

Supporting Online Information

**Remarkable Stability of High Energy
Conformers in Self Assembled Monolayers of a
Bistable Electro- and Photoswitchable
Overcrowded Alkene**

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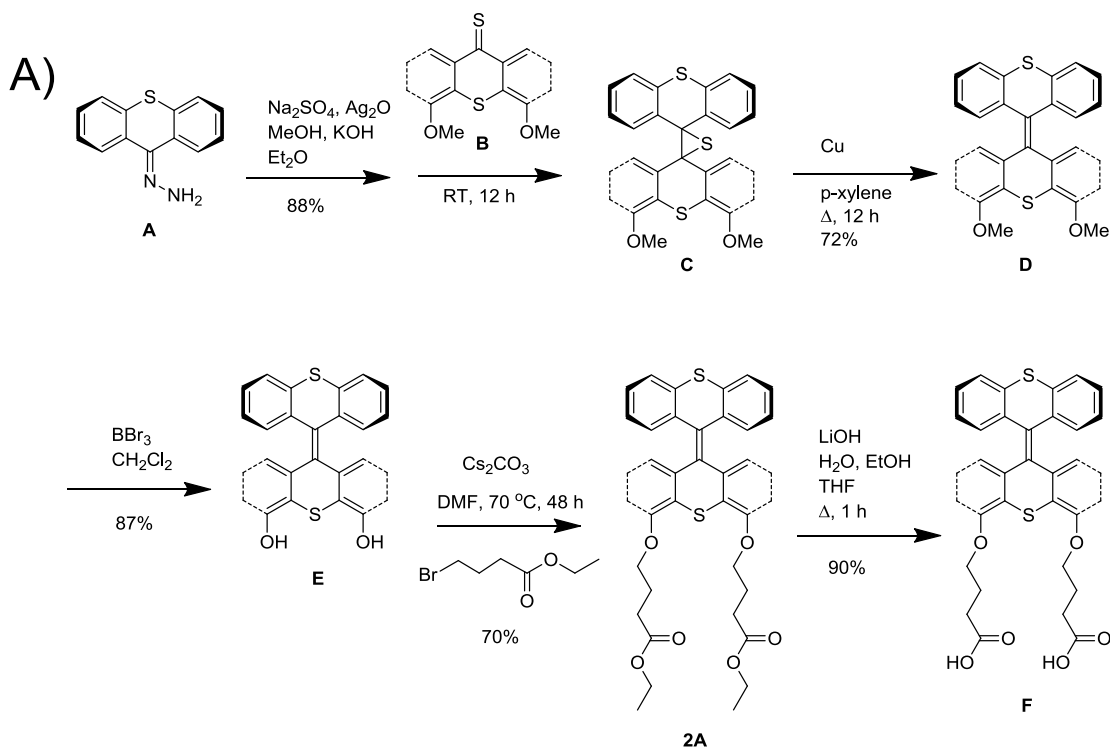
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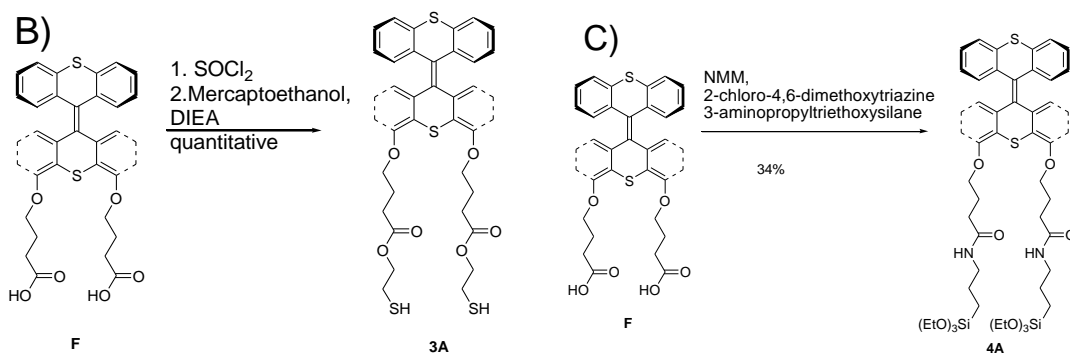
Synthesis and characterization

All chemicals were purchased from commercial sources (Sigma Aldrich, Acros) and used as received without further purification unless stated otherwise. All solvents used for spectroscopic and electrochemical measurements were UVASOL grade (Merck) unless stated otherwise.

^1H NMR spectra were recorded using a Varian Mercury Plus spectrometer (300 or 400 MHz). Chemical shifts are relative to the residual solvent peak ($\text{CDCl}_3 = 7.26$ ppm, $\text{d}_6\text{-DMSO} = 2.49$ ppm).

The divergent synthetic route taken to preparing compounds **2-4** from **A** is shown below.





Dispiro[4,5-dimethoxy-9H-thioxanthene-9, 2'-thiirane-3', 9''-(9''H)-thioxanthene]

(C) Under a nitrogen atmosphere, thioxanthen-9-ylidene-hydrazine **A**^[1] (0.75 g, 3.32 mmol) was dissolved in diethyl ether (50 mL). Na₂SO₄ (1.8 g), Ag₂O (1.8 g) and KOH (1 mL of saturated solution in methanol) were added and the mixture was stirred at room temperature until a deep blue, violet color was observed (~1 h). 4,5-Dimethoxy-thioxanthene-9-thione **B**^[2] (400 mg, 1.39 mmol) was added and evolution of N₂ was observed. The mixture was stirred over night at room temperature. Product **C** precipitated and was collected on a glass filter, dried and obtained pure as a slightly yellowish powder (590 mg, 1.22 mmol, 88% based on thioketone). ¹H NMR (300 MHz, CDCl₃, 25°C) δ 7.64 – 7.62 (m, 2H), 7.30 (dd, *J* = 8.1, 1.1 Hz, 2H), 7.13 – 7.11 (m, 2H), 6.96 – 6.91 (m, 4H), 6.87 (dd, *J* = 8.1, 8.1 Hz, 2H), 6.51 (dd, *J* = 1.1, 8.1 Hz, 2H), 3.77 (s, 6H); ¹³C NMR (50 MHz, CDCl₃, 25°C) δ 172.10 (s), 154.28 (s), 135.78 (s), 131.91 (s), 131.77 (s), 130.44 (d), 126.54 (d), 125.85 (d), 125.15 (d), 125.05 (d), 124.04 (s), 123.05 (d), 108.33 (d), 66.81 (s), 66.18 (s), 56.04 (q); HRMS calcd for C₂₈H₂₀O₂S₃: 484.06253; found: 484.06313.

4,5-Dimethoxy-[9,9']bithioxanthenylidene (D) Under a nitrogen atmosphere, **C** (580 mg, 1.20 mmol) was dissolved in *p*-xylene (20 mL) and Cu-bronze (763, mg, 12.0 mmol)

was added. The mixture was heated at reflux overnight. After cooling, the mixture was filtered and the filtrate was concentrated *in vacuo* to yield **D** (390 mg, 0.86 mmol, 72%) as a yellow solid. ^1H NMR (300 MHz, CDCl_3 , 25°C) δ 7.49 (d, $J = 7.7$ Hz, 2H), 7.09 (dd, $J = 7.7, 7.3$ Hz, 2H), 6.90 – 6.77 (m, 6H), 6.67 (d, $J = 8.1$ Hz, 2H), 6.42 (d, $J = 7.7$ Hz, 2H), 3.95 (s, 6H); ^{13}C NMR (50 MHz, CDCl_3 , 25°C) δ 155.71 (s), 136.41 (s), 136.27 (s), 135.62 (s), 133.27 (s), 129.76 (d), 126.99 (d), 126.54 (d), 126.08 (d), 125.58 (d), 123.87 (s), 122.25 (d), 107.96 (d), 55.93 (q), one aromatic singlet was not observed; HRMS calcd for $\text{C}_{28}\text{H}_{20}\text{O}_2\text{S}_2$: 452.09046; found: 452.09089.

[9,9']Bithioxanthenylidene-4,5-diol (E) Under a nitrogen atmosphere, **D** (360 mg, 0.80 mmol) was dissolved in CH_2Cl_2 (20 mL) and the mixture was cooled to 0°C . BBr_3 (2.4 mL of 1.0 M solution in CH_2Cl_2 , 2.4 mmol) was added and the mixture was stirred overnight at room temperature. Water (20 mL) was added and the mixture was extracted with CH_2Cl_2 (2×20 mL). The combined organic layers were washed with water (20 mL) and brine (20 mL), dried (Na_2SO_4) and concentrated *in vacuo* to yield **E** (294 mg, 87%) as a yellowish powder. ^1H NMR (300 MHz, $\text{DMSO}-d_6$, 25°C) δ 10.12 (b, 2H, OH), 7.57 (d, $J = 8.1$ Hz, 2H), 7.17 (dd, $J = 7.7, 6.6$ Hz, 2H), 6.95 (dd, $J = 7.3, 7.7$ Hz, 2H), 6.78 – 6.64 (m, 6H), 6.11 (d, $J = 7.7$ Hz, 2H); no ^{13}C NMR spectrum was recorded due to low solubility. HRMS calcd for $\text{C}_{26}\text{H}_{16}\text{O}_2\text{S}_2$: 424.05916; found: 424.05719.

4-[5-(3-Ethoxycarbonyl-propoxy)-[9,9']bithioxanthenyliden-4-yloxy]-butyric acid ethyl ester (2A) Under a nitrogen atmosphere, a mixture of **E** (250 mg, 0.59 mmol), Cs_2CO_3 (576 mg, 1.77 mmol), 4-bromo-butyric acid ethyl ester (345 mg, 1.77 mmol) and DMF (15 mL) were heated at 70°C over night. After cooling, water (15 mL) was added and the mixture was extracted with ethyl acetate (3×20 mL). The combined organic

layers were washed with 10% HCl_(aq) (20 mL), water (20 mL), NaHCO₃ (aq, sat.) and brine (20 mL), dried (Na₂SO₄) and concentrated *in vacuo* to yield a yellowish powder. The powder was washed twice with pentane (10 mL) by stirring (10 min.) and subsequent filtration to yield **2A** (270 mg, 0.41 mmol, 70%) as a yellowish powder. ¹H NMR (300 MHz, CDCl₃, 25°C) δ 7.49 (d, *J* = 7.3 Hz, 2H), 7.09 (ddd, *J* = 8.3 6.6, 1.2, Hz, 2H), 6.90 – 6.78 (m, 6H), 6.66 (d, *J* = 7.3 Hz, 2H), 6.40 (dd, *J* = 7.7, 1.2 Hz, 2H), 4.25 – 4.01 (m, 8H), 2.77 – 2.58 (m, 4H), 2.27 – 2.18 (m, 4H), 1.26 (t, *J* = 7.0 Hz, 6H); ¹³C NMR (50 MHz, CDCl₃, 25°C) δ 173.27 (s), 154.90 (s), 136.25 (s), 136.25 (s), 135.58 (s), 133.26 (s), 133.11 (s), 129.71 (d), 126.95 (d), 126.49 (d), 125.89 (d), 125.55 (d), 124.71 (s), 122.39 (d), 109.29 (d), 67.74 (t), 60.35 (t), 30.74 (t), 24.64 (t), 14.22 (q); HRMS calcd for C₃₈H₃₆O₆S₂: 652.19530; found: 652.19412.

4-[5-(3-Carboxy-propoxy)-[9,9']bithioxanthenyliden-4-yloxy]-butyric acid (F)

Under a nitrogen atmosphere, **2A** (264 mg, 0.40 mmol), was heated at reflux for 1 h in a mixture of water (3 mL), THF (3 mL) and ethanol (3 mL). After cooling, the mixture was acidified with 2 M HCl (aq.) and the precipitate was collected on a glass filter, washed with methanol and diethyl ether and dried to yield **F** (215 mg, 0.36 mmol, 90%) as a yellow powder. An impurity [~10%, probably a lithium salt with THF; ¹H NMR (300 MHz, CDCl₃, 25°C) δ 3.58 (m, 4H), 1.74 (m, 4H)] was found. **F** was used for further modification without additional purification. ¹H NMR (300 MHz, DMSO-d₆, 25°C) δ 12.71 (b, 2H, OH), 7.60 (d, *J* = 7.7 Hz, 2H), 7.19 (dd, *J* = 7.7, 7.7 Hz, 2H), 6.97 (dd, *J* = 7.7, 7.7 Hz, 2H), 6.91 – 6.87 (m, 4H), 6.65 (d, *J* = 7.7 Hz, 2H), 6.24 (dd, *J* = 6.4, 2.4 Hz, 2H), 4.25 – 4.18 (m, 2H), 4.06 – 3.98 (m, 2H), 2.53 – 2.43 (m, 4H, hidden under

DMSO absorption), 2.06 – 1.99 (m, 4H); HRMS calcd for C₃₄H₂₈O₆S₂: 596.13270; found: 596.13399.

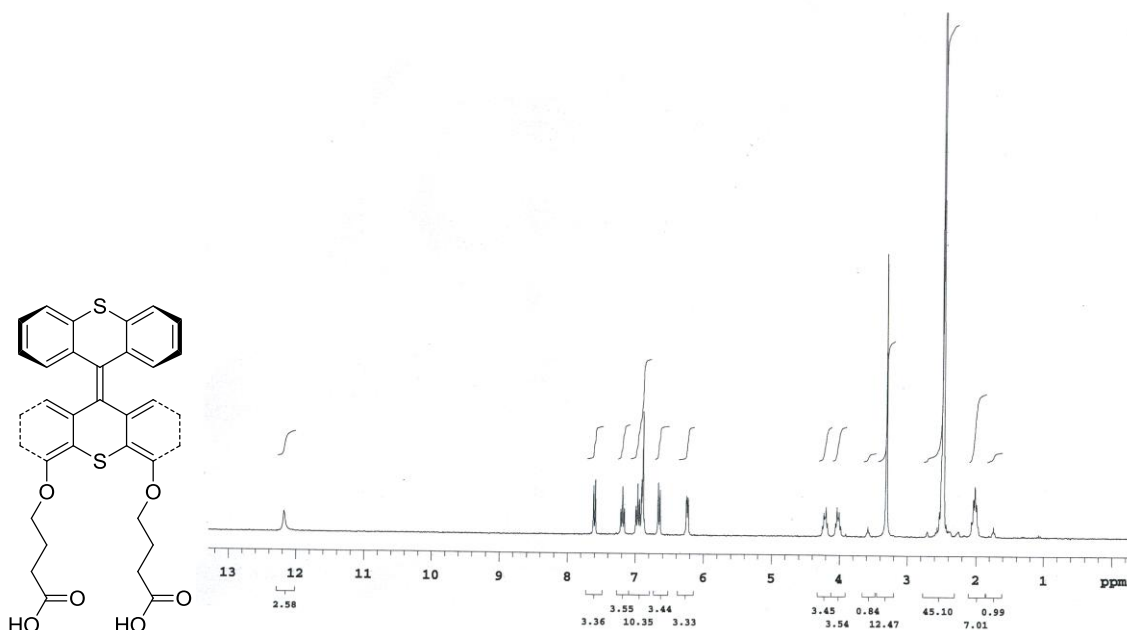


Figure S1. ¹H NMR spectrum of F in DMSO-d₆

bis(2-mercaptoethyl)-4,4'-((2,3,6,7-tetrahydro-[9,9'-bithioxanthenylydene]-4,5-diyl)bis(oxy))dibutanoate (3A) Acid F (20 mg, 3.35 x 10⁻⁵ mol) was dissolved in 2 mL freshly distilled CH₂Cl₂ under a nitrogen atmosphere. SOCl₂ (30 μL) was added to this solution, and the mixture was subsequently heated at reflux for 1 h followed by cooling slowly to room temperature. The solvent was removed in vacuo. The resulting brown colored residue was redissolved in 2 mL dry CH₂Cl₂ and 22 μL mercaptoethanol and 11 μL N,N-diisopropylethylamine (DIEA) were added. The solution was then placed under a nitrogen atmosphere and heated at reflux for 1 h. After cooling, the organic phase was washed with sat. aq. NaHCO₃ solution and brine and dried over Na₂SO₄. The solvent was removed in vacuo and the resulting residue dried overnight under vacuum. The crude product was dissolved in CH₂Cl₂ and passed through a silica gel plug to remove

unreacted mercaptoethanol to obtain the **3A** quantitatively. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C) δ 7.52 (d, $J = 7.6$ Hz, 2H), 7.11 (dd, $J = 8$ Hz, 2H), 6.84 (m, 4H), 6.69 (d, $J = 8$ Hz, 2H), 6.44 (d, $J = 8$ Hz, 2H), 4.26-4.22 (m, 8H), 4.08-4.06 (m, 4H), 2.78-2.71 (m, 8H), 2.27-2.24 (m, 4H), 1.50 (t, $J = 8.8$ Hz, 2H). $^{13}\text{C NMR}$ (50 MHz, CDCl_3) δ 173.02 (s), 154.84 (s), 136.29 (d), 135.59 (s), 133.18 (s), 129.74 (s), 127.01 (s), 126.55 (s), 125.98 (s), 125.60 (s), 124.56 (s), 122.51 (s), 109.24 (s), 67.60 (s), 65.73 (s), 30.66 (s), 24.62 (s), 23.29 (s), HRMS calcd. For $\text{C}_{38}\text{H}_{36}\text{Na}_2\text{O}_6\text{S}_4$ (Na adduct): 762.1190 found 762.2339. Molar absorptivity in CH_2Cl_2 , $10300\text{ M}^{-1}\text{ cm}^{-1}$ @ 348 nm and $13800\text{ M}^{-1}\text{ cm}^{-1}$ @ 301 nm.

4,4'-((2,3,6,7-tetrahydro-[9,9'-bithioxanthenylidene]-4,5-diyl)bis(oxy))bis(N-(3-(triethoxysilyl)propyl)butanamide) (4)

The diacid **F** (35 mg, 58 μmol) was dissolved in dry CH_2Cl_2 (5 mL). This solution was cooled to 0°C and stirred for 5 min under N_2 and N-methylmorpholine (25 μL , 270 μmol) and 2-chloro-4,6-dimethoxytriazine (20 mg, 114 μmol) were added. The solution was then stirred for 4 h at 0°C under N_2 . Additional N-methyl morpholine (25 μL , 270 μmol) was added followed by 3-aminopropyltriethoxysilane (54 μL , 230 μmol). The mixture was stirred for 1 h at 0°C and then overnight at room temperature. The solvent was removed under reduced pressure to yield a white semi-solid which was purified by column chromatography (SiO_2 , 2:1 EtOAc/Pentane) to give the desired product (yield 20 mg, 20 μmol , 34%). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C) δ 7.51 (d, $J = 8.5$ Hz, 2H), 7.11 (dd, $J = 8.5$ Hz, 2H), 6.90 (dd, $J = 7.4$ Hz, 2H), 6.85 (t, $J = 12$ Hz, 2H), 6.81 (d, $J = 6.5$ Hz, 2H), 6.68 (d, $J = 12$ Hz, 2H), 6.43 (d, $J = 12$ Hz, 2H), 4.26-4.22 (m, 8H), 4.08-4.06 (m, 4H), 2.78-2.71 (m, 8H), 2.27-2.24 (m, 4H), 1.50 (t, $J = 8.8$ Hz, 2H), 4.03 (m, 12 H), 3.75 (m, 4H), 2.46 (m, 4H), 2.31

(m, 4H), 1.48 (m, 4H), 1.27 (t, $J = 8.0$ Hz, 18 H), 0.54 (m, 4H). Monolayer formation on cleaned ITO and quartz slides (vide infra) were prepared by heating the slides at reflux in toluene with **4** overnight followed by rinsing with toluene, dichloromethane and drying in an argon gas stream.

Preparation of compound $2^{2+}(\text{PF}_6^-)_2$

The dication of **2A** was prepared by bulk oxidation in CH_3CN with 0.1 M KPF_6 and isolated as its PF_6^- salt as described earlier for compound **1**.³

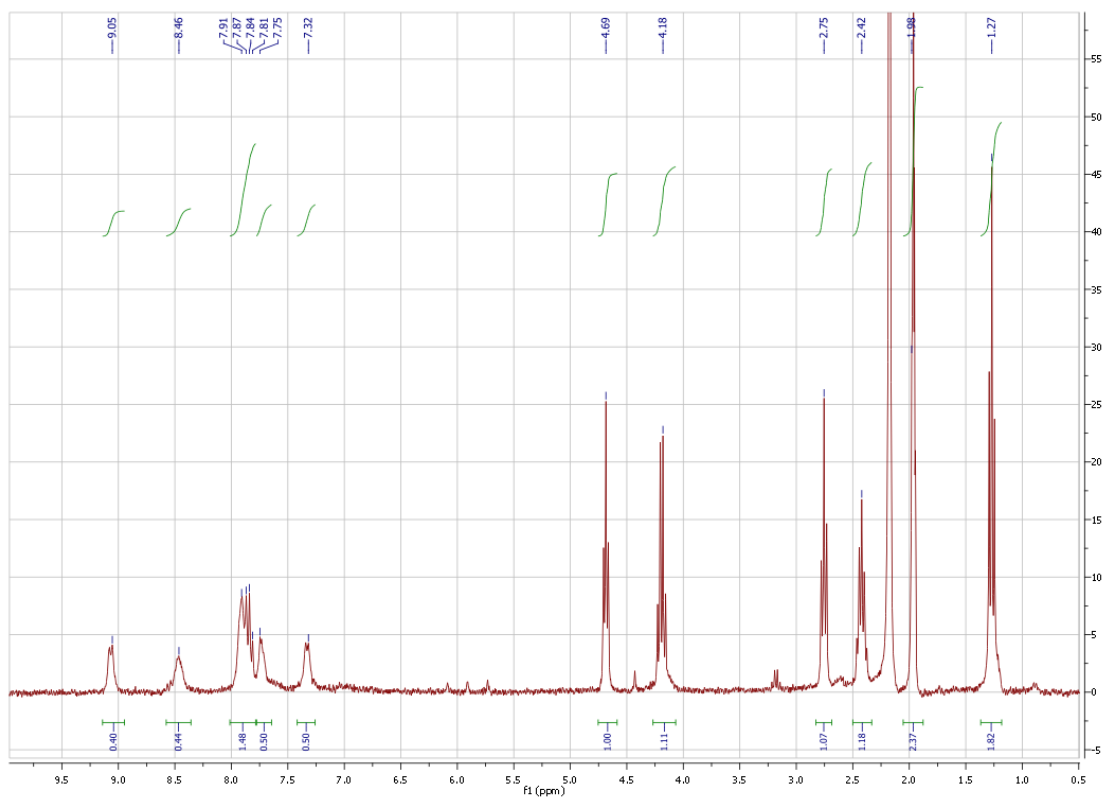


Figure S2. ^1H NMR spectrum of 2^{2+} in CD_3CN

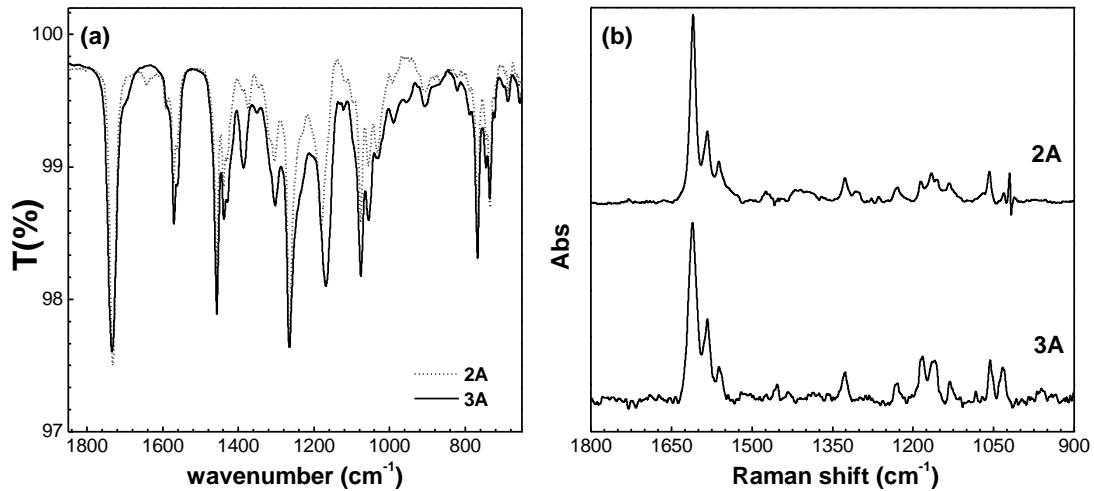


Figure S3. (a) FTIR and (b) Raman (λ_{exc} 785) spectra of **2A** and **3A** at 298 K.

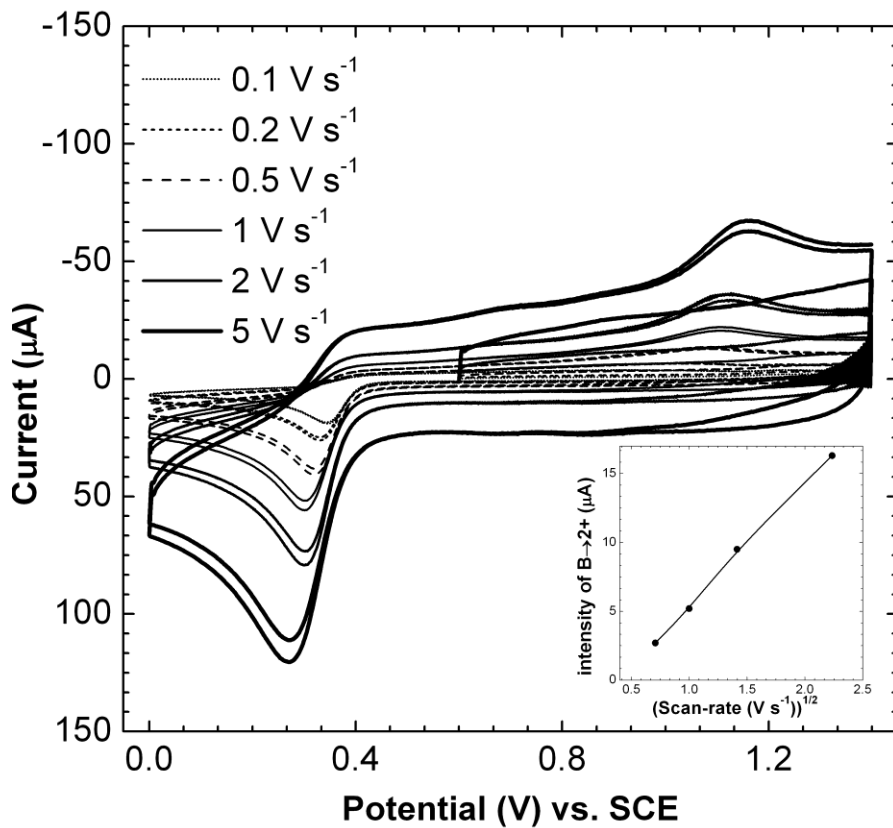


Figure S4. Cyclic voltammetry of **2**²⁺(PF₆⁻)₂ (inset: current vs sqrt(scan rate)) in CH₃CN (0.1 M TBAPF₆).

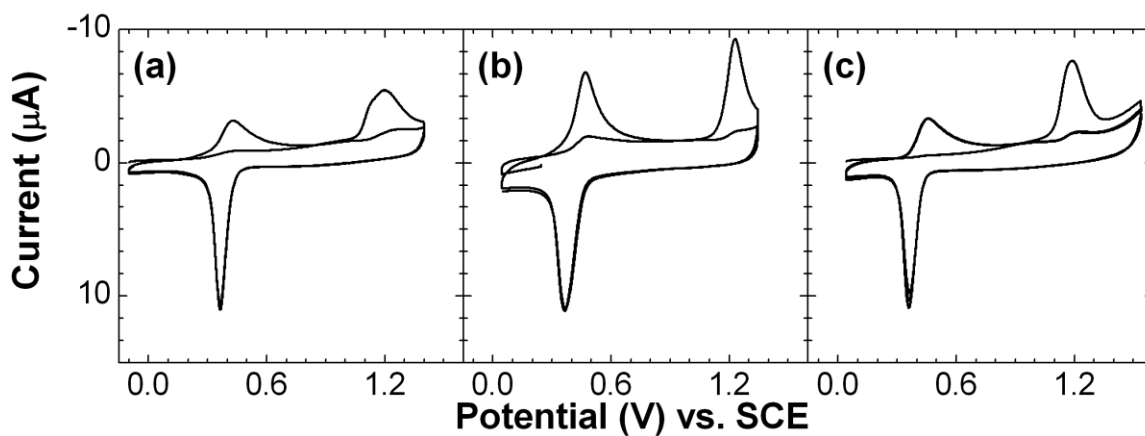


Figure S5. Cyclic voltammogram of a SAM of 3A on a Au bead in (a) CH₃CN (0.1 M TBAPF₆), (b) CH₂Cl₂ (0.1 M TBAPF₆) and (c) CH₃CN (0.1 M LiClO₄) ($\Gamma = 1 \times 10^{-10}$ mol cm⁻²).

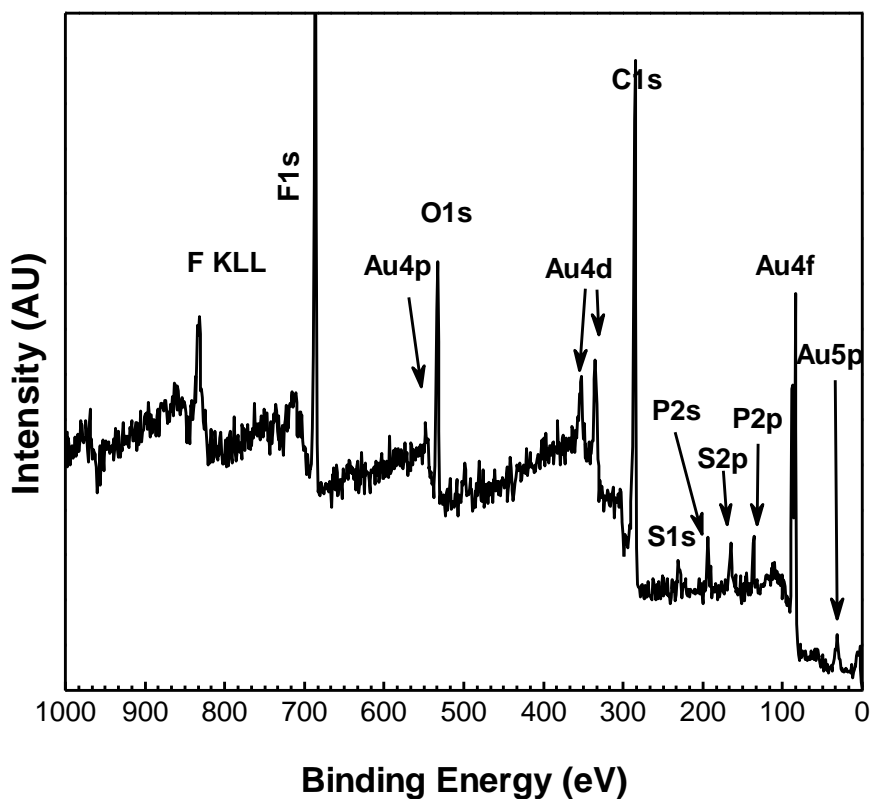


Figure S6. XPS overview scan spectrum for a thick film $2^{2+}(\text{PF}_6)^{-}2$ on Au on mica.

Preparation of the substrates. 150 nm thick polycrystalline gold films on mica (grade V-1, TED PELLA) were prepared in a home-built deposition system by sublimation of 99.99% gold (SCHÖNE EDELMETAAL B.V). To obtain atomically flat Au(111) substrates, sublimation was carried out at a base pressure of 10^{-7} Torr onto freshly cleaved mica sheets kept at 650 K, which had been pre-heated at the same temperature for 16 h in order to degas environmental impurities. The substrate was cooled down to room temperature over a period of 8 h.

For XPS, ellipsometry and contact angle measurements the gold layer was formed on mica. For spectroelectrochemical measurements a 200 nm film of gold was deposited with a 2 nm chromium interlayer on a glass microscope slide (Knittel Glass). Prior to gold evaporation, the slide was cleaned with 10% hydrochloric acid for 10 min, rinsed with water, acetone and ethanol for 2 min, followed by drying under a stream of nitrogen. The slides were then subjected to air plasma cleaning (Diener) for 1 min. ITO and quartz substrates were prepared by treatment as described earlier (see for example Markovich et al.⁴). Gold bead working electrodes for spectro/electrochemical measurements were prepared from 0.5 mm 99.999% Au wire (SCHÖNE EDELMETAAL B.V), which was melted in a H₂ gas flame to form a bead with a diameter of 2-3 mm. The freshly prepared bead was cleaned chemically and electrochemically. Roughening of the gold bead electrode was performed according to the procedure described by Tian et al.⁵ SERS active surfaces were obtained after 9 cycles and the measured electrochemically active surface area did not change significantly with further cycling. Immediately after cleaning, the substrates were immersed into a solution of the compound for subsequent monolayer formation.

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