

**Redox, Acid–Base Chemistry,
Electrochemical Synthesis and
Characterization of Materials Based on
TCNQF₄ and TCNQ**



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(M.Sc.)

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Abbreviations

ω	angular rotation rate of the electrode
ΔE_p	peak-to-peak separation
A	area of electrode
BAS	Bioanalytical Systems
D	diffusion coefficient
DCTC ⁻	α,α -dicyano-p-toluoylcyanide
E^0	formal potential
$E_{1/2}$	half-wave potential
EDXS	energy-dispersive X-ray spectroscopy
E_m	midpoint potential
E_p	peak potential
EQCM	electrochemical quartz crystal microbalance
ESI-MS	electrospray ionization mass spectrometry
F	Faraday constant
FT-IR	Fourier transform infrared
i_{lim}	limiting current
i_p	peak current
IR	infrared
ITO	indium tin oxide
k^0	standard electron transfer rate constant
R	gas constant
r	radius of microdisk electrode
RDE	rotating disc electrode
SEM	scanning electron microscopy
SPR	surface plasmon resonance
T	temperature (K)
TCNQ	7,7,8,8-tetracyanoquinodimethane
TCNQF ₄	2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane
TFA	trifluoroacetic acid
TGA	thermogravimetric analysis
UV-vis	Ultraviolet-visible
ν	scan rate
ν	kinematic viscosity
λ_{max}	maximum absorption wavelength

Abstract

Redox and acid–base chemistry of 7,7,8,8-tetracyanoquinodimethane (TCNQ), 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (TCNQF₄), and their mono- and di-anions in acetonitrile in the presence or absence of trifluoroacetic acid (TFA) have been studied systematically. In acetonitrile containing supporting electrolyte, both compounds undergo two electrochemically and chemically reversible one-electron reduction steps. The reversible formal potentials associated with these reductions of TCNQF₄ are 0.36 and 0.37 V more positive than those for TCNQ. This result is consistent with the higher electron affinity of TCNQF₄ than TCNQ due to the strong electron withdrawing effect of the fluorine atoms. The underlying mechanisms for the electrochemistry and the acid–base chemistry of TCNQ, TCNQF₄ and their anions have been proposed and supported by digital simulations. A wealth of thermodynamic and kinetic parameters has been revealed from the experimental and simulated data. A comparison of the redox and acid–base chemistry between TCNQ and TCNQF₄ as well as their anions also has been discussed.

Studies of chemical and electrochemical synthesis of new materials based on TCNQF₄ in combination with Li⁺, Pr₄N⁺, Ag⁺, Cu⁺, Co²⁺ and Ni²⁺ have been undertaken. In acetonitrile, I[−] (as the I[−] salt) reduces TCNQF₄ to TCNQF₄^{•−} or TCNQF₄^{2−} depending on the reaction conditions. At low temperature (0 °C) and using the molar ratio I[−]:TCNQF₄ ≤ 3:2, TCNQF₄ is reduced to the TCNQF₄^{•−} monoanion. In contrast, at higher temperatures (50–60 °C) and using the molar ratio > 3:1, the major product is the TCNQF₄^{2−} dianion. The LiTCNQF₄ and Li₂TCNQF₄ thus generated were used to chemically synthesize Pr₄NTCNQF₄ and (Pr₄N)₂TCNQF₄. TCNQF₄ can also be electrochemically reduced in acetonitrile to afford either TCNQF₄^{•−} or TCNQF₄^{2−} by applying different potentials. This electrosynthetic approach has, therefore, been applied to crystallize a family of charge-transfer, semiconducting materials, including AgTCNQF₄, Ag₂TCNQF₄, CuTCNQF₄, Cu₂TCNQF₄, CoTCNQF₄ and NiTCNQF₄ onto an electrode surface. The electrodeposition of these compounds has been monitored using cyclic voltammetry, surface plasmon resonance and electrochemical quartz crystal microbalance. The solubility of these compounds has been determined in acetonitrile in the presence or absence of 0.1 M Bu₄NPF₆ supporting electrolyte and found to increase in the presence of the supporting electrolyte as a result of ion pairing between ions from the electrolyte and the complexes. These metal-organic charge-transfer complexes also have been chemically synthesized

from acetonitrile solutions of the corresponding TCNQF₄ anion and metal cation. A wide range of microscopic and spectroscopic techniques has been applied to characterize the newly generated compounds.

Besides synthesis of TCNQF₄-based compounds in acetonitrile, a new complex Ni(TCNQF₄)₂(H₂O)₂ has been electrochemically synthesized in aqueous media via the reduction of TCNQF₄ solid immobilized onto an electrode surface and placed in contact with a Ni²⁺_(aq) solution. The solid-solid state transformation TCNQF₄/Ni(TCNQF₄)₂(H₂O)₂ has been explored via cyclic voltammetry and chronoamperometry. The electrosynthesis involves a one-electron reduction of TCNQF₄ to TCNQF₄^{•-}, accompanied with the ingress of Ni²⁺_(aq) from the bulk solution. This transformation is governed by a nucleation and growth mechanism, and is independent of the electrode material and the identity of Ni²⁺_(aq) counter anion, but strongly dependent on Ni²⁺_(aq) concentration and scan rate. The composition, structure, magnetic and conducting properties of the Ni(TCNQF₄)₂(H₂O)₂ complex have been determined.

The disproportionation reaction of TCNQF₄^{•-} and TCNQ^{•-} (both designated as TCNQ(F₄)^{•-}) in the presence of Zn²⁺ is reported. Acetonitrile solutions containing TCNQ(F₄)^{•-} and Zn²⁺ form dissolved TCNQ(F₄) and ZnTCNQ(F₄) precipitates. The neutral TCNQ(F₄) dissolved in acetonitrile was detected using UV-vis spectroscopy and steady-state voltammetry, whilst the presence of TCNQ(F₄)²⁻ in the precipitates was confirmed by infrared spectroscopy, and also by showing that the precipitates reacts with TCNQ(F₄) in the presence of water to form TCNQ(F₄)^{•-}. Interestingly, the extent of the disproportionation decreases upon addition of water; ≥ 3% (v/v) of water results in no disproportionation. A mechanism for the disproportionation has been proposed and is attributed to the precipitation of ZnTCNQ(F₄), which shifts the equilibrium $2\text{TCNQ}(\text{F}_4)^{\bullet-} \rightleftharpoons \text{TCNQ}(\text{F}_4) + \text{TCNQ}(\text{F}_4)^{2-}$ to the right-hand side. However, the solubility of ZnTCNQ(F₄) in water is higher than in acetonitrile, and hence the disproportionation is less favored in the presence of water.

Electrochemical and spectroscopic identification of TCNQF₄ redox levels are reviewed. Steady-state voltammetry and UV-vis spectroscopy are simple and powerful techniques for the qualitative and quantitative detection of TCNQF₄ and its anions (TCNQF₄^{•-} and TCNQF₄²⁻) since each species has a characteristic fingerprint. Infrared spectroscopy has been applied extensively and successfully in the qualitative determination

of the redox levels of TCNQF₄ in a range of compounds. Predominately, the frequency of the C≡N stretch is diagnostic of the redox level. Raman vibration modes for the C≡N and C=C ring stretches also are sensitive to the TCNQF₄ redox levels.

Declaration for thesis based or partially based on conjointly published or unpublished work

General Declaration

In accordance with Monash University Doctorate Regulation 17/ Doctor of Philosophy and Master of Philosophy (MPhil) regulations the following declarations are made:

I hereby declare that this thesis contains no material which has been accepted for the award of any other degree or diploma at any university or equivalent institution and that, to the best of my knowledge and belief, this thesis contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

This thesis includes four original papers published in peer reviewed journals and six unpublished pieces of work (including one accepted paper). The core theme of the thesis is Eletrochemical Synthesis and Characterization of New Materials Based on TCNQF₄. The ideas, development and writing up of all the papers in the thesis were the principal responsibility of myself, the candidate, working within the School of Chemistry under the supervision of A.Prof. Lisandra L. Martin and Prof. Alan M. Bond.

The inclusion of co-authors reflects the fact that the work came from active collaboration between researchers and acknowledges their input into team-based research.

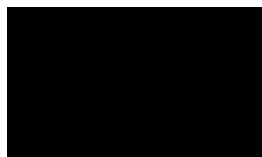
In all chapters of this thesis, my contribution to the work involved the following:

Thesis chapter	Publication title	Publication status	Nature and extent of candidate's contribution
3	Detailed Electrochemical Analysis of the Redox Chemistry of Tetrafluorotetracyanoquinodimethane TCNQF ₄ , the Radical Anion TCNQF ₄ ^{•-} , and the Dianion TCNQF ₄ ²⁻ in the Presence of Trifluoroacetic Acid	Published	Initiation, key ideas, experimental work, writing up – 85%

3	Redox and Acid–Base Chemistry of 7,7,8,8-Tetracyanoquinodimethane, 7,7,8,8-Tetracyanoquinodimethane Radical Anion, 7,7,8,8-Tetracyanoquinodimethane Dianion, and Dihydro-7,7,8,8-Tetracyanoquinodimethane in Acetonitrile	Published	Initiation, key ideas, experimental work, writing up – 75%
4	Synthesis, X-ray Crystallographic Characterization and Electrochemical Studies of TCNQF ₄ Complexes with Li ⁺ or Pr ₄ N ⁺	Draft	Initiation, key ideas, experimental work, writing up – 35%
4	A New Method for Electrocrystallization of AgTCNQF ₄ and Ag ₂ TCNQF ₄ (TCNQF ₄ = 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane) in Acetonitrile	Published	Initiation, key ideas, experimental work, writing up – 85%
4	Electrochemically Directed Synthesis and Characterization of Cu(I) Derivatives of TCNQF ₄ ^{•−} or TCNQF ₄ ^{2−} (TCNQF ₄ = 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane) in Acetonitrile	Draft	Initiation, key ideas, experimental work, writing up – 85%
4	Electrochemically Directed Synthesis of Co ²⁺ and Ni ²⁺ Complexes with TCNQF ₄ ^{2−} (TCNQF ₄ = 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane)	Draft	Initiation, key ideas, experimental work, writing up – 90%

5	Electrochemical Synthesis and Characterization of Semiconducting $\text{Ni}(\text{TCNQF}_4)_2(\text{H}_2\text{O})_2$ (TCNQF_4 = 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane)	Published	Initiation, key ideas, experimental work, writing up – 80%
6	Solvent Controlled Reversible Disproportionation of $\text{TCNQF}_4^{\bullet-}$ and $\text{TCNQ}^{\bullet-}$ in the Presence of Zn^{2+}	Draft	Initiation, key ideas, experimental work, writing up – 80%
7	Spectroscopic and Electrochemical Fingerprints Available for Identification of TCNQF_4 Redox Levels	Draft	Initiation, key ideas, experimental work, writing up – 90%
Appendix	Novel Semiconducting Biomaterials Derived from a Proline Ester and Tetracyanoquinodimethane (TCNQ) Identified by <i>Hand-Picked</i> Selection of Individual Crystals	Accepted	Key ideas, experimental work, writing up – 10%

Signed:



Date: 06/06/2012

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I would like to say much more but I cannot express all of my thoughts here.



“Electrochemistry – in the broadest sense – will be one of the great achievements in chemistry in the next millennium, and one should prepare our people for it.”¹

Peter William Atkins

(1) Bond, A. M. *Broadening Electrochemical Horizons: Principles and Illustration of Voltammetric and Related Techniques*; Oxford University Press Inc.: New York 2002.

Chapter 1

Introduction

1.1. Introduction

Electrochemistry has been established for over 200 years and is now a mature scientific discipline.¹ It concerns the interrelationship of electrical and chemical reactions. This field explores primarily chemical changes resulting from an electric current and the production of electrical energy by chemical reactions. Electrochemical measurements on chemical systems are made for a variety of reasons, such as obtaining thermodynamic data about a reaction, generating and studying an unstable intermediate, analyzing a solution for trace amounts of metal ions or organic species, electrochemically synthesizing new products, and many others. Electrochemistry also has been applied in electrophoresis, corrosion, electrochromic displays, sensors, batteries, fuel cells.^{1,2}

Using electrochemistry as the key technique of sample interrogation, this thesis studies the redox and acid–base chemistry of 7,7,8,8-tetracyanoquinodimethane (TCNQ) and 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (TCNQF₄) (structures given in Figure 1.1), and electrochemical synthesis as well as characterization of new materials based on TCNQF₄ or TCNQ. Cyclic voltammetry has been intensively used to explore the redox chemistry and formation of these compounds. In addition, electrochemical quartz crystal microbalance (EQCM) and surface plasmon resonance (SPR) have been utilized to monitor the mass change on the surface of an electrode during the course of electrochemical experiments. In addition, the chemically and electrochemically synthesized materials have been characterized using a wide range of spectroscopic and microscopic techniques.

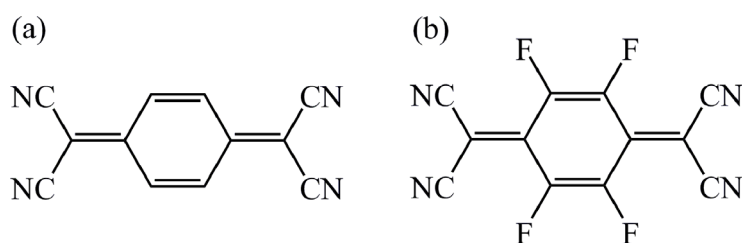


Figure 1.1. Molecular structures of (a) TCNQ and (b) TCNQF₄

1.2. Recent studies of TCNQ and TCNQF₄

TCNQ has been studied widely by electrochemical and spectroscopic techniques since the 1960s.³⁻⁹ In acetonitrile, TCNQ is chemically and electrochemically reversible sequentially reduced in two one-electron steps (equations 1.1 and 1.2).¹



Metal-organic charge-transfer salts, network polymers and organometallic compounds based on TCNQ usually exhibit novel conducting, optical and/or magnetic properties.^{1,10-17} Consequently, these materials have been used in optical and electrical media recording,¹⁸⁻²² energy and data storage,^{8,23,24} sensor and catalysis,²⁵⁻²⁷ organic field-effect transistors,^{28,29} as well as electrochromic and magnetic devices^{30,31} for over several decades. Semiconductors based on TCNQ^{•-} and monocations of metal (Na⁺, K⁺, Rb⁺, Cs⁺, Cu⁺ and Ag⁺) or tetraalkyl ammonium origin have been synthesized and characterized, extensively.¹ In recent times, the binary MTCNQ₂^{1,6,8,32-36} or MTCNQ^{34,37,38} based materials (M^{II} = first row transition metals) have also shown interesting semiconductivity and a wide range of magnetic properties with demonstrated relevance to the field of molecular magnets. Furthermore, some lanthanide derived TCNQ-based materials can behave as molecular magnets under designated conditions as well.³⁹

TCNQ is a strong π -acceptor⁴⁰ with the electron affinity of ~2.9 eV.^{41,42} However substitution of the four hydrogens by four electronegative fluorine atoms yielding TCNQF₄, which has an even stronger electron affinity (~3.3 eV).⁴²⁻⁴⁴ In acetonitrile (0.1 M Bu₄NClO₄) solution, TCNQF₄ undergoes two chemically and electrochemically reversible one-electron reduction processes and the reversible formal potentials for the first and second processes are 0.36 and 0.37 V, respectively more positive than those for TCNQ.⁴⁴ Recently, studies have focused on the synthesis and optically induced transformation,^{45,46} structure and magnetic properties⁴⁷⁻⁴⁹ of TCNQF₄-based charge-transfer complexes. For example, several charge-transfer compounds based on TCNQF₄, such as Ag-TCNQF₄,^{43,45,47,50} Cu-TCNQF₄,^{50,51} Mn-TCNQF₄⁵² and lanthanide-TCNQF₄⁵³ have been chemically synthesized and characterized. These TCNQF₄ derivatives exhibit even more interesting and unexpected properties than the TCNQ parent molecule. However, to date there are relatively too few studies of TCNQF₄-based materials undertaken – a situation addressed here in this thesis.

1.3. Thesis Objectives

The primary aim of this thesis is to investigate the chemistry and redox behaviors of TCNQF₄ compounds in detail:

- i) to understand the kinetics, thermodynamics and mechanisms associated with reduction of TCNQF₄ (compared with TCNQ) dissolved in acetonitrile in the presence or absence of an acid or a metal cation, or while immobilized on the surface of an electrode and placed in contact with an aqueous solution containing a metal cation.
- ii) to electrochemically and chemically synthesize new materials based on the monoanions or dianions of TCNQF₄ or TCNQ.
- iii) to characterize the structures, magnetic properties, conductivities and morphologies of the new materials.

1.4. Thesis Outline

- i) Chapter 1 provides a general introduction about the importance and applications of electrochemistry, followed by the objectives and outline of the thesis. Previous studies of TCNQ, TCNQF₄ and their complexes are reviewed in this chapter.
- ii) Chapter 2 describes the experimental techniques used in the thesis.
- iii) Chapter 3 focuses on the redox and the acid-based chemistry of TCNQ and TCNQF₄ in acetonitrile in the presence or absence of trifluoroacetic acid. Mechanisms associated with the protonation of the mono- and dianions of TCNQ and also TCNQF₄ have been investigated and several valuable kinetic and thermodynamic parameters have been revealed from this investigation.
- iv) Chapter 4 describes the methods applied to electrochemically and/or chemically synthesize and characterize materials based on TCNQF₄^{•-} or TCNQF₄²⁻ in combination with Li⁺, Pr₄N⁺, Ag⁺, Cu⁺, Co²⁺ or Ni²⁺ cations. These compounds were formed through electrochemical or chemical reduction of TCNQF₄ in acetonitrile in the presence of these cations.
- v) In chapter 5, electrochemistry of an electrode modified with TCNQF₄ solid in contact with an aqueous Ni²⁺ electrolyte is described. A mechanism for the solid-solid phase transformation of TCNQF₄/Ni(TCNQF₄)₂(H₂O)₂, and investigation of the structure and properties of the Ni(TCNQF₄)₂(H₂O)₂ complex are described in detail.

- vi) Chapter 6 describes the unexpected disproportionation of the $\text{TCNQF}_4^{\bullet-}$ and $\text{TCNQ}^{\bullet-}$ radical monoanions in acetonitrile in the presence of Zn^{2+} . A mechanism for this disproportionation reaction has been proposed.
- vii) The distinction of the redox levels of TCNQF_4 in its compounds using electrochemistry, UV-vis, infrared and Raman spectroscopies are reviewed in chapter 7. In particular, it is shown how TCNQF_4 and its anions present in a new material can be distinguished using steady-state voltammetry and/or UV-vis spectroscopy.
- viii) A summary of the main findings of this thesis together with suggestions for future work are presented in Chapter 8.
- ix) An appendix section presents two novel semiconducting biomaterials, which were derived from *N,N*-dimethyl-D-proline-dimethylester ($\text{Pro}(\text{CH}_3)_3^+$) iodide and LiTCNQ . Crystals of the two compounds ($\text{Pro}(\text{CH}_3)_3\text{TCNQ}$ and $(\text{Pro}(\text{CH}_3)_3)_2(\text{TCNQ})_3$) were collected by hand-picked selection. The crystal structures and other properties of the new compounds have been determined.

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Chapter 2

Experimental Techniques and Simulation Software

2.1. Introduction

A wide range of techniques has been used to explore the redox chemistry of TCNQ and TCNQF₄ as well as the electrocrystallization of materials based on TCNQF₄ in combination with transition metals, such as Ag, Cu, Co and Ni. This chapter describes the basis of voltammetry; electrochemical quartz crystal microbalance; surface plasmon resonance; thermogravimetric analysis; microscopic and spectroscopic techniques; and simulation software, which were used in this thesis.

2.2. Experimental Techniques

2.2.1. Voltammetry

In dynamic electrochemistry, experiments are generally conducted in a three-electrode cell (Figure 2.1) using a potentiostatted form of instrumentation. In this configuration, reactions of interest occur at the working electrode while the current is passed between the working and counter electrodes. The potential at the working electrode is compared with that of the reference electrode. In order to minimize the solution resistance, reduce the migration of electroactive species and establish a well defined double layer, a supporting electrolyte with a concentration of ≥ 0.01 M is usually added to the solution.¹ In addition, the reference electrode is placed as closely as possible to the working electrode surface to minimize the uncompensated potential (Ohmic, IR) drop. The cell has an inlet and outlet for purging with an inert gas to displace any electroactive oxygen present in the solution.

Cyclic voltammetry has been used widely for initial electrochemical studies of new materials and has proven to be very useful in gaining a rapid understanding of qualitative aspects of the electrode mechanism.^{2,3} In cyclic voltammetric experiments, the potential at the working electrode is usually swept from an initial to a switching potential at a constant scan rate and then the direction of the sweep is reversed and the potential returns to the initial value. However, the potential sometimes is scanned back to another value, which differs from the initial value. In addition, the potential can be cycled several times to examine the stability of products formed via an electron transfer reaction and to detect any new electroactive products formed from their decomposition.^{1,2,4} Hence, use of cyclic

voltammetry has provided a great deal of valuable information about thermodynamic, kinetic and mechanistic aspects of the redox chemistry in this thesis.

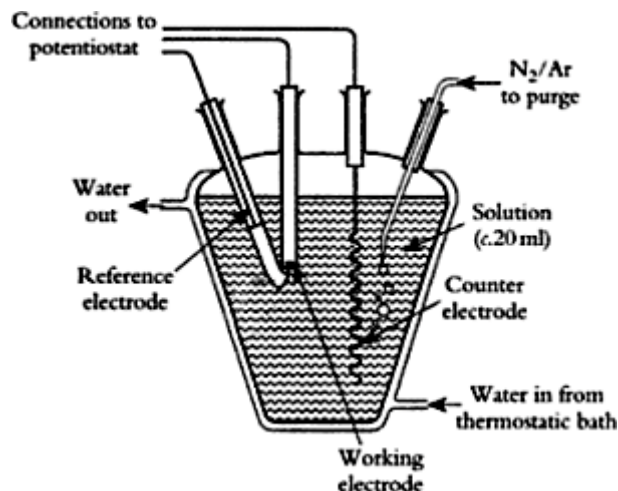
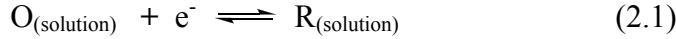


Figure 2.1. Schematic diagram of a three-electrode cell configuration (reproduced from reference 1).

Two major classes of voltammetry are transient and steady-state voltammetry. Which method is employed depends on the experimental conditions, mass transport type of analyte and the size of the working electrode.^{1,4} Figure 2.2a shows a typical transient peak-shaped cyclic voltammogram for the reduction of the dissolved species O to the dissolved R (equation 2.1) obtained at a macrodisc electrode under stationary electrode conditions, whilst sigmoidal shaped Figure 2.2b represents steady-state voltammetry for this reaction obtained with a stationary microdisc electrode. Transient cyclic voltammetry is characterized by peak potentials (or a midpoint potential E_m , which is the average of the oxidation (E_p^{ox}) and reduction (E_p^{red}) peak potentials, $E_m = (E_p^{ox} + E_p^{red})/2$), and peak currents. The peak-to-peak separation ΔE_p for a reversible process depends on the number of electrons transferred (n) and is represented by equation 2.2.¹ Therefore, ΔE_p sometimes can be used to determine the number of electrons of an electroactive species transferred at the working electrode. However, when the rate of electron transfer is not fast enough to achieve reversibility and/or the resistance of the solution is too high, the peak-to-peak separation becomes larger. The dependence of the peak current (i_p) on variable parameters for a diffusion controlled reversible process is represented by the Randles-Sevcik relationship (equation 2.3). In contrast, the important parameters in a steady-state voltammogram are the limiting current (i_{lim}) and the half-wave potential ($E_{1/2}$), where the current equals one-half of the limiting current. The limiting currents obtained with a

microelectrode ($i_{\text{lim(microelectrode)}}$) or a rotating macrodisc electrode ($i_{\text{lim(RDE)}}$) under steady-state conditions are given by equations 2.4 and 2.5 (Levich equation), respectively.



$$\Delta E_p = E_p^{\text{ox}} - E_p^{\text{red}} = \frac{56}{n} \text{ mV} \quad (\text{at } 25^\circ\text{C}) \quad (2.2)$$

$$i_p = 0.4463nFAC(nFvD/RT)^{1/2} \quad (2.3)$$

$$i_{\text{lim(microelectrode)}} = 4nFrCD \quad (2.4)$$

$$i_{\text{lim(RDE)}} = 0.620nFACD^{2/3}\nu^{-1/6}\omega^{1/2} \quad (2.5)$$

where, n = number of electrons transferred, F = Faraday constant, A = area of macroelectrode, C = analyte concentration, D = diffusion coefficient, R = gas constant, T = temperature, r = microelectrode radius, ω = angular rotation rate of the electrode, ν = scan rate (for equation 2.3) or kinematic viscosity of the solution (for equation 2.5).

When the electron transfer rates of the forward and backward are both rapid, the system is described as being electrochemically reversible. If the species R generated electrochemically from reduction of O converts to Z, then the overall reaction $\text{O} \longrightarrow \text{Z}$ is defined to be chemically irreversible.¹

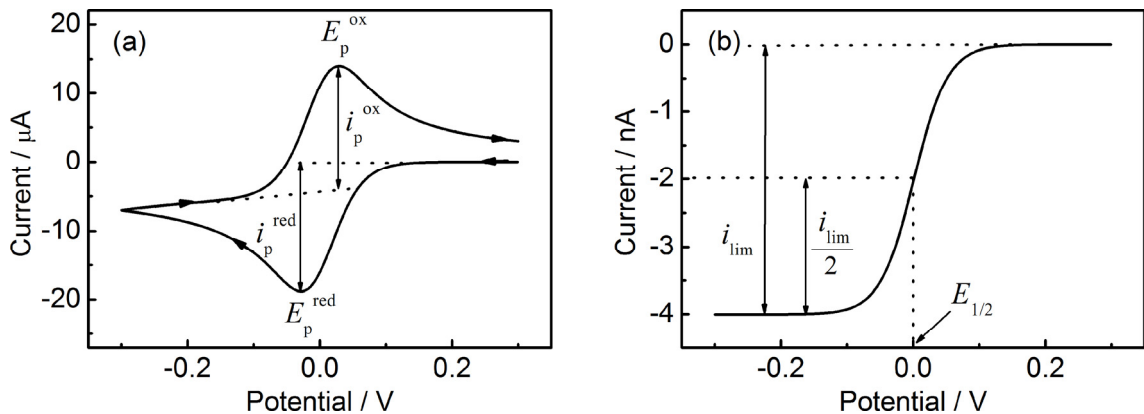


Figure 2.2. Typical current-potential responses for (a) transient cyclic voltammogram and (b) steady-state voltammogram.

If both oxidized (O) and reduced (R) species are confined to an electrode surface, which is placed in a solution containing an electrolyte, the electron transfer reaction occurs within the solid phase to give a diffusionless system.¹ However, in order to achieve charge neutralization, charge transport must still occur across the redox active solid(s)-electrode-solution interface.¹ In other words, both electron and ionic transport processes occur within

the attached solid(s) in this circumstance. The solid(s) may be adsorbed or attached to the electrode surface by chemical or physical methods to give monolayer or even multilayer coverage with each layer having a different level of activity. The solid also may be attached to the surface of the electrode as arrays of microcrystals with random forms of electrode coverage resulting. Therefore, studies on the voltammetry of a surface confined process are much more complicated than that for redox active species, which are dissolved in a solution.^{1,4} Here, only the simplest case of the redox chemistry for a monolayer thin film with a non-interacting surface is considered. The cyclic voltammogram for the one-electron reduction of an adsorbed species O to adsorbed R is shown in Figure 2.3a, whilst Figure 2.3b presents a cyclic voltammogram of an electrochemically irreversible reaction, in which only adsorbed O is electroactive. The peak current (i_p) and peak potential (E_p) associated with these processes are given by equations 2.6 to 2.9^{1,4} (subscripts *rev* and *irr* refer to reversible and irreversible processes, respectively). The peak current associated with the reduction or oxidation of an adsorbed species is proportional to the scan rate, in contrast to the square root of the scan rate dependence for a diffusion controlled process in solution (equation 2.3).

$$i_{p(rev)} = \frac{F^2}{4RT} \nu A (\Gamma_O + \Gamma_R) \quad (2.6)$$

$$E_{p(rev)} = E^{0'} - \frac{RT}{F} \ln \frac{\beta_O \Gamma_O}{\beta_R \Gamma_R} \quad (2.7)$$

$$i_{p(irr)} = \frac{\alpha F^2}{2.718RT} \nu A (\Gamma_O + \Gamma_R) \quad (2.8)$$

$$E_{p(irr)} = E^{0'} + \frac{RT}{\alpha F} \ln \left(\frac{RT}{\alpha F} \frac{k^0}{\nu} \right) \quad (2.9)$$

where F , R , T , ν , A were described in equation 2.3; Γ_O , Γ_R are the surface coverage by O and R, respectively; $E^{0'}$ is formal potential, β_O , β_R are the activity coefficients of O and R, respectively, α is the charge transfer coefficient, k^0 is the standard charge transfer rate constant.

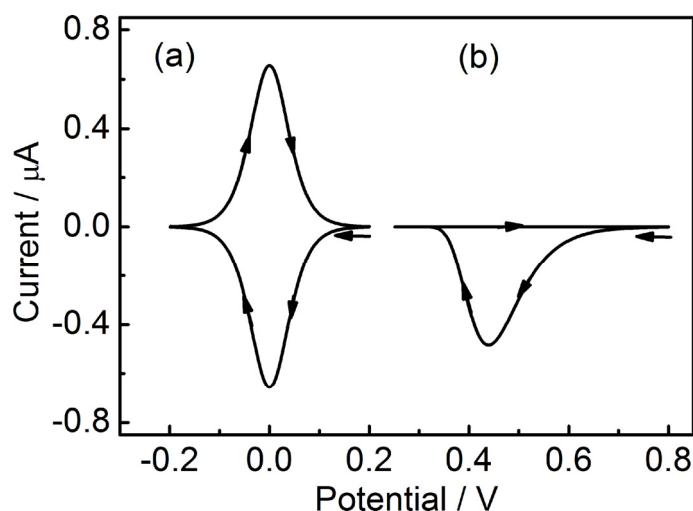


Figure 2.3. Cyclic voltammograms for reduction of adsorbed A to adsorbed B: (a) reversible process, (b) irreversible process. Voltammograms are obtained by using DigiElch software with electrode area = 0.07 cm^2 , scan rate = 0.1 V s^{-1} , surface coverage of A and B = $1.0 \times 10^{-10} \text{ moles cm}^{-2}$, $E^0 = 0.0 \text{ V}$, $\alpha = 0.5$, $k^0 = 1.0 \times 10^4 \text{ s}^{-1}$, temperature = 298.2 K .

The double-potential step chronoamperometric technique was applied to explore the nucleation and growth process of $\text{Ni}(\text{TCNQF}_4)_2(\text{H}_2\text{O})_2$ in chapter 5.2. In this technique, the potential is first set at an initial value (E_{ini}) for a quiet time, t_{quiet} (Figure 2.4a), at which no Faradaic process occurs. The potential is then stepped to potential (E_1) and held at this value for a fixed time t_1 to induce a Faradaic current due to oxidation or reduction of the species of interest. Finally, the potential is switched to the second step value E_2 (which may be the same as or different from the initial potential E_{ini}) and held there for time t_2 . During this experiment, the current is recorded as a function of time (Figure 2.4b).

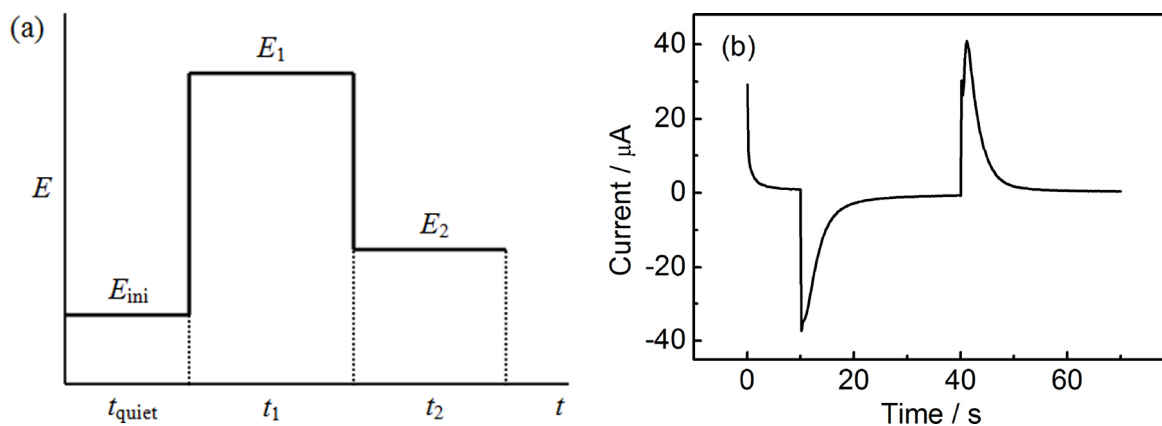


Figure 2.4. (a) Potential waveform for double-step potential chronoamperometry, (b) double-potential step chronoamperogram obtained with a drop-cast TCNQF₄-modified 3.0 mm diameter glassy carbon electrode in contact with a 0.1 M Ni(NO₃)₂ aqueous electrolyte solution: potential (vs. Ag/AgCl) stepped from $E_{ini} = 800$ mV (held for 10 s) to 345 mV (for 30 s) and then back to 575 mV (for 30 s).

2.2.2. Electrochemical Quartz Crystal Microbalance

The mass change on the surface of a working electrode when Cu₂TCNQF₄ was electrocrystallized and stripped off in an acetonitrile solution containing TCNQF₄ and Cu(MeCN)₄⁺ (Chapter 4.4) was monitored with an electrochemical quartz crystal microbalance (EQCM). The mass change, as a result of deposition or loss of material from an electrode surface during the course of electrochemical experiments, is often of interest and EQCM is a powerful technique for the detection of mass change.⁴ The quartz crystal microbalance is based on the piezoelectric properties of a quartz crystal. The particular mechanical resonant mode of a bare quartz crystal depends on its size and thickness.⁴ The quartz crystal used in the EQCM experiment has a diameter of 1.3 cm and coated with 5.0 mm diameter gold discs on both sides (see Figure 2.5a). One side is in contact with the solution of interest and acts as a working electrode, while the other side is exposed to air (Figure 2.5b). When applying a sinusoidal electrical signal of a frequency f_0 to the gold contacts of the quartz crystal, the quartz crystal will oscillate at the same frequency. The mass changes on the surface of the quartz crystal during the course of experiment results in a frequency change (Δf) of the quartz crystal oscillation and is represented by the Sauerbrey equation (2.10).⁴ Consequently, the mass change can be determined from the frequency change of the quartz crystal. Thus, EQCM can measure simultaneously mass change on the surface of the electrode, current, potential and time during voltammetric experiments.

$$\Delta f = -2f_0^2 mn/(\rho\mu)^{1/2} = -C_f m \quad (2.10)$$

where, m is mass change per unit area to the crystal surface, n is the harmonic number of the oscillation, ρ is the density of quartz, μ is the shear modulus of quartz. Normally, the constants are grouped together to form a single constant C_f (sensitive factor).

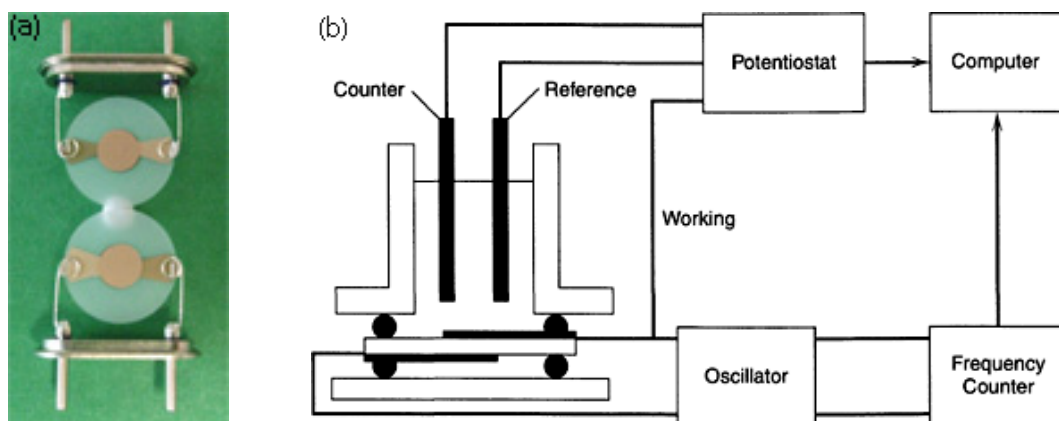


Figure 2.5. (a) Photo of the two sides of a quartz crystal coated with gold discs, (b) schematic diagram of EQCM instrumentation (reproduced from reference 4).

2.2.3. Surface Plasmon Resonance

In situ cyclic voltammetric and surface plasmon resonance (SPR, the excitation of surface plasmon by light⁵) experiments on gold coated-glass electrodes also were used to explore the mass change due to deposition onto or stripping of solid from an electrode surface.^{4,6,7} However, it needs to be recognized that unlike EQCM, changes in the solution near the electrode surface also may affect the SPR intensity.⁶ Figure 2.6a shows the schematic arrangement for measuring the SPR signal in an electrochemical cell. The working electrode is a gold thin film (~50 nm) coated on a glass plate. When *p*-polarized light (polarization is parallel to the plane of incidence) from a laser source is shone through a hemispherical prism to the backside of the gold thin film, the light will be reflected. By changing the angle of incidence (θ) over a range of a few degrees and monitoring the intensity of the reflected light, the reflected light intensity will pass through a minimum (Figure 2.6b, line A) as the light excites surface plasmon and induces surface plasmon resonance (Krestchmann configuration).⁴ The angle at which the intensity of the reflected light becomes smallest is called the resonance or SPR angle. The SPR angle is dependent on the refractive indices of the media on both sides of the gold film. The refractive index of one side contacting the prism does not change, while the refractive index in the immediate vicinity of the gold electrode surface, where electrochemical processes occur, will change

during the course of voltammetry when solid is adsorbed onto it. As a result, the SPR angle is shifted (Figure 2.6b, line B) as the surface plasmon resonance conditions change. Consequently, the SPR signal can provide information about the changes due to materials bound to the electrode surface.^{4,5}

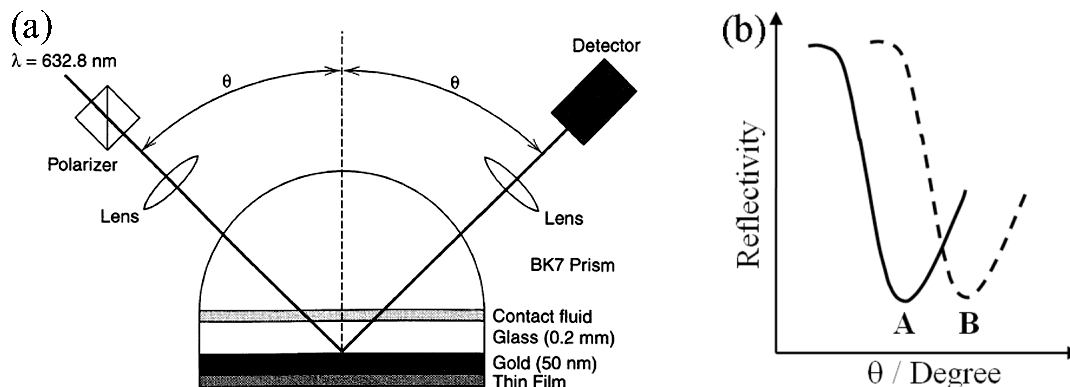


Figure 2.6. (a) Schematic diagram of a prism and gold electrode arrangement for *in situ* electrochemical and SPR experiments. The layer designated as “thin film” is an adsorbed or deposited layer on a gold electrode (reproduced from reference 4), (b) the shift of the incident angle from A to B as a change in refractive index at the gold electrode surface.

2.2.4. Thermogravimetric Analysis

The number of coordinated water and acetonitrile molecules present in the electrochemically synthesized $\text{Ni}(\text{TCNQF}_4)_2(\text{H}_2\text{O})_2$ and $\text{Cu}_2\text{TCNQF}_4(\text{CH}_3\text{CN})_2$, respectively was determined by thermogravimetric analysis (TGA). In TGA, the temperature is increased or decreased with time at a fixed rate of temperature change or held at a constant value⁸ and the mass change of a sample is monitored with an accurate, sensitive and reliable analytical balance.^{8,9} TGA has been applied widely in analysis and characterization of materials, such as polymers, pharmaceuticals, ceramics, metals and alloys.^{8,9} It may be used to determine absorbed moisture content of inorganic or organic components, solvent residues and decompositions points of materials.^{8,9}

2.2.5. Spectroscopy and Microscopy

In this thesis, Ultraviolet-visible (UV-vis), Fourier transform infrared (FT-IR) and Raman spectroscopies have been utilized to characterize and to determine the redox levels of TCNQ and TCNQF_4 in the synthesized compounds. Additionally, UV-vis spectroscopy also was used to quantify TCNQ, TCNQF_4 and their anions using calibration curves as the absorbance of a species in a solution at a certain maximum absorption wavelength is proportional to its concentration.

UV-vis spectroscopy typically refers to absorption spectroscopy in the spectral region of 190 to 800 nm and is due to electronic transitions from the ground state to higher energy states.^{10,11} The transitions involving non-bonding electrons or electrons in molecular orbitals of unsaturated molecules give rise to UV-vis absorptions by organic compounds.¹⁰ In the case of ions and complexes of elements of the first two transition series, the absorption involves the transitions between filled and unfilled *d*-orbitals with energy depending on the ligands coordinated to the metal ions.¹¹ UV-vis spectroscopy has been used for qualitative as well as quantitative determinations of different analytes¹¹ since each species may absorb UV-vis light at different wavelength(s) to give absorption peak(s) (λ_{max}). The absorbance of a species dissolved in solution, at a certain λ_{max} , is proportional to its concentration and the path length (the Beer-Lambert law, equation 2.11).

$$A = \varepsilon CL \quad (2.11)$$

where, *A* is the absorbance, ε is the molar extinction coefficient, *C* is the concentration of the analyte and *L* is the path length.

IR spectroscopy is one of the most powerful techniques for determining the structure of organic as well as inorganic compounds since most molecules absorb infrared radiation, except a few homonuclear molecules, such as O₂, N₂ and Cl₂.^{11,12} Infrared radiation can excite vibrational and rotational transitions.¹¹ Basically, IR spectroscopy measures relative radiation absorption, i.e. the absorption is derived indirectly by comparing the radiation from a source transmitted through the sample with the unattenuated radiation from the same source in the range of 400 to 4000 cm⁻¹.^{8,12} All IR spectra presented in this thesis were recorded with a Fourier transform spectrometer. This kind of spectrometer offers several benefits, such as high sensitivity, resolution and speed of data acquisition.¹¹

Raman spectroscopy, which is complementary to IR, has been used to study vibrational and rotational modes in molecules. Raman spectra are recorded as a wavelength (frequency) shift from a well-defined, fixed wavelength due to inelastic scattering of light (usually from a monochromatic laser source in the UV-vis or near infrared ranges⁸) by the molecules.^{8,12} The frequency of the laser photon changes to lower or higher values and are small compared with the original frequency.¹² Information about the vibrational modes in the molecules studied can be obtained from the energy shift. Because the regular Raman effect is very weak, Raman spectroscopy can only be used analytically for the study of major components.⁸

Optical microscopy was used to record images of the electrocrystallized AgTCNQF₄ sample on an ITO electrode surface since these crystals are particularly large. However, other electrocrystallized samples were much smaller and needed higher resolution imaging. Scanning electron microscopy (SEM) was the technique routinely used to image the morphology of these materials. The surface of a sample is scanned in a raster pattern with a very high energy (0.1 – 30 keV), finely focused electron beam (< 10 nm), which is accelerated at a high positive voltage and focused by a set of magnetic lenses and apertures (Figure 2.7).¹³ The electron beam strikes the sample with a sample interaction depth of approximately 1 μm and ejects more electrons from the sample, which can be sensed by a detector and then amplified to reconstruct an image which is displayed on a viewing screen.¹³ The SEM instrumentation can be used for identification of the elements present in the sample using energy-dispersive X-ray spectroscopy (EDXS). This technique is a powerful tool for qualitative X-ray microanalysis.¹³ The interaction between electron beam and sample produces X-rays emitted from the sample with the energies of these X-rays depending on the difference in binding energies of the outer and inner shells where electrons are transferred. Because each element has specific energy levels, the energy of the emitted X-rays can be used to identify the presence of particular element(s) in the sample.^{13,14}

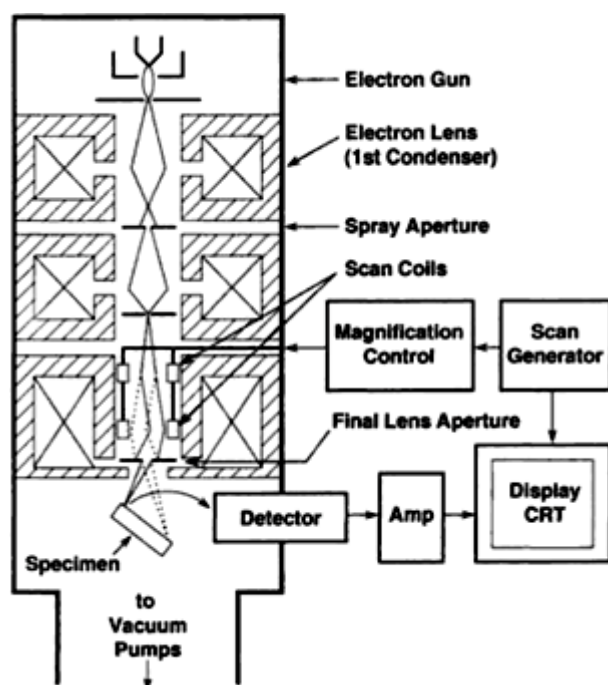


Figure 2.7. Schematic diagram of the electron beam path from electron gun to specimen and electron detector in SEM (reproduced from reference 13).

2.2.6. Simulations of Voltammetry

The outcome of experimental electrochemical data are affected by various parameters, such as the area of electrode surface, rate of electron transfer, diffusion coefficient of analytes, solution resistance, capacitance, temperature, etc.^{3,4,15} Therefore, voltammetry simulation software has been developed to model complex voltammetric responses. The simulation software DigiSim 3.03 distributed by Bioanalytical Systems (BAS) was used to support the proposed mechanisms for the redox chemistry of TCNQ, TCNQF₄ and their anions in acetonitrile in the presence of trifluoroacetic acid (TFA) in chapter 3, whilst DigiElch 6.F software (BAS) was utilized to simulate the electrocrystallization of Cu₂TCNQF₄ on the surface of an electrode in acetonitrile (0.1 M Bu₄NPF₆) when reduction of TCNQF₄ occurs in the presence of Cu(MeCN)₄⁺ (chapter 4.4).

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Chapter 3

Redox and Acid–Base Chemistry of TCNQF₄ and TCNQ

3.1. Introduction

This chapter provides a comparison of the electrochemistry and acid–base properties of TCNQF₄, TCNQ as well as their radical monoanions and dianions. In acetonitrile, both TCNQF₄ and TCNQ can be reduced in two electrochemically and chemically reversible one-electron processes with the reversible formal potentials associated with the first and second processes for TCNQF₄ are 0.36 and 0.37 V more positive than those for TCNQ, respectively, i.e. TCNQF₄ is a much stronger acceptor than TCNQ. TCNQF₄ and TCNQ do not react with TFA, whilst their anions react with this acid with different vigor. For anions of both compounds, radical monoanions are protonated much weaker than dianions. Consequently, in the presence of TFA, the first reduction processes are not significantly affected, whilst the potentials associated with the second processes shift to more positive values markedly. The TCNQF₄^{•−}/TCNQ^{•−} radical monoanions react with proton to produce TCNQF₄/TCNQ and H₂TCNQF₄/H₂TCNQ. The TCNQF₄^{2−}/TCNQ^{2−} dianions can be sequentially protonated in two steps to form HTCNQF₄[−]/HTCNQ[−] and H₂TCNQF₄/H₂TCNQ. H₂TCNQF₄/H₂TCNQ are electroinactive in the potential range for the reductions of TCNQF₄/TCNQ to their mono- and dianions, whilst HTCNQF₄[−]/HTCNQ[−] are oxidized at the same potentials for the oxidations of TCNQF₄^{•−}/TCNQ^{•−}. A mechanism for the redox chemistry of TCNQF₄, TCNQ and their anions in acetonitrile in the presence of TFA have been proposed and supported by excellent agreements between experimental and simulated cyclic voltammograms.

Declaration for Thesis Chapter 3.2

Declaration by candidate

In the case of Chapter 3.2, the nature and extent of my contribution to the work was the following:

Nature of contribution	Extent of contribution (%)
Initiation, key ideas, experimental work, writing up	85

The following co-authors contributed to the work.

Name	Nature of contribution
Ayman Nafady	Initiation, key ideas, experimental work, writing up
Xiaohu Qu	Initiation, key ideas
Lisandra L. Martin	Initiation, key ideas, writing up
Alan M. Bond	Initiation, key ideas, writing up

Candidate's Signature

06/06/2012

Declaration by co-authors

The undersigned hereby certify that:

- (1) the above declaration correctly reflects the nature and extent of the candidate's contribution to this work, and the nature of the contribution of each of the co-authors.
- (2) they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;
- (3) they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
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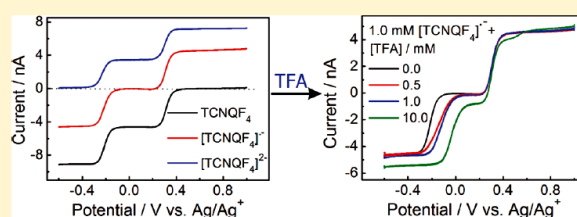
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Detailed Electrochemical Analysis of the Redox Chemistry of Tetrafluorotetracyanoquinodimethane TCNQF₄, the Radical Anion [TCNQF₄]^{•−}, and the Dianion [TCNQF₄]^{2−} in the Presence of Trifluoroacetic Acid

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ABSTRACT: The electrochemistry of 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (TCNQF₄), [TCNQF₄]^{•−}, and [TCNQF₄]^{2−} have been studied in acetonitrile (0.1 M [Bu₄N][ClO₄]). Transient and steady-state voltammetric techniques have been utilized to monitor the generation of [TCNQF₄]^{•−} and [TCNQF₄]^{2−} anions as well as their reactions with trifluoroacetic acid (TFA). In the absence of TFA, the reduction of TCNQF₄ occurs via two, diffusion controlled, chemically and electrochemically reversible, one-electron processes where the reversible formal potentials are 0.31 and −0.22 V vs Ag/Ag⁺. Unlike the TCNQ analogues, both [TCNQF₄]^{•−} and [TCNQF₄]^{2−} are persistent when generated via bulk electrolysis even under aerobic conditions. Voltammetric and UV–vis data revealed that although the parent TCNQF₄ does not react with TFA, the electrochemically generated radical anion and dianion undergo facile protonation to yield [HTCNQF₄][•], [HTCNQF₄][−] and H₂TCNQF₄ respectively. The voltammetry can be simulated to give a complete thermodynamic and kinetic description of the complex, coupled redox and acid–base chemistry. The data indicate dramatically different equilibrium and rate constants for the protonation of [TCNQF₄]^{•−} ($K_{\text{eq}} = 3.9 \times 10^{-6}$, $k_{\text{f}} = 1.0 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$) and [TCNQF₄]^{2−} ($K_{\text{eq}} = 3.0 \times 10^3$, $k_{\text{f}} = 1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) in the presence of TFA.



As a natural extension of widespread importance of 7,7,8,8-tetracyanoquinodimethane (TCNQ, Figure 1a) in various areas of chemistry, the tetrafluorinated derivative (TCNQF₄, Figure 1b) has attracted significant interest in recent years.^{1–4} The delocalized electronic structure, combined with the large electron-withdrawing effect of the fluorine atoms makes TCNQF₄ one of the strongest organic electron acceptors; the electron affinity of TCNQ is 2.88 eV whereas for TCNQF₄ it is ~3.28 eV.^{3,5} On the basis of these properties, TCNQF₄ has been widely utilized in organic light-emitting diodes to reduce the hole injection barrier by formation of a narrow space-charge region near the metal contact.⁶ Additionally, TCNQF₄ has been employed for preparation of new charge-transfer complexes either with organic electron donors⁷ or with metal ions.³ The most extensively studied charge-transfer systems so far are CuTCNQF₄ and AgTCNQF₄ semiconducting solids.^{3,8} The interest in these systems is driven by their optical and electrical bistable switching

properties as well as their potential applications in many fields such as sensors, catalysis, light-emitting diodes and field effect transistors.^{3,8}

Despite substantial efforts exploring the fundamental properties, such as conductivity, magnetism, and switching effects of TCNQF₄-based materials,^{3,6–8} studies on the effect of acid, i.e., proton transfer, on the redox chemistry of TCNQF₄ and its anions, [TCNQF₄]^{•−} and [TCNQF₄]^{2−}, are surprisingly rare. Previous studies of the acid effect and redox equilibria on compounds such as fullerene (C₆₀),^{9,10} quinones,^{11,12} TCNQ,¹³ and related redox polymer films¹⁴ have shown that the interplay of electron and proton transfer reactions is critical in controlling the redox chemistry, stability of radicals, and also the transitions between the insulating and conducting states in electroactive materials.¹⁴

In this paper, we report a detailed voltammetric investigation of TCNQF₄, [TCNQF₄]^{•−} and [TCNQF₄]^{2−} in the presence of acid. Anhydrous trifluoroacetic acid (TFA) was chosen as the proton source in order to avoid addition of water, which is known to affect the electrochemical behavior of quinone derivatives.¹⁵ Furthermore, the trifluoroacetate anion is not electroactive in the potential range of interest. A mechanism that accounts for the dependence of the voltammetry of TCNQF₄ and its reduced

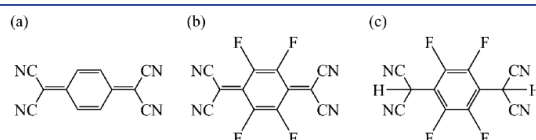


Figure 1. Molecular structures of (a) TCNQ, (b) TCNQF₄, and (c) H₂TCNQF₄.

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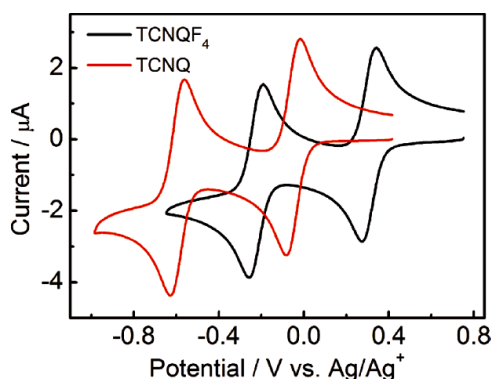


Figure 2. Cyclic voltammograms of 1.0 mM TCNQ and 1.0 mM TCNQF₄ in acetonitrile (0.1 M [Bu₄N][ClO₄]) obtained with a 1.0 mm diameter glassy carbon electrode at a scan rate of 100 mV s⁻¹.

forms on the concentration of TFA is proposed and supported by close agreement of simulated and experimental data.

In the absence of acid, both TCNQ and TCNQF₄ undergo two chemically and electrochemically reversible one-electron reduction processes under voltammetric conditions (Figure 2) when dissolved in acetonitrile (0.1 M [Bu₄N][ClO₄]) to give the processes summarized in eqs 1 and 2, where T = TCNQ or its fluorinated derivative, TCNQF₄. The reversible formal potentials (E_f^0) for [TCNQF₄]^{0/+•-} and [TCNQF₄]^{•-/2-} redox couples are 0.31 and -0.22 V vs Ag/Ag⁺, which are 0.36 and 0.37 V more positive, as expected for the strong electron withdrawing effect of fluorine atoms, than the corresponding couples of TCNQ with E_f^0 (1) = -0.05 and E_f^0 (2) = -0.59 V vs Ag/Ag⁺. However, in the presence of TFA, while the first reduction of TCNQF₄ to [TCNQF₄]^{•-} is affected very weakly, the second process [TCNQF₄]^{•-/2-} is modified and dependent on concentrations of TFA as well as TCNQF₄.



EXPERIMENTAL SECTION

Reagents and Procedures. TCNQ (Aldrich, 97%), TCNQF₄ (98%, Beijing Health), acetonitrile (HPLC grade, Omnisolv), and trifluoroacetic acid (TFA) were used as received from commercial sources. [Bu₄N][ClO₄] (Aldrich) was used as the supporting electrolyte and was recrystallized twice from 96% ethanol. The [TCNQF₄]^{•-} radical anion was prepared quantitatively by exhaustive bulk electrolysis (in a three-compartment cell described in more detail below) of a 1.0 mM solution of TCNQF₄ in acetonitrile (0.1 M [Bu₄N][ClO₄]) at an applied constant potential of 0.1 V vs Ag/Ag⁺. Quantitative conversion of the green [TCNQF₄]^{•-} solution to the colorless [TCNQF₄]²⁻ dianion was achieved by applying a more negative constant potential of -0.5 V vs Ag/Ag⁺.

Instrumentation. Electrochemical experiments were carried out at room temperature (22 ± 3 °C) in a drybox using an Epsilon (BAS) electrochemical workstation. A standard three-electrode cell configuration was used for cyclic and linear sweep voltammetric experiments. The working electrodes were 1.0 or 3.0 mm diameter glassy carbon (GC) macrodisc electrodes or a

12.0 μm diameter (determined using limiting current (i_L) magnitude in K₃[Fe(CN)₆] aqueous solution and relation $i_L = 4nFCDr$, where $n = 1$, F = Faraday constant, $C = [\text{Fe(CN)}_6]^{3-}$ concentration, D = diffusion coefficient, r = electrode radius) carbon fiber microelectrode (BAS, diameter quoted is 11 ± 2 μm). The Ag/Ag⁺ reference electrode (RE) was constructed from a Ag wire which was immersed in an acetonitrile containing 1.0 mM AgNO₃ and 0.1 M [Bu₄N][ClO₄] and separated from the test solution by a salt bridge containing CH₃CN (0.1 M [Bu₄N][ClO₄]). The potential of this RE is -0.14 V vs the ferrocene/ferrocenium (Fc^{0/+}) couple. The counter electrode was made of a Pt wire. For controlled potential electrolysis, a three-compartment cell was utilized with both the reference and counter electrodes being separated by a salt bridge from the test solution containing the working electrode. The Ag/Ag⁺ reference electrode was the same as that used in voltammetric studies, while the working and counter electrodes were both constructed from platinum mesh. UV-vis spectra were recorded in a 1.0 cm path length cuvette using a Varian Cary 5000 UV-vis-NIR spectrophotometer.

Simulation Software. DigiSim 3.03 distributed by BAS was used to simulate the experimental cyclic voltammograms.

RESULTS AND DISCUSSION

Voltammetry of TCNQF₄, [TCNQF₄]^{•-}, and [TCNQF₄]²⁻ in Acetonitrile. Transient cyclic voltammograms at a macroelectrode and near steady-state voltammograms obtained with a microelectrode for 1.0 mM TCNQF₄, [TCNQF₄]^{•-}, and [TCNQF₄]²⁻ in acetonitrile (0.1 M [Bu₄N][ClO₄]) are shown in Figure 3. TCNQF₄ and its anions each give rise to the expected

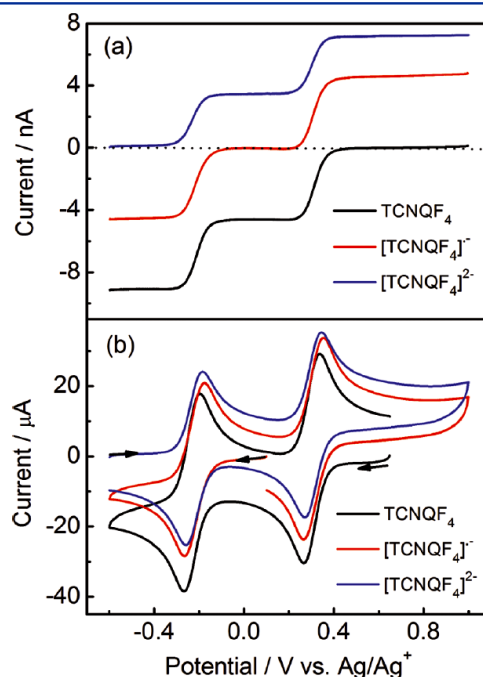


Figure 3. Voltammograms obtained from 1.0 mM TCNQF₄, [TCNQF₄]^{•-}, and [TCNQF₄]²⁻ in acetonitrile (0.1 M [Bu₄N][ClO₄]): (a) near steady-state voltammograms with a 12.0 μm diameter carbon fiber microdisc electrode ($\nu = 20 \text{ mV s}^{-1}$) and (b) transient cyclic voltammograms with a 3.0 mm diameter GC macrodisc electrode ($\nu = 100 \text{ mV s}^{-1}$).

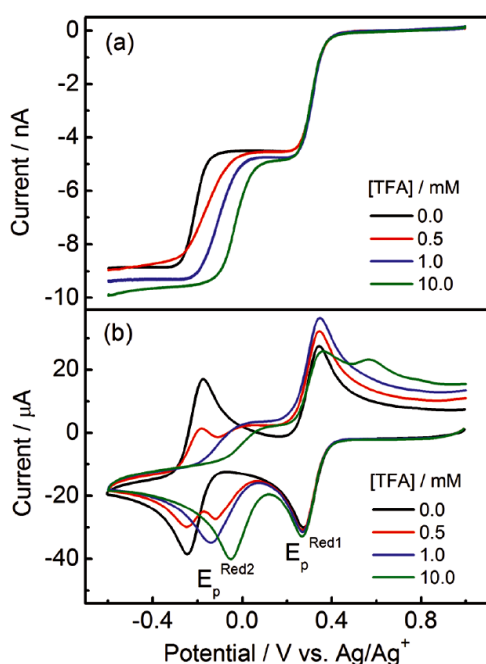


Figure 4. Voltammograms obtained from 1.0 mM TCNQF₄ in the presence of designated TFA concentrations: (a) near steady-state voltammograms with a 12.0 μ m diameter carbon fiber microelectrode ($\nu = 20$ mV s⁻¹) and (b) transient cyclic voltammograms with a 3.0 mm diameter GC electrode ($\nu = 100$ mV s⁻¹).

two electrochemically reversible one-electron processes. The half-wave potentials ($E_{1/2}$, where the current equals one-half of the limiting value in steady-state voltammetry, Figure 3a) or the midpoint potentials (E_m , calculated from the average of the reduction and oxidation peak potentials recorded under transient conditions) for TCNQF₄/[TCNQF₄]^{•-} and [TCNQF₄]^{•-}/[TCNQF₄]²⁻ redox couples are essentially identical, irrespective of initial redox state. Equating $E_{1/2}$ and E_m to the reversible formal potential (E_f^0) gives $E_f^0(1) = 0.31$ V and $E_f^0(2) = -0.22$ V vs Ag/Ag⁺, respectively, so that the formal potential separation $\Delta E_f^0 = E_f^0(1) - E_f^0(2) = 0.53$ V. From Figure 3a, it is also apparent on the basis of the magnitudes of the relevant limiting current values that the diffusion coefficients (D) for TCNQF₄ and [TCNQF₄]^{•-} are almost the same, but also both are substantially larger than that of [TCNQF₄]²⁻.

In order to ensure the lower limiting current value for [TCNQF₄]²⁻ is not an artifact arising from diffusion of either TCNQF₄ or [TCNQF₄]^{•-} into the counter or reference electrode compartments or from kinetic instability, [TCNQF₄]²⁻ was converted (oxidized) back to [TCNQF₄]^{•-} and then to neutral TCNQF₄ by applying a controlled potential of 0.1 and 0.5 V vs Ag/Ag⁺, respectively. The steady-state voltammograms obtained before and after reoxidation provided limiting currents that are almost identical (data not shown) confirms that [TCNQF₄]²⁻ has a significantly smaller diffusion coefficient than either TCNQF₄ or [TCNQF₄]^{•-}. An analogous phenomenon is also found for TCNQ and its anions with $D(\text{TCNQ}) \approx D(\text{TCNQ}^{\bullet-}) > D(\text{TCNQ}^{2-})$.¹⁶ The diffusion coefficients of TCNQF₄, [TCNQF₄]^{•-}, and [TCNQF₄]²⁻ calculated from cyclic and steady-state voltammograms shown in Figure 3 are 2.0×10^{-5} , 1.9×10^{-5} , and 1.5×10^{-5} cm² s⁻¹, respectively.

Voltammetry of TCNQF₄ and Its Anions in Acetonitrile after Addition of Trifluoroacetic Acid (TFA). The steady-state and transient voltammetry of TCNQF₄ as a function of TFA concentration give rise to current–potential plots presented in Figure 4. Addition of TFA does not modify the first [TCNQF₄]^{0/•-} reduction process; $E_{1/2}$ and E_m values are independent of TFA concentration and full reversibility is retained. In contrast, the peak currents and potentials ($E_{1/2}$ and E_m) for the second process [TCNQF₄]^{•-/2-} are dramatically changed. Thus, upon addition of 1.0 equiv of TFA, the $E_{1/2}$ value for the [TCNQF₄]^{•-/2-} reduction process shifts to more positive potentials as the concentration of TFA increases (Figure 4a). Under transient conditions, the process then loses its chemical reversibility in the presence of excess TFA and finally an irreversible oxidation process emerges at a more positive potential ($E_p^{\text{ox}} \sim 0.56$ V). The process at ~ 0.56 V presumably arises from the oxidation of the monoprotonated form of [TCNQF₄]²⁻ dianion. This behavior is characteristic of an electron transfer process (E step) coupled with proton transfer (C step) to give an (EC) mechanism.¹⁷ That is, [TCNQF₄]²⁻ dianions, generated by reduction of [TCNQF₄]^{•-} radical anions, rapidly react with the protons from TFA to give a protonated form(s) of the dianion. Clearly, upon an increase in the concentration of TFA from 0.0 to 10 mM, the $E_{1/2}$ value (steady-state) for the second process shifts by 184 mV in the positive direction from -215 to -31 mV vs Ag/Ag⁺ (Figure 4a). The corresponding changes in the transient (cyclic voltammetry) behavior are more complex, as the [TCNQF₄]^{•-/2-} process is replaced by an irreversible reduction process on addition of acid. Thus, probing of the reduction peak potential of the second process E_p^{red} (Figure 4b), rather than trying to determine its E_m values as a function of TFA concentration, becomes more relevant under these conditions. This potential shifts 196 mV to more positive potentials upon increasing the TFA concentration from 0.0 to 10.0 mM.

In order to gain additional insights into the protonation of the [TCNQF₄]²⁻ dianion, as implied by voltammetric investigations on reduction of TCNQF₄ in the presence of TFA, studies on [TCNQF₄]²⁻ in the bulk solution, involving direct protonation with TFA, were explored. The influence of TFA concentration on the voltammetric oxidation of [TCNQF₄]²⁻ is shown in Figure 5. The effect of adding acid differed distinctly from that found for the voltammetric reduction of TCNQF₄. Under steady-state conditions (Figure 5a), as the TFA concentration is increased, the limiting current for the [TCNQF₄]^{2-/•-} process ($E_{1/2} \sim -0.22$ V) now decreases dramatically. This is as expected if the [TCNQF₄]²⁻ anion is protonated, thereby lowering the concentration of [TCNQF₄]²⁻ in the bulk solution. The steady-state voltammetry at more positive potentials is now more complex, but ultimately the process in the [TCNQF₄]^{•-/0} region diminishes and is replaced by a new process at a more positive potential. Similarly, cyclic voltammetric studies conducted under transient voltammetric conditions imply that the [TCNQF₄]²⁻ concentration in bulk solution becomes smaller when the TFA concentration is increased, as the oxidation peak current I^{ox1} (at ~ -0.18 V) for [TCNQF₄]^{2-/•-} oxidation process decreases. In addition, the oxidation peak current I^{ox2} is enhanced when small TFA concentrations (up to 2.0 mM) are added and then decreases at higher TFA levels, with the emergence of process I^{ox3} .

These transient and steady-state voltammetric findings imply that the electrochemically generated [TCNQF₄]²⁻ dianion is most likely protonated in two steps to form [HTCNQF₄]⁻ and H₂TCNQF₄ (the probable structure of electroinactive

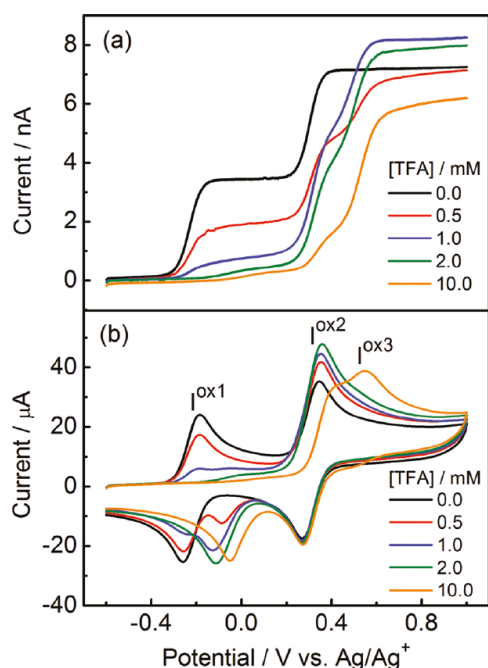


Figure 5. Voltammograms obtained from 1.0 mM $[\text{TCNQF}_4]^{2-}$ in acetonitrile (0.1 M $[\text{Bu}_4\text{N}][\text{ClO}_4]$) containing designated concentrations of TFA: (a) steady-state voltammograms with a 12.0 μm diameter carbon fiber microelectrode ($\nu = 20 \text{ mV s}^{-1}$) and (b) transient cyclic voltammograms with a 3.0 mm diameter GC electrode ($\nu = 100 \text{ mV s}^{-1}$).

H_2TCNQF_4 is given in Figure 1c,¹⁸ and this should be a very stable compound). These reactions are represented by eqs 3 and 4 where the equilibrium constant K_1 is much larger than K_2 , as reported in a study involving H_2TCNQF_4 with $\text{p}K_{\text{a}}$ values of H_2TCNQF_4 in N,N -dimethylformamide (DMF) are $\text{p}K_{\text{a}1} = 4.01$ and $\text{p}K_{\text{a}2} = 7.20$.¹⁸ Furthermore, $[\text{HTCNQF}_4]^-$ appears to be oxidized almost at the same potential as $[\text{TCNQF}_4]^{*-}$ is oxidized, whereas H_2TCNQF_4 apparently is significantly more difficult to oxidize than $[\text{HTCNQF}_4]^-$. Importantly, when the initial positive potential scan direction for $[\text{TCNQF}_4]^{2-}$ is switched at 1.0 V and scanned back in the negative direction, the generated voltammograms closely resemble those found in the case of parent TCNQF_4 with added TFA. This implies that $[\text{HTCNQF}_4]^-$ is oxidized to neutral TCNQF_4 and H^+ when the potential is sufficiently positive. The fact that the limiting current for steady-state voltammograms decreases (Figure 5a) when excess of TFA is added to $[\text{TCNQF}_4]^{2-}$ solution (even more pronounced when the TFA concentration in the solution is 100 mM, voltammogram not shown) implies that H_2TCNQF_4 is electroinactive at potentials up to +1.0 V vs Ag/Ag^+ .



For completeness and also in order to obtain further understanding of the reduction pathways, the influence of acid on the voltammetry of the $[\text{TCNQF}_4]^{*-}$ radical anion was studied.

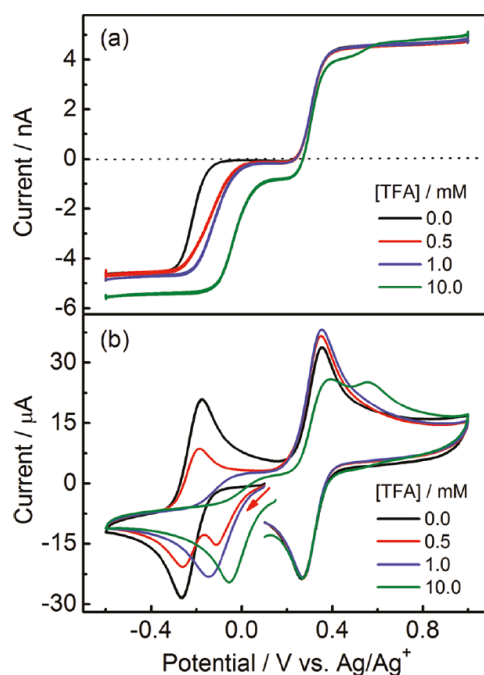


Figure 6. Voltammograms obtained from 1.0 mM $[\text{TCNQF}_4]^{*-}$ in acetonitrile (0.1 M $[\text{Bu}_4\text{N}][\text{ClO}_4]$) containing designated concentrations of TFA: (a) steady-state voltammograms with a 12.0 μm diameter carbon fiber microelectrode ($\nu = 20 \text{ mV s}^{-1}$) and (b) transient cyclic voltammograms with a 3.0 mm diameter GC electrode ($\nu = 100 \text{ mV s}^{-1}$).

Results are displayed in Figure 6. In the steady-state case outcome obtained with a microelectrode (Figure 6a) and in the absence of TFA, the zero current lies midway between the positive current for the $[\text{TCNQF}_4]^{*-/0}$ oxidation and the negative current for the $[\text{TCNQF}_4]^{*-/2-}$ reduction process. However, significantly, the current between the two major processes is no longer zero and becomes negative when a significant amount of acid is present. In addition, when an excess of TFA is present, the total limiting current for the process with $E_{1/2}$ at 0.31 V increases. All these observations imply that the concentration of neutral TCNQF_4 in bulk solution has increased when increasing the concentration of acid. The most likely scenario is that $[\text{TCNQF}_4]^{*-}$ radical anions react with protons to produce TCNQF_4 and H_2TCNQF_4 (eq 5), which parallels the reaction of $[\text{TCNQ}]^{*-}$ radical anions with protons.^{13,19} This is supported by the detection of TCNQF_4 under these conditions by UV-vis spectra (vide infra). Since neutral TCNQF_4 is only detected when an excess of TFA (5 equiv) was added to $[\text{TCNQF}_4]^{*-}$, it can be assumed that the equilibrium constant (K_3) for the reaction given in eq 5 is relatively small.

Transient cyclic voltammograms for 1.0 mM $[\text{TCNQF}_4]^{*-}$ resemble those for TCNQF_4 and $[\text{TCNQF}_4]^{2-}$ when TFA is present at the same concentrations (compare Figures 6b with 4b and 5b). This highlights differences in the steady-state condition, where bulk solution concentrations are very important, compared with transient technique, where the concentrations of species at the electrode surface dominate the outcome.



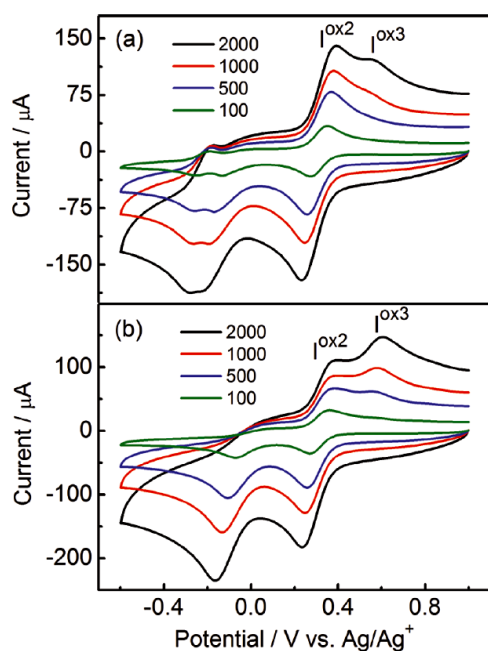


Figure 7. Cyclic voltammograms obtained from 1.0 mM TCNQF₄ in the presence of (a) 0.5 mM and (b) 5.0 mM TFA in acetonitrile (0.1 M [Bu₄N][ClO₄]) with a 3.0 mm diameter GC electrode at designated scan rates (mV s⁻¹).

Scan Rate and TCNQF₄ Concentration Effects under Transient Cyclic Voltammetric Conditions. Figure 7 provides examples of transient cyclic voltammograms of 1.0 mM TCNQF₄ in acetonitrile (0.1 M [Bu₄N][ClO₄]) in the presence of 0.5 or 5.0 mM TFA. As the scan rate is increased, oxidation process $I^{\text{ox}3}$ at ~ 0.56 V emerges at scan rates ≥ 1.0 V s⁻¹ (Figure 7a). As the concentration of TFA is increased to 5.0 mM, process $I^{\text{ox}3}$ is even detected at much slower scan rates ($\nu \geq 0.5$ V s⁻¹) (Figure 7b) and its peak current magnitude is increased relative to that for process $I^{\text{ox}2}$ (~ 0.34 V). This behavior implies that oxidation process $I^{\text{ox}2}$ is followed by both electrochemical and chemical reactions. Plausibly, after oxidation of [HTCNQF₄]⁻ to [HTCNQF₄][•] ($I^{\text{ox}2}$ process), [HTCNQF₄][•] can be further oxidized to [HTCNQF₄]⁺ ($I^{\text{ox}3}$ process) or deprotonated to form [TCNQF₄]^{•-} and H⁺, the latter process being more dominant at slower scan rates, while the former dominates at higher scan rates. The hypothesis that the deprotonation of [HTCNQF₄][•] occurs is supported by noting the increase in the peak current of $I^{\text{ox}3}$ when the [TFA]/[TCNQF₄] concentration ratio is increased (see Figures 7a, b). In other words, formation of [HTCNQF₄][•] and its oxidation is favored by the higher acid concentrations.

Cyclic voltammetry in the presence of TFA was also explored as a function of the TCNQF₄ concentration. Thus, Figure 8 provides results when the TFA concentration was kept constant at 1.0 mM, while the TCNQF₄ concentration was varied from 0.5 to 5.0 mM. These experiments lead to the conclusion that three reduction processes are only observed when the ratio of [TFA]/[TCNQF₄] is <1, as also observed in Figure 7a. These data further support the hypothesis that the protonation of [TCNQF₄]²⁻ to form [HTCNQF₄]⁻ is strongly favored.

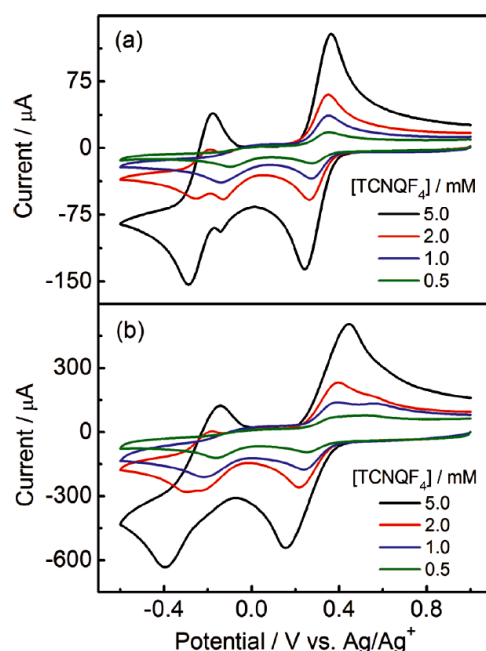


Figure 8. Cyclic voltammograms obtained in acetonitrile (0.1 M [Bu₄N][ClO₄]) containing 1.0 mM TFA and designated concentrations of TCNQF₄ with a 3.0 mm diameter GC electrode at scan rate of (a) 100 and (b) 2000 mV s⁻¹.

UV–Visible Spectra of TCNQF₄, [TCNQF₄]^{•-}, and [TCNQF₄]²⁻ in the Absence and Presence of TFA. The UV–vis spectrophotometric technique was also used to explore the reactivity of TCNQF₄ and the reduced anions [TCNQF₄]^{•-} and [TCNQF₄]²⁻ with TFA under the same conditions used for voltammetry. Thus, acetonitrile (0.1 M [Bu₄N][ClO₄]) solutions containing 1.0 mM TCNQF₄, [TCNQF₄]^{•-}, or [TCNQF₄]²⁻ without and with TFA were prepared as for the electrochemical experiments. However, with this technique, the concentrations of TCNQF₄, [TCNQF₄]^{•-}, and [TCNQF₄]²⁻ in solutions had to be diluted to 0.02 mM in order to measure their UV–vis spectra. Inspection of these results (Figure 9) reveals that the UV–vis spectra of TCNQF₄ solutions are not affected by TFA. In contrast, UV–vis spectra for [TCNQF₄]^{•-} and [TCNQF₄]²⁻ containing solutions are function of TFA concentration. For [TCNQF₄]^{•-}, when the TFA concentration is raised, the absorbances of the bands with λ_{max} at 411, 686, and 752 nm^{20–22} decrease, while two new bands appear at 386 and 365 nm, which correspond to the formation of neutral TCNQF₄. This confirms a conclusion from the voltammetric studies that [TCNQF₄]^{•-} reacts with TFA to form TCNQF₄ and H₂TCNQF₄. Again, in agreement with the voltammetric results, the quantity of [TCNQF₄]^{•-} converted to TCNQF₄ is small when the concentration of TFA is less than 10 mM. The [TCNQF₄]²⁻ dianion exhibits a well-defined band with λ_{max} at 333 nm.²¹ The absorbance of this band decreases upon increasing the TFA concentration, confirming that the [TCNQF₄]²⁻ concentration also decreases in the higher TFA concentration range. When a large excess of TFA is present, a new absorbance band with λ_{max} at 278 nm appears and then increases upon further addition of TFA (see Figure 9c). Since the UV–vis spectrum of H₂TCNQ in acetonitrile has a value λ_{max} at 270 nm,¹³ the 278 nm band is assigned to the generation of H₂TCNQF₄. In addition, the extinction

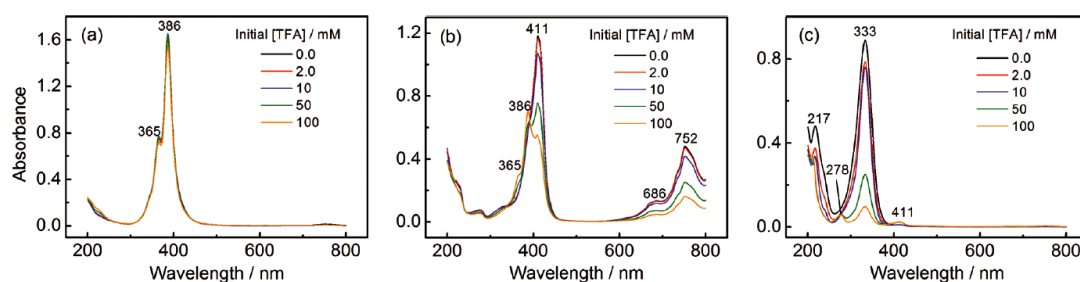


Figure 9. UV-vis spectra obtained after addition of designated TFA concentrations to 1.0 mM (a) TCNQF₄, (b) [TCNQF₄]^{•−}, (c) [TCNQF₄]^{2−} in acetonitrile (0.1 M [Bu₄N][ClO₄]) followed by a 50-fold dilution to provide 0.02 mM TCNQF₄, [TCNQF₄]^{•−}, or [TCNQF₄]^{2−} solutions.

Table 1. Parameters ^a Used to Simulate the Mechanism (Equations 6–15) Proposed to Describe the Voltammetry of TCNQF₄ and Its Anions [TCNQF₄]^{•−} and [TCNQF₄]^{2−} in Acetonitrile (0.1 M [Bu₄N][ClO₄]) Solutions in the Presence of TFA ^b

reaction	E^0/V	$k_s/(\text{cm s}^{-1})$	K_{eq}	$k_t/(\text{M}^{-1} \text{s}^{-1})$
1 $T + e = T^{•−}$	0.305	0.1 ^c		
2 $T^{•−} + e = T^{2−}$	−0.220	0.1 ^c		
3 $T^{•−} + HA = HT^{•} + A^{−}$			3.9×10^{-6} ^d	1×10^{-3}
4 $HT^{•} + HT^{•} = H_2T + T$			2.1×10^5 ^d	1×10^7 ^c
5 $T^{2−} + HA = HT^{−} + A^{−}$			3×10^3	1×10^{10} ^c
6 $T^{2−} + H_2T = HT^{−} + HT^{•}$			3×10^3 ^d	1×10^{10} ^c
7 $HT^{−} + HA = H_2T + A^{−}$			1.0	1×10^7 ^c
8 $HT^{−} = HT^{•} + e$	0.30	0.1 ^c		
9 $HT^{•} = HT^{+} + e$	0.50	0.1 ^c		
10 $HT^{+} + A^{−} = T + HA$			5.5×10^8 ^d	1×10^5 ^c

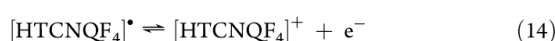
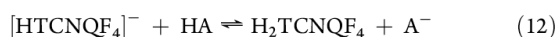
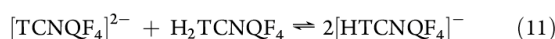
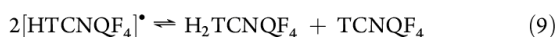
^aThe parameters used in the simulation are $\alpha = 0.50$, $T = 295$ K, $D(\text{TCNQF}_4) = 2.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $D([\text{TCNQF}_4]^{•−}) = 1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $D([\text{TCNQF}_4]^{2−}) = 1.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$; $D(\text{HA}) = D(A^{−}) = 3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$; area of electrode = 0.075 cm²; $R_s = 150 \Omega$.

^b $T = \text{TCNQF}_4$ and all potentials are versus Ag/Ag⁺. ^cSome parameters may be modified slightly from tabular values to provide enhanced agreement between experimental and simulated cyclic voltammograms. Thus, k_s values of 0.1 cm s^{−1} for the electron transfer rate imply that this reaction is reversible. In addition, simulations are not sensitive to this parameter in the sense that use of larger k_s values result in a very minor influence on simulations. k_t values need to be very fast but should not exceed value for diffusion control of about $10^{10} \text{ M}^{-1} \text{ s}^{-1}$. Furthermore, $C_{dl} = 2 \times 10^{-5} \text{ F}$ is used for the TCNQF₄ simulation and $1 \times 10^{-5} \text{ F}$ for simulations of the voltammetry of [TCNQF₄]^{•−} and [TCNQF₄]^{2−}. DigiSim requires C_{dl} to be independent of potential. In practice, this parameter varies with potential and hence simulated and experimental data may differ because of this limitation. ^dValue automatically determined by DigiSim software from other input parameters (thermodynamically related data).

coefficient of the band at 270 nm for H₂TCNQ is ~200-fold smaller than that for TCNQ at 395 nm¹³ explains the very weak absorbance intensity observed at 278 nm even when a large excess of TFA has been added into the [TCNQF₄]^{2−} solution.

Simulation of the Voltammetry of TCNQF₄ and Its Anions in the Presence of TFA. All voltammetric and UV-vis data lead to the following conclusions: (i) neutral TCNQF₄ does not react with TFA, (ii) the [TCNQF₄]^{•−} radical anion reacts with TFA to form TCNQF₄ and H₂TCNQF₄, (iii) the

[TCNQF₄]^{2−} dianion can be protonated in two sequential steps to give [HTCNQF₄][−] and H₂TCNQF₄ with the equilibrium constant for the first protonation step being much larger than that for the second, (iv) the [HTCNQF₄][−] protonated anion is oxidized to [HTCNQF₄][•] at a potential coincident with that where [TCNQF₄]^{•−} is oxidized, (v) [HTCNQF₄][•] generated radicals are further oxidized to transiently form [HTCNQF₄]⁺ or deprotonate to yield [TCNQF₄]^{•−} and H⁺. On the basis of all these findings, a mechanism for voltammetry of TCNQF₄ and its anions is postulated to occur via the reactions given in eqs 6–15.



where HA and A[−] represent TFA and CF₃COO[−], respectively, and noting that since TFA is a weak acid in acetonitrile (pK_a = 12.7)²³ that the H⁺ concentration from this source is very low.

This mechanism was supported by simulations of cyclic voltammograms obtained for the TCNQF₄, [TCNQF₄]^{•−} radical anion, and [TCNQF₄]^{2−} dianion over a range of concentrations and scan rates. Use of simulation parameters provided in Table 1 and the caption to Figure 10 allowed very good agreement between experiment and theory to be achieved. The usual concern that accompanies simulations involving many steps applies in this case. That is, it is very difficult to be absolutely sure that a unique set of parameters have been chosen to fit all the experimental data. Furthermore, thermodynamically allowed cross redox reactions and other complexities could have been added. However, despite these limitations, the

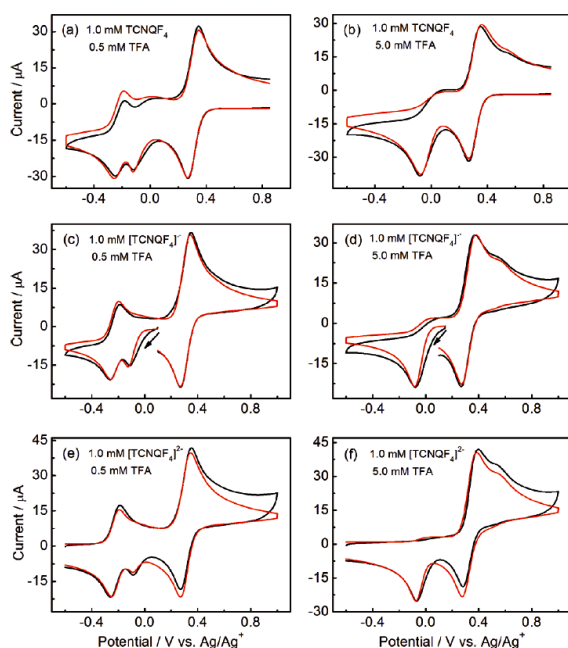


Figure 10. Comparison of simulated (red line) and experimental (black line) cyclic voltammograms obtained with a 3.0 mm diameter GC electrode at a scan rate of 100 mV s^{-1} for (a, b) 1.0 mM TCNQF_4 , (c, d) $1.0 \text{ mM [TCNQF}_4\text{]}^{\bullet-}$ and (e, f) $1.0 \text{ mM [TCNQF}_4\text{]}^{2-}$ in acetonitrile ($0.1 \text{ M [Bu}_4\text{N][ClO}_4\text{]}$) containing 0.5 or 5.0 mM TFA.

simulation–experimental correlation is very good and provides support that the basic features of the mechanism postulated are correct. Importantly, these simulations allowed the estimation of the protonation rate and equilibrium constants for both $[\text{TCNQF}_4]^{\bullet-}$ radical anion and $[\text{TCNQF}_4]^{2-}$ dianion.

CONCLUSIONS

The electrochemical reduction of TCNQF_4 in acetonitrile ($0.1 \text{ M [Bu}_4\text{N][ClO}_4\text{]}$) in the absence and the presence of TFA has been explored. Voltammetric as well as UV–vis data have shown that TCNQF_4 as well as the radical anion $[\text{TCNQF}_4]^{\bullet-}$ and dianion $[\text{TCNQF}_4]^{2-}$ are stable and do not rapidly decompose upon exposure to air. In the absence of acid, the reduction of TCNQF_4 takes place via two well resolved diffusion controlled, chemically and electrochemically reversible, one-electron processes. The E_f^0 values for the $[\text{TCNQF}_4]^{0/\bullet-}$ and $[\text{TCNQF}_4]^{\bullet-/2-}$ redox couples are 0.31 and -0.22 V vs Ag/Ag^+ , respectively, which are 0.36 and 0.37 V more positive than found for the corresponding TCNQ couples.

In the presence of TFA, TCNQF_4 is inert but its radical anion and dianion afford protonated species identified as $[\text{HTCNQF}_4]^{\bullet}$, $[\text{HTCNQF}_4]^-$, and H_2TCNQF_4 . Formation of these protonated species is assumed to occur via a sequence of electron and coupled proton transfer reactions. Simulations support the mechanism postulated to describe the voltammetric behavior of TCNQF_4 , $[\text{TCNQF}_4]^{\bullet-}$, and $[\text{TCNQF}_4]^{2-}$ in the presence of TFA and demonstrate a significant redox level dependence on the equilibrium and rate constants. Thus, the rate and equilibrium constants proposed for the protonation of the dianion $[\text{TCNQF}_4]^{2-}$ to $[\text{HTCNQF}_4]^-$ are significantly higher than that for protonation of $[\text{TCNQF}_4]^{\bullet-}$. Importantly, the substantial kinetic and thermodynamic stabilization of the reduced forms

of TCNQF_4 relative to that found in the case of TCNQ is a consequence of the electron-withdrawing effect of the fluorine atoms in the quinone ring.

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Declaration for Thesis Chapter 3.3

Declaration by candidate

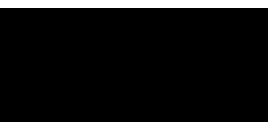
In the case of Chapter 3.3, the nature and extent of my contribution to the work was the following:

Nature of contribution	Extent of contribution (%)
Initiation, key ideas, experimental work, simulation, writing up	75

The following co-authors contributed to the work.

Name	Nature of contribution
Ayman Nafady	Initiation, key ideas, experimental work, writing up
Xiaohu Qu	Initiation, key ideas, experimental work, writing up
Lisandra L. Martin	Initiation, key ideas, writing up
Alan M. Bond	Initiation, key ideas, writing up

Candidate's Signature

	06/06/2012
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Declaration by co-authors

The undersigned hereby certify that:

- (1) the above declaration correctly reflects the nature and extent of the candidate's contribution to this work, and the nature of the contribution of each of the co-authors.
- (2) they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;
- (3) they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
- (4) there are no other authors of the publication according to these criteria;
- (5) potential conflicts of interest have been disclosed to (a) granting bodies, (b) the editor or publisher of journals or other publications, and (c) the head of the responsible academic unit; and
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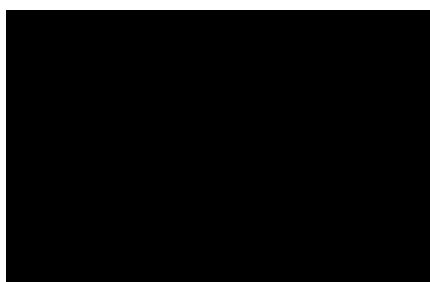
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Redox and Acid–Base Chemistry of 7,7,8,8-Tetracyanoquinodimethane, 7,7,8,8-Tetracyanoquinodimethane Radical Anion, 7,7,8,8-Tetracyanoquinodimethane Dianion, and Dihydro-7,7,8,8-Tetracyanoquinodimethane in Acetonitrile

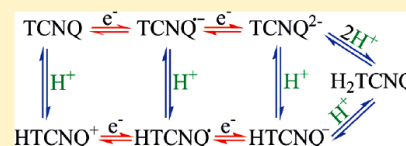
Thanh Hai Le, Ayman Nafady, Xiaohu Qu, Alan M. Bond,* and Lisandra L. Martin*

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S *Supporting Information*

ABSTRACT: The chemistry and electrochemistry of TCNQ (7,7,8,8-tetracyanoquinodimethane), $\text{TCNQ}^{\bullet-}$, TCNQ^{2-} , and H_2TCNQ in acetonitrile (0.1 M Bu_4NPF_6) solution containing trifluoroacetic acid (TFA) has been studied by transient and steady-state voltammetric methods with the interrelationship between the redox and the acid–base chemistry being supported by simulations of the cyclic voltammograms. In the absence of acid, TCNQ and its anions undergo two electrochemically and chemically reversible one-electron processes.

However, in the presence of TFA, the voltammetry is considerably more complex. The TCNQ^{2-} dianion is protonated to form HTCNQ^- , which is oxidized to $\text{HTCNQ}^\bullet$, and H_2TCNQ which is electroinactive over the potential range of -1.0 to $+1.0$ V versus Ag/Ag^+ . The monoreduced $\text{TCNQ}^{\bullet-}$ radical anion is weakly protonated to give $\text{HTCNQ}^\bullet$, which disproportionates to TCNQ and H_2TCNQ . In acetonitrile, H_2TCNQ deprotonates slowly, whereas in *N,N*-dimethylformamide or tetrahydrofuran, rapid deprotonation occurs to yield HTCNQ^- as the major species. H_2TCNQ is fully deprotonated to the TCNQ^{2-} dianion in the presence of an excess concentration of the weak base, CH_3COOLi . Differences in the redox and acid-base chemistry relative to the fluorinated derivative TCNQF_4 are discussed in terms of structural and electronic factors.



Molecular materials based on TCNQ (TCNQ = 7,7,8,8-tetracyanoquinodimethane) or its derivatives, such as TCNQF₄, TCNQCl₂, and TCNQBr₂, are of considerable current interest due to their intriguing structural, physical, and chemical properties.^{1–5} In this context, a great deal of research effort has been directed toward the development of new synthetic routes and methodologies that could provide precise control of conductivity, magnetism, and electronic properties.^{6–8} In spite of the remarkable progress in this area, very little attention has been paid to fundamentally important properties such as the effect of acid (proton-transfer) on the redox chemistry and stability of TCNQ and its anions, TCNQ^{•−} and TCNQ^{2−} (structures given in Figure 1a–c), since the initial work of Yamagishi and co-workers in the 1970s.^{9–11} In these pioneering studies, the kinetics of protonation of TCNQ^{•−} in the presence of HCl in water and organic solvents such as methanol, ethanol, and acetonitrile were reported.^{9–11} The rate of protonation was found to be first order in HCl and second order in the TCNQ^{•−} radical anion in methanol, whereas in acetonitrile, which is the solvent relevant to the present study, it deviates from second order with respect to the anion.⁹ These kinetics were explained in terms of the rapid formation of HTCNQ[•] species (TCNQ^{•−} + H⁺ ⇌ HTCNQ[•]). This and related studies on TCNQ-based redox polymers^{12,13} have revealed that the interplay of electron- and proton-transfer reactions is crucial to control the redox chemistry and stability of generated anions.

The importance of protonation of the dianionic species TCNQ^{2-} has been more difficult to establish than is the case with the monoanion since it rapidly decomposes into α,α -dicyano-*p*-toluoylcyanide (DCTC⁻, Figure 1e) in the presence of atmospheric oxygen.^{14,15} The challenge to generate a persistent solution of TCNQ^{2-} has hampered research efforts on this dianion in a new generation of TCNQ-based network polymers. However, elegant work by the Robson group^{16,17} has shown that air-stable H_2TCNQ (structure d in Figure 1) provides a facile route to the dianion. The strategy is to use in situ deprotonation of H_2TCNQ in the presence of the desired metal ions to give robust TCNQ^{2-} -based materials. Through this approach, a wide range of TCNQ-based coordination polymers containing $[\text{M}^{2+}(\text{TCNQ}^{2-})]$ ($\text{M}^{2+} = \text{Mn}^{2+}$, Fe^{2+} , Co^{2+} , Zn^{2+} , and Cd^{2+}) sheets in three-dimensional (3D) network arrangements, having unusual and potentially useful structural properties, have been synthesized.

Following our recent studies on the effect of trifluoroacetic acid (TFA) on the tetrafluoro, TCNQF_4 ($\text{TCNQF}_4 = 2,3,5,6$ -tetrafluoro-7,7,8,8-tetracyanoquinodimethane), and its anions in acetonitrile (0.1 M Bu_4NClO_4),¹⁸ where TCNQF_4^{2-} is air-stable, we have now undertaken a detailed voltammetric study on TCNQ , H_2TCNQ , and electrochemically generated $\text{TCNQ}^{\cdot-}$, TCNQ^{2-} anions under drybox conditions. A

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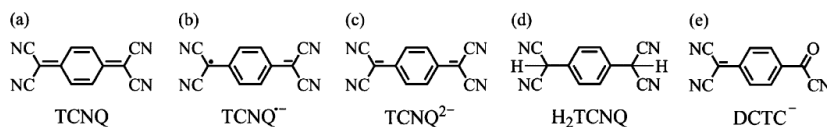


Figure 1. Molecular structures of (a) TCNQ, (b) TCNQ^{•-}, (c) TCNQ²⁻, (d) H₂TCNQ, and (e) DCTC⁻.

mechanism that takes into account the effects of protonation on the above-mentioned TCNQ species has been proposed and is supported by digital simulations. The thermodynamic and kinetic parameters associated with the redox couples and acid–base equilibria are compared with those reported for the TCNQF₄ analogues. Interesting differences in reactivity with protons are detected and explained in terms of the electronic and structural differences between TCNQ and TCNQF₄.^{18–20}

EXPERIMENTAL SECTION

Chemicals. TCNQ (98%, Aldrich) was recrystallized from hot acetonitrile prior to use. Acetonitrile (HPLC grade, Omnisolv), ferrocene (Merck, >98%), *N,N*-dimethylformamide (DMF) (>99.9%, Aldrich), tetrahydrofuran (THF) (extra pure, Merck), acetone (Suprasolv, Merck), and trifluoroacetic acid (99.0%, Aldrich) were used as received from the manufacturers. H₂TCNQ and LiTCNQ were synthesized via literature methods.^{1,21} Bu₄NPF₆ (Aldrich), used as the supporting electrolyte, was recrystallized twice from 96% ethanol (Merck) and then dried at 100 °C under vacuum for 24 h. The 1.0 mM TCNQ^{•-} solution was prepared quantitatively by exhaustive bulk electrolysis of a 1.0 mM solution of TCNQ in acetonitrile (0.1 M Bu₄NPF₆) in a three-compartment electrochemical cell using a platinum gauze working electrode at a constant potential of –300 mV versus Ag/Ag⁺. Electrolysis was terminated when the final current reached 0.1% of the initial value. The 1.0 mM solution of the TCNQ²⁻ dianion in acetonitrile was prepared in the same electrochemical cell by reduction of 1.0 mM TCNQ^{•-} in acetonitrile containing 0.1 M Bu₄NPF₆ supporting electrolyte at a potential of –800 mV versus Ag/Ag⁺ until the current again decayed to 0.1% of the initial value. Aqueous solutions were prepared from water that had been purified (resistivity of 18.2 MΩ cm) by a Sartorius Arium 611 system (Sartorius, Germany).

Instrumentation. Voltammetric experiments were carried out at room temperature (22 ± 2 °C) in a drybox using a Bioanalytical System (BAS) Epsilon electrochemical workstation with a standard three-electrode cell configuration. The working electrodes (BAS) were 1.0 mm diameter (determined area = 0.0081 cm²) glassy carbon (GC) and 1.6 mm diameter gold macrodisc electrodes, 10.0 μm diameter Pt or 12.0 μm diameter carbon fiber microelectrodes. The area of the macrodisc GC electrode was determined from peak currents derived from cyclic voltammograms of a 1.0 mM K₃[Fe(CN)₆] aqueous solution (1.0 M KCl) obtained at different scan rates using the Randles–Sevcik relationship, and the diameters of the microelectrodes were determined as described elsewhere.¹⁸ The Ag/Ag⁺ reference electrode was constructed from Ag wire immersed in an acetonitrile solution containing 1.0 mM AgNO₃ and 0.1 M Bu₄NPF₆ and separated from the test solution by a glass frit. The potential of this reference electrode is –135 ± 5 mV versus the ferrocene/ferrocenium (Fc^{0/+}) couple. The counter electrode was made of a platinum wire (1.0 mm diameter). Working electrodes were polished with 0.3 μm alumina slurry on a Microcloth polishing cloth, washed with

water, and then sonicated in an ultrasonic bath for 1 min before being used for voltammetric experiments. In the case of bulk electrolysis experiments, an “H-type” three-compartment cell separated by fine frits was used to minimize cathode and anode solution mixing. Platinum baskets were employed as the working and counter electrodes along with a Ag/Ag⁺ reference electrode.

UV–vis spectra were recorded in a 1.0 cm path length cuvette using a Varian Cary 5000 UV–vis–NIR spectrophotometer. DigiSim 3.03 (BAS) software was used to simulate voltammograms.

RESULTS AND DISCUSSION

Voltammetry of TCNQ and its Anions (TCNQ^{•-} and TCNQ²⁻) in Acetonitrile (0.1 M Bu₄NPF₆). Transient cyclic voltammograms for 1.0 mM TCNQ and near-steady-state voltammograms for 1.0 mM solutions of TCNQ, TCNQ^{•-}, and TCNQ²⁻ in acetonitrile (0.1 M Bu₄NPF₆) are shown in Figure 2. As expected, TCNQ, in each of its redox levels,

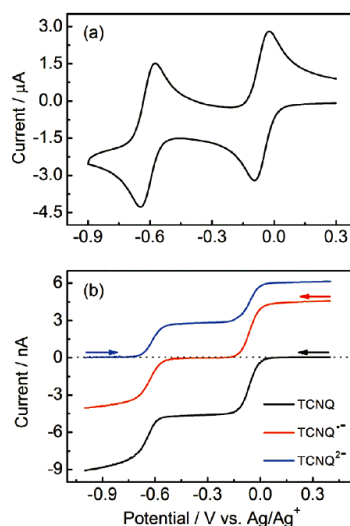


Figure 2. Voltammograms in acetonitrile (0.1 M Bu₄NPF₆): (a) cyclic voltammetry for reduction of 1.0 mM TCNQ at a 1.0 mm diameter GC electrode using a scan rate of 100 mV s⁻¹; (b) near-steady-state voltammograms for reduction of 1.0 mM TCNQ, reduction and oxidation of 1.0 mM TCNQ^{•-}, and oxidation of 1.0 mM TCNQ²⁻ at a 12.0 μm diameter carbon fiber microelectrode using a scan rate of 20 mV s⁻¹.

exhibits two reversible one-electron processes.^{22,23} The midpoint potentials E_m , which are derived from the average of the reduction and oxidation peak potentials, $(E_p^{\text{red}} + E_p^{\text{ox}})/2$, are –60 and –610 mV versus Ag/Ag⁺, respectively, for the TCNQ^{0/•-} and TCNQ^{•-/2-} redox processes (eqs 1 and 2). E_m is approximately equal to the reversible formal potential E_f^0 . The separation (ΔE_m) of 550 mV is in excellent agreement

Table 1. Diffusion Coefficient Values ($\text{cm}^2 \text{s}^{-1}$) Reported in the Literature for TCNQ, $\text{TCNQ}^{\bullet-}$, and TCNQ^{2-} in Acetonitrile

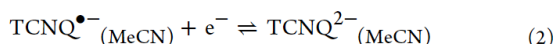
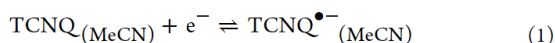
reference	present work ^a	ref 25 ^b	ref 26 ^b	ref 23 ^c	ref 27 ^b	ref 28 ^d	ref 29 ^e
TCNQ/ 10^{-5}	1.9	2.0	1.98	1.8	1.66	1.6 ± 0.2	1.44
$\text{TCNQ}^{\bullet-}/10^{-5}$	1.7	1.6	<i>f</i>	<i>f</i>	1.47	1.4 ± 0.2	1.35
$\text{TCNQ}^{2-}/10^{-5}$	1.2	<i>f</i>	<i>f</i>	<i>f</i>	1.05	<i>f</i>	0.91

^aDetermined as described in the section entitled Voltammetry of TCNQ and Its Anions ($\text{TCNQ}^{\bullet-}$ and TCNQ^{2-}) in Acetonitrile (0.1 M Bu_4NPF_6) in the Presence of Trifluoroacetic Acid. ^bDetermined from limiting currents obtained with microelectrodes. ^cDetermined from limiting current derived from a channel flow cell voltammogram. ^dDetermined from transient voltammetric peak currents using the Randles–Sevcik relationship. ^e D for TCNQ was determined using single-potential-step chronoamperometry, whereas values of D for $\text{TCNQ}^{\bullet-}$ and TCNQ^{2-} relative to TCNQ were deduced from normal pulse voltammetry. ^fNo value reported.

with other studies,^{22,24} while the absolute E_m values are in reasonable agreement.

Inspection of the limiting currents in Figure 2b reveals that the magnitude derived from neutral TCNQ is slightly larger than that from $\text{TCNQ}^{\bullet-}$ and almost 1.6 times larger than when TCNQ^{2-} is present in the bulk solution. This behavior implies that the diffusion coefficients of TCNQ and $\text{TCNQ}^{\bullet-}$ are similar to each other, but significantly larger than that for TCNQ^{2-} . In order to ensure the smaller limiting current value for the dianion is not an artifact related to decomposition, TCNQ^{2-} was oxidized back to $\text{TCNQ}^{\bullet-}$ and then TCNQ. Limiting currents derived from steady-state voltammograms for TCNQ obtained before and after back-oxidation agree within 2%, confirming that the lower limiting current for TCNQ^{2-} arises from the smaller diffusion coefficient for this species.

The diffusion coefficient (D) values of TCNQ, $\text{TCNQ}^{\bullet-}$, and TCNQ^{2-} , calculated from transient voltammogram using the Randles–Sevcik relationship $i_p = 0.4463nFAC(nFvD/RT)^{1/2}$ and near-steady-state voltammogram using the equation $i_L = 2nFdCD$ (where i_p and i_L are peak and limiting currents, respectively, $n = 1$, F = Faraday constant, A = area of macroelectrode, C = analyte concentration, v = scan rate, R = universal gas constant, T = temperature (K), d = microelectrode diameter), are summarized in Table 1. In this study, D values obtained by both methods agree to two significant figures, but D values for TCNQ, $\text{TCNQ}^{\bullet-}$, and TCNQ^{2-} vary and appear to be highly sensitive to experimental conditions (electrolyte, TCNQ purity, electrode, method or electrode dimension calibration, voltammetric technique, and temperature), so variation over a range of 25% is evident in data summarized in Table 1.



Voltammetry for TCNQ and Its Anions in Acetonitrile (0.1 M Bu_4NPF_6) in the Presence of Trifluoroacetic Acid.

The addition of TFA strongly influences the transient and near-steady-state voltammeters for TCNQ and its anions, but in a distinctly different manner (see Figure 3). In the steady-state voltammogram obtained when neutral TCNQ is present in the bulk solution, the half-wave potential $E_{1/2}^1$ (potential where the current equals half the limiting value) associated with the first reduction of TCNQ to $\text{TCNQ}^{\bullet-}$ is almost unaffected by the presence of TFA, whereas $E_{1/2}^2$ for the second $\text{TCNQ}^{\bullet-}/2-$ process is shifted by 235 mV in the positive direction (from -615 to -380 mV) upon addition of 5.0 mM TFA (Figure 3a). The large positive shift of $E_{1/2}^2$ implies that TCNQ^{2-} is strongly protonated by TFA.^{18,30} The virtual independence of $E_{1/2}^1$ on the TFA concentration suggests that protonation of $\text{TCNQ}^{\bullet-}$ either does not occur or is very weak.

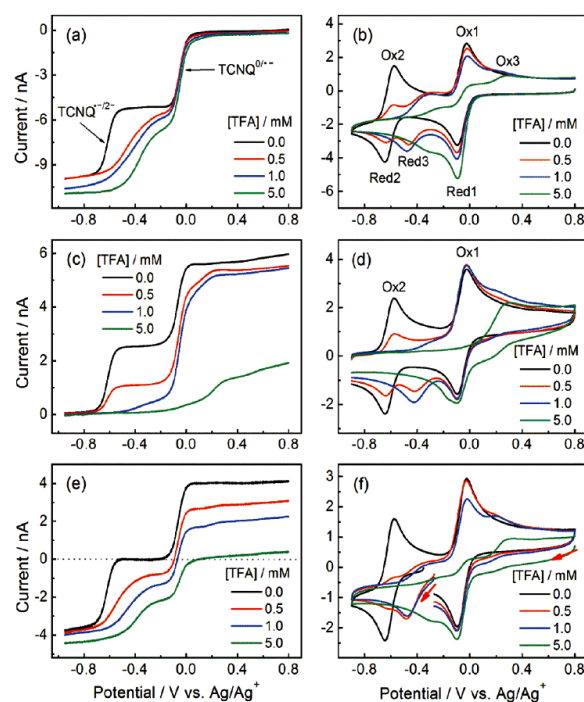
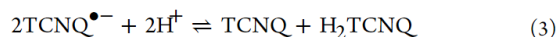


Figure 3. Near-steady-state (a, c, e) linear sweep voltammograms obtained with a $12.0 \mu\text{m}$ diameter carbon fiber microelectrode at a scan rate of 20 mV s^{-1} and transient (b, d, f) cyclic voltammograms using a 1.0 mm diameter GC at a scan rate of 100 mV s^{-1} for 1.0 mM TCNQ (a and b), TCNQ^{2-} (c and d), and $\text{TCNQ}^{\bullet-}$ (e and f), respectively, in acetonitrile (0.1 M Bu_4NPF_6) with designated concentrations of TFA.

However, even though $E_{1/2}^1$ is not shifted markedly when the concentration of TFA is increased, the limiting current associated with the $\text{TCNQ}^{\bullet-}$ process does increase. This is consistent with $\text{TCNQ}^{\bullet-}$ reacting with TFA to produce neutral TCNQ and H_2TCNQ via a disproportionation reaction as described in eq 3. This type of reaction has been proposed to occur in solvents such as acetonitrile,^{9,10} methanol, ethanol,⁹ and water.¹¹ The increase in the current associated with the reduction of TCNQ to $\text{TCNQ}^{\bullet-}$ (Red1) upon addition of TFA also is observed in transient cyclic voltammograms obtained with a 1.0 mm diameter GC electrode in acetonitrile (0.1 M Bu_4NPF_6) (Figure 3b).



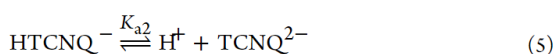
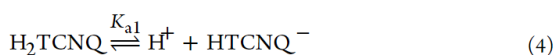
Upon addition of a half molar equivalence of TFA to a TCNQ solution (0.5 mM TFA/ 1.0 mM TCNQ), the peak currents associated with the reduction (Red2) and oxidation

(Ox2) processes for the $\text{TCNQ}^{\bullet-/-2-}$ couple are still observed under transient cyclic voltammetric conditions but are much smaller than obtained in the absence of TFA. Furthermore, a new reduction process (Red3) emerges at a potential more positive than Red2 process (Figure 3b). As the molar ratio of TFA/TCNQ increases to ≥ 1.0 , processes Red2 and Ox2 eventually disappear in a manner which implies facile protonation^{18,30} of TCNQ^{2-} to form electroactive HTCNQ^- and electroinactive H_2TCNQ (this assumption is fully confirmed below). Importantly, upon increasing the concentration of TFA, the oxidation peak currents associated with the $\text{TCNQ}^{2-/\bullet-}$ (Ox2) and $\text{TCNQ}^{\bullet-/0}$ (Ox1) processes diminish, while another oxidation process at ~ 0.2 V (Ox3) emerges and increases in magnitude. The process Ox3 is attributed to the oxidation of the monoprotonated HTCNQ^- . Analogous behavior also is observed in the TCNQF_4 case.¹⁸

Steady-state voltammograms obtained with a carbon fiber microelectrode ($12.0\ \mu\text{m}$ diameter) for solutions of $1.0\ \text{mM}$ TCNQ^{2-} in the presence of TFA further support the hypothesis that H_2TCNQ is electroinactive in the designated potential range, as minimal limiting current is detected in the presence of $5.0\ \text{mM}$ TFA (Figure 3c). The decrease in steady-state limiting and transient peak currents associated with the oxidation of TCNQ^{2-} to $\text{TCNQ}^{\bullet-}$ (Ox2) upon addition of TFA is shown in Figure 3, parts c and d. Interestingly, after protonation of TCNQ^{2-} to form HTCNQ^- , the current associated with oxidation process at $-25\ \text{mV}$ remains (labeled Ox1 in Figure 3d), whereas in the case where the molar ratio of TFA/TCNQ ≤ 1.0 , the magnitude is even slightly greater than that found for TCNQ^{2-} in the absence of TFA. Apparently, HTCNQ^- is oxidized to $\text{HTCNQ}^{\bullet}$ at a potential similar to that for the oxidation of $\text{TCNQ}^{\bullet-}$ to TCNQ , and the generated $\text{HTCNQ}^{\bullet}$ is further oxidized at $\sim 0.2\ \text{V}$ (the process Ox3).

Near-steady-state and transient voltammograms for acetonitrile solution containing $1.0\ \text{mM}$ $\text{TCNQ}^{\bullet-}$ in the presence and absence of TFA are shown in Figure 3, parts e and f. Figure 3e reveals that, upon increasing the TFA concentration, the limiting current magnitude for the oxidation of $\text{TCNQ}^{\bullet-}$ to TCNQ decreases, whereas that for the reduction of $\text{TCNQ}^{\bullet-}$ to TCNQ^{2-} increases as a result of the reaction between $\text{TCNQ}^{\bullet-}$ and TFA to generate TCNQ and electroinactive H_2TCNQ as described in eq 3. The presence of this and other reactions established qualitatively by the above results will be incorporated into a mechanism developed in the section entitled Mechanism and Digital Simulation of the Voltammetry of TCNQ in the Presence of TFA and used in simulations of the cyclic voltammetric results.

Deprotonation of H_2TCNQ . Colorless TCNQ^{2-} rapidly reacts with oxygen to afford the orange-colored DCTC^- .^{14,15} In contrast, H_2TCNQ , a derivative of TCNQ^{2-} , is air-stable.¹⁶ Structurally, H_2TCNQ differs significantly from TCNQ and TCNQ^{2-} (Figure 1). However, the protons in H_2TCNQ can be dissociated to give HTCNQ^- and TCNQ^{2-} (via eqs 4 and 5) under basic conditions.^{31,32} In DMF/ H_2O mixed solvent, the first acid-dissociation constant K_{a1} for H_2TCNQ (eq 4) is ca. 2000-fold larger than the second dissociation constant K_{a2} (eq 5).^{31–33}



Solvents that are more basic than acetonitrile, such as DMF and THF,³⁴ afford well-defined and stable voltammetric responses, immediately upon dissolution of H_2TCNQ (Figure 4). In DMF ($0.1\ \text{M}$ Bu_4NPF_6), the cyclic voltammogram

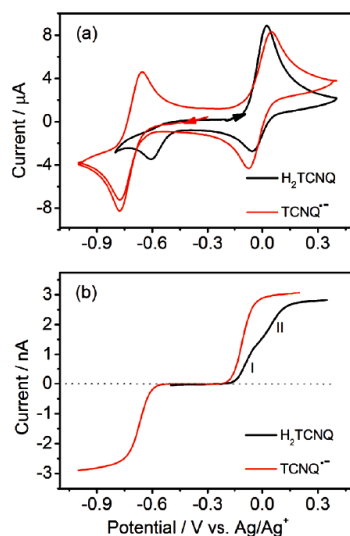
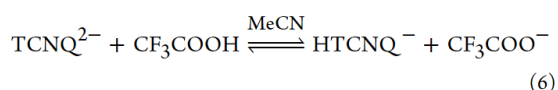


Figure 4. (a) Cyclic voltammograms for $1.0\ \text{mM}$ H_2TCNQ (black line) and $1.0\ \text{mM}$ $\text{TCNQ}^{\bullet-}$ (red line) in DMF ($0.1\ \text{M}$ Bu_4NPF_6) obtained with a $1.6\ \text{mm}$ diameter Au electrode at a scan rate of $100\ \text{mV s}^{-1}$ and (b) near-steady-state voltammograms derived from a $10.0\ \mu\text{m}$ diameter Pt microdisc electrode at a scan rate of $50\ \text{mV s}^{-1}$.

consists of an oxidation process with a peak potential at $-10\ \text{mV}$ and two reduction processes at -88 and $-640\ \text{mV}$ (Figure 4a). The current magnitude for the sole oxidation peak at $-10\ \text{mV}$ is significantly larger than that of its reduction counterpart at $-88\ \text{mV}$. This cyclic voltammetric behavior resembles that found in an acetonitrile ($0.1\ \text{M}$ Bu_4NPF_6) solution containing $1.0\ \text{mM}$ TCNQ^{2-} and $1.0\ \text{mM}$ TFA (Figure 3d), thereby implying that deprotonation of H_2TCNQ in DMF produces HTCNQ^- (eq 4). In principle, this is equivalent to TCNQ^{2-} being protonated by TFA to form HTCNQ^- (eq 6) when equimolar TCNQ and TFA are present in acetonitrile.

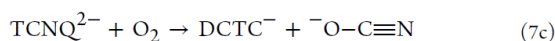
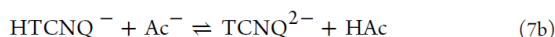
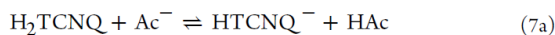


Close inspection of voltammograms obtained with a Pt microelectrode under near-steady-state conditions over the potential range of 200 to $-200\ \text{mV}$ (Figure 4b) reveals the presence of two closely spaced oxidation processes (labeled I and II in Figure 4b) having approximately equal limiting current values. These two oxidation processes are merged into one under transient conditions (Figure 4a), leading to a larger oxidation peak current compared to its reduction counterpart. For comparison, the steady-state voltammogram derived from a $1.0\ \text{mM}$ solution of $\text{TCNQ}^{\bullet-}$ in DMF ($0.1\ \text{M}$ Bu_4NPF_6) also was investigated. The $E_{1/2}$ for $\text{TCNQ}^{\bullet-/0}$ process matches that found for process I, again implying that the oxidations of $\text{TCNQ}^{\bullet-}$ to TCNQ and HTCNQ^- to $\text{HTCNQ}^{\bullet}$ occur at the same potential. However, the magnitude of the limiting current associated with the first oxidation of H_2TCNQ (in fact, oxidation of the deprotonated species HTCNQ^-) in DMF is

much smaller than that for $\text{TCNQ}^{\bullet-}$, which indicates that the deprotonation of H_2TCNQ to HTCNQ^- in DMF is incomplete.

Cyclic voltammograms obtained for a freshly dissolved H_2TCNQ in acetonitrile (0.1 M Bu_4NPF_6) do not show any redox activity at the beginning of the experiment. However, after 2 h, the cyclic voltammograms are similar to the black curves shown in Figure 4, parts a and b, implying that the monodeprotonation of H_2TCNQ is kinetically controlled, being fast in DMF and slow in acetonitrile.

To achieve complete deprotonation of H_2TCNQ , CH_3COOLi (LiAc) is used as a base. In the presence of equimolar LiAc/ H_2TCNQ , only the monodeprotonated species is present, even after 1 h of reaction time (voltammetric evidence, data not shown). When an excess of LiAc (molar ratio LiAc/ H_2TCNQ > 5:1) is added to the H_2TCNQ solution (DMF or MeCN) in the presence of air, the initially colorless solution of H_2TCNQ gradually turns orange. The UV-vis spectrum of the solution exhibits a major absorption band at 470 nm, consistent with the generation of the decomposition product DCTC^- .^{14,35} Detection of DCTC^- implies that dideprotonation of H_2TCNQ to air-sensitive TCNQ^{2-} occurs as an intermediate step in the reaction sequence given in eqs 7a–c. Dideprotonation of H_2TCNQ in the presence of excess LiAc is shown to occur under anaerobic conditions by steady-state voltammetry (Figure 5), which confirms that the major species formed in the absence of oxygen is the two-electron reduced form TCNQ^{2-} .^{15,36}



The information contained in the sections entitled Voltammetry for TCNQ and Its Anions in Acetonitrile (0.1 M Bu_4NPF_6) in the Presence of Trifluoroacetic Acid and Deprotonation of H_2TCNQ forms the basis of the mechanism proposed in the section Mechanism and Digital Simulation of the Voltammetry of TCNQ in the Presence of TFA below which in turn is used to simulate the voltammetry of the $\text{TCNQ}^{0/\bullet-/2-}$ system in acidified acetonitrile solutions.

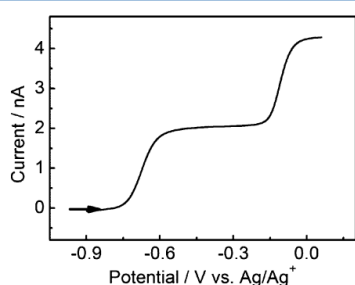


Figure 5. Near-steady-state voltammogram obtained with a 10.0 μm Pt microelectrode at a scan rate of 50 mV s^{-1} in DMF (0.1 M Bu_4NPF_6) solution containing 1.0 mM H_2TCNQ and a 5-fold excess LiAc.

Mechanism and Digital Simulation of the Voltammetry of TCNQ in the Presence of TFA. Details of the mechanism proposed to describe the voltammetry of TCNQ (T), as well as $\text{TCNQ}^{\bullet-}$ and TCNQ^{2-} in the presence of TFA in acetonitrile (0.1 M Bu_4NPF_6) are provided in Table 2 and

Scheme 1. An important assumption associated with the reactions in Table 2 is that TFA (designated as HA) is a very weak acid in acetonitrile ($\text{pK}_a = 12.7^{37}$ or 14^{38}) and hence undissociated. Note that, in order to simplify the description of the chemical reaction Scheme 1, H^+ is used instead of HA.

The proposed mechanism consists of the following steps: steps 1 and 2, electrochemically reversible processes for $\text{TCNQ}^{0/\bullet-/2-}$ steps; steps 3 and 4, $\text{TCNQ}^{\bullet-}$ reacts with TFA to form $\text{HTCNQ}^{\bullet}$, which undergoes a disproportionation reaction to produce TCNQ and H_2TCNQ as described in earlier studies; steps 5 and 6, monoprotection of TCNQ^{2-} by TFA and H_2TCNQ forms HTCNQ^- ; step 7, protonation of HTCNQ^- forms H_2TCNQ ; step 8, HTCNQ^- formed in steps 5 and 6 is oxidized to $\text{HTCNQ}^{\bullet}$ at a potential coincident with that for the oxidation of $\text{TCNQ}^{\bullet-}$ to TCNQ; step 9, $\text{HTCNQ}^{\bullet}$ produced in step 8 is further oxidized to HTCNQ^+ when the potential is scanned to more positive values ($\text{HTCNQ}^{\bullet}$ also rapidly releases protons to CF_3COO^- (A^-) via the reverse of step 3); step 10, HTCNQ^+ deprotonates to the CF_3COO^- anion to generate TCNQ and TFA.

The mechanism is supported by good agreement obtained between simulated and experimental cyclic voltammograms irrespective of whether TCNQ, $\text{TCNQ}^{\bullet-}$, or TCNQ^{2-} is present in the bulk solution and for a wide range of TFA concentrations and scan rates. As noted in the footnotes to Table 2, the simulated capacitance of the double layer C_{dl} is required to be independent of potential, whereas in practice, the value exhibits a substantial dependence. The majority of the difference in simulated and experimental data arises from this discrepancy. The footnotes to Table 2 also detail some other assumptions and issues relevant to the fidelity of the simulations. Figure 6 provides a comparison of experimental cyclic voltammograms obtained for 1.0 mM TCNQ (Figure 6a–c), $\text{TCNQ}^{\bullet-}$ (Figure 6d), and TCNQ^{2-} (Figure 6, parts e and f) for a range of scan rates and TFA concentrations in acetonitrile (0.1 M Bu_4NPF_6) with those obtained from digital simulations based on the aforementioned mechanism and parameters. Supporting Information Figure S-1 provides further comparisons with different sets of conditions.

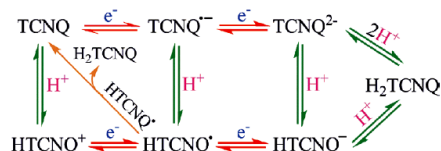
The fact that, generally excellent agreement between experimental and simulated cyclic voltammograms is observed using the mechanism described in Table 2 with the six chemical equilibrium constants listed in this table over a wide range of conditions gives some confidence that a unique set of parameters has been selected. However, a common warning that needs to accompany simulations of very complex mechanism should be kept in mind. That is, there is no guarantee that another set of different parameters could be available that provides an equally good or even better fit to the experimental data.

Simulations derived from TCNQ and TCNQ^{2-} in the bulk solution are relatively straightforward, apart from a minor problem associated with double layer capacitance, which is treated as a constant in the simulation, whereas it is potential-dependent in the experimental data. Significantly, when either TCNQ or TCNQ^{2-} is used as the starting material, simulated cyclic voltammograms obtained when the pre-equilibrium function available in DigiSim is enabled or disabled are identical as the initial potential is chosen to be at a value where no electrochemical process occurs. However, there is a problem with use of this function in the simulation of cyclic voltammograms when $\text{TCNQ}^{\bullet-}$ is the species present in the bulk solution. The question that arises is how to best deal with

Table 2. Mechanism Proposed to Describe the Electrochemistry of $\text{TCNQ}^{0/\bullet-/-2-}$ (T , $\text{T}^{\bullet-}$, T^{2-}) in the Presence of TFA (HA) and a Summary of Parameters Used to Simulate the Cyclic Voltammetry^a

step	reaction	E^0/V	$k_s/(\text{cm s}^{-1})$	K_{eq}	$k_t/(\text{M}^{-1} \text{s}^{-1})$
1	$\text{T} + \text{e} = \text{T}^{\bullet-}$	-0.06	0.1^b		
2	$\text{T}^{\bullet-} + \text{e} = \text{T}^{2-}$	-0.61	0.1^b		
3	$\text{T}^{\bullet-} + \text{HA} = \text{HT}^{\bullet} + \text{A}^-$			4×10^{-2c}	3×10^{3b}
4	$\text{HT}^{\bullet} + \text{HT}^{\bullet} = \text{H}_2\text{T} + \text{T}$			5×10^{4c}	1×10^{9b}
5	$\text{T}^{2-} + \text{HA} = \text{HT}^{2-} + \text{A}^-$			1×10^8	1×10^{10b}
6	$\text{T}^{2-} + \text{H}_2\text{T} = \text{HT}^{2-} + \text{HT}^{\bullet}$			5×10^{5c}	1×10^{10b}
7	$\text{HT}^{2-} + \text{HA} = \text{H}_2\text{T} + \text{A}^-$			2×10^2	1×10^{7b}
8	$\text{HT}^{\bullet} = \text{HT}^+ + \text{e}$	-0.06	0.1^b		
9	$\text{HT}^+ = \text{HT}^{\bullet} + \text{e}$	0.12	0.1^b		
10	$\text{HT}^+ + \text{A}^- = \text{T} + \text{HA}$			3×10^{4c}	1×10^{4b}

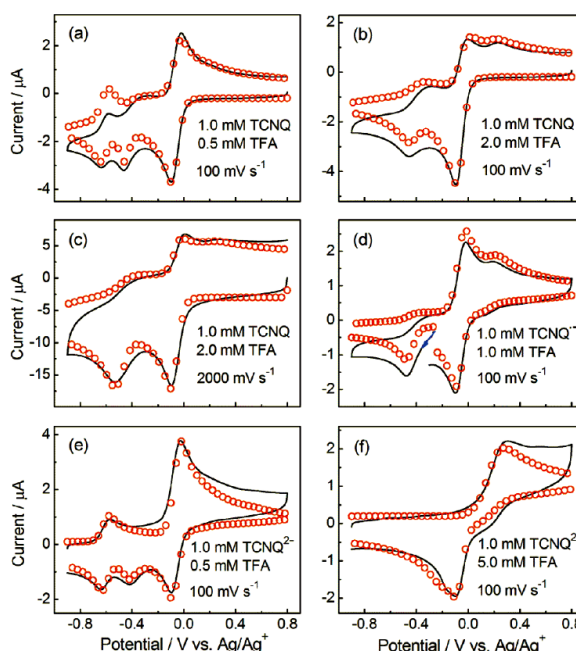
^aDiffusion coefficients $D(\text{TCNQ}) = 1.9 \times 10^{-5}$, $D(\text{TCNQ}^{\bullet-}) = 1.7 \times 10^{-5}$, $D(\text{TCNQ}^{2-}) = 1.2 \times 10^{-5}$, $D(\text{HA}) = D(\text{A}^-) = 3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, electrode area = 0.0081 cm^2 , $T = 295 \text{ K}$, $\alpha = 0.5$, $R_u = 200 \Omega$, $C_{\text{dl}} = 2 \times 10^{-6} \text{ F}$. C_{dl} is required to be independent of potential in DigiSim software. However, in practice, C_{dl} varies with the potential and this causes the majority of the differences between experimental and simulated data. E^0 is the formal potential of the redox couple. k_t values for coupled chemical reactions need to be fast to model these processes but have been set so that they do not exceed the diffusion controlled limit of $\sim 1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. ^bThis parameter may be varied from the value in the table to slightly enhance the agreement between the experimental and simulated cyclic voltammograms under some circumstances. For example, the standard heterogeneous electron-transfer rate constant (k_s) value of 0.1 cm s^{-1} implies that these reactions are close to the reversible limit and hence only minimally sensitive to input of larger values in simulations. ^cValues determined by DigiSim simulation software via a thermodynamic relationship available with other parameters.

Scheme 1. Schematic Representation of the Mechanism for Electron- and Proton-Transfer Reactions That Occur in the Voltammetry of TCNQ, $\text{TCNQ}^{\bullet-}$, and TCNQ^{2-} in Acetonitrile (0.1 M Bu_4NPF_6)

the chemical reaction between $\text{TCNQ}^{\bullet-}$ and TFA to produce TCNQ and H_2TCNQ when the initial potential is set at -0.27 V , a value which lies between the $\text{TCNQ}^{0/\bullet-}$ and $\text{TCNQ}^{\bullet-/2-}$ processes. If the pre-equilibrium function is employed at this initial potential, almost all TCNQ produced from the reaction between $\text{TCNQ}^{\bullet-}$ and TFA, in the bulk solution should be reduced to $\text{TCNQ}^{\bullet-}$ before commencing the simulation. In fact, TCNQ always exists in the bulk solution at the time the experiment commences. In contrast, if the pre-equilibrium function is disabled, no reaction between $\text{TCNQ}^{\bullet-}$ and TFA will have occurred when the simulation commences. In the experiment, a rest period of 10 s was used, which is not long enough to reach the equilibrium position provided by the simulation. Nevertheless, better agreement in the first cycle of potential between simulated and experimental cyclic voltammograms is found when the pre-equilibrium function is enabled as shown by a comparison of Figure 6d and Supporting Information Figure S-2. Interestingly, upon cycling the potential, simulations with the pre-equilibrium function enabled or disabled closely mimic the experimental data, so this is the regime of greatest importance in experiment–simulation comparison when both $\text{TCNQ}^{\bullet-}$ and TFA are present in bulk solution.

■ COMPARISON OF THE REDOX AND ACID–BASE CHEMISTRY OF TCNQ AND TCNQF_4

Comparative analysis of the voltammetric data obtained for TCNQF_4 ¹⁸ and TCNQ under similar conditions allows several

**Figure 6.** Experimental (black line) and simulated (red circles) cyclic voltammograms obtained in acetonitrile (0.1 M Bu_4NPF_6) with 1.0 mM TCNQ (a–c), $\text{TCNQ}^{\bullet-}$ (d), or TCNQ^{2-} (e and f) at designated TFA concentrations and scan rates using a 1.0 mm diameter GC electrode.

important observations to be made. First, both TCNQ and TCNQF_4 undergo two diffusion-controlled, chemically and electrochemically reversible one-electron reduction processes in acetonitrile (supporting electrolyte). Second, E_f^0 values for the $\text{TCNQ}^{0/\bullet-}$ and $\text{TCNQ}^{\bullet-/2-}$ redox couples are $\sim 0.37 \text{ V}$ more negative than the corresponding ones for TCNQF_4 . This difference in E_f^0 arises from the strong electron-withdrawing effect of the fluorine atoms in TCNQF_4 , thereby making its anions thermodynamically more stable than the corresponding

TCNQ anions. Third, although both $\text{TCNQ}^{\bullet-}$ and $\text{TCNQF}_4^{\bullet-}$ monoanions are highly stable, even in air for prolonged periods of time, the kinetic stability of the dianions of the two congeners differs dramatically. Thus, the TCNQF_4^{2-} dianion is stable under aerobic conditions for several hours, whereas TCNQ^{2-} decomposes rapidly into DCTC^- upon contact with air (oxygen). This enhanced stability represents a major advantage of the fluorinated derivatives of TCNQ and should provide more ready access to dianion chemistry. Finally, in the presence of TFA, both TCNQ^{2-} and TCNQF_4^{2-} dianions (designated as T^{2-}) can be protonated sequentially and rapidly to form HT^- and H_2T . However, the equilibrium constants associated with protonation of the dianions by TFA differ significantly, with values of 1×10^8 and 2×10^2 for TCNQ^{2-} and 3×10^3 and 1 for TCNQF_4^{2-} . Thus, in acetonitrile, there is greater tendency for TCNQ^{2-} to react with protons than TCNQF_4^{2-} . This finding is consistent with data available in a DMF/ H_2O mixture, where $\text{p}K_{\text{a}}$ values for H_2TCNQ ($\text{p}K_{\text{a}1} = 7.10$, $\text{p}K_{\text{a}2} = 10.30$) are much larger than those for H_2TCNQF_4 ($\text{p}K_{\text{a}1} = 4.01$, $\text{p}K_{\text{a}2} = 7.20$).^{31,33} The implication is that H_2TCNQ is a much weaker acid than H_2TCNQF_4 , or in other words, TCNQ^{2-} is a much stronger base than TCNQF_4^{2-} . It therefore also follows that extent of the disproportionation of the monoanion $\text{TCNQ}^{\bullet-}$ in acid to produce neutral TCNQ and H_2TCNQ is much stronger than applies to the corresponding fluorinated analogue. Thus, after addition of 10.0 mM TFA into 1.0 mM $\text{TCNQF}_4^{\bullet-}$ in acetonitrile, only a relatively small amount of TCNQF_4 is produced,¹⁸ whereas in the presence of only 5.0 mM TFA, almost all of the 1.0 mM $\text{TCNQ}^{\bullet-}$ present in acetonitrile is converted to TCNQ and H_2TCNQ .

CONCLUSIONS

Transient cyclic voltammetric studies at a macroelectrode and steady-state studies at a microelectrode confirm that TCNQ and its $\text{TCNQ}^{\bullet-}$ and TCNQ^{2-} anions undergo two electrochemically reversible one-electron processes; two reductions for TCNQ, one reduction and one oxidation for $\text{TCNQ}^{\bullet-}$, and two oxidations for TCNQ^{2-} . In the presence of TFA, both voltammetric methods show that $\text{TCNQ}^{\bullet-}$ is weakly protonated to form $\text{HTCNQ}^{\bullet}$, which rapidly disproportionates to TCNQ and H_2TCNQ . In contrast, TCNQ^{2-} is a much stronger base and is protonated in two steps, first forming HTCNQ^- and then H_2TCNQ with the equilibrium constant for the first step being much larger than the second one. H_2TCNQ is electroinactive in acetonitrile (0.1 M Bu_4NPF_6) within the potential range of -1.0 V to $+1.0$ V versus Ag/Ag^+ , whereas HTCNQ^- is oxidized to $\text{HTCNQ}^{\bullet}$ at a similar potential to where $\text{TCNQ}^{\bullet-}$ is oxidized to TCNQ. $\text{HTCNQ}^{\bullet}$ generated from this reaction can release a proton, forming $\text{TCNQ}^{\bullet-}$, or it can be further oxidized to neutral TCNQ and a proton when the potential is scanned to more positive values. The postulated mechanism is supported by simulations that mimic the experimental cyclic voltammograms satisfactorily over a wide range of scan rates and concentration ratios of TCNQ or TCNQ^{2-} and TFA. Studies on the deprotonation of H_2TCNQ reveal that H_2TCNQ is partially monodeprotonated upon dissolution in DMF or THF very rapidly, while this process occurs much more slowly in acetonitrile. In the presence of a molar excess of LiAc, H_2TCNQ completely deprotonates to form TCNQ^{2-} . When this experiment is undertaken in the presence of oxygen, further reaction occurs leading to formation of DCTC^- . This outcome differs

remarkably from TCNQF_4^{2-} which is persistent in aerobic ambient conditions for several hours. Additionally, the extent of reaction between $\text{TCNQ}^{\bullet-}$ and TFA to form TCNQ and H_2TCNQ , as well as the protonation of TCNQ^{2-} , is much stronger than analogous reactions with TCNQF_4 .

ASSOCIATED CONTENT

Supporting Information

Figures S-1 and S-2, which provide further comparisons of experimental and simulated cyclic voltammograms. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Supporting Information

Redox and Acid – Base Chemistry of TCNQ, TCNQ^{•-}, TCNQ²⁻ and H₂TCNQ

(TCNQ = 7,7,8,8-tetracyanoquinodimethane) in Acetonitrile

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The Supporting Information contains further comparisons of simulated and experimental cyclic voltammograms. Figure S-1 provides comparisons of simulated and experimental cyclic voltammograms obtained at a glassy carbon (GC) electrode for acetonitrile (0.1 M Bu₄NPF₆) solutions containing (a, b) 1.0 mM TCNQ and 2.0 mM trifluoroacetic acid (TFA) at scan rates of 1000 and 5000 mV s⁻¹, (c, d) 1.0 mM TCNQ²⁻ and 1.0 mM TFA at scan rates of 100 and 200 mV s⁻¹. Figure S-2 provides a comparison of experimental cyclic voltammogram obtained at a GC electrode for acetonitrile (0.1m Bu₄NPF₆) solution containing 1.0 mM TCNQ^{•-} and 1.0 mM TFA and simulated data obtained when the pre-equilibrium function available in DigiSim software is disabled.

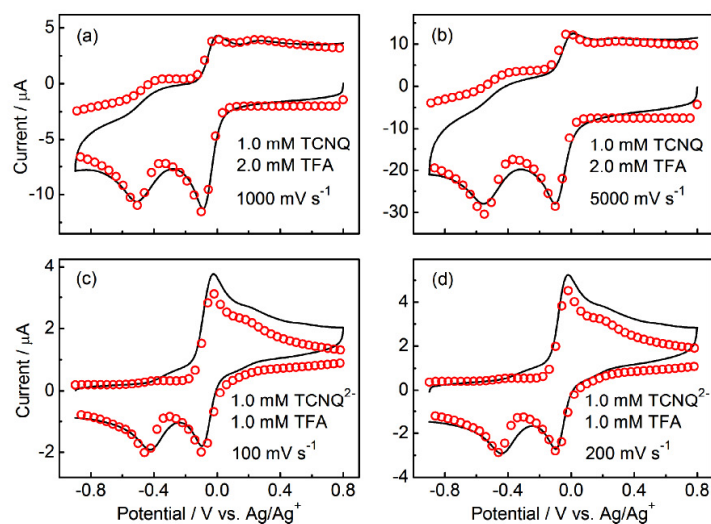


Figure S-1. Comparison of simulated ($\circ \circ \circ$) and experimental cyclic voltammograms (—) obtained with a GC electrode (0.0081 cm^2) in acetonitrile ($0.1 \text{ M Bu}_4\text{NPF}_6$) containing (a, b) 1.0 mM TCNQ and 2.0 mM TFA , (c, d) 1.0 mM TCNQ^{2-} and 1.0 mM TFA at designated scan rates.

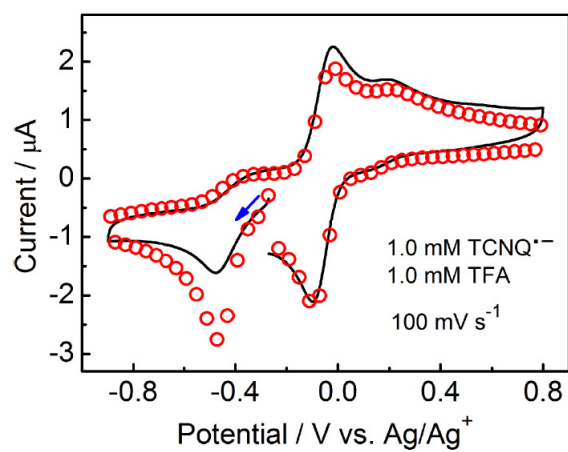


Figure S-2. A comparison between experimental cyclic voltammogram (—) for acetonitrile solution (0.1 M Bu₄NPF₆) containing 1.0 mM TCNQ^{•-} in the presence of 1.0 mM TFA using a GC electrode (0.0081 cm²) at 100 mV s⁻¹ with simulation (○ ○ ○) obtained when the pre-equilibrium is disabled.

Chapter 4

Synthesis and Characterization of TCNQF₄-Based Materials in Acetonitrile

4.1. Introduction

This chapter details how to control the synthesis of materials based on either TCNQF₄^{•-} or TCNQF₄²⁻ in acetonitrile via a chemical reaction between LiI and TCNQF₄, or using an electrochemical method. In the case of chemical synthesis, the molar ratio of the reactants and temperature are the most important parameters. When LiI and TCNQF₄ are mixed together with a molar ratio of 3:2 in cold acetonitrile and stirred for 30 min under N₂ gas, only LiTCNQF₄ is produced. In contrast, when LiI and TCNQF₄ are used with a molar ratio > 3:1 and at temperature from 50–60 °C, the major product is Li₂TCNQF₄ along with a small amount of LiTCNQF₄. The generated LiTCNQF₄ and Li₂TCNQF₄ were then used as starting materials for the chemical synthesis of Pr₄NTCNQF₄ and (Pr₄N)₂TCNQF₄. LiTCNQF₄, Li₂TCNQF₄, Pr₄NTCNQF₄ and (Pr₄N)₂TCNQF₄ have been characterized via electrochemistry and a wide range of spectroscopic techniques. The structures of the Pr₄N-TCNQF₄ compounds were also described using single crystal X-ray diffraction.

The electrocrystallization of AgTCNQF₄, Ag₂TCNQF₄, CuTCNQF₄, Cu₂TCNQF₄, CoTCNQF₄ and NiTCNQF₄ from the reduction of TCNQF₄ in acetonitrile (0.1 M Bu₄NPF₆) in the presence of an appropriate metal cation also is described in this chapter. As mentioned in chapter 3, in acetonitrile, TCNQF₄ can be sequentially reduced to TCNQF₄^{•-} and TCNQF₄²⁻ depending on the magnitude of the applied potential. Therefore, in the presence of a metal cation, the electrochemically generated TCNQF₄^{•-} or TCNQF₄²⁻ may react with the metal cation to form crystals onto the electrode surface when the solubility product of the compound is exceeded. The solubility and solubility product of the metal-TCNQF₄ compounds in acetonitrile in the presence and absence of 0.1 M Bu₄NPF₆ supporting electrolyte have been determined, and revealed that their solubility in the presence of the supporting electrolyte is higher than in neat solvent. As the solubility of a TCNQF₄²⁻-based compound is lower than that of the TCNQF₄^{•-} one, with the same metal cation, the electrochemical synthesis of TCNQF₄²⁻ compounds can occur at lower concentrations of TCNQF₄ and metal cations. However, Co(TCNQF₄)₂ and Ni(TCNQF₄)₂

are found to be quite soluble in acetonitrile and these compounds cannot be electrocrystallized under the experimental conditions used in this Chapter.

Along with cyclic voltammetry, the electrocrystallization processes for the metal-TCNQF₄ compounds in acetonitrile have been explored using a wide range of techniques, such as (i) *in situ* SPR and EQCM to monitor the mass change on the electrode surface due to the deposition and stripping of the compounds during the course of the electrochemical processes, (ii) UV-vis, FT-IR and Raman spectroscopies to characterize the synthesized materials, (iii) optical and SEM for morphological determination, (iv) EDXS for the identification of the elements in the electrocrystallized materials, (v) elemental analysis, and (vi) digital simulation has been used to support a proposed mechanism for the electrocrystallization of Cu₂TCNQF₄ from TCNQF₄ and Cu(MeCN)₄⁺ using the software DigiElch.

AgTCNQF₄, Ag₂TCNQF₄, CuTCNQF₄, Cu₂TCNQF₄, CoTCNQF₄ and NiTCNQF₄ also were chemically synthesized. Firstly, TCNQF₄ in acetonitrile (0.1 M Bu₄NPF₆) was electrochemically reduced to TCNQF₄^{•-} or TCNQF₄²⁻ by applying suitable potentials. Secondly, each generated solution was mixed with an acetonitrile solution containing an appropriate metal cation to produce the corresponding precipitate. Finally, the solid was washed with acetonitrile several times before being characterized using spectroscopic techniques.

Declaration for Thesis Chapter 4.2

Declaration by candidate

In the case of Chapter 4.2, the nature and extent of my contribution to the work was the following:

Nature of contribution	Extent of contribution (%)
Initiation, key ideas, experimental work, writing up	35

The following co-authors contributed to the work.

Name	Nature of contribution
Jinzheng Lu	Initiation, key ideas, experimental work, writing up
Daouda Traore	Initiation, key ideas, experimental work, writing up
Matthew Wilce	Initiation, key ideas, experimental work, writing up
Alan M. Bond	Initiation, key ideas, writing up
Lisandra L. Martin	Initiation, key ideas, writing up

Candidate's Signature

	06/06/2012
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Declaration by co-authors

The undersigned hereby certify that:

- (1) the above declaration correctly reflects the nature and extent of the candidate's contribution to this work, and the nature of the contribution of each of the co-authors.
- (2) they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;
- (3) they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
- (4) there are no other authors of the publication according to these criteria;
- (5) potential conflicts of interest have been disclosed to (a) granting bodies, (b) the editor or publisher of journals or other publications, and (c) the head of the responsible academic unit; and
- (6) the original data are stored at the following location and will be held for at least five years from the date indicated below:

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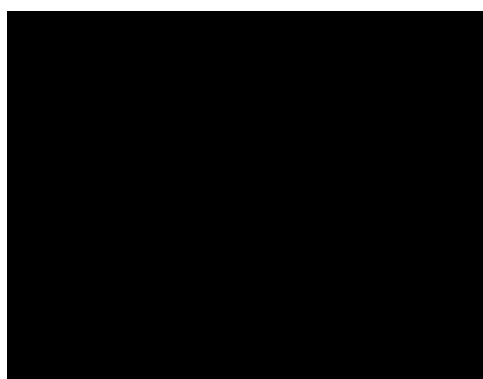
Jinzheng Lu

Daouda Traore

Matthew Wilce

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Lisandra L. Martin

	22/5/2012
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	23/5/12

Synthesis, X-ray Crystallographic Characterization and Electrochemical Studies of TCNQF₄ Complexes with Li⁺ or Pr₄N⁺

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Abstract

Careful control of the reaction stoichiometry and conditions enables the synthesis of both LiTCNQF₄ and Li₂TCNQF₄ to be achieved. Reaction of LiI with TCNQF₄, in a 4:1 molar ratio, in boiling acetonitrile yields Li₂TCNQF₄. However, deviation from this ratio or the reaction temperature gives either LiTCNQF₄ or a mixture of Li₂TCNQF₄ and LiTCNQF₄. This is the first report of the large scale chemical synthesis of Li₂TCNQF₄. Attempts to prepare a single crystal of Li₂TCNQF₄ have been unsuccessful, although the air stable (Pr₄N)₂TCNQF₄ was obtained by mixing Pr₄NBr with Li₂TCNQF₄ in aqueous solution. Similarly, Pr₄NTCNQF₄ was also obtained by reaction of LiTCNQF₄ with Pr₄NBr in water. Li₂TCNQF₄, (Pr₄N)₂TCNQF₄ and Pr₄NTCNQF₄ have been characterized by UV-vis, FT-IR, Raman and NMR spectroscopies, high resolution electrospray ionization mass spectrometry and electrochemistry. The structures of single crystals of (Pr₄N)₂TCNQF₄ and Pr₄NTCNQF₄ have been determined by X-ray crystallography. These TCNQF₄²⁻ salts will provide useful precursors for the synthesis of derivatives of the dianions.

Key words: Li₂TCNQF₄, LiTCNQF₄, (Pr₄N)₂TCNQF₄, Pr₄NTCNQF₄, TCNQF₄²⁻ dianion, synthetic precursors.

1. Introduction

7,7,8,8-tetracyanoquinodimethane (TCNQ) has been a molecule of great of interest as it is a strong electron acceptor.^{1,2} However, the tetrafluorinated TCNQ derivative, 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (TCNQF₄) is an even stronger electron acceptor than TCNQ with a higher electron affinity (~ 3.3 eV³⁻⁵ compared with ~ 2.9 eV for TCNQ^{5,6}). Despite this, to date, TCNQF₄-based charge transfer (CT) complexes have been much less studied than their TCNQ counterparts. The radical monoanions of TCNQ and TCNQF₄ are stable in air at least for several hours and can be synthesized by chemical or electrochemical reduction of TCNQ or TCNQF₄. Thus, metal and organic derivatives based on either TCNQ^{•-} or TCNQF₄^{•-} have been prepared and their physical properties, such as, magnetism,⁷⁻¹⁰ electronic conductivity^{3,11-14} and electric switching as bulk materials^{15,16} have been widely studied. In contrast, studies of materials derived from TCNQ²⁻ as well as TCNQF₄²⁻ dianions are limited.

There have been several reports of X-ray crystal structures of TCNQ²⁻-based complexes.¹⁷⁻²⁴ In comparison, only coordination polymers containing TCNQF₄²⁻ have been fully characterized by X-ray crystallography; Mn₂(TCNQF₄²⁻)(solvent)(TCNQF₄^{•-})₂,²⁵ and [(Me₅Cp)₂M]TCNQF₄ (M^{II}: Fe, Co).²⁶ In these studies the TCNQ²⁻/TCNQF₄²⁻ dianions resulted from either disproportionation of LiTCNQ/LiTCNQF₄ or direct two-electron reduction of TCNQ/TCNQF₄ by reactive metallocenes (Fe and Co). The reason for the disproportionation of TCNQ^{•-}/TCNQF₄^{•-} to dianions of TCNQ/TCNQF₄ is yet not fully understood.

In solution, the TCNQ²⁻ dianion is sensitive to air and rapidly decomposes into α,α -dicyano-p-toluoylcyanide (DCTC⁻).^{27,28} As a result, syntheses of complexes based on the TCNQ²⁻ dianion are much more difficult than those for the radical monoanion. However, recently, Robson and co-workers have successfully used the air stable H₂TCNQ as a starting material to produce both metal and organic based TCNQ²⁻ complexes.²¹⁻²⁴ In an organic solution in the presence of a weak base, H₂TCNQ undergoes sequential deprotonations to TCNQ²⁻. The generated dianion then combines with metal or organic cations *in situ* to form new the materials. These metal-TCNQ²⁻-based coordination polymers have an ability to establish 3D networks which intercalate redox-active species into the structural units and which may lead to these solid materials having interesting electronic and magnetic properties.²⁴ Although the TCNQ²⁻ complexes also have attractive

features, which differ significantly from the better known TCNQ $\bullet^-$ -based materials. For example, TCNQ $^{2-}$ can bind strongly to the metal ion^{21,23} and is free from π - π contacts.^{23,24} Consequently, new types of coordination polymers can be formed with intercalation of oxidants or reductants into the structure, which may change the electric conductivity of these materials.^{21,23} Here, we report the one step, direct chemical synthesis as well as the characterization and stability of two new complexes based on the TCNQF $_4^{2-}$ dianion, i.e. Li $_2$ TCNQF $_4$, (Pr $_4$ N) $_2$ TCNQF $_4$, which can be used as starting reagents to synthesize both metal- and organic-TCNQF $_4^{2-}$ -based materials. To the best of our knowledge, this is the first report of the chemical synthesis, in high yield of Li $_2$ TCNQF $_4$ and (Pr $_4$ N) $_2$ TCNQF $_4$. In addition, single crystals of both (Pr $_4$ N) $_2$ TCNQF $_4$ and the radical monoanion derivative Pr $_4$ N⁺TCNQF $_4$, were structurally characterized by X-ray diffraction methods.

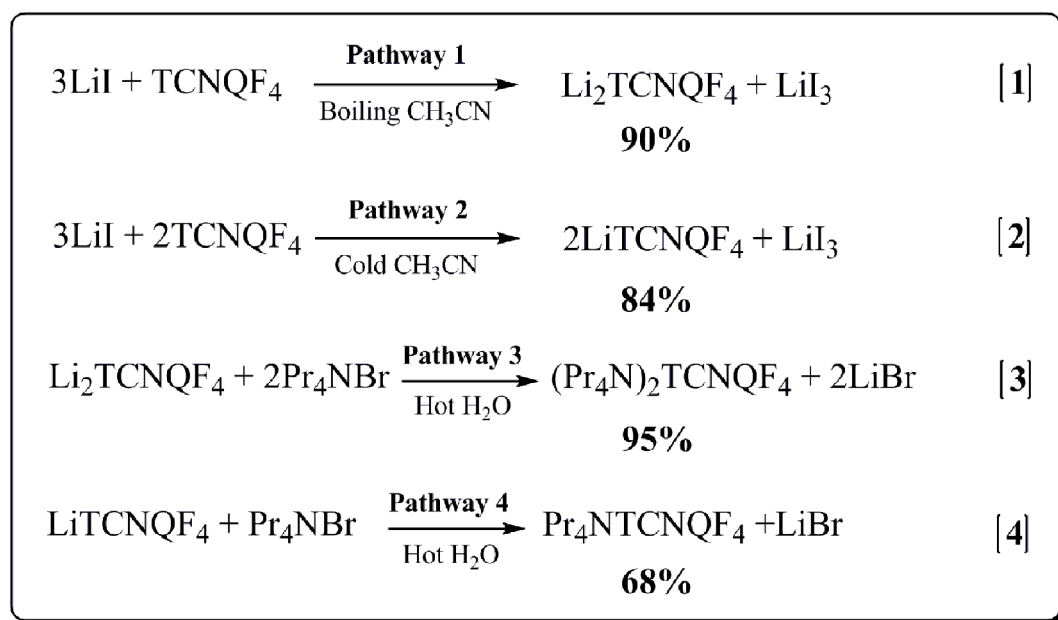
2. Results and Discussion

2.1. Synthesis

As noted already, LiTCNQF $_4$ is an important starting reagent for the synthesis of TCNQF $_4^{\bullet-}$ -based materials. Our initial attempts to synthesize LiTCNQF $_4$ was based on the literature procedure described for the preparation of LiTCNQ.² However, it was found that these reaction conditions produced a mixture of LiTCNQF $_4$ and Li $_2$ TCNQF $_4$ as proved by UV-vis spectroscopy and electrochemistry (see below). Subsequently, it was shown that the synthetic conditions could be optimized to favor the formation of Li $_2$ TCNQF $_4$, which can be an important starting salt for the synthesis of TCNQF $_4^{2-}$ dianion coordination polymers. This optimization study has demonstrated that the ratio of Li $_2$ TCNQF $_4$ and LiTCNQF $_4$ generated depends on the reaction temperature, duration of the reaction and the molar ratio of the reactants used in the synthesis.

A straightforward method for the synthesis of Li $_2$ TCNQF $_4$ is summarized in Pathway 1 (Scheme 1). Thus, a boiling solution of LiI (273 mg, 2.04 mmol) in acetonitrile (15 mL) was added dropwise to a boiling solution of TCNQF $_4$ (142 mg, 0.51 mmol) in acetonitrile (15 mL). The resulting mixture was stirred for 1 h at 50–60 °C under N $_2$. The suspension was cooled to room temperature before filtration to collect the solid. The crude product was washed with diethyl ether (dried and degassed prior to use) until no LiI $_3$ was detected in the solution. A creamy white solid (134 mg, 90%) was obtained after drying under vacuum over P $_2$ O $_5$ for three hours. The solid was then characterized using FT-IR, Raman, UV-vis spectroscopies and electrochemistry (see below). These data indicate that

$\text{Li}_2\text{TCNQF}_4$ is free of LiTCNQF_4 . High resolution electrospray ionization mass spectrometry (ESI-MS) also confirms that the charge on the TCNQF_4 moiety is 2- (Calculated for $\text{C}_{12}\text{F}_4\text{N}_4^{2-}$: m/z 138.0030 (100%); found: m/z 138.0026 (100%)). However, $\text{Li}_2\text{TCNQF}_4$ is unstable in air, even in the solid state, and over time is gradually converted to LiTCNQF_4 (see Figure S1). Efforts to grow a single crystal of $\text{Li}_2\text{TCNQF}_4$ have proved unsuccessful. The same reaction conditions, but using a 3:1 molar ratio of LiI and TCNQF_4 yielded a mixture of $\text{Li}_2\text{TCNQF}_4$ and LiTCNF_4 . The mixture was quantitatively analyzed using UV-vis spectroscopy and electrochemistry. $\text{Li}_2\text{TCNQF}_4$ was found to be produced under these conditions at a level of 90-95% (molar %) with the remainder of the sample being LiTCNQF_4 (Figures S2 and S3).



Scheme 1. Summary of reaction pathways used for synthesis of $\text{Li}_2\text{TCNQF}_4$, LiTCNQF_4 , $(\text{Pr}_4\text{N})_2\text{TCNQF}_4$ and $\text{Pr}_4\text{N}^+\text{TCNQF}_4$.

In order to favor the reduction of TCNQF_4 to $\text{TCNQF}_4^{\bullet-}$ rather than to TCNQF_4^{2-} , the reaction conditions used for the synthesis of $\text{Li}_2\text{TCNQF}_4$ needed to be modified. Thus, the molar ratio of LiI and TCNQF_4 was changed to 3:2 and the reaction was carried out with cold solutions (Pathway 2, Scheme 1). 3 mL of a cold (0 °C) acetonitrile solution containing LiI (75.4 mg, 0.57 mmol) was added dropwise into 8 mL of a cold acetonitrile solution of TCNQF_4 (104 mg, 0.38 mmol). The resulting mixture was placed in an ice bath and stirred under N_2 for 30 min. The precipitate that formed was isolated rapidly by vacuum filtration, followed by washing with acetonitrile (3×3 mL), diethyl ether (3×5 mL), and dried over P_2O_5 under vacuum overnight. The purple solid obtained (89.5 mg,

84%) was studied using a wide range of spectroscopic techniques and electrochemistry. These data (see below) confirmed that LiTCNQF₄ was the only product produced in Pathway 2. Clearly, the reduction of TCNQF₄ is thermodynamically controlled, so an excess of LiI gives rise to the further reduction of TCNQF₄^{•-} to TCNQF₄²⁻ as illustrated in Pathway 1 of Scheme 1.

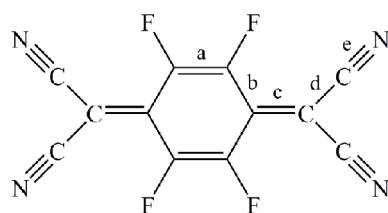
Both Li₂TCNQF₄ and LiTCNQF₄ directly reacted with Pr₄NBr in water (Pathways 3 and 4, Scheme 1) to yield colourless crystals of (Pr₄N)₂TCNQF₄, and a blue powder for Pr₄NTCNQF₄. Single crystals of (Pr₄N)₂TCNQF₄ and Pr₄NTCNQF₄ suitable for X-ray crystallographic analysis were obtained by either diffusion of n-pentane into an acetone solution of (Pr₄N)₂TCNQF₄, or diffusion of diethyl ether into a methanol solution of Pr₄NTCNQF₄. The polycrystalline solids of both (Pr₄N)₂TCNQF₄ and Pr₄NTCNQF₄ are stable in air and characterised by ¹⁹F NMR, FT-IR, Raman, UV-vis spectroscopy and electrochemistry. All these data are consistent with the single crystal structures.

2.2. X-ray Structural Characterization of (Pr₄N)₂TCNQF₄ and Pr₄NTCNQF₄

Colorless diamond-like (Pr₄N)₂TCNQF₄ crystallized in the monoclinic space group *P*2₁/*n*. The asymmetric unit contains one Pr₄N⁺ cation and a half TCNQF₄ moiety as shown in Figure 1a. The structure of (Pr₄N)₂TCNQF₄ is comprised of a 3D layered network supported by hydrogen bonding (Figure 1b). The charge (ρ) on the TCNQF₄ moieties in (Pr₄N)₂TCNQF₄ has been estimated by the mean bond lengths of TCNQF₄ (Table 1) using the Kistenmacher relationship, $\rho = A[c/(b+d)] + B$, ($A = -46.729$ and $B = 22.308$, A , B were determined from neutral TCNQF₄ ($\rho = 0$),²⁹ and TCNQF₄^{•-} monoanion in n-Bu₄NTCNQF₄ ($\rho = -1$).³⁰ The calculated ρ value (-1.92) supports the assignment of TCNQF₄²⁻ dianions. Moreover, the structural parameters in (Pr₄N)₂TCNQF₄ are consistent with those for TCNQF₄²⁻ species reported by Miller *et al.*²⁶ (Table 1). The TCNQF₄ moieties in (Pr₄N)₂TCNQF₄ are not planar since the –C(CN)– groups apparently lie away from phenyl plane with a diangle of 17°. Each TCNQF₄ moiety interacts with seven Pr₄N⁺ cations via hydrogen bond interactions between the CN/F groups of the TCNQF₄ moieties and the CH groups from the Pr₄N⁺ cations (Figure 1c). Moreover, the adjacent TCNQF₄²⁻ layers are separated by Pr₄N⁺ cation layers and oriented with an angle between the respective phenyl planes of about 59.2° (Figure 1d). In addition, the Pr₄N⁺ cations and the TCNQF₄²⁻ anions are connected by hydrogen bonding to form a 3D network (Figure 1b and Table S1).

Dark-blue needles of $\text{Pr}_4\text{NTCNQF}_4$ crystallizes in the monoclinic space group $P2_1/n$ and the 3D H-bonded network structure consists of $(\text{TCNQF}_4^{\bullet-})_2$ dimers and Pr_4N^+ cations (Figure 1f and Table S2). The asymmetric unit of $\text{Pr}_4\text{NTCNQF}_4$ is shown in Figure 1e. Each TCNQF_4 anion is almost planar with a slight bowing of the $\text{C}\equiv\text{N}$ groups away from the phenyl plane. The two neighboring $\text{TCNQF}_4^{\bullet-}$ anions eclipse to form a face-to-face π -stacked dimer with an inter-planar distance of 3.147 Å; a remarkably short spacing compared with that of normal π - π stacked TCNQ or TCNQF_4 dimers (ca 3.30 Å).^{7-8,11,30} The overlap of the dimer is ring over bond mode. The degree of charge transfer of TCNQF_4 species in $\text{Pr}_4\text{NTCNQF}_4$ has been determined using the same method applied to $(\text{Pr}_4\text{N})_2\text{TCNQF}_4$ and found to be -0.94. Therefore, the TCNQF_4 moieties in $\text{Pr}_4\text{NTCNQF}_4$ can be described as the $\text{TCNQF}_4^{\bullet-}$ radical monoanion. The structural parameters for $\text{Pr}_4\text{NTCNQF}_4$ also agree well with those expected for $\text{TCNQF}_4^{\bullet-}$ (Table 1) and found in related complexes reported by us and others.^{7-8,30,32,34}

Table 1. Some examples of intramolecular bond distances reported for TCNQF_4 , $\text{TCNQF}_4^{\bullet-}$ and TCNQF_4^{2-}



	a / Å	b / Å	c / Å	d / Å	e / Å	ρ	Ref.
TCNQF_4^{2-}	1.377	1.403	1.456	1.406	1.161	-1.92	This work
$\text{TCNQF}_4^{\bullet-}$	1.357	1.419	1.415	1.424	1.152	-0.94	This work
TCNQF_4^0	1.334	1.437	1.372	1.437	1.140	0.00	26
$\text{TCNQF}_4^{\bullet-}$	1.360	1.420	1.429	1.435	1.140	-1.00	30
TCNQF_4^{2-}	1.373	1.398	1.457	1.403	1.154	-2.00	26

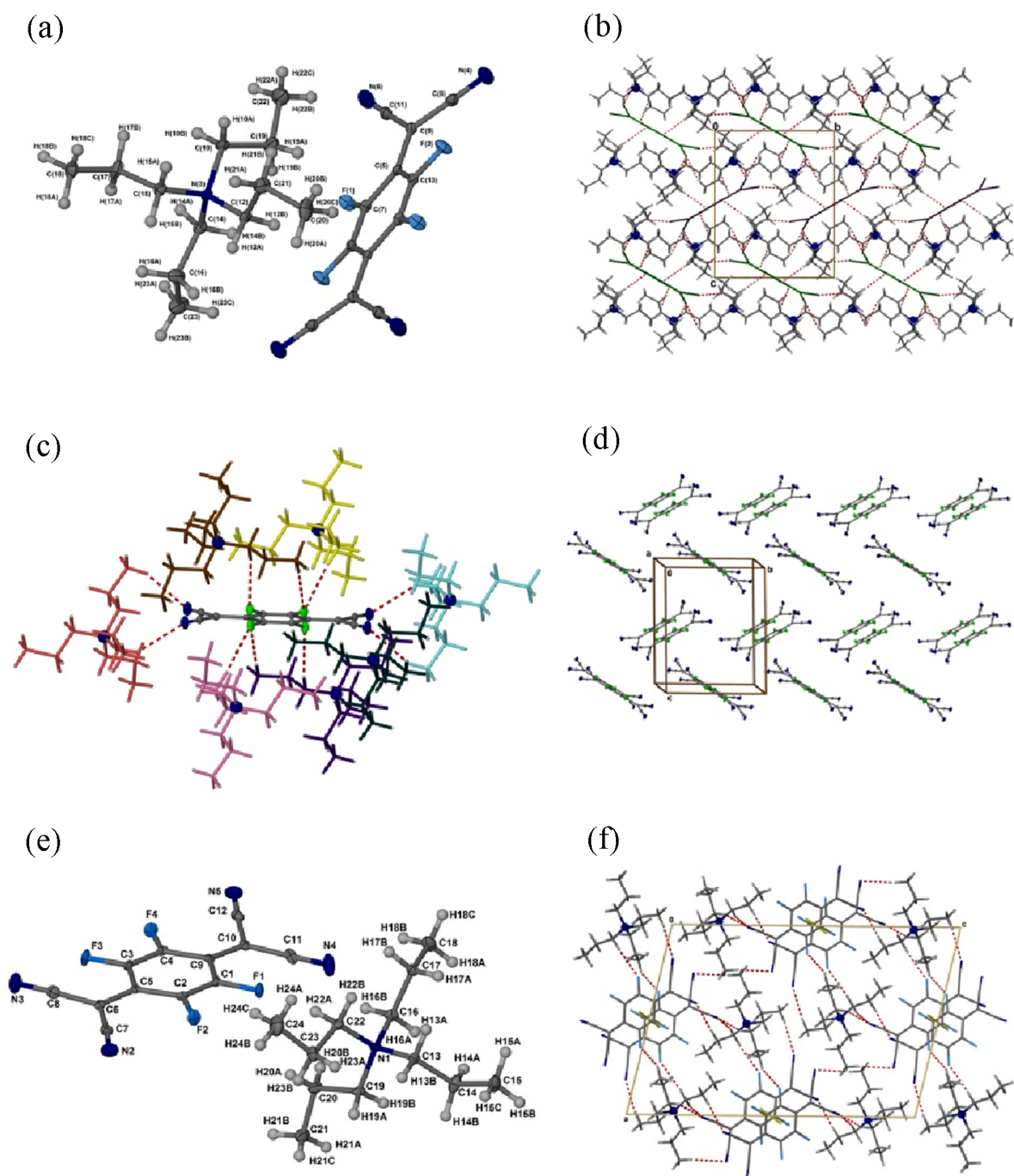


Figure 1. X-ray single crystal structures; (a) asymmetric unit of $(\text{Pr}_4\text{N})_2\text{TCNQF}_4$; (b) packing diagram of $(\text{Pr}_4\text{N})_2\text{TCNQF}_4$ viewed along the a axis; (c) hydrogen-bonding interactions in $(\text{Pr}_4\text{N})_2\text{TCNQF}_4$; (d) packing diagram of TCNQF_4^{2-} anions in $(\text{Pr}_4\text{N})_2\text{TCNQF}_4$; (e) the asymmetric unit of $\text{Pr}_4\text{NTCNQF}_4$; and (f) the packing diagram of $\text{Pr}_4\text{NTCNQF}_4$ viewed along the b axis.

2.3. FT-IR and Raman spectroscopies

IR and Raman spectroscopies have been used widely to determine the redox state of TCNQF₄ in previously synthesized materials.^{25,31,32} IR and Raman bands associated with the C≡N stretch are especially sensitive to the redox level. Generally, these bands are shifted to lower frequency regions as the negative charge on TCNQF₄ increases.

Table 2 summarizes the pertinent FT-IR spectroscopic data for the complexes synthesized in this study. In FT-IR spectra obtained for Li₂TCNQF₄ and (Pr₄N)₂TCNQF₄, the C≡N stretch bands are observed at the lowest wavenumbers of the compounds we studied and located at ~2160 and ~2100 cm⁻¹, indicating the presence of the TCNQF₄²⁻ dianion.^{25,26,33} In contrast, the FT-IR bands for the C≡N stretch in Pr₄NTCNQF₄ and LiTCNQF₄, are observed at ~2205 and ~2183 cm⁻¹, which are characteristic of the TCNQF₄^{•-} monoanion.^{7,30,32,34}

Table 2. Some characteristic FT-IR bands for TCNQF₄, LiTCNQF₄, Li₂TCNQF₄, (Pr₄N)₂TCNQF₄ and Pr₄NTCNQF₄.

Compound	$\nu(\text{C}\equiv\text{N}) / \text{cm}^{-1}$	$\nu(\text{C}=\text{C}) / \text{cm}^{-1}$	$\delta(\text{C}-\text{F}) / \text{cm}^{-1}$
TCNQF ₄	2225	1493	1193
LiTCNQF ₄	2204, 2184	1507	1204
Li ₂ TCNQF ₄	2154, 2127	1486	1262
(Pr ₄ N) ₂ TCNQF ₄	2164, 2132, 2093	1473	1236
Pr ₄ NTCNQF ₄	2205, 2182	1499	1204

Three characteristic Raman bands for TCNQF₄ located at 2226, 1665 and 1457 cm⁻¹ are assigned to C≡N, C=C ring and C–CN wing stretches.^{3,31,32,34} These vibration modes for Li₂TCNQF₄ (Figure 2a) are observed at 2119, 1658 and 1436 cm⁻¹ and (Pr₄N)₂TCNQF₄ has similarly located diagnostic Raman bands (Figure 2b). The bands associated with the C≡N and C–CN wing stretches are found at lower energy regions compared to those for neutral TCNQF₄ and LiTCNQF₄ (2223, 1443 cm⁻¹, see Figure 2c) or Pr₄NTCNQF₄ (2205 and 1443 cm⁻¹, see Figure 2d). The location of the Raman bands for LiTCNQF₄ and Pr₄NTCNQF₄ are also consistent with the presence of the TCNQF₄^{•-} monoanion.^{3,32,34} Interestingly, the Raman band for the C=C ring stretch of the TCNQF₄²⁻ dianion in

$\text{Li}_2\text{TCNQF}_4$ (1658 cm^{-1}) and $(\text{Pr}_4\text{N})_2\text{TCNQF}_4$ (1648 cm^{-1}) is found at lower frequencies in the $\text{TCNQF}_4^{\bullet-}$ monoanions of LiTCNQF_4 (1638 cm^{-1}) and $\text{Pr}_4\text{NTCNQF}_4$ (1641 cm^{-1}), but at higher frequency (1665 cm^{-1}) for neutral TCNQF_4 .

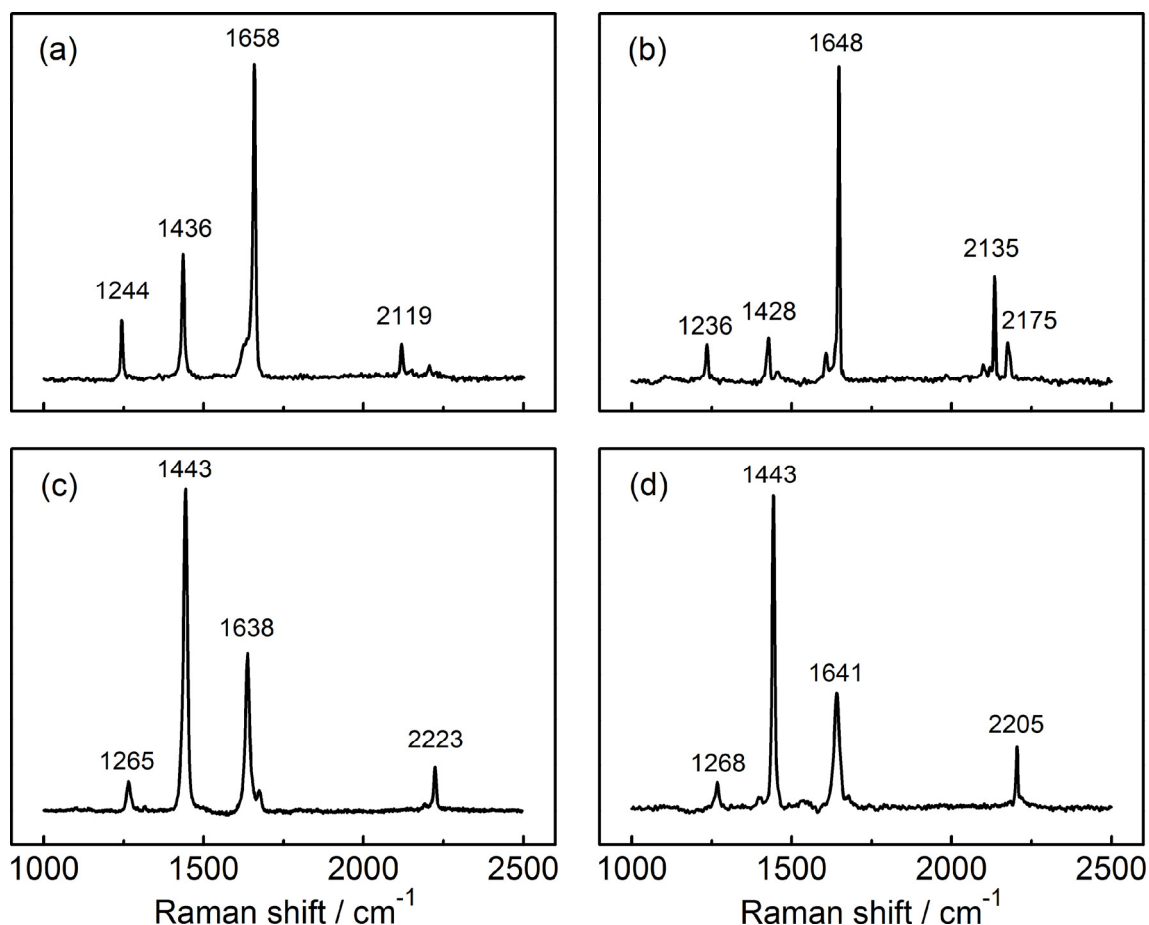


Figure 2. Raman spectra for (a) $\text{Li}_2\text{TCNQF}_4$, (b) $(\text{Pr}_4\text{N})_2\text{TCNQF}_4$, (c) LiTCNQF_4 and (d) $\text{Pr}_4\text{NTCNQF}_4$.

2.4. Studies in Solution

UV-vis spectra for $\text{Li}_2\text{TCNQF}_4$, $(\text{Pr}_4\text{N})_2\text{TCNQF}_4$, $\text{Pr}_4\text{NTCNQF}_4$ and LiTCNQF_4 dissolved in acetonitrile are shown in Figure 3. The spectra derived from LiTCNQF_4 and $\text{Pr}_4\text{NTCNQF}_4$ have two intense bands with peaks (λ_{max}) at 752, 411 nm, which are characteristic for $\text{TCNQF}_4^{\bullet-}$,⁴ whilst $\text{Li}_2\text{TCNQF}_4$ and $(\text{Pr}_4\text{N})_2\text{TCNQF}_4$ both exhibit two λ_{max} values at 333 and 218 nm, which is consistent with the presence of only the TCNQF_4^{2-} dianion species.⁴

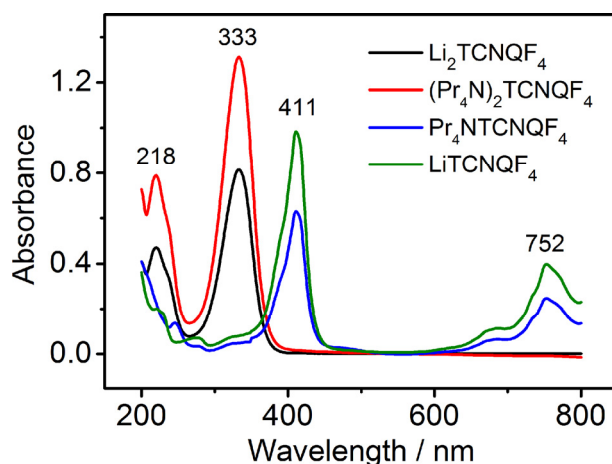


Figure 3. UV-vis spectra for designated compounds dissolved in acetonitrile.

^{19}F -NMR spectroscopy was employed to study the solution behaviour of $\text{Li}_2\text{TCNQF}_4$, $(\text{Pr}_4\text{N})_2\text{TCNQF}_4$ and $\text{Pr}_4\text{NTCNQF}_4$ in methanol- d_4 . The ^{19}F -NMR spectrum for $\text{Pr}_4\text{NTCNQF}_4$ in methanol- d_4 contains broad and weak signals (Figure 4a), implying the presence of paramagnetic $\text{TCNQF}_4^{\bullet-}$. In contrast, the ^{19}F -NMR spectrum for $(\text{Pr}_4\text{N})_2\text{TCNQF}_4$ in methanol- d_4 exhibits a sharp singlet (Figure 4b), indicating the presence of only one TCNQF_4 -based species which is diamagnetic. The ^{19}F -NMR spectrum for LiTCNQF_4 is similar to $\text{Pr}_4\text{NTCNQF}_4$, also paramagnetically shifted as seen in Figure 4c. However, the ^{19}F -NMR spectrum for $\text{Li}_2\text{TCNQF}_4$ does not provide the expected sharp singlet resonance as observed for $(\text{Pr}_4\text{N})_2\text{TCNQF}_4$. Instead three weak signals are observed, also paramagnetically broadened and shifted upfield compared with those observed for LiTCNQF_4 (Figures 5a and b). This observation may be attributed to rapid electron exchange between TCNQF_4^{2-} and $\text{TCNQF}_4^{\bullet-}$ ($\text{TCNQF}_4^{\bullet-}$ is formed by the oxidation of $\text{Li}_2\text{TCNQF}_4$ in solution as mentioned in Section 2.1).

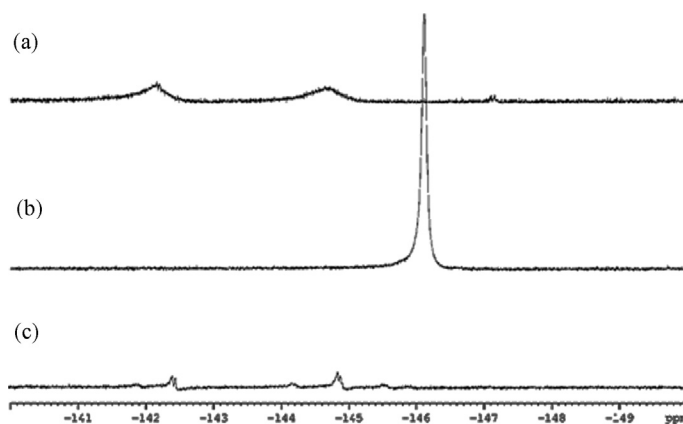


Figure 4. ^{19}F -NMR spectra for (a) $\text{Pr}_4\text{NTCNQF}_4$, (b) $(\text{Pr}_4\text{N})_2\text{TCNQF}_4$ and (c) LiTCNQF_4 in methanol- d_4 .

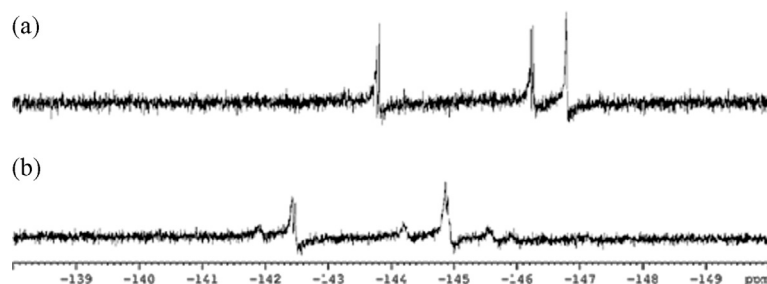


Figure 5. ^{19}F -NMR spectra for (a) $\text{Li}_2\text{TCNQF}_4$, (b) LiTCNQF_4 in methanol- d_4 .

Steady-state voltammetry also was used to determine the redox levels of TCNQF_4 in the synthesized materials. Figure 6a shows near a steady-state voltammogram for an acetonitrile (0.1 M Bu_4NPF_6) solution containing the product formed via Pathway 1 (Scheme 1). Clearly, the product obtained in boiling acetonitrile with a 4:1 molar ratio of LiI and TCNQF_4 contains only TCNQF_4^{2-} , devoid of $\text{TCNQF}_4^{\bullet-}$ as only oxidation current associated with the $\text{TCNQF}_4^{2-/\bullet-}$ and $\text{TCNQF}_4^{\bullet-/0}$ processes are detected. Figure 6b shows the near steady-state voltammogram in acetonitrile (0.1 M Bu_4NPF_6) after dissolution of LiTCNQF_4 solid, synthesized via Pathway 2. In this case, only $\text{TCNQF}_4^{\bullet-}$ is present as the zero current position lies midway between the currents for the $\text{TCNQF}_4^{\bullet-/2-}$ reduction and the $\text{TCNQF}_4^{\bullet-/0}$ oxidation processes. The same steady-state voltammetric behavior is observed for the product formed via Pathway 4 (Figure S4), confirming that only the $\text{TCNQF}_4^{\bullet-}$ species and no TCNQF_4^{2-} is present in the original solid $\text{Pr}_4\text{N}^+\text{TCNQF}_4^-$. The near steady-state voltammogram for $(\text{Pr}_4\text{N})_2\text{TCNQF}_4$ (Figure 6c) in acetonitrile (0.1 M Bu_4NPF_6) is similar to that for $\text{Li}_2\text{TCNQF}_4$. The result implies that only TCNQF_4^{2-} is present in this synthesized solid.

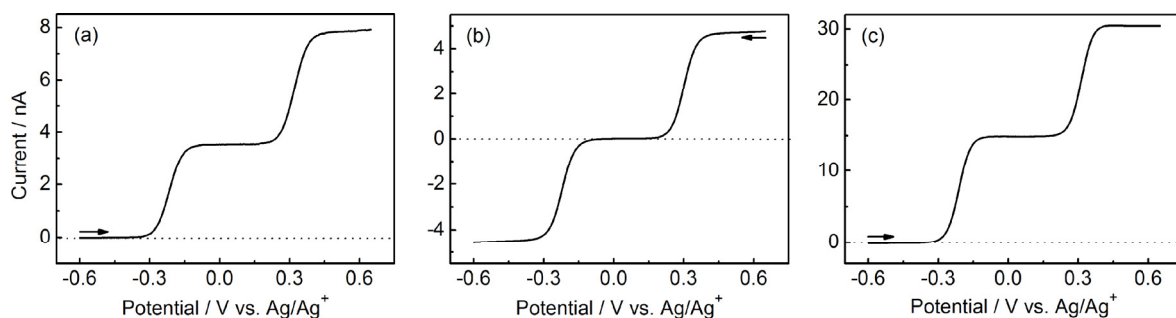


Figure 6. Near steady-state voltammograms of (a) 1.0 mM $\text{Li}_2\text{TCNQF}_4$, (b) 1.0 mM LiTCNQF_4 and (c) 4.5 mM $(\text{Pr}_4\text{N})_2\text{TCNQF}_4$ in acetonitrile (0.1 M Bu_4NPF_6) obtained with a 12.0 μm diameter carbon fiber microelectrode at a scan rate of 20 mV s^{-1} .

3. Conclusions

The reduction of TCNQF₄ by lithium iodide is a thermodynamically favorable process. Hence, either LiTCNQF₄ or Li₂TCNQF₄ can be generated by controlling the reaction temperature and the molar ratio of the reaction of TCNQF₄ with LiI. This appears to be the first report of the chemical synthesis of Li₂TCNQF₄ in high yield. Li₂TCNQF₄ is slowly oxidized to LiTCNQF₄ in air. However, (Pr₄N)₂TCNQF₄ is stable in air and is recommended as a synthetic precursor for the synthesis of a range of materials based on TCNQF₄²⁻. The X-ray structural analysis of single crystals of both (Pr₄N)₂TCNQF₄ and Pr₄N⁺TCNQF₄²⁻ show the presence of 3D H-supported networks. Electrochemical data, Raman, FT-IR, UV-vis spectra and elemental analysis are all consistent with the formulations derived from the crystal structures of (Pr₄N)₂TCNQF₄ and Pr₄N⁺TCNQF₄²⁻. ¹⁹F-NMR spectra obtained from Li₂TCNQF₄, (Pr₄N)₂TCNQF₄ and Pr₄N⁺TCNQF₄²⁻ dissolved in methanol-d₆ confirm that TCNQF₄²⁻ is diamagnetic and TCNQF₄^{•-} is paramagnetic.

4. Experimental Section

Chemicals

Tetrapropylammonium bromide, lithium iodide, n-pentane, methanol, acetone and TCNQF₄ were used as received. Acetonitrile and diethyl ether were dried before use. Bu₄NPF₆ was recrystallized twice from ethanol. All aqueous solutions were prepared from high purity water (resistivity of 18.2 MΩ·cm). All reactions were performed under N₂ using standard Schlenk techniques.

Synthesis of Li₂TCNQF₄ (Pathway 1, Scheme 1)

A boiling solution of LiI (273 mg, 2.04 mmol) in acetonitrile (15 ml) was added dropwise to a boiling solution of TCNQF₄ (142 mg, 0.51 mmol) in acetonitrile (15ml). The resulting mixture was stirred for 1h at 50-60°C under N₂. The suspension was cooled to room temperature before filtration to collect the solid. The crude product was washed with diethyl ether (dried and degassed prior use) until no LiI₃ was detected in the solution. Thus pure Li₂TCNQF₄, was obtained as a creamy white solid after drying under vacuum over P₂O₅ for three hours (134 mg, 90%). FT-IR (ν/cm⁻¹): CN: 2154 (s, TCNQF₄²⁻), 2134 (s, TCNQF₄²⁻). UV-vis (λ_{max} nm): 333 (TCNQF₄²⁻), 218 (TCNQF₄²⁻). HRMS: Calcd for (C₁₂F₄N₄)²⁻ m/z 138.0030; found: m/z 138.0026 (100%).

Synthesis of LiTCNQF₄, (Pathway 2, Scheme 1)

3 mL of a cold (0°C) acetonitrile solution containing LiI (75.4 mg, 0.57 mmol) was added dropwise into 8 mL of a cold acetonitrile solution of TCNQF₄ (104 mg, 0.38 mmol). The resulting mixture was placed in an ice bath and stirred under N₂ for 30 min. The precipitate that formed was isolated rapidly by vacuum filtration, followed by washing with acetonitrile (3 × 3 mL), diethyl ether (3 × 5 mL), and dried over P₂O₅ under vacuum overnight. The purple solid was obtained (89.5 mg, 84%). FT-IR (v/cm⁻¹): 2204(s, TCNQF₄^{•-}), 2198 (s, TCNQF₄^{•-}), High resolution HRMS: Calcd for (C₁₂F₄N₄)^{•-} m/z 276.0059; found: m/z 276.0140 (100%). UV-vis (λ_{max}nm): 752 (TCNQF₄^{•-}), 411 (TCNQF₄^{•-}).

Synthesis of (Pr₄N)₂TCNQF₄, (Pathway 3, Scheme 1)

Pr₄NBr (84.8 mg, 0.32 mmol) was dissolved in hot water (5 ml, degassed), and added to a aqueous solution of Li₂TCNQF₄ (30 mg, 0.11 mmol, in 5 mL of degassed hot water). The white precipitates that formed immediately was filtered and washed with hot water (3 × 10 mL) and diethyl ether (3 × 15 mL), and dried over P₂O₅ under vacuum overnight (62.5 mg, 93%). The colorless single crystals of (Pr₄N)₂(TCNQF₄) suitable for X-ray crystallographic analysis were obtained by diffusion of n-pentane into a methanol solution of (Pr₄N)₂TCNQF₄ over 5 days. ¹⁹F-NMR (282 MHz, δ/ppm, methanol-d₄): -146.10 (s). FT-IR (v/cm⁻¹): 2979 (m) 2949 (w), 2885 (w), 2164(s, CN), 2132 (s, CN), 2093 (w, CN) 1473 (s), 1387 (w), 1304 (w), 1287(w), 1222 (s), 1134 (s), 1106 (w), 1038 (w), 987 (m), 972(m), 956(s), 874 (w), 853 (w), 781 (s), 762 (m), 751 (m). UV-vis (nm): 333 (TCNQF₄²⁻), 218 (TCNQF₄²⁻). Anal. Calcd. for (Pr₄N)₂TCNQF₄ [C₃₆H₅₆F₄N₆]: C, 66.64, H 8.70, N, 12.95. Found: C, 66.49, H 9.01, N, 13.31.

Synthesis of Pr₄NTCNQF₄, (Pathway 4, Scheme 1)

5 mL of a hot aqueous solution of Pr₄NBr (51.7 mg, 0.19 mmol) was added into 5 mL of a hot aqueous solution of LiTCNQF₄ (50 mg, 0.18 mmol). The dark blue solid that formed immediately was filtered and washed with hot water (3 × 15 mL) and diethyl ether (3 × 15 mL), and then dried over P₂O₅ under vacuum overnight (43 mg, 68%). The dark blue needle crystals of Pr₄NTCNQF₄ suitable for X-ray crystallography were obtained by diffusion of diethyl ether into a methanol solution of Pr₄NTCNQF₄ over a week. ¹⁹F-NMR (282 MHz, δ/ppm, methanol-d₄): -142.19 (weak, broad), -144.64 (weak, broad). FT-IR (v/cm⁻¹): 2975 (m) 2943 (w), 2881 (w), 2200 (s, CN), 2182 (s, CN), 1633 (s), 1603 (w),

1536 (s), 1502 (m), 1472(m), 1459 (m), 1390 (s), 1347 (m), 1337 (m), 1265(m), 1204(m), 1142 (m), 1107 (w), 1039 (w), 967 (s), 872 (w), 853 (m), 756 (m), 716 (s). UV-vis (nm): 752 (TCNQF₄^{•-}), 411 (TCNQF₄^{•-}). Anal. Calcd. for P₄NTCNQF₄, [C₂₄H₂₈F₄N₅]: C, 62.32, H 6.10, N, 15.14. Found: C, 62.49, H 6.25, N, 15.31.

Electrochemical Procedure and Instrumentation

Voltammetric experiments under near steady-state conditions were conducted in acetonitrile (0.1 M Bu₄NPF₆) with an electrochemical workstation using a standard three-electrode cell configuration at room temperature (22 ± 2 °C). The working electrode (WE) was calibrated to be a 12.0 μm diameter carbon fiber microelectrode (diameter is 11 ± 2 μm). A platinum wire was used as the counter electrode. A silver wire immersed in acetonitrile solution containing 1.0 mM AgNO₃ and 0.1 M Bu₄NPF₆ was used as an Ag/Ag⁺ reference electrode (RE) (the potential is -135 ± 5 mV versus the ferrocene/ferrocenium couple Fc^{0/+}). The RE was separated from the test solution by a salt bridge containing the relevant supporting electrolyte.

Physical Characterization Procedures

FT-IR spectra were recorded using an ATR Instrument. Raman spectra were acquired with a spectrometer and microscope using 633 nm laser line. ¹⁹F-NMR spectra were recorded using a 300 MHz spectrometer at 282 MHz with chemical shifts reported relative to an external reference of CFCl₃ at 0.00 ppm. Mass spectra were acquired on an electrospray ionization mass spectrometer by direct infusion using a syringe pump and the spectra were run in positive ion mode. X-ray structural data were collected at the Australian Synchrotron using the PX1 beam-line operating at 15 KeV (λ = 0.7292 Å). The collection temperature was maintained at 100 K using an open-flow N₂ cryostream. Initial data processing was carried out using XDS software.³⁵ Both structures were solved by direct methods using SHELXS-97.³⁶ Least-squares refinements against F² were carried out using SHELXL-97, using the program X-Seed as a graphical interface.³⁷ All hydrogen atoms were placed in idealized positions and refined using a riding model. Documentations CCDC-831469 (for (Pr₄N)₂TCNQF₄) and 831468 (for Pr₄NTCNQF₄) contain the supplementary crystallographic data obtained for this report. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

Financial support from the Australian Research Council (ARC) to A.M.B and L.L.M is gratefully acknowledged. T.H.L is very appreciative of a graduate scholarship from Danang City in Vietnam and a stipend provided by the Monash University, Faculty of Science Dean's International Postgraduate Research Scholarship. D.A.K.T would like to thank the ARC Super Science Fellowship. The authors also express their appreciation to the Australian Synchrotron for the beam-time.

Supporting information includes the following: Figure S1: Stability of $\text{Li}_2\text{TCNQF}_4$; Figure S2: UV-vis Study of a Mixture of $\text{Li}_2\text{TCNQF}_4$ and LiTCNQF_4 ; Figure S3: Electrochemical Study of a Mixture of $\text{Li}_2\text{TCNQF}_4$ and LiTCNQF_4 ; Figure S4: Electrochemistry of $\text{Pr}_4\text{NTCNQF}_4$ and crystallographic information for $(\text{Pr}_4\text{N})_2\text{TCNQF}_4$ and $\text{Pr}_4\text{NTCNQF}_4$. This material is available free of charge via the internet at <http://pubs.acs.org>.

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Supporting Information

Synthesis, X-ray Crystallographic Characterization and Electrochemical Studies of TCNQF₄ Complexes with Li⁺ or Pr₄N⁺

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Stability of Li₂TCNQF₄

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Electrochemistry of Pr₄N⁺TCNQF₄

¹⁹F NMR spectrum for (Pr₄N)₂TCNQF₄

X-ray Crystallographic Data

Reference

Stability of Li₂TCNQF₄

The UV-vis spectrum for freshly synthesized Li₂TCNQF₄ dissolved in acetonitrile has two absorption bands at $\lambda_{\text{max}} = 333$ and 218 nm (Figure S1 - black curve), which is characteristic of TCNQF₄²⁻.^{S1} However, on exposure of the Li₂TCNQF₄ solid to air over 15 days before dissolution in acetonitrile, two new bands appear with $\lambda_{\text{max}} = 411$ and 752 nm (Figure S1 - red curve), which indicates that the Li₂TCNQF₄ has been partially converted to TCNQF₄^{•-}-based material.^{S1}

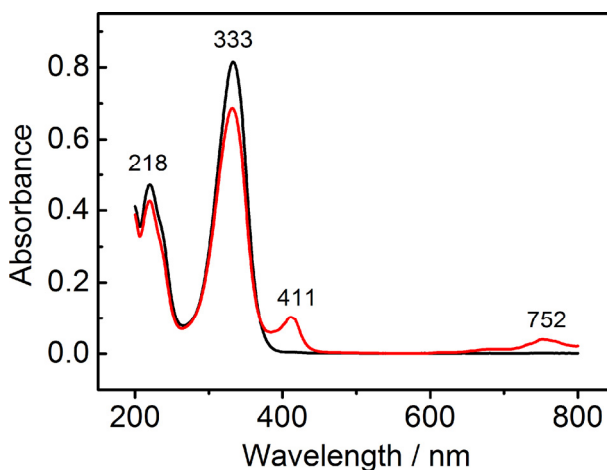


Figure S1. UV-vis spectra for Li₂TCNQF₄ in acetonitrile. Black curve, is for freshly prepared solid, and the red curve results after 15 days exposure to air.

UV-vis Study of a Mixture of Li₂TCNQF₄ and LiTCNQF₄

Absorption (UV-vis) spectroscopy was used for the quantitative determination of both TCNQF₄²⁻ and TCNQF₄^{•-}, present in a mixture of Li₂TCNQF₄ and LiTCNQF₄. The absorption bands at 333 and 411 nm^{S1} were utilized with reference to calibration curves. Figure S2 shows a typical experiment in which the crude product, generated via Pathway 1 (Scheme 1) using a 3:1 molar ratio of LiI and TCNQF₄, contained ~95% of TCNQF₄²⁻ and ~5% of TCNQF₄^{•-} (mole percent).

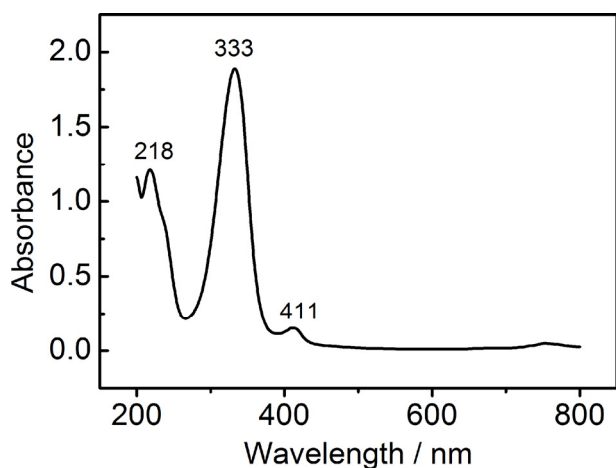


Figure S2. UV-vis spectrum in acetonitrile for the crude LiTCNQF₄ product produced from reaction of a 3:1 molar ratio of LiI and TCNQF₄ as shown in Pathway 1 (Scheme 1).

Electrochemical Study of a Mixture of Li₂TCNQF₄ and LiTCNQF₄

Steady-state voltammetry also was used to quantify the proportion of Li₂TCNQF₄ and LiTCNQF₄ present in the sample referred to in Figure S2. The limiting current data (Figure S3) confirm the conclusion from UV-vis spectroscopy that the crude product contained ~95% of Li₂TCNQF₄ and ~5% of LiTCNQF₄.

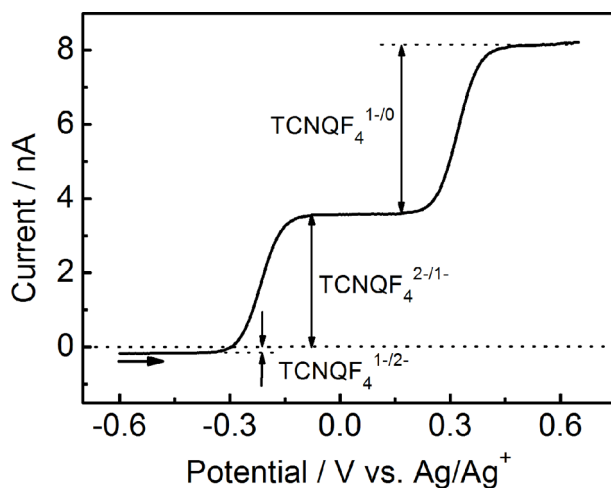


Figure S3. Near steady-state voltammogram for the product, synthesized via Pathway 1 (Scheme 1) using a 3:1 molar ratio of LiI and TCNQF₄ in acetonitrile (0.1 M Bu₄NPF₆) obtained with a 12.0 μ m diameter carbon fiber microelectrode at a scan rate of 20 mV s⁻¹.

Electrochemistry of $\text{Pr}_4\text{NTCNQF}_4$

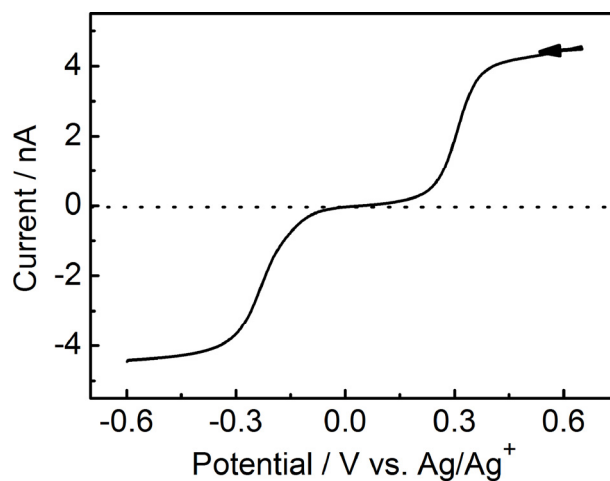


Figure S4. Near steady-state voltammogram for a 1.0 mM solution of $\text{Pr}_4\text{NTCNQF}_4$ in acetonitrile (0.1 M Bu_4NPF_6) obtained with a 12.0 μm diameter carbon fiber microelectrode at a scan rate of 20 mV s^{-1} .

^{19}F NMR spectrum for $(\text{Pr}_4\text{N})_2\text{TCNQF}_4$

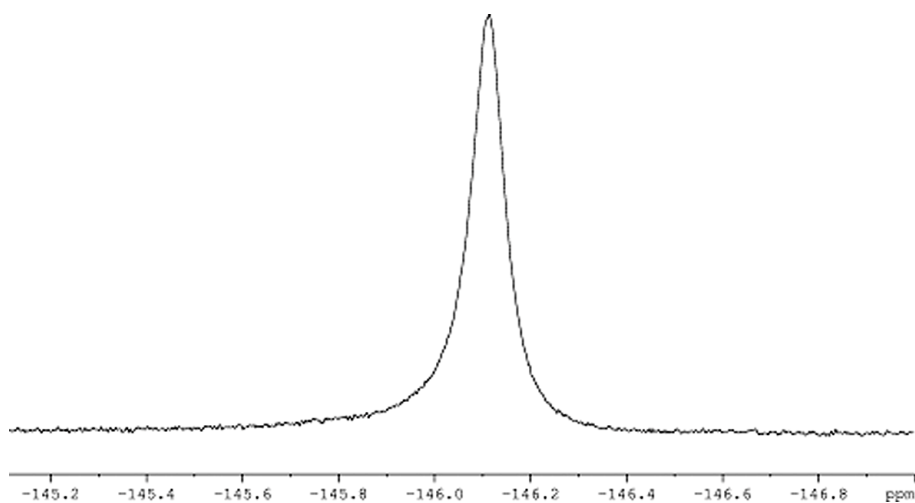


Figure S5. ^{19}F NMR spectrum for $(\text{Pr}_4\text{N})_2\text{TCNQF}_4$ in Methanol- d_4

X-ray Crystallographic Data

Table S1. Bond distances (Å) and angles (°) of hydrogen bonds for relevant crystallographic interactions for (Pr₄N)₂TCNQF₄. The identity of each atom is shown in Figure 1a. D represents donor atom and A is the acceptor atom.

D-H----A	d(D-H) (Å)	d(H-A) (Å)	d(D-A) (Å)	<(DHA) (°)	Symmetry code
C12-H12C----F1	0.980	2.620	3.582	166.9	$\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$
C15-H15C----F1	0.980	2.629	3.584	164.9	2-x, 1-y, -z
C13-H13A----N1	0.990	2.707	3.512	138.7	x, y-1, $\frac{1}{2}-z$
C7-H7A----N2	0.990	2.559	3.509	161.1	$\frac{3}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$
C12-H12A----N2	0.980	2.744	3.652	154.4	x, y-1, z
C16-H16B----N2	0.990	2.603	3.503	151	$\frac{3}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$

Table S2. Bond distances (Å) and angles (°) of hydrogen bonds for relevant crystallographic interactions for Pr₄NTCNQF₄. The identity of each atom is shown in Figure 1a. D represents donor atom and A is the acceptor atom.

D-H----A	d(D-H) Å	d(H-A) Å	d(D-A) Å	<(DHA) °	Symmetry code
C22-H22A----F1	0.990	2.609	3.589	170.5	x, y, z
C21-H21B----F3	0.980	2.571	3.308	132.0	1-x, 1-y, -z
C19-H19A----N2	0.990	2.574	3.497	160.8	$\frac{2}{3}-x, \frac{1}{2}+y, \frac{1}{2}-z$
C19-H22B----N2	0.990	2.455	3.431	168.8	$\frac{2}{3}-x, \frac{1}{2}+y, \frac{1}{2}-z$
C15-H15C----N3	0.980	2.724	3.611	174.5	1+x, y, z
C18-H18B----N4	0.980	2.731	3.629	152.3	x, y, z
C23-H23A----N5	0.990	2.610	3.404	137.2	$\frac{1}{2}+x, \frac{3}{2}-y, \frac{1}{2}+z$

Crystal data for (Pr₄N)₂TCNQF₄ (CCDC: 831469): C₁₈H₂₈F₂N₃, *M* = 324.43, colorless block, 0.22 × 0.19 × 0.15 mm³, monoclinic, space group *P*2₁/*n* (No. 14), *a* = 10.591(2), *b* = 11.791(2), *c* = 14.954(3) Å, β = 103.94(3)°, *V* = 1812.5(6) Å³, *Z* = 4, *D*_c = 1.189 g/cm³, *F*₀₀₀ = 700, MoKα radiation, λ = 0.77343 Å, *T* = 123(2)K, 2θ_{max} = 50.0°, 11403 reflections collected, 2478 unique (*R*_{int} = 0.0352). Final *GoF* = 1.054, *RI* = 0.0445, *wR*2 = 0.1078, *R* indices based on 2902 reflections with *I* > 2σ(*I*) (refinement on *F*²), 212 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.085 mm⁻¹.

Crystal data for Pr₄NTCNQF₄ (CCDC: 831468): C₂₄H₂₈F₄N₅, *M* = 462.51, blue needle, 0.09 × 0.03 × 0.01 mm³, monoclinic, space group *P*2₁/*n* (No. 14), *a* = 14.946(3), *b* = 7.1680(14), *c* = 22.136(4) Å, β = 103.01(3)°, *V* = 2310.6(8) Å³, *Z* = 4, *D*_c = 1.330 g/cm³, *F*₀₀₀ = 972, ADSC Quantum 210r Detector, Synchrotron radiation, λ = 0.77343 Å, *T* = 123(2)K, 2θ_{max} = 50.0°, 14654 reflections collected, 3145 unique (*R*_{int} = 0.0478). Final *GoF* = 1.048, *RI* = 0.0426, *wR*2 = 0.1087, *R* indices based on 3582 reflections with *I* > 2σ(*I*) (refinement on *F*²), 302 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.103 mm⁻¹.

Reference

(S1) Le, T. H.; Nafady, A.; Qu, X.; Martin, L. L.; Bond, A. M. *Anal. Chem.* **2011**, 83, 6731-6737.

Declaration for Thesis Chapter 4.3

Declaration by candidate

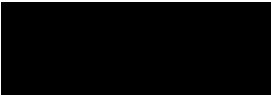
In the case of Chapter 4.3, the nature and extent of my contribution to the work was the following:

Nature of contribution	Extent of contribution (%)
Initiation, key ideas, experimental work, writing up	85

The following co-authors contributed to the work.

Name	Nature of contribution
Anthony P. O'Mullane	Initiation, key ideas, experimental work, writing up
Lisandra L. Martin	Initiation, key ideas, writing up
Alan M. Bond	Initiation, key ideas, writing up

Candidate's Signature

	06/06/2012
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Declaration by co-authors

The undersigned hereby certify that:

- (1) the above declaration correctly reflects the nature and extent of the candidate's contribution to this work, and the nature of the contribution of each of the co-authors.
- (2) they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;
- (3) they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
- (4) there are no other authors of the publication according to these criteria;
- (5) potential conflicts of interest have been disclosed to (a) granting bodies, (b) the editor or publisher of journals or other publications, and (c) the head of the responsible academic unit; and
- (6) the original data are stored at the following location and will be held for at least five years from the date indicated below:

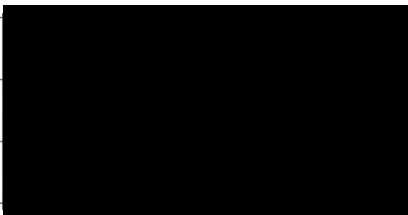
Location

School of Chemistry, Monash University, Clayton

Anthony P. O'Mullane

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Alan M. Bond

	07/05/2012
	23/5/12
	18/5/12

A new method for electrocrystallization of AgTCNQF₄ and Ag₂TCNQF₄ (TCNQF₄ = 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane) in acetonitrile

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Lisandra L. Martin · Alan M. Bond

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Abstract Semiconducting AgTCNQF₄ (TCNQF₄=2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane) has been electrocrystallized from an acetonitrile (0.1 M Bu₄NPF₆) solution containing TCNQF₄ and Ag(MeCN)₄⁺. Reduction of TCNQF₄ to the TCNQF₄¹⁻ anion, followed by reaction with Ag(MeCN)₄⁺ forms crystalline AgTCNQF₄ on the electrode surface. Electrochemical synthesis is simplified by the reduction of TCNQF₄ prior to Ag(MeCN)₄⁺ compared with the analogous reaction of the parent TCNQ to form AgTCNQ, where these two processes are coincident. Cyclic voltammetry and surface plasmon resonance studies reveal that the electrocrystallization process is slow on the voltammetric time scale (scan rate=20 mV s⁻¹) for AgTCNQF₄, as it requires its solubility product to be exceeded. The solubility of AgTCNQF₄ is higher in the presence of 0.1 M Bu₄NPF₆ supporting electrolyte than in pure solvent. Cyclic voltammetry illustrates a dependence of the reduction peak potential of Ag(MeCN)₄⁺ to metallic Ag on the electrode material with the ease of reduction following the order Au<Pt<GC<ITO. Ultraviolet-visible, Fourier transform infrared, and Raman spectra confirmed the formation of reduced TCNQF₄¹⁻ and optical microscopy showed needle-shaped morphology for the electrocrystallized AgTCNQF₄. AgTCNQF₄ also can be formed by solid–solid transformation at a TCNQF₄-modified

electrode in contact with aqueous media containing Ag⁺ ions. Chemically and electrochemically synthesized AgTCNQF₄ are spectroscopically identical. Electrocrystallization of Ag₂TCNQF₄ was also investigated; however, this was found to be thermodynamically unstable and readily decomposed to form AgTCNQF₄ and metallic Ag, as does chemically synthesized Ag₂TCNQF₄.

Keywords AgTCNQF₄ · Ag₂TCNQF₄ ·
Electrocrystallization

Introduction

Metal-organic charge-transfer (CT) complexes based on TCNQ (7,7,8,8-tetracyanoquinodimethane) have been intensively studied due to their novel conducting and/or magnetic properties [1–4]. TCNQ-based materials have been used for data storage [5, 6], in catalysis [7–9], and in magnetic and sensor devices [10, 11]. In contrast, investigation of TCNQF₄-based CT complexes (TCNQF₄=2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane) are much more limited, although some materials have been synthesized and characterized [12–19]. One of these is AgTCNQF₄, a metal-organic CT semiconducting material [16] which is regarded as an excellent candidate for field-emission cathodes [17], reversible bi-stable electrical and optical switches, as well as memory storage [16]. The chemical synthesis of AgTCNQF₄ has been reported by mixing the Ag⁺ cation and the TCNQF₄¹⁻ radical anion in acetonitrile [13], spontaneous redox reaction by placing Ag foil in a dry and degassed acetonitrile solution containing saturated TCNQF₄, and then heating to about 90 °C to achieve a film of AgTCNQF₄ on the Ag substrate [20]. Alternatively, a solid-phase reaction between TCNQF₄

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powder and Ag metal is possible by precisely controlling the temperature and time [16, 17]. AgTCNQF₄ also has been electrochemically synthesized by slow reduction of TCNQF₄ at an Ag electrode with a constant current in a two-compartment cell configuration containing acetonitrile [13]. The single-crystal X-ray structure of the electrocrystallized AgTCNQF₄ has been determined and is not isostructural with AgTCNQ [13]. The silver cations have a pseudotetrahedral geometry and the TCNQF₄^{1−} anions are nearly perfectly eclipsed and exhibit a high degree of dimerization, which results in the compound being essentially diamagnetic [13]. Ag₂TCNQF₄ also has been chemically synthesized by direct reaction of thin films of TCNQF₄ and Ag at 100 °C for approximately 100 s, where it was found to photodecompose to AgTCNQF₄ and metallic Ag [12].

In this paper, a potentiostatic electrochemical method for synthesizing AgTCNQF₄ and Ag₂TCNQF₄ in acetonitrile is reported. Thus, AgTCNQF₄ and Ag₂TCNQF₄ were electrocrystallized onto the surface of an inert electrode by sequential reduction of TCNQF₄ to TCNQF₄^{1−} and then to TCNQF₄^{2−} in acetonitrile (0.1 M Bu₄NPF₆), followed by combination with Ag(MeCN)₄⁺ also present in the solution to form AgTCNQF₄ and Ag₂TCNQF₄, respectively. Factors potentially affecting the electrochemical synthesis, such as the concentrations of TCNQF₄ and Ag(MeCN)₄⁺, scan rate, and electrode material have been explored. The isolated electrocrystallized AgTCNQF₄ complex was characterized by a range of microscopic and spectroscopic techniques, and in situ by surface plasmon resonance (SPR). Electrochemical synthesis of bulk Ag₂TCNQF₄ is complicated by the close proximity of the TCNQF₄^{1−/2−} process and the reduction of Ag(MeCN)₄⁺ to Ag metal. The solubility and solubility product of AgTCNQF₄ in acetonitrile with and without 0.1 M Bu₄NPF₆ supporting electrolyte also have been determined, but efforts to determine the solubility of Ag₂TCNQF₄ have not been successful because of thermodynamic instability, in which Ag₂TCNQF₄ undergoes an internal redox reaction to generate AgTCNQF₄ (as detected by UV-vis and FTIR spectroscopy) and metallic Ag.

Materials and methods

Chemicals

Ag(MeCN)₄BF₄ (98%, Aldrich), AgNO₃ (99.998%, Aldrich), TCNQF₄ (97%, Aldrich), acetonitrile (HPLC grade, Omnisolv), acetone (Suprasolv, Merck KGaA), and isopropanol (BDH) were used as received from the manufacturers. Bu₄NPF₆ (Aldrich) was recrystallized twice from 96% ethanol (Merck) and then dried at 100 °C under vacuum for 24 h.

Electrochemistry

Voltammetric measurements were carried out at room temperature (22±2 °C) with a Bioanalytical Systems (BAS) 100W electrochemical workstation and a standard three-electrode cell configuration. Working electrodes (WEs) were 3.0-mm diameter glassy carbon (GC) (BAS), gold or platinum (1.6-mm diameter, BAS) disks, or indium tin oxide (ITO)-coated glass plates (0.1–0.2 cm²) with a resistance of 10 Ω/sq (as quoted by the manufacturer, Prazisions Glas und Optik GmbH). All working electrodes, except for ITO, were polished with 0.3 μm alumina slurry on Microcloth polishing cloth, washed with deionized water (purified from a Millipore system, resistivity of 18.2 MΩ cm) and then sonicated in an ultrasonic bath for 5 min. ITO electrodes were cleaned by sonication in isopropanol and acetone for 5 and 10 min, respectively, and then washed with deionized water and dried under a stream of nitrogen gas. A silver wire placed in an acetonitrile solution containing 1.0 mM AgNO₃ and 0.1 M Bu₄NPF₆ was used to form an Ag/Ag⁺ reference electrode (RE) (the potential of this RE is −0.14 V versus the ferrocene/ferrocenium (Fc^{0/+}) couple). The counter electrode (CE) was platinum wire (1.0-mm diameter). In the case of rotating disk electrode (RDE) experiments, the Ag/Ag⁺ and Pt wire mentioned above also were used as reference and counter electrodes, while the working electrode was a 3.0-mm diameter GC electrode attached to BAS RDE-2 RDE assembly. In case of solid–solid state transformation experiments, TCNQF₄ crystals, physically adhered to GC and ITO electrode surfaces, were used as the working electrodes, the reference electrode was aqueous Ag/AgCl (3.0 M KCl) (BAS) and Pt wire (1.0-mm diameter) was used as the counter electrode. In bulk electrolysis experiments, a three-compartment cell was used with each of the working (Pt foil), reference (Ag/Ag⁺), and counter (Pt mesh) electrodes placed in one compartment of the cell. Stirring via a magnetic bar in the working electrode compartment was used during the course of bulk electrolysis. These bulk electrolysis experiments were stopped when the current decreased to 0.1% of the initial value. Nitrogen gas was used to purge solutions of oxygen prior to commencing electrochemical experiments. A stream of this gas was maintained above the solution during the course of the experiments.

In situ SPR experiments were carried out using an AutoLab ESPRIT system, interfaced to an AutoLab PGSTAT100 potentiostat. A 50-nm thick gold film coated on a glass plate was used as both the SPR substrate and working electrode (all instrumentations and electrodes for SPR experiments were supplied by ECO-Chemie). The angle of the minimum reflection in the Kretschmann configuration [21] was used to examine the SPR response

during the course of electrochemical experiments. Platinum wires were used as quasi-reference and counter electrodes in the SPR-electrochemical measurements.

Other instrumentation

UV-vis spectra were recorded with a Varian Cary 5000 UV-vis NIR spectrophotometer on solutions contained in a 1.0-cm path length cuvette. FTIR spectra were obtained with a Varian UMA600 IR microscope and FTS7000 optics bench using 128 scans and a resolution of 8 cm^{-1} . A Renishaw Invia Raman spectrograph, using an Argon ion laser excitation at 633 nm, was used to measure Raman spectra. Optical microscopic images were collected with an Olympus BX51M optical microscope at a magnification factor of 20. SEM image was recorded with a FEI Nova SEM instrument.

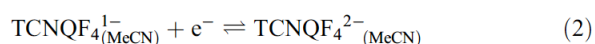
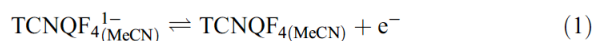
Results and discussion

Solubility of AgTCNQF₄ in acetonitrile

A 10.0 mM TCNQF₄¹⁻ solution was prepared by exhaustive reductive electrolysis of 5.0 mL of 10.0 mM TCNQF₄ acetonitrile solution (0.1 M Bu₄NPF₆) with the potential of the Pt working electrode held at 100 mV vs. Ag/Ag⁺ (all potentials in this paper are reported versus Ag/AgNO₃ (1.0 mM) in acetonitrile containing 0.1 M Bu₄NPF₆ unless otherwise stated). 1.0 mL of 100 mM Ag(MeCN)₄⁺ acetonitrile solution was then added into the TCNQF₄¹⁻ solution with stirring for 1 min. A dark blue precipitate formed immediately and was collected after centrifugation and the solid was washed three times with 1.0 mL of acetonitrile to ensure removal of excess Ag(MeCN)₄⁺ and Bu₄NPF₆ supporting electrolyte. Finally, 2.0 mL of acetonitrile was added into the test tube containing pure solid AgTCNQF₄, followed by sonication for 5 min to achieve good mixing with the dissolved material. The AgTCNQF₄ saturated acetonitrile solution and solid AgTCNQF₄ were separated by centrifugation and filtration. The solid AgTCNQF₄ was placed on an ITO surface and dried under vacuum prior to characterization by spectroscopic and microscopic techniques (see section “Chemically synthesized AgTCNQF₄”). The concentration of the TCNQF₄¹⁻ remaining in the saturated solution was determined by UV-vis spectroscopy and measuring the absorbance at 411 nm and subsequent reference to a calibration curve, and found to be $7.08 \pm 0.16 \times 10^{-4}\text{ M}$. Consequently, the values for the solubility and solubility product of AgTCNQF₄ in acetonitrile are $7.08 \pm 0.16 \times 10^{-4}\text{ M}$ and $5.01 \pm 0.22 \times 10^{-7}\text{ M}^2$, respectively.

RDE voltammetry also was used to determine the concentration of TCNQF₄¹⁻. TCNQF₄¹⁻ is oxidized to

neutral TCNQF₄ (Eq. 1) in acetonitrile (0.1 M Bu₄NPF₆) under RDE conditions to give a limiting current that is proportional to the concentration of TCNQF₄¹⁻. Solid Bu₄NPF₆ was added to a saturated acetonitrile solution of AgTCNQF₄ to give the 0.1 M electrolyte concentration needed for RDE experiments. A 3.0-mm diameter GC RDE was used at a rotation rate of 1,000 rpm and scan rate of 10 mV s^{-1} , and gave well-defined limiting currents (see Fig. 1) for the three processes given in Eqs. 1 to 3. The solubility and solubility product values were found to be the same as determined by UV-vis spectroscopy.



The solubility of AgTCNQF₄ was then re-determined in an acetonitrile solution containing 0.1 M Bu₄NPF₆ electrolyte. In this case, 2.0 mL of acetonitrile containing 0.1 M Bu₄NPF₆ was used for RDE and UV-vis methods and the concentration of TCNQF₄¹⁻ in the saturated solution was determined to be $1.10 \pm 0.04 \times 10^{-3}\text{ M}$. This value translates to a solubility product for AgTCNQF₄ of $1.22 \pm 0.08 \times 10^{-6}\text{ M}^2$, indicating that the solubility of AgTCNQF₄ in the presence of 0.1 M Bu₄NPF₆ is higher than that in neat solvent. This enhancement in solubility also has been observed for AgTCNQ and CuTCNQ [22, 23] in the presence of electrolyte and, in this case, can be attributed to the ion pairing of Ag(MeCN)₄⁺ with PF₆⁻ and TCNQF₄¹⁻ with Bu₄N⁺, which favors the dissociation of AgTCNQF₄ to Ag(MeCN)₄⁺ and TCNQF₄¹⁻ [22].

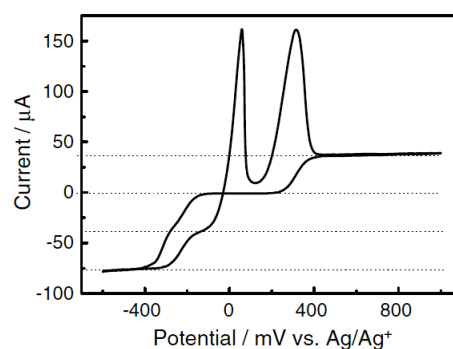


Fig. 1 Cyclic voltammogram obtained with a 3.0-mm diameter GC electrode RDE (1,000 rpm, 10 mV s^{-1}) for AgTCNQF₄ dissolved in acetonitrile (0.1 M Bu₄NPF₆)

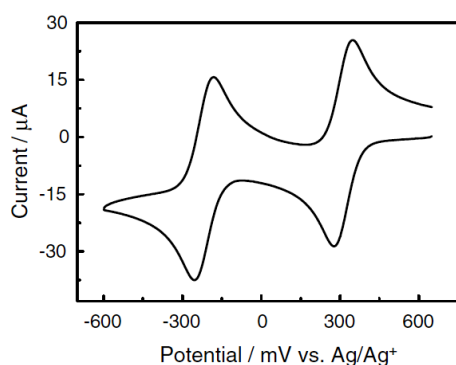


Fig. 2 Cyclic voltammogram obtained with a 3.0-mm diameter GC electrode at a scan rate of 100 mV s^{-1} for 1.0 mM TCNQF_4 in acetonitrile ($0.1 \text{ M Bu}_4\text{NPF}_6$)

Cyclic voltammetric study of the electrocrystallization of AgTCNQF_4 and $\text{Ag}_2\text{TCNQF}_4$ in acetonitrile

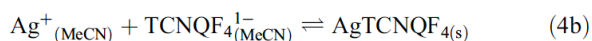
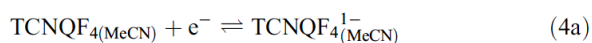
Voltammetry of TCNQF_4 and $\text{Ag}(\text{MeCN})_4^+$ in acetonitrile ($0.1 \text{ M Bu}_4\text{NPF}_6$) solution

The limited solubility of AgTCNQF_4 in acetonitrile ($0.1 \text{ M Bu}_4\text{NPF}_6$) indicated that electrocrystallization of AgTCNQF_4 should be possible. A cyclic voltammogram of 1.0 mM TCNQF_4 in acetonitrile ($0.1 \text{ M Bu}_4\text{NPF}_6$) using a GC electrode recorded at a scan rate of 100 mV s^{-1} is shown in Fig. 2. TCNQF_4 underwent the two chemically and electrochemically reversible one-electron reduction processes (reverse of Eq. 1 and Eq. 2) as expected [24]. The mid-point potentials E_m for these processes at GC, Au, Pt, and ITO electrodes are given in Table 1 (where $E_m^1 = (E_{p1}^{\text{red}} + E_{p1}^{\text{ox}})/2$ and $E_m^2 = (E_{p2}^{\text{red}} + E_{p2}^{\text{ox}})/2$, and E_p^{red} and E_p^{ox} are reduction and oxidation peak potentials, respectively, for processes related to Eqs. 1 and 2). E_m , as expected, is almost independent of electrode material.

Cyclic voltammograms for $2.0 \text{ mM Ag}(\text{MeCN})_4^+$ in acetonitrile ($0.1 \text{ M Bu}_4\text{NPF}_6$) are shown in Fig. 3. In the case of reduction of $\text{Ag}(\text{MeCN})_4^+$ to Ag metal, the process is strongly dependent on the nature of the electrode material. Thus, $\text{Ag}(\text{MeCN})_4^+$ cations follow the ease of reduction

order, $\text{Au} < \text{Pt} < \text{GC} < \text{ITO}$ (Fig. 3e). Moreover, E_p^{red} for reduction of $\text{Ag}(\text{MeCN})_4^+$ in the first cycle of potential is always more negative than in subsequent cycles. For example, at a GC electrode in the first cycle with a scan rate of 100 mV s^{-1} , E_p^{red} for the reduction of $\text{Ag}(\text{MeCN})_4^+$ to metallic Ag is at -331 mV , whereas in the second cycle, E_p^{red} is -140 mV . Additionally, a sharp oxidation peak for stripping silver occurs at 68 mV and current crossover is detected at -260 and -77 mV in the first cycle. These results imply that the reduction of $\text{Ag}(\text{MeCN})_4^+$ to Ag metal occurs via a nucleation and growth process [23]. A comparison with TCNQ shows the reduction to TCNQ^{1-} occurs at a potential value slightly more positive than for $\text{Ag}(\text{MeCN})_4^+$ reduction [23]. For TCNQF_4 , the first reduction process is now well removed from that of $\text{Ag}(\text{MeCN})_4^+$ (compare Figs. 2 and 3). Consequently, AgTCNQF_4 can be readily electrosynthesized via scheme 1. However, in principle, $\text{Ag}_2\text{TCNQF}_4$ cannot be electrochemically synthesized at Au or Pt electrodes where $\text{Ag}(\text{MeCN})_4^+$ is reduced prior to the TCNQF_4^{1-} process, although at GC or ITO electrodes, this is now possible (via scheme 2) because the reduction of TCNQF_4^{1-} to TCNQF_4^{2-} is slightly more positive than that of $\text{Ag}(\text{MeCN})_4^+$. However, efforts to achieve electrochemical synthesis of bulk $\text{Ag}_2\text{TCNQF}_4$ on GC and ITO have not been successful as the potentials for reduction of TCNQF_4^{1-} and $\text{Ag}(\text{MeCN})_4^+$ on GC and ITO are still very close. Furthermore, $\text{Ag}_2\text{TCNQF}_4$ is not a stable species in acetonitrile (see section “Chemically synthesized $\text{Ag}_2\text{TCNQF}_4$ ”).

Scheme 1



Scheme 2

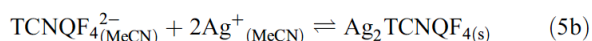
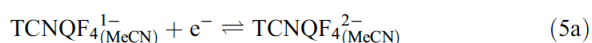


Table 1 Summary of voltammetric data obtained at a scan rate of 100 mV s^{-1} for TCNQF_4 and $\text{Ag}(\text{MeCN})_4^+$ in acetonitrile ($0.1 \text{ M Bu}_4\text{NPF}_6$) with GC, Au, Pt, and ITO electrodes (potential (millivolts) vs. Ag/Ag^+)

WE	Compound							$\text{Ag}(\text{MeCN})_4^+$ (1st cycle)			
	TCNQF_4										
	E_p^{red1}	E_p^{ox1}	E_m^1	E_p^{red2}	E_p^{ox2}	E_m^2	ΔE^0	E_p^{red}	E_p^{ox}	E_m	ΔE_p
GC	277	345	311	-255	-185	-220	531	-331	68	-132	399
Au	277	343	310	-255	-185	-220	530	-99	79	-10	178
Pt	277	343	310	-256	-186	-221	531	-133	59	-37	192
ITO	201	406	304	-335	-157	-246	550	-447	34	-207	481

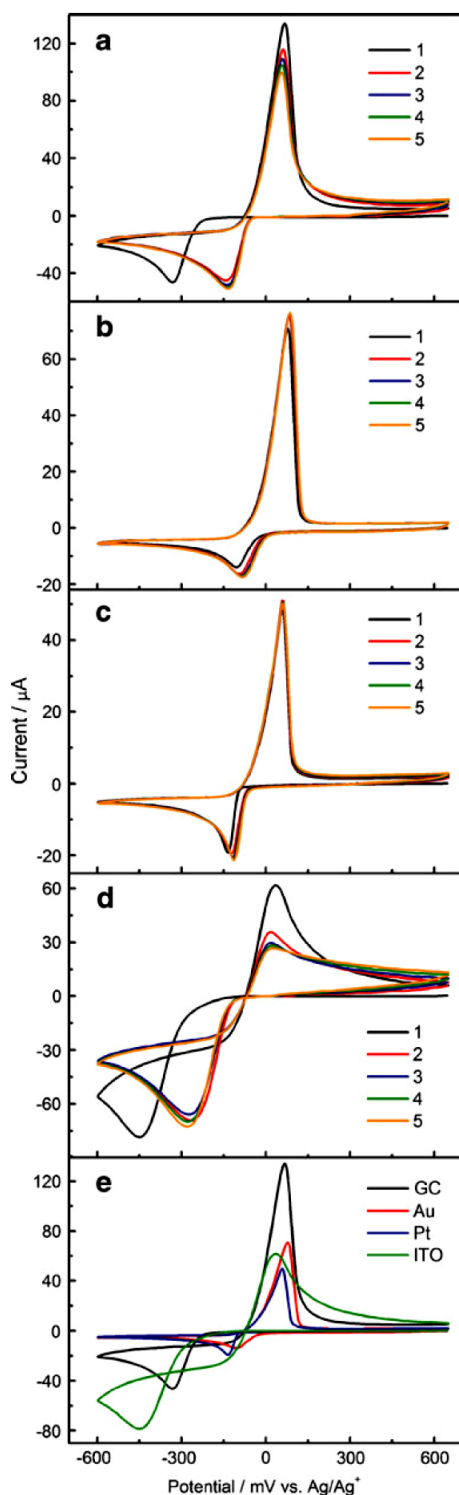


Fig. 3 Cyclic voltammograms obtained at a scan rate of 100 mV s^{-1} at GC, Au, Pt, ITO electrodes for $2.0 \text{ mM Ag(MeCN)}_4^+$ in acetonitrile ($0.1 \text{ M Bu}_4\text{NPF}_6$) **a–d** represent number of cycles across potential range at GC, Au, Pt, ITO, **e** first cycle for each electrode

Cyclic voltammetry of TCNQF_4 in the presence of Ag(MeCN)_4^+ in acetonitrile ($0.1 \text{ M Bu}_4\text{NPF}_6$)

1. Reduction of TCNQF_4 to TCNQF_4^{1-} in the presence of Ag(MeCN)_4^+

In order to ensure electrocrystallization of AgTCNQF_4 rather than $\text{Ag}_2\text{TCNQF}_4$ occurs, the potential was switched at 50 mV , which lies between the $\text{TCNQF}_4^{0/1-}$ and $\text{TCNQF}_4^{1-/2-}$ processes. The concentration ratios of TCNQF_4 and Ag(MeCN)_4^+ were varied to produce the cyclic voltammetric behavior exhibited in Fig. 4a, b and c. Clearly, when the Ag(MeCN)_4^+ concentration is constant and that of TCNQF_4 is increased, the ratio of oxidation and reduction peak current ($i_p^{\text{ox}}/i_p^{\text{red}}$) decreases, which is expected if reduction of TCNQF_4 to TCNQF_4^{1-} is followed by electrocrystallization of AgTCNQF_4 (scheme 1) [25]. However, electrocrystallization can only occur when the solubility product of AgTCNQF_4 is exceeded at the electrode surface and if the rate of precipitation is sufficiently fast. Studies with 2.0 mM TCNQF_4 and $100 \text{ mM Ag(MeCN)}_4^+$ in acetonitrile ($0.1 \text{ M Bu}_4\text{NPF}_6$) solution show that the precipitation kinetics are relatively slow as the $i_p^{\text{ox}}/i_p^{\text{red}}$ ratio approaches unity at high scan rate of $>2 \text{ V s}^{-1}$ (data not shown). Interestingly, no well-defined stripping peak was found when the potential was scanned in the positive direction to very positive potentials under conditions relevant to Fig. 4c. This behavior implies that AgTCNQF_4 either does not precipitate on the time scale of cyclic voltammetry or predominantly precipitates away from the surface of the electrode (under conditions of Fig. 4c, a dark blue precipitate is observed in the solution if a potential of 150 mV is applied for 15 min). However, when a solution of 2.0 mM TCNQF_4 and $100 \text{ mM Ag(MeCN)}_4^+$ is used, a broad oxidation stripping process is detected at around 770 mV on the reverse scan (Fig. 4d), implying that AgTCNQF_4 is now electrocrystallized onto the electrode surface and oxidized back to neutral TCNQF_4 .

2. Reduction of TCNQF_4^{1-} to TCNQF_4^{2-} in the presence of Ag(MeCN)_4^+

When the switching potential was set at -170 mV , and hence slightly more negative than the onset of the $\text{TCNQF}_4^{1-/2-}$ process, with 1.0 mM TCNQF_4 and $10.0 \text{ mM Ag(MeCN)}_4^+$ present, the cyclic voltammograms at a GC electrode become much more complicated. On the first scan in the negative potential direction, the $\text{TCNQF}_4^{0/1-}$ reduction process is still located at its normal position; in contrast, the second $\text{TCNQF}_4^{1-/2-}$ process is modified and now found at -147 mV . On reversing the scan direction, a sharp stripping oxidation process at 215 mV is followed by the $\text{TCNQF}_4^{1-}/$

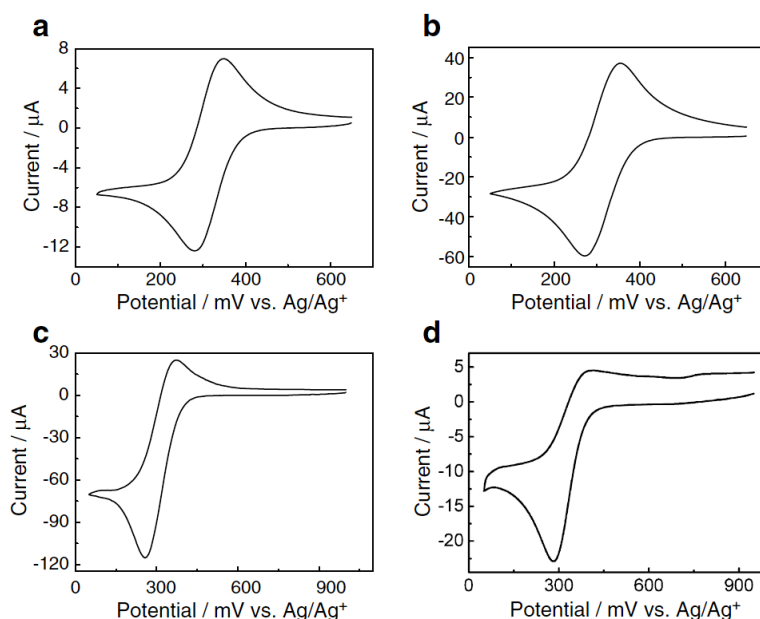


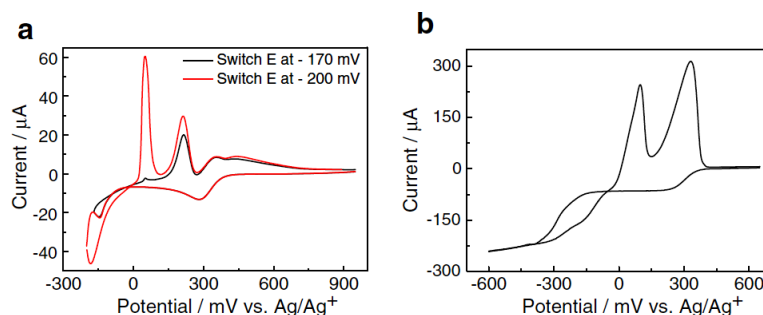
Fig. 4 Cyclic voltammograms obtained at a scan rate of 20 mV s^{-1} with a 3.0-mm diameter GC electrode in acetonitrile (0.1 M Bu_4NPF_6) containing **a–c** 10.0 mM $\text{Ag}(\text{MeCN})_4^+$ and 1.0, 5.0, 10.0 mM TCNQF_4 , respectively, **d** 100 mM $\text{Ag}(\text{MeCN})_4^+$ and 2.0 mM TCNQF_4

TCNQF_4 process (Fig. 5a, black curve). The new oxidation process is assumed to be associated with stripping of electrocrystallized solid $\text{Ag}_2\text{TCNQF}_4$, which was formed via scheme 2. When the potential was switched at the more negative value of -200 mV , on scanning in the positive potential direction, a current loop and a sharp stripping process at 50 mV were detected (Fig. 5a, red curve) in addition to the $\text{Ag}_2\text{TCNQF}_4$ stripping process. The current loop is due to the nucleation and growth of metallic Ag on the GC electrode surface [26–28] (Eq. 3). In the reverse potential scan direction, a broad oxidation process also is detected at around 450 mV . This process is presumed to result from the oxidation of AgTCNQF_4 , which is formed by the oxidation of TCNQF_4^{2-} in $\text{Ag}_2\text{TCNQF}_4$ back to TCNQF_4^{1-} , followed by reaction in Eq. 4b. However, the potential for the oxidation process is less

positive than that of $\sim 770 \text{ mV}$ that is detected when the potential is switched at 50 mV (Fig. 4d). Therefore, AgTCNQF_4 derived from the oxidation of $\text{Ag}_2\text{TCNQF}_4$ rather than from combination of $\text{Ag}(\text{MeCN})_4^+$ and TCNQF_4^{1-} in the negative potential direction scan may exist in a different phase. Interestingly, two AgTCNQ oxidation processes also were seen in the cyclic voltammetry in acetonitrile solutions containing TCNQ and $\text{Ag}(\text{MeCN})_4^+$ [23].

The deposition of $\text{Ag}_2\text{TCNQF}_4$ and Ag onto the electrode surface was confirmed by cyclic voltammetric experiments using a RDE. Figure 5b shows GC RDE voltammograms in acetonitrile (0.1 M Bu_4NPF_6) containing 1.0 mM TCNQF_4 with 1.0 mM $\text{Ag}(\text{MeCN})_4^+$. When scanning the potential in the negative direction, reduction of TCNQF_4 to TCNQF_4^{1-} and then TCNQF_4^{2-} is followed by reduction of $\text{Ag}(\text{MeCN})_4^+$

Fig. 5 Cyclic voltammograms obtained in acetonitrile (0.1 M Bu_4NPF_6) with **a** a 3.0-mm diameter GC electrode at a scan rate of 20 mV s^{-1} for 1.0 mM TCNQF_4 and 10.0 mM $\text{Ag}(\text{MeCN})_4^+$, **b** a 3.0-mm diameter GC RDE (1,000 rpm, 10 mV s^{-1}) for 1.0 mM TCNQF_4 and 1.0 mM $\text{Ag}(\text{MeCN})_4^+$



to metallic silver. On reversing the scan direction, stripping of Ag and $\text{Ag}_2\text{TCNQF}_4$ formed at the surface occurs when the potential was scanned in the positive direction.

The electrocrystallization and stripping of $\text{Ag}_2\text{TCNQF}_4$ were also explored as a function of scan rate and other parameters. Cyclic voltammograms in Fig. 6a reveal that for 1.0 mM TCNQF_4 and 2.0 mM $\text{Ag}(\text{MeCN})_4^+$ at a GC electrode (scan rate = 20 mV s^{-1} , potential range +650 to –600 mV), reduction of TCNQF_4^{1-} occurs just prior to that of $\text{Ag}(\text{MeCN})_4^+$ in the first cycle, but in later cycles of potential, both processes are almost coincident. This change is expected on the basis of the voltammetry of $\text{Ag}(\text{MeCN})_4^+$ (Fig. 3a). However, the potentials for stripping of Ag and $\text{Ag}_2\text{TCNQF}_4$ do not change upon cycling the potential. Besides Ag and $\text{Ag}_2\text{TCNQF}_4$ stripping, only one other oxidation process at –200 mV is observed, which corresponds to the oxidation of $\text{TCNQF}_4^{2-}(\text{MeCN})$ to $\text{TCNQF}_4^{1-}(\text{MeCN})$ (Fig. 6a dark yellow curve).

In another series of experiments with 1.0 mM TCNQF_4 and 2.0 mM $\text{Ag}(\text{MeCN})_4^+$, the magnitude of the $\text{Ag}_2\text{TCNQF}_4$ stripping peak was investigated as a function of electrocrystallization time. In this case, the potential was set at –170 mV for a certain time before sweeping the potential in the positive direction. Under these conditions, the peak current at 230 mV for stripping $\text{Ag}_2\text{TCNQF}_4$ from the electrode increases with deposition time (Fig. 6b). In contrast, increasing the scan rate under cyclic voltammetric conditions decreases the oxidation of $\text{Ag}_2\text{TCNQF}_4$ (Fig. 6c), which implies that its deposition onto the electrode surface also is kinetically controlled.

Role of working electrode material

Cyclic voltammograms for 1.0 mM TCNQF_4 and 2.0 mM $\text{Ag}(\text{MeCN})_4^+$ in acetonitrile (0.1 M Bu_4NPF_6) at GC, Au, Pt, and ITO electrodes are shown in Fig. 7. Since the reduction

of $\text{Ag}(\text{MeCN})_4^+$ to Ag on Au electrode occurs prior to that for the reduction of TCNQF_4^{1-} to TCNQF_4^{2-} by about 200 mV, $\text{Ag}_2\text{TCNQF}_4$ cannot be formed, as indicated in scheme 2. Hence, no $\text{Ag}_2\text{TCNQF}_4$ stripping process was detected in the positive potential scans at the Au electrode (Fig. 7b). In contrast, $\text{Ag}_2\text{TCNQF}_4$ can be electrocrystallized directly onto GC, Pt, and ITO electrodes as $\text{Ag}_2\text{TCNQF}_4$ stripping process is observed when scanning the potential in the positive direction (Fig. 7a, c, d), even though the reduction of $\text{Ag}(\text{MeCN})_4^+$ cations occurs slightly before that of the TCNQF_4^{1-} at the Pt electrode. Since the reduction of TCNQF_4^{1-} occurs slightly before that of $\text{Ag}(\text{MeCN})_4^+$ at GC and ITO electrodes, these electrode materials are preferable for electrochemical synthesis of $\text{Ag}_2\text{TCNQF}_4$.

The influence of $\text{Ag}(\text{MeCN})_4^+$ concentration on the formation of $\text{Ag}_2\text{TCNQF}_4$

Voltammograms derived from 1.0 mM TCNQF_4 (Fig. 8) reveal that the second TCNQF_4^{1-} reduction peak potential ($E_{\text{p}}^{\text{Red2}}$) depends markedly on the $\text{Ag}(\text{MeCN})_4^+$ concentration. In contrast, the peak potential for the first TCNQF_4 to TCNQF_4^{1-} reduction ($E_{\text{p}}^{\text{Red1}}$) is independent of the $\text{Ag}(\text{MeCN})_4^+$ concentration. $E_{\text{p}}^{\text{Red2}}$ shifted 78 mV to more positive potential when $\text{Ag}(\text{MeCN})_4^+$ concentration was increased from 0.0 to 10.0 mM. The shift of $E_{\text{p}}^{\text{Red2}}$ to more positive potential is consistent with the combination of TCNQF_4^{2-} and $\text{Ag}(\text{MeCN})_4^+$ [25].

The influence of scan rate

Peak potentials $E_{\text{p}}^{\text{Red1}}$, $E_{\text{p}}^{\text{Red2}}$, and $E_{\text{p}}^{\text{Red3}}$ shift 15, 15, and 181 mV, respectively, to more negative potential when the scan rate is increased from 20 to 500 mV s^{-1} at a GC electrode under conditions described in Fig. 9. Thus, although a small IR_{u} drop may be present, the scan rate does not significantly affect the first and second reduction peak potentials ($E_{\text{p}}^{\text{Red1}}$ and $E_{\text{p}}^{\text{Red2}}$). In contrast, $E_{\text{p}}^{\text{Red3}}$

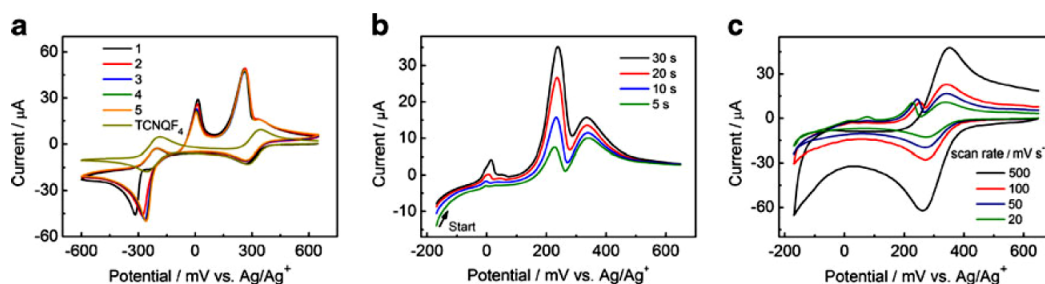
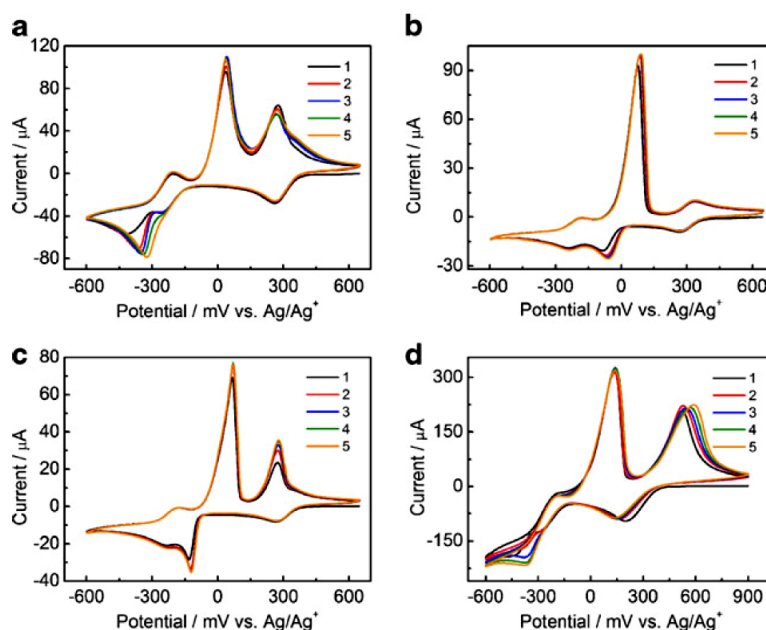


Fig. 6 Voltammograms obtained in acetonitrile (0.1 M Bu_4NPF_6) with a 3.0-mm diameter GC electrode **a** cyclic voltammetry at a scan rate of 20 mV s^{-1} for 1.0 mM TCNQF_4 and 2.0 mM $\text{Ag}(\text{MeCN})_4^+$ (First five cycles of potential compared to 1.0 mM TCNQF_4), **b** solution as in **a**

but potential held at –170 mV for designated times before sweeping the potential to 650 mV (scan rate = 20 mV s^{-1}), **c** cyclic voltammetry for 1.0 mM TCNQF_4 and 5.0 mM $\text{Ag}(\text{MeCN})_4^+$ at designated scan rates

Fig. 7 Cyclic voltammograms (first five cycles of potential) for 1.0 mM TCNQF₄ and 2.0 mM Ag(MeCN)₄⁺ in acetonitrile (0.1 M Bu₄NPF₆) using **a** GC, **b** Au, **c** Pt, and **d** ITO electrode at a scan rate of 100 mV s⁻¹



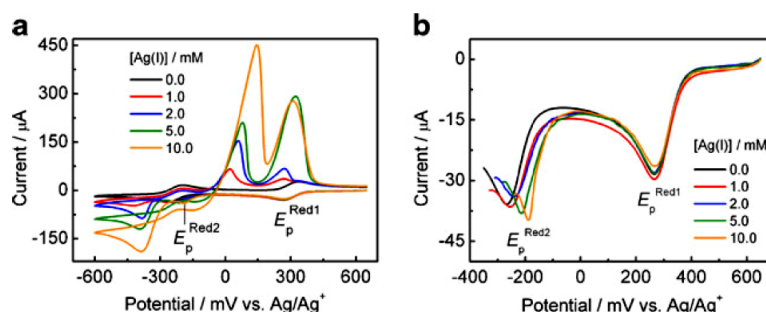
attributed to the reduction of Ag(MeCN)₄⁺ to Ag metal is strongly dependent on scan rate as expected for a nucleation and growth mechanism [26, 27].

Surface plasmon resonance study

In situ cyclic voltammetric and SPR experiments on gold-coated glass electrodes have been used to monitor mass change due to deposition onto or stripping from an electrode surface [21, 23], although caution is needed in the interpretation of these data since the changes in the solution near the electrode surface also may affect the SPR intensity [21]. SPR monitoring of cyclic voltammograms in acetonitrile (0.1 M Bu₄NPF₆) containing either 1.0 mM TCNQF₄ and 2.0 mM Ag(MeCN)₄⁺, or 10.0 mM TCNQF₄ and 10.0 mM Ag(MeCN)₄⁺ is shown in Fig. 10. Clearly, no evidence for AgTCNQF₄ deposition on the gold electrode surface is found when the potential was switched prior to the

reduction of TCNQF₄¹⁻ to TCNQF₄²⁻ (compare Fig. 10a with c, and e with f) because the SPR behaviors for mixtures of TCNQF₄ and Ag(MeCN)₄⁺ are very similar to those found for solutions containing only TCNQF₄. Interestingly, the i_p^{ox} value for the mixture of 10.0 mM TCNQF₄ and 10.0 mM Ag(MeCN)₄⁺ is less than that for pure 10.0 mM TCNQF₄ (170 vs. 230 μA from baseline), while i_p^{red} values are the same (255 μA). This implies that TCNQF₄¹⁻ has reacted with Ag(MeCN)₄⁺ to form AgTCNQF₄ near to the electrode surface, but the solid has not adhered to the electrode surface. In contrast, when the potential range was extended to more negative values, a large change in the SPR signal accompanied the deposition and stripping of metallic Ag. The cyclic voltammetric and SPR response in these experiments are consistent with data derived from a 1.6-mm diameter Au disk electrode (Fig. 7b). That is, Ag deposition occurs before reduction of the TCNQF₄¹⁻ to the TCNQF₄²⁻.

Fig. 8 **a** Cyclic voltammograms obtained in acetonitrile (0.1 M Bu₄NPF₆) with a 3.0-mm diameter GC electrode (scan rate= 100 mV s⁻¹) for 1.0 mM TCNQF₄ and designated concentrations of Ag(MeCN)₄⁺, **b** is identical to **a** but only the two reduction processes are presented



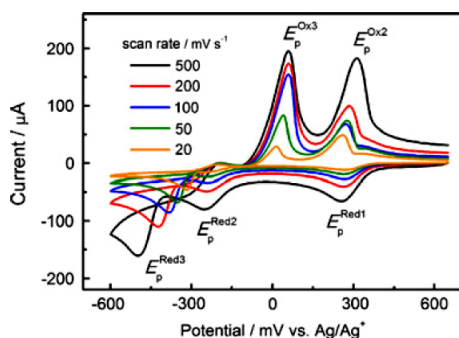


Fig. 9 Cyclic voltammograms for 1.0 mM TCNQF₄ and 2.0 mM Ag(MeCN)₄⁺ in acetonitrile (0.1 M Bu₄NPF₆) obtained with a 3.0-mm diameter GC electrode at designated scan rates

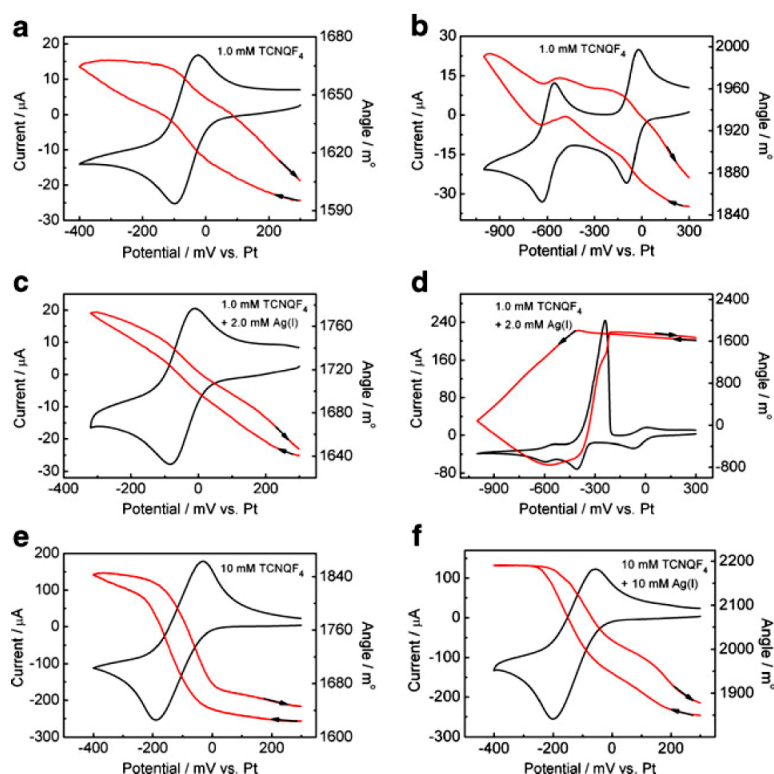
Characterization of Ag-TCNQF₄ compounds by spectroscopic and microscopic techniques

Chemically synthesized AgTCNQF₄

The single crystal X-ray structure of AgTCNQF₄ electrochemically synthesized by reduction of TCNQF₄ at an Ag electrode in acetonitrile at a constant current has been determined [13]. The TCNQF₄¹⁻ anions are nearly perfectly eclipsed with a high degree of dimerization, which results in this compound being essentially diamagnetic.

Here, AgTCNQF₄ was chemically synthesized as described in the section “Solubility of AgTCNQF₄ in acetonitrile”, and characterized by UV-vis, FTIR, and Raman spectra as shown in Fig. 11. The UV-vis spectrum of AgTCNQF₄ dissolved in acetonitrile has three absorption bands with $\lambda_{\max}$ at 411, 686, and 752 nm (Fig. 11a), which is consistent with the presence of only TCNQF₄¹⁻ [29–31]. In solid-state, X-ray structure [13] shows that TCNQF₄¹⁻ is better represented as (TCNQF₄)₂²⁻ dimer, although for convenience, sometimes referred to this species as TCNQF₄¹⁻. The IR bands for the solid material are at 2,221, 2,210, and 2,195 cm⁻¹ (Fig. 11b) can be assigned to the C≡N stretch in the (TCNQF₄)₂²⁻ dimer [13, 32] with the splitting being the result of coordination of TCNQF₄¹⁻ to the Ag⁺ cation via the CN groups [33]. The locations of these bands are the same as those reported for AgTCNQF₄ in ref. [13] (i.e., 2,220, 2,213, and 2,197 cm⁻¹), within experimental error. The IR band at 1,501 cm⁻¹ for AgTCNQF₄ is typical of the π (C=C) ring stretch and is usually found at higher energy than that for TCNQF₄ (1,493 cm⁻¹). The presence of this band also implies that the TCNQF₄ units in AgTCNQF₄ are present in the reduced form of TCNQF₄¹⁻ [13, 16, 32]. The C–F out of plane bending mode is located at 1,205 cm⁻¹ [13, 17], shifted to higher energy by 15 cm⁻¹ compared with TCNQF₄ (1,190 cm⁻¹). The Raman spectrum for the chemically synthesized solid AgTCNQF₄ exhibits three bands at

Fig. 10 In situ cyclic voltammetric (black) (scan rate=100 mV s⁻¹) and SPR (red) data obtained on a gold electrode for **a, b** 1.0 mM TCNQF₄, **c, d** 1.0 mM TCNQF₄ and 2.0 mM Ag(MeCN)₄⁺, **e** 10.0 mM TCNQF₄ and 10.0 mM Ag(MeCN)₄⁺ in acetonitrile (0.1 M Bu₄NPF₆)



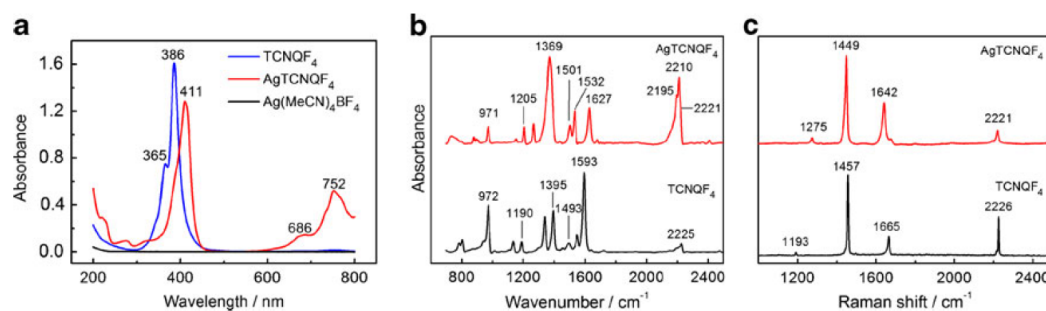


Fig. 11 Characterization of chemically synthesized AgTCNQF₄ by **a** UV-vis spectra (solution), **b** FTIR spectra (solid), **c** Raman spectra (solid) compared with TCNQF₄

2,221, 1,642, and 1,449 cm⁻¹, which respectively correspond to C≡N, C=C ring, and C–CN wing stretches [16, 17]. Compared with TCNQF₄ (2,226, 1,665, and 1,457 cm⁻¹), all three of these Raman vibration modes exhibit lower Raman shift as a result of the reduction of TCNQF₄ to TCNQF₄¹⁻ [16, 17]. A relative decrease in the intensity of the C≡N stretch band also is a spectroscopic fingerprint for the formation of TCNQF₄¹⁻ reduced form [17].

Electrochemically synthesized AgTCNQF₄

AgTCNQF₄ can be electrochemically synthesized and deposited on the surface of an electrode under conditions in which the solubility product of AgTCNQF₄ is exceeded. Hence, acetonitrile (0.1 M Bu₄NPF₆) solutions containing 2.0 mM TCNQF₄ and 10.0 mM Ag(MeCN)₄⁺ were used to electrocrystallize AgTCNQF₄ onto an ITO electrode surface. A constant potential of 100 mV was applied to the ITO electrodes for 30 min to reduce TCNQF₄ to TCNQF₄¹⁻. The electrocrystallized material was rinsed with ethanol, dried under a nitrogen gas stream for 10 min, and then under vacuum for 5 h prior to characterization. An optical microscopic image shows that the morphology of the sample on ITO is needle-shaped with crystal lengths of

~200 μm (see Fig. 12a). UV-vis, FTIR, and Raman spectra for the electrochemically synthesized AgTCNQF₄ are identical to the chemically synthesized AgTCNQF₄ (see Fig. 11). It is likely that the AgTCNQF₄ samples chemically or electrochemically synthesized exist in the same phase. Interestingly, UV-vis, FTIR, and Raman spectra for AgTCNQF₄ electrochemically synthesized by reduction of immobilized solid TCNQF₄ on an ITO electrode surface placed in a 0.1 M AgNO₃ aqueous solution at a potential of 550 mV vs. Ag/AgCl are also the same as the chemically synthesized AgTCNQF₄, within experimental error. Figure 12b shows a SEM image for the AgTCNQF₄ electrochemically synthesized onto a GC electrode surface via solid–solid phase transformation under conditions described in Fig. 12b.

Chemically synthesized Ag₂TCNQF₄

Ag₂TCNQF₄ was chemically synthesized by mixing 2.0 mL of 5.0 mM TCNQF₄²⁻ acetonitrile solution, which was prepared by exhaustive reductive electrolysis of 5.0 mM TCNQF₄ at a Pt foil electrode in acetonitrile (0.1 M Bu₄NPF₆) at -400 mV vs. Ag/Ag⁺, with 2.0 mL of 10.0 mM Ag(MeCN)₄BF₄ in acetonitrile. A white precipitate of

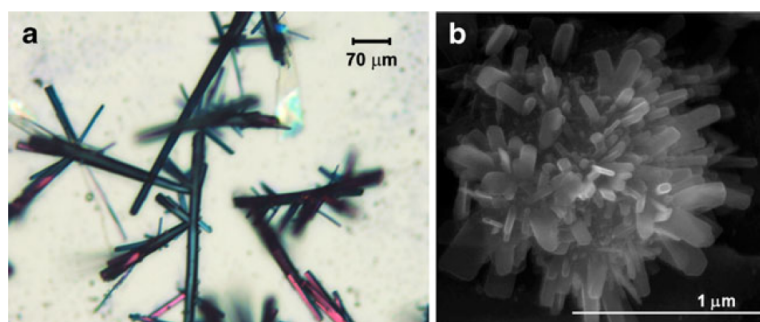
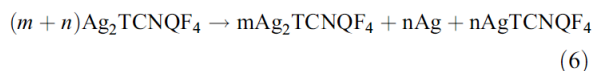


Fig. 12 **a** Optical microscopic image of AgTCNQF₄ electrocrystallized onto ITO electrode surface from acetonitrile (0.1 M Bu₄NPF₆) containing 2.0 mM TCNQF₄ and 10.0 mM Ag(MeCN)₄⁺ by holding the potential at 100 mV for 30 min, **b** SEM image of AgTCNQF₄

electrochemically synthesized by reduction of solid TCNQF₄, which was physically immobilized on a GC electrode surface and placed in a 0.1 M AgNO₃ aqueous solution, at 550 mV vs. Ag/AgCl for 10 min

$\text{Ag}_2\text{TCNQF}_4$ formed immediately, but gradually changed to pale green within a few minutes. The color of the solution also turned green. The precipitate was collected by centrifugation and washed three times with acetonitrile before filtration to obtain the solid and solution. UV-vis spectroscopy reveals the presence of both TCNQF_4^{1-} and TCNQF_4^{2-} (a specific band for TCNQF_4^{2-} [29] was observed with λ_{max} at 333 nm) in the filtered solution. The washed solid was dried under a stream of N_2 gas for 10 min and in vacuum for 1 h before being characterized by FTIR spectroscopy. Four IR bands associated with the $\text{C}\equiv\text{N}$ stretch are observed at 2,212, 2,193 cm^{-1} (which accord with the presence of TCNQF_4^{1-}), 2,159 and 2,127 cm^{-1} (which are characteristics for TCNQF_4^{2-} dianion [18, 29]). Apparently, the TCNQF_4^{2-} dianion rapidly reacts with the Ag^+ cation in acetonitrile to form a white precipitate of $\text{Ag}_2\text{TCNQF}_4$. However, this solid is not thermodynamically stable and gradually decomposes via a redox reaction (Eq. 6) to produce AgTCNQF_4 and metallic Ag. This internal redox reaction is thermodynamically allowed since the potentials for the oxidation of TCNQF_4^{2-} and reduction of $\text{Ag}(\text{MeCN})_4^+$ in acetonitrile are very close (see section “Voltammetry of TCNQF_4 and $\text{Ag}(\text{MeCN})_4^+$ in acetonitrile (0.1 M Bu_4NPF_6) solution”). However, on the voltammetric time scale (scan rate = 20 mV s^{-1}), $\text{Ag}_2\text{TCNQF}_4$ can be formed on the electrode surface so that a stripping process associated with $\text{Ag}_2\text{TCNQF}_4$ is observed in the positive potential direction scan (see section “Cyclic voltammetry of TCNQF_4 in the presence of $\text{Ag}(\text{MeCN})_4^+$ in acetonitrile (0.1 M Bu_4NPF_6)”). The transformation of $\text{Ag}_2\text{TCNQF}_4$ to metallic Ag and AgTCNQF_4 also was observed to be catalyzed when exposing a thin film of $\text{Ag}_2\text{TCNQF}_4$ to low-power visible laser radiation [12].



Conclusions

Electrocrystallization of the dark blue AgTCNQF_4 solid onto electrode surfaces can be achieved in acetonitrile containing TCNQF_4 and $\text{Ag}(\text{MeCN})_4^+$, as confirmed by UV-vis, FTIR, and Raman spectra. The electrocrystallization of AgTCNQF_4 occurs via the two processes given in Eqs. 4a and 4b.

In the solid phase, TCNQF_4^{1-} anions in AgTCNQF_4 exist in dimer form [13]. The potential for reduction of $\text{Ag}(\text{MeCN})_4^+$ to Ag metal is much more negative than that for the $\text{TCNQF}_4^{0/1-}$ reduction process. Therefore, electrochemical synthesis of AgTCNQF_4 is easy to perform in acetonitrile via the above method without concern for overlap with reduction of $\text{Ag}(\text{MeCN})_4^+$. However, electrocrystallization can only occur when the solubility product

of AgTCNQF_4 is exceeded and if the kinetics of precipitation of AgTCNQF_4 is sufficiently fast. The solubility and solubility product of AgTCNQF_4 in acetonitrile in the presence or absence of 0.1 M Bu_4NPF_6 supporting electrolyte were determined to be $1.10 \pm 0.04 \times 10^{-3}$ M and $1.22 \pm 0.08 \times 10^{-6}$ M^2 or $7.08 \pm 0.16 \times 10^{-4}$ M and $5.01 \pm 0.22 \times 10^{-7}$ M^2 , respectively, allowing conditions to be identified that allow AgTCNQF_4 to be electrocrystallized.

The reversible potentials for the $\text{TCNQF}_4^{0/1-}$ and $\text{TCNQF}_4^{1-/2-}$ reduction processes are almost independent of GC, Au, Pt, and ITO electrodes, while the peak potential for reduction of $\text{Ag}(\text{MeCN})_4^+$ to metallic Ag is strongly dependent on electrode material. Comparing the potential for reduction of TCNQF_4^{1-} to TCNQF_4^{2-} , the reduction of $\text{Ag}(\text{MeCN})_4^+$ occurs about 200 mV more positive at a Au electrode, slightly more positive at a Pt electrode and a little more negative at GC and ITO electrodes. Therefore, electrochemical synthesis of bulk $\text{Ag}_2\text{TCNQF}_4$ on Au and Pt substrates is difficult, and even on GC and ITO electrodes because of the close proximity of potentials for reduction of TCNQF_4^{1-} and $\text{Ag}(\text{MeCN})_4^+$, but it can be formed transiently. Another complication in electrocrystallization of $\text{Ag}_2\text{TCNQF}_4$ is that this material is not stable and decomposes gradually through a redox reaction to generate AgTCNQF_4 and Ag. The presence of AgTCNQF_4 generated via the internal redox reaction in chemically synthesized $\text{Ag}_2\text{TCNQF}_4$ is detected via UV-vis and FTIR spectroscopy.

Optical microscopic image shows that the morphology of AgTCNQF_4 electrocrystallized onto ITO is needle-shaped. UV-vis, FTIR, and Raman spectra for AgTCNQF_4 electrochemically synthesized from TCNQF_4 and $\text{Ag}(\text{MeCN})_4^+$ in acetonitrile, electrochemically synthesized AgTCNQF_4 from solid TCNQF_4 immobilized on an ITO electrode surface placed in 0.1 M AgNO_3 aqueous solution and chemically synthesized AgTCNQF_4 are spectroscopically indistinguishable. It seems that all the AgTCNQF_4 complexes exist in the same phase.

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Declaration for Thesis Chapter 4.4

Declaration by candidate

In the case of Chapter 4.4, the nature and extent of my contribution to the work was the following:

Nature of contribution	Extent of contribution (%)
Initiation, key ideas, experimental work, writing up	85

The following co-authors contributed to the work.

Name	Nature of contribution
Ayman Nafady	Initiation, key ideas
Lisandra L. Martin	Initiation, key ideas, writing up
Alan M. Bond	Initiation, key ideas, writing up

Candidate's Signature

		06/06/2012
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Declaration by co-authors

The undersigned hereby certify that:

- (1) the above declaration correctly reflects the nature and extent of the candidate's contribution to this work, and the nature of the contribution of each of the co-authors.
- (2) they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;
- (3) they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
- (4) there are no other authors of the publication according to these criteria;
- (5) potential conflicts of interest have been disclosed to (a) granting bodies, (b) the editor or publisher of journals or other publications, and (c) the head of the responsible academic unit; and
- (6) the original data are stored at the following location and will be held for at least five years from the date indicated below:

Location

School of Chemistry, Monash University, Clayton

Ayman Nafady

Lisandra L. Martin

Alan M. Bond

	30/4/12
	23/5/12
	18/5/12

Electrochemically Directed Synthesis and Characterization of Cu(I) Derivatives of TCNQF₄^{•-} or TCNQF₄²⁻ (TCNQF₄ = 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane) in Acetonitrile

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Abstract

CuTCNQF₄ and Cu₂TCNQF₄ (TCNQF₄ = 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane) can be synthesized by electrochemically directed synthesis based on reduction of TCNQF₄ in acetonitrile (0.1 M Bu₄NPF₆) solution containing Cu(MeCN)₄⁺. In one scenario, TCNQF₄^{•-} or TCNQF₄²⁻ are quantitatively formed by bulk electrolysis of TCNQF₄ followed by addition of Cu(MeCN)₄⁺ to form the Cu(I)-TCNQF₄^{•-} or Cu(I)-TCNQF₄²⁻ coordination polymers. In a second scenario, TCNQF₄ is reduced *in situ* at glassy carbon, gold, platinum or indium tin oxide electrode surfaces to TCNQF₄^{•-} or TCNQF₄²⁻, followed by reaction with the Cu⁺ cations present in the solution to form crystalline CuTCNQF₄ or Cu₂TCNQF₄. The solubility of both solids has been determined in acetonitrile. The higher solubility of CuTCNQF₄ allows its precipitation to be avoided during the course of electrochemical generation of Cu₂TCNQF₄. The presence of TCNQF₄^{•-} or TCNQF₄²⁻ in the CuTCNQF₄ and Cu₂TCNQF₄ materials was confirmed by Ultraviolet-visible, infrared and Raman spectroscopies. Cu₂TCNQF₄ can be photochemical transformation to CuTCNQF₄ and Cu metal. Voltammetric experiments suggest that two distinct phases of Cu₂TCNQF₄ are formed when TCNQF₄²⁻ is formed on the electrode surface in the presence of Cu(MeCN)₄⁺. The kinetically favored form being rapidly converted to the thermodynamically favored one. The postulated mechanism is supported by simulations that are in excellent agreement with the experimental voltammograms. Scanning electron microscopy images reveal that CuTCNQF₄ is electrocrystallized with a cubic shape (~3 μm), whilst the electrocrystallized Cu₂TCNQF₄ has a rod-like morphology. Thermogravimetric and elemental analysis data indicate the presence of two moles of CH₃CN in the Cu₂TCNQF₄ material.

1. Introduction

The properties of organic charge-transfer complexes containing conjugated π -electron systems have been widely investigated in the last few decades¹⁻³ because of their technologically important optical, electrical and magnetic properties.^{2,4,5} Of relevance to the present studies, it is noted that metal-organic charge-transfer TCNQ-based materials (TCNQ = 7,7,8,8-tetracyanoquinodimethane, Figure 1a) have been of considerable interest in energy and data storage,^{6,7} optical and electrical media recording,⁸ catalysis,⁹⁻¹¹ light emitting, magnetic and sensor device applications.^{8,12-14} Recently, a series of studies have been published that have focused on the synthesis, structure, magnetic properties and optically induced transformation as well as applications of TCNQF₄-based materials (TCNQF₄ = 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane, Figure 1b).^{2,15-20} For instance, AgTCNQF₄, and CuTCNQF₄ exhibit electrical switching phenomena, memory storage capability²¹ and are potential candidates for use in reversible bistable electrical and optical switches, memory effects^{2,21} and field-emission cathodes.¹⁷

TCNQF₄ is a far stronger electron acceptor than TCNQ with the reversible formal potentials for the first and second reduction processes in acetonitrile (0.1 M Bu₄NClO₄) being 0.36 and 0.37 V more positive, respectively.²² In principle, the substituent effect produced by the introduction of fluorine should lead to enhance the stability of the dianion TCNQF₄²⁻.²²

CuTCNQF₄ has been chemically synthesized by tuning the temperature for the reaction of TCNQF₄ powder and Cu foil in a ceramic boat¹⁷ or by placing a polished Cu metal substrate in a dry and degassed acetonitrile solution containing saturated TCNQF₄.²¹ In this study, both CuTCNQF₄ and Cu₂TCNQF₄ complexes have been synthesized by mixing an acetonitrile solution of Cu(MeCN)₄⁺ with electrochemically generated and air stable TCNQF₄^{•-} or TCNQF₄²⁻ in acetonitrile, which were produced by reduction of TCNQF₄ in acetonitrile (0.1 M Bu₄NPF₆) at a Pt foil electrode. Electrochemical methods also have been used to electrocrystallize CuTCNQF₄ and Cu₂TCNQF₄ directly onto an electrode surface. Thus, TCNQF₄ present in acetonitrile (0.1 M Bu₄NPF₆) solution containing Cu(MeCN)₄⁺ is reduced at a controlled potential to TCNQF₄^{•-} or TCNQF₄²⁻, coupled by reaction with Cu⁺_(MeCN) at the electrode-solution interface to form CuTCNQF₄ or Cu₂TCNQF₄ which are deposited onto the electrode surface under suitable conditions. Electrocrystallizations can only occur when the solubility products of CuTCNQF₄ or Cu₂TCNQF₄ are exceeded, so the knowledge of reactant concentrations and control of

electrochemical conditions allows selective deposition to be achieved. The role of working electrode material also was explored. The CuTCNQF_4 and $\text{Cu}_2\text{TCNQF}_4$ complexes synthesized by electrochemically directed methods have been characterized by Ultraviolet-visible (UV-vis), Fourier transform infrared (FT-IR) and Raman spectroscopies. Scanning electron microscopy (SEM) images of electrode surfaces were used to define the morphology of the electrocrystallized materials. Electrochemically generated TCNQF_4^{2-} is seen to provide a facile route to the synthesis of dianion based metal complexes because of the much greater stability than the TCNQ^{2-} analogues, which have proved difficult to isolate because of instability associated with aerial oxidation.²³⁻²⁵

2. Experimental Section

2.1. Chemicals

$\text{Cu}(\text{MeCN})_4\text{PF}_6$ (98%, Aldrich), TCNQF_4 (98%, Beijing Health), acetonitrile (HPLC grade, Omnisolv), isopropanol (BHD) and acetone (Suprasolv, Merck KGaA) were used as received from the manufacturer. Bu_4NPF_6 (Wako), used as the supporting electrolyte in voltammetric and electrodeposition studies was recrystallized twice from 96% ethanol (Merck) and then dried at 100°C under vacuum for 24 h.

CuTCNQF_4 was prepared in bulk quantities by electrochemically directed synthesis involving reaction of $\text{TCNQF}_4^{\bullet-}$ and $\text{Cu}(\text{MeCN})_4^+$ in acetonitrile. Thus, 5.0 mL of 5.0 mM $\text{TCNQF}_4^{\bullet-}$ was quantitatively prepared by reduction of 5.0 mM TCNQF_4 in acetonitrile (0.1 M Bu_4NPF_6) with the potential of the Pt foil working electrode being held at 100 mV vs. Ag/Ag^+ , which lies between the $\text{TCNQF}_4^{0/\bullet-}$ and $\text{TCNQF}_4^{\bullet-/2-}$ processes. The prepared $\text{TCNQF}_4^{\bullet-}$ solution was then mixed with 0.25 mL of 100 mM $\text{Cu}(\text{MeCN})_4^+$ in acetonitrile. The black precipitate that was formed immediately was collected and washed with 4×2 mL of acetonitrile. The solid was used directly for determination of the solubility of CuTCNQF_4 in acetonitrile or dried under vacuum overnight before spectroscopic characterization (see Section 3).

Electrochemically directed synthesis of $\text{Cu}_2\text{TCNQF}_4$ was achieved in an analogous manner to that for CuTCNQF_4 . In this case, reaction of 2.0 mL of 5.0 mM TCNQF_4^{2-} (synthesized from exhaustive reductive electrolysis of $\text{TCNQF}_4^{\bullet-}$ in acetonitrile (0.1 M Bu_4NPF_6) at -400 mV vs. Ag/Ag^+) and 0.20 mL of 100 mM $\text{Cu}(\text{MeCN})_4^+$ was used. $\text{Cu}_2\text{TCNQF}_4$ was formed and collected as a white precipitate.

2.2. Electrochemistry

Voltammetric experiments were undertaken at room temperature ($22 \pm 2^\circ\text{C}$) with a Bioanalytical Systems (BAS) 100W electrochemical workstation using a standard three-electrode cell configuration. Working electrodes (WEs) were BAS glassy carbon (GC, 3.0 mm diameter), gold or platinum (1.6 mm diameter) disks, carbon fiber microelectrode ($11 \pm 2 \mu\text{m}$ diameter as quoted) or indium tin oxide (ITO)-coated glass plates ($0.1 - 0.2 \text{ cm}^2$) with a resistance of $10 \Omega/\text{sq}$ as specified by the manufacturer (Prazisions Glas und Optik GmbH). The procedures for polishing the WEs are as described elsewhere.²⁶ A silver wire in contact with acetonitrile containing 1.0 mM AgNO_3 and 0.1 M Bu_4NPF_6 , separated from the test solution by a salt bridge was used as a reference electrode (potential of this reference electrode is $-135 \pm 5 \text{ mV}$ vs. the couple Ferrocene/Ferrocenium, $\text{Fc}^{0/+}$). The counter electrode was made of a 1.0 mm diameter platinum wire. Solutions used in voltammetric studies were purged with nitrogen gas for 10 min; a stream of nitrogen was then maintained above the solutions during the course of voltammetric experiments. In bulk electrolysis and *in situ* surface plasmon resonance (SPR) studies, a platinum foil and a gold film coated on a glass plate were used as working electrodes, respectively; along with reference, counter electrodes and other features described in reference 26. Electrochemical quartz crystal microbalance (EQCM) experiment was undertaken with an ELCHEMA EQCN-701 quartz crystal microbalance and a PS-205 potentiostat connected to a computer via an Advantech PCI-1711 DAQ device. In this case, a 5.0 mm diameter Au electrode, formed as a film on 1.3 cm diameter quartz crystal was used as the working electrode, Ag/Ag^+ as the reference electrode and a platinum wire as the counter electrode.

2.3. Other Instrumentation

Instrumentation used in UV-vis, FT-IR and Raman spectroscopic experiments is the same as detailed elsewhere.²⁶ After being coated with Pt, SEM images were collected with a JEOL JSM 7001F FEGSEM instrumentation using an accelerating voltage of 15.0 kV. This instrumentation coupled with Bruker EDXS software suite was used for Energy Dispersive X-Ray Spectroscopy (EDXS) analysis of electrocrystallized samples. Thermogravimetric analysis (TGA) was undertaken in a flow of dry nitrogen atmosphere (30 mL min^{-1}) over the temperature range from 25 to 350°C at a rate of 5°C min^{-1} using aluminium pans and a Mettler-Toledo model TGA-DSC1 instrumentation. The reported TGA data was deduced after subtraction blank data (obtained with an empty aluminium pan) from raw data (obtained with the aluminium pan containing the studied material).

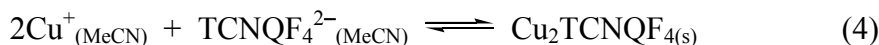
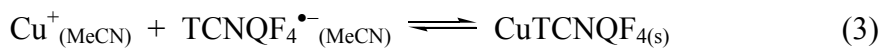
Simulation software DigiElch 6.F distributed by Gamry Instruments was used to simulate cyclic voltammograms.

3. Results and Discussion

3.1. Electrocrystallization of CuTCNQF₄ and Cu₂TCNQF₄ in Acetonitrile

3.1.1. Voltammetry of TCNQF₄ and Cu(MeCN)₄⁺ in Acetonitrile (0.1 M Bu₄NPF₆)

A cyclic voltammogram for the reduction of 1.0 mM TCNQF₄ to TCNQF₄^{•-} and then TCNQF₄²⁻ (equations 1 and 2) in acetonitrile (0.1 M Bu₄NPF₆) at a GC electrode is shown in Figure 2a, whilst Figure 2b represents the oxidation of 2.0 mM Cu⁺_(MeCN) to Cu²⁺_(MeCN) as well as its reduction to copper metal under the same conditions. The TCNQF₄^{0/•-} and TCNQF₄^{•-/2-} processes represent ideal reversible one-electron processes. In contrast, the cyclic voltammetry of Cu(MeCN)₄⁺ is more complex. As shown in Figure 2b, on scanning the potential in the negative direction, Cu(MeCN)₄⁺ is reduced to metallic Cu which deposits onto the electrode surface. On scanning back in the positive potential direction, a sharp and large Cu stripping peak is detected. At much more positive potential, the oxidation of Cu⁺_(MeCN) to Cu²⁺_(MeCN) occurs. However, the potentials for both the reduction and oxidation of Cu⁺_(MeCN) are well removed from the reduction of TCNQF₄ to TCNQF₄^{•-} and TCNQF₄^{•-} to TCNQF₄²⁻ (see Figure 2 and Table 1). Consequently, the electrocrystallization of CuTCNQF_{4(s)} (via equations 1 and 3) and Cu₂TCNQF_{4(s)} (via equations 1, 2 and 4) via reduction of TCNQF₄ in acetonitrile (0.1 M Bu₄NPF₆) in the presence of Cu⁺_(MeCN) are possible if the potential is maintained in the region between the reduction and oxidation of Cu⁺_(MeCN). Nevertheless, the electrocrystallization of Cu₂TCNQF_{4(s)} will require discrimination against the formation of CuTCNQF_{4(s)} if the reaction sequence 1, 2 and 4 is to be employed.



3.1.2. ElectrocrySTALLIZATION OF CuTCNQF_{4(s)} AND Cu₂TCNQF_{4(s)} IN ACETONITRILE (0.1 M Bu₄NPF₆) CONTAINING TCNQF₄ AND Cu(MeCN)₄⁺

a) CuTCNQF_{4(s)}

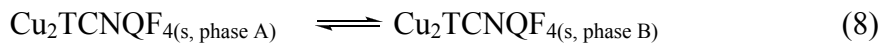
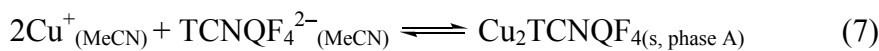
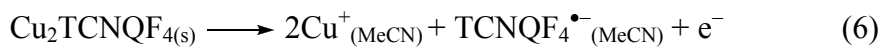
Figure 3 shows cyclic voltammograms derived from acetonitrile (0.1 M Bu₄NPF₆) solutions containing both 10.0 mM Cu(MeCN)₄⁺ and either 1.0; 5.0 or 10.0 mM TCNQF₄ using a 3.0 mm diameter GC electrode at a scan rate of 20 mV s⁻¹. The potential was switched at 50 mV (vs. Ag/Ag⁺) in order to ensure TCNQF₄ was reduced to TCNQF₄^{0•-} rather than TCNQF₄²⁻. The cyclic voltammogram at the 1.0 mM TCNQF₄ concentration retains the fully diffusion controlled process associated with the TCNQF₄^{0•-} couple (Figure 3a). When the concentration of TCNQF₄ is increased from 1.0 to 10.0 mM, the oxidation and reduction peak current ratio ($i_p^{\text{ox}}/i_p^{\text{red}}$) decreases from close to unity to about 0.69. A loss of TCNQF₄^{•-}(MeCN) and hence its oxidation peak current is as expected if the reduction of TCNQF₄ to TCNQF₄^{•-} is followed by rapid formation of CuTCNQF_{4(s)}. However, electrocrystallization of CuTCNQF_{4(s)} may only occur under conditions where the concentration product of TCNQF₄ and Cu(MeCN)₄⁺ exceeds the solubility product of CuTCNQF_{4(s)} in acetonitrile. Apparently, electrocrystallized CuTCNQF_{4(s)} is oxidized when the potential was scanned in the positive direction, as evidenced by the emergence of a broad peak at 515 mV when the concentration of TCNQF₄ is sufficiently high (Figures 3b and c). The oxidative stripping of the electrocrystallized CuTCNQF_{4(s)} from the electrode surface occurs as described in equation 5. If the concentrations of both Cu(MeCN)₄⁺ and TCNQF₄ in the bulk solution are low, the electrocrystallization process is not favored. The formation of a substantial amount of CuTCNQF_{4(s)} does indeed follow the reduction of 2.0 mM TCNQF₄ in the presence of 100 mM Cu(MeCN)₄⁺ at slow cyclic voltammetric scan rates as the reduction of TCNQF₄ to TCNQF₄^{•-} is irreversible at a scan rate of 10 mV s⁻¹. However, $i_p^{\text{ox}}/i_p^{\text{red}}$ ratio reverts to unity at faster scan rates ($v \geq 1 \text{ V s}^{-1}$) (data not show) as expected if the TCNQF₄^{0•-} electrochemical process is followed by a kinetically controlled electrodeposition.²⁷



b) Cu₂TCNQF_{4(s)}

In order to electrocrystallize Cu₂TCNQF_{4(s)}, the negative potential range used in the voltammetry was extended to -600 mV. Requirements to achieve this outcome are that Cu₂TCNQF_{4(s)} need to be significantly less soluble than CuTCNQF_{4(s)} in a thermodynamic

sense or that rate of the formation of $\text{CuTCNQF}_{4(s)}$ is so slow, that conditions can be chosen where $\text{Cu}_2\text{TCNQF}_{4(s)}$ can be formed but $\text{CuTCNQF}_{4(s)}$ does not electrocrystallize prior to $\text{TCNQF}_4^{\bullet-}$ being reduced to TCNQF_4^{2-} . Voltammograms for 1.0 mM TCNQF_4 and 2.0 mM $\text{Cu}(\text{MeCN})_4^+$ in acetonitrile (0.1 M Bu_4NPF_6) under a range of conditions that meet the requirement of the reversible $\text{TCNQF}_4^{0/\bullet-}$ solution phase process are shown in Figures 4a–c. As seen on examination of Figure 4a (black curve), on scanning in the negative direction at a low scan rate (20 mV s^{-1}), two processes associated with the reduction of TCNQF_4 to $\text{TCNQF}_4^{\bullet-}$ (Red1) and then $\text{TCNQF}_4^{\bullet-}$ to TCNQF_4^{2-} (Red2) are found. However, the process for oxidation of TCNQF_4^{2-} to $\text{TCNQF}_4^{\bullet-}$, seen in the absence of $\text{Cu}(\text{MeCN})_4^+$ (Figure 2a), is replaced by a sharp stripping peak at 280 mV (designated as Ox2). This outcome implies that TCNQF_4^{2-} has rapidly combined with $\text{Cu}^+_{(\text{MeCN})}$ to form solid $\text{Cu}_2\text{TCNQF}_4$ (confirmed below), which is adhered to the electrode surface, and that $\text{Cu}_2\text{TCNQF}_{4(s)}$ is oxidized back to $\text{TCNQF}_4^{\bullet-}_{(\text{MeCN})}$ and $\text{Cu}^+_{(\text{MeCN})}$ (equation 6) at 280 mV (Ox2) as the potential is reversed in the positive direction. Interestingly, upon increasing the scan rate, a new oxidation process at $\sim -130 \text{ mV}$ (designated as Ox3) is detected and increases at the expense of the oxidation process Ox2 (Figure 4b). This behavior is consistent with the existence of 2 phases of $\text{Cu}_2\text{TCNQF}_{4(s)}$. Thus, the kinetically favored phase is rapidly formed from TCNQF_4^{2-} and $\text{Cu}(\text{MeCN})_4^+$ (phase A) and then converted to the thermodynamically stable phase of $\text{Cu}_2\text{TCNQF}_{4(s)}$ (phase B) as described in the reaction sequence given in equations 7 and 8. This hypothesis is supported by simulations (see Section 3.3).



Another series of experiments were conducted in which the potential was held at -400 mV for a period of time to electrocrystallize $\text{Cu}_2\text{TCNQF}_{4(s)}$ onto the GC electrode surface, followed by scanning the potential in the positive direction at variable scan rate. Thus, when the potential was maintained at -400 mV for 1 s and then scanned in the positive direction (Figure 4c), the peak current associated with the oxidation of $\text{Cu}_2\text{TCNQF}_{4(s)}$ phase A (Ox3) increased significantly with scan rate, whilst that for the oxidation of $\text{Cu}_2\text{TCNQF}_{4(s)}$ phase B (Ox2) was no longer seen at fast scan rate. In addition,

the peak asymmetry and other characteristics of the oxidation peaks Ox2 and Ox3 indicate that these processes are irreversible²⁷ as described in equation 6.

In order to establish that the stoichiometry for the combination of Cu^+ and TCNQF_4^{2-} is 2:1, cyclic voltammograms for a variety of initial concentrations of $\text{Cu}(\text{MeCN})_4^+$ and TCNQF_4 in acetonitrile (0.1 Bu_4NPF_6) solutions were recorded. When the concentration ratio $\text{Cu}(\text{MeCN})_4^+:\text{TCNQF}_4 < 2:1$, in the reverse scan of the potential, the oxidation peak at -185 mV (Figure 4a – peak A on red curve) associated with the $\text{TCNQF}_4^{2-/•-}$ diffusion controlled process is observed, implying that $\text{Cu}(\text{MeCN})_4^+$ concentration is not sufficient to react with all the TCNQF_4^{2-} , generated in the forward scan (Red2). In other words, to consume one TCNQF_4^{2-} anion, two $\text{Cu}(\text{MeCN})_4^+$ ions are required.

3.1.3. Influence of Working Electrode Material on the Electrocrystallization of $\text{Cu}_2\text{TCNQF}_{4(s)}$

Cyclic voltammograms (first 5 cycles of the potential) for an acetonitrile (0.1 M Bu_4NPF_6) solution containing both 1.0 mM TCNQF_4 and 2.0 mM $\text{Cu}(\text{MeCN})_4^+$ at scan rate of 20 and 100 mV s^{-1} are shown in Figure 5 as a function of electrode material. The cyclic voltammetric behavior at the GC and Pt electrodes are very similar. However, at the Au electrode, the oxidation process Ox3 is more strongly favored at higher scan rates (compare Figures 5d and 5f for example). This implies that phase A of $\text{Cu}_2\text{TCNQF}_{4(s)}$ formed on the Au electrode surface is relatively more stable than when adhered to the Pt or GC electrodes. However, the cyclic voltammetric behavior at all WE materials is highly reproducible, implying that TCNQF_4 and $\text{Cu}(\text{MeCN})_4^+$ are both regenerated at the end of each cycle.

3.1.4. Impact of $\text{Cu}(\text{MeCN})_4^+$ Concentration and Scan Rate on the Electrocrystallization of $\text{Cu}_2\text{TCNQF}_{4(s)}$

Cyclic voltammetric studies on the reduction of 1.0 mM TCNQF_4 in the presence of variable concentrations of $\text{Cu}(\text{MeCN})_4^+$ in acetonitrile (0.1 M Bu_4NPF_6) reveal that the peak potential for the $\text{TCNQF}_4^{0/•-}$ reduction process is almost independent of $\text{Cu}(\text{MeCN})_4^+$ concentration, as expected if the $\text{TCNQF}_4^{•-}$ monoanion either does not react or interact only weakly with the $\text{Cu}(\text{MeCN})_4^+$ cation. In contrast, the peak potential associated with the reduction of $\text{TCNQF}_4^{•-}$ to TCNQF_4^{2-} shifts by 97 mV to more positive value when the concentration of $\text{Cu}(\text{MeCN})_4^+$ is increased from 0.0 mM to 10.0 mM (Figures 6a, b). Examination of Figure 6a also reveals that the peak current associated with the stripping of

phase A of $\text{Cu}_2\text{TCNQF}_{4(s)}$ decreases, whilst that for phase B of $\text{Cu}_2\text{TCNQF}_{4(s)}$ increases as the concentration of $\text{Cu}(\text{MeCN})_4^+$ is increased.

The results shown in Figures 6c and d are consistent with those in Figure 6a. Thus, for fixed scan rates from 20 to 500 mV s^{-1} , upon increasing the $\text{Cu}(\text{MeCN})_4^+$ concentration from 2.0 to 5.0 mM, the peak currents associated with the oxidation of $\text{Cu}_2\text{TCNQF}_{4(s)}$ phases A and B decrease and increase, respectively. The results of this series of experiments also are consistent with the hypothesis that phase A of $\text{Cu}_2\text{TCNQF}_{4(s)}$ is initially formed but is thermodynamically unstable and hence converts to the phase B form. Analogous behavior to that shown at the GC electrode also was found at Pt and Au electrodes (data not shown), although there is a quantitative difference at the Au electrode as mentioned above.

3.2. *In situ* Surface Plasmon Resonance and Electrochemical Quartz Crystal Microbalance Studies

The *in situ* mass change taking place on an electrode surface as a function of potential during the course of cyclic voltammetric experiments at a gold coated-glass electrode can be deduced by measurement of the concomitant change in the surface plasmon resonance (SPR), although the changes in the solution near the electrode surface also may affect the SPR intensity.^{26,28,29} Figure 7 provides cyclic voltammetric-SPR responses at the gold electrode for 1.0 mM TCNQF_4 in acetonitrile (0.1 M Bu_4NPF_6) in the presence and absence of 2.0 mM $\text{Cu}(\text{MeCN})_4^+$. Upon reversing the potential scan direction between the $\text{TCNQF}_4^{0/\bullet-}$ and $\text{TCNQF}_4^{\bullet-/2-}$ reduction processes, the SPR signals obtained in the presence and absence of $\text{Cu}(\text{MeCN})_4^+$ are almost indistinguishable (compare Figures 7a and c), implying that under these conditions, $\text{CuTCNQF}_{4(s)}$ does not deposit onto the electrode surface. In contrast, when the potential is scanned to around -600 mV vs. Pt wire in order to encompass the $\text{TCNQF}_4^{\bullet-/2-}$ process, the SPR angle decreases severely to values that lie outside the detection capability of the instrument. Significantly, the SPR signal reverts to its initial value when the potential returns back to the initial value (Figure 7d). These data confirm that mass increase occurs when the TCNQF_4^{2-} dianion is generated and the electrocrystallization of $\text{Cu}_2\text{TCNQF}_{4(s)}$ occurs on the electrode surface at negative potentials, and that mass is lost as the deposited solid is stripped from the surface. The data also confirms that controlled conditions avoiding the electrocrystallization of $\text{CuTCNQF}_{4(s)}$ are available.

The EQCM technique also was applied to monitor the formation and stripping of the $\text{Cu}_2\text{TCNQF}_{4(s)}$ from the surface of a gold electrode during the course of cyclic voltammetric experiments. Figure 8 shows the cyclic voltammogram (black curve) and mass change (red curve) for an acetonitrile (0.1 M Bu_4NPF_6) solution containing 1.0 mM TCNQF_4 in the presence of 2.0 mM $\text{Cu}(\text{MeCN})_4^+$. The results are consistent with the SPR study. Thus, during the forward scan of the potential, no mass change on the electrode surface is observed until the reduction of $\text{TCNQF}_4^{\bullet-}$ to TCNQF_4^{2-} occurs. This result confirms that under these experimental conditions, the electrocrystallization of $\text{CuTCNQF}_{4(s)}$ does not occur, whilst $\text{Cu}_2\text{TCNQF}_{4(s)}$ is electrocrystallized onto the electrode surface. When the potential was scanned back to the initial potential, the mass on the electrode surface initially continued increasing and then decreased as the potential reached the values where $\text{Cu}_2\text{TCNQF}_{4(s)}$ was stripped from the electrode. However, a residual $\text{Cu}_2\text{TCNQF}_{4(s)}$ remained on the electrode surface as the mass change did not quite revert to zero.

3.3. Simulations of the Cyclic Voltammetry

DigiElch software was used to mimic the voltammetry associated with the formation of the phases A and B of electrocrystallized $\text{Cu}_2\text{TCNQF}_{4(s)}$ on an electrode surface that accompanies the reduction of TCNQF_4 to TCNQF_4^{2-} in the presence of $\text{Cu}(\text{MeCN})_4^+$ in acetonitrile (0.1 M Bu_4NPF_6). A comparison of simulated and experimental cyclic voltammograms is shown in Figure 9 over a range of scan rates. The hypothesis used in the simulation is that the kinetically favored phase A of $\text{Cu}_2\text{TCNQF}_{4(s)}$ is formed initially from the reaction of TCNQF_4^{2-} and $\text{Cu}(\text{MeCN})_4^+$, and this phase rapidly converts to the thermodynamically stable phase B of $\text{Cu}_2\text{TCNQF}_{4(s)}$ as in equations 7 and 8. Table 2 summarizes the parameters used to simulate the cyclic voltammograms that mimic the reduction of 1.0 mM TCNQF_4 in the presence of 2.0 mM $\text{Cu}(\text{MeCN})_4^+$ in acetonitrile (0.1 M Bu_4NPF_6) at a 3.0 mm diameter GC electrode over the scan rate range of 20 to 500 mV s^{-1} . Clearly, the simulated and experimental cyclic voltammograms are in excellent agreement for the first and also subsequent cycles (data not shown) of the potential.

In principle, $\text{TCNQF}_4^{\bullet-}$ can react with $\text{Cu}(\text{MeCN})_4^+$ to form $\text{CuTCNQF}_{4(s)}$. However, the experimental conditions were chosen in order to minimize the contribution from this reaction (see Section 3.1.2a). This feature also simplifies the mechanism required for the simulations.

3.4. Characterization of the CuTCNQF_{4(s)} and Cu₂TCNQF_{4(s)} Prepared by Electrocrystallization and Electrochemically Directed Synthesis

EDXS was used to confirm the presence of the elements Cu, C, N and F in all the electrocrystallized CuTCNQF_{4(s)} and Cu₂TCNQF_{4(s)} samples. However, in order to confirm the TCNQF₄ redox levels and establish more details, UV-vis^{2,31,32}, FT-IR^{2,15-17,19,20} and Raman^{2,17} spectroscopic and SEM imaging techniques were applied to bulk solids prepared by electrochemically directed synthesis and electrocrystallization.

3.4.1. Electrochemically Directed Synthesis of CuTCNQF_{4(s)}

Bulk quantities of CuTCNQF_{4(s)} were synthesized by the electrochemically directed approach as described in Section 2.1. As predicted from analysis of the cyclic voltammetry, CuTCNQF_{4(s)} has a finite level of solubility in acetonitrile. The UV-vis spectrum for the prepared CuTCNQF_{4(s)}, dissolved in acetonitrile, has three absorption bands with λ_{max} values at 411, 686 and 752 nm (Figure S1a) confirming that the TCNQF₄^{•-} radical anion is present after dissolution.^{4,26,32} In the FT-IR spectrum for the solid (Figure S1b), the bands associated with the C≡N stretch are located at 2214 and 2187 cm⁻¹, which are similar to those at 2215 cm⁻¹ and ~2190 cm⁻¹ for CuTCNQF₄ reported in a previous study,¹⁷ and typical for the monoanion¹⁶ rather than the TCNQF₄²⁻ dianion, where the IR bands are expected at ~2167 and ~2133 cm⁻¹.^{32,33} The splitting of the C≡N stretch indicates that TCNQF₄^{•-} is coordinated to Cu⁺ through the CN groups in the CuTCNQF_{4(s)} complex.³⁴ The Raman spectrum for CuTCNQF_{4(s)} (Figure S1c) exhibits bands at 2221 (C≡N stretch), 1641 (C=C ring stretch), 1439 (C–CN wing stretch)^{2,17} and 1273 cm⁻¹ (this band could be attributed to C–F bending out of plane, as its energy is close to that band in the FT-IR spectrum for this compound). The Raman band at 1273 cm⁻¹ is shifted to higher energy compared to that of 1193 cm⁻¹ found for TCNQF₄, whilst the other three bands are located at lower energy, again as expected for the presence of the TCNQF₄^{•-} monoanion in the CuTCNQF_{4(s)}.^{2,17}

In order to confirm that the molar ratio Cu⁺:TCNQF₄^{•-} in the synthesized CuTCNQF_{4(s)} is 1:1, the solid was dissolved in acetonitrile with assistance of sonication for 5 min. Bu₄NPF₆ was then added into the saturated solution of CuTCNQF₄ to provide 0.1 M Bu₄NPF₆ as the supporting electrolyte before recording steady-state voltammogram with a microdisk electrode. The obtained data are shown in Figure 10a. Clearly, the limiting currents associated with the reduction of TCNQF₄^{•-} and Cu(MeCN)₄⁺ are consistent with

the ratio $\text{Cu}^+:\text{TCNQF}_4^{\bullet-}$ of 1:1 as the relative limiting currents are the same as those found for solutions of either 1.0 mM $\text{TCNQF}_4^{\bullet-}$ or $\text{Cu}(\text{MeCN})_4^+$ (Figure 10b).

Elemental analysis (%C = 41.95, % H = 0.59, %N = 16.47) for the synthesized $\text{CuTCNQF}_{4(s)}$ compound also supports the 1:1 molar ratio of Cu^+ and $\text{TCNQF}_4^{\bullet-}$. Based on the elemental analysis data, the compound is formulated as $\text{CuTCNQF}_4 \cdot 0.6\text{H}_2\text{O} \cdot 0.3\text{CH}_3\text{CN}$ (calculated: %C = 41.71, %H = 0.58, %N = 16.60). This result also implies that there was a relative small amount of uncoordinated H_2O and CH_3CN when $\text{CuTCNQF}_{4(s)}$ was precipitated.

3.4.2. Electrocrystallized $\text{CuTCNQF}_{4(s)}$

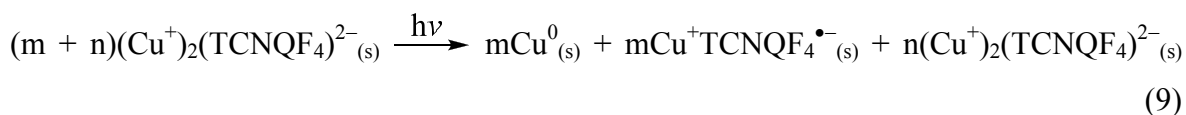
$\text{CuTCNQF}_{4(s)}$ was electrocrystallized onto the surface of an ITO electrode by reduction of 2.0 mM TCNQF_4 in acetonitrile (0.1 M Bu_4NPF_6) containing 10.0 mM $\text{Cu}(\text{MeCN})_4^+$. In this case, the potential at the ITO electrode was held at 100 mV for 15 min. The electrocrystallized solid was rinsed with ethanol, dried under a stream of N_2 gas for 10 min and finally placed in vacuum overnight before being characterized. UV-vis, FT-IR and Raman spectra for the electrocrystallized $\text{CuTCNQF}_{4(s)}$ are indistinguishable from those reported above for the electrochemically directed synthesis of $\text{CuTCNQF}_{4(s)}$.

The morphology of the $\text{CuTCNQF}_{4(s)}$ electrocrystallized onto the ITO electrode surface was probed via the use of the SEM imaging technique. A film of closely packed microcrystals of micron size was formed (Figure 11).

3.4.3. Characterization of $\text{Cu}_2\text{TCNQF}_{4(s)}$

In order to determine whether there is any solvent present with $\text{Cu}_2\text{TCNQF}_{4(s)}$, electrochemically prepared by directed bulk electrolysis as mentioned in Section 2.1, TGA experiments were undertaken over the temperature range of 25 to 350 °C. TGA experiments show that at about 140 °C, the compound loses 17.0 ± 1 % of its mass (Figure S2). This is consistent with the empirical formula of the compound being $\text{Cu}_2\text{TCNQF}_4 \cdot 2\text{CH}_3\text{CN}$ as the calculated mass due to CH_3CN is 16.92 %. Elemental analysis for this compound further supports this empirical formula (see below). The mass loss due to CH_3CN occurs at such high temperature relevant to the solvent boiling point of 82 °C, that the CH_3CN molecules are likely to be coordinated to the Cu^+ cation in the form of $[\text{Cu}(\text{CH}_3\text{CN})_2]^+$.

FT-IR spectrum for the synthesized $\text{Cu}_2\text{TCNQF}_{4(s)}$ material is shown in Figure S3a. IR bands associated with the $\text{C}\equiv\text{N}$ stretch are located at 2204, 2162 and 2135 cm^{-1} . The bands at 2162 and 2135 cm^{-1} are in accord with the presence of the TCNQF_4^{2-} dianion as reported in studies on $[\text{Fe}(\text{C}_5\text{Me}_5)_2^+]_2(\text{TCNQF}_4)^{2-}$ and $[\text{Co}(\text{C}_5\text{Me}_5)_2^+]_2(\text{TCNQF}_4)^{2-}$ (~2167 and 2133 cm^{-1}),³² $[\text{Ni}(\text{C}_5\text{Me}_5)_2^+]_2(\text{TCNQF}_4)^{2-}$ (2167 and 2131 cm^{-1}),³³ or a Mn(II)- TCNQF_4 based compound (2161 cm^{-1}).²⁰ The IR band at 2204 cm^{-1} is attributed to the presence of photogenerated $\text{TCNQF}_4^{\bullet-}$,^{16,18,20} resulting from photoinduced transformation of TCNQF_4^{2-} to $\text{TCNQF}_4^{\bullet-}$ (via the internal redox reaction summarized in equation 9). The phototransformation is facilitated when the sample is irradiated by the laser beam used to record the IR spectra as reported in a previous study on $\text{Cu}_2\text{TCNQF}_{4(s)}$ ¹⁵ and also for $\text{Ag}_2\text{TCNQF}_{4(s)}$.^{15,26} However, the rate of the transformation of TCNQF_4^{2-} in $\text{Cu}_2\text{TCNQF}_{4(s)}$ to $\text{TCNQF}_4^{\bullet-}$ under white light is very slow compared to that found with $\text{Ag}_2\text{TCNQF}_{4(s)}$.²⁶ Slow photochemical conversion has been confirmed by UV-vis spectroscopy. Thus, after being synthesized as in Section 2.1, the $\text{Cu}_2\text{TCNQF}_4$ solid was dissolved in acetonitrile and centrifuged to provide a saturated solution. Although the solubility of $\text{Cu}_2\text{TCNQF}_{4(s)}$ is very low, it is still sufficient for detection by UV-vis spectroscopy, along with a very small amount of $\text{TCNQF}_4^{\bullet-}$ ($\lambda_{\text{max}} = 411 \text{ nm}$)^{22,26} relative to TCNQF_4^{2-} ($\lambda_{\text{max}} = 333 \text{ nm}$)²². However, on leaving the sample for several days, even under vacuum, the relative amount of $\text{TCNQF}_4^{\bullet-}$ in the solid increases (data not show).



A related photoinduced transformation also is found in the case of $\text{Cu}^+\text{TCNQ}^{\bullet-}$.³⁵⁻³⁷ Thus, $\text{Cu}^+\text{TCNQ}^{\bullet-}$ undergoes the transformation given in equation 10 when irradiated with either visible light,³⁵ or exposed to green to red lights used to record Raman spectra when above a threshold powers,³⁶ or laser diode beam.³⁷ However, the transformation of $\text{Cu}_2\text{TCNQF}_4$ is thermodynamically more favored as E_m for the $\text{TCNQF}_4^{\bullet-/2-}$ process is -170 mV more negative than that for the $\text{TCNQ}^{0/\bullet-}$,²² i.e. TCNQF_4^{2-} is a stronger reductant than $\text{TCNQ}^{\bullet-}$.



The IR bands at 1475 and 1489 cm^{-1} also are characteristic of TCNQF_4^{2-} , as found at 1477 and 1495 cm^{-1} in $\text{Ag}_2\text{TCNQF}_4$.¹⁵ The analogous bands¹⁵ are located at 1494 and 1528

cm^{-1} in CuTCNQF_4 (see Figure S1b), so in $\text{Cu}_2\text{TCNQF}_{4(s)}$, they are shifted by 19 and 39 cm^{-1} , respectively to lower energy. A similar shift also is found in comparing IR spectra for AgTCNQF_4 and $\text{Ag}_2\text{TCNQF}_4$.¹⁵ Although the TGA experiment and elemental analysis indicate the presence of two moles of CH_3CN to give a $[\text{Cu}(\text{CH}_3\text{CN})_2]^+$ cation, neither IR bands at around 2300 cm^{-1} for the $\text{C}\equiv\text{N}$ stretch in coordinated CH_3CN (at 2290 cm^{-1} in $\text{Cr}(\text{TCNQ})_2(\text{CH}_3\text{CN})_2$,³⁸ nor at 2274, 2302 and 2310 cm^{-1} in $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$) have been detected.

The Raman vibration region for the $\text{C}\equiv\text{N}$ stretch in the $\text{Cu}_2\text{TCNQF}_{4(s)}$ consists of three bands located at 2218, 2170 and 2141 cm^{-1} (Figure S4a). The vibration mode at 2218 cm^{-1} is consistent with the presence of $\text{TCNQF}_4^{\bullet-}$,^{2,17,26} again confirming the photoinduced transformation of TCNQF_4^{2-} to $\text{TCNQF}_4^{\bullet-}$ during recording of the Raman spectrum, while the two bands located at lower energy are consistent for TCNQF_4^{2-} -based material. The Raman bands at 1655, 1435 and 1246 cm^{-1} are attributed to $\text{C}=\text{C}$ ring, $\text{C}-\text{CN}$,^{2,17,26} and $\text{C}-\text{F}$ stretches, respectively in TCNQF_4^{2-} , while other bands at 1643, 1443 and 1273 cm^{-1} are in accord with these stretches in $\text{TCNQF}_4^{\bullet-}$ as discussed in Section 3.4.1.

$\text{Cu}_2\text{TCNQF}_{4(s)}$ electrocrystallized onto an ITO electrode surface from 1.0 mM TCNQF_4 and 2.0 mM $\text{Cu}(\text{MeCN})_4^+$ in acetonitrile (0.1 M Bu_4NPF_6) by reduction of TCNQF_4 to TCNQF_4^{2-} at a constant potential of -500 mV for 15 min was rinsed with 3×3 mL of acetonitrile and dried under a stream of N_2 gas for 10 min and then under vacuum overnight before being spectroscopically characterized. FT-IR, Raman and UV-vis spectra for this electrocrystallized $\text{Cu}_2\text{TCNQF}_4$ are respectively identical (within experimental error) with those for the $\text{Cu}_2\text{TCNQF}_{4(s)}$ synthesized by electrochemically directed method (see Figures S3 and S4, UV-vis spectra not shown). Spectroscopic data imply that Cu^+ - TCNQF_4^{2-} -based compounds isolated by the two methods have the same phase and both are prone to optically induced transformation to CuTCNQF_4 and Cu metal. SEM images reveal that the rod-like morphology of the electrocrystallized $\text{Cu}_2\text{TCNQF}_4$ (Figure 12) differs from that for electrocrystallized CuTCNQF_4 (closely packed cubic particles - Figure 11).

Elemental analysis data for the $\text{Cu}_2\text{TCNQF}_{4(s)}$ synthesized by the electrochemically directed method from acetonitrile solutions of $\text{Cu}(\text{MeCN})_4^+$ and TCNQF_4^{2-} are %C = 39.50; %H = 1.26; %N = 17.48, which is consistent with the formulation being

$\text{Cu}_2\text{TCNQF}_4 \cdot 2\text{CH}_3\text{CN}$ (calculated: %C = 39.59, %H = 1.25, %N = 17.32). The two moles of CH_3CN are as deduced from the TGA experiment.

Efforts to obtain single crystals of $\text{Cu}_2\text{TCNQF}_4 \cdot 2\text{CH}_3\text{CN}$ have been unsuccessful. However, a powder diffraction pattern for the compound was obtained (Figure S5a). In related collaborative work, single crystals of $\text{Me}_4\text{N}[\text{Cu}^{\text{I}}(\text{TCNQF}_4)]$ have been obtained and the crystal structure has been elucidated. A representation of the structure of $\text{Me}_4\text{N}[\text{Cu}^{\text{I}}(\text{TCNQF}_4)]$ is presented in Figure S6. In this structure, Cu(I) centres are bound to four different TCNQF_4 dianions and each dianion coordinates to four Cu(I) centres. The four nitrogen centres bound to each Cu(I) form a slightly distorted tetrahedral environment around the Cu(I) centre. Each TCNQF_4 dianion is planar and binds to Cu(I) centres at the corners of a rectangle of approximate dimensions $7.3 \times 11.1 \text{ \AA}$. Me_4N^+ cations, which are required to balance the charge of the anionic framework, are located within the intersecting channels of the infinite network as can be seen in Figure S6. From a topological perspective, the structure is analogous to platinum(II) sulfide which has an infinite network structure consisting of square planar Pt(II) centres linked by tetrahedral sulfide anions. When a range of other countercations are used in place of NMe_4^+ , similar 3D anionic networks are obtained but they differ with respect to the orientations of the TCNQF_4 dianions.

Whilst there is a clear difference in the formulation of $\text{Me}_4\text{N}[\text{Cu}^{\text{I}}(\text{TCNQF}_4)]$ and $\text{Cu}_2\text{TCNQF}_4 \cdot 2\text{CH}_3\text{CN}$, we believe there is a distinct possibility that crystalline $\text{Cu}_2\text{TCNQF}_4 \cdot 2\text{CH}_3\text{CN}$ consists of a 3D anionic framework of composition $[\text{Cu}(\text{TCNQF}_4)]^-$, either similar or closely related to that described above, but with a solvated Cu(I) centre ($[\text{Cu}^{\text{I}}(\text{CH}_3\text{CN})_2]^+$) serving as the countercation in place of Me_4N^+ . A comparison of the diffraction patterns obtained from the powdered $\text{Cu}_2\text{TCNQF}_4 \cdot 2\text{CH}_3\text{CN}$ sample and that generated from the single crystal data for $\text{Me}_4\text{N}[\text{Cu}^{\text{I}}(\text{TCNQF}_4)]$ (Figure S5b) is inconclusive in terms of confirming an isostructural anionic network although we do note some similarity in the positions of some diffraction peaks.

3.5. Solubility of $\text{CuTCNQF}_{4(s)}$ and $\text{Cu}_2\text{TCNQF}_{4(s)}$ in Acetonitrile

The solubility of $\text{CuTCNQF}_{4(s)}$ in acetonitrile in the presence and absence of 0.1 M Bu_4NPF_6 supporting electrolyte was determined. Thus, 2.0 mL of acetonitrile containing 0.1 M Bu_4NPF_6 supporting electrolyte or neat acetonitrile were used to dissolve $\text{CuTCNQF}_{4(s)}$ synthesized as described in Section 2.1. The mixtures were then sonicated

for 5 min to achieve equilibrium between the solid and solution phases. The concentration of $\text{TCNQF}_4^{\bullet-}$ in the saturated solutions were determined by UV-vis spectroscopy using the absorption band with λ_{max} at 411 nm and reference to a calibration curve. In this manner, the solubility of $\text{CuTCNQF}_{4(s)}$ was determined to be $1.95 \pm 0.06 \times 10^{-4}$ M and $1.14 \pm 0.03 \times 10^{-4}$ M in the presence and absence of 0.1 M Bu_4NPF_6 , respectively. Consequently, the solubility products of the $\text{CuTCNQF}_{4(s)}$ in acetonitrile containing 0.1 M Bu_4NPF_6 supporting electrolyte and in neat solvent are $3.81 \pm 0.25 \times 10^{-8} \text{ M}^2$ and $1.30 \pm 0.07 \times 10^{-8} \text{ M}^2$, respectively.

The solubility of $\text{Cu}_2\text{TCNQF}_{4(s)}$ in acetonitrile in the presence and absence of 0.1 M Bu_4NPF_6 was determined in a similar manner to that for the $\text{CuTCNQF}_{4(s)}$. However, in order to achieve a saturated $\text{Cu}_2\text{TCNQF}_4$ solution, instead of sonication, a mixture of $\text{Cu}_2\text{TCNQF}_4$ solid and acetonitrile was purged with N_2 gas for 10 minutes in order to achieve equilibration (TCNQF_4^{2-} slowly decomposes in the presence of the air). The concentration of TCNQF_4^{2-} in each of the $\text{Cu}_2\text{TCNQF}_4$ saturated solutions after filtration was determined by UV-vis spectroscopy using the band with λ_{max} at 333 nm and a calibration curve, and found to be $1.59 \pm 0.06 \times 10^{-5}$ M and $7.29 \pm 0.46 \times 10^{-6}$ M in 0.1 M Bu_4NPF_6 containing and neat acetonitrile, respectively, leading to $\text{Cu}_2\text{TCNQF}_{4(s)}$ solubility products of $1.61 \times 10^{-14} \text{ M}^3$ and $1.55 \times 10^{-15} \text{ M}^3$, respectively. The solubility of $\text{CuTCNQF}_{4(s)}$ and $\text{Cu}_2\text{TCNQF}_{4(s)}$ in the presence of 0.1 M Bu_4NPF_6 supporting electrolyte is higher than that in neat acetonitrile. The enhanced solubility, also found for $\text{AgTCNQ}_{(s)}$ and $\text{CuTCNQ}_{(s)}$, is attributed to the ion pairing^{26,39} of Cu^+ , $\text{TCNQF}_4^{\bullet-}$ and TCNQF_4^{2-} with counterions provided by the Bu_4NPF_6 supporting electrolyte.

4. Conclusions

Electrochemically directed synthesis of $\text{CuTCNQF}_{4(s)}$ and $\text{Cu}_2\text{TCNQF}_{4(s)}$ has been achieved via reduction of TCNQF_4 to $\text{TCNQF}_4^{\bullet-}$ and TCNQF_4^{2-} , respectively in acetonitrile (0.1 M Bu_4NPF_6), followed by combination with $\text{Cu}(\text{MeCN})_4^+$. The solubility of the $\text{CuTCNQF}_{4(s)}$ and $\text{Cu}_2\text{TCNQF}_{4(s)}$ in acetonitrile in the presence and absence of 0.1 M Bu_4NPF_6 supporting electrolyte has been determined, to be $1.95 \pm 0.06 \times 10^{-4}$ M and $1.14 \pm 0.03 \times 10^{-4}$ M (for $\text{CuTCNQF}_{4(s)}$), and $1.59 \pm 0.06 \times 10^{-5}$ M and $7.29 \pm 0.46 \times 10^{-6}$ M (for $\text{Cu}_2\text{TCNQF}_{4(s)}$), respectively. Thus, $\text{Cu}_2\text{TCNQF}_{4(s)}$ is more than 10-fold less soluble than $\text{CuTCNQF}_{4(s)}$. This allows $\text{Cu}_2\text{TCNQF}_4$ to be electrocrystallized from low concentrations of TCNQF_4 and $\text{Cu}(\text{MeCN})_4^+$, whilst CuTCNQF_4 may be

electrocrystallized from higher concentration environments. UV-vis, IR and Raman spectra confirm the presence of either $\text{TCNQF}_4^{\bullet-}$ or TCNQF_4^{2-} as appropriate in all materials, synthesized by electrochemically directed synthesis or electrocrystallization. $\text{Cu}_2\text{TCNQF}_{4(s)}$ undergoes slowly photoinduced transformation to $\text{CuTCNQF}_{4(s)}$ and metallic Cu via an internal redox reaction. Electrocrystallized $\text{CuTCNQF}_{4(s)}$ produced cubic particles ($\sim 3 \mu\text{m}$), whilst $\text{Cu}_2\text{TCNQF}_{4(s)}$ formed with a rod-shaped morphology. A simulation that mimics the electrocrystallization of $\text{Cu}_2\text{TCNQF}_{4(s)}$ from the reduction of TCNQF_4 to TCNQF_4^{2-} in the presence of $\text{Cu}(\text{MeCN})_4^+$ in acetonitrile (0.1 M Bu_4NPF_6) is proposed and describes most of the features present in experimental cyclic voltammograms over a range of scan rates. Electrocrystallization experiments imply that $\text{Cu}_2\text{TCNQF}_{4(s)}$ is initially formed in a thermodynamically unstable form which rapidly converts to a stable phase. TGA experiment, elemental analysis, FT-IR and XRD data reveal that the TCNQF_4^{2-} -based material may be formed as $[\text{Cu}^{\text{I}}(\text{CH}_3\text{CN})_2][\text{Cu}^{\text{I}}(\text{TCNQF}_4)]$. Importantly, electrochemical synthesis of TCNQF_4^{2-} complexes is facilitated relative to TCNQ^{2-} -based materials due to their much reduced level of reactivity with oxygen.

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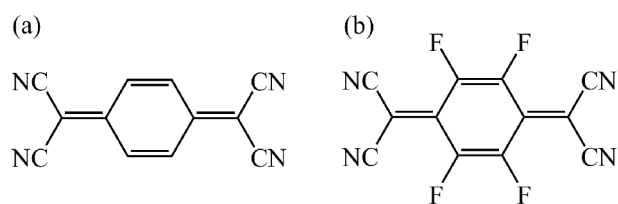


Figure 1. Molecular structures of (a) TCNQ and (b) TCNQF₄.

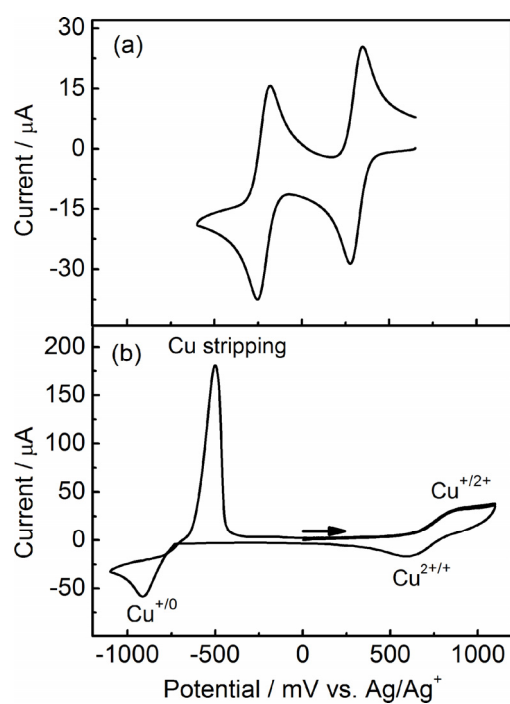


Figure 2. Cyclic voltammograms for (a) 1.0 mM TCNQF₄ and (b) 2.0 mM Cu(MeCN)₄⁺ in acetonitrile (0.1 M Bu₄NPF₆) obtained with a 3.0 mm diameter GC electrode at a scan rate of 100 mV s⁻¹.

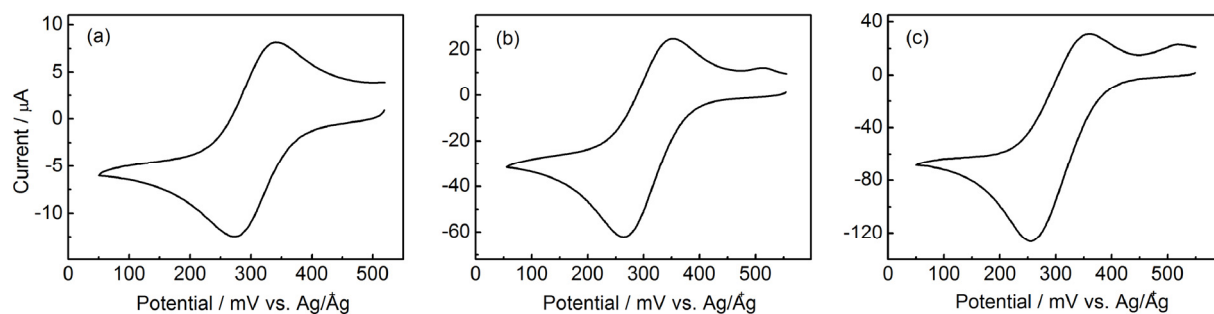


Figure 3. Cyclic voltammograms for acetonitrile (0.1 M Bu_4NPF_6) solutions containing 10.0 mM $\text{Cu}(\text{MeCN})_4^+$ and (a) 1.0, (b) 5.0, (c) 10.0 mM TCNQF_4 using a 3.0 mm diameter GC electrode ($\nu = 20 \text{ mV s}^{-1}$).

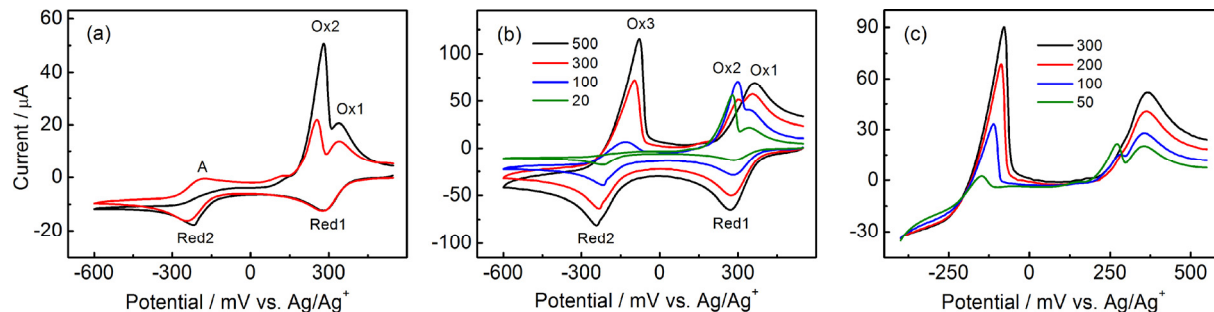


Figure 4. Voltammograms obtained with a 3.0 mm diameter GC electrode in acetonitrile (0.1 M Bu_4NPF_6) solutions containing (a) 1.0 mM TCNQF_4 in the presence of 2.0 mM $\text{Cu}(\text{MeCN})_4^+$ (black curve) or 1.0 mM $\text{Cu}(\text{MeCN})_4^+$ (red curve) at a scan rate of 20 mV s^{-1} , (b) 1.0 mM TCNQF_4 and 2.0 mM $\text{Cu}(\text{MeCN})_4^+$ at designated scan rates (mV s^{-1}), (c) under conditions as (b) but the potential was held at -400 mV for 1 s and then scanned in positive direction at designated scan rates (mV s^{-1}).

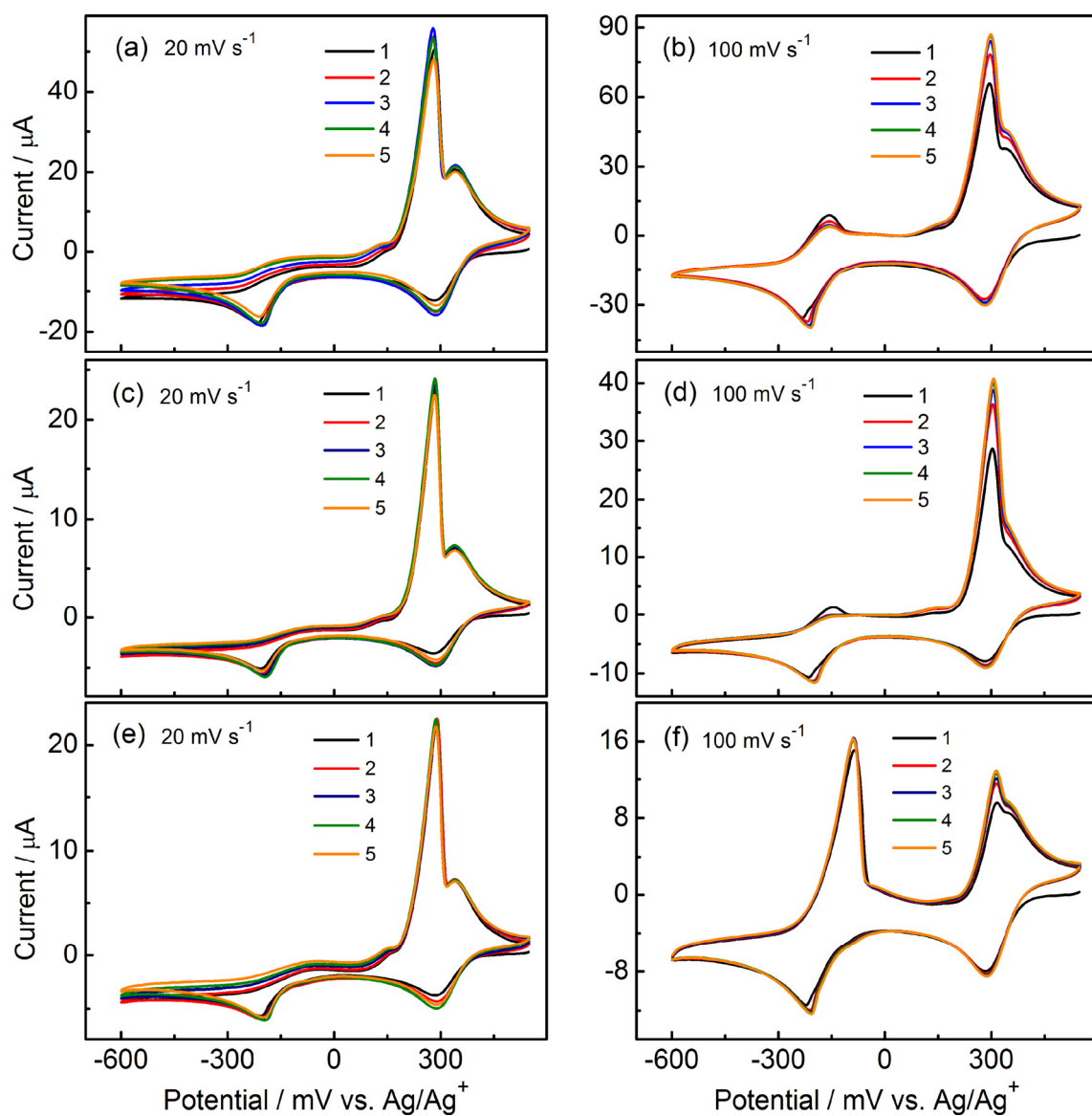


Figure 5. Cyclic voltammograms (first five cycles) obtained at (a, b) 3.0 mm diameter GC, (c, d) 1.6 mm diameter Pt and (e, f) 1.6 mm diameter Au electrodes in an acetonitrile (0.1 M Bu₄NPF₆) solution containing 1.0 mM TCNQF₄ and 2.0 mM Cu(MeCN)₄⁺ at scan rates of 20 and 100 mV s⁻¹.

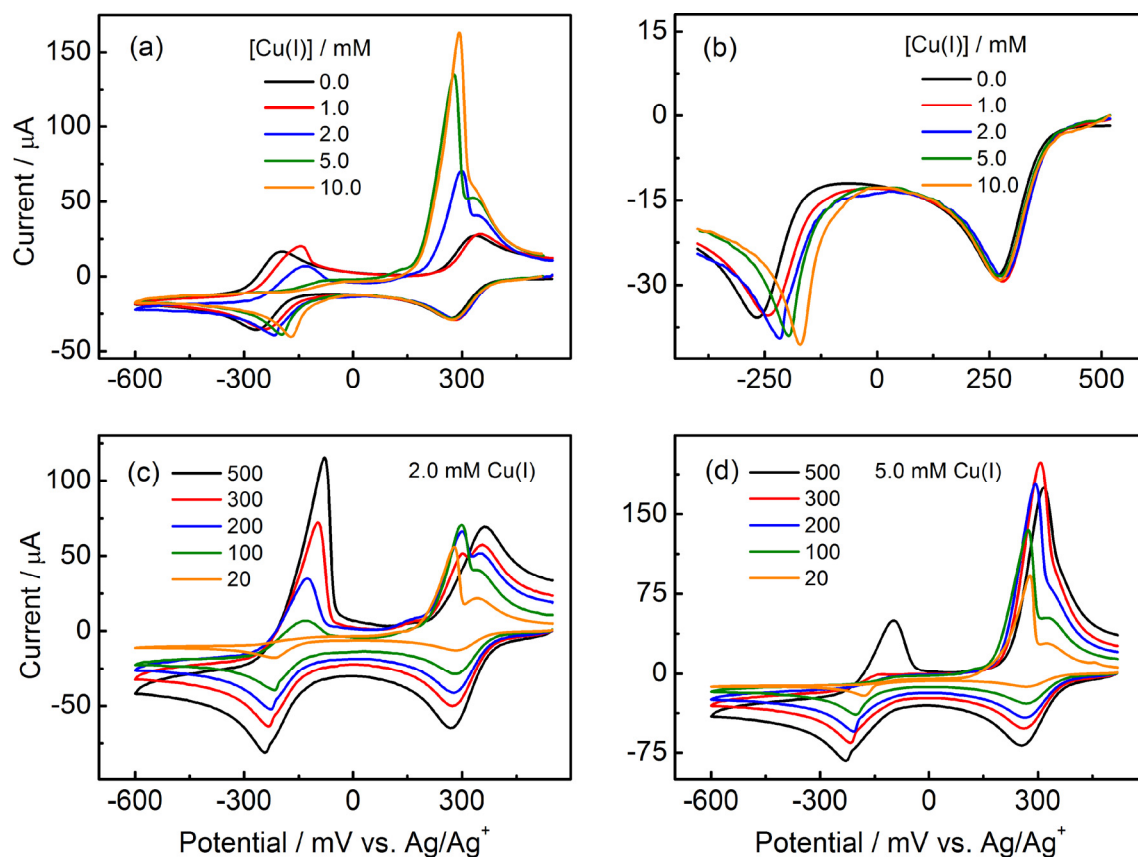


Figure 6. (a) Cyclic voltammograms for 1.0 mM TCNQF₄ in the presence of designated $\text{Cu}(\text{MeCN})_4^+$ concentrations in acetonitrile (0.1 M Bu_4NPF_6) obtained with a 3.0 mm diameter GC electrode ($\nu = 100 \text{ mV s}^{-1}$), (b) as for (a) but only reduction components are shown, (c, d) as for (a) but at designated scan rates and $\text{Cu}(\text{MeCN})_4^+$ concentrations.

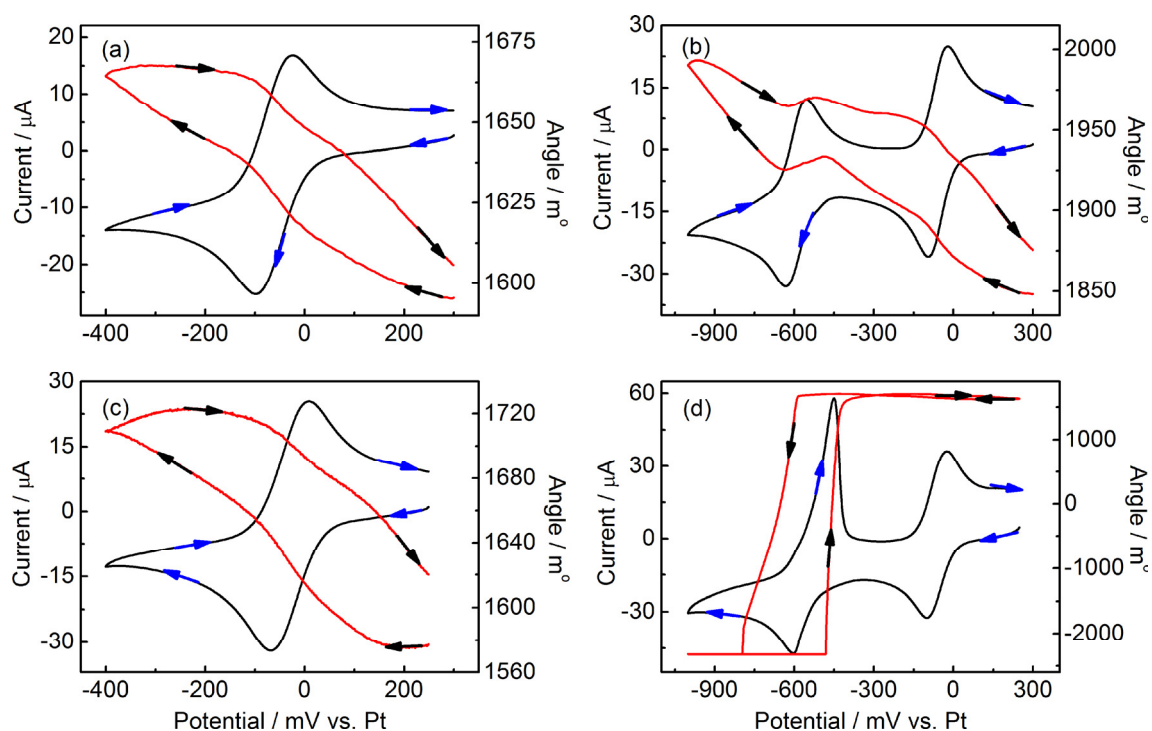


Figure 7. *In situ* cyclic voltammetric (—) and SPR (—) data obtained at a scan rate of 100 mV s^{-1} and as a function of switching potential when a gold coated-glass electrode was in contact with acetonitrile ($0.1 \text{ M Bu}_4\text{NPF}_6$) solutions containing 1.0 mM TCNQF_4 in (a, b) the absence and (c, d) the presence of $2.0 \text{ mM Cu(MeCN)}_4^+$.

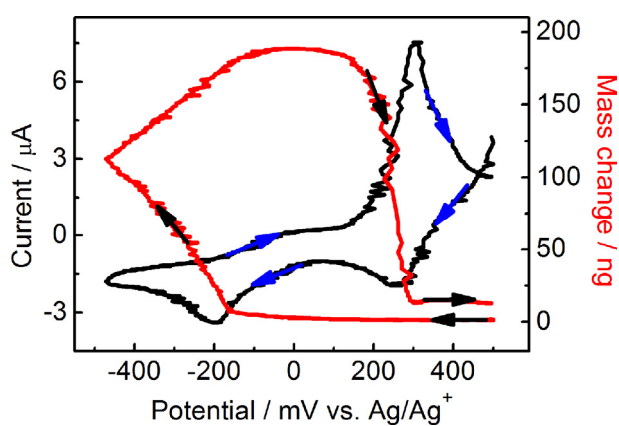


Figure 8. EQCM (current —, mass change —) data obtained with a 5.0 mm diameter Au electrode ($\nu = 20 \text{ mV s}^{-1}$) for an acetonitrile ($0.1 \text{ M Bu}_4\text{NPF}_6$) solution containing 1.0 mM TCNQF_4 and $2.0 \text{ mM Cu(MeCN)}_4^+$.

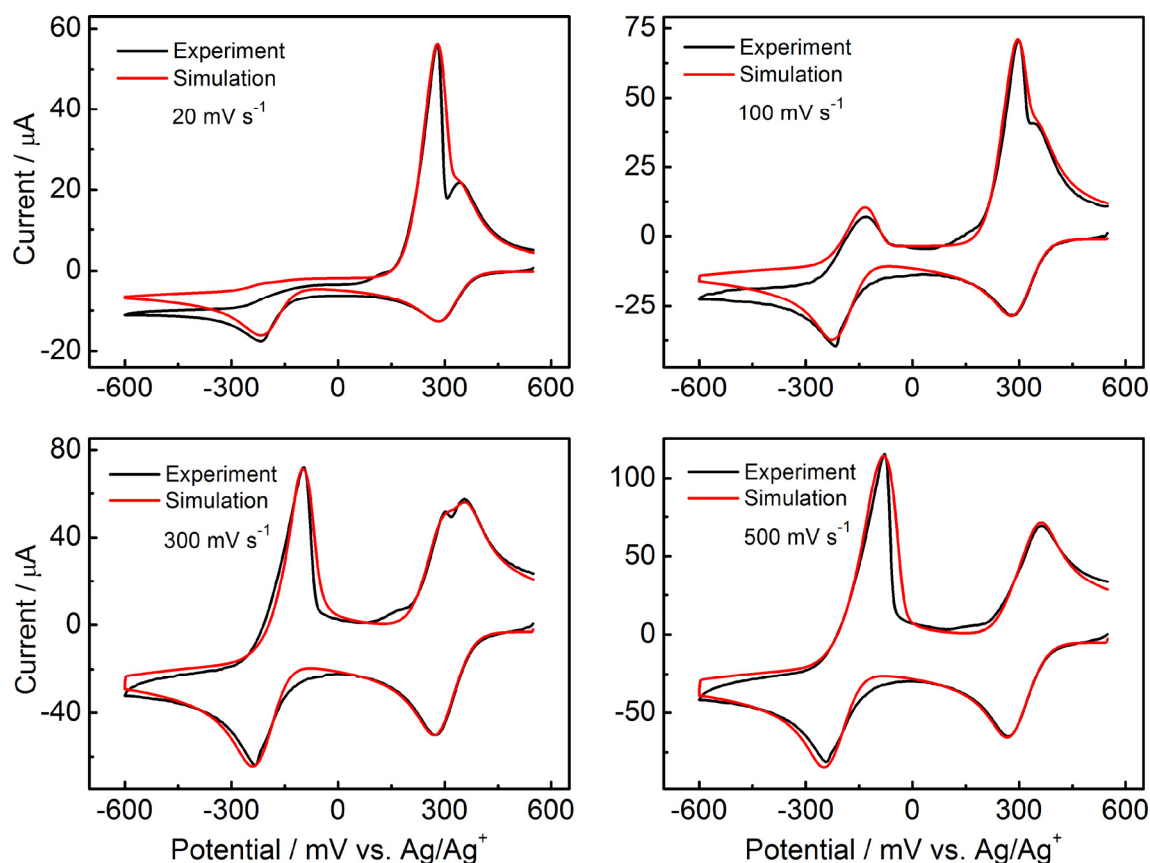


Figure 9. Comparison of simulated (—) and experimental (—) cyclic voltammograms obtained for 1.0 mM TCNQF₄ in the presence of 2.0 Cu(MeCN)₄⁺ in acetonitrile (0.1 M Bu₄NPF₆) using a 3.0 mm diameter GC electrode at designated scan rates. Simulation parameters are provided in Table 2.

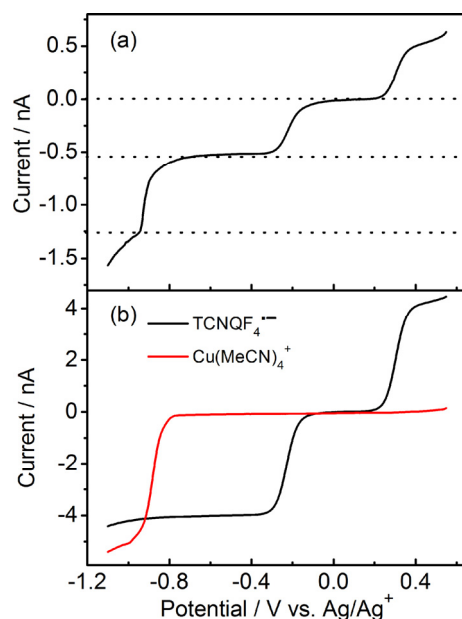


Figure 10. Near steady-state voltammograms obtained with a 11 μm diameter carbon fiber microelectrode ($\nu = 20 \text{ mV s}^{-1}$) for acetonitrile (0.1 Bu_4NPF_6) solutions containing (a) saturated CuTCNQF_4 , (b) 1.0 mM $\text{TCNQF}_4^{\bullet-}$ and 1.0 mM $\text{Cu}(\text{MeCN})_4^+$.

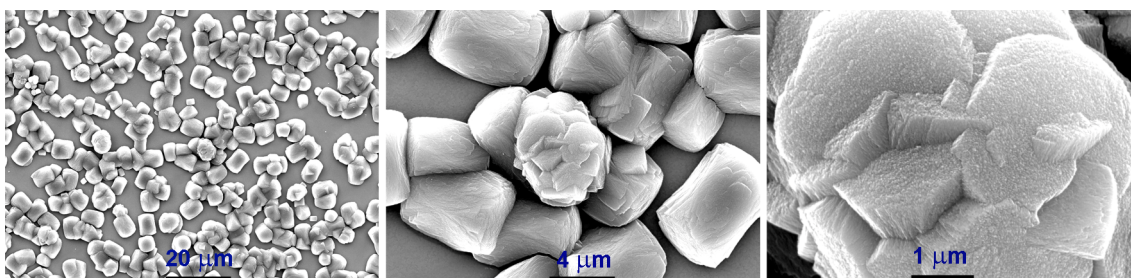


Figure 11. SEM images with (left to right) increasing levels of magnification for CuTCNQF_4 electrocrystallized onto an ITO electrode surface from an acetonitrile (0.1 M Bu_4NPF_6) solution containing 2.0 mM TCNQF_4 and 10.0 mM $\text{Cu}(\text{MeCN})_4^+$. Reductive electrolysis of TCNQF_4 to $\text{TCNQF}_4^{\bullet-}$ was for 15 min at 100 mV.

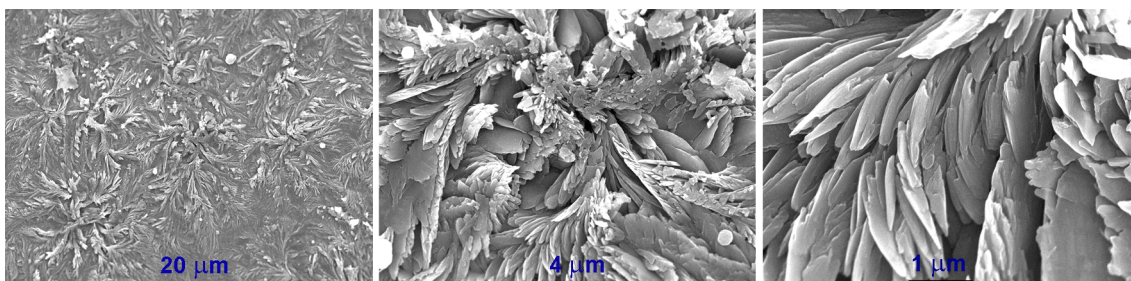


Figure 12. SEM images at increasing magnification (left to right) for $\text{Cu}_2\text{TCNQF}_{4(s)}$ electrocrystallized onto an ITO electrode surface by reductive electrolysis of 1.0 mM TCNQF_4 at -500 mV for 15 min in an acetonitrile (0.1 M Bu_4NPF_6) solution containing 2.0 mM $\text{Cu}(\text{MeCN})_4^+$.

Table 1. Midpoint Potentials (E_m)^(a, b) Derived from Cyclic Voltammograms Obtained for 1.0 mM TCNQF₄ and 2.0 mM Cu(MeCN)₄⁺ in Separate Acetonitrile (0.1 M Bu₄NPF₆) Solutions at GC, Au, Pt and ITO Electrodes

WE	Process			
	TCNQF ₄ ^{0/•-}	TCNQF ₄ ^{•-/2-}	Cu ^{+/0}	Cu ^{+/2+}
GC	311	-220	-706	748
Au	310	-220	-630	560
Pt	310	-221	-659	545
ITO	304	-246	-640	725

^(a) Midpoint potential is the average of the reduction E_p^{red} and oxidation E_p^{ox} peak potentials for a redox couple, i.e. $E_m = (E_p^{\text{red}} + E_p^{\text{ox}})/2$.

^(b) Potentials in mV vs. Ag/Ag⁺.

Table 2. Parameters Used to Simulate Cyclic Voltammograms that Mimic the Reduction of 1.0 mM TCNQF₄ in the Presence of 2.0 mM Cu(MeCN)₄⁺ in Acetonitrile (0.1 Bu₄NPF₆) When Using a 3.0 mm Diameter GC Electrode

Step	Reaction	E^0 / V	k_s	K_{eq}	$k_f^{(a)}$
1.	$\text{T} + \text{e}^- = \text{T}^{\bullet-}$	0.315	$0.1 \text{ cm s}^{-1 (b)}$		
2.	$\text{T}^{\bullet-} + \text{e}^- = \text{T}^{2-}$	-0.225	$0.1 \text{ cm s}^{-1 (b)}$		
3.	$\text{T}^{2-} + \text{Cu}^+ = \text{CuT}^-$			1×10^8	$1 \times 10^{5 (b)}$
4.	$\text{CuT}^- + \text{Cu}^+ = \text{Cu}_2\text{TA}$			1×10^6	1×10^{10}
5.	$\text{Cu}_2\text{TA} = \text{Cu}_2\text{TB}$			1×10^{15}	$1^{(b)}$
6.	$\text{Cu}_2\text{TA} = \text{Cu}_2\text{TA}^*$			1×10^{15}	1×10^{10}
7.	$\text{Cu}_2\text{TB} = \text{Cu}_2\text{TB}^*$			1×10^{20}	1×10^{10}
8.	$\text{Cu}_2\text{TA} = \text{Cu}_2\text{TA}^+ + \text{e}^-$	-1.30	$0.0 \text{ cm s}^{-1 (c)}$		
9.	$\text{Cu}_2\text{TB} = \text{Cu}_2\text{TB}^+ + \text{e}^-$	-1.16	$0.0 \text{ cm s}^{-1 (c)}$		
10.	$\text{Cu}_2\text{TA}^* = \text{Cu}_2\text{TA}^{*+} + \text{e}^-$	-0.117 ^(d)	$50 \text{ s}^{-1 (b)}$		
11.	$\text{Cu}_2\text{TB}^* = \text{Cu}_2\text{TB}^{*+} + \text{e}^-$	0.319 ^(d)	$50 \text{ s}^{-1 (b)}$		
12.	$\text{Cu}_2\text{TA}^{*+} = \text{Cu}_2\text{TA}^+$			1×10^5	$1 \times 10^{2 (b)}$
13.	$\text{Cu}_2\text{TB}^{*+} = \text{Cu}_2\text{TB}^+$			1×10^5	1×10^2
14. ^(e)	$\text{Cu}_2\text{TA}^+ \Rightarrow \text{T}^{\bullet-} + \text{Cu}_2^{2+}$			1×10^{15}	1×10^6
15. ^(e)	$\text{Cu}_2\text{TB}^+ \Rightarrow \text{T}^{\bullet-} + \text{Cu}_2^{2+}$			232.3 ^(d)	1×10^6
16. ^(e)	$\text{Cu}_2^{2+} \Rightarrow \text{Cu}^+ + \text{Cu}^+$			6.8×10^{-48} (d)	1×10^{12}

T = TCNQF₄; Cu₂TA = Phase A of Cu₂TCNQF_{4(s)}; Cu₂TB = Phase B of Cu₂TCNQF_{4(s)}

^(a) k_f has unit of M⁻¹ s⁻¹ for steps 3 and 4 (second-order reactions) and s⁻¹ for other steps (first-order reactions).

^(b) In some cases, the value of this parameter may be slightly varied from those stated to provide enhanced agreement between simulated and experimental cyclic voltammograms; in other cases, simulation can be insensitive to particular value, e.g. in steps 1 and 2, any k_s values of $> 0.1 \text{ cm s}^{-1}$ allows excellent agreement between simulation and experiment to be obtained, so that the value of 0.1 cm s^{-1} represents a lower limit.

^(c) Oxidation of $\text{Cu}_2\text{TCNQF}_4$ phases A and B in solution is switched off in the simulation, i.e. $\text{Cu}_2\text{TCNQF}_{4(s)}$ phase A and B are strongly adhered to the electrode surface. However, the E^0 values for these processes have to be included to generate E^0 values (created automatically by software) for steps 10 and 11.

^(d) Values of these parameters are automatically computed by the DigiElch software from other input parameters (thermodynamically related data).

^(e) The $\text{Cu}_2\text{TCNQF}_4^+$ cation might fully dissociate into $\text{TCNQF}_4^{\bullet-}$ and 2Cu^+ in a single step, but the simulation software does not allow for this possibility.

Other parameters used in the simulation are: $\alpha = 0.50$, $T = 295 \text{ K}$, Area of electrode = 0.074 cm^2 ; uncompensated resistance $R_u = 200 \Omega$; double layer capacitance $C_{dl} = 1 \times 10^{-5} \text{ F}$; diffusion coefficients: $\text{TCNQF}_4 = 2.0 \times 10^{-5}$, $\text{TCNQF}_4^{\bullet-} = 1.9 \times 10^{-5}$, $\text{TCNQF}_4^{2-} = 1.5 \times 10^{-5}$,²² $\text{Cu}^+ = 2.3 \times 10^{-5}$ (determined from peak currents derived from cyclic voltammograms for reduction of $2.0 \text{ mM Cu}(\text{MeCN})_4^+$ in acetonitrile ($0.1 \text{ M Bu}_4\text{NPF}_6$) obtained with a 3.0 mm diameter GC electrode at different scan rates using the Randles-Sevcik relationship $i_p = 0.4463nFAC(nFvD/RT)^{1/2}$; this value is consistent with a previous report³⁰ for diffusion coefficient of $\text{Cu}(\text{MeCN})_4^+$ in acetonitrile being $2.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 38°C), and $1.0 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for all other species (note that varying the diffusion coefficient of intermediate species almost does not affect the simulated cyclic voltammetric behavior), the maximum surface coverage = $\sim 10^{-9} \text{ moles cm}^{-2}$, self-interaction parameter $a^* = 0$.

Supporting Information

Electrochemically Directed Synthesis and Characterization of Cu(I) Derivatives of TCNQF₄^{•-} or TCNQF₄²⁻ (TCNQF₄ = 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane) in Acetonitrile

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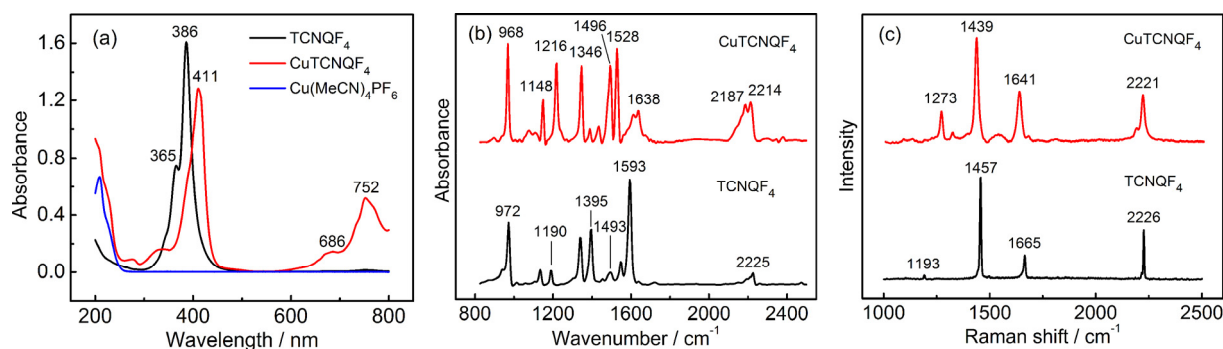


Figure S1. (a) UV-vis spectra (in acetonitrile), (b) FT-IR spectra (solid) and (c) Raman spectra (solid) for TCNQF₄ and CuTCNQF₄ prepared by electrochemically directed synthesis.

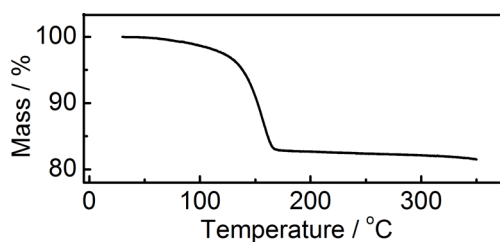


Figure S2. TGA data for the Cu⁺-TCNQF₄²⁻ material, which was prepared from Cu(MeCN)₄⁺ and electrochemically generated TCNQF₄²⁻ acetonitrile solutions.

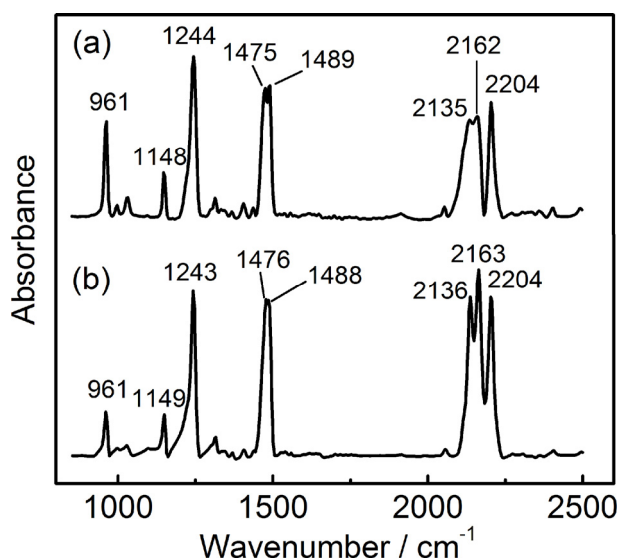


Figure S3. FT-IR spectra for (a) $\text{Cu}_2\text{TCNQF}_{4(s)}$ synthesized from reaction of TCNQF_4^{2-} and $\text{Cu}(\text{MeCN})_4^+$ in acetonitrile, (b) $\text{Cu}_2\text{TCNQF}_{4(s)}$ electrocrystallized onto an ITO electrode surface by reductive electrolysis of 1.0 mM TCNQF_4 at -500 mV for 15 min in an acetonitrile (0.1 M Bu_4NPF_6) solution containing 2.0 mM $\text{Cu}(\text{MeCN})_4^+$.

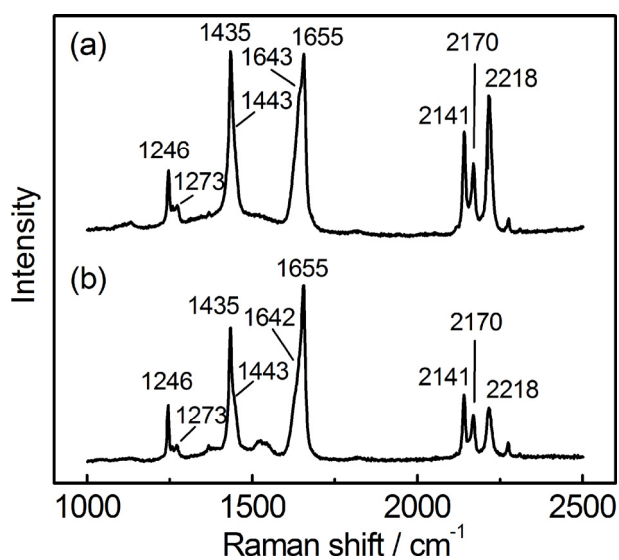


Figure S4. Raman spectra for $\text{Cu}_2\text{TCNQF}_{4(s)}$ as mentioned in the caption to Figure S3.

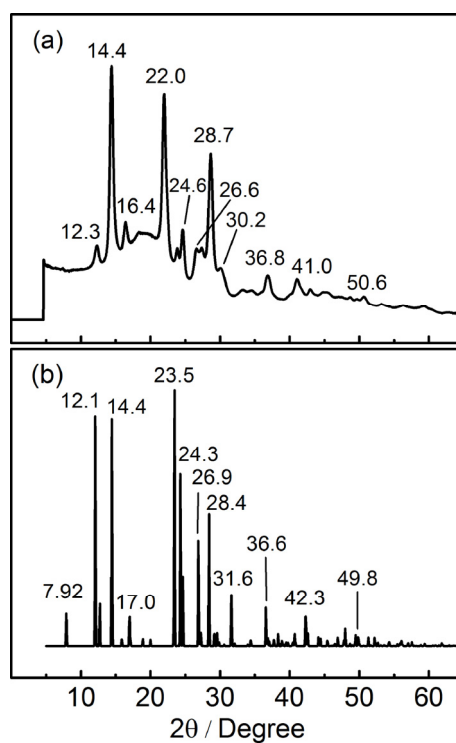


Figure S5. X-ray powder diffractograms (a) for $\text{Cu}_2\text{TCNQF}_4 \cdot 2\text{CH}_3\text{CN}$ powder synthesized from $\text{Cu}(\text{MeCN})_4^+$ and TCNQF_4^{2-} in acetonitrile, (b) generated from the single crystal data for $\text{Me}_4\text{N}[\text{Cu}(\text{TCNQF}_4)]$, prepared by layering an acetonitrile solution containing $\text{Cu}(\text{MeCN})_4^+$ and LiCH_3COO onto a dimethylformamide solution of H_2TCNQF_4 .

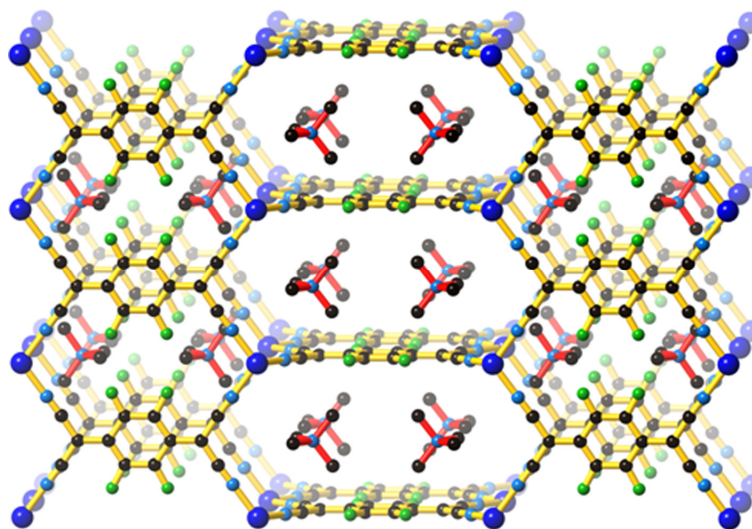


Figure S6. The crystal structure of $\text{Me}_4\text{N}[\text{Cu}^{\text{I}}(\text{TCNQF}_4)]$. The bonds in the anionic $[\text{Cu}^{\text{I}}(\text{TCNQF}_4)]^-$ network are represented by gold connections; the C–N bonds of the Me_4N^+ cations are represented by red connections. Color code: Cu blue, F green; N light blue, C black; hydrogen atoms have been omitted for clarity.

Declaration for Thesis Chapter 4.5

Declaration by candidate

In the case of Chapter 4.5, the nature and extent of my contribution to the work was the following:

Nature of contribution	Extent of contribution (%)
Initiation, key ideas, experimental work, writing up	90

The following co-authors contributed to the work.

Name	Nature of contribution
Ayman Nafady	Initiation, key ideas
Lisandra L. Martin	Initiation, key ideas, writing up
Alan M. Bond	Initiation, key ideas, writing up

Candidate's Signature

	06/06/2012
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Declaration by co-authors

The undersigned hereby certify that:

- (1) the above declaration correctly reflects the nature and extent of the candidate's contribution to this work, and the nature of the contribution of each of the co-authors.
- (2) they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;
- (3) they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
- (4) there are no other authors of the publication according to these criteria;
- (5) potential conflicts of interest have been disclosed to (a) granting bodies, (b) the editor or publisher of journals or other publications, and (c) the head of the responsible academic unit; and
- (6) the original data are stored at the following location and will be held for at least five years from the date indicated below:

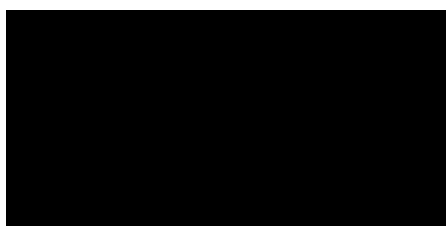
Location

School of Chemistry, Monash University, Clayton

Ayman Nafady

Lisandra L. Martin

Alan M. Bond

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	18/5/12

Electrochemically Directed Synthesis of Co^{2+} and Ni^{2+} Complexes with TCNQF_4^{2-} (TCNQF_4 = 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane)

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Key words: CoTCNQF_4 / NiTCNQF_4 / TCNQF_4^{2-} / electrochemical synthesis.

Abstract

The electrocrystallization of transition metal coordination polymers containing the TCNQF_4^{2-} dianion and M^{2+} cation, MTCNQF_4 (TCNQF_4 = 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane, $\text{M} = \text{Co}$ or Ni) has been achieved in acetonitrile (0.1 M Bu_4NPF_6) at glassy carbon and indium tin oxide electrodes with the reaction pathway being monitored by cyclic voltammetry and surface plasmon resonance. TCNQF_4 is sequentially reduced to $\text{TCNQF}_4^{\bullet-}$ and then TCNQF_4^{2-} . In the presence of M^{2+} , TCNQF_4^{2-} formation is accompanied by electrocrystallization of the sparingly soluble MTCNQF_4 solid onto the electrode surface. Cyclic voltammetric studies reveal that two phases of the MTCNQF_4 are formed. One is kinetically favoured and rapidly converts to a second thermodynamically stable phase. The formation of MTCNQF_4 is possible due to the relatively high solubility of $\text{M}(\text{TCNQF}_4)_2$ derivatives. The solubilities of CoTCNQF_4 and NiTCNQF_4 are 8.6×10^{-6} and 9.2×10^{-6} M, respective in neat acetonitrile, and 2.2×10^{-5} and 2.4×10^{-5} M in acetonitrile (0.1 Bu_4NPF_6). The presence of the TCNQF_4^{2-} dianion rather than the $\text{TCNQF}_4^{\bullet-}$ monoanion in the coordination polymers was confirmed by UV-visible, infrared and Raman spectroscopies. Scanning electron microscopy images show that the morphology depends on the applied potential for electrocrystallized CoTCNQF_4 , but not for the NiTCNQF_4 complex.

1. Introduction

In recent years, a number of TCNQF₄-based complexes (TCNQF₄ = 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane) have been synthesized, and their structures and physical properties explored.^[1-6] These materials are currently of interest for application to optical and electrical bistable switches, light-emitting diodes, field effect transistors, sensors and catalysis.^[1, 5] However, the number of TCNQF₄-based complexes is still small compared with the TCNQ (7,7,8,8-tetracyanoquinodimethane) analogues, that have been widely studied for several decades.^[7-12] To date, most studies have focused on complexes and materials based on the monoanions of TCNQ or TCNQF₄, although recently, a number of air stable TCNQ²⁻ complexes have been reported.^[13-17] In these cases, the starting materials used in the synthesis have been LiTCNQ^[13] or H₂TCNQ,^[14-17] both being stable under ambient conditions. However, it is difficult to synthesize complexes directly from TCNQ²⁻ as it is unstable in the air. In contrast, TCNQF₄²⁻ is stable in air over several hours,^[18] so it provides an excellent starting material for the preparation of TCNQF₄²⁻-based materials.

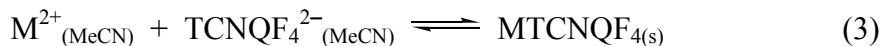
In this study, the electrochemical synthesis and characterization of two transition metal complexes of TCNQF₄²⁻, i.e. CoTCNQF₄ and NiTCNQF₄, are reported. To achieve this outcome, TCNQF₄ dissolved in acetonitrile (0.1 M Bu₄NPF₆) solution was sequentially reduced to TCNQF₄^{•-} and finally to TCNQF₄²⁻. If Co²⁺ or Ni²⁺ is also present in the solution, the solid CoTCNQF₄ or NiTCNQF₄, respectively crystallize onto the surface of the electrodes. Electrochemically directed methods were also used to synthesize these compounds. In this approach, an acetonitrile solution of TCNQF₄²⁻, prepared by exhaustive bulk electrolysis of TCNQF₄ in acetonitrile (0.1 M Bu₄NPF₆), was mixed with an equimolar acetonitrile solution of either Co(ClO₄)₂·6H₂O or Ni(ClO₄)₂·6H₂O under atmospheric conditions to immediately form a precipitate of CoTCNQF₄ or NiTCNQF₄. The Co and Ni complexes were characterized by Ultraviolet-visible (UV-vis), Fourier transform infrared (FT-IR) and Raman spectroscopies, and elemental analysis, whilst the morphology of the electrocrystallized materials on ITO electrode surfaces was imaged using scanning electron microscopy (SEM).

2. Results and Discussion

2.1. Electrocrystallization of MTCNQF₄ in Acetonitrile (0.1 M Bu₄NPF₆)

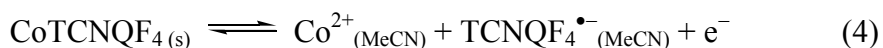
2.1.1. Cyclic Voltammetry of TCNQF₄ in the Presence of Co²⁺ or Ni²⁺

In the absence of M²⁺, TCNQF₄ undergoes two electrochemically reversible one-electron processes (Figure 1a) represented by equations 1 and 2.^[18, 19] Figure 1a also shows that Ni²⁺ and Co²⁺ are electroinactive over the potential range where TCNQF₄ is reduced. Importantly, the presence of 100 mM M²⁺ does not influence the cyclic voltammogram associated with the first TCNQF₄^{0/•-} reduction process derived from 2.0 mM TCNQF₄ in acetonitrile (0.1 M Bu₄NPF₆) (Figure 1b), which implies that TCNQF₄^{•-} does not combine with M²⁺ under the cyclic voltammetric conditions relevant to Figure 1b. This observation is consistent with solubility studies of M(TCNQF₄)₂ in acetonitrile (discussed later), where no precipitate is detected after preparing acetonitrile solutions containing 100 mM M²⁺ and 2.0 mM TCNQF₄^{•-}.



In contrast, the cyclic voltammetric behaviour for the TCNQF₄^{•-/2-} process in the presence of M²⁺ changes significantly when the potential is extended to more negative values, even when the concentration of M²⁺ is much lower than 100 mM (Figures 2a–c). Firstly, cyclic voltammograms for TCNQF₄ in the presence of Co²⁺ are described. In the presence of a 1:2 ratio of Co²⁺:TCNQF₄, three reduction processes are observed (designated as Red1, Red2, Red3 in Figure 2a) as the potential is scanned cathodically. Processes Red1 and Red3 at 280 and –260 mV are assigned to the reduction of TCNQF₄ to TCNQF₄^{•-} and the TCNQF₄^{•-} to TCNQF₄²⁻, respectively. Furthermore, as the Co²⁺:TCNQF₄ ratio increases to > 1.0, process Red3 vanishes and only reduction processes Red1 and Red2 are observed. Additionally, no evidence for the oxidation of TCNQF₄²⁻ to TCNQF₄^{•-} (at –190 mV) is detected (Figure 2b). Thus, Red2 is attributed to the reduction of TCNQF₄^{•-} to TCNQF₄²⁻, accompanied by reaction with Co²⁺ to form CoTCNQF₄ as described by the combination of equations 2 and 3. This assignment is consistent with other studies in where the reduction peak potential has shifted anodically.^[6, 18, 20]

For a 1.0 mM TCNQF₄ and 1.0 mM Co²⁺ acetonitrile (0.1 M Bu₄NPF₆) solution, the reverse positive potential direction scan has two oxidation processes at 350 and 390 mV (Ox1 and Ox2 in Figure 2b). The peak current observed for Ox2 is much greater than those for reduction processes Red1 and Red3, implying that the CoTCNQF₄ has deposited onto the electrode surface during the cathodic scan and is stripped from the electrode in the oxidative scan (equation 4). Process Ox1 is attributed to the oxidation of TCNQF₄^{•-} to TCNQF₄ (i.e. the reverse of equation 1). Interestingly, upon increasing the scan rate, another oxidation process at ~250 mV emerges (designated as Ox3 in Figure 2c), whilst the two processes Ox1 and Ox2 now overlap. Furthermore, as the scan rate is increased, the peak current for the process Ox3 increases relative to those for Ox2 and Ox1. This result implies that there are two phases of CoTCNQF₄ solid formed on the surface of electrode during the reductive scan. One phase is a kinetically favoured form (phase A) which rapidly converts to a thermodynamically stable structure (phase B). Process Ox3 is associated with the oxidation of phase A, while stripping of phase B gives rise to process Ox2. The formation of two phases with (Cu^I)₂TCNQF₄ in acetonitrile also has been observed.^[21] The existence of two phases is also supported by data obtained in Figure 2d. Thus, when the potential was held at -600 mV for 1 s and then scanned in the positive direction at a range of scan rates. Under these conditions, the peak current associated with stripping of phase A increases with scan rate more rapidly than that for phase B.



Importantly, the cyclic voltammograms remain close to constant even with extensive cycling of the potential (Figure 2b), indicating that neutral TCNQF₄ and the Co²⁺_(MeCN) cation are regenerated quantitatively when the potential is returned to its initial value.

Related cyclic voltammetric behaviour is observed when Ni²⁺ is present instead of Co²⁺ (Figure 3). However, in this case, the rate of the conversion between the two NiTCNQF₄ phases is slower than for the CoTCNQF₄ case since two sharp stripping peaks are observed in the anodic scan at 20 mV s⁻¹ compared to only the stripping process for phase B with Co²⁺ case under conditions, where the acetonitrile solution contains 1.0 TCNQF₄ and 1.0 mM Ni²⁺ or 1.0 mM Co²⁺ (compare Figure 3b (green curve) with Figure 2b). The scan rate dependence supports the hypothesis of the slow transition between the two NiTCNQF₄ phases as no stripping process is detected for the thermodynamically stable form of NiTCNQF₄ (phase B) when scan rates ≥ 500 mV s⁻¹ are employed (Figure 3b).

The response of the two phases of the MTCNQF₄ has been explored as a function of switching potential at a scan rate of 20 mV s⁻¹ (Figure 4). In the Co²⁺ case (Figure 4a), when the potential is switched at 55 mV (the foot of the onset of Red2 – green curve), no anodic stripping process Ox2 associated with the oxidation of phase B is detected. However, as the potential is switched at the slightly more negative value of 0.0 mV, both stripping processes Ox3 and Ox2 are detected. In contrast, when the potential is switched at a much more negative value (≤ -300 mV), only stripping of CoTCNQF₄ phase B is observed. Conversely, in the presence of Ni²⁺, as the potential is switched at -75 mV, only the stripping process due to phase A is observed, whilst the stripping of both phases A and B are detected when the switching potential is ≤ -300 mV (Figure 4b). Importantly, the cyclic voltammetric behaviour is identical when starting with a solution containing 1.0 mM TCNQF₄^{•-} instead of TCNQF₄ and 1.0 mM M²⁺ under the same potential scanning conditions (compare Figures 4b and c for Ni²⁺).

The voltammograms obtained for the electrocrystallization of CoTCNQF₄ in this study by reduction of TCNQF₄ in the presence of Co²⁺ have similar characteristics to those reported for the analogous TCNQ case.^[10] However, in the TCNQ based study, product formed in the second reduction process was identified as Co(TCNQ)₂(H₂O)₂. That is, a second pathway was proposed for formation of the TCNQ^{•-} derivative. On the basis of the present studies with air and moisture stable TCNQF₄²⁻ derivatives, it was concluded likely that CoTCNQ could have been formed on the electrode surface. The electrocrystallization studies reported in reference [10] were therefore repeated under dry box conditions, where the formation of the TCNQ²⁻ derivative was confirmed as the product of the second reduction process. However, on removal of the ITO electrode containing adhered TCNQ²⁻ solid from the dry box environment, rapid transformation to blue Co(TCNQ)₂(H₂O)₂ occurred. Ex situ methods of characterization (Raman, IR) revealed that the final product formed is indeed the TCNQ^{•-} derivative as reported in the electrochemical studies undertaken under ambient conditions.

2.1.2. Influence of M²⁺ and TCNQF₄ Concentrations

An increase in either the concentration of M²⁺ or TCNQF₄ does not change the peak potential or wave shape for the first reduction TCNQF₄^{0/•-} process at 280 mV (Red1). However, as expected an increase in current magnitude occurs when additional TCNQF₄ is present. In contrast, the peak potential for the second process (Red2) associated with the

formation of MTCNQF₄ shifts anodically (Figure 5). When the TCNQF₄ concentration is held at 1.0 mM, the potential for Red2 peak shifts anodically by 48 mV as the concentration of Co²⁺ is increased from 0.25 to 2.0 mM (Figure 5a). On the other hand, maintaining the Co²⁺ concentration at 5.0 mM and increasing the TCNQF₄ concentration from 0.5 to 5.0 mM shifts the Red2 peak potential anodically by 86 mV (Figure 5b). The potential shift in Red2 to more positive values upon increasing the concentration of Co²⁺ and/or TCNQF₄ imply that insoluble CoTCNQF₄ formation follows the reduction of TCNQF₄ to TCNQF₄²⁻ via TCNQF₄^{•-}.^[18, 20] An analogous situation prevails for the Ni²⁺ case.

2.2. *In situ* Surface Plasmon Resonance

In situ cyclic voltammetry combined with surface plasmon resonance (SPR) experiments at a gold coated-film glass electrode were used to monitor the mass change on the surface of the electrode.^[6, 22, 23] Figure 6 provides the *in situ* cyclic voltammetric-SPR data for acetonitrile (0.1 M Bu₄NPF₆) solutions containing 1.0 mM TCNQF₄ in the presence of 1.0 mM Co²⁺ (Figure 6a) or 1.0 mM Ni²⁺ (Figure 6b). Early in the negative potential scan direction mode, the SPR response increases in magnitude by a small amount. This increase is attributed to the change of the solution composition near to the electrode surface rather than to a mass change.^[6, 22, 23] However, the SPR signal decreases dramatically as the potential is scanned to values where MTCNQF₄ has been postulated to be electrocrystallized. On reversing the scan direction, the SPR signal ultimately returns to the initial value when the potential is sufficiently positive. In addition, if the switching potential is extended cathodically by 50 mV or more beyond those presented in Figures 6a and b, the SPR response exceeds the detection limit of the instrumentation. However, even under these conditions, the SPR signal returns to the initial value after the potential scanning direction is reversed and the original potential is reached (data not shown). All these data support the hypothesis that M²⁺ does not form a precipitate with TCNQF₄^{•-}, but only combines with TCNQF₄²⁻ to form MTCNQF₄ solid which deposits onto the electrode surface after TCNQF₄^{•-} is reduced to TCNQF₄²⁻. The solid is then stripped from the electrode as the potential is swept anodically.

2.3. Solubility of M(TCNQF₄)₂ and MTCNQF₄ in Acetonitrile

Exhaustive reductive electrolysis was used to prepare a 2.0 mM TCNQF₄^{•-} solution from 2.0 mM TCNQF₄ in acetonitrile (0.1 M Bu₄NPF₆). The prepared solution (2.0 mL) was

mixed with $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (100 mM) in acetonitrile (2.0 mL). A similar reaction was carried out with LiTCNQF_4 (2.0 mM) and $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (100 mM) or $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (100 mM) in acetonitrile (2.0 mL). In both cases, no precipitate was detected. These results confirm that $\text{Co}^{\text{II}}\text{-TCNQF}_4^{\bullet-}$ and $\text{Ni}^{\text{II}}\text{-TCNQF}_4^{\bullet-}$ derivatives are soluble in acetonitrile.

In contrast, when TCNQF_4^{2-} (2.0 mM) in acetonitrile (2.0 mL), which was prepared by exhaustive bulk electrolysis of $\text{TCNQF}_4^{\bullet-}$ (2.0 mM) in acetonitrile (0.1 M Bu_4NPF_6), was mixed with Co^{2+} (10.0 mM) in acetonitrile (0.4 mL), a dark coloured precipitate formed immediately. This precipitate was collected via centrifugation and washed with acetonitrile (4×1.5 mL) to remove the supporting electrolyte. Nitrogen purged acetonitrile (2.0 mL) or acetonitrile (2.0 mL) containing Bu_4NPF_6 (0.1 M) was then added into the test tube containing CoTCNQF_4 solid. Further purging with N_2 gas for 10 min was undertaken to achieve CoTCNQF_4 saturated acetonitrile solutions in the presence and absence of 0.1 M Bu_4NPF_6 . N_2 gas was used to enhance the rate of equilibration and also to eliminate oxygen in order to avoid slow TCNQF_4^{2-} oxidation that occurs in the presence of air. The solution, saturated with dissolved solid was separated from the residual solid by centrifugation, followed by filtration. The concentration of TCNQF_4^{2-} present in the CoTCNQF_4 saturated acetonitrile solutions was determined by UV-vis spectroscopy and reference to a calibration curve based on the absorption for TCNQF_4^{2-} at 333 nm. The concentration of TCNQF_4^{2-} determined in this manner was $8.59 \pm 0.68 \times 10^{-6}$ and $2.20 \pm 0.20 \times 10^{-5}$ M in neat or 0.1 M Bu_4NPF_6 containing acetonitrile, respectively. The solid component obtained by filtration was washed with neat acetonitrile and placed onto an ITO electrode surface, dried under vacuum for 5 h (a dark solid was obtained) and then characterized by FT-IR and Raman spectroscopic techniques (see Section 2.6).

The solubility of NiTCNQF_4 in acetonitrile was determined in a similar manner to CoTCNQF_4 , and found to be $9.16 \pm 0.86 \times 10^{-6}$ and $2.41 \pm 0.18 \times 10^{-5}$ M in neat or 0.1 M Bu_4NPF_6 containing acetonitrile, respectively. In this case, a dark brown precipitate was formed immediately after mixing acetonitrile solutions of TCNQF_4^{2-} and Ni^{2+} , and after being dried, the solid appeared to be black. The solubility of NiTCNQF_4 in acetonitrile in the presence or absence of 0.1 M Bu_4NPF_6 is therefore similar to that of CoTCNQF_4 . Furthermore, in both cases, the solubility of MTCNQF_4 is higher in the presence of 0.1 M Bu_4NPF_6 supporting electrolyte than in the neat solvent. An increase in solubility in the

presence of 0.1 M Bu₄NPF₆ supporting electrolyte also was found for AgTCNQ,^[23] CuTCNQ,^[24] AgTCNQF₄,^[6] CuTCNQF₄ and Cu₂TCNQF₄.^[21] This increased solubility is attributed to the ion pairing of the metal cations and TCNQF₄ anions with PF₆⁻ and Bu₄N⁺ provided by the supporting electrolyte.^[6, 24] The solubility products calculated from the solubility data are $7.42 \pm 1.16 \times 10^{-11}$ and $4.85 \pm 0.85 \times 10^{-10} \text{ M}^2$ (for CoTCNQF₄), and $8.43 \pm 1.56 \times 10^{-11}$ and $5.81 \pm 0.84 \times 10^{-10} \text{ M}^2$ (for NiTCNQF₄), respectively in neat acetonitrile and acetonitrile containing 0.1 M Bu₄NPF₆.

2.4. Elemental Analysis

MTCNQF₄ samples used for elemental analysis were prepared by mixing acetonitrile solutions containing M²⁺ (10.0 mM in 5.0 mL) and TCNQF₄²⁻ (10.0 mM in 5.0 mL) (prepared in the same manner described in Section 2.3), followed by washing the collected precipitate with acetonitrile (5 × 2 mL) and then drying overnight under vacuum. The microanalytical data are consistent with the formulae CoTCNQF₄ and NiTCNQF₄. The experimental data (calculated based on the formulae) are C% = 43.02 (43.01); N% = 16.59 (16.72) and C% = 43.19 (43.04); N% = 16.45 (16.73), respectively.

2.5. Electrocrystallization of Bulk MTCNQF₄

Bulk MTCNQF₄ samples also were prepared by electrocrystallization onto ITO electrode surfaces by controlled potential reductive electrolysis of TCNQF₄ (1.0 mM) in acetonitrile (0.1 M Bu₄NPF₆) in the presence of M²⁺ (1.0 mM). To achieve this outcome, the potential was held for 10 min at either the peak potential for the second reduction process Red2 (cyclic voltammetric behaviour obtained with an ITO electrode is similar to that shown in Figure 2a with a GC electrode) or at 260 mV more negative than this value. Thus, in the case of CoTCNQF₄, the potential was held at either -40 mV or -300 mV, whilst for NiTCNQF₄, the potential values were either -140 or -400 mV. The four MTCNQF₄ samples electrocrystallized onto the ITO electrode surfaces in the above mentioned manner were rinsed with acetonitrile (3 × 3 mL), dried under a stream of N₂ gas for 10 min, further dried under vacuum for 5 h and then characterized by FT-IR, Raman spectroscopies and SEM imaging (see Section 2.6). However, characterization by UV-vis spectroscopy was undertaken immediately following electrocrystallization by dissolving the solids in acetonitrile with the assistance of a N₂ gas purge for 10 min.

2.6. Spectroscopic and Microscopic Studies on Electrocrystallized MTCNQF₄

EDXS was used to confirm the presence of the elements C, N, F and Co or Ni in the electrochemically synthesized MTCNQF₄. However, in order to confirm the redox level of TCNQF₄ and more fully characterize the MTCNQF₄ solids, probing by UV-vis, FT-IR and Raman spectroscopies was utilized.^[5, 6] SEM imaging was also used to obtain morphological details of the electrocrystallized MTCNQF₄.

UV-vis spectra for all the prepared MTCNQF₄ solids dissolved in acetonitrile have a characteristic absorption band with λ_{max} at 333 nm, indicating the presence of TCNQF₄²⁻ dianion.^[6, 18, 25]

FT-IR spectra for the CoTCNQF₄ and NiTCNQF₄, synthesized as described in Section 2.3, are provided in Figures 7a and b, respectively. The major IR bands are very similar for both compounds. The most diagnostically useful bands are located at ~ 2136 and ~ 2162 cm⁻¹, and characteristic of the C $\equiv$ N stretch in the TCNQF₄²⁻ dianion.^[3, 6, 25, 26] Further evidence for the presence of TCNQF₄²⁻ is available via detection of the two bands at ~ 1485 and ~ 1495 cm⁻¹, that are consistent with those reported previously for Ag₂TCNQF₄ (1477 and 1495 cm⁻¹)^[27] and Cu₂TCNQF₄ (1475 and 1489 cm⁻¹)^[21]. The IR spectra for the MTCNQF₄ solids (~ 3400 cm⁻¹) indicate the presence of very small amount of H₂O.^[28-30] Importantly, the FT-IR spectra for all the CoTCNQF₄ compounds, prepared by electrochemically directed method or electrocrystallization, are identical within experimental error, as also applies for the prepared NiTCNQF₄ solids.

Three characteristic and diagnostic Raman vibration modes, associated with C $\equiv$ N, C=C ring and C-CN wing stretches^[4, 6] are located at (2118, 2082), 1653 and 1440 cm⁻¹, respectively for the CoTCNQF₄ prepared by electrochemically directed synthesis. The Raman mode for the C $\equiv$ N stretch is split into 2 bands and shifted to lower energy compared to TCNQF₄ (2226 cm⁻¹) and TCNQF₄^{•-} (~ 2220 cm⁻¹).^[4, 6] A similar splitting and shift in this Raman band is also found for (Cu^I)₂TCNQF₄ and (Pr₄N)₂TCNQF₄ solids.^[21] In these materials, the C $\equiv$ N stretch is located at (2170, 2141) and (2175, 2135) cm⁻¹, respectively. Furthermore, the Raman band for the C=C ring stretch in CoTCNQF₄ is consistent with that reported for (Cu^I)₂TCNQF₄ (1655 cm⁻¹), (Pr₄N)₂TCNQF₄ (1648 cm⁻¹) and Li₂TCNQF₄ (1658 cm⁻¹).^[21] As for IR spectroscopic data, Raman spectra for the CoTCNQF₄ compounds, whether electrocrystallized at different potentials or prepared by electrochemically directed synthesis, are identical within experimental error. The same

situation applies to Raman spectra for all NiTCNQF₄ compounds, synthesized by different mentioned methods, where the Raman bands for the C≡N, C=C ring and C–CN wing stretches are found at $\sim(2111, 2082)$, ~ 1650 and $\sim 1440\text{ cm}^{-1}$, respectively.

The morphologies of MTCNQF₄ electrocrystallized onto ITO electrode surfaces were characterized by the SEM images shown in Figure 8. CoTCNQF₄ electrocrystallized at -40 mV as a thin film with fractures across the surface (Figures 8a and b), whereas CoTCNQF₄ formed at -300 mV exhibited needle crystals (Figures 8c and d). Although these electrochemically synthesized CoTCNQF₄ solids are spectroscopically identical, their morphologies differ significantly. In contrast, the morphology of the NiTCNQF₄ materials electrocrystallized at -140 mV and -400 mV are similar and provide non-uniform morphologies (Figures 8e and f).

3. Conclusions

Sparingly soluble MTCNQF₄ (M = Co or Ni) solids have been electrocrystallized after reduction of TCNQF₄ to TCNQF₄²⁻ in the presence of M²⁺ in acetonitrile (0.1 M Bu₄NPF₆). The electrocrystallization of MTCNQF₄ onto an electrode can be monitored voltammetrically and by *in situ* SPR experiments. Cyclic voltammetry demonstrates that TCNQF₄ is reduced to TCNQF₄²⁻ dianion via the TCNQF₄^{•-} monoanion, prior to interaction with M²⁺ to initially produce a kinetically favoured phase of MTCNQF₄ on the electrode surface. This phase (A) is rapidly converted to phase (B), which is the thermodynamically stable form. The MTCNQF₄ complexes also have been synthesized by an electrochemically directed method using 2.0 mM electrochemically generated TCNQF₄²⁻ and 10.0 mM M²⁺ acetonitrile solutions. In contrast, no precipitate is observed upon mixing 2.0 mM TCNQF₄^{•-} with 100 mM Co²⁺ or Ni²⁺ acetonitrile solutions. The solubility of MTCNQF₄ in acetonitrile in the presence and absence of 0.1 M Bu₄NPF₆ was determined to be $2.20 \pm 0.20 \times 10^{-5}\text{ M}$ and $8.59 \pm 0.68 \times 10^{-6}$ (for CoTCNQF₄); and $2.41 \pm 0.18 \times 10^{-5}\text{ M}$ and $9.16 \pm 0.86 \times 10^{-6}$ (for NiTCNQF₄), respectively. Thus, the solubility of both Co and Ni-TCNQF₄ compounds is almost the same. Use of physicochemical characterization techniques (UV-vis, Raman and IR spectroscopies) confirms the presence of the TCNQF₄²⁻ dianion in all the MTCNQF₄ materials, which were synthesized by different methods. SEM images show variation morphology for CoTCNQF₄ electrocrystallized at -40 mV and at -300 mV . In contrast, SEM images of the electrocrystallized NiTCNQF₄ indicate that its morphology is not sensitive to the applied

potentials. Unfortunately, no crystals suitable for X-ray diffraction structural determination could be obtained, but the materials are about certainly coordination polymers.

4. Experimental Section

4.1. Chemicals

Co(ClO₄)₂·6H₂O (Aldrich), Ni(ClO₄)₂·6H₂O (≥ 98.0%, Aldrich), AgNO₃ (99.998%, Aldrich), TCNQF₄ (97%, Aldrich), ferrocene (98%, EGA-Chemie), acetonitrile (HPLC grade, Omnisolv), acetone (Suprasolv, Merck KGaA) and isopropanol (BDH) were used as received from the manufacturer. Bu₄NPF₆ (Wako) was recrystallized twice from 96% ethanol (Merck) and then dried at 100°C under vacuum for 24 h, and stored until required. LiTCNQF₄ was prepared from LiI (99%, Aldrich) and TCNQF₄ as detailed elsewhere.^[28]

4.2. Electrochemistry

Voltammograms were recorded at room temperature (22 ± 2°C) with a Bioanalytical Systems (BAS) 100W electrochemical workstation using a standard three-electrode cell configuration. Working electrodes were 3.0 mm diameter glassy carbon (GC) disk (BAS), or Prazisions Glas und Optik GmbH indium tin oxide (ITO)-coated glass plates (0.1 – 0.2 cm²) with a resistance of 10 Ω/sq. The working electrodes were cleaned prior to being used as described elsewhere.^[6] A silver wire in contact with acetonitrile containing 1.0 mM AgNO₃ and 0.1 M Bu₄NPF₆ was used as an Ag/Ag⁺ reference electrode. The reversible potential of this electrode is -0.135 ± 5 mV versus the ferrocene/ferrocenium couple (Fc^{0/+}). The counter electrode was a Pt wire (1.0 mm diameter). In bulk electrolysis experiments, each of the working (Pt mesh), reference (Ag/Ag⁺) and counter (Pt mesh) electrodes were placed in an H-type three-compartment cell. The solution of interest was agitated during the course of the bulk electrolysis using a magnetic stirrer. In order to prepare TCNQF₄^{•-} from TCNQF₄ in acetonitrile (0.1 M Bu₄NPF₆), the potential at the working electrode was held at 100 mV, while TCNQF₄²⁻ was generated by further reduction of TCNQF₄^{•-} at -400 mV. The bulk electrolysis experiments were stopped when the current decreased to 0.1% of the initial value. All solutions for electrochemical experiments were purged with nitrogen gas for 10 min prior to commencing the experiments. During the course of the experiments, a stream of nitrogen was maintained above the solution.

Surface plasmon resonance (SPR) experiments were undertaken with an AutoLab ESPRIT system interfaced to an AutoLab PGSTAT100 potentiostat. A glass disk coated

with a 50 nm thick gold film used as both the SPR substrate and the working electrode (ECO-Chemie). During the course of the SPR experiments, the response was monitored via the angle of the minimum reflection in the Kreschmann configuration.^[6, 22] In these SPR experiments, platinum wires were used as both the quasi-reference and the counter electrodes.

4.3. Other Instrumentation

Instrumentation for UV-vis, FT-IR and Raman spectroscopies, SEM imaging and Energy Dispersive X-Ray Spectroscopy (EDXS) analysis are as described elsewhere.^[6, 28]

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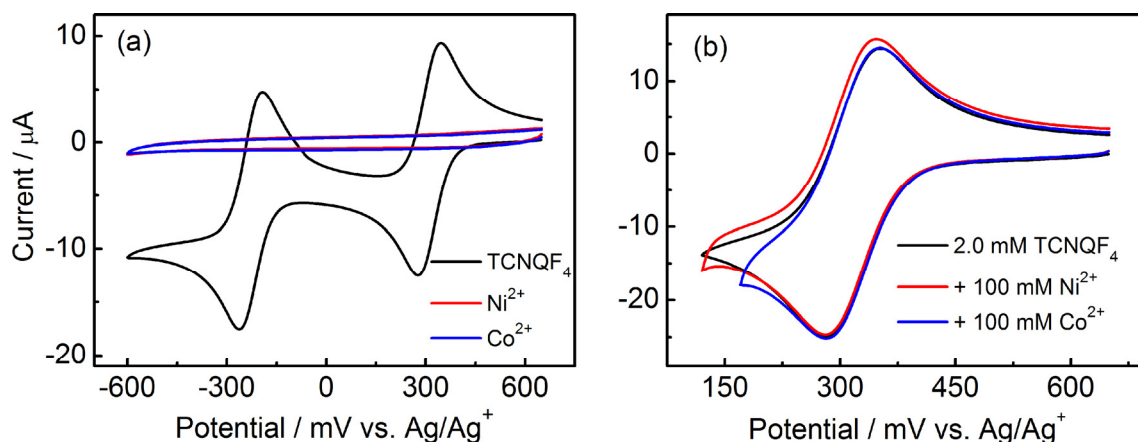


Figure 1. Cyclic voltammograms in acetonitrile (0.1 M Bu₄NPF₆) obtained with a GC electrode at a scan rate of 20 mV s⁻¹ for (a) 1.0 mM TCNQF₄, Ni²⁺ and Co²⁺, (b) 2.0 mM TCNQF₄ with and without the presence of 100 mM Ni²⁺ or Co²⁺.

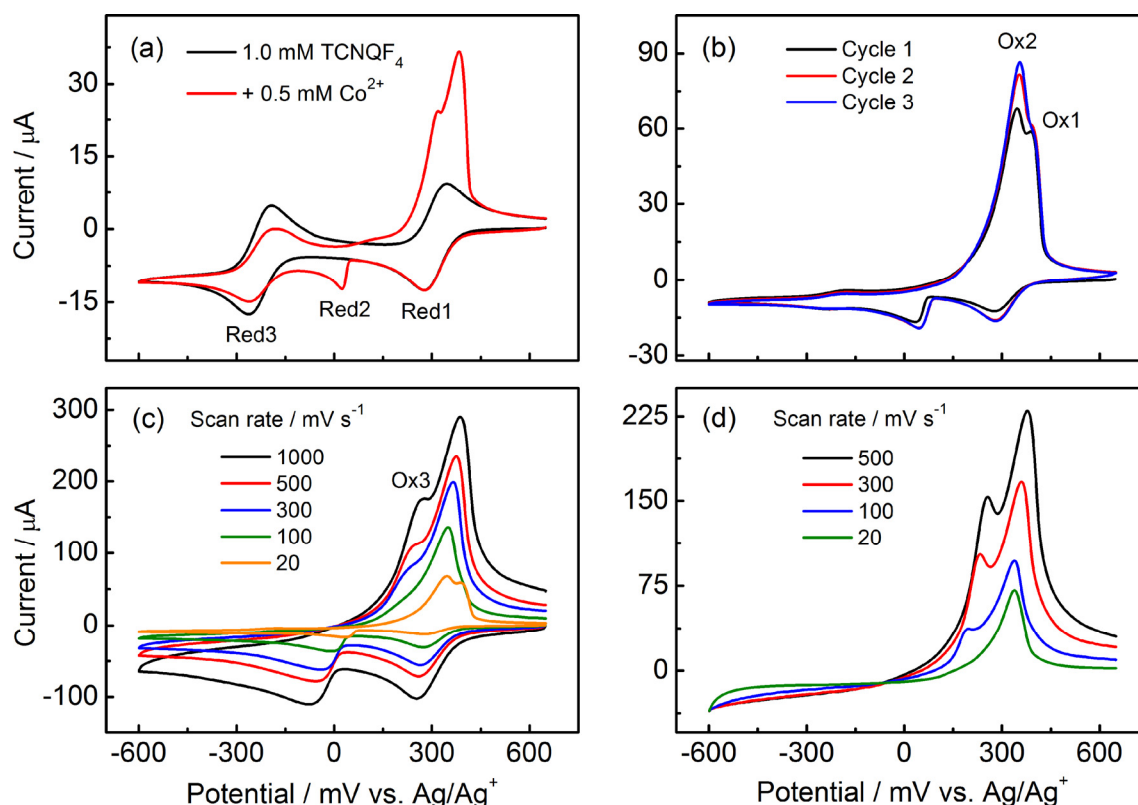


Figure 2. Cyclic voltammograms in acetonitrile (0.1 M Bu₄NPF₆) obtained with a GC electrode at a scan rate of 20 mV s⁻¹ for (a) 1.0 mM TCNQF₄ (—), and 1.0 mM TCNQF₄ in the presence of 0.5 mM Co²⁺ (—), (b) 1.0 mM TCNQF₄ in the presence of 1.0 mM Co²⁺. (c) same conditions as for (b) but at designated scan rates. (d) same conditions as for (a) but with the potential held at -600 mV for 1s before commencement of the anodic scan at designated scan rates.

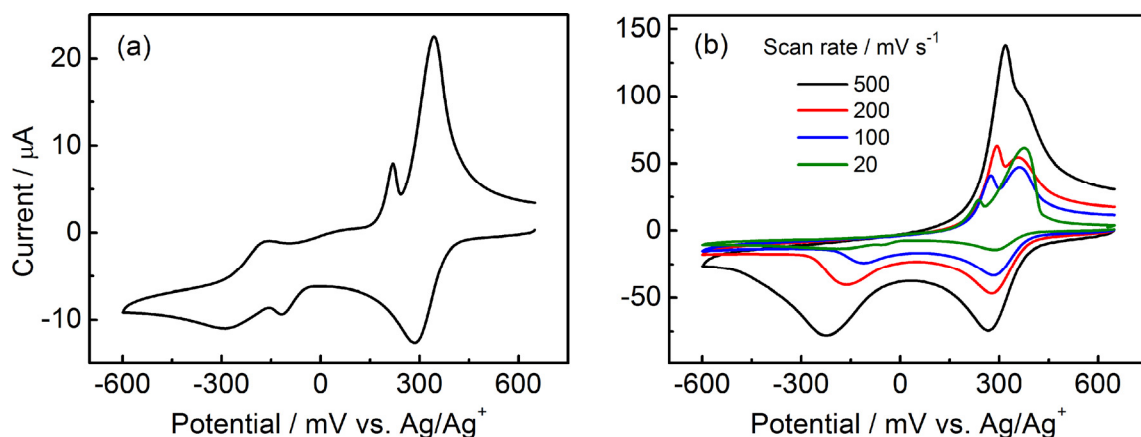


Figure 3. Cyclic voltammograms obtained with a GC electrode in acetonitrile (0.1 M Bu₄NPF₆) containing 1.0 mM TCNQF₄ in the presence of (a) 0.5 mM Ni²⁺ at a scan rate of 20 mV s⁻¹, (b) 1.0 mM Ni²⁺ at designated scan rates.

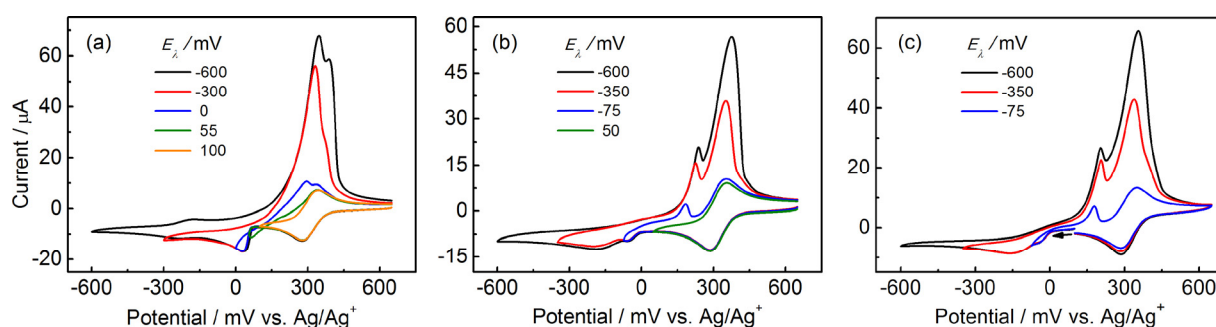


Figure 4. Cyclic voltammograms in acetonitrile (0.1 M Bu₄NPF₆) obtained with a GC electrode at a scan rate of 20 mV s⁻¹ with designated switching potentials (E_{λ}) for (a) 1.0 mM TCNQF₄ in the presence of 1.0 mM Co²⁺, (b) 1.0 mM TCNQF₄ in the presence of 1.0 mM Ni²⁺, (c) 1.0 mM TCNQF₄^{•-} in the presence of 1.0 mM Ni²⁺.

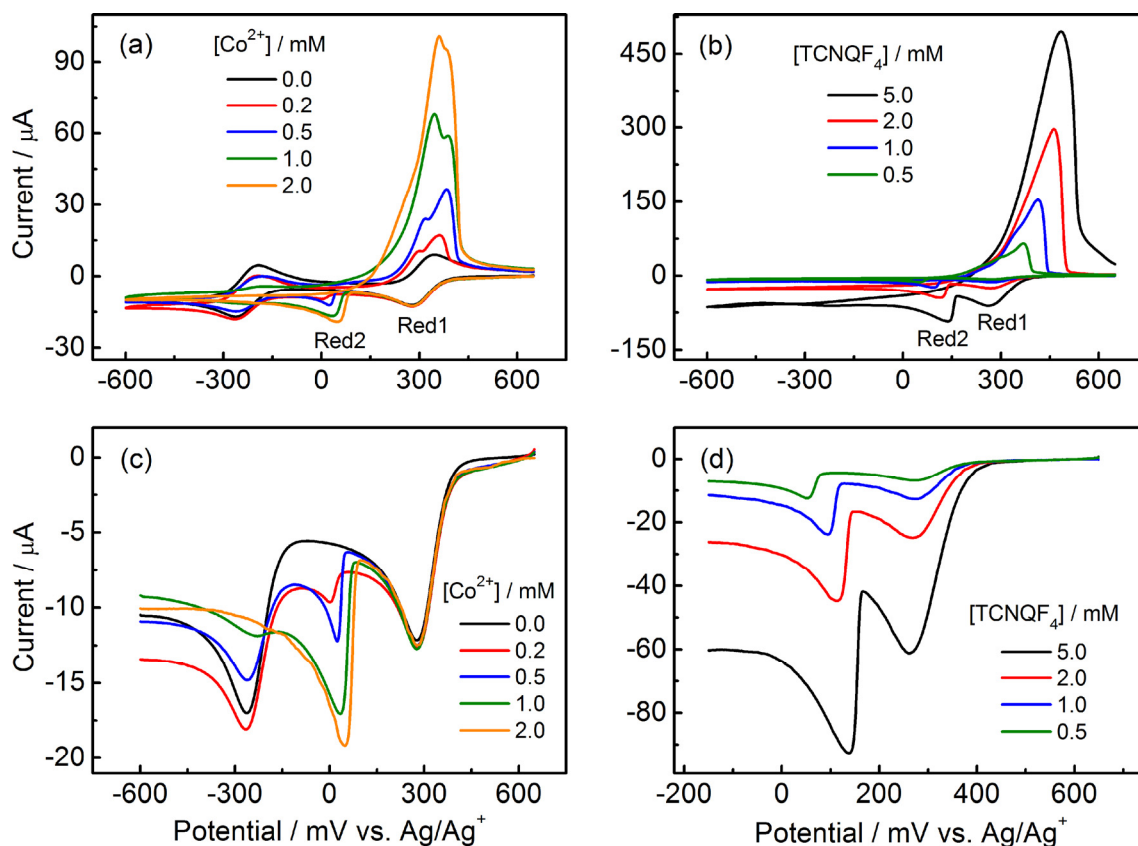


Figure 5. Cyclic voltammograms obtained at a scan rate of 20 mV s^{-1} with a GC electrode in acetonitrile ($0.1 \text{ M Bu}_4\text{NPF}_6$) solutions containing (a) 1.0 mM TCNQF_4 with designated concentrations of Co^{2+} , (b) 5.0 mM Co^{2+} with designated TCNQF_4 concentrations. (c) and (d) as for (a) and (b) with only the reduction processes presented for clarity.

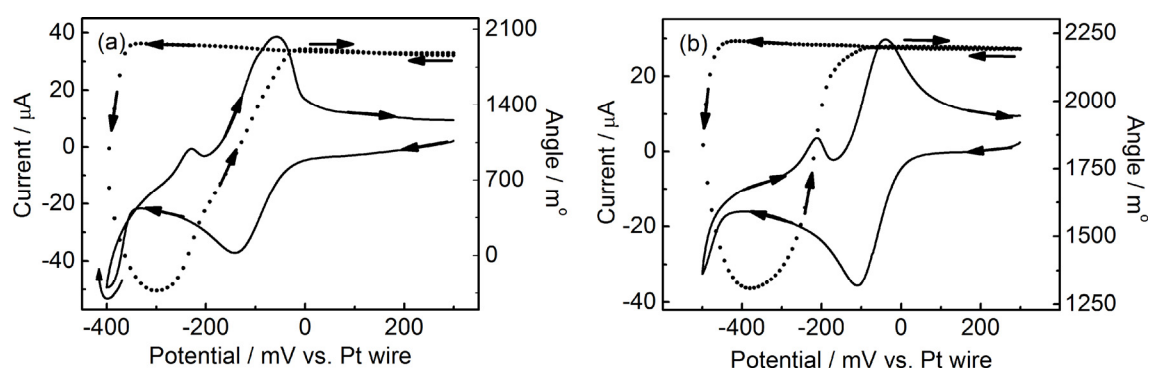


Figure 6. *in situ* cyclic voltammetric (—) and SPR (.....) responses obtained in acetonitrile ($0.1 \text{ M Bu}_4\text{NPF}_6$) solutions with a gold-coated glass electrode (scan rate = 100 mV s^{-1}) for 1.0 mM TCNQF_4 in the presence of (a) 1.0 mM Co^{2+} and (b) 1.0 mM Ni^{2+} .

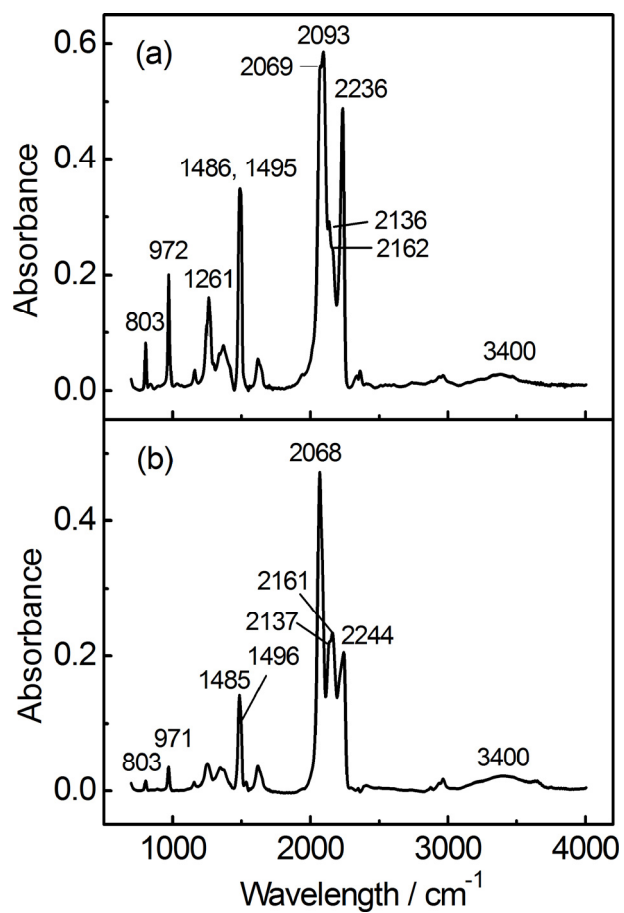


Figure 7. FT-IR spectra for (a) CoTCNQF₄ and (b) NiTCNQF₄, prepared by electrochemically directed synthesis.

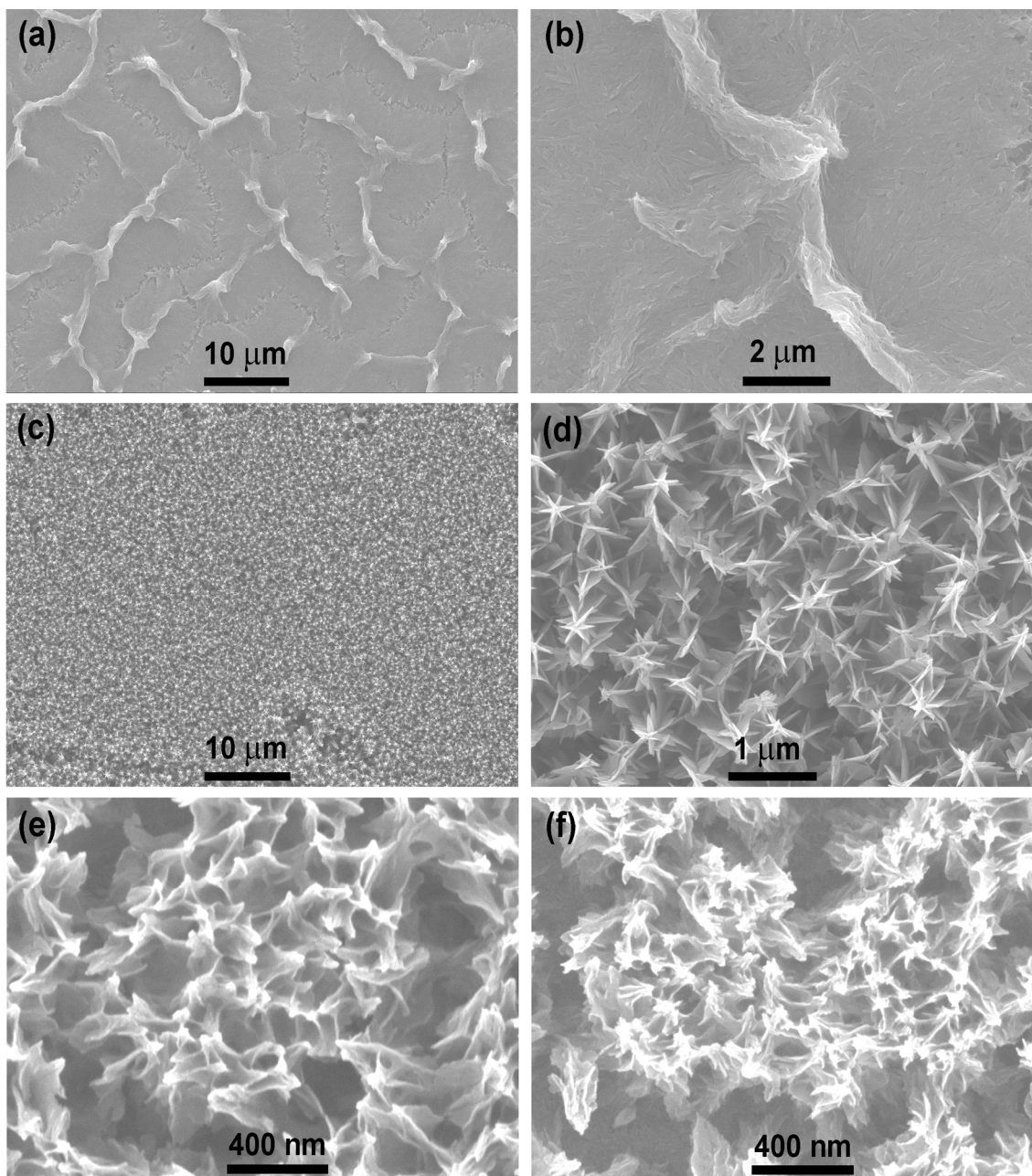


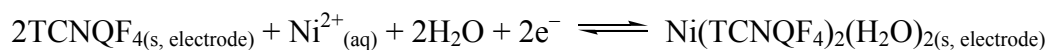
Figure 8. SEM images for MTCNQF₄ solids electrocrystallized onto ITO electrode surfaces when 1.0 mM TCNQF₄ in acetonitrile (0.1 M Bu₄NPF₆) was reduced at a controlled potential (E) in the presence of 1.0 mM M²⁺: (a, b) CoTCNQF₄ ($E = -40$ mV), (c, d) CoTCNQF₄ ($E = -300$ mV) at different magnifications, (e) NiTCNQF₄ ($E = -140$ mV) and (f) NiTCNQF₄ ($E = -400$ mV).

Chapter 5

Electrocrystallization of Ni(TCNQF₄)₂(H₂O)₂ in Aqueous Media

5.1. Introduction

The electrochemical conversion of solid TCNQF₄ into solid Ni(TCNQF₄)₂(H₂O)₂ using a TCNQF₄ chemically modified electrode in contact with aqueous electrolyte is reported. In particular, crystalline TCNQF₄ was immobilized onto a glassy carbon or indium tin oxide electrode surface and then electrochemically reduced to TCNQF₄^{•-} monoanion in an aqueous solution containing Ni²⁺_(aq) electrolyte to form Ni(TCNQF₄)₂(H₂O)₂ on the electrode surface. The empirical formula of Ni(TCNQF₄)₂(H₂O)₂ has been established using thermogravimetric and elemental analyses. The overall reaction is the following:



Cyclic voltammetry and chronoamperometry were used to understand the mechanism of the solid-solid phase transformation. The results indicate that the transformation is governed by nucleation and growth kinetics, and is independent of Ni²⁺_(aq) counter anion and working electrode material, but dependent on the concentration of Ni²⁺_(aq) electrolyte and scan rate.

Microscopic and spectroscopic techniques, such as UV-vis, FT-IR, Raman, EDXS and SEM, as well as magnetic and conductivity measurements have been utilized to characterize the electrocrystallized Ni(TCNQF₄)₂(H₂O)₂ complex. The data show that the material is paramagnetic and semiconducting, and electrocrystallizes onto the electrode surface in thin film morphology.

Declaration for Thesis Chapter 5.2

Declaration by candidate

In the case of Chapter 5.2, the nature and extent of my contribution to the work was the following:

Nature of contribution	Extent of contribution (%)
Initiation, key ideas, experimental work, writing up	80

The following co-authors contributed to the work.

Name	Nature of contribution
Ayman Nafady	Initiation, key ideas, experimental work, writing up
Jinzheng Lu	Experimental work, writing up
Germanas Peleckis	Experimental work, writing up
Alan M. Bond	Initiation, key ideas, writing up
Lisandra L. Martin	Initiation, key ideas, writing up

Candidate's Signature

	06/06/2012
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Declaration by co-authors

The undersigned hereby certify that:

- (1) the above declaration correctly reflects the nature and extent of the candidate's contribution to this work, and the nature of the contribution of each of the co-authors.
- (2) they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;
- (3) they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
- (4) there are no other authors of the publication according to these criteria;
- (5) potential conflicts of interest have been disclosed to (a) granting bodies, (b) the editor or publisher of journals or other publications, and (c) the head of the responsible academic unit; and
- (6) the original data are stored at the following location and will be held for at least five years from the date indicated below:

Location

School of Chemistry, Monash University, Clayton

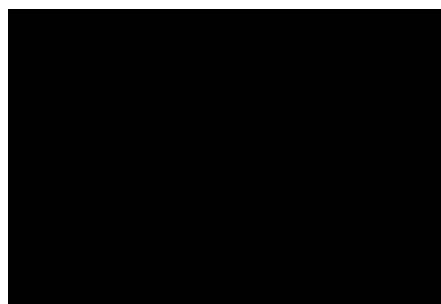
Ayman Nafady

Jinzheng Lu

Germanas Peleckis

Alan M. Bond

Lisandra L. Martin

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	18/5/12

Electrochemical Synthesis and Characterization of Semiconducting $\text{Ni}(\text{TCNQF}_4)_2(\text{H}_2\text{O})_2$ (TCNQF_4 = 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane)

Thanh Hai Le,^[a] Ayman Nafady,^[a] Jinzhen Lu,^[a] Germanas Peleckis,^[b] Alan M. Bond,^{*,[a]} and Lisandra L. Martin^{*,[a]}

Keywords: Nickel / Solid-phase synthesis / Electrochemistry / Semiconducting properties / Magnetism

An electrochemical technique has been used to synthesize $\text{Ni}(\text{TCNQF}_4)_2(\text{H}_2\text{O})_2$ (TCNQF_4 = 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane). The method involves the reduction of solid TCNQF_4 immobilized on an electrode surface in contact with $\text{Ni}^{2+}(\text{aq.})$ -containing electrolyte. The electrochemically irreversible, but chemically reversible solid–solid $\text{TCNQF}_4/\text{Ni}(\text{TCNQF}_4)_2(\text{H}_2\text{O})_2$ interconversion process is governed by nucleation and growth kinetics and is represented by the overall reaction: $2\text{TCNQF}_4(\text{s, electrode}) + \text{Ni}^{2+}(\text{aq.}) + 2\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{Ni}(\text{TCNQF}_4)_2(\text{H}_2\text{O})_2(\text{s, electrode})$. Thus, the formation of $\text{Ni}(\text{TCNQF}_4)_2(\text{H}_2\text{O})_2$ involves the one-electron reduction of TCNQF_4 to $[\text{TCNQF}_4]^-$ coupled with an ingress of $\text{Ni}^{2+}(\text{aq.})$ from the aqueous electrolyte, while the reverse scan represents the oxidation of $[\text{TCNQF}_4]^-$ to TCNQF_4 coupled with the egress of $\text{Ni}^{2+}(\text{aq.})$. Cyclic voltam-

mograms for the $\text{TCNQF}_4/\text{Ni}(\text{TCNQF}_4)_2(\text{H}_2\text{O})_2$ solid–solid phase transformation are independent of the electrode material and the identity of the $\text{Ni}^{2+}(\text{aq.})$ counteranion but are strongly dependent on the concentration of $\text{Ni}^{2+}(\text{aq.})$ and the scan rate. UV/Vis, infrared, and Raman spectra confirm the presence of $[\text{TCNQF}_4]^-$ in the newly synthesized material. The composition of $\text{Ni}(\text{TCNQF}_4)_2(\text{H}_2\text{O})_2$ was deduced from thermogravimetric and elemental analyses. Scanning electron microscopic images of $\text{Ni}(\text{TCNQF}_4)_2(\text{H}_2\text{O})_2$ electrocrystallized onto the surface of an indium tin oxide electrode show a thin film morphology. Magnetic and conductivity data demonstrate that the complex behaves as a classical paramagnet and is a typical semiconductor with a band gap close to that of an insulator.

1. Introduction

The organic molecule 7,7,8,8-tetracyanoquinodimethane (TCNQ) is a strong electron acceptor.^[1] When the four hydrogen atoms are substituted by fluorine to form 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (TCNQF_4), even stronger electron affinity is achieved.^[2–6] This is evidenced by the fact that a positive shift in the reversible formal potentials for the $[\text{TCNQF}_4]^{0/-}$ and $[\text{TCNQF}_4]^{-/2-}$ couples of 0.36 and 0.37 V, respectively, is observed in acetonitrile (0.1 M Bu_4NClO_4) relative to those for the corresponding TCNQ processes.^[6]

In view of the close to ideal electrochemistry, particularly for the $[\text{TCNQ}]^{0/-}$ couple, chemically modified TCNQ-based electrodes have been widely utilized for voltammetric sensing and related applications.^[7–14] Importantly, M–TCNQ compounds (M = group I cations, transition metals, and lanthanides) have been extensively studied by numerous electrochemical and spectroscopic techniques since the ini-

tial synthesis of this class of material by Melby et al. in 1960.^[15–25] This research has led to the emergence of a wide range of TCNQ-based metal–organic charge-transfer salts, network polymers, and organometallic compounds that exhibit interesting conducting and/or magnetic properties.^[26–30] Consequently, TCNQ-based materials have been employed in optical and electrical recording,^[31–35] data storage,^[36,37] organic field-effect transistors,^[38,39] catalysis,^[40–42] as well as in electrochromic, magnetic, and sensor devices.^[43,44]

Recently, a series of studies have focused on the structure, magnetic properties,^[45–47] synthesis, and optically induced transformation^[48] of TCNQF_4 -based materials. These investigations suggest that important new advances may emerge from using the tetrafluorinated derivative. Metal complexes with TCNQF_4 that have been chemically synthesized and characterized include Ag–TCNQF_4 , Cu–TCNQF_4 ,^[5,45,48–51] Mn–TCNQF_4 ,^[52] and lanthanide– TCNQF_4 .^[53] However, Ni– TCNQF_4 -based materials have not been reported, although in the case of Ni with TCNQ, several examples are known which include the binary hydrated $\text{Ni}(\text{TCNQ})_2(\text{H}_2\text{O})_2$,^[54] nonhydrated $\text{Ni}(\text{TCNQ})_2$,^[55] and other Ni–TCNQ derivatives.^[30]

In this paper, the synthesis of the semiconducting $\text{Ni}(\text{TCNQF}_4)_2(\text{H}_2\text{O})_2$ has been achieved by electrochemical

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reduction of TCNQF₄ to [TCNQF₄]^{•−} through a solid–solid phase transformation. The water-insoluble, crystalline TCNQF₄ was immobilized onto a working electrode, and the chemically modified electrode was immersed into an aqueous solution containing Ni²⁺(aq.) cations. The solid TCNQF₄ was reduced to [TCNQF₄]^{•−}, which was accompanied by ingress of Ni²⁺(aq.) from the aqueous electrolyte to form Ni(TCNQF₄)₂(H₂O)₂. The composition and morphology of the Ni²⁺–[TCNQF₄]^{•−} derivative were established by UV/Vis, FTIR, and Raman spectroscopy, thermogravimetric and elemental analyses, and scanning electron microscopy (SEM). The magnetic susceptibility and conductivity of the complex were also measured over a wide range of temperatures.

2. Results and Discussion

2.1. Voltammetric Studies with Electrodes Chemically Modified with TCNQF₄

2.1.1. Cyclic Voltammetry in Aqueous Ni²⁺(aq.) Electrolyte

Cyclic voltammogram obtained with a bare GC electrode in contact with a Ni²⁺(aq.) aqueous solution revealed that Ni²⁺(aq.) is electroinactive over a potential range from 800 to −100 mV. In contrast, a TCNQF₄-modified GC electrode immersed in aqueous Ni(NO₃)₂ electrolyte shows two reduction processes (Red1 and Red2) and two oxidation processes (Ox1 and Ox2) over the potential range (Figure 1a).

The first reduction process (Red1) is attributed to the reduction of TCNQF₄(s) to [TCNQF₄]^{•−}, coupled with ingress of Ni²⁺(aq.) to form a Ni²⁺–[TCNQF₄]^{•−}-based material through a solid–solid transformation process. The second reduction step (Red2) is consistent with further reduction of [TCNQF₄]^{•−} to [TCNQF₄]^{2−}. On reversing the scan direction, the generated Ni²⁺–[TCNQF₄]^{•−}-based material is oxidized at approximately 570 mV (process Ox1) back to the neutral TCNQF₄. The Ni²⁺–[TCNQF₄]^{2−} product, unlike the [TCNQF₄]^{•−} derivative, is soluble in water, as evidenced by noting that the reduction and oxidation peak currents diminish on repetitive cycling of the potential and almost disappear after 50 cycles (see Figure 1a). In contrast, switching the potential at 220 mV, after the first [TCNQF₄]^{0/•−} reduction, has a much smaller effect on repetitive cycling the potential (Figure 1b), which implies a much lower level of dissolution. Thus, in aqueous electrolyte, only the first reduction process could be investigated in detail in terms of solid–solid interconversion.

Since a very well-defined reduction (Red1) and oxidation (Ox1) couple is evident after five to ten cycles of the potential (Figure 1c), voltammetric data derived from the fifth cycle are reported (unless otherwise stated). For this cycle, reduction (E_p^{red}) and oxidation (E_p^{ox}) peak potentials at a scan rate of 20 mV s^{−1} are 355 and 578 mV, respectively, giving an E_m value [$(E_p^{\text{red}} + E_p^{\text{ox}})/2$] of 467 mV, which is 374 mV more positive than the value of E_m reported for the analogous TCNQ-modified electrode in a Ni²⁺(aq.) aqueous solution.^[56] This difference in E_m values obtained at TCNQF₄ and TCNQ-modified electrodes is similar to the

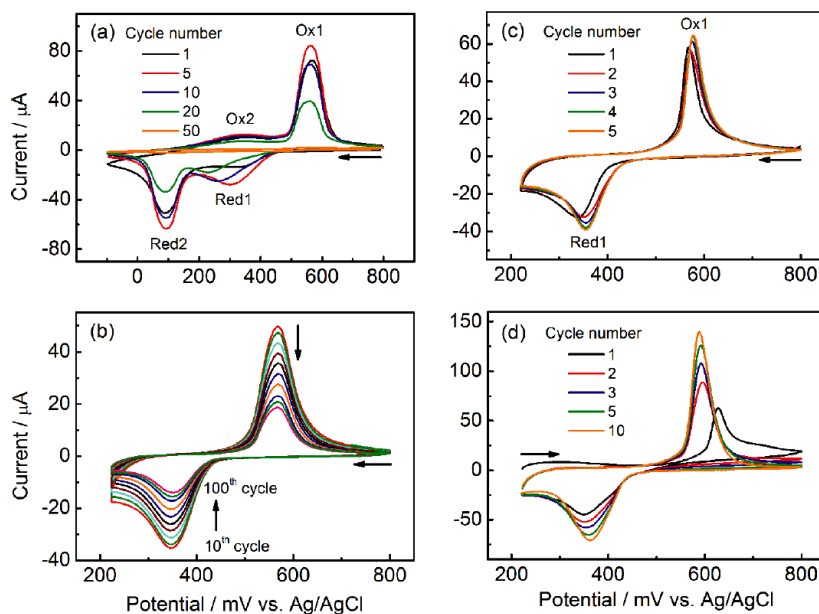
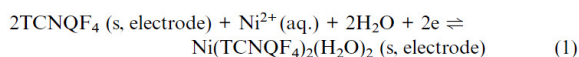


Figure 1. Cyclic voltammograms obtained at a scan rate of 20 mV s^{−1}: (a) for a TCNQF₄-modified GC electrode placed in contact with aqueous 0.1 M Ni(NO₃)₂ electrolyte; (b) as for (a) but over a potential range restricted to the first reduction process and showing every tenth cycle of potential, from 10 to 100 cycles; (c) as in (b), but the first five cycles shown; (d) under the same conditions as for (b) but the GC electrode was modified with chemically synthesized Ni(TCNQF₄)₂(H₂O)₂.

value of 360 mV found in acetonitrile (0.1 M Bu₄NClO₄).^[6] The peak-to-peak separation or “inert zone” is also large ($\Delta E_p = E_p^{\text{ox}} - E_p^{\text{red}} = 223$ mV) and consistent with the solid–solid phase transformation of TCNQF₄/Ni(TCNQF₄)₂ governed by nucleation and growth kinetics. This electrochemical behavior resembles that found for the solid–solid interconversion of a number of TCNQ-based transformations, TCNQ/M(TCNQ)₂(H₂O)₂ (M = Fe²⁺, Co²⁺, Ni²⁺) and TCNQ/M(TCNQ) (M = Na⁺, K⁺, Cs⁺, Cu⁺).^[7,20,56–58] Interestingly, ΔE_p for TCNQF₄ in 0.1 M Ni²⁺(aq.) is substantially larger than that for the analogous TCNQ ($\Delta E_p = 164$ mV),^[56] thereby implying that the kinetics of transformation are slower in the TCNQF₄ case.

It will emerge from evidence below that the Ni²⁺–[TCNQF₄][–] material is Ni(TCNQF₄)₂(H₂O)₂, so that the solid–solid phase transformation can be described by Equation (1).



Thus, in the negative-potential-direction scan, at approximately 450 mV, TCNQF₄ is reduced to [TCNQF₄][–], which is combined with Ni²⁺(aq.) to form solid Ni(TCNQF₄)₂(H₂O)₂ on the surface of the working electrode. In the oxidation component, Ni(TCNQF₄)₂(H₂O)₂ is converted back to TCNQF₄ with the egress of Ni²⁺(aq.) cations back into the solution phase. The magnitudes of the charge for the reduction and oxidation components for a given cycle are almost equal. For example, the charge associated with both the reduction (and oxidation) for the fifth cycle in Figure 1c is approximately 2.25×10^{-4} C. Thus, the solid–solid transformation of solid TCNQF₄ and Ni(TCNQF₄)₂(H₂O)₂ is a chemically reversible process.^[56,58]

The reaction in Equation (1) is supported by examination of the cyclic voltammograms (Figure 1d) obtained from a GC electrode modified with chemically synthesized Ni(TCNQF₄)₂(H₂O)₂. The Ni(TCNQF₄)₂(H₂O)₂-modified electrode was placed in an aqueous solution of 0.1 M Ni(NO₃)₂, and the potential was now initially scanned in the positive direction, from 220 to 800 mV for ten cycles at a scan rate of 20 mV s^{–1}. After seven cycles, the cyclic voltammograms were highly reproducible and similar to those based on a TCNQF₄-modified electrode described in Figure 1c.

2.1.2. Role of Electrode Material

GC, Pt, Au, and indium tin oxide (ITO) electrodes were modified with solid TCNQF₄ and placed in contact with aqueous 0.1 M Ni(NO₃)₂ electrolyte. The data derived from the tenth cycle of potential over the range from 800 to 220 mV are summarized in Table 1. These results indicate that the redox-based TCNQF₄/Ni(TCNQF₄)₂(H₂O)₂ solid–solid phase transformation is essentially independent of the electrode material. The slightly larger ΔE_p value for the ITO electrode is attributed to the larger Ohmic drop (IR_u) encountered when using this larger-area electrode.

Table 1. Voltammetric parameters obtained at a scan rate of 20 mV s^{–1} with GC, Pt, Au, and ITO electrodes modified with solid TCNQF₄ and placed in aqueous 0.1 M Ni(NO₃)₂ solution.

Electrode material	Area /cm ²	E_p^{red} /mV	E_p^{ox} /mV (vs. Ag/AgCl)	E_m /mV	ΔE_p /mV
GC	0.07	355	578	467	223
Pt	0.02	358	574	466	216
Au	0.02	357	576	467	219
ITO	ca. 0.4	345	585	465	240

2.1.3. Influence of Ni²⁺ (aq.) Concentration

The effect of Ni²⁺(aq.) concentration on cyclic voltammograms for the TCNQF₄/Ni(TCNQF₄)₂(H₂O)₂ solid–solid phase transformation is shown in Figure 2a. The voltammetric parameters derived from these experiments are summarized in Table 2. The peak-to-peak separation (ΔE_p) increases from 172 to 266 mV as the concentration of

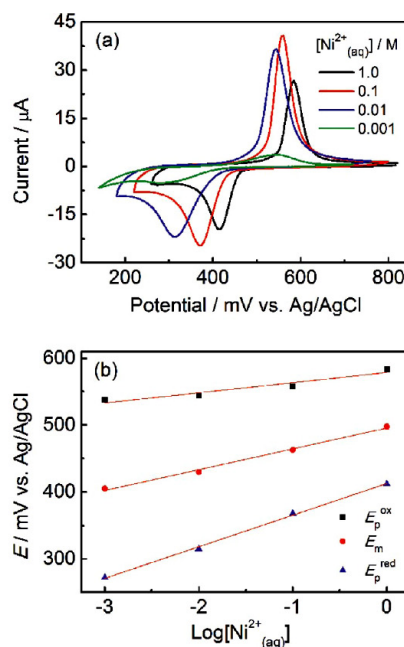


Figure 2. (a) Cyclic voltammograms obtained at a scan rate of 10 mV s^{–1} [fifth cycle with 1.0, 0.1, 0.01 M Ni²⁺(aq.) and second cycle with 0.001 M Ni²⁺(aq.)] with a TCNQF₄-modified GC electrode in contact with aqueous Ni(NO₃)₂ electrolyte; (b) dependence of E_p^{ox} , E_p^{red} , and E_m on $\log[\text{Ni}^{2+} (\text{aq.})]$.

Table 2. Voltammetric parameters obtained at a scan rate of 10 mV s^{–1} with a TCNQF₄-modified GC electrode in contact with variable concentrations of aqueous Ni(NO₃)₂ electrolyte.

[Ni ²⁺ (aq.)] /M	E_p^{red} /mV	E_p^{ox} /mV (vs. Ag/AgCl)	E_m /mV	ΔE_p /mV
1.0	412	584	498	172
0.1	368	558	463	190
0.01	315	544	430	229
0.001	272	538	405	266

$\text{Ni}^{2+}(\text{aq.})$ decreases from 1.0 to 0.001 M, which is attributed predominantly to an increase in the uncompensated resistance, which is particularly important at very low concentrations of $\text{Ni}^{2+}(\text{aq.})$.^[56–58] For the reaction given in Equation (1), $E_{\text{p}}^{\text{red}}$ and E_{p}^{ox} are expected to depend on the concentration of $\text{Ni}^{2+}(\text{aq.})$, as described in Equations (2) and (3).

$$E_{\text{p}}^{\text{red}} = \text{Constant} + S \log[\text{Ni}^{2+}(\text{aq.})] - \eta_{\text{crit}}^{\text{red}} - E_{\text{ohmic}}^{\text{red}} \quad (2)$$

$$E_{\text{p}}^{\text{ox}} = \text{Constant} + S \log[\text{Ni}^{2+}(\text{aq.})] + \eta_{\text{crit}}^{\text{ox}} + E_{\text{ohmic}}^{\text{ox}} \quad (3)$$

where S is the slope, $\eta_{\text{crit}}^{\text{red}}$ and $\eta_{\text{crit}}^{\text{ox}}$ are critical nucleation overpotentials, and $E_{\text{ohmic}}^{\text{red}}$ and $E_{\text{ohmic}}^{\text{ox}}$ are IR_{u} terms associated with the reduction and oxidation processes, respectively. Equation (4) gives the peak-to-peak separation (ΔE_{p}) as the difference between Equations (2) and (3). Thus,

$$\Delta E_{\text{p}} = E_{\text{p}}^{\text{ox}} - E_{\text{p}}^{\text{red}} = (\eta_{\text{crit}}^{\text{ox}} + \eta_{\text{crit}}^{\text{red}}) + (E_{\text{ohmic}}^{\text{ox}} + E_{\text{ohmic}}^{\text{red}}) \quad (4)$$

Thus, when the $\text{Ni}^{2+}(\text{aq.})$ electrolyte concentration is low, the solution conductivity is low, so that IR_{u} is high. If η_{crit} as well as IR_{u} values for both reduction and oxidation processes are equal in magnitude, then the midpoint potential E_{m} , which should approximate the reversible potential $E^{0'}$, is given by Equation (5).

$$E_{\text{m}} = (E_{\text{p}}^{\text{red}} + E_{\text{p}}^{\text{ox}})/2 = \text{Constant} + S \log[\text{Ni}^{2+}(\text{aq.})] \quad (5)$$

The slope (S) of a plot of E_{m} vs. $\log[\text{Ni}^{2+}(\text{aq.})]$ (Figure 2b) is 31 ± 2 mV, which agrees with the Nernst relationship [Equation (6)] for a two-electron transfer process described by Equation (1) where the slope of $2.303(RT/2F)$ is predicted to be 29.3 mV at 22 °C ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$; $T = 295.15 \text{ K}$; $F = 96485 \text{ C mol}^{-1}$).

$$E = E^{0'} + 2.303(RT/2F) \log[\text{Ni}^{2+}(\text{aq.})] \quad (6)$$

2.1.4. Influence of Counteranion

The peak potential and wave shape data derived from cyclic voltammograms (Figure 3) obtained with a TCNQF₄-modified GC electrode in contact with 0.1 M $\text{Ni}(\text{NO}_3)_2$, NiCl_2 , $\text{Ni}(\text{ClO}_4)_2$, or NiSO_4 aqueous electrolytes show minimal dependence on the identity of the counteranion. Thus, the anion is assumed to play no major role in the insertion of $\text{Ni}^{2+}(\text{aq.})$ cations into the $[\text{TCNQF}_4]^-$ crystal lattice during the reduction step nor in its release from solid $\text{Ni}(\text{TCNQF}_4)_2(\text{H}_2\text{O})_2$ in the oxidation process, thereby implying that processes involving $\text{Ni}^{2+}(\text{aq.})$ and not the counteranion are the rate-determining steps.^[58]

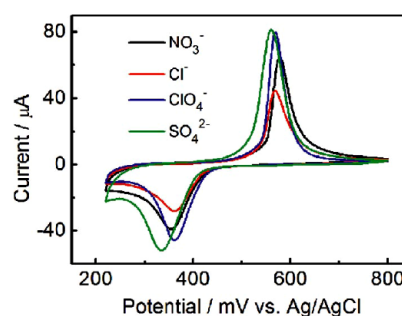


Figure 3. Cyclic voltammograms (fifth cycle) obtained at a scan rate of 20 mV s^{-1} when a TCNQF₄-modified GC electrode was immersed in aqueous 0.1 M $\text{Ni}(\text{NO}_3)_2$, NiCl_2 , $\text{Ni}(\text{ClO}_4)_2$, or NiSO_4 electrolyte.

2.2. Nucleation and Growth Processes Associated with the Interconversion between TCNQF₄ (s) and $\text{Ni}(\text{TCNQF}_4)_2(\text{H}_2\text{O})_2$ (s)

2.2.1. Effect of the Scan Rate

Figure 4 contains cyclic voltammograms obtained as a function of scan rate when a TCNQF₄-modified GC was immersed in a 0.1 M $\text{Ni}(\text{NO}_3)_2$ aqueous solution. Both reduction and oxidation peak potentials depend on scan rate in a manner which is characteristic of nucleation and growth kinetics.^[20,21] However, E_{m} is almost independent of scan rate, which is as required if this parameter approximates $E^{0'}$ and hence has thermodynamic significance.

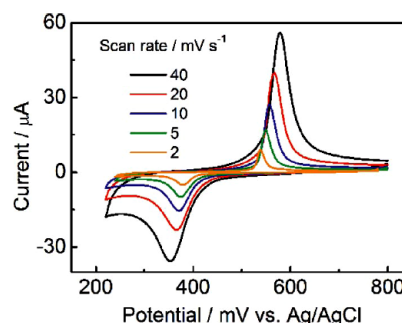


Figure 4. Cyclic voltammograms obtained at designated scan rates from a TCNQF₄-modified GC electrode in contact with aqueous 0.1 M $\text{Ni}(\text{NO}_3)_2$ electrolyte.

At higher scan rates, the peak-to-peak potential separation increases. Since the current magnitude also increases with scan rate, the peak-to-peak separation could arise in part from an increase in IR_{u} . However, IR_{u} is believed to only provide a small contribution to the scan rate dependence when aqueous 0.1 M $\text{Ni}^{2+}(\text{aq.})$ is present as the supporting electrolyte.

2.2.2. Effect of the Switching Potential

Further evidence of a nucleation and growth mechanism is found by switching the potential at the onset of the re-

duction or the oxidation processes. As shown in Figure 5a (reduction step) and Figure 5b (oxidation step), current loops are detected (more readily, as shown in the inset to Figure 5a), which are diagnostic of nucleation and growth kinetics.^[20,21,59]

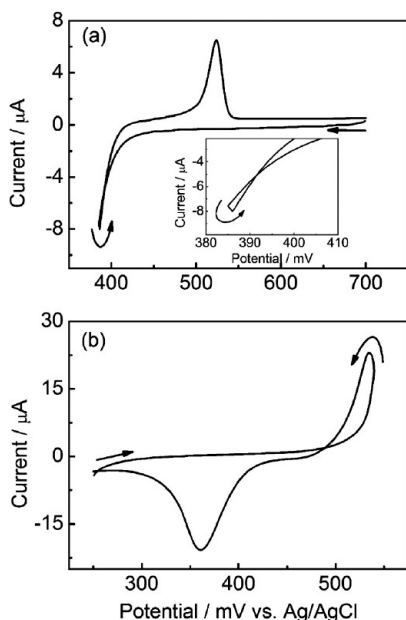


Figure 5. Cyclic voltammogram obtained at a scan rate of 5 mV s^{-1} (fifth cycle of potential) with a TCNQF_4 -modified GC electrode in contact with aqueous $0.1 \text{ M Ni}(\text{NO}_3)_2$ electrolyte when the potential was switched just past the foot of (a) the reduction and (b) the oxidation processes.

2.2.3. Chronoamperometry

Double-potential step chronoamperometric experiments are extremely sensitive to nucleation and growth processes.^[20,21,59] Figure 6a shows the result of a double-potential step chronoamperometric measurement when a TCNQF_4 -modified GC electrode was placed in contact with aqueous $0.1 \text{ M Ni}(\text{NO}_3)_2$ electrolyte and the potential was cycled five times from 800 to 220 mV at a scan rate of 20 mV s^{-1} . The potential was then held at an initial value of 800 mV , where TCNQF_4 is electroinactive, for 10 seconds. The potential was then stepped to 345 mV for 30 seconds, when solid TCNQF_4 was transformed to solid $\text{Ni}(\text{TCNQF}_4)_2(\text{H}_2\text{O})_2$. The potential was then stepped back to 575 mV for 30 seconds to induce oxidation of solid $\text{Ni}(\text{TCNQF}_4)_2(\text{H}_2\text{O})_2$ to solid TCNQF_4 , accompanied by egress of $\text{Ni}^{2+}(\text{aq.})$ cations into the solution phase. The detection of current maxima in the current–time curves (Figure 6) is strong proof for nucleation and growth kinetics in both the reduction and oxidation solid–solid state transformation.^[20,21,59]

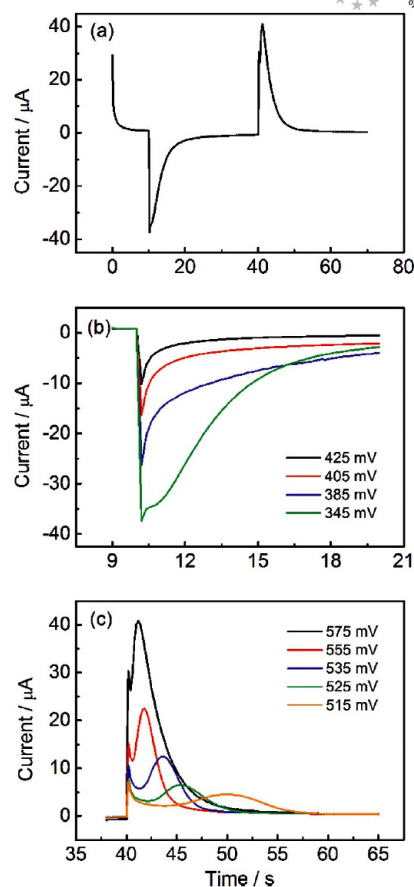


Figure 6. Double-potential step chronoamperograms obtained by using a TCNQF_4 -modified GC electrode in contact with aqueous $0.1 \text{ M Ni}(\text{NO}_3)_2$ electrolyte: (a) potential stepped from $E_i = 800$ to 345 mV for 30 s and then back to 575 mV for 30 s ; (b) as for (a) but potential stepped to a series of designated potentials; (c) as for (a) but with the second potential step set to a series of designated potentials.

In summary, the $\text{TCNQF}_4/\text{Ni}(\text{TCNQF}_4)_2(\text{H}_2\text{O})_2$ solid–solid phase electrochemical transformation is governed by nucleation and growth kinetics as found in the $\text{TCNQ}-\text{Ni}(\text{TCNQ})_2(\text{H}_2\text{O})_2$ case.^[56] Both TCNQ and TCNQF_4 give rise to a chemically reversible and electrochemically irreversible solid–solid conversion processes, which are independent of electrode material and counteranion but depend on $\text{Ni}^{2+}(\text{aq.})$ concentration and scan rate.

2.3. Spectroscopic and Microscopic Characterization of $\text{Ni}(\text{TCNQF}_4)_2(\text{H}_2\text{O})_2$

Electrochemically synthesized $\text{Ni}(\text{TCNQF}_4)_2(\text{H}_2\text{O})_2$ (see below) dissolved in acetonitrile gives three UV/Vis absorption bands with λ_{max} values at 411 , 686 , and 752 nm . This UV/Vis spectrum is consistent with literature data for $[\text{TCNQF}_4]^-$,^[6,51,60,61] confirming that the electrochemically generated $\text{Ni}-\text{TCNQF}_4$ complex contains the monoanion

$[\text{TCNQF}_4]^-$ and not $[\text{TCNQF}_4]^{2-}$, which has a λ_{max} value of 333 nm.^[6,51,61]

The IR bands at 2190 and 2207 cm^{-1} , assigned to the $\text{C}\equiv\text{N}$ stretch in the $\text{Ni}(\text{TCNQF}_4)_2(\text{H}_2\text{O})_2$ complex (Figure 7a) are also in good agreement with data for other $[\text{TCNQF}_4]^-$ salts.^[5,45,50–53] The band at 2227 cm^{-1} is also assigned to the $\text{C}\equiv\text{N}$ stretch. This band is shifted to slightly higher energy compared with that for neutral TCNQF_4 . Interestingly, in the analogous $\text{Ni}(\text{TCNQ})_2(\text{H}_2\text{O})_2$ material, the $\text{C}\equiv\text{N}$ stretch is split into three bands located at 2177, 2208, and 2226 cm^{-1} .^[54] The absence of bands at approximately 2167 and 2133 cm^{-1} again implies that the $[\text{TCNQF}_4]^{2-}$ dianion is not produced.^[51,52,61] Another diagnostic band for the out-of-plane $\text{C}-\text{F}$ bending^[50] in $[\text{TCNQF}_4]^-$ found at 1207 cm^{-1} is shifted by 17 cm^{-1} to higher wavenumbers relative to the band at 1190 cm^{-1} for TCNQF_4 . A similar shift in this band relative to TCNQF_4 also is observed for AgTCNQF_4 .^[45,51] Finally, the presence of the broad absorption band at approximately 3400 cm^{-1} is indicative of coordinated water.^[56–58]

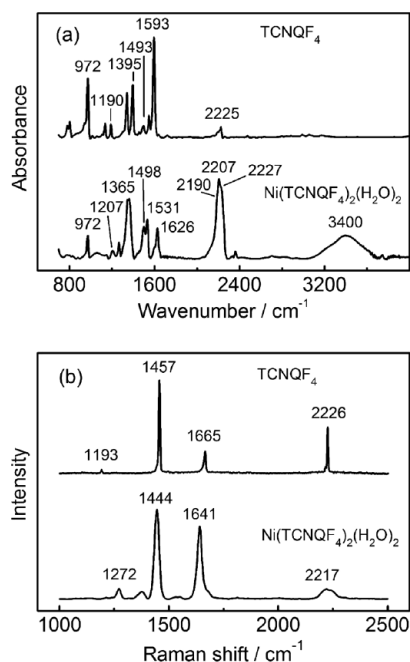


Figure 7. FTIR (a) and Raman (b) spectra for TCNQF_4 and $\text{Ni}(\text{TCNQF}_4)_2(\text{H}_2\text{O})_2$ electrochemically synthesized by exhaustive reduction of TCNQF_4 immobilized onto an ITO electrode surface, which was immersed in aqueous 0.1 M $\text{Ni}(\text{NO}_3)_2$ electrolyte at a constant potential of 300 mV.

Support for the composition $\text{Ni}(\text{TCNQF}_4)_2(\text{H}_2\text{O})_2$ also can be obtained by using Raman spectroscopy.^[5,50] Three Raman-active bands for TCNQF_4 found at 2226, 1665, and 1457 cm^{-1} (Figure 7b) are associated with $\text{C}\equiv\text{N}$, $\text{C}=\text{C}$ ring, and $\text{C}-\text{CN}$ wing stretches respectively.^[5,50,51] These three diagnostic Raman vibration modes for the $\text{Ni}(\text{TCNQF}_4)_2$ -

$(\text{H}_2\text{O})_2$ complex are redshifted, and located at 2217, 1641, and 1444 cm^{-1} , as a result of the conversion of TCNQF_4 to $[\text{TCNQF}_4]^-$.^[5,50,51] A relatively large decrease in intensity of the band due to the $\text{C}\equiv\text{N}$ stretch is also a spectroscopic fingerprint of $[\text{TCNQF}_4]^-$.^[50,51]

Figures 8a and 8b provide SEM images at different magnifications when TCNQF_4 is drop-casted onto an ITO electrode while Figures 8c and 8d present the SEM images when $\text{Ni}(\text{TCNQF}_4)_2(\text{H}_2\text{O})_2$ is electrocrystallized by solid-solid conversion on an ITO electrode surface. The nickel complex is formed as a thin film of microcrystals. EDXS elemental analysis of the electrochemically synthesized nickel complex confirms the presence of Ni, C, N, F, and O.

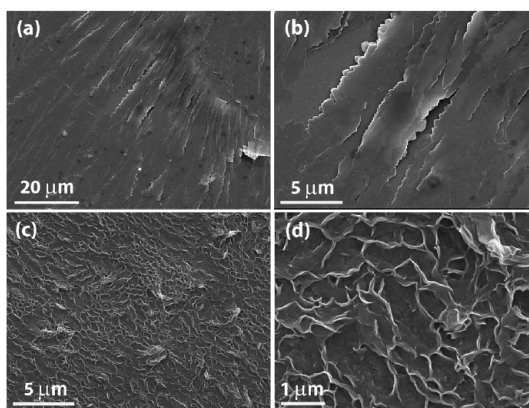


Figure 8. SEM images at different magnifications of (a, b) solid TCNQF_4 drop-casted onto an ITO electrode. (c, d) $\text{Ni}(\text{TCNQF}_4)_2(\text{H}_2\text{O})_2$ formed when a drop-casted TCNQF_4 -modified ITO electrode was immersed into an aqueous solution of 0.1 M $\text{Ni}(\text{NO}_3)_2$ and the potential was held at 300 mV for 10 min.

2.4. Thermogravimetry and Elemental Analysis

A TGA experiment for $\text{Ni}-\text{TCNQF}_4$ material electrochemically generated on an ITO electrode surface was carried out over the temperature range of 25 to 420 $^{\circ}\text{C}$. The result illustrated in Figure 9 reveals that the $\text{Ni}-\text{TCNQF}_4$ compound loses $5.5 \pm 0.1\%$ of its mass over the temperature range of 140 to 230 $^{\circ}\text{C}$. On the basis of an empirical

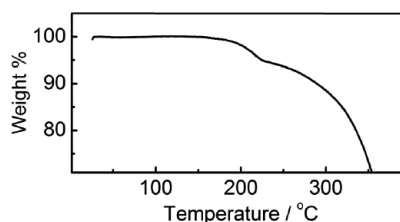
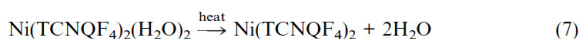


Figure 9. TGA data for $\text{Ni}-\text{TCNQF}_4$ material that was obtained by controlled potential reduction of TCNQF_4 immobilized onto an ITO electrode in contact with aqueous 0.1 M $\text{Ni}(\text{NO}_3)_2$ electrolyte. A potential of 300 mV was applied until the current was 0.5% of the initial value.

formula of Ni(TCNQF₄)₂(H₂O)₂, the mass proportion of water is calculated to be 5.57%. Thus, the mass decrease is attributed to the loss of the two coordinated water molecules as in Equation (7). This TGA behavior is similar to that found for chemically synthesized Ni(TCNQ)₂(H₂O)₂, for which the analogous dehydration reaction also occurs in a single step.^[54]



Elemental analysis was used to fully confirm the empirical formula of the Ni–TCNQF₄ compound. In order to obtain a solid of sufficient quality for this experiment, the same compound formed electrochemically was chemically synthesized as described in the Experimental Section. The experimental (and calculated) results for elemental analysis (% weight) are C 44.55 (44.44), H 0.62 (0.69), N 17.32 (17.36), and F 23.49 (23.27). This result is fully consistent with the formulation Ni(TCNQF₄)₂(H₂O)₂.

2.5. Conductivity and Magnetic Properties

Figure 10 shows a plot of magnetic molar susceptibility χ_M' (corrected for diamagnetism) vs. temperature for the Ni–TCNQF₄ complex. The susceptibility–temperature dependence corresponds to that expected for a classical paramagnetic material, which implies that the Ni atoms in the structure are magnetically dilute and do not participate in short- or long-range ordering. Over the temperature range, 6 to 300 K, the effective magnetic moment rises from 3.1 to 3.8 B.M., which is close to that expected for a magnetically dilute Ni²⁺ ion. The magnetic behavior for the Ni(TCNQ)₂·(H₂O)₂ derivative is similar, with an essentially temperature-independent value of approximately 3.0 B.M. found over a similar range of temperatures.^[54] In the case of Ni(TCNQ)₂·(MeOH)₂, the magnetic moment is a little higher (ca. 3.4 B.M.).^[54] However, all these Ni–TCNQ materials behave as essentially magnetically isolated ions.

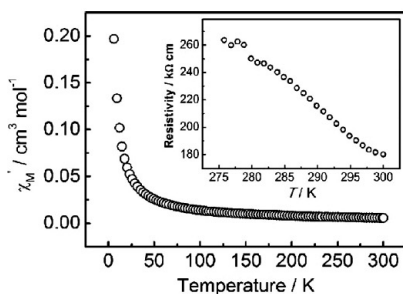


Figure 10. The dependence of magnetic molar susceptibility and resistivity (inset) on temperature for Ni(TCNQF₄)₂(H₂O)₂.

The plot of electrical resistivity vs. temperature for a pressed pellet (inset in Figure 10) indicates that the Ni–TCNQF₄ complex is semiconducting, as shown by the increase of electrical resistivity with decreasing temperature. It is a typical semiconductor with a band gap close to that of an insulator, since the electrical resistance is large, with

the resistivity at 275 K already beyond the range accessible with the equipment used for these measurements. This result can be explained in part by the fact that the pressed pellet provides poor connectivity between the grains. Measurement of the electrical conductivity of a single crystal would provide a better assessment of the conductivity. Unfortunately, all efforts to obtain such a crystal were unsuccessful.

3. Conclusions

The combination of voltammetric, spectroscopic, microscopic, TGA, and elemental analysis studies has revealed that Ni(TCNQF₄)₂(H₂O)₂ can be electrochemically generated as a dark blue solid by one-electron reduction of solid TCNQF₄ immobilized on a working electrode surface in contact with aqueous Ni²⁺(aq.) electrolyte. Reduction of TCNQF₄ to [TCNQF₄]^{•−} is accompanied by the facile incorporation of the Ni²⁺(aq.) cation, from the electrolyte solution, to form solid Ni(TCNQF₄)₂(H₂O)₂ on the electrode surface. Scanning the potential back to sufficiently positive values causes [TCNQF₄]^{•−} to be reoxidized to TCNQF₄ with the egress of Ni²⁺(aq.) ions to the solution phase. UV/Vis, FTIR, and Raman spectra confirm that the [TCNQF₄]^{•−} monoanion, rather than the [TCNQF₄]^{2−} dianion, has been formed under the experimental conditions. The overall electrochemically irreversible, but chemically reversible, TCNQF₄/Ni(TCNQF₄)₂(H₂O)₂ solid–solid transformation process is governed by a nucleation and growth mechanism. Importantly, the voltammetric behavior is independent of the electrode material and the identity of the Ni²⁺(aq.) counteranion, but it shows strong dependence on the Ni²⁺(aq.) concentration and the scan rate. TGA results indicate that there are two coordinated water molecules in the electrochemically synthesized compound. SEM images reveal that Ni(TCNQF₄)₂(H₂O)₂ is formed as a thin film of microcrystals on the electrode surface. Ni(TCNQF₄)₂·(H₂O)₂ exhibits weakly semiconducting properties. Ni atoms in the complex are magnetically dilute and are not involved in short- or long-range ordering.

4. Experimental Section

4.1. Chemicals

Analytical grade hydrated nickel salts Ni(NO₃)₂·6H₂O, NiCl₂·6H₂O, Ni(ClO₄)₂·6H₂O, NiSO₄·6H₂O, LiI (Aldrich, 99%), as well as TCNQF₄ (97%, Aldrich), and the solvents acetonitrile (HPLC grade, Omnisolv), acetone (Suprasolv, Merck), 2-propanol (BDH), and 96% ethanol (Merck) were used as received from the manufacturer.

4.2. Electrochemistry

Voltammetric measurements were carried out at room temperature (22 ± 2 °C) with a Bioanalytical Systems (BAS) 100 W electrochemical workstation. Chronoamperometric experiments were conducted by using an AutoLab PGSTAT 100 (ECO-Chemie) potentiostat. A standard three-electrode cell configuration (working, reference, and counter electrodes) was used. Working elec-

trodes were (BAS) 3.0 mm diameter glassy carbon (GC), gold, or platinum (1.6 mm diameter) disks or indium tin oxide (ITO)-coated glass plates (area 0.2–0.4 cm²) with a resistance of 10 Ω /sq (as quoted by the manufacturer, Präzisions Glas und Optik GmbH). The working electrodes were cleaned as described elsewhere.^[51] An aqueous Ag/AgCl (3.0 M KCl) electrode (BAS) and platinum wire (1.0 mm diameter) were used as reference and counter electrodes, respectively. Aqueous electrolyte solutions were prepared by using purified water from a Millipore system (resistivity 18.2 M Ω cm). Nitrogen gas was used to purge the aqueous solutions prior to conducting the electrochemical experiments, and a stream of this gas was maintained above the solution during the course of these measurements.

4.3. Electrode Modification

GC, Au, or Pt electrodes modified with TCNQF₄ were prepared by immersion of these electrodes into an acetone solution containing TCNQF₄ (10.0 mM). The electrodes were then removed from the solution and suspended with the electrode surface face down. In the case of ITO electrodes, an acetone solution of TCNQF₄ (15 μ L, 10.0 mM) was drop-cast onto the surface. The TCNQF₄-modified electrodes were then dried in air for several minutes to allow the acetone to evaporate, leaving behind an array of TCNQF₄ microcrystals on the electrode surface.

A Ni(TCNQF₄)₂(H₂O)₂-modified 3.0 mm diameter GC electrode was prepared by immersion of the bare electrode into an acetonitrile solution containing Ni(TCNQF₄)₂(H₂O)₂ (5.0 mM). After removal from solution, the chemically modified electrode was dried under a stream of N₂ gas for 10 min.

4.4. Electrochemical and Chemical Synthesis of Ni(TCNQF₄)₂(H₂O)₂

Ni(TCNQF₄)₂(H₂O)₂ was electrochemically synthesized by placing a TCNQF₄-modified ITO electrode in an aqueous Ni(NO₃)₂ solution (0.1 M). The potential was then maintained at 300 mV vs. Ag/AgCl until the current decreased to 0.5% of its initial value (ca. 20 min). A dark blue solid formed on the surface of the ITO electrode. This solid was gently rinsed with deionized water and ethanol, and then dried initially under a stream of nitrogen gas for 10 min, then more thoroughly under vacuum for 24 h. The solid, which was still attached to the ITO electrode, was removed from the electrode surface by using a spatula and then characterized by UV/Vis, FTIR, Raman spectroscopy, SEM and thermogravimetric analysis (TGA).

LiTCNQF₄ used for chemical synthesis of Ni(TCNQF₄)₂(H₂O)₂ was prepared from TCNQF₄ and LiI. TCNQF₄ (104 mg, 0.38 mmol) was dissolved in cold acetonitrile (8.0 mL), and a solution of LiI (75.4 mg, 0.56 mmol) in cold acetonitrile (3.0 mL) was added dropwise. The mixture that generated LiTCNQF₄ was stirred under N₂ for 30 min, and the LiTCNQF₄ solid was collected by filtration. The solid was washed with acetonitrile (3 $\times$ 2 mL) and diethyl ether (2 $\times$ 2 mL), and then dried overnight with P₂O₅ under vacuum. A dark purple solid was obtained (89.5 mg, yield 84%). Ni(TCNQF₄)₂(H₂O)₂ was then chemically synthesized (for elemental analysis) by using aqueous solutions of LiTCNQF₄ and Ni(NO₃)₂. In this case, water (5.0 mL) containing LiTCNQF₄ (23.10 mg, 0.082 mmol) was mixed with water (0.5 mL) containing Ni(NO₃)₂·6H₂O (11.85 mg, 0.041 mmol). A dark blue precipitate formed immediately, which was collected by filtration, washed with water (3 $\times$ 2 mL), and then dried under vacuum for 24 h (19.20 mg, yield 73%). The UV/Vis, FTIR, Raman spectra, and all other physical and chemical properties of the solid prepared electrochemically or chemically are identical within experimental error.

4.5. Other Instrumentation

Details of the instrumentation used in UV/Vis, FTIR, and Raman spectroscopic experiments are available elsewhere.^[51] SEM images of samples coated with a thin film of Pt were obtained by using a JEOL JSM 7001F FEGSEM microscope with an accelerating voltage of 15.0 kV. This instrument was also used to confirm the elemental composition (except H) of materials by the energy dispersive X-ray spectroscopy (EDXS) analysis technique and the Bruker EDXS software suite.

TGA was undertaken in a flow-through dry nitrogen atmosphere (50 mLmin⁻¹) over the temperature range from 25 to 420 °C at a rate of 10 °Cmin⁻¹ by using platinum pans and a Perkin-Elmer Pyris TGA1 instrument. Calibration was achieved by using the Curie points of four reference materials: Alumel, Perkin alloy, iron, and nickel. C, H, N, F elemental analysis was carried out at the Campbell Microanalytical Laboratory, Chemistry Department, University of Otago, New Zealand.

Magnetic data were obtained with a 5 T Magnetic Property Measurement System (Quantum Design, USA), by using a known mass of the sample, which was wrapped into nonmagnetic material. Magnetic susceptibility vs. temperature measurements were undertaken with a 1000 Oe applied magnetic field by sweeping the temperature at a rate of 3 Kmin⁻¹ from 6 to 300 K [zero-field-cooled (ZFC) measurement] and 300 to 6 K [field-cooled (FC) measurement].

Four-probe electrical resistivity measurements utilized a 14 T Physical Property Measurement System (Quantum Design, USA). The powder was placed into a rectangular tungsten carbide die and then pressed into a rectangular shaped pellet under 4 MPa pressure. No further sintering was used to avoid possible decomposition of the material. The four contacts with the pellet were achieved with a 50 μ m Au wire and Ag paste.

Acknowledgments

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Chapter 6

Disproportionation of $\text{TCNQF}_4^{\bullet-}$ and $\text{TCNQ}^{\bullet-}$ in Acetonitrile in the Presence of Zn^{2+}

6.1. Introduction

Disproportionation of $\text{TCNQF}_4^{\bullet-}$ and $\text{TCNQ}^{\bullet-}$ in organic solvents in the presence of a metal cation has been implied in several studies leading to the synthesis of TCNQF_4^{2-} or TCNQ^{2-} -metal derivatives, but to the best of our knowledge, no details of the mechanism has been proposed. This chapter describes a study of the disproportionation of $\text{TCNQF}_4^{\bullet-}$ and $\text{TCNQ}^{\bullet-}$ (both designated as $\text{TCNQ}(\text{F}_4)^{\bullet-}$) in acetonitrile in the presence of Zn^{2+} . $\text{TCNQ}(\text{F}_4)^{\bullet-}$ are very stable in acetonitrile and do not disproportionate to $\text{TCNQ}(\text{F}_4)$ and $\text{TCNQ}(\text{F}_4)^{2-}$ since the equilibrium constants (K_{disp}) for the disproportionation reaction $2\text{TCNQ}(\text{F}_4)^{\bullet-} \rightleftharpoons \text{TCNQ}(\text{F}_4) + \text{TCNQ}(\text{F}_4)^{2-}$ are extremely small ($K_{\text{disp}} \approx 5 \times 10^{-10}$). However, in the presence of Zn^{2+} , the disproportionation is driven thermodynamically by precipitation of the highly insoluble $\text{ZnTCNQ}(\text{F}_4)$. The hypothesis for the disproportionation is confirmed by simultaneous detection of neutral $\text{TCNQ}(\text{F}_4)$ along with the precipitation of $\text{ZnTCNQ}(\text{F}_4)$ solids. Intriguingly, the disproportionation reaction is reversed upon addition of water. In the presence of $\geq 3\%$ (v/v) water, the disproportionation of $\text{TCNQ}(\text{F}_4)$ does not occur. This impact of the addition of water to the system is attributed to the higher solubility of $\text{ZnTCNQ}(\text{F}_4)$ in water than in acetonitrile. As a consequence, in the presence of only water, $\text{ZnTCNQ}(\text{F}_4)$ suspensions in acetonitrile are stable. In contrast, in the presence of both water and neutral $\text{TCNQ}(\text{F}_4)$, the formation of $\text{TCNQ}(\text{F}_4)^{\bullet-}$ is detected, so that the disproportionation reaction is now reversible.

Declaration for Thesis Chapter 6.2

Declaration by candidate

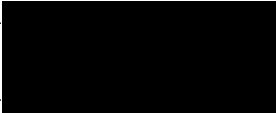
In the case of Chapter 6.2, the nature and extent of my contribution to the work was the following:

Nature of contribution	Extent of contribution (%)
Initiation, key ideas, experimental work, writing up	80

The following co-authors contributed to the work.

Name	Nature of contribution
Ayman Nafady	Initiation, key ideas, experimental work, writing up
Lisandra L. Martin	Initiation, key ideas, writing up
Alan M. Bond	Initiation, key ideas, writing up

Candidate's Signature

	06/06/2012
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Declaration by co-authors

The undersigned hereby certify that:

- (1) the above declaration correctly reflects the nature and extent of the candidate's contribution to this work, and the nature of the contribution of each of the co-authors.
- (2) they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;
- (3) they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
- (4) there are no other authors of the publication according to these criteria;
- (5) potential conflicts of interest have been disclosed to (a) granting bodies, (b) the editor or publisher of journals or other publications, and (c) the head of the responsible academic unit; and
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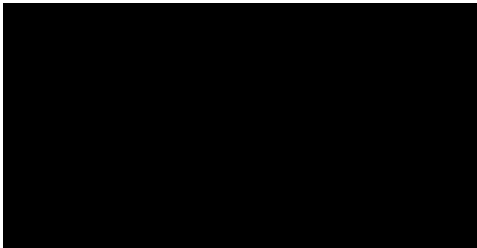
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	18/5/12

Solvent Controlled Reversible Disproportionation of TCNQF₄^{•-} and TCNQ^{•-} in the Presence of Zn²⁺

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Abstract

An explanation as to why both TCNQ²⁻ and TCNQF₄²⁻ (TCNQ = 7,7,8,8-tetracyanoquinodimethane, TCNQF₄ = 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane, both designated as TCNQ(F₄)²⁻) containing coordination polymers may be generated from TCNQ(F₄)^{•-} reactants has been provided in terms of a solvent dependent dynamic disproportionation reaction. A systematic study of reactions associated electrochemically generated acetonitrile solutions of TCNQ(F₄)^{•-}_(MeCN) revealed that disproportionation of TCNQ(F₄)^{•-}_(MeCN) radical anions is facilitated by the presence of Zn²⁺_(MeCN). Thus, while the disproportionation reaction $2\text{TCNQ}(\text{F}_4)^{\bullet-}_{(\text{MeCN})} \rightleftharpoons \text{TCNQ}(\text{F}_4)_{(\text{MeCN})} + \text{TCNQ}(\text{F}_4)^{2-}_{(\text{MeCN})}$ is thermodynamically very unfavorable (equilibrium constant of $\sim 5 \times 10^{-10}$), preferential precipitation of ZnTCNQ(F₄)_(s) drives the reaction: $\text{Zn}^{2+}_{(\text{MeCN})} + 2\text{TCNQ}(\text{F}_4)^{\bullet-}_{(\text{MeCN})} \rightleftharpoons \text{ZnTCNQ}(\text{F}_4)_{(\text{s})} + \text{TCNQ}(\text{F}_4)_{(\text{MeCN})}$. Formation of soluble TCNQ(F₄)_(MeCN) and insoluble ZnTCNQ(F₄)_(s), and loss of TCNQ(F₄)^{•-}_(MeCN) in the regarded stoichiometries was verified by UV-visible and infrared spectroscopies and steady-state voltammetry. Importantly, comproportionation rather than disproportionation becomes favored in the presence of water, owing to the increased solubility of solid ZnTCNQ(F₄)_(s). Thus, an environment containing $\geq 3\%$ (v/v) water produces Zn²⁺_(MeCN) and TCNQ(F₄)^{•-}_(MeCN) from ZnTCNQ(F₄)_(s) and TCNQ(F₄)_(MeCN). An important conclusion from this work is that the redox level of TCNQ(F₄)-based materials synthesized from mixing solutions of metal cations and TCNQ(F₄)^{•-} can be governed by control of the solvent dependent disproportionation/comproportionation reaction to favor formation of solids containing the monoanion radical, the dianion or even a mixture of both.

1. Introduction

Coordination polymers based on TCNQ $\bullet^-$ radical monoanion and its fluorinated derivative TCNQF $_4\bullet^-$ (TCNQ = 7,7,8,8-tetracyanoquinodimethane, TCNQF $_4$ = 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane) are of significant interest because of their fascinating structural architectures and intriguing conductivity, magnetic, and electronic properties.¹⁻⁶ Although there has been an emphasis on applications of CuTCNQ and AgTCNQ for electronic switching and magnetic data storage, recent research has been directed towards the fluorinated analogues CuTCNQF $_4$ and AgTCNQF $_4$. Additionally, TCNQ-based materials containing divalent transition metals (e.g. Mn, Fe, Co, Ni, Cd, Zn) and lanthanides also hold promise for applications in diverse fields, such as energy and data storage, electrochromic and magnetic devices, biosensors, catalysis and photovoltaic cells.⁷⁻⁹ Advances in industrial and technological applications require a fundamental understanding of rational methods of synthesis and mechanistic details associated with their formation and reactivity.

Metal-TCNQ derivatives are readily accessible because of the availability of highly stable TCNQ $\bullet^-$ and TCNQF $_4\bullet^-$ radical anion sources. Thus, in addition to (1:1) CuTCNQ(F $_4$) and AgTCNQ(F $_4$) (TCNQ(F $_4$) designates both TCNQ and TCNQF $_4$ here), the binary (1:2) M(TCNQ) $_2$ (M^{II} = V, Mn, Fe, Co, Ni and Zn) family in different forms, including nonsolvated M(TCNQ) $_2$ (M^{II} = Mn, Fe, Co, Ni) “glassy magnets”^{10,11} and solvated M(TCNQ) $_2$ (S) $_2$, (S = MeOH or H $_2$ O)¹² congeners have been synthesized from a range of TCNQ $\bullet^-$ sources. Similarly, TCNQF $_4\bullet^-$ radical anion sources have been successfully utilized to synthesize Ni(TCNQF $_4$) $_2$ (H $_2$ O) $_2$,¹³ as well as a homologous heterospin series of mononuclear [M(TCNQF $_4$) $_2$ (H $_2$ O) $_x$] $\bullet$ (TCNQF $_4$)(3H $_2$ O), x = 6, 7 complexes with trivalent lanthanides (M^{III} = La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er and Yb).⁵

Although the majority of the compounds chemically synthesized by existing methods are expected to solely contain the monoanionic radicals, detection of solids containing the TCNQ(F $_4$) $^{2-}$ dianions in addition to the TCNQ(F $_4$) $\bullet^-$ radical monoanions has been noted.^{10,14} For example, when methanol solutions of Mn(CH $_3$ CN) $_4$ (BF $_4$) $_2$ and LiTCNQF $_4$ were allowed to react in a 1:1 ratio, dark blue crystals of the “glassy magnet” {[Mn $_2$ (TCNQF $_4$)(CH $_3$ OH) $_{7.5}$ (H $_2$ O) $_{0.5}$](TCNQF $_4$) $_2$ •7.5CH $_3$ OH} $_\infty$ were isolated.¹⁴ Structural analysis of single crystals by X-ray diffraction revealed the presence of both the (μ_4 -TCNQF $_4$) $^{2-}$ dianions in the form of a 2-D honeycomb-like net, along with TCNQF $_4\bullet^-$

radical anions residing between the layers. The presence of TCNQF_4^{2-} in the product was postulated to be a consequence of disproportionation of the $\text{TCNQF}_4^{\bullet-}$ radical anion.¹⁴ A related finding also has been reported when an acetonitrile solution of either $\text{Mn}(\text{CH}_3\text{CN})_6(\text{SbF}_6)_2$ or $\text{Ni}(\text{CH}_3\text{CN})_6(\text{SbF}_6)_2$ (1 equiv) was mixed with a slight excess of Bu_4NTCNQ to afford $\text{M}(\text{TCNQ})_x$ -based materials ($\text{M}^{\text{II}} = \text{Mn}$ or Ni) with $1 < x < 2$, indicative of the presence of the TCNQ^{2-} dianion along with the $\text{TCNQ}^{\bullet-}$ monoanion in the isolated products.¹⁰

Clearly, the synthesis of purely TCNQ^{2-} containing materials is more likely when the starting material is $\text{TCNQ}^{\bullet-}$,³ but this approach is rare. Thus, Kitagawa *et al.* have synthesized the 3D coordination polymer, $[\text{Zn}(\text{TCNQ})\text{bpy}]\cdot 6\text{CH}_3\text{OH}$ (bpy = 4,4'-bipyridine) by reacting hydrated $\text{Zn}(\text{NO}_3)_2$ with LiTCNQ and bpy in methanol. Generation of the TCNQ^{2-} dianion under these conditions was unexpected, but assumed to arise from the disproportionation of $\text{TCNQ}^{\bullet-}$.³ However, no experimental evidence for disproportionation was provided. The same group, again using LiTCNQ as a reagent were able to obtain TCNQ^{2-} -containing $[\text{M}(\text{TCNQ})\text{bpy}]$ ($\text{M} = \text{Fe}, \text{Zn}, \text{Mn}, \text{Co}$ and Cd) porous coordination polymers having 3D pillared layer structures.⁶

In this study, a quantitative investigation of disproportionation reactions in which $\text{TCNQ}(\text{F}_4)^{\bullet-}_{(\text{MeCN})}$ radical anions are converted into neutral $\text{TCNQ}(\text{F}_4)_{(\text{MeCN})}$ and solid dianionic $\text{TCNQ}(\text{F}_4)^{2-}$ materials in acetonitrile upon addition of $\text{Zn}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ is reported. The disproportionation/comproportionation reactions that are sensitive to experimental conditions give rise to precipitation of $\text{ZnTCNQ}(\text{F}_4)_{(\text{s})}$ ($\text{s} = \text{solid}$), which have been isolated and characterized by elemental analysis, ultraviolet-visible (UV-vis) and Fourier transform infrared (FT-IR) spectroscopies. The concomitant formation of neutral $\text{TCNQ}(\text{F}_4)_{(\text{MeCN})}$ was quantitatively demonstrated by UV-vis spectroscopy and electrochemistry. The fact that the disproportionation of dissolved $\text{TCNQ}(\text{F}_4)^{\bullet-}_{(\text{MeCN})}$ to $\text{TCNQ}(\text{F}_4)_{(\text{MeCN})}$ and $\text{TCNQ}(\text{F}_4)^{2-}_{(\text{MeCN})}$ is highly unfavorable in a thermodynamic sense highlights the crucial role of Zn^{2+} and other cations in facilitating the formation of insoluble coordination polymers. A mechanism that involves the reaction of $\text{Zn}^{2+}_{(\text{MeCN})}$ with $\text{TCNQ}(\text{F}_4)^{2-}_{(\text{MeCN})}$ available from a dynamic disproportionation reaction to form $\text{Zn}^{2+}\text{-TCNQ}(\text{F}_4)^{2-}_{(\text{s})}$ is proposed. Intriguingly, addition of water to the reaction media reverses the disproportionation reaction, so that comproportionation to generate $\text{TCNQ}(\text{F}_4)^{\bullet-}_{(\text{MeCN})}$ becomes the favored pathway. Thus, results presented in this paper offer insights into the

role of water in controlling the direction of disproportionation/comproportionation reactions, thereby determining whether dianions (in the absence of water) or the monoanions (in the presence of water) are present in the synthesized Zn-TCNQ(F₄) coordination polymer based materials.

2. Experimental Section

2.1. Chemicals

Zn(ClO₄)₂·6H₂O (Aldrich), ferrocene (98%, EGA-Chemie), acetonitrile (HPLC grade, Omnisolv), isopropanol (BHD) and acetone (Suprasolv, Merck) were used as received by the manufacturer. TCNQ (98%, Aldrich), TCNQF₄ (98%, Beijing Health) were recrystallized twice from boiling acetonitrile or dichloromethane (Suprasolv, Merck), respectively prior to use. Bu₄NPF₆ (Wako) was recrystallized twice from 96% ethanol (Merck) and then dried at 100 °C under vacuum for 24 h before being used as the supporting electrolyte in the electrochemical experiments.

2.2. Procedures

Acetonitrile solutions containing either 10.0 mM TCNQF₄^{•-}_(MeCN) or 10.0 mM TCNQ^{•-}_(MeCN) were quantitatively prepared by exhaustive electrochemical reduction of 10.0 mM TCNQF₄_(MeCN) or TCNQ_(MeCN) in acetonitrile (0.1 M Bu₄NPF₆) at a Pt mesh working electrode using applied potentials (*E*_{appl}) of 100 mV vs. Ag/Ag⁺ for the former and -300 mV (vs. Ag/Ag⁺) for the latter. An analogous protocol was applied to prepare a 10.0 mM solution of TCNQF₄²⁻_(MeCN). In this case, after quantitative generation of the monoanion, *E*_{appl} was set to -400 mV to convert TCNQF₄^{•-}_(MeCN) to TCNQF₄²⁻_(MeCN). Controlled potentials were maintained until the current decreased to 0.1% of its initial value. UV-vis spectroscopy was utilized to confirm that all the starting material was reduced to the required product in the bulk electrolysis experiments.

Zn-TCNQF_{4(s)} material, characterized by elemental analysis, was obtained by mixing 10.0 mL solutions of the electrochemically generated TCNQF₄^{•-}_(MeCN) or TCNQF₄²⁻_(MeCN) (10.0 mM) in acetonitrile (0.1 M Bu₄NPF₆) with 5.0 mL (2:1 ratio) or 10.0 mL (1:1 ratio) acetonitrile solutions containing 10.0 mM Zn²⁺_(MeCN), followed by stirring for 5 min. The rapidly formed precipitates were collected by centrifugation, washed with 5 × 2 mL of acetonitrile and dried overnight under vacuum. No single crystals suitable for structural analysis by X-ray diffraction could be obtained.

2.3. Electrochemistry

Voltammetric experiments were undertaken with a Bioanalytical Systems (BAS) Epsilon electrochemical workstation at room temperature ($22 \pm 2^\circ\text{C}$) using a standard three-electrode cell configuration. The working electrode was a BAS carbon fiber microelectrode ($11 \pm 2 \mu\text{m}$ diameter as quoted). The counter electrode was 1.0 mm diameter Pt wire. The reference electrode consisted of a Ag wire placed in acetonitrile solution containing 1.0 mM AgNO_3 and 0.1 M Bu_4NPF_6 , and separated from the test solution by a glass frit. Conversion to Fc/Fc^+ reference scale can be achieved by addition of -135 mV . In the case of bulk electrolysis experiments, a three-compartment “H-type” cell configuration with Pt mesh working and counter electrodes and the same Ag/Ag^+ reference electrode employed in voltammetric studies were used. Solutions for electrochemical measurements were purged with nitrogen gas for 10 min before commencing the experiments.

2.4. Other Instrumentation

Elemental (C, H, N, Zn) analysis was carried out at the Campbell Microanalytical Laboratory, Chemistry Department, University of Otago, New Zealand. UV-vis and FT-IR instrumentation are as detailed elsewhere.¹⁵

3. Results and Discussion

3.1. Electrochemical and UV-vis Monitoring of the Reactions between $\text{Zn}^{2+}_{(\text{MeCN})}$ and $\text{TCNQ}(\text{F}_4)^{\bullet-}_{(\text{MeCN})}$ Radical Anions

As described in the Experimental Section 2.2, 10.0 mM solutions of either $\text{TCNQF}_4^{\bullet-}_{(\text{MeCN})}$ or $\text{TCNQ}^{\bullet-}_{(\text{MeCN})}$ in acetonitrile (0.1 M Bu_4NPF_6) were generated electrochemically. As can be seen in Figure 1, after bulk electrolysis, both $\text{TCNQF}_{4(\text{MeCN})}$ (Figure 1a) and $\text{TCNQ}_{(\text{MeCN})}$ (Figure 1b) were quantitatively converted to $\text{TCNQF}_4^{\bullet-}_{(\text{MeCN})}$ and $\text{TCNQ}^{\bullet-}_{(\text{MeCN})}$ respectively, as evidenced by the change in location of the zero current position. Further proof was obtained by noting that UV-vis spectral bands characteristic for neutral $\text{TCNQF}_{4(\text{MeCN})}$ ($\lambda_{\text{max}} = 365$ and 386 nm) and $\text{TCNQ}_{(\text{MeCN})}$ ($\lambda_{\text{max}} = 374$ and 393 nm) completely disappeared after the one-electron reduction electrolysis and were replaced by new ones at $\lambda_{\text{max}} = 411$ and 752 nm for the fluorinated and 420 and 743 nm for the $\text{TCNQ}_{(\text{MeCN})}$ radical monoanions¹⁵⁻¹⁸ (Figure 2). Figure 3 shows the color change that occurs when neutral $\text{TCNQ}_{(\text{MeCN})}$ solution is electrochemically reduced to $\text{TCNQ}^{\bullet-}_{(\text{MeCN})}$.

Interestingly, when 2.0 mL of the electrochemically prepared 10.0 mM $\text{TCNQF}_4^{\bullet-}(\text{MeCN})$ or 10.0 mM $\text{TCNQ}^{\bullet-}(\text{MeCN})$ in acetonitrile (0.1 M Bu_4NPF_6) were mixed with 2.0, 1.0 or 0.5 mL of 10.0 mM $\text{Zn}^{2+}(\text{MeCN})$ in acetonitrile (0.1 M Bu_4NPF_6) to give 2:2, 2:1 or 2:0.5 $\text{TCNQ}(\text{F}_4)^{\bullet-}(\text{MeCN}) : \text{Zn}^{2+}(\text{MeCN})$ stoichiometric ratios, pale green precipitates were formed immediately on addition of $\text{TCNQF}_4^{\bullet-}(\text{MeCN})$, whereas for $\text{TCNQ}^{\bullet-}(\text{MeCN})$, ~5 min was required to convert the brown precipitate, formed immediately on mixing the solutions, to a pale green precipitate (Figure 4). After centrifugation to separate the solids, the supernatant solutions were examined by UV-vis spectroscopy. Remarkably, the UV-vis spectra (Figure 5) contain the characteristic absorption bands for neutral dissolved $\text{TCNQF}_4(\text{MeCN})$ ($\lambda_{\text{max}} = 386$ and 365 nm) or dissolved $\text{TCNQ}(\text{MeCN})$ ($\lambda_{\text{max}} = 374$ and 393 nm), thereby implying the generation of the neutral forms as a result of the reaction of the monoanionic radicals with $\text{Zn}^{2+}(\text{MeCN})$. The concentration of $\text{TCNQ}(\text{F}_4)(\text{MeCN})$ and remaining (unreacted) $\text{TCNQ}(\text{F}_4)^{\bullet-}(\text{MeCN})$ radical anions was quantitatively determined via UV-vis spectroscopy, by measuring the absorbance at 386 and 752 nm for $\text{TCNQF}_4(\text{MeCN})$ and $\text{TCNQF}_4^{\bullet-}(\text{MeCN})$, respectively or at 393 and 743 nm for $\text{TCNQ}(\text{MeCN})$ and $\text{TCNQ}^{\bullet-}(\text{MeCN})$, respectively by reference to appropriate calibration curves for these species. The results are summarized in Table 1. From these data, it can be concluded that both $\text{TCNQF}_4^{\bullet-}(\text{MeCN})$ and $\text{TCNQ}^{\bullet-}(\text{MeCN})$ radical monoanions react with $\text{Zn}^{2+}(\text{MeCN})$ in a 2:1 stoichiometric ratio to afford ~50% of the neutral $\text{TCNQ}(\text{F}_4)(\text{MeCN})$ species together with a $\text{Zn-TCNQ}(\text{F}_4)_{(s)}$ -based solid material.

Steady-state voltammetry was used to assess the redox level of $\text{TCNQ}(\text{F}_4)$ species formed after mixing the $\text{TCNQ}(\text{F}_4)^{\bullet-}(\text{MeCN})$ monoanions with $\text{Zn}^{2+}(\text{MeCN})$ in acetonitrile (0.1 M Bu_4NPF_6). In this case, after removal of the solids, the supernatant solutions could be studied without dilution. Figure 6 shows near steady-state voltammograms obtained with designated concentration ratios of $\text{TCNQ}(\text{F}_4)^{\bullet-}(\text{MeCN})$ and $\text{Zn}^{2+}(\text{MeCN})$. When the concentration ratios of $\text{TCNQ}(\text{F}_4)^{\bullet-}(\text{MeCN}) : \text{Zn}^{2+}(\text{MeCN})$ were 2:2 or 2:1, the residual $\text{TCNQ}(\text{F}_4)^{\bullet-}(\text{MeCN})$ concentration remaining after reaction with $\text{Zn}^{2+}(\text{MeCN})$ was very small. This conclusion was based on the fact the anodic (positive) currents associated the oxidation of the radical anions back to neutral forms were small relative to the negative currents for the reduction of the $\text{TCNQ}(\text{F}_4)(\text{MeCN})$ reaction products. In contrast, when the concentration ratio of $\text{TCNQ}(\text{F}_4)^{\bullet-}(\text{MeCN})$ to $\text{Zn}^{2+}(\text{MeCN})$ was 2:0.5, the oxidation currents for the $\text{TCNQ}(\text{F}_4)^{\bullet-/0}(\text{MeCN})$ processes are almost twice those of the reduction currents for the

TCNQ(F₄)^{0/•-}_(MeCN) processes, implying that after reaction with Zn²⁺_(MeCN), the concentrations of TCNQF₄^{•-}_(MeCN) and TCNQ^{•-}_(MeCN) remaining are about twice those of their neutral forms. These steady-state results confirm the conclusions drawn from UV-vis data and clearly that the reactions between the TCNQ(F₄)^{•-}_(MeCN) anionic radicals and Zn²⁺_(MeCN) cation occur via a 2:1 TCNQ(F₄)^{•-}_(MeCN) : Zn²⁺_(MeCN) stoichiometric ratio to generate ~50% of neutral TCNQ(F₄)_(MeCN) dissolved in acetonitrile along with pale green Zn-TCNQ(F₄)_(s)-based solids.

In the case of 2:2 TCNQ(F₄)^{•-}_(MeCN) : Zn²⁺_(MeCN) stoichiometry, voltammograms containing peaks were observed. The voltammetric features are attributed to the disproportionation of TCNQ(F₄)^{•-}_(MeCN), generated by reduction of TCNQ(F₄)_(MeCN) when the potential is scanned to more negative values, accompanied by precipitation of ZnTCNQ(F₄) solid (see further details below). Deposition of the solid onto the electrode surface may cause a decrease in active area of the electrode and/or in diffusion of TCNQ(F₄)_(MeCN) from the bulk solution to the electrode surface, and hence a decrease in the current.

3.2. Characterization of the Solid Products

IR spectroscopy allows the redox level of TCNQ(F₄) in the solids to be established since the vibrational modes for the C≡N and π(C=C) ring stretches are strongly sensitive to the degree of charge transfer.^{3,13-15,19} The IR spectra for all solids obtained from mixing TCNQF₄^{•-}_(MeCN) (or TCNQ^{•-}_(MeCN)) and Zn²⁺_(MeCN) solutions at different ratios are identical within experimental error.

Figure 7 shows the IR spectra for solids derived from a 2:1 ratio. IR spectrum for the Zn-TCNQF_{4(s)} based solid (Figure 7a) contains two ν(C≡N) bands at lower frequency (2165 and 2137 cm⁻¹) than might be expected for the TCNQF₄^{•-} monoanion. However, the frequencies agree well with those reported for [Co(C₅Me₅)₂⁺]₂(TCNQF₄)²⁻ (ν(C≡N) = 2168 and 2133 cm⁻¹)¹⁷ and [Ni(C₅Me₅)₂⁺]₂(TCNQF₄)²⁻ (ν(C≡N) = 2167 and 2131 cm⁻¹).²⁰ Therefore, they are assigned to the presence of the TCNQF₄²⁻ dianion. Furthermore, these frequencies are close to those (2161 and 2136 cm⁻¹, see Figure S1) obtained from the ZnTCNQF₄ solid material formed by direct reaction with TCNQF₄²⁻_(MeCN), generated electrochemically in acetonitrile (0.1 M Bu₄NPF₆) by exhaustive electrolysis, when Zn²⁺_(MeCN) is added at a 1:1 concentration ratio. The ν(C≡N) band at 2181 cm⁻¹, which is at

a higher frequency than found for TCNQF_4^{2-} but lower than that for neutral TCNQF_4 (2225 cm^{-1})^{9,15}, implies that the solid also may contain a small amount of $\text{TCNQF}_4^{\bullet-}$, probably having the composition $\text{Zn}(\text{TCNQF}_4)_2(\text{H}_2\text{O})_2$. Further support for this conclusion was obtained via UV-vis spectroscopy as the characteristic bands^{15,16} for $\text{TCNQF}_4^{\bullet-}(\text{MeCN})$ with λ_{max} values of 411 and 752 nm were observed upon dissolving the solid in acetonitrile. The weak and broad IR absorption band located at $\sim 3450\text{ cm}^{-1}$, is indicative of the presence of a small amount of water.^{19,21} Three very weak bands at 2874, 2930 and 2968 cm^{-1} are indicative of trace Bu_4N^+ , postulated to be derived from the electrolyte (0.1 M Bu_4NPF_6), as IR bands for $\text{Bu}_4\text{NPF}_6(\text{s})$ are located at 2878, 2938 and 2966 cm^{-1} (data not shown). No IR bands for the $\text{C}\equiv\text{N}$ stretch for coordinated CH_3CN , expected at 2270 to 2215 cm^{-1} ,^{10,22} were detected.

In the case of the Zn-TCNQ based solid, IR data (Figure 7b) contain two characteristic low energy bands at 2156 and 2116 cm^{-1} , confirming the presence of TCNQ^{2-} .^{3,23,24} These frequencies are in good agreement with those reported for Na_2TCNQ (2164 and 2096 cm^{-1}),²³ $\text{Zn}(\text{TCNQ})\text{bpy}\cdot 6\text{CH}_3\text{OH}$ (2194 and 2121 cm^{-1})³ and the newly synthesized series of TCNQ^{2-} -based compounds by Robson *et al.* (2152 – 2194 and 2100 – 2166 cm^{-1}).²⁴ Further support of the presence of the dianion was also obtained by the location of IR bands at 814 and 1053 cm^{-1} associated with the ring bending $\delta(\text{C-H})$. These bands are in excellent agreement with those of 815 and 1050 cm^{-1} reported for $\text{Ni}^{2+}\text{TCNQ}^{2-}$.²⁵

As applies in the Zn- TCNQF_4 case, the IR signature for the presence of $\text{TCNQ}^{\bullet-}$ in the Zn-TCNQ solid also was evident by the $\nu(\text{C}\equiv\text{N})$ stretch at 2225 cm^{-1} , which is consistent with the frequencies of 2196 , 2222 , 2224 and 2226 cm^{-1} , reported for solvated $\text{Zn}(\text{TCNQ})_2(\text{H}_2\text{O})_2$,²⁶ $\text{Zn}(\text{TCNQ})_2(\text{MeOH})_2$, $\text{Ni}(\text{TCNQ})_2(\text{MeOH})_2$ and $\text{Ni}(\text{TCNQ})_2(\text{H}_2\text{O})_2$ analogues, respectively.¹² The presence of a broad band at $\sim 3450\text{ cm}^{-1}$ implies the presence of water.^{19,21} In the spectrum, the three weak characteristic bands for Bu_4N^+ (as mentioned above) are also detected, indicating the presence of a small amount this cation, probably in form of Bu_4NPF_6 , in the solid.

In summary, the IR data implies that the solids contain the dianions, $\text{TCNQ}(\text{F}_4)^{2-}$ as $\text{ZnTCNQ}(\text{F}_4)$ together with small quantities of the $\text{TCNQ}(\text{F}_4)^{\bullet-}$ monoanion radicals, probably in the form of hydrated $\text{Zn}(\text{TCNQF}_4)_2(\text{H}_2\text{O})_2$ or $\text{Zn}(\text{TCNQ})_2(\text{H}_2\text{O})_2$ and Bu_4NPF_6 from the electrolyte.

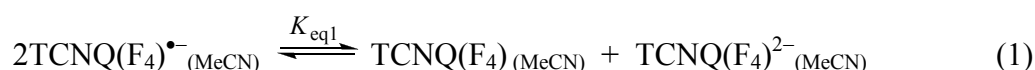
Elemental analysis data for the solid obtained by reacting $\text{TCNQF}_4^{\bullet-}(\text{MeCN})$ with $\text{Zn}^{2+}(\text{MeCN})$ in a 2:1 ratio (see Section 2.2) have been used to determine the empirical formula of the solid. Accordingly, the solid can be approximately represented as $\text{Zn}^{2+}\text{TCNQF}_4^{2-} \cdot 0.05\text{Zn}^{2+}(\text{TCNQF}_4^{\bullet-})_2(\text{H}_2\text{O})_2 \cdot 0.06\text{Bu}_4\text{NPF}_6 \cdot 0.3\text{H}_2\text{O}$ since experimental (calculated) data are %C: 42.65 (42.21), %H: 0.80 (0.74), %N: 15.55 (15.51), %Zn: 16.67 (17.05). The presence of small amounts of $\text{TCNQF}_4^{\bullet-}$, Bu_4N^+ and H_2O , as detected in the FT-IR spectrum, can be attributed to co-crystallization of these compounds during the precipitation of the dominant ZnTCNQF_4 solid product. The elemental analysis data confirm that the major TCNQF_4 based species in the solid is the TCNQF_4^{2-} dianion with a small amount of the monoanion being present.

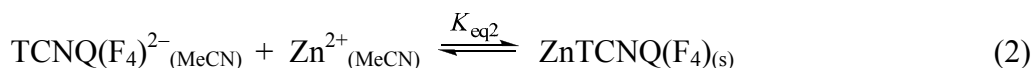
The elemental analysis results are consistent with data revealed from examination of the UV-vis spectroscopic and steady-state voltammetric experiments. Thus, all the evidence implies that in the presence of $\text{Zn}^{2+}(\text{MeCN})$ cations, the $\text{TCNQ}(\text{F}_4)^{\bullet-}(\text{MeCN})$ radical anion disproportionates to $\text{TCNQ}(\text{F}_4)^{2-}$ dianion (in form of $\text{ZnTCNQ}(\text{F}_4)_{(\text{s})}$) and neutral $\text{TCNQ}(\text{F}_4)_{(\text{MeCN})}$.

In the majority of cases, reaction of $\text{TCNQF}_4^{\bullet-}$ or $\text{TCNQ}^{\bullet-}$ with a transition metal cation leads to formation of a coordination polymer containing the monoanion. Nevertheless, detection of both the monoanions and dianions in chemically synthesized products has been also reported. For instance, Dunbar *et al.* showed that when methanol solutions of LiTCNQF_4 and $\text{Mn}(\text{CH}_3\text{CN})_4(\text{BF}_4)_2$ were reacted in a 1:1 ratio for two weeks, a compound containing both $\text{TCNQF}_4^{\bullet-}$ and TCNQF_4^{2-} was isolated.¹⁴ Similarly, Miller *et al.* reported that upon mixing acetonitrile solutions of Bu_4NTCNQ and $\text{M}(\text{CH}_3\text{CN})_6\text{SbF}_6$ ($\text{M}^{\text{II}} = \text{Mn}$ or Ni), solids having empirical formulae $\text{Mn}(\text{TCNQ})_{1.38}(\text{Bu}_4\text{N})_{0.1}(\text{SbF}_6)_{0.34} \cdot 1.32\text{CH}_3\text{CN}$ and $\text{Ni}(\text{TCNQ})_{1.32}(\text{Bu}_4\text{N})_{0.04}(\text{SbF}_6)_{0.24} \cdot 0.54\text{CH}_3\text{CN}$ were produced,¹⁰ although no rationalization of these stoichiometries was proposed.

3.3. Mechanistic Aspects of the Dianion Generation

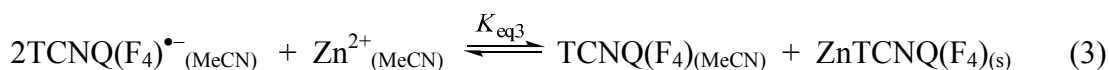
A mechanism that accounts for the disproportionation of the $\text{TCNQ}(\text{F}_4)^{\bullet-}(\text{MeCN})$ monoanionic radicals in acetonitrile solution containing $\text{Zn}^{2+}(\text{MeCN})$ is represented via equations 1 and 2.



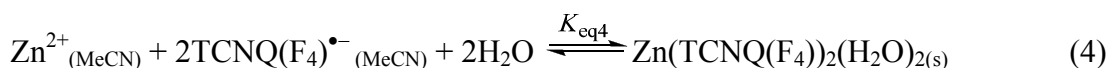


where, $K_{\text{eq}1} = 10^{-\frac{F}{2.303RT}(E_1^0 - E_2^0)}$, $27,28$ or $10^{-\frac{E_1^0 - E_2^0}{0.0585}}$ at 295 K (22 °C), F = Faraday constant, R = universal gas constant, T = temperature (K), E_1^0 and E_2^0 are the reversible formal potentials for the $\text{TCNQ}(\text{F}_4)^{0/\bullet-}_{(\text{MeCN})}$ and $\text{TCNQ}(\text{F}_4)^{\bullet-/2-}_{(\text{MeCN})}$ processes, respectively and $K_{\text{eq}2} = K_{\text{sp}}^{-1}$ (K_{sp} = solubility product of $\text{ZnTCNQ}(\text{F}_4)_{(\text{s})}$).

The equilibrium constants for the disproportionation reaction in equation 1 ($K_{\text{eq}1} = 9 \times 10^{-10}$ for TCNQF_4 as $E_1^0 - E_2^0 = 0.53 \text{ V}^{15}$ or 4×10^{-10} for TCNQ as $E_1^0 - E_2^0 = 0.55 \text{ V}^{29,30}$) are both very small. Since the disproportionation is not favored in the absence of process 2, K_{sp} has to be sufficiently small in order to facilitate the formation of $\text{ZnTCNQ}(\text{F}_4)_{(\text{s})}$. Combining equations 1 and 2 yields equation 3, the net reaction that leads to formation of $\text{ZnTCNQ}(\text{F}_4)_{(\text{s})}$ and neutral $\text{TCNQ}(\text{F}_4)_{(\text{MeCN})}$.



In practice, a small amount of $\text{TCNQ}(\text{F}_4)^{\bullet-}$ is observed, presumably due to the reaction given in equation 4.



where the water comes from the $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ salt.

The solubility of $\text{ZnTCNQF}_4_{(\text{s})}$ has been varified by mixing 10.0 mM acetonitrile solutions of $\text{Zn}^{2+}_{(\text{MeCN})}$ and the air stable dianion,¹⁶ $\text{TCNQF}_4^{2-}_{(\text{MeCN})}$ generated electrochemically in acetonitrile (0.1 M Bu_4NPF_6), in a molar ratio of 1:1. A precipitate formed immediately when the two solutions were mixed together. The solid was collected and washed 5 times with acetonitrile and then shaken vigorously in acetonitrile for several minutes. The solution obtained after centrifugation was studied by UV-vis spectroscopy. No characteristic absorption bands for $\text{TCNQF}_4^{2-}_{(\text{MeCN})}$ dianion could be detected, implying that the solubility of $\text{ZnTCNQF}_4_{(\text{s})}$ (the formula is confirmed below) is extremely low in acetonitrile.

The IR spectrum for the $\text{ZnTCNQF}_4_{(\text{s})}$ material, which was “chemically” synthesized by addition of 10.0 mM $\text{Zn}^{2+}_{(\text{MeCN})}$ to 10.0 mM electrochemically generated $\text{TCNQF}_4^{2-}_{(\text{MeCN})}$ solution at a 1:1 molar ratio, exhibits only the two characteristic $\nu(\text{C}\equiv\text{N})$ bands for TCNQF_4^{2-} dianion,^{17,20} at 2161 and 2136 cm^{-1} and also provides no evidence for

the $\text{TCNQF}_4^{\bullet-}$ radical monoanion (Figure S1). Thus, this solid is a TCNQF_4^{2-} derivative devoid of any $\text{TCNQF}_4^{\bullet-}$. Elemental analysis is consistent with the empirical formula $\text{ZnTCNQF}_4 \cdot 0.03\text{Bu}_4\text{NPF}_6 \cdot 0.3\text{H}_2\text{O}$ (found: %C: 41.24, %H: 0.53, %N: 15.94 and %Zn: 17.91; and calculated: %C: 41.80, %H: 0.47, %N: 15.65 and %Zn: 18.24). Traces of Bu_4N^+ and H_2O were detected in the IR spectrum.

Although monoanion disproportionation (equation 1) is facilitated by the presence of $\text{Zn}^{2+}_{(\text{MeCN})}$ in acetonitrile, the extent to which this reaction occurs is strongly dependent upon the concentration of water present. The presence of trace amounts of hydrated $\text{Zn}(\text{TCNQ}(\text{F}_4))_2(\text{H}_2\text{O})_2$ is a consequence of the reaction in equation 4, which occurs in competition with disproportionation. The Zn^{2+} salt, $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ provides a source of water and the acetonitrile solvent contains adventitious water which allow the hydrated $\text{TCNQ}(\text{F}_4)$ solid to be formed. Consistent with this hypothesis, it was established that upon deliberate addition of water, the disproportionation of $\text{TCNQ}(\text{F}_4)^{\bullet-}_{(\text{MeCN})}$ in the presence of $\text{Zn}^{2+}_{(\text{MeCN})}$ (equation 3) becomes disfavored, whilst the reverse (comproportionation) reaction is now favored. Consequently, the concentration of the $\text{TCNQ}(\text{F}_4)^{\bullet-}_{(\text{MeCN})}$ monoanions remaining in solution increases upon increasing the concentration of water. This is supported by the increase in the absorbance at 411 and 752 nm or 420 and 743 nm (Figure 8), which are characteristic λ_{max} values for $\text{TCNQF}_4^{\bullet-}_{(\text{MeCN})}$ or $\text{TCNQ}^{\bullet-}_{(\text{MeCN})}$, respectively. Importantly, when the water content is $\geq 3\%$ (v/v), no precipitation of $\text{ZnTCNQ}(\text{F}_4)_{(\text{s})}$ or any other solids are observed; and the concentration of the $\text{TCNQ}(\text{F}_4)^{\bullet-}_{(\text{MeCN})}$ monoanions in solutions in the presence or absence of both $\text{Zn}^{2+}_{(\text{MeCN})}$ and $\geq 3\%$ H_2O remain constant as evidenced by UV-vis spectroscopic data (see Figure S2).

The fact that the disproportionation of the $\text{TCNQ}(\text{F}_4)^{\bullet-}$ monoanions can be inhibited by addition of water is attributed to the enhanced solubility of $\text{ZnTCNQF}_4_{(\text{s})}$. This conclusion is further supported by a series of experiments described below:

(i) Mixing acetonitrile $\text{TCNQ}(\text{F}_4)^{\bullet-}_{(\text{MeCN})}$ radical anions with $\text{Zn}^{2+}_{(\text{MeCN})}$ in a 2:1 molar ratio yields, in principle, via disproportionation, soluble $\text{TCNQ}(\text{F}_4)_{(\text{MeCN})}$ and solid $\text{ZnTCNQ}(\text{F}_4)_{(\text{s})}$. The suspensions were diluted 100-fold and then UV-vis spectra were recorded before and after addition of water (Figure 9). Clearly, increasing the water content results in a marked increase in the concentration of $\text{TCNQ}(\text{F}_4)^{\bullet-}_{(\text{MeCN})}$ with a concomitant decrease in $\text{TCNQ}(\text{F}_4)_{(\text{MeCN})}$ concentrations. This observation is supported visually by inspection of photographs in Figure 10. Thus, addition of 10 % (v/v) water

gives rise to a change from a green suspension of $\text{ZnTCNQ}_{(s)}$ and dissolved $\text{TCNQ}_{(\text{MeCN})}$ to a clear solution of the monoanion.

(ii) $\text{ZnTCNQ}(\text{F}_4)$ solids prepared from $\text{TCNQ}(\text{F}_4)^{\bullet-}_{(\text{MeCN})}$ and $\text{Zn}^{2+}_{(\text{MeCN})}$ acetonitrile solutions at a 2:1 molar ratio were washed with 5×2 mL of acetonitrile and then added into neat acetonitrile to give suspensions. After addition of 3% (v/v) water and shaking for 2 min, no prominent UV-vis bands were detected in the solution phase (Figures 11a and b – black curves). Known concentrations of $\text{TCNQ}(\text{F}_4)_{(\text{MeCN})}$ were then added. After shaking the suspensions for a further 2 min, UV-vis spectra were recorded (Figure 11 – red, blue and green curves) and confirmed that the addition of $\text{TCNQ}(\text{F}_4)_{(\text{MeCN})}$ led to formation of $\text{TCNQ}(\text{F}_4)^{\bullet-}_{(\text{MeCN})}$ in solution as evidenced by the increase in the absorbance at 752(743) nm.

(iii) Suspensions of $\text{ZnTCNQ}(\text{F}_4)$ solids were prepared in acetonitrile as in (ii). However, this time, water was added after the addition of $\text{TCNQ}(\text{F}_4)_{(\text{MeCN})}$. Prior to addition of water, only UV-vis absorption bands for neutral $\text{TCNQ}(\text{F}_4)_{(\text{MeCN})}$ were detected. Upon addition of water, the absorbance from neutral $\text{TCNQ}(\text{F}_4)_{(\text{MeCN})}$ decreased, whilst that for $\text{TCNQ}(\text{F}_4)^{\bullet-}_{(\text{MeCN})}$ increased (data not shown).

(iv) In acetonitrile solutions containing a suspension of $\text{ZnTCNQF}_{4(s)}$ in the presence (3% v/v) or absence of water, no UV-vis spectrum for the $\text{TCNQF}_4^{2-}_{(\text{MeCN})}$ dianion could be detected. This result attests to the very low solubility of $\text{ZnTCNQF}_{4(s)}$ in acetonitrile, even following the addition of 3% (v/v) water. However, when neutral $\text{TCNQF}_{4(\text{MeCN})}$ was added to the 3% water/acetonitrile $\text{ZnTCNQF}_{4(s)}$ suspension, absorbance bands due to the presence of dissolved $\text{TCNQF}_4^{\bullet-}_{(\text{MeCN})}$ were observed, thereby again confirming that the comproportionation reaction is favored under these conditions.

The combination of observations from experiments (i), (ii), (iii) and (iv) attests to the fact that the solubility of solid $\text{ZnTCNQ}(\text{F}_4)$ increases on addition of water, thereby disfavoring the disproportionation reaction and regenerating $\text{TCNQ}(\text{F}_4)^{\bullet-}_{(\text{MeCN})}$ via the comproportionation reaction.

The significant outcome of this study is a new understanding and rationalization of how to control and quantitatively probe the role of the disproportionation reactions involving the $\text{TCNQ}(\text{F}_4)^{\bullet-}_{(\text{solvent})}$, neutral $\text{TCNQ}(\text{F}_4)_{(\text{solvent})}$ and $\text{TCNQ}(\text{F}_4)^{2-}_{(\text{solvent})}$ dianions. The disproportionation of $\text{TCNQ}(\text{F}_4)^{\bullet-}_{(\text{solvent})}$ is promoted by the precipitation of insoluble metal- $\text{TCNQ}(\text{F}_4)^{2-}$ coordination polymers. Solvent dependent disproportionation–

comproportionation reactions in combination with solubility issues can explain why different redox levels are detected in the synthesis of TCNQ(F₄)-based materials when the preparative methods involve the reaction of the radical anions with metal cation precursors.

4. Conclusions

This study highlights the crucial role that metal ions and water have on promoting and controlling the extent of the disproportionation reactions associated with the TCNQ(F₄)^{•-}_(solvent) monoanionic radicals and ultimately the solid products isolated from reactions with the radical anions. In the absence of a precipitation reaction, e.g. when generated electrochemically in acetonitrile (0.1 M Bu₄NPF₆), the radical anions are thermodynamically very stable with respect to the disproportionation. In the absence of water, addition of Zn²⁺_(MeCN) promotes the disproportionation of TCNQ(F₄)^{•-}_(MeCN) radicals, leading to generation of the neutral TCNQ(F₄)_(MeCN) and precipitation of sparingly soluble ZnTCNQ(F₄)_(s). However, deliberate addition of water can be used to prevent the disproportionation reaction since the reverse (comproportionation) reaction is now favored giving rise to soluble mixture of Zn²⁺_(MeCN) and TCNQ(F₄)^{•-}_(MeCN) or hydrated Zn(TCNQ(F₄))₂(H₂O)₂ congeners. This study clarifies the interplay between the identity of the metal ion and presence of water in controlling the disproportionation/comproportionation reactions encountered in many TCNQ(F₄) chemical syntheses and provides a rationale for control of products. Importantly, this work has resolved not only the ambiguity arising from formation of TCNQ(F₄)-based materials in different redox levels when mixing solutions of metal cations and TCNQ(F₄)^{•-}, but also opens up the possibility to tune the composition of the final products. Rational rather than empirical methods of synthesis could be attractive in developing targeted strategies for generation of new TCNQ(F₄)-based materials, which may form the basis for molecular electronic, sensing or other devices (see introduction).

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Supporting Information Available: Figure S1 providing an FT-IR spectrum for a solid synthesized from TCNQF₄²⁻_(MeCN) and Zn²⁺_(MeCN) acetonitrile solutions, and Figure S2

which provides a comparison of UV-vis spectra for a $\text{TCNQF}_4^{\bullet-}(\text{MeCN})$ acetonitrile solution and a solution obtained by mixing $\text{TCNQF}_4^{\bullet-}(\text{MeCN})$ and $\text{Zn}^{2+}(\text{MeCN})$ acetonitrile solutions at a 2:1 molar ratio in the presence of 3% water. This material is free of charge via the Internet at <http://pubs.acs.org>.

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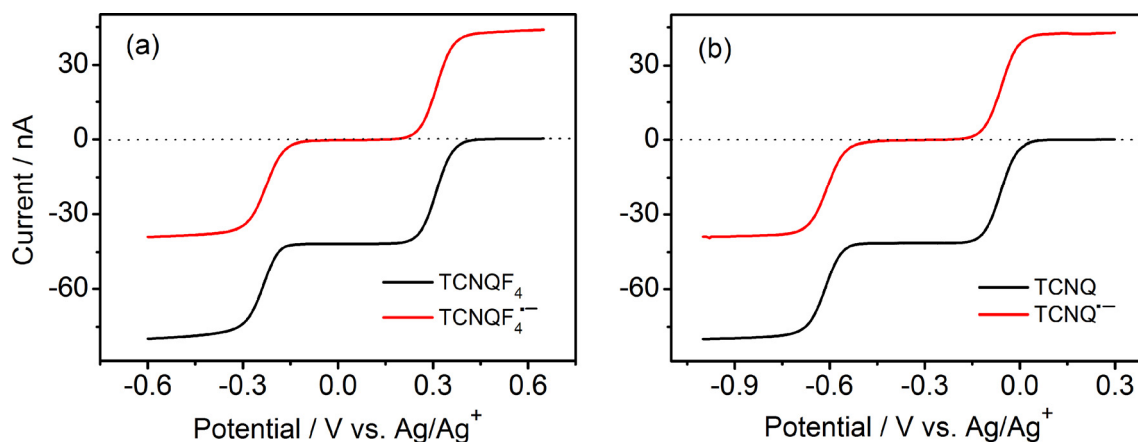


Figure 1. Near steady-state voltammograms obtained with a 11 μm diameter carbon fiber microelectrode at a scan rate of 20 mV s^{-1} for (a) $10.0 \text{ mM TCNQF}_4(\text{MeCN})$ and (b) $10.0 \text{ mM TCNQ}(\text{MeCN})$ in acetonitrile ($0.1 \text{ M Bu}_4\text{NPF}_6$) before (—) and after (—) bulk electrolysis.

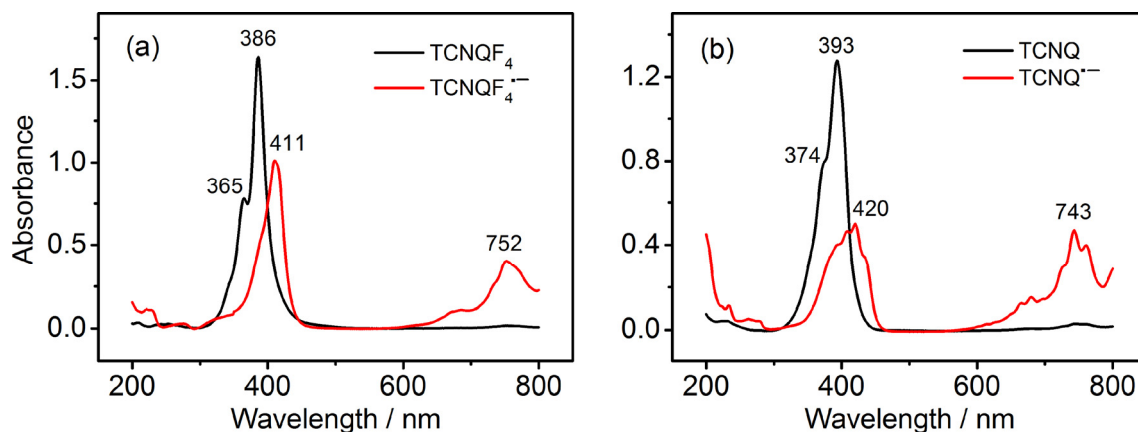


Figure 2. UV-vis spectra for (a) $0.02 \text{ mM TCNQF}_4(\text{MeCN})$ and (b) $0.02 \text{ mM TCNQ}(\text{MeCN})$ in acetonitrile ($0.1 \text{ M Bu}_4\text{NPF}_6$) recorded before and after exhaustive bulk electrolysis.

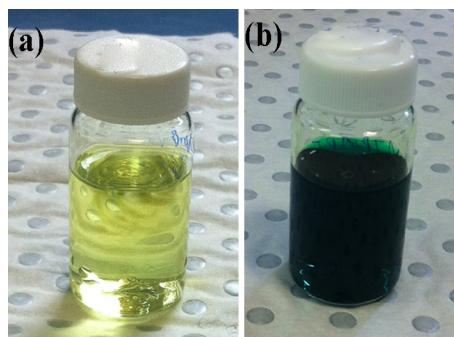


Figure 3. Photographs of solutions of $10.0 \text{ mM TCNQ}(\text{MeCN})$ in acetonitrile ($0.1 \text{ M Bu}_4\text{NPF}_6$) before (a) and after (b) exhaustive bulk electrolysis to reduce $\text{TCNQ}(\text{MeCN})$ to $\text{TCNQ}^{\bullet-}(\text{MeCN})$.

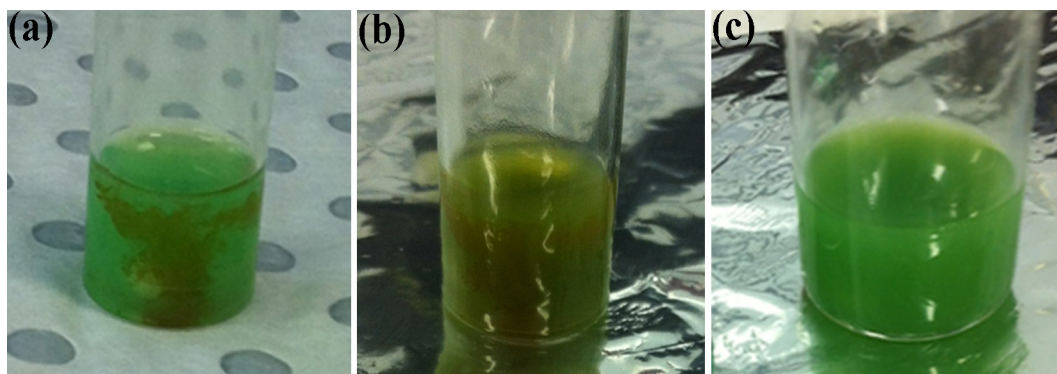


Figure 4. Photographs showing changes that take place when 0.5 equiv of $\text{Zn}^{2+}_{(\text{MeCN})}$ in acetonitrile is added dropwise into 1.0 equiv of $\text{TCNQ}^{\bullet-}_{(\text{MeCN})}$ acetonitrile solution: (a) just after addition of a few drops of $\text{Zn}^{2+}_{(\text{MeCN})}$ solution, (b) just after addition of all the $\text{Zn}^{2+}_{(\text{MeCN})}$ solution, (c) 5 min after addition of all the $\text{Zn}^{2+}_{(\text{MeCN})}$ solution.

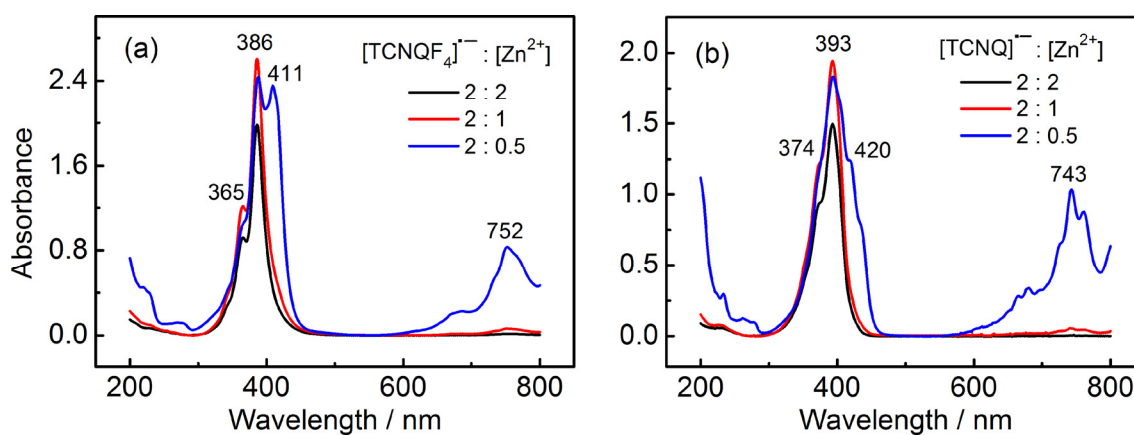


Figure 5. UV-vis spectra obtained after mixing acetonitrile solutions of (a) $\text{TCNQF}_4^{\bullet-}_{(\text{MeCN})}$ or (b) $\text{TCNQ}^{\bullet-}_{(\text{MeCN})}$ and $\text{Zn}^{2+}_{(\text{MeCN})}$ with designated ratios of initial concentrations (the solutions were diluted 100-fold before recording the spectra).

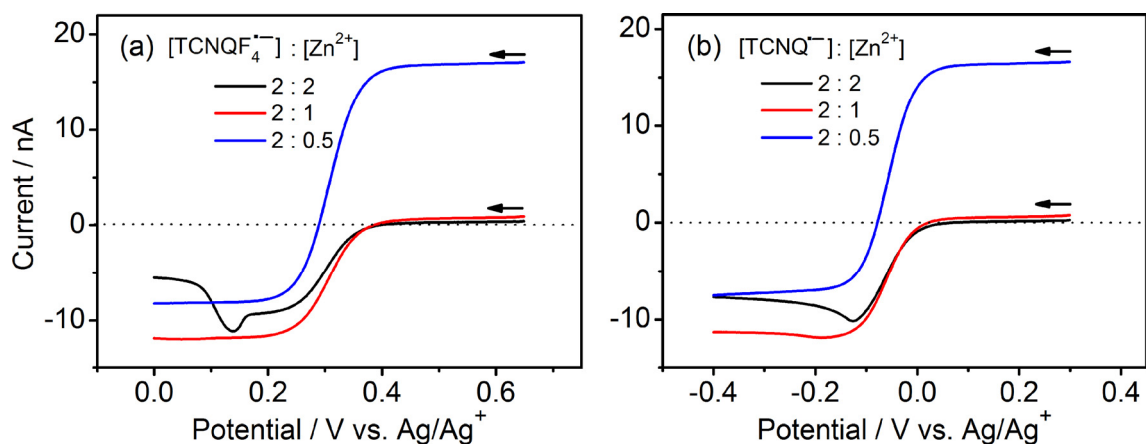


Figure 6. Near steady-state voltammograms obtained after mixing (a) TCNQF₄^{•-}_(MeCN) or (b) TCNQ^{•-}_(MeCN) with Zn²⁺_(MeCN) at designated concentration ratios when using a carbon fiber microelectrode (11 μm diameter) at a scan rate of 20 mV s⁻¹.

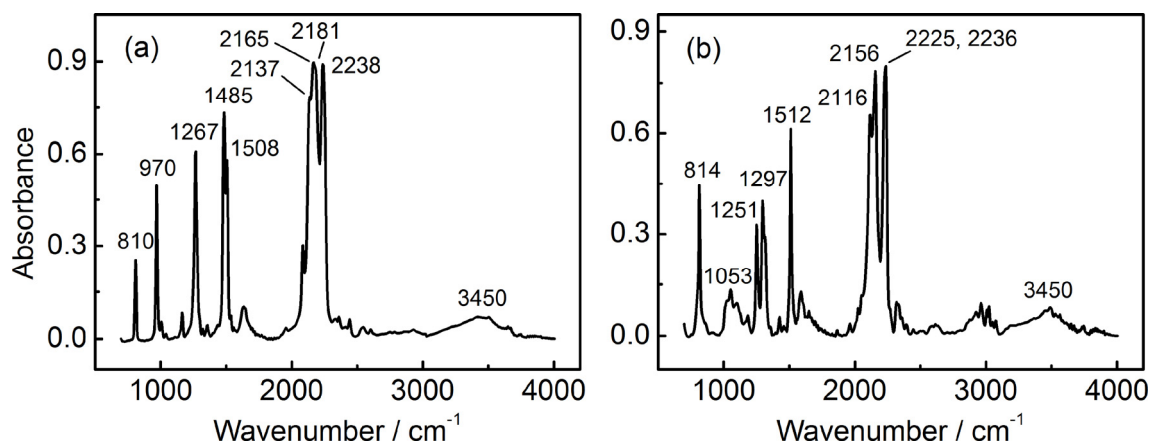


Figure 7. IR spectra for the solids obtained by mixing 5.0 mL of 10.0 mM Zn²⁺_(MeCN) and 10.0 mL of (a) 10.0 mM TCNQF₄^{•-}_(MeCN), (b) 10.0 mM TCNQ^{•-}_(MeCN).

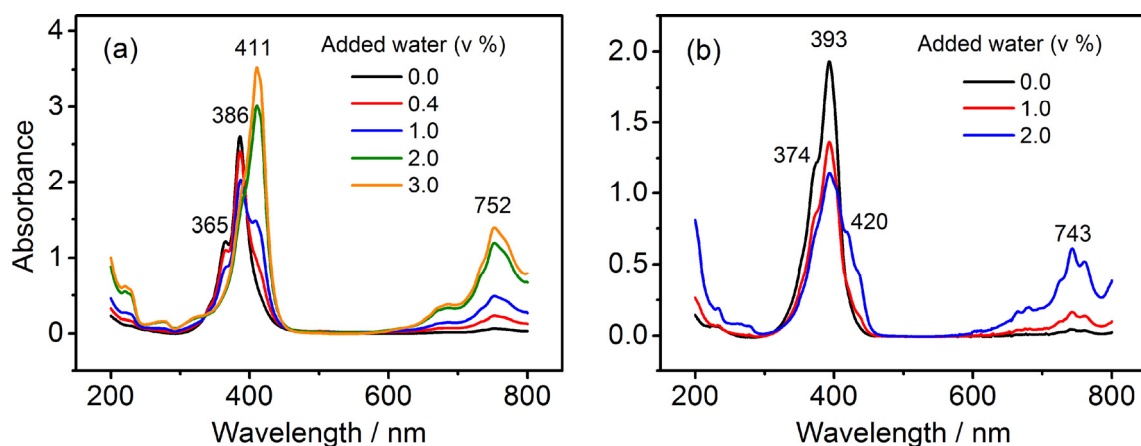


Figure 8. UV-vis spectra for solutions obtained after mixing (a) TCNQF₄^{•-}_(MeCN) and (b) TCNQ^{•-}_(MeCN) solutions with Zn²⁺_(MeCN) solution using a molar ratio of 2:1 in the presence of the designated percentage of added water.

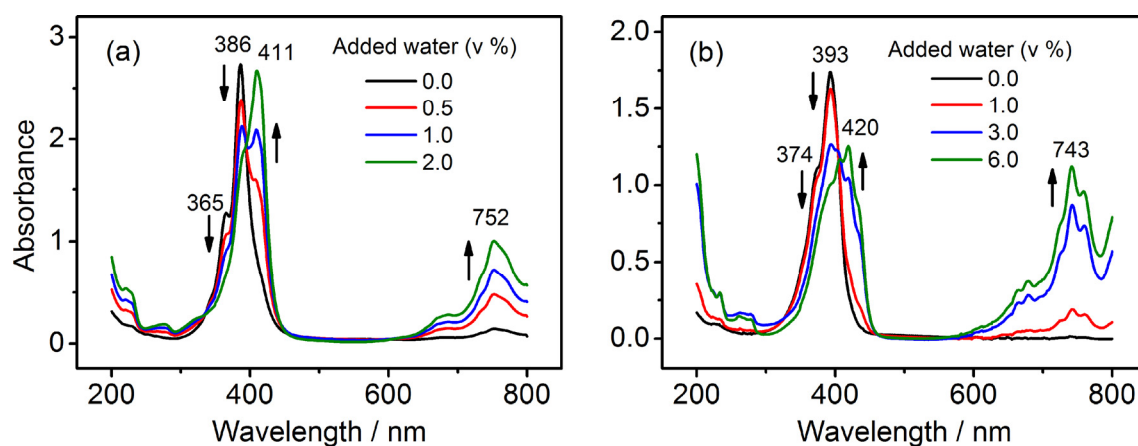


Figure 9. (a) UV-vis spectra for diluted (100-fold) suspension containing soluble $\text{TCNQF}_{4(\text{MeCN})}$ and solid $\text{ZnTCNQF}_{4(\text{s})}$, obtained by mixing acetonitrile solutions of $\text{TCNQF}_{4\bullet-}(\text{MeCN})$ and $\text{Zn}^{2+}(\text{MeCN})$ in a 2:1 molar ratio, followed by addition of designated amount of water, (b) as for (a) but TCNQ-based compounds instead of TCNQF_4 ones.

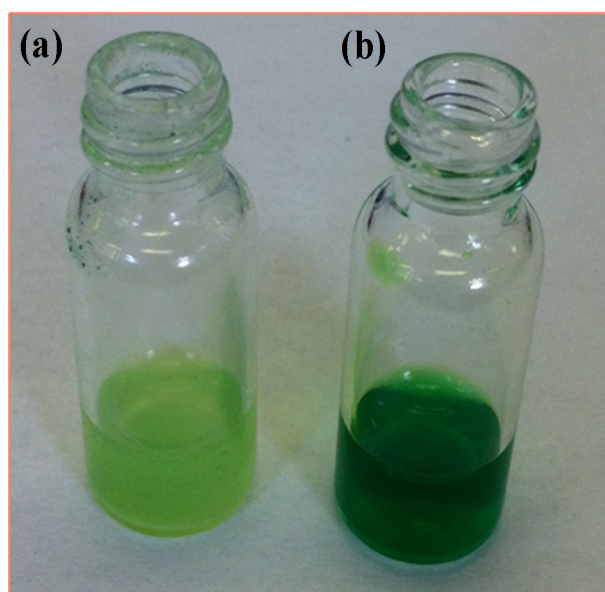


Figure 10. The color change of the suspension (a), obtained from mixing acetonitrile solutions of 1.0 equiv of $\text{TCNQ}\bullet- (\text{MeCN})$ and 0.5 equiv of $\text{Zn}^{2+}(\text{MeCN})$, after addition of 10 % (v/v) water (b).

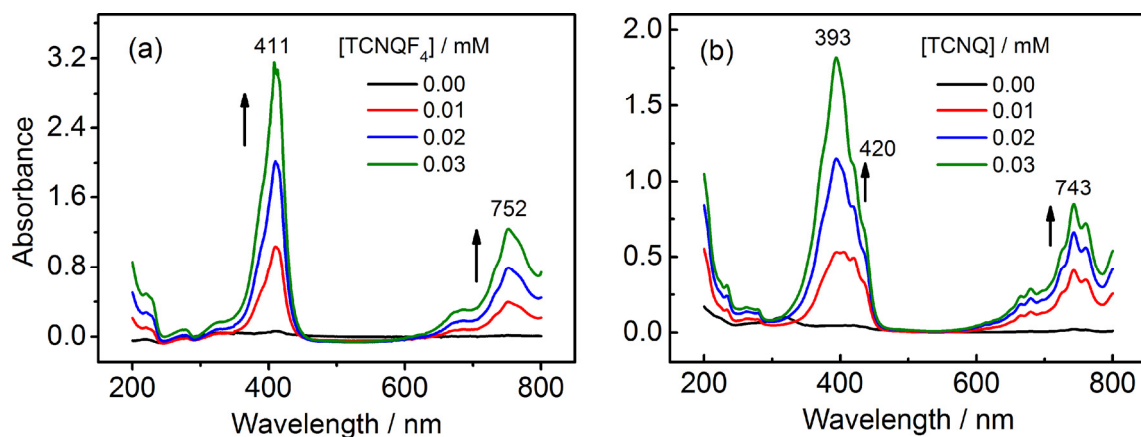


Figure 11. (a) UV-vis spectra derived from a suspension of $\text{ZnTCNQF}_{4(s)}$, formed from mixing $\text{TCNQF}_4^{\bullet-}(\text{MeCN})$ and $\text{Zn}^{2+}(\text{MeCN})$ acetonitrile solutions, in acetonitrile containing 3.0 % (v/v) water before and after addition of $\text{TCNQF}_{4(\text{MeCN})}$ at designated concentrations, (b) as for (a) but with TCNQ used instead of TCNQF_4 .

Table 1. Dependence of $\text{TCNQ}(\text{F}_4)_{(\text{MeCN})}$ and unreacted $\text{TCNQ}(\text{F}_4)^{\bullet-}(\text{MeCN})$ concentrations on the volumes of $\text{TCNQ}(\text{F}_4)^{\bullet-}(\text{MeCN})$ and $\text{Zn}^{2+}(\text{MeCN})$ solutions mixed together.

Experiment	10.0 mM $\text{TCNQ}(\text{F}_4)^{\bullet-}$ (mL)	10.0 mM Zn^{2+} (mL)	Initial $\text{TCNQ}(\text{F}_4)^{\bullet-}$ (mM)	Initial Zn^{2+} (mM)	Produced $\text{TCNQ}(\text{F}_4)$ (mM)	Unreacted $\text{TCNQ}(\text{F}_4)^{\bullet-}$ (mM)
1	2.0	2.0	5.0	5.0	2.3 (2.4) ^(a)	0.05 (0.05)
2	2.0	1.0	6.7	3.3	3.0 (3.1)	0.3 (0.3)
3	2.0	0.5	8.0	2.0	1.8 (1.8)	4.3 (4.2)

^(a) Values in parentheses are for TCNQF_4 species

Supporting Information

Solvent Controlled Reversible Disproportionation of TCNQF₄^{•-} and TCNQ^{•-} in the Presence of Zn²⁺

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The Supporting Information contains Figure 1 which is a FT-IR spectrum of ZnTCNQF₄ solid, obtained by mixing acetonitrile solutions of Zn²⁺_(MeCN) and TCNQF₄²⁻_(MeCN) in a molar ratio of 1:1 (Figure S1). Figure S2 provides a comparison of UV-vis spectra obtained by mixing acetonitrile solutions of TCNQF₄^{•-}_(MeCN) and Zn²⁺_(MeCN) in a 2:1 molar ratio in the presence of 3% (v/v) water, and an acetonitrile solution containing only the same concentration of TCNQF₄^{•-}_(MeCN).

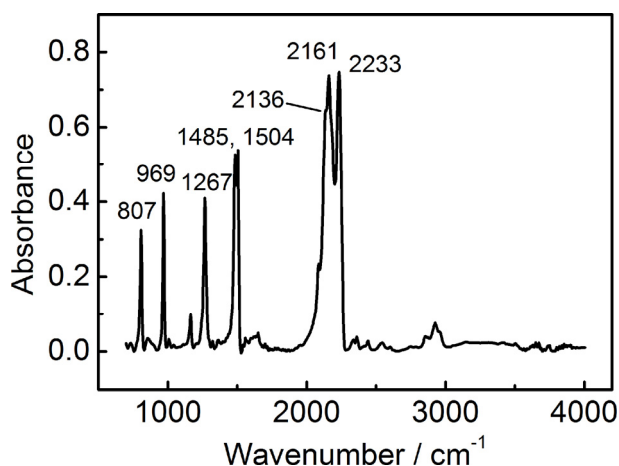


Figure S1. FT-IR spectrum for the solid obtained by mixing 10.0 mL of acetonitrile (0.1 M Bu_4NPF_6) solution containing 10.0 mM $\text{TCNQF}_4^{2-}(\text{MeCN})$ with 10.0 mL of 10.0 mM $\text{Zn}^{2+}(\text{MeCN})$ in acetonitrile.

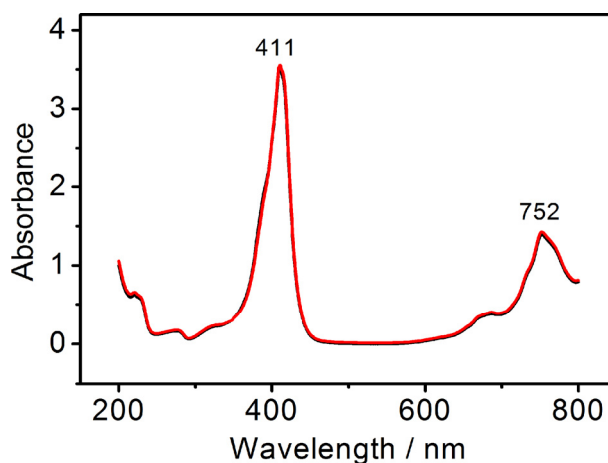


Figure S2. UV-vis spectra obtained after mixing acetonitrile solution containing 2.0 mL of 10.0 mM $\text{TCNQF}_4^{\bullet-}(\text{MeCN})$ with 1.0 mL of 10.0 mM $\text{Zn}^{2+}(\text{MeCN})$ solution to give a 2:1 molar ratio with 3% (v/v) water also present, followed by 100-fold dilution with acetonitrile (black curve). The red curve is for a pure $\text{TCNQF}_4^{\bullet-}(\text{MeCN})$ solution mixed with acetonitrile to provide the same dilution level, but without any water or $\text{Zn}^{2+}(\text{MeCN})$ being present. The two spectra are experimentally indistinguishable.

Chapter 7

Fingerprints for Identification of TCNQF₄ Redox Levels

7.1. Introduction

This chapter provides an overview range of spectroscopic and electrochemical techniques that can be used for the identification of the redox levels in TCNQF₄-based materials. Infrared (IR) spectroscopy is a powerful technique for the redox level identification, generally via the C≡N stretch. Ultraviolet-visible (UV-vis) and also Raman spectroscopy have been used less frequently than IR spectroscopy. However, investigations in this thesis have revealed that TCNQF₄, and its anions (TCNQF₄^{•-} and TCNQF₄²⁻) present in a compound can be qualitatively and quantitatively identified using UV-vis spectroscopy or steady-state voltammetry. In the case of UV-vis spectroscopy, TCNQF₄ in each redox level has two characteristic wavelengths of maximum absorption (λ_{max}). The maximum absorbance of the strongest band can be used for quantitative determination using the Beer-Lambert law. Under steady-state voltammetric conditions, TCNQF₄ undergoes two well separated reduction processes, TCNQF₄^{•-} can be either reduced or oxidized, whilst TCNQF₄²⁻ can only be oxidized in two steps to return to TCNQF₄. Consequently, TCNQF₄ and its anions can be electrochemically detected. Furthermore, the relationship of the limiting current and concentration of TCNQF₄, TCNQF₄^{•-} and TCNQF₄²⁻ in a solution can be applied for quantitative determination. The redox level(s) of TCNQF₄ moieties within a material also can be distinguished using Raman spectroscopy, specifically via the vibration modes for C≡N and/or C=C ring stretches.

Declaration for Thesis Chapter 7.2

Declaration by candidate

In the case of Chapter 7.2, the nature and extent of my contribution to the work was the following:

Nature of contribution	Extent of contribution (%)
Initiation, key ideas, experimental work, writing up	90

The following co-authors contributed to the work.

Name	Nature of contribution
Lisandra L. Martin	Initiation, key ideas, writing up
Alan M. Bond	Initiation, key ideas, writing up

Candidate's Signature

	06/06/2012
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Declaration by co-authors

The undersigned hereby certify that:

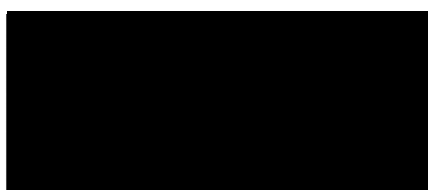
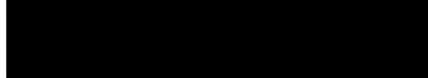
- (7) the above declaration correctly reflects the nature and extent of the candidate's contribution to this work, and the nature of the contribution of each of the co-authors.
- (8) they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;
- (9) they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
- (10) there are no other authors of the publication according to these criteria;
- (11) potential conflicts of interest have been disclosed to (a) granting bodies, (b) the editor or publisher of journals or other publications, and (c) the head of the responsible academic unit; and
- (12) the original data are stored at the following location and will be held for at least five years from the date indicated below:

Location

School of Chemistry, Monash University, Clayton

Lisandra L. Martin

Alan M. Bond

	23/5/12
	18/5/12

Spectroscopic and Electrochemical Fingerprints Available for Identification of TCNQF₄ Redox Levels (TCNQF₄ = 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane)

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Abstract

Solution and solid state fingerprints for the identification of 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (TCNQF₄) redox levels by spectroscopic and electrochemical techniques are described. Unlike reduced TCNQ (7,7,8,8-tetracyanoquinodimethane) analogues, both TCNQF₄^{•-} and TCNQF₄²⁻ are stable for hours even when dissolved in an organic solution under aerobic conditions. Consequently, all these redox levels are readily accessible. UV-vis spectroscopy provides a simple and very sensitive method for the qualitative and quantitative determination of TCNQF₄ and its anions, TCNQF₄^{•-} and TCNQF₄²⁻, via their distinctly different wavelengths of maximum absorption and known molar extinction coefficients at these wavelengths. Steady-state voltammetry is also a valuable technique for the distinction of TCNQF₄ redox levels as well as qualitative and quantitative determination. TCNQF₄ is sequentially reduced to TCNQF₄^{•-} and TCNQF₄²⁻ by two one-electron reduction processes; TCNQF₄^{•-} can be either reduced to TCNQF₄²⁻ or oxidized to TCNQF₄, whilst TCNQF₄²⁻ can undergo two one-electron oxidation processes. Infrared spectroscopy has been successfully used for the determination of the TCNQF₄ redox states via the measurement of the frequency of the C≡N stretch. The IR bands for this stretch shift to lower energy upon increasing the negative charge on the series TCNQF₄, TCNQF₄^{•-} and TCNQF₄²⁻. To date, studies with a wide range of inorganic and organic TCNQF₄-based materials have revealed that TCNQF₄ redox levels can be readily distinguished by Raman spectroscopy. As with IR spectra, Raman vibration modes for the C≡N stretch exhibit lower energy as the negative charge on TCNQF₄ increases. The Raman C=C ring stretch band also is sensitive to the redox levels and occurs at around 1665, 1640 and 1650 cm⁻¹ for TCNQF₄, TCNQF₄^{•-} and TCNQF₄²⁻, respectively.

1. Introduction

7,7,8,8-tetracyanoquinodimethane (TCNQ) chemistry is now well established as being of substantial fundamental and applied interest^{1,2} with characteristics and properties being strongly dependent of the redox level (TCNQ, TCNQ^{•-} and TCNQ²⁻).³⁻⁵ Recently, charge-transfer materials containing reduced 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (TCNQF₄) and organic or metal electron donors have also become of wide interest and extensively studied^{6,7} in the context of the systematic synthesis and structural characterization.⁸⁻¹⁰ Physical properties of TCNQF₄-based materials such as conductivity,^{11,12} magnetism,^{13,14} field-emission,⁶ and their use in electrical switching and memory storage¹² are now established and as is the case with TCNQ materials. TCNQF₄ is a much stronger electron acceptor than TCNQ due to the combination of delocalized electronic structure and the powerful electron-withdrawing effect of the four fluorine atoms^{7,15} (Figure 1a). TCNQF₄ can be readily reduced to form the TCNQF₄^{•-} monoanion and the TCNQF₄²⁻ dianion (see structures in Figures 1b and c). Ideally, following their synthesis, TCNQF₄-based materials would be characterized by single crystal X-ray analysis to determine the structural organization and the redox levels of the TCNQF₄ units. The redox levels can be estimated from the crystal structure using the Kistenmacher relationship, which correlates the bond lengths between atoms in TCNQF₄ units.^{8,9} However, single crystal structures of many TCNQF₄ materials often cannot be obtained. Under these circumstances, spectroscopic techniques need to be used to estimate the redox level of the TCNQF₄ moieties present in these materials. Possible use of Ultraviolet-visible (UV-vis), infrared (IR) and Raman spectroscopies, and electrochemical methods for the identification of TCNQF₄ redox levels is established in this study.

2. UV-vis Spectroscopy

TCNQF₄^{•-} and TCNQF₄²⁻ are stable for several hours under aerobic conditions.⁷ In contrast, TCNQ²⁻ rapidly decomposes to give orange colored α , α -dicyano-p-toluoylcyanide (DCTC⁻)^{17,18} on exposure to air. Thus, TCNQF₄-based materials can be dissolved in organic solvents and easily studied in the solution phase. UV-vis spectra for TCNQF₄, TCNQF₄^{•-} and TCNQF₄²⁻ dissolved in acetonitrile under aerobic condition are shown in Figure 2.⁷ Each species has two well defined maximum absorption wavelengths (λ_{max}) that differ with the redox level. In the case of neutral TCNQF₄, λ_{max} is located at 365 and 386 nm, whilst those for the TCNQF₄^{•-} anion and TCNQF₄²⁻ dianion are at (411 and

752 nm) and (217 and 333 nm), respectively. Clearly, UV-vis spectroscopy should provide a sensitive method for the identification of the TCNQF₄ redox levels after dissolution of TCNQF₄-based materials.

The Beer-Lambert law (equation 1) was used to determine the molar extinction coefficients (ε) of the above mentioned absorption bands for TCNQF₄, TCNQF₄^{•-} and TCNQF₄²⁻ at 386, 411 and 333 nm, respectively and found to be $8.18 \pm 0.13 \times 10^4$, $5.08 \pm 0.17 \times 10^4$ and $4.06 \pm 0.12 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, respectively.

$$A = \varepsilon LC \quad (1)$$

where, A is absorbance, ε is the molar extinction coefficient, L is the sample pathlength and C is the concentration of TCNQF₄, TCNQF₄^{•-} and TCNQF₄²⁻.

3. Steady-State Voltammetry

Steady-state voltammetry also is a powerful technique for the identification of TCNQF₄ redox levels in dissolved samples as TCNQF₄ and its anions undergo two electrochemically and chemically reversible one-electron processes in solution.⁷ TCNQF₄ can only be reduced sequentially to TCNQF₄^{•-} and TCNQF₄²⁻, whilst TCNQF₄^{•-} can be reduced to TCNQF₄²⁻ or oxidized to TCNQF₄. In the case of TCNQF₄²⁻, this dianion can be oxidized to TCNQF₄^{•-} and then TCNQF₄. Consequently, the steady-state current responses associated with TCNQF₄, TCNQF₄^{•-} and TCNQF₄²⁻ voltammetry in solution are all significantly different with respect to the sign of the current (see Figure 3).

Steady-state voltammetry also may be applied for the quantitative determination of TCNQF₄ and its anions. The steady-state limiting current (i_{lim}) is proportional to the concentration of TCNQF₄, TCNQF₄^{•-} as well as TCNQF₄²⁻ in solution, which is described by equation 2. Thus, the concentration of TCNQF₄ and/or its anions in a solution can be determined from the limiting current.

$$i_{\text{lim}} = 4nFCDr \quad (2)$$

where, n is the number of electron transferred, F is the Faraday constant, C is the concentration of the analyze, D is the diffusion coefficient of the analyte, r is the electrode radius.

4. IR Spectroscopy

The most widely used technique for the determination of the redox level in TCNQF₄-based materials is IR spectroscopy. Bands for the C≡N stretch together with the $\pi(\text{C}=\text{C})$ ring stretch have been used most commonly. The C–F out of plane bend also has been employed. Table 1 contains IR frequencies associated with these stretches, whilst Table 2 provides the C≡N IR data for a range of TCNQF₄-based derivatives. The C≡N IR bands shift to lower energy as the charge on TCNQF₄ becomes more negative. Thus, this band for neutral TCNQF₄ is located at 2225 cm⁻¹, while that for TCNQF₄^{•-} is usually split into several bands around 2200 cm⁻¹. In the case of the TCNQF₄²⁻ dianion, the bands are usually observed in the region of ~2167 and ~2133 cm⁻¹. The frequency shift occurs in the opposite direction with the C–F out of plane bend and this band is located at ~1190, ~1210 and 1244-1262 cm⁻¹ for TCNQF₄, TCNQF₄^{•-} and TCNQF₄²⁻, respectively. Finally, the IR band for the C=C stretch in TCNQF₄ is observed at ~1490 cm⁻¹, whilst for TCNQF₄^{•-}, it shifts to higher energy (~1500 cm⁻¹); whereas, for TCNQF₄²⁻ this band occurs at lower wavenumbers (~1480 cm⁻¹).

5. Raman spectroscopy

Raman spectroscopy has not been widely used for the determination of TCNQF₄ redox levels, especially that of TCNQF₄²⁻. However, we have found Raman spectroscopy to provide a well resolved fingerprint for each redox level of TCNQF₄. Raman vibration modes for TCNQF₄ located at about 2226, 1665 and 1460 cm⁻¹ (Figure 4a and Table 3) are associated with C≡N, (C=C) ring and C–CN wing stretches.^{6,11,16} As for the IR spectra, upon increasing the negative charge, the Raman bands for the C≡N stretch shift to lower energy and for TCNQF₄^{•-} occur at 2205 – 2224 cm⁻¹, and for TCNQF₄²⁻ at 2082 – 2217 cm⁻¹. Another Raman mode that may be useful for the assignment of the redox levels is the C=C ring stretch, which for TCNQF₄^{•-} and TCNQF₄²⁻ occur at ~1640 and ~1650 cm⁻¹, respectively, whilst for neutral TCNQF₄, it is at ~1665 cm⁻¹ (see Table 3).

6. Conclusions

Examination of a range of TCNQF₄ materials has revealed that UV-vis, IR and Raman spectroscopies, and electrochemistry can be used for the identification of all three TCNQF₄ redox levels. Each of TCNQF₄, TCNQF₄^{•-} or TCNQF₄²⁻ has two specific UV-vis wavelengths of maximum absorption at (386 and 365 nm), (411, 752 nm) or (333, 217

nm), respectively. In acetonitrile with supporting electrolyte, under steady-state voltammetric conditions, TCNQF₄ undergoes two one-electron reduction processes, TCNQF₄^{•-} can be either reduced or oxidized, whilst TCNQF₄²⁻ can only be sequentially oxidized back to TCNQF₄ via TCNQF₄^{•-}. Unlike TCNQ²⁻, TCNQF₄²⁻ is stable in aerobic conditions for several hours. Therefore, UV-vis spectroscopy and electrochemistry provide simple and sensitive techniques for qualitative and quantitative determination of TCNQF₄ and its anions upon dissolution of solids into organic solvents. The strongest UV-vis absorbance for TCNQF₄, TCNQF₄^{•-} and TCNQF₄²⁻ dissolved in acetonitrile are at wavelengths of 386, 411 and 333 nm with molar extinction coefficients of $8.18 \pm 0.13 \times 10^4$, $5.08 \pm 0.17 \times 10^4$ and $4.06 \pm 0.12 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, respectively. By applying the relationship between limiting current and concentration under steady-state voltammetric conditions, the concentration of TCNQF₄, TCNQF₄^{•-} and/or TCNQF₄²⁻ can be determined. IR spectroscopy also may be used to determine the redox levels of TCNQF₄ in its materials, generally, on the basis of the IR bands associated with the C≡N stretch. These bands shift to lower frequency with the negative charge on TCNQF₄. Raman spectroscopy, although not as widely used as IR spectroscopy, is probably even more valuable than IR spectroscopy for probing the redox levels of TCNQF₄ in solid phases. As in IR spectroscopy, Raman modes for the C≡N stretch shift to lower energy as the negative charge on TCNQF₄ increases. However, the most characteristic Raman bands available for this purpose are associated with the C=C ring stretch, which occur at around 1665, 1640 and 1650 cm⁻¹ for TCNQF₄, TCNQF₄^{•-} and TCNQF₄²⁻, respectively.

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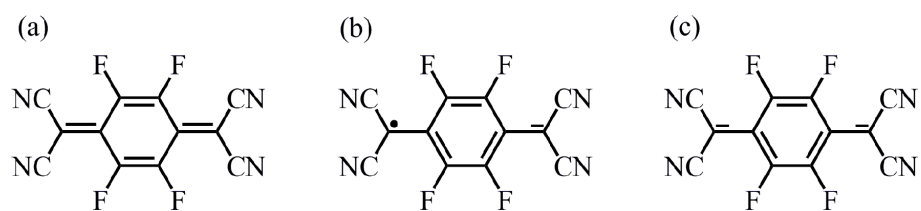


Figure 1. Molecular structures of (a) TCNQF₄, (b) TCNQF₄^{•-} and TCNQF₄²⁻.

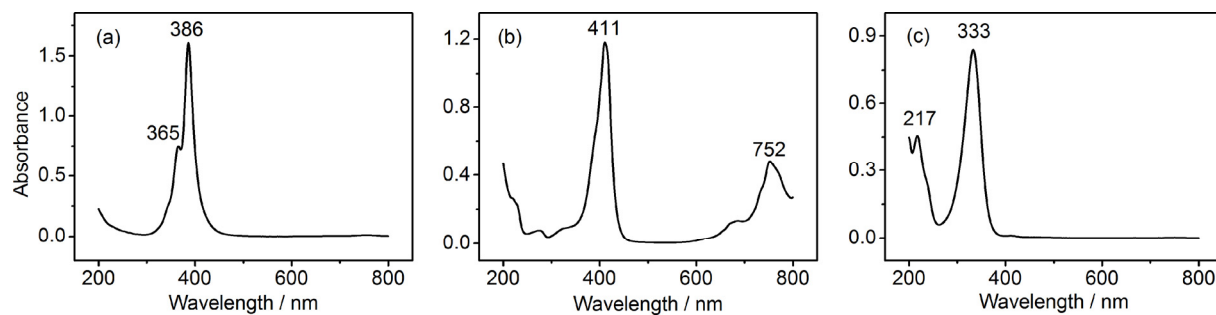


Figure 2. UV-vis spectra for 0.02 mM (a) TCNQF₄, (b) TCNQF₄^{•-} and (c) TCNQF₄²⁻ in acetonitrile using a 1.0 cm pathlength cuvette.⁷

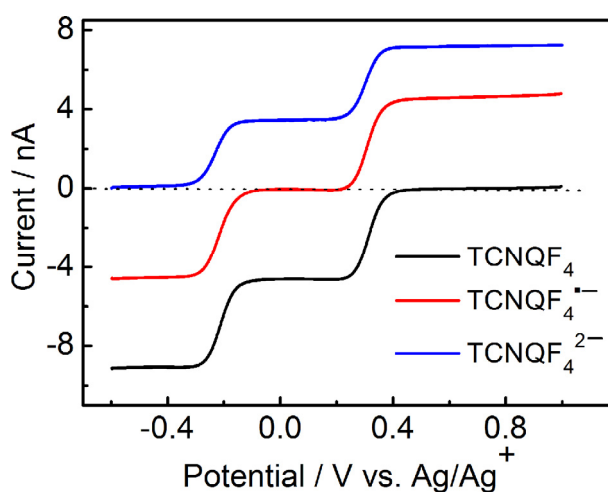


Figure 3. Near steady-state voltammograms obtained with a 12 μm diameter carbon fiber microdisk electrode at a scan rate of 20 mV s^{-1} for 1.0 mM TCNQF₄, TCNQF₄^{•-}, and TCNQF₄²⁻ in acetonitrile (0.1 M Bu₄NClO₄).⁷

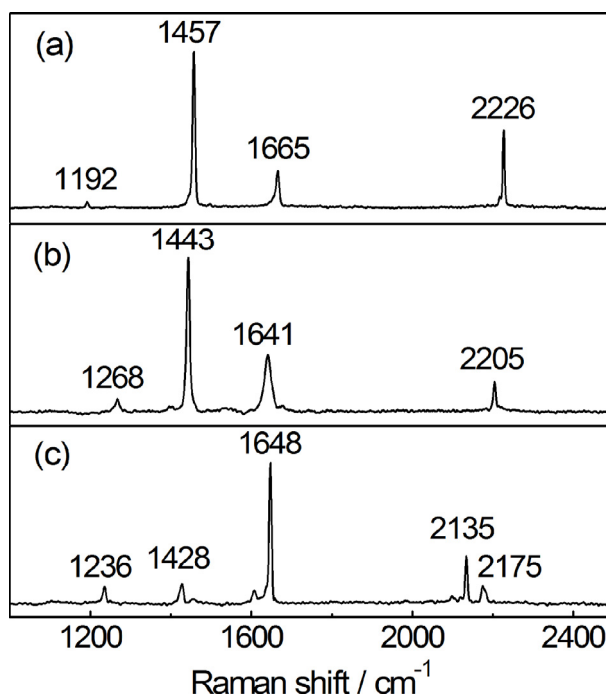


Figure 4. Raman spectra for (a) TCNQF₄, (b) Pr₄NTCNQF₄ and (c) (Pr₄N)₂TCNQF₄ solids.

Table 1. Frequencies for IR Bands Associated with the C≡N, π (C=C) Stretches and C–F out of Plane Bend in TCNQF₄-Based Materials

Compound	TCNQF ₄ charge	ν (C≡N) (cm ⁻¹)	ν (C=C) (cm ⁻¹)	δ (C–F) (cm ⁻¹)	Ref.
TCNQF ₄	0	2225	1493	1190	16
TCNQF ₄	0	2225	1489	1192	6
LiTCNQF ₄	-1	2204, 2184	1507	1204	This work
Pr ₄ NTCNQF ₄	-1	2205, 2182	1499	1204	This work
AgTCNQF ₄	-1	2221, 2210, 2195	1501	1205	16
AgTCNQF ₄	-1	2220, 2213, 2197	1501	1208	14
AgTCNQF ₄	-1	2213, 2197	1502	^a	11
CuTCNQF ₄	-1	2215, ~2190	1500	1213	6
CuTCNQF ₄	-1	2214, 2187	1496	1216	This work
Ni(TCNQF ₄) ₂ (H ₂ O) ₂	-1	2207, 2190	1498	1207	19
Li ₂ TCNQF ₄	-2	2154, 2127	1486	1262	This work
(Pr ₄ N) ₂ TCNQF ₄	-2	2164, 2132	1473	1236	This work
Cu ₂ TCNQF ₄	-2	2162, 2135	1475	1244	This work
CoTCNQF ₄	-2	2162, 2136	1486	1260	This work
NiTCNQF ₄	-2	2161, 2137	1485	1261	This work

^a Not available

Table 2. Frequencies for IR Bands Associated with the C≡N Stretch in TCNQF₄-Based Materials

Compound	TCNQF ₄ charge	$\nu(\text{C}\equiv\text{N})$ (cm ⁻¹)	Ref.
LiTCNQF ₄	-1	2198	9
{La[TCNQF ₄] ₂ [H ₂ O] ₇ }.(TCNQF ₄)(3H ₂ O)	-1	2209, 2190	8
{Pr[TCNQF ₄] ₂ [H ₂ O] ₇ }.(TCNQF ₄)(3H ₂ O)	-1	2204, 2189	8
{Nd[TCNQF ₄] ₂ [H ₂ O] ₇ }.(TCNQF ₄)(3H ₂ O)	-1	2214, 2199, 2190	8
{Sm[TCNQF ₄] ₂ [H ₂ O] ₇ }.(TCNQF ₄)(3H ₂ O)	-1	2209, 2202, 2189	8
{Eu[TCNQF ₄] ₂ [H ₂ O] ₇ }.(TCNQF ₄)(3H ₂ O)	-1	2201, 2189	8
{Gd[TCNQF ₄] ₂ [H ₂ O] ₆ }.(TCNQF ₄)(3H ₂ O)	-1	2207	8
{Dy[TCNQF ₄] ₂ [H ₂ O] ₆ }.(TCNQF ₄)(3H ₂ O)	-1	2208, 2196, 2186, 2179	8
{Ho[TCNQF ₄] ₂ [H ₂ O] ₆ }.(TCNQF ₄)(3H ₂ O)	-1	2207, 2196, 2186, 2179	8
{Er[TCNQF ₄] ₂ [H ₂ O] ₆ }.(TCNQF ₄)(3H ₂ O)	-1	2207, 2196, 2186, 2179	8
{Yb[TCNQF ₄] ₂ [H ₂ O] ₆ }.(TCNQF ₄)(3H ₂ O)	-1	2208, 2195, 2187, 2179	8
{Y[TCNQF ₄] ₂ [H ₂ O] ₆ }.(TCNQF ₄)(3H ₂ O)	-1	2201, 2193	8
{Tb[TCNQF ₄] ₂ [H ₂ O] ₆ }.(TCNQF ₄)(3H ₂ O)	-1	2207, 2196, 2187, 2180	13
[Fe(C ₅ Me ₅) ₂] ₂ (TCNQF ₄) ₂	-1	2198, 2195, 2178	10
[Co(C ₅ Me ₅) ₂] ₂ (TCNQF ₄) ₂	-1	2196, 2179	10
[Cr(C ₅ Me ₅) ₂] ₂ (TCNQF ₄) ₂	-1	2196, 2179	10
[Fe(C ₅ Me ₅) ₂] ₂ TCNQF ₄	-2	2167, 2133	10
[Co(C ₅ Me ₅) ₂] ₂ TCNQF ₄	-2	2168, 2133	10
[Ni(C ₅ Me ₅) ₂] ₂ TCNQF ₄	-2	2167, 2131	20
[Fe(C ₅ H ₅) ₂] ₂ (TCNQF ₄) ₂ (TCNQF ₄)	-1 and 0	2225, 2195, 2179	21
[Mn ₂ (TCNQF ₄)(CH ₃ OH) _{7.5} (H ₂ O) _{0.5}] (TCNQF ₄) ₂ .(7.5CH ₃ OH)	-2 and -1	2211, 2202, 2161	9

Table 3. Frequencies of Raman Vibration Modes for the C≡N, (C=C) Ring and C–CN Wing Stretches in TCNQF₄-Based Materials

Compound	TCNQF₄ charge	$\nu(\text{C}\equiv\text{N})$ (cm⁻¹)	$\nu(\text{C}=\text{C})$ (cm⁻¹)	$\nu(\text{C}-\text{CN})$ (cm⁻¹)	Ref.
TCNQF ₄	0	2226	1665	1457	16
TCNQF ₄	0	2227	1664	1461	6
LiTCNQF ₄	-1	2223	1638	1443	This work
Pr ₄ NTCNQF ₄	-1	2205	1641	1443	This work
AgTCNQF ₄	-1	2221	1642	1449	16
AgTCNQF ₄	-1	2220	1639	1447	6
AgTCNQF ₄	-1	2224	1644	1453	11
CuTCNQF ₄	-1	2222	1641	1439	This work
CuTCNQF ₄	-1	2220	1638	1451	6
Ni(TCNQF ₄) ₂ (H ₂ O) ₂	-1	2217	1641	1444	This work
(Pr ₄ N) ₂ TCNQF ₄	-2	2175, 2135	1648	1428	This work
Cu ₂ TCNQF ₄	-2	2170, 2141	1655	1435	This work
CoTCNQF ₄	-2	2118, 2082	1653	1440	This work
NiTCNQF ₄	-2	2111, 2082	1650	1440	This work

Chapter 8

Conclusions and Future Work

8.1. Conclusions

Electrochemistry has been shown to be a very powerful technique for the study of both dynamic and thermodynamic aspects of the redox chemistry of TCNQ or TCNQF₄-based materials. An initial electron transfer process, followed by a chemical reaction can be investigated to reveal the properties of an intermediate, such as stability and/or reactivity, and facilitate identification of associated mechanistic steps. In this thesis, electrochemistry has been the primary tool to study the redox and acid–base chemistry of TCNQ, TCNQF₄ and their anions in acetonitrile, and also used in the synthesis of new materials based on TCNQF₄. In fact, the synthesis of complexes based on either TCNQF₄^{•−} or TCNQF₄^{2−} can be controlled by applying the potential needed to produce the required compound. For instance, Cu(I) compounds based on TCNQF₄^{•−} or TCNQF₄^{2−} can be electrocrystallized from acetonitrile solution containing TCNQF₄ in the presence of Cu(MeCN)₄⁺ by control of the applied potential, i.e. at 100 mV or −500 mV versus Ag/Ag⁺, respectively.

TCNQ-based materials have been widely studied over many decades due to the extensive number of charge-transfer complexes, network polymers and organometallic compounds, many of which exhibit novel conductive, optical and magnetic properties. These materials have been applied in fields as diverse as optical and electrical recording; energy and data storage; catalysis; electrochromic, magnetic and sensor devices; However, studies using the tetrafluorinated derivative (TCNQF₄) are far less extensive than for TCNQ, although recently there has been a significant increase in reports of the synthesis, characterization and physical properties of TCNQF₄-based materials. Therefore, although some aspects of TCNQ chemistry are explored, this thesis has primarily focused on the electrochemistry and acid–base properties of TCNQF₄ as well as electrochemical synthesis and characterization of TCNQF₄-based materials. The research described in this thesis covers five topics.

8.1.1. Redox and Acid–Base Chemistry of TCNQF₄ and TCNQ in the Presence of Trifluoroacetic Acid

The electrochemistry of TCNQF₄, TCNQ and their anions (mono- and dianions) has been studied. In acetonitrile, both TCNQF₄ and TCNQ undergo two electrochemically and chemically reversible one-electron reduction steps with the reversible formal potentials associated with the first and second processes for TCNQF₄ are 0.36 and 0.37 V, respectively more positive than for TCNQ. This feature indicates that TCNQF₄ is a much stronger electron acceptor than TCNQ. TCNQF₄ and its anions are shown to be stable under aerobic ambient conditions. In contrast, TCNQ²⁻ rapidly reacts with oxygen to produce DCTC⁻, although TCNQ and TCNQ^{•-} are also air stable and persistent in solution. Proton transfers between TFA and either TCNQF₄ or TCNQ and their anions have also been described and compared. A mechanism for the electrochemistry of these species in acetonitrile in the presence of TFA has been proposed based on the experimental data and excellent agreement with simulation.

An important finding in this study is the stability of TCNQF₄²⁻ in an organic solvent under aerobic condition, which differs dramatically from the analogous TCNQ²⁻ dianion. Thus, this has opened up an easy approach for the synthesis of materials based on TCNQF₄²⁻ in the air as described in chapters 4 and 6.

8.1.2. Synthesis and Characterization of TCNQF₄-Based Materials in Acetonitrile

Chemical synthesis of LiTCNQF₄ and Li₂TCNQF₄ from LiI and TCNQF₄ in acetonitrile has been achieved. In cold acetonitrile, using LiI and TCNQF₄ with a molar ratio of 3:2, TCNQF₄ is reduced to only TCNQF₄^{•-}. In contrast, Li₂TCNQF₄ is formed if the molar ratio of LiI:TCNQF₄ is increased to > 3:1 and a higher temperature (50–60°C) is used. In addition, Pr₄N⁺TCNQF₄⁻ and (Pr₄N)₂TCNQF₄ have been chemically synthesized by mixing aqueous solutions of Pr₄NBr and LiTCNQF₄ or Li₂TCNQF₄. Single crystals of the Pr₄N⁺TCNQF₄⁻ compounds have been prepared and their structures were determined by single crystal X-ray diffraction techniques.

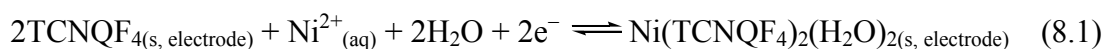
A combination of cyclic voltammetry, EQCM and SPR techniques has been employed to explore the electrocrystallization of AgTCNQF₄, Ag₂TCNQF₄, CuTCNQF₄, Cu₂TCNQF₄, CoTCNQF₄ and NiTCNQF₄ from TCNQF₄ in acetonitrile (0.1 Bu₄NPF₆) in the presence of the appropriate metal cation. Electrocristallization can only occur when the concentration product of TCNQF₄ and the metal cation exceeds the solubility product. The

solubility of these compounds in acetonitrile has been determined using UV-vis spectroscopy and hence, the solubility products have been deduced. The metal-TCNQF₄ complexes with different redox levels of TCNQF₄ were electrochemically and controllably synthesized by applying a suitable potential at a working electrode to induce the reduction of TCNQF₄ to either TCNQF₄^{•-} or TCNQF₄²⁻, coupled by reaction with an appropriate metal cation present in the same solution to produce crystals on the electrode surface. These metal-TCNQF₄ complexes also were chemically synthesized by mixing acetonitrile solutions of TCNQF₄^{•-} or TCNQF₄²⁻ and the appropriate metal cation to form a precipitate of the corresponding compound.

The chemically and electrochemically synthesized compounds were characterized using a wide range of spectroscopic and microscopic techniques and other analytical methods.

8.1.3. Electrochemistry of a TCNQF₄-Modified Electrode in Contact with an Aqueous Ni²⁺ Solution

The solid TCNQF₄-solid Ni(TCNQF₄)₂(H₂O)₂ transformation (equation 8.1) has been studied in aqueous media. Thus, an electrode surface was modified with crystalline TCNQF₄ and immersed in aqueous Ni²⁺ electrolyte. The electrode potential was first scanned in the negative direction to induce the reduction of TCNQF₄ to TCNQF₄^{•-}, which was accompanied with the ingress of Ni²⁺_(aq) from the bulk solution to form solid Ni(TCNQF₄)₂(H₂O)₂ on the electrode surface. The reverse process occurred as the potential was returned to the initial value and involved the reoxidation of TCNQF₄^{•-} from the newly generated complex back to the solid TCNQF₄, coupled with the egress of Ni²⁺_(aq) to the solution phase. This transformation is independent of working electrode material and Ni²⁺ counter anion, but does depend on the concentration of Ni²⁺_(aq) and scan rate. The voltammetric studies have revealed that the solid-solid conversion is electrochemically irreversible, chemically reversible and governed by nucleation and growth kinetics, as described in equation 8.1.



A wide range of microscopic, spectroscopic and analytical techniques has been used to determine the empirical formula, structure and physical properties of the electrochemically synthesized complex. SEM images have shown that the material electrocrystallizes onto the electrode surface in a thin film of microcrystals.

8.1.4. Disproportionation of $\text{TCNQF}_4^{\bullet-}$ and $\text{TCNQ}^{\bullet-}$ in Acetonitrile in the Presence of Zn^{2+}

The disproportionation of $\text{TCNQF}_4^{\bullet-}$ and $\text{TCNQ}^{\bullet-}$ in acetonitrile occurs in the presence of Zn^{2+} to form dissolved TCNQF_4 or TCNQ and a precipitate of ZnTCNQF_4 or ZnTCNQ as described in chapter 6. A mechanism for this reaction also has been proposed. Importantly, in the absence of Zn^{2+} , the disproportionation $2\text{TCNQ}(\text{F}_4)^{\bullet-} \rightleftharpoons \text{TCNQ}(\text{F}_4) + \text{TCNQ}(\text{F}_4)^{2-}$ is thermodynamically unfavorable ($\text{TCNQ}(\text{F}_4) = \text{TCNQ}$ or TCNQF_4). However, addition of Zn^{2+} to an acetonitrile solution of $\text{TCNQ}(\text{F}_4)^{\bullet-}$ results in pale green precipitates. Examination of the supernatant solutions reveals the presence of neutral $\text{TCNQ}(\text{F}_4)$. The precipitates were collected by filtration, washed with acetonitrile and characterized using infrared spectroscopy and elemental analysis. These data confirm the formation of $\text{ZnTCNQ}(\text{F}_4)$ solids by the disproportionation reaction. Importantly, addition of water decreases the extent of the disproportionation. If the amount of water is $\geq 3\%$ (v/v), the disproportionation of $\text{TCNQ}(\text{F}_4)^{\bullet-}$ does not occur and the reverse comproportionation reaction is favored. This interesting result is attributed to the higher solubility of $\text{ZnTCNQ}(\text{F}_4)$ in water than in acetonitrile. Thus, in the presence of water, the formation of $\text{ZnTCNQ}(\text{F}_4)$ solids via the disproportionation reaction are not favored.

8.1.5. Fingerprints for Identification of TCNQF_4 Redox Levels

This research, together with that of other workers, has revealed that UV-vis, IR and Raman spectroscopies as well as electrochemistry can be used to distinguish the redox level(s) of TCNQF_4 present in a compound. The UV-vis spectrum for each redox level, i.e. TCNQF_4 , $\text{TCNQF}_4^{\bullet-}$ or TCNQF_4^{2-} , in acetonitrile has two specific wavelengths of maximum absorption that depend on the redox levels. Thus, these λ_{max} values for TCNQF_4 , $\text{TCNQF}_4^{\bullet-}$ and TCNQF_4^{2-} are found at (365, 386), (411, 752) and (217, 333) cm^{-1} , respectively. Consequently, UV-vis spectroscopy is a simple and sensitive technique for the identification of the presence of TCNQF_4 and its anions in newly synthesized materials. In addition, UV-vis spectroscopy also can be utilized for quantitative analysis of these species using the Beer-Lambert law.

IR spectroscopy has been widely applied for the determination of TCNQF_4 redox levels. In particular, the IR bands associated with the $\text{C}\equiv\text{N}$ stretch are often used for this purpose. As the negative charge on TCNQF_4 increases, the IR bands shift to lower energy, from 2225 cm^{-1} (TCNQF_4) to ~ 2200 cm^{-1} ($\text{TCNQF}_4^{\bullet-}$) and ~ 2167 , ~ 2133 cm^{-1}

(TCNQF₄²⁻). Furthermore, the IR bands associated with the $\pi(\text{C}=\text{C})$ stretch and the C–F out of plane bend may be used for the distinction of the redox levels. For neutral TCNQF₄, these bands are at 1493 and 1190 cm⁻¹, whilst for TCNQF₄^{•-} and TCNQF₄²⁻, they are at (~1500, ~1205) and (~1490, ~1250) cm⁻¹, respectively,

Raman spectroscopy has been successfully used for the redox level assignment. Notably, there are not many prior studies in which the redox levels of TCNQF₄ have been assigned by Raman spectroscopy. In Raman spectroscopy, vibrational modes associated with the C $\equiv$ N and/or C=C ring stretches are characteristic of the redox levels. As the negative charge on TCNQF₄ increases, the Raman modes for the C $\equiv$ N stretch shift to lower energy, as also occurs in IR spectra. Raman bands for the C=C ring are also characteristic for the determination of TCNQF₄ redox levels as the locations of these bands are at ~1665, ~1640 and ~1650 cm⁻¹ relatively for TCNQF₄, TCNQF₄^{•-} and TCNQF₄²⁻.

As in the case with UV-vis spectroscopy, electrochemistry has been shown to be a very sensitive and simple technique that can be applied to the qualitative and quantitative determination of the TCNQF₄ redox levels on dissolved samples. In acetonitrile with supporting electrolyte, TCNQF₄ can be reduced in two well-resolved steps, TCNQF₄^{•-} can be either reduced or oxidized, whilst TCNQF₄²⁻ can oxidized back to TCNQF₄^{•-} and TCNQF₄. Limiting current derived from steady-state voltammogram can be utilized for quantitative analysis using the relationship between the limiting current and concentration of the analyte.

8.2. Future Work

This thesis has focused on the application of electrocrystallization, chemical synthesis (in acetonitrile) and physicochemical characterization of materials based on TCNQF₄ anions in combination with either Li⁺, Pr₄N⁺, Ag⁺, Cu⁺, Co⁺, Ni²⁺ or Zn²⁺ cations. In addition, the solid-solid phase transformation of TCNQF₄/Ni(TCNQF₄)₂(H₂O)₂ also has been studied in aqueous media. However, many opportunities remain to investigate the synthesis (in organic and aqueous media), structure and properties of compounds based on TCNQF₄; in particular combination with other transition or lanthanide metals can be studied in the future. An important outcome is the discovery of the air stability of TCNQF₄²⁻ in solution, which has encouraged the pursuit of synthesis and characterization of new materials based on TCNQF₄²⁻ under the ambient atmospheric conditions.

Recent studies by Robson *et al.* have shown that the coordination polymers based on

TCNQ²⁻ could be readily prepared and crystallized from H₂TCNQ, which was dissolved in an organic solvent and then layered with another organic solution containing a suitable metal-based cation and a weak base.¹⁻³ H₂TCNQ is readily deprotonated by the weak base to form TCNQ²⁻, which upon reaction with suitable cations forms coordination polymers. This strategy could be applied for the synthesis of a wide range of TCNQF₄²⁻-based coordination polymers, and this may be more favorable since H₂TCNQF₄ is a stronger acid and TCNQF₄²⁻ is much more stable in air than the TCNQ analogues.^{4,5} If possible, structural data of these generated complexes should be acquired by single crystal X-ray diffraction.

Exciting opportunities also exist for the formation of complexes with biomolecules following the recent reports of charge-transfer complexes based on both amino acid and TCNQ.⁶⁻⁸ These reports have opened a new direction for future work in studies of semiconductors based on amino acids and TCNQ or TCNQF₄, which are potential candidates for biodegradable semiconductors and also can be utilized for biosensors and bioreactor applications.⁶

Furthermore, applications of newly synthesized materials based on TCNQ and TCNQF₄ need to be explored. These materials might exhibit novel physically and/or chemically exciting properties of substantial technological significance as is the case with TCNQ-based materials as mentioned in chapter 1.

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Appendix

Declaration for Thesis Appendix

Declaration by candidate

In the case of Appendix, the nature and extent of my contribution to the work was the following:

Nature of contribution	Extent of contribution (%)
Key ideas, experimental work, writing up	10

The following co-authors contributed to the work.

Name	Nature of contribution
Lisandra L. Martin	Initiation, key ideas, writing up
Jinzhen Lu	Initiation, key ideas, experimental work, writing up
Ayman Nafady	Key ideas, experimental work, writing up
Amal I. Siriwardana	Initiation, key ideas, experimental work, writing up
Xiaohu Qu	Initiation, key ideas, experimental work
Daouda A. K. Traore	Key ideas, experimental work, writing up
Matthew Wilce	Key ideas, experimental work, writing up
Alan M. Bond	Initiation, key ideas, writing up

Candidate's Signature

		06/06/2012
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Declaration by co-authors

The undersigned hereby certify that:

- (13) the above declaration correctly reflects the nature and extent of the candidate's contribution to this work, and the nature of the contribution of each of the co-authors.
- (14) they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;
- (15) they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;
- (16) there are no other authors of the publication according to these criteria;
- (17) potential conflicts of interest have been disclosed to (a) granting bodies, (b) the editor or publisher of journals or other publications, and (c) the head of the responsible academic unit; and
- (18) the original data are stored at the following location and will be held for at least five years from the date indicated below:

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	18/5/12

Novel Semiconducting Biomaterials Derived from a Proline Ester and Tetracyanoquinodimethane (TCNQ) Identified by *Hand-picked* Selection of Individual Crystals*

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*** The authors wish to dedicate this manuscript to Professor Allan White on the occasion of his 75th birthday. Professor Raymond L. Martin wishes to acknowledge that Professor Allan White was one of his most productive PhD students; 9 papers during the period 1964-1969.**

Key words: amino acid esters, tetracyanoquinodimethane, semi-conductivity, biomaterials, hand-picked crystals of different stoichiometry

Abstract

Complex mixtures of cation:anion stoichiometries often result from the synthesis of TCNQ salts, and often these can't be easily separated. In this study, the reaction of *N,N*-dimethyl-*D*-proline-methylester ($\text{Pro}(\text{CH}_3)_3^+$) with LiTCNQ (TCNQ = tetracyanoquinodimethane) resulted in a mixture of crystals. Hand selection and characterisation of each crystal type by X-ray, IR, Raman and electrochemistry has provided two stoichiometries, 1:1 [$\text{Pro}(\text{CH}_3)_3\text{TCNQ}$] and 2:3 ($[(\text{Pro}(\text{CH}_3)_3)_2(\text{TCNQ})_3]$) where a detailed comparison of these structures is provided. The electrochemical method provides an exceptionally sensitive method of distinguishing differences in stoichiometry. Conductivity of the mixture is $3.1 \times 10^{-2} \text{ S cm}^{-1}$ which lies in the semi-conducting range.

Introduction

One of the most famous examples of separation science was when Louis Pasteur *hand-selected* single crystals, to optically resolve tartaric acid in 1847. Pasteur's method sometimes proves to be the only one available to separate co-crystallised mixtures from the same solution. Over 150 years later this feature is a highlight of the present contribution.

The significance of various electroactive molecules in supramolecular chemistry¹ and molecular electronics² is now well recognised and 7,7,8,8-tetracyanoquinodimethane (TCNQ) occupies a prominent position among these redox-active building blocks as a result of the extreme ease of reduction which makes TCNQ a suitable acceptor for charge transfer (CT).³ The properties of TCNQ-based molecular materials (such as ion-pair complexes, organometallic compounds, and coordination polymers) have generated a great deal of interest over the past four decades,⁴⁻⁸ in particular for storage and light emitting devices, catalysis, electronics, magnetism and sensing applications,⁸⁻¹² Another significant feature of this electron acceptor is the tendency for the pi-delocalized system to overlap with neighbouring molecules, to form stacks with different degrees of electron delocalization.^{8,13-15}

Despite the long history of TCNQ chemistry, anion-radical salts of TCNQ with amino acid derivatives as a cation have had few examples until recently. In 2004, Jiang *et al.* reported some interesting results of colorimetric detection of cysteine using the molecular complex of dihydroxymethyl-di-(2-pyrrolyl)methane with TCNQ. Padhiyar *et al.* reported that CT complexes of four amino acids are formed with TCNQ, as indicated by IR spectroscopy.¹⁶ Recently, we reported the preparation and characterization of a novel

bio-organic TCNQ material $[\text{Pro}_2\text{H}^+]_2[\text{TCNQ}^{\bullet-}]_2\text{TCNQ}$, (Pro = proline) formed as a charge transfer compound.¹⁷ In this case, it is reasonable to assume that TCNQ layers interact with the cationic proline sheets via the extensive hydrogen bonding between the $\text{C}\equiv\text{N}$ groups of $\text{TCNQ}/\text{TCNQ}^{1-}$ and the proline ammonium groups.

In this paper, we report the reaction of *N,N*-dimethyl-*D*-proline-methylester ($\text{Pro}(\text{CH}_3)_3^+$) with Li TCNQ (TCNQ = tetracyanoquinodimethane), see Figure 1, affording a mixture of two novel semiconducting, $[\text{Pro}(\text{CH}_3)_3\text{TCNQ}]$ and $[(\text{Pro}(\text{CH}_3)_3)_2(\text{TCNQ})_3]$ compounds referred to as 1:1 ProTCNQ and 2:3 ProTCNQ, respectively. X-ray structures of hand selected single crystals showed an extended H-bonding network resulting in unusual properties. Spectroscopic characterisation of these single crystals has also been undertaken. Electrochemical characterisation of the dissolved crystals readily discriminated between the stoichiometries and could be used more widely for the analysis of such mixtures especially when no suitable crystals are available for X-ray structure analysis.

Experimental Section

Chemicals

TCNQ compounds were synthesized from the following chemicals: *N*-methyl-*D*-proline methyl ester (> 99%), iodomethane (99%), potassium carbonate (98%), lithium iodide (99%), TCNQ and HPLC grade acetonitrile (CH_3CN), methanol (CH_3OH), acetone (CH_3COCH_3), from Aldrich (Australia). All of the chemicals were used as received from the manufacturer except TCNQ which was recrystallized from acetonitrile and tetra-*n*-butylammonium hexafluorophosphate (Bu_4NPF_6) which was recrystallized from ethanol three times and vacuum dried. Water used was purified by a Sartorius Arium 611 system (resistivity of 18.2 $\text{M}\Omega\text{ cm}$).

Synthesis

N,N-Dimethyl-*D*-proline methyl ester iodide

K_2CO_3 (1.0 mmol) was added into a solution of *N*-methyl-*D*-proline methylester (1.0 mmol) and CH_3CN (150 mL). After stirring the mixture for 1.5 hr at room temperature, CH_3I (15.5 mL) was added dropwise. One day later, the required solid was collected by filtration. Additional material was obtained following concentration of the supernatant under reduced pressure. The required product, *N,N*-dimethyl-*D*-proline methylester iodide, was obtained in high yield.

LiTCNQ

The LiTCNQ was synthesised by the reaction of neutral TCNQ with LiI in methanol. The product was isolated and washed with cold solvent until the colour due to the I_3^- was absent.

1:1 and 2:3 ProTCNQ

N,N-dimethyl-*D*-proline methylester iodide (1.0 mmol) was dissolved in 10 mL of H_2O under a nitrogen atmosphere. LiTCNQ (1.0 mmol), dissolved in 15 mL of H_2O was added slowly to the *N,N*-dimethyl-*D*-proline methyl iodide aqueous solution at room temperature. The crude dark brown microcrystalline solid precipitated immediately and after 1 hr it was collected by filtration, washed with 5 mL of diethylether and dried in vacuum at 40 °C for one day. Purification of the crude material was achieved by washing repeatedly with diethylether, until no yellow colour was observed in the diethyl ether phase. This solid material was then dissolved in acetone and MeOH (3:1) and diffusion of *n*-pentane into this solution over 4 days, gave a mixture of solids containing two slightly different morphologies. The 1:1 ProTCNQ was a block-like crystal ($0.25 \times 0.12 \times 0.03$ mm) while the 2:3 ProTCNQ was a thin plate morphology ($0.09 \times 0.08 \times 0.01$ mm). These were separated by hand and both were characterised by X-ray crystallography and other methods.

Raman and IR Spectroscopies and Mass Spectrometry

IR spectra were recorded on the solids using a Spectrac Diamond ATR Instrument spectrometer and positive and negative ion electrospray mass spectra with a Micromass Platform 2 ESI-MS instrument. A Renishaw Invia Raman spectrograph was used to measure Raman spectra of the solids using an argon ion laser excitation at 633 nm.

Conductivity

Room temperature conductivity measurements were carried out on a pressed pellet of a mixture of 1:1 and 2:3 ProTCNQ with a Jandel RM3–AR Four–Point Probe Test Meter.

Electrochemistry

Electrochemical measurements were undertaken at room temperature of 22 ± 2 °C with an Epsilon Electrochemical Analyzer (Bioanalytical Systems) and a standard three-electrode cell configuration. Glassy carbon (Bioanalytical Systems, diameter = 1.5 mm) or platinum microelectrode (home built, diameter = 10 μ m) were used as the working electrodes. The

reference electrode was a silver wire coated with AgCl and placed in contact with 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile, separated from the test solution by a frit. The potential of the reference electrode is -0.37 V vs. $\text{Fc}^{0/+}$ (Fc = ferrocene). The counter electrode consisted of a large area platinum mesh.

X-ray structural determination of the ProTCNQ complexes

1:1 ProTCNQ

A single crystal of 1:1 ProTCNQ was mounted on a fine glass fibre using viscous hydrocarbon oil. Data were collected using a Bruker X8 ApexII diffractometer equipped with graphite monochromated Mo-K α radiation. Data collection temperatures were maintained at 123 K using an open-flow N₂ cryostream. Initial data processing was carried out using the Bruker ApexII software suite for the instruments.

2:3 ProTCNQ

The crystal data for the 2:3 ProTCNQ were collected at the Australian Synchrotron using the PX1 beam-line operating at 15 KeV ($\lambda = 0.7292$ Å). The collection temperature was maintained at 100 K using an open-flow N₂ cryostream. Initial data processing was carried out using XDS software.¹⁸

Both structures were solved by direct methods using SHELXS-97.¹⁹ Least-squares refinements against F^2 were carried out using SHELXL-97 with the program X-Seed as a graphical interface.²⁰ Hydrogen atoms were anisotropically refined, and placed in their calculated positions and were refined following the riding model.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers 874315 and 874316 for 2:3 ProTCNQ and 1:1 ProTCNQ respectively. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: (+44) 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

Crystal data for 1:1 ProTCNQ: C₂₀H₂₀N₅O₂, $M = 362.41$, dark purple block, $0.25 \times 0.12 \times 0.03$ mm³, monoclinic, space group $P2_1$ (No. 4), $a = 10.3031(13)$, $b = 6.8566(8)$, $c = 15.5118(19)$ Å, $\beta = 101.946(4)^\circ$, $V = 1072.1(2)$ Å³, $Z = 2$, $D_c = 1.123$ g/cm³, $F_{000} = 382$, CCD area detector, MoK α radiation, $\lambda = 0.71073$ Å, $T = 123(2)$ K, $2\theta_{\text{max}} = 50.0^\circ$, 6871 reflections collected, 3531 unique ($R_{\text{int}} = 0.0400$). Final $\text{Goof} = 1.033$, $RI = 0.0826$, $wR2$

= 0.2286, R indices based on 2562 reflections with $I > 2\sigma(I)$ (refinement on F^2), 247 parameters, 1 restraint. L_p and absorption corrections applied, $\mu = 0.076 \text{ mm}^{-1}$.

Crystal data for 2:3 ProTCNQ: $\text{C}_{26}\text{H}_{22}\text{N}_7\text{O}_2$, $M = 464.51$, $0.26 \times 0.29 \times 0.01 \text{ mm}^3$, monoclinic, space group $P2_1/c$ (No. 14), $a = 7.2910(15)$, $b = 29.534(6)$, $c = 12.701(4) \text{ \AA}$, $\beta = 122.37(2)^\circ$, $V = 2309.9(10) \text{ \AA}^3$, $Z = 4$, $D_c = 1.336 \text{ g/cm}^3$, $F_{000} = 972$, MoK α radiation, $\lambda = 0.7292 \text{ \AA}$, $T = 100 \text{ K}$, $2\theta_{\text{max}} = 50.0^\circ$, 28502 reflections collected, 4015 unique ($R_{\text{int}} = 0.0551$). Final $\text{Goof} = 1.096$, $RI = 0.1016$, $wR2 = 0.2206$, R indices based on 3716 reflections with $I > 2\sigma(I)$ (refinement on F^2), 319 parameters, 0 restraints. L_p and absorption corrections applied, $\mu = 0.089 \text{ mm}^{-1}$.

Results and Discussion

The TCNQ proline ester material was synthesized by the simple metathesis reaction of the ester iodide with the lithium salt of the TCNQ monoanion (Scheme 1). Mass spectrometry showed that the cation and anion were present in both crystal morphologies. Characterisation details of the hand-picked crystals follow.

X-ray Structural Analysis of 1:1 ProTCNQ

A dark purple single crystal of 1:1 ProTCNQ was hand picked following diffusion of *n*-pentane into an acetone and methanol (v/v=3:1) solution of the crude solid. The 1:1 ProTCNQ crystallises in the monoclinic space group $P2_1$, with the asymmetric unit consisting of one $\text{Pro}(\text{CH}_3)_3$ cation and one TCNQ anion (Figure 2). The crystal structure reveals a layered structure (Figure 3).

The charge transfer degree (ρ) of the TCNQ moieties was deduced from the mean bond lengths of TCNQ, which is -1.07, and is indicative of the presence of the radical monoanion TCNQ^{1-} (Table 1). Each TCNQ monoanion was almost planar with a slight bowing of the CN groups away from the phenyl plane. The two neighboring TCNQ^{1-} monoanions form a π -stacked dimer and the interplanar distance between these two TCNQ moieties is $3.404 \text{ \AA}$, and an intra-dimer distance is $3.446 \text{ \AA}$. Thus there are columns of TCNQ^{1-} dimers that are equally spaced along the b axis direction. In addition, the $\text{Pro}(\text{CH}_3)_3$ cations are connected via an extensive hydrogen bond network to create a 2D sheet (Table 2). Finally, TCNQ^{1-} monoanion columns and $\text{Pro}(\text{CH}_3)_3$ cation sheets interact via hydrogen bonding to form a 2D layered network (Table 2, Figure 3).

A dark purple single crystal of 2:3 ProTCNQ was also hand picked following the procedure described for the 1:1 ProTCNQ above. It crystallised in the monoclinic space group $P2_1/c$, with the asymmetric unit containing one $\text{Pro}(\text{CH}_3)_3^+$ cation and two crystallographically independent TCNQ moieties (Figure 4), namely TCNQ-A and TCNQ-B, respectively.

The structure consists of alternating layers of $\text{Pro}(\text{CH}_3)_3^+$ and $(\text{TCNQ})_3^{2-}$. From the analysis of the mean bond lengths of each TCNQ moiety, the charge transfer degree (ρ) can be deduced as -0.30 for TCNQ-A and -0.94 for TCNQ-B respectively (see Table 1). Thus, TCNQ-A can be approximated as a neutral TCNQ species, while TCNQ-B is close to radical anion TCNQ^{1-} .

In each case the TCNQ moieties are very close to planar. The two types of TCNQ form two separate 1D chains defined by weak H-bonding interactions between the $\text{C}\equiv\text{N}$ and H groups of each TCNQ moiety (Table 3, Figure 5), and are almost parallel to each other (dihedral angle of TCNQ-A and TCNQ-B planes is 2.34°). These TCNQ chains are stacked along the c direction to create a 2D layer with a triad pattern -ABB- (Figure 6). There are strong π - π interactions among the chains containing the TCNQ-A and TCNQ-B moieties. The mean inter-planar separation within the two overlapping pairs of TCNQ (dimers) are 3.24 Å for TCNQ-AB, and 3.18 Å for TCNQ-BB, respectively. The TCNQ layer is orientated with neighbouring TCNQ layers at an angle of 143° (Figure 6). The $\text{Pro}(\text{CH}_3)_3^+$ cations are linked by hydrogen bonding again forming a 2D sheet (Figure 6, Table 3). Finally, the TCNQ layers interact with the cationic $\text{Pro}(\text{CH}_3)_3^+$ sheets via weak hydrogen bonds between the CN groups of the TCNQ anions and the $\text{Pro}(\text{CH}_3)_3$ cationic CH groups (see Table 3) thus building the layered structure (Figure 6).

3.2. Raman Spectra

Raman spectra of individual 1:1 and 2:3 ProTCNQ crystals together with TCNQ are shown in Figure 7. The four characteristic bands for TCNQ at 1206, 1454, 1602 and 2227 cm^{-1} that correspond to $\text{C}=\text{C}-\text{H}$ bending, $\text{C}-\text{CN}$ wing stretch, $\text{C}=\text{C}$ ring stretch and $\text{C}\equiv\text{N}$ stretch^{2,23,24}, respectively, are clearly seen. The Raman spectra for both 1:1 and 2:3 ProTCNQ are similar with all vibration modes for $\text{C}=\text{C}-\text{H}$ bending, $\text{C}-\text{CN}$ wing stretch and $\text{C}\equiv\text{N}$ stretch shifted to lower energy compared with those for neutral TCNQ. This spectra change is attributed to the presence of the TCNQ radical monoanion and is consistent with previous studies.^{2,23,24} In particular, the $\text{C}\equiv\text{N}$ stretch band of TCNQ at 2227

cm^{-1} is red-shifted by $\sim 32 \text{ cm}^{-1}$ to 2195 cm^{-1} , while the C–CN wing stretches of the 1:1 and 2:3 stoichiometries are shifted by 58 and 62 cm^{-1} respectively. The relative reduction of intensity for the $\text{C}\equiv\text{N}$ stretch band is also another spectroscopic fingerprint for the presence of the TCNQ radical monoanion.²

In the case of the 2:3 ProTCNQ, there are 3 vibration bands for the $\text{C}\equiv\text{N}$ stretch at 2192, 2207 and 2225 cm^{-1} and another 3 bands for C–CN wing stretch at 1296, 1350 and 1388 cm^{-1} . This could be due to the special crystal structure of compound 2:3 ProTCNQ where three TCNQ moieties share two negative charges to form π - π stacks, in which these charges are unevenly distributed, see structural discussion above.

The FT-IR spectrum for 1:1 ProTCNQ supported the presence of TCNQ^{1-} using the diagnostic $\nu(\text{C}\equiv\text{N})$ bands at 2188, 2178 and 2161 cm^{-1} together with the $\delta(\text{C–H})$ at 819 cm^{-1} . Similarly, the two sharp and characteristic bands at 2189 and 2172 cm^{-1} for $\text{C}\equiv\text{N}$ were observed and the strong absorption at 823 cm^{-1} due to C–H for the 2:3 ProTCNQ. Interestingly, the 2:3 ProTCNQ does not exhibit any bands in the FT-IR spectrum attributed to a partial distribution of charge (< 1.0) as observed for related TCNQ compounds in previous studies.²⁵

Electrochemistry

Transient voltammetry

The electrochemical behaviour of solutions of the hand-picked single crystals of 1:1 and 2:3 ProTCNQ in CH_3CN (0.1 M TBAPF₆) exhibit similar cyclic voltammetric characteristics. They give rise to two diffusion-controlled chemically and electrochemically reversible processes indicative of the presence of TCNQ^0 or reduced TCNQ^{1-} derived from the two crystals. This is shown clearly in the transient cyclic voltammograms presented in Figure 8a for 1:1 ProTCNQ by scanning the potential from the position of zero current resulting in the detection of one reversible oxidation ($E_1^0 = 0.177 \text{ V}$) and one reversible reduction ($E_2^0 = -0.372 \text{ V}$) process over the scan rate range from 100 to 1000 mV s^{-1} . The separation in the potential of the two processes ($\Delta E^0 = E_1^0 - E_2^0$) is 0.549 V, as found for the sequential one-electron reductions of the parent TCNQ under the same electrochemical conditions, thereby indicating that the hand-picked crystals of 1:1 ProTCNQ are completely dissociated in acetonitrile solution. Importantly, the detection of only two reversible processes over $\sim 4 \text{ V}$ potential window implies the absence

of any other redox active species, including iodide from materials used in the synthesis, in the solution derived from the single crystals.

Steady state voltammetry

Although it is possible to qualitatively assign the process detected at 0.177 V to the oxidation of TCNQ^{1-} anion to neutral TCNQ^0 and the one at -0.372 V to the reduction of TCNQ^{1-} anion to TCNQ^{2-} dianion, the definitive and quantitative determination of the redox level of TCNQ can be gained by steady state voltammetry. In principle, one-electron reduction of TCNQ^0 to TCNQ^{1-} monoanion is anticipated to yield negative (reduction) current for the $\text{TCNQ}^{0/1-}$ process over the potential range of -100 to 600 mV. In contrast, if the starting material contains only TCNQ^{1-} , as is the case of 1:1 material, the steady-state current over the same potential range should be positive for the $\text{TCNQ}^{1-/0}$ oxidation process.

Inspection of the position of zero current of the steady-state voltammograms obtained for the hand-picked crystals of the 1:1 ProTCNQ using a $10\text{ }\mu\text{m}$ Pt microelectrode (Figure 8b) reveals that the solution contains purely ($\sim 100\%$) TCNQ^{1-} monoanion which can be either oxidized to neutral TCNQ^0 , giving rise to positive (oxidative) current or reduced further to the dianion (TCNQ^{2-}) as the position of zero current lies exactly between the $\text{TCNQ}^{0/1-}$ and $\text{TCNQ}^{1-/2-}$ processes. This voltammetric finding is completely consistent with the IR, Raman and X-ray structural data thereby confirming that the stoichiometric ratio of this crystal is fully 1:1.

The steady-state voltammogram (Figure 8c) obtained for a solution of the hand-picked crystal of 2:3 ProTCNQ reveals the presence of neutral TCNQ^0 in addition to TCNQ^{1-} monoanion in the sample. Quantitative analysis of the current associated with the first process reveals that the oxidative current arising from TCNQ^{1-} monoanion represents approximately 67% (two thirds) of the total current whereas the remaining $\sim 33\%$ (one third) is reductive current arising from the presence of neutral TCNQ^0 . This oxidative/reductive current ratio attests to the fact that the stoichiometry of this crystal is 2:3. Finally we noted that there was no evidence for TCNQ^{2-} in any of the solutions derived from the single crystals.

Conclusions

The reaction mixture of *N,N*-dimethyl-*D*-proline methylester with LiTCNQ afforded a mixture of crystals with two cation:anion stoichiometries. These were separated by hand and each crystal form subjected to a series of analyses including single crystal X-ray diffraction, IR, Raman in the solid state and solution electrochemistry. This analysis demonstrated the existence of two stoichiometries; the 1:1 [Pro(CH₃)₃TCNQ] and 2:3 [(Pro(CH₃)₃)₂(TCNQ)₃]. Interestingly, the electrochemical method provided an exceptionally sensitive method of distinguishing these two stoichiometries and is definitive with or without X-ray crystallographic characterisation. Interestingly, the conductivity of the mixture of crystals ($3.1 \times 10^{-2} \text{ S cm}^{-1}$) was found to lie in the range observed for a semi-conductor.

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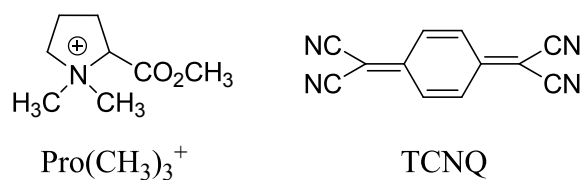


Figure 1: Structures and abbreviations of the *N,N*-dimethyl-D-proline-methylester, Pro(CH₃)₃⁺ and tetracyanoquinodimethane, TCNQ.

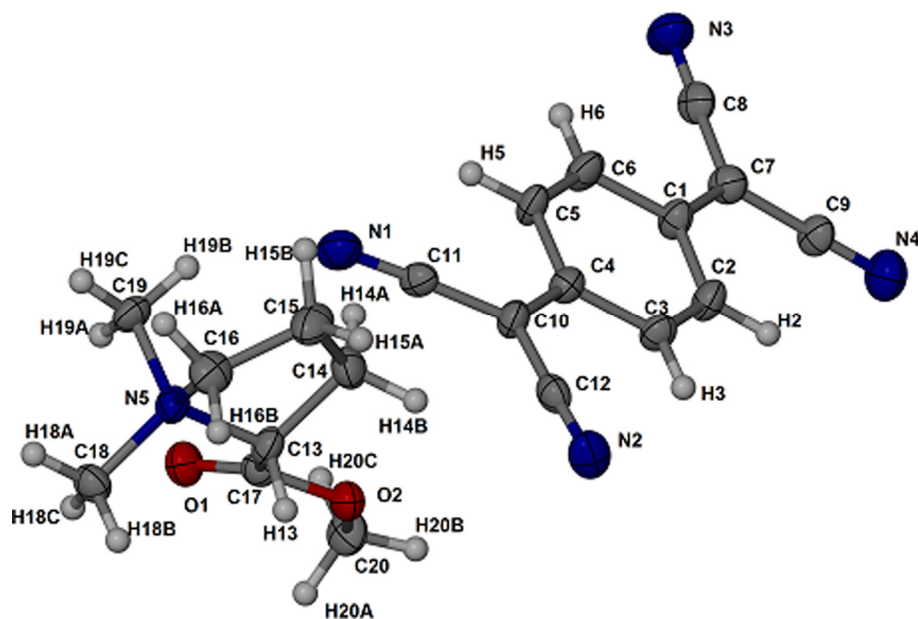


Figure 2: Asymmetric unit of the 1:1 ProTCNQ.

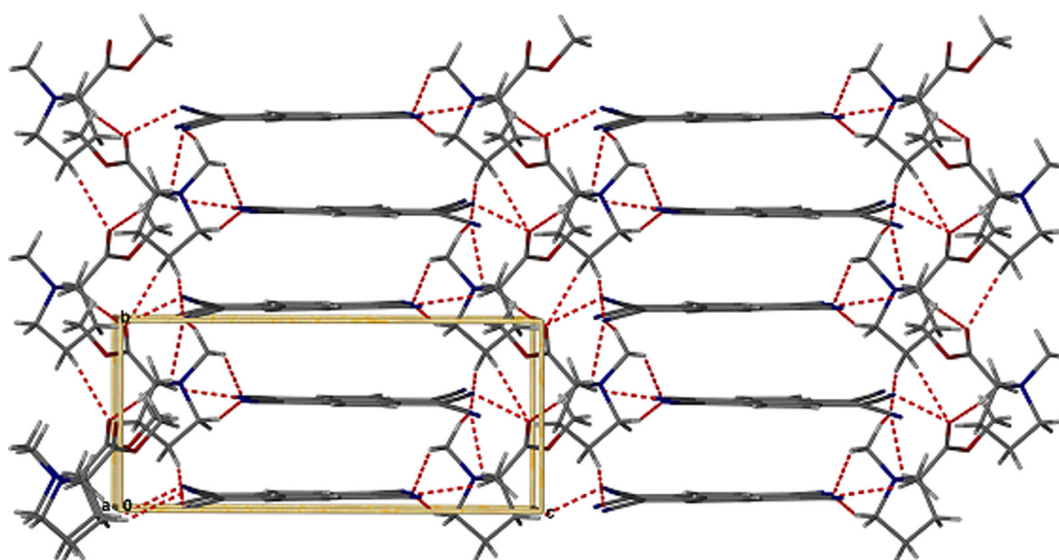


Figure 3: The view of the packing along the *bc* plane in the 1:1 ProTCNQ.

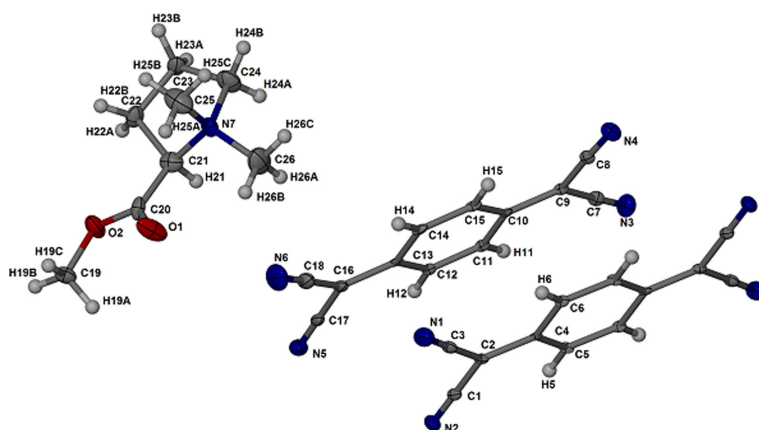


Figure 4: Asymmetric unit of the 2:3 ProTCNQ.

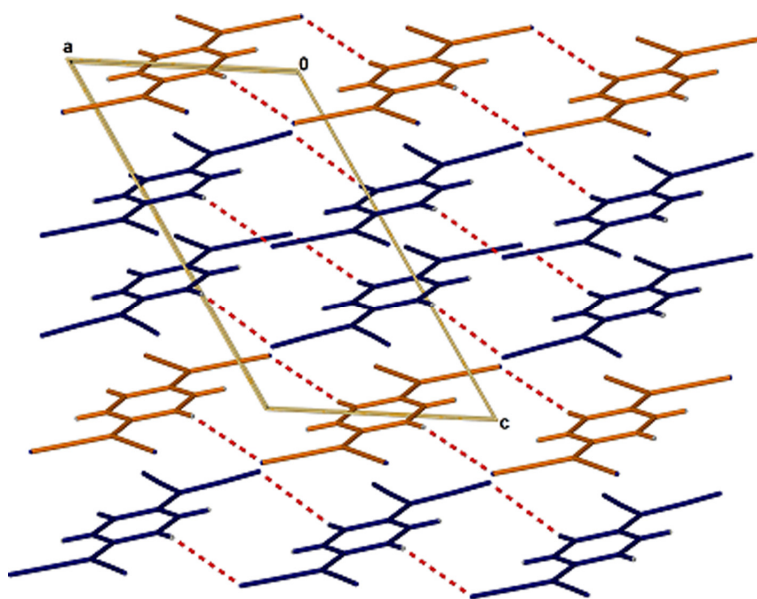


Figure 5: View of the TCNQ chains in 2: 3 ProTCNQ, TCNQ-A (orange), TCNQ-B (dark blue).

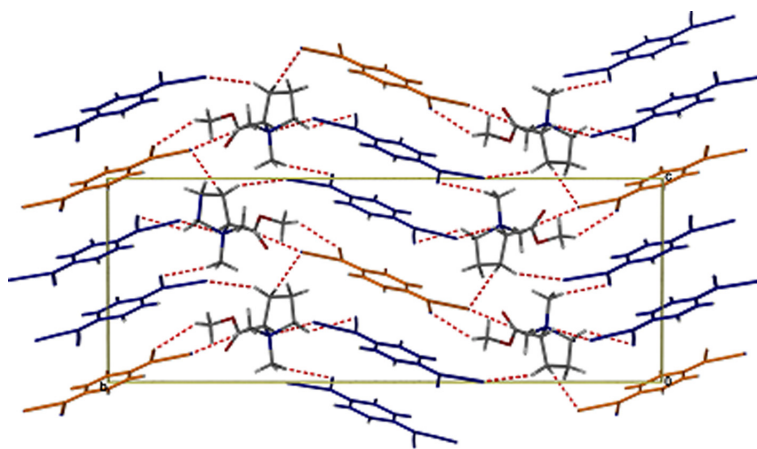


Figure 6: View of the 2:3 ProTCNQ crystal packing, viewed along the a axis; TCNQ-A (orange), TCNQ-B (dark blue).

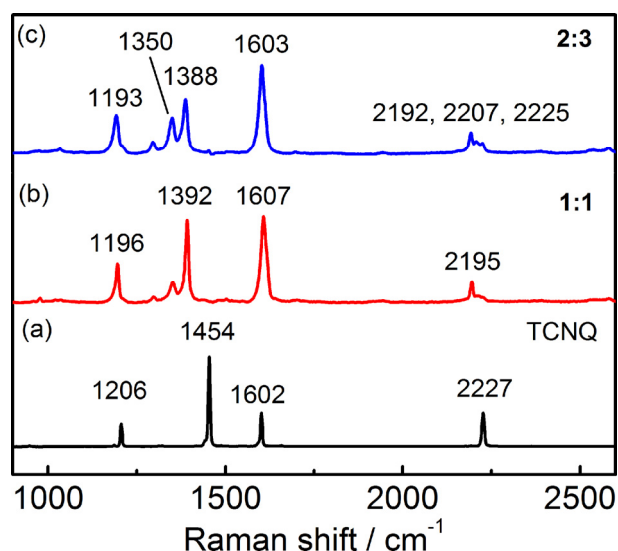


Figure 7: Raman spectra for (a) neutral TCNQ and hand-selected crystals of (b) 1:1 and (c) 2:3 ProTCNQ.

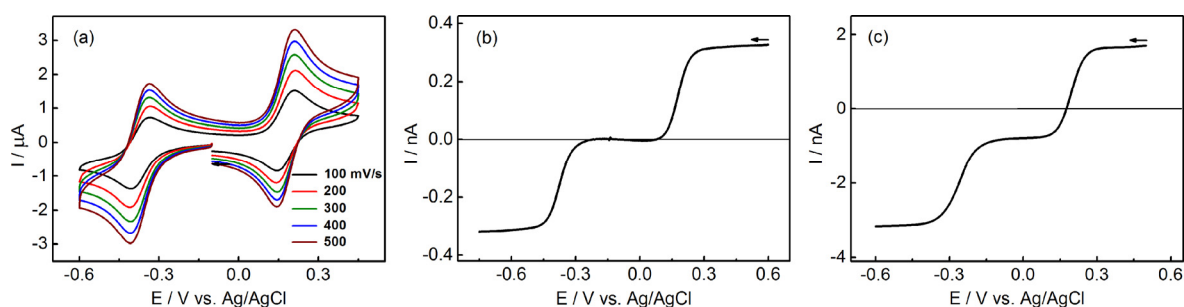
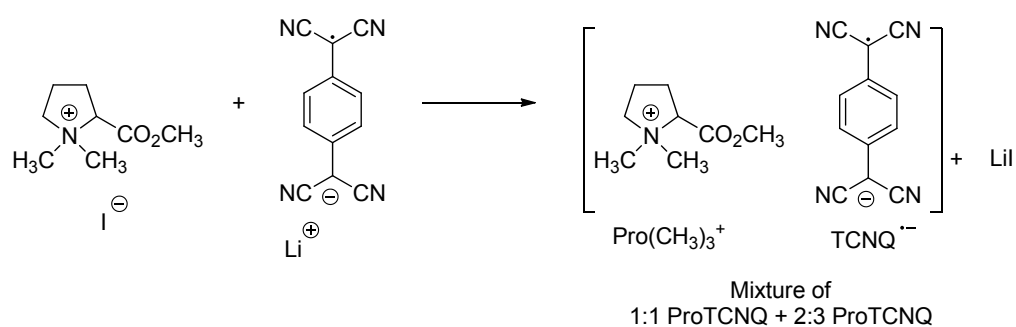
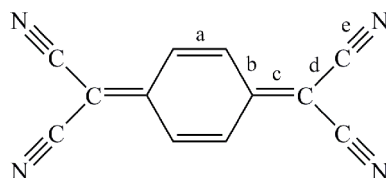


Figure 8: (a) Transient cyclic voltammograms of hand-picked single crystals of 1:1 ProTCNQ (~ 0.2 mM) in acetonitrile (0.1M Bu_4NPF_6) using 1.5 mm GC electrode at designated scan rates. (b) Steady-state voltammogram of the same sample obtained under the same conditions with a 10 μm Pt microelectrode at scan rate of 100 mV s^{-1} . (c) Steady-state voltammogram of hand-picked single crystals of 2:3 ProTCNQ (~ 0.3 mM) obtained from acetonitrile (0.1M Bu_4NPF_6) with a 10 μm Pt microelectrode at scan rate of 100 mV s^{-1} .



Scheme 1: Synthesis of proline ester TCNQ materials.

Table 1: C–C and C≡N mean bond lengths [Å] for 1:1 ProTCNQ and 2:3 ProTCNQ



	a	b	c	d	e	ρ^*
1:1 ProTCNQ	1.3665	1.4170	1.4150	1.4192	1.1635	-1.07
2:3 ProTCNQ-A	1.3430	1.4415	1.3860	1.4330	1.1450	-0.30
2:3 ProTCNQ-B	1.3690	1.4253	1.4130	1.4235	1.1543	-0.94
$^{21}\text{TCNQ}^0$	1.346	1.448	1.374	1.440	1.138	0
$^{22}\text{TCNQ}^{1-}$	1.362	1.424	1.413	1.417	1.149	-1.00

* $\rho = -(r-r^0)/(r^1-r^0)$; $r = c/(b+d)$; r^1 , r^0 values are those calculated for TCNQ^{1-} and TCNQ^0 , respectively.

Table 2: Distances [Å] and Angles [°] within the hydrogen bonding network for 1:1 ProTCNQ

D-H...A	d (D-H) (Å)	d (H...A) (Å)	d (D...A) (Å)	<(DHA) (°)	Symmetry code
C ₁₅ H _{15B} ...O ₁	0.990	2.444	2.982	113.60	x, y-1, -z
C ₁₉ H _{19B} ...O ₁	0.981	2.457	2.937	119.87	-x-1, y- ¹ / ₂ , -z
C ₁₄ H _{14A} ...N ₁	0.990	2.723	3.631	152.71	x, y, z
C ₁₃ H ₁₃ ...N ₂	1.000	2.587	3.269	125.37	-x, ¹ / ₂ +y, -z
C ₁₅ H _{15A} ...N ₂	0.990	2.577	3.532	161.92	-x, y- ¹ / ₂ , -z
C ₁₆ H _{16A} ...N ₃	0.990	2.495	3.398	151.54	x, y, z-1
C ₁₆ H _{16B} ...N ₄	0.990	2.666	3.473	138.89	x-1, y, z-1
C ₁₈ H _{18A} ...N ₄	0.980	2.696	3.542	144.67	x-1, y, z-1
C ₁₉ H _{19C} ...N ₄	0.980	2.587	3.455	147.80	x-1, y, z-1

Table 3: Distances [Å] and Angles [°] of selected hydrogen bonds for the 2:3 ProTCNQ

D-H...A	d (D-H) (Å)	d (H...A) (Å)	d (D...A) (Å)	<(DHA) °	Symmetry code
C ₂₃ H _{23B} ...O ₁	0.990	2.573	3.529	162.21	x, ¹ / ₂ -y, z- ¹ / ₂
C ₂₅ H _{25A} ...N ₁	0.979	2.484	3.439(3)	165.04	x, ¹ / ₂ -y, z- ¹ / ₂
C ₂₂ H _{22A} ...N ₁	0.990	2.612	3.412 (3)	137.97	x-1, y, z-1
C ₆ H ₆ ...N ₂	0.950	2.703	3.439	134.73	1+x, y, z
C ₁₉ H _{19C} ...N ₂	0.979	2.661	3.352	127.8	x, ¹ / ₂ -y, z- ¹ / ₂
C ₂₁ H ₂₁ ...N ₃	1.000	2.352	3.185(3)	140.29	-x, -y, 1-z
C ₁₁ H ₁₁ ...N ₄	0.950	2.821	3.437	123.41	x-1, y, z
C ₁₄ H ₁₄ ...N ₅	0.950	2.668	3.272	121.92	1+x, y, z