Ni(III)/(IV) Bis(dicarbollide) as a Fast, Non-Corrosive Redox Shuttle for Dye-Sensitized Solar Cells

Tina C. Li,[†] Alexander M. Spokoyny,[‡] Chunxing She,[†] Omar K. Farha,[‡] Chad A. Mirkin,^{*,‡} Tobin J. Marks,^{*,†} and Joseph T. Hupp^{*,†,‡}

[†]Department of Chemistry, Argonne-Northwestern Solar Energy Research Center (ANSER), and the [‡]International Institute for Nanotechnology, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113

Experimental Section

All reactions were carried out under an inert atmosphere of nitrogen using standard Schlenk techniques and dry solvents; work-up and all post-reaction manipulations were done at ambient conditions, unless specifically noted otherwise. Solvents were purified by standard procedures. All reagents were used as received from Aldrich Chemical Company. Electrospray ionization (ESI) mass spectra were recorded on an Agilent ESI-MS MSD1100 mass spectrometer. Elemental analyses (C, H, N) were performed by Quantitative Technologies (Intertek), Whitehouse, NJ. Thermogravimetric analyses (TGA) were performed on a Mettler-Toledo TGA/SDTA851e. Samples placed in alumina pans were heated from 25 °C to 700 °C at 10 °C/minute under N₂ flow.

Nickel bis(dicarbollide) synthesis

Compound **1** was purchased from Sigma-Aldrich and used as received. Compound **2** was synthesized via procedure established by Hawthorne et al.^{S1} Next, **2** was reacted with NiCl₂ hexahydrate in 40% aq. NaOH solution to afford crude compound **3**, as described previously by Hawthorne et al.^{S2} Crude **3** was oxidized by aqueous FeCl₃, to afford crude **4**.^{S2} Crude **4** was subsequently filtered, washed with excess of water, dried and purified on the silica column with 1:1 mixture of hexanes/benzene, to afford

analytically pure **4** as light orange crystalline solid (70% yield based on **1**). Compound **4** was subsequently reduced in MeOH using 1.5 equiv. of NaBH₄ almost quantitatively within 5 min, the solvent was removed *in vacuo*, and residue dissolved in water and precipitated with slight excess of Me₄NCl. The precipitate was washed with excess of water and recrystallized from a mixture of dichloromethane/methanol/pentane to afford analytically pure **3** (96% based on **4**).

Anal. Calcd for C₈H₃₄B₁₈NNi (**3**): C, 24.16; H, 8.62; N, 3.52 Found: C, 24.04; H, 8.57; N, 3.52. ESI-MS: m/z (negative mode) 323.6 [**3**-Me₄N]⁻. Anal. Calcd for C₄H₂₂B₁₈Ni (**4**): C, 14.85; H, 6.85 Found: C, 14.92; H, 7.12. ESI-MS: m/z (negative mode) 323.3 [**4**]⁻.

Solar cell fabrication

The photoanodes were prepared on fluorine-doped tin oxide coated on glass (8 Ω/cm², Hartford Glass) with a 14 nm TiO₂ blocking layer deposited by atomic layer deposition (Savannah 100, Cambridge Nanotech Inc.) using alternating pulses of titanium isopropoxide (Aldrich) and water. The films were grown at a flow rate of 15 sccm at 200 °C with reactant exposure times of 1 s each. Transparent colloidal titania paste (Dyesol, DSL-90T) was next screen-printed to achieve ~5 μm film thicknesses and repeated for thicker films. Thicknesses were characterized by profilometry (Tencor Model P10) after sintering at 500 °C for 30 min. The films were then soaked in 40 mM TiCl₄ in <10% HCl at 60 °C for 30 min, rinsed with water and isopropanol and re-sintered at 500 °C prior to dye loading. For the ALD Al₂O₃ modified substrates, trimethylaluminum (Aldrich) and water were used as precursors to grow the films at 200°C, with reactant exposure times of 10 s each. The films were held at 90 °C before immersing in a solution of 0.3 mM of *cis*-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) bis-tetrabutylammonium (Dyesol, N719) for 24 h.

An adhesive polymer spacer (Solaronix SX1170-25, 25 μm) was used to sandwich the sensitized photoanode to the pre-drilled, metal-coated FTO counterelectrode (15 Ω/cm², Hartford Glass). Platinum, gold, and silver counterelectrodes were respectively deposited on the FTO by drop-casting H₂PtCl₆ solution,^{S3} vapor depositing 45 nm gold (base pressure <10⁻⁵ Torr), or sputter coating 45 nm

silver (base pressure 10^{-3} Torr). The electrolyte, which contained a ratio of 0.50 M TMA-Ni(III) bis(dicarbollide) **3** salt (TMA = tetramethylammonium) and 0.030 M Ni(IV) bis(dicarbollide) **4**, with additives such as 0.10 M LiBF₄, 0.10 M TMABF₄ and/or 0.60 M tert-butylpyridine in 85:15 acetonitrile/valeronitrile solution was conducted into the cell by vacuum-filling. For I/I₃⁻ cells, 0.60 M 1-butyl-3-methylimidazolium iodide (BMII), 0.030 M I₂, 0.10 M guanidinium thiocyanate, 0.50 M tert-butylpyridine was used and 0.10 M Fc, 0.010 M FcBF₄, 0.20 M TBABF₄ for Fc/Fc⁺ cells.

Characterization

DSC *J-V* characteristics were measured for the completed cells under AM 1.5 conditions (Class A Spectra Nova Technologies, 995 W/m²). Open-circuit voltage decay (OCVD) measurements were made with a CH Instruments 1202 potentiostat and a Jobin Yvon Spex FluoroLog-3 fluorimeter equipped with a Xe lamp and an AM 1.5 solar filter. Incident photon-to-current conversion efficiency (IPCE) spectra were obtained by monitoring the current responses, averaged over 10 s increments at each wavelength from 400 nm – 800 nm. The spectral spacing between each wavelength was set to 10 nm.

Transient absorbance kinetic measurements were performed with a nanosecond transient absorption detection system, Proteus (Ultrafast Systems Inc., FL, USA), equipped with a Xe arc lamp (75 W) and a Si photodiode. Samples were excited with pulses from the second harmonic (532 nm, 10 ns, 20-30 mJ/pulse) from a Q-switched Nd:YAG laser (Continuum) and were probed at 500 nm. Optical density of N719/TiO₂ samples is 0.3-0.5 at 532 nm.

Figure S1. Cyclic voltammogram of Ni bis(dicarbollide) with 0.2 M TBABF₄ in deaerated acetonitrile, with ferrocene as an internal reference. Cyclic voltammograms were obtained at a scan rate of 0.1 V/s with a CH Instruments 900 Electrochemical Analyzer using Ag/AgCl as the reference and Pt wire as the working electrode.

Figure S2. Thermogravimetric analyses of Ni bis(dicarbollide).

Figure S3. Current-transients at 10 s intervals of DSCs using 0.50 M/0.030 M **3/4**, 0.10 M TMABF₄, 0.50 M *tert*-butylpyridine in 85:15 acetonitrile:valeronitrile, at (a) 2 nm, 4 nm, 6 nm, 8 nm, and 10 nm slit widths, corresponding to (b) light intensities between 1/10 and 1 sun illuminations.

J_{sc} values at various light intensities did not appear to have noticeable deviation from linearity, in contrast to DSCs utilizing cobalt-based shuttles, where diffusion of the polypyridyl cobalt (III) complex through the titania framework is reported to limit the currents attainable at 1 sun.^{S4} Slow diffusion with cobalt shuttles relative to I^-/I_3^- is attributed not only to their larger size, but also because of their cationic nature, causing Co(III) species to preferentially bind at the titania photoanode at higher light intensities^{S5} and making it difficult for cells to sustain initial current spikes. The anionic nature of the nickel bis(dicarbollide) redox couple prevents it from electrostatically binding to the titania surface.

Figure S4. J - V characteristics of $3/4$ with electrolyte concentrations of 0.50 M/0.030 M $3/4$, 0.10 M TMABF₄, 0.50 M *tert*-butylpyridine in 85:15 acetonitrile:valeronitrile, with 0 (green solid), 1 (black dotted), and 2 (red dashed) cycles of Al₂O₃ ALD on the TiO₂ nanoparticle framework. J_{sc} has 1.26 mA/cm² with no ALD treatment and 3.10 mA/cm² with 1 cycle Al₂O₃.

Figure S5. J - V characteristics of DSCs with 0.50 M/0.030 M $3/4$ couple, with 0 ALD cycles, using Au (top red solid), Ag (middle grey solid), and Pt (bottom black solid line) and 1 cycle Al₂O₃, using Au (top red dotted), Pt (middle black dotted), and Pt (bottom gray dotted).

Figure S6. *J-V* characteristics of **3/4** with 2 ALD cycles of Al_2O_3 on the TiO_2 nanoparticle framework with Au (red), Ag (gray), and Pt (black-dashed line) counterelectrodes.

References

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