Supplementary Data for

Intramolecular electron transfer in the photodimerisation product of a tetrathiafulvalene derivative in solution and on surface

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Experimental Details

Synthesis of dimethyl 2,5-bis(benzo[d][1,3]dithiol-2-ylidene)tetrahydrocyclobuta[1,2-d:3,4-d']bis([1,3]dithiole)-3a,3b-dicarboxylate ***(2).*** Tetrathiafulvalene (methyl 2-(benzo[d][1,3]dithiol-2-ylidene)-1,3-dithiole-4-carboxylate) **1** (510 mg, 1.6 mmol) was grated to a thin powder and left undisturbed in the sunlight for 24 hours. A colour change of the solid from the initial orange to yellow was observed and after purification in a silica-gel chromatographic column (eluent CH_2Cl_2), **2** was obtained in 75% (375 mg) yield together with recovered tetrathiafulvalene **1** (112 mg, 22 %).

IR (ν/cm^{-1}): 3052 (w), 2924 (w), 2852 (w), 1740 (s), 1445 (m), 1254 (s), 1207(w), 1156(m), 1076 (w), 734(m); **^{1}HNMR** (250 MHz; $CDCl_3$) (δ/ppm): 6.87-6.70 (m, 8H), 5.35 (s, 2H), 3.82 (s, 6H); **UV-Vis** (CH_2Cl_2) (λ/nm (logε)): 244 (4.481), 292 (4.449), 410 (313); **Elemental analysis**: calculated: C (46.13%), H (2.58%); experimental C (46.27%), H (2.30%); **LDI-TOF** (m/z): calculated: 623.9; experimental: 396.2 ([M$^+$-PhTTF]); **CV** (0.1 M TBAHFP in CH_2Cl_2 *vs.* Ag/AgCl): two reversible waves at $E^{1/2}$= +0.75 V and $E^{1/2}$= +1.10 V and one irreversible wave at $E^{1/2}$= +1.60 V.

Synthesis of (2,5-bis(benzo[d][1,3]dithiol-2-ylidene)tetrahydrocyclobuta[1,2-d:3,4-d']bis([1,3]dithiole)-3a,3b-diyl)dimethanol ***(3).*** In an anhydrous system under argon, diisobutylaluminium hydride (1 M in CH_2Cl_2, 0.7 mL, 0.7 mmol) was added drop wise to a solution of **2** (50 mg, 0.08 mmol) in dry dichloromethane (10 mL) and the mixture was cooled at -78ºC in a $CO_{2(s)}$:acetone bath. After 5 hours, the mixture was treated with a mixture of 6 M aqueous HCI and MeOH (1:1) (10 mL) and then allowed to reach room temperature. Dichloromethane (100 mL) was added and the organic layer was washed with 1 M aqueous HCl (2 x 50 mL), then with water, dried with $MgSO_4$, filtered and concentrated under reduced pressure. The yellow solid was purified through a silica gel chromatographic column (70-230 mesh, eluent initially CH_2Cl_2 increasing polarity up to CH_2Cl_2:acetone (1:1)). Initial diester was recovered in 10% yield (5 mg), the mono-reduced compound was separated in 25% yield (12 mg) and the desired di-alcohol compound **3** was obtained in 45% yield (20.5 mg).

IR (ν/cm^{-1}): 3242 (m), 2917 (w), 2856 (w), 1594 (w), 1458 (m), 1444 (s), 1429 (s), 1373 (s), 1283 (m), 1257 (m), 1119 (s), 1092 (s), 1017 (s), 969 (m), 712 (s); **^{1}HNMR** (250 MHz; CD_3OD) (δ/ppm): 6.90-6.84 (m, 8H), 5.54 (s, 2H), 3.82 (s, 4H), 2.88 (s, 2H); **UV-Vis** (CH_2Cl_2) (λ/nm (logε)): 244 (4.726), 290 (4.703), 400 (339); **Elemental analysis**: calculated: C (46.45%), H (2.83%); experimental: C (45.95%), H (2.72%); **LDI-TOF** (m/z): calculated: 567.9; experimental: 565.92 ([M$^+$]); **CV** (0.1 M TBAHFP in CH_2Cl_2 *vs.* Ag/AgCl): two reversible waves at $E^{1/2}$= +0.65 V and $E^{1/2}$= +0.90 V and one irreversible oxidation wave at $E^{1/2}$= + 1.51 V.

Synthesis of (2,5-bis(benzo[d][1,3]dithiol-2-ylidene)tetrahydrocyclobuta[1,2-d:3,4-d']bis([1,3]dithiole)-3a,3b-diyl)bis(methylene) bis((3-(triethoxysilyl)propyl)carbamate) ***(4).*** In an anhydrous system, alcohol **3** (25 mg; 0.044 mmol) in dry THF (3 mL) was poured inside a 10 mL three-neck round-bottom flask with a refrigerator column. Then, 3-isocyanatopropyltriethoxysilane (ICTES) (25 μL; 0.10 mmol) and triethylamine (14 μL; 0.10 mmol) were added while stirring and the mixture was refluxed overnight. The solvent was evaporated at reduced pressure and the resulting yellow oil was cooled at 5ºC overnight. Purification through a reverse phase silica-gel chromatographic column (CH_3CN:Acetone (1:4) as eluent) afforded compound **4** in 45% yield (21 mg).

IR (ν/cm^{-1}): 3326 (w), 2974 (w), 2927 (w), 2884 (w), 1626 (m), 1583 (m), 1441 (w), 1389 (w), 1282 (w), 1189 (m), 1073(s), 955 (s), 775 (m); **^{1}HNMR** (250 MHz; $CDCl_3$) (δ/ppm): 6.90-6.79 (m, 8H), 4.72 (s, 2H), 3.81-3.62 (m, 12 H), 3.10 (q, 4H, J= 6.2 Hz), 1.64-1.45 (m, 4H), 1.03-1.1 (m, 18H), 0.63-0.54 (m, 4H); **^{29}Si NMR** (360 MHz; CDCl3) (δ/ppm): -99; **UV-Vis** (CH_2Cl_2) (λ/nm (logε)): 255 (3.950), 280 (3.899), 307 (3.599), 420 (257); **Elemental analysis**: calculated: C (47.43%), H (5.50%), S (24.12%); Si (5.28%); experimental C (48.06%), H (5.70%), S (24.21%); Si (5.02%); **LDI-TOF** (m/z): calculated: 1063.6; experimental: 1034.26 ([M$^+$- C_2H_5]); **CV** (0.1 M TBAHFP in CH_2Cl_2 *vs.* Ag/AgCl): two reversible waves at $E^{1/2}$= + 0.48V and $E^{1/2}$= + 0.80 V.

Self-Assembled Monolayer Preparation: The ITO substrates were purchased to Delta Technologies, LTD (USA), as double-face coated ITO over unpolished float glass showing a resistance of 15-25 Ω. The dimensions of the substrates were of 7x50x0.5(mm) for electrochemical and UV-Vis experiments and 3x150x0.5(mm) for EPR measurements. The ITO substrates were firstly degreased in ultra-sonic bath using a solvent series with increased polarity: dichloromethane, acetone and then ethanol for fifteen minutes each. The substrates were then rinsed with pure ethanol and dried under a nitrogen stream. Secondly, the substrates were treated in an oxidising bath of NH_4OH:H_2O_2:H_2O (1:1:5) at 80ºC for 30 minutes and washed thoroughly with millipore distilled water, rinsed with ethanol and then dried under nitrogen stream. The freshly cleaned ITO substrates were immersed in a 1 mM solution of **4** in freshly distilled toluene, in a vessel under argon atmosphere. The first 3 hours the solution was kept in a thermostatized oil bath at 80ºC and then it was left at room temperature overnight. The substrates were then washed thoroughly with toluene and dried under nitrogen stream giving **S-4**.

A *TOF-SIMS* IV mass spectrometer (Ion-Tof GmbH, Münster, Germany) equipped with a bismuth cluster (Bi3+) ion source in pulses of 15 ns was used for these experiments. The sample was scanned under these conditions in a 125x125 μm^2 area for 30 seconds with a mass resolution of 10^5 m/z. The secondary ions emitted were accelerated to 2 keV, the mass analysed during the time of flight and post-accelerated to 10 keV after detection. The abundance of the ions detected was normalized to the total ion abundance.

Contact angle measurements were performed with Millipore water on a contact angle measuring system DSA 100 from KRÜSS using the SCA20 software.

X-ray Photoelectron Spectroscopy (XPS) experiments were performed using *PHI 5500 Multitechnique System* (from *Physical Electronics*) with a monochromatic X-ray source (Al K α line of 1486.6 eV energy and 350 W power), placed perpendicular to the analyzer axis and calibrated using the $3d_{5/2}$ Ag line with a full width at half maximum (FWHM) of 0.8 eV. The analyzed area was a circle of 0.8 mm diameter, and the selected resolution for the spectra was 187.5 eV of *pass energy* and 0.8 eV/step for the general spectra and 23.5 eV of *pass energy* and 0.1 eV/step for the spectra of the different elements. All measurements were made at a pressure between $5x10^{-9}$ and $2x10^{-8}$ torr inside an ultra-high vacuum chamber.

Cyclic Voltammetry (CV) with the functionalised surfaces was used to characterize the SAM employing a potentiostat-galvanostast *VersaSTAT* from *Princeton Applied Research.* The functionalized surfaces were used as working electrode, a silver wire as pseudo-reference electrode, and a degassed solution of 0.02 M TBAHFP in acetonitrile as electrolyte solution. The same equipement was used for the chronomperometric experiments in solution

EPR spectra were obtained at room temperature using a Bruker ELEXYS E500 X band spectrometer. A rectangular TE102 cavity was used for the measurements. The signal to noise ratio of spectra was increased by accumulation of scans using the F/F lock accessory to guarantee large field reproducibility. Precautions to avoid undesirable spectral distortions and line broadenings, such as those arising from microwave power saturation and magnetic field over modulation, were also taken into account. To avoid dipolar line broadening from dissolved oxygen, solutions were always carefully degassed with pure Argon. EPR of neutral and oxidized SAM were performed inside a rectangular quartz holder filled with argon.

UV-Vis absorbance measurements to optically characterise the materials were performed in a *Cary 5000* UV-Vis-NIR spectrophotometer using the double beam mode.

*X-ray Crystallography***.** Crystals of **2** suitable for X-ray diffraction study were mounted on a loop with protective oil. X-ray data were collected at 150K on a Bruker AXS-KAPPA APEX II diffractometer using graphite monochromated Mo-Kα radiation (λ=0.71069 Å) and operating at 50kV and 30 mA. Cell parameters were retrieved using Bruker SMART[1] software and refined using Bruker SAINT[2] on all observed reflections. Absorption corrections were applied using SADABS[3]. Structure solution and refinement were performed using direct methods with program SIR97[4] and SHELXL97[5], both included in the package of programs WINGX-Version 1.80.05[6]. A full-matrix least-squares refinement was used for the non-hydrogen atoms with anisotropic thermal parameters, except for one carbon of the solvent that is refined isotropically. All hydrogen atoms were inserted in idealized positions and allowed to refine riding in the parent carbon atom.

Crystallographic data for **2** (CCDC 876433): $C_{24}H_{16}O_4S_8$, (C_2O), fw=664.87, triclinic, space group P-1, a=6.0600(6) Å, b=12.2550(7) Å, c=19.5350(9) Å, α=79.509(4) °, β= 81.926(6) °, γ=76.549(5) °, V =1380.07(17) Å^3, Z=2, T=150K, d_{calc}=1.600 mg.m^{-3}, μ =0.685 mm^{-1}, F(000)=680, yellow crystal (0.10 x 0.04 x 0.02 mm). Of 9389 reflections collected, 5549 were independent (Rint= 0.1835); 350 variables refined with 5549 reflections to final R indices $R_1(I > 2\sigma(I))$=0.1673, $wR_2(I > 2\sigma(I))$=0.4192, R_1(all data)=0.3373, wR_2(all data)=0.4702, GOF= 1.038.

Due to the very poor quality of the crystals and their low diffraction power, no better refinement was possible. The solvent molecule (ethanol) is disordered nearby an inversion centre and no better model was possible to obtain.

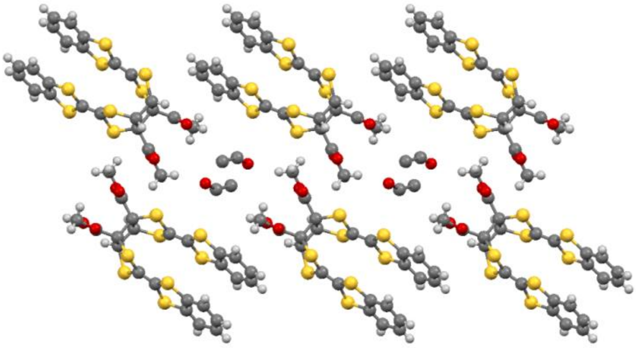

Figure S1. Crystal packing of **2** in a view along the a axis, showing the ethanol molecules lying in the space left by the $(TTFH)_2$ molecules, without establishing intermolecular interactions amongst them. The only classical hydrogen bonds are ethanol···ethanol.

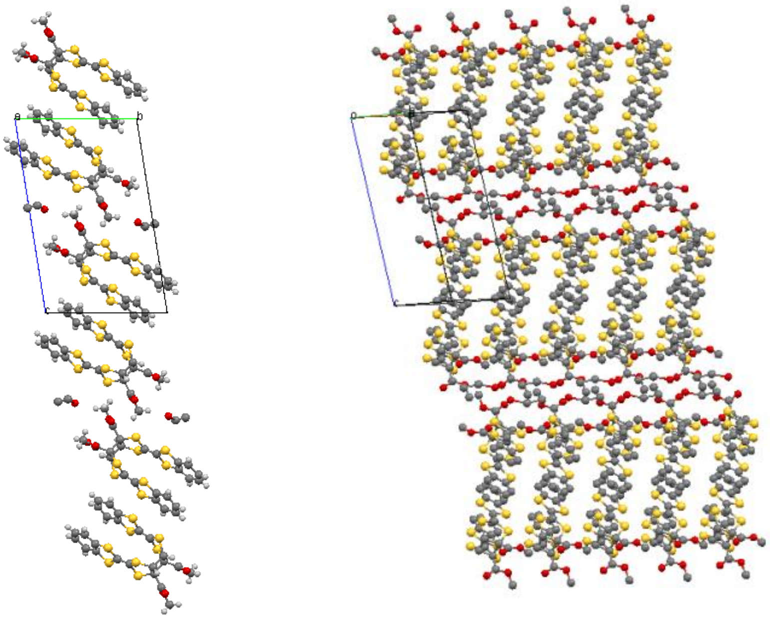

Figure S2. Crystal packing of **2** showing the cisoid arrangement of the head-to-tail dimers along *a* (left) and the *ab* plane (right). A 2D sheet is formed showing the alternation of the layer of head to tail dimers and ethanol molecules.

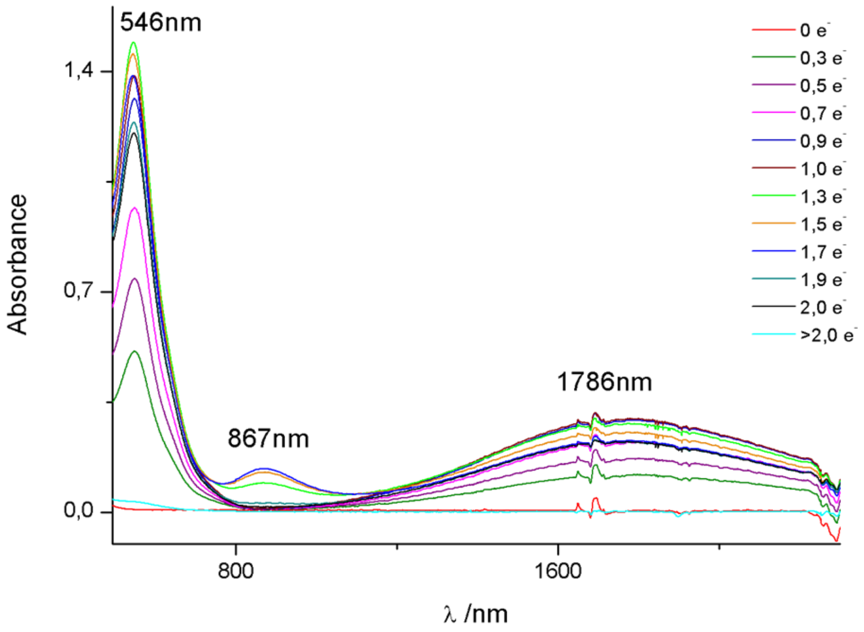

Figure S3. Vis-NIR spectra of compound **2** in its neutral state and at different stages of the chronoamperometric oxidation.

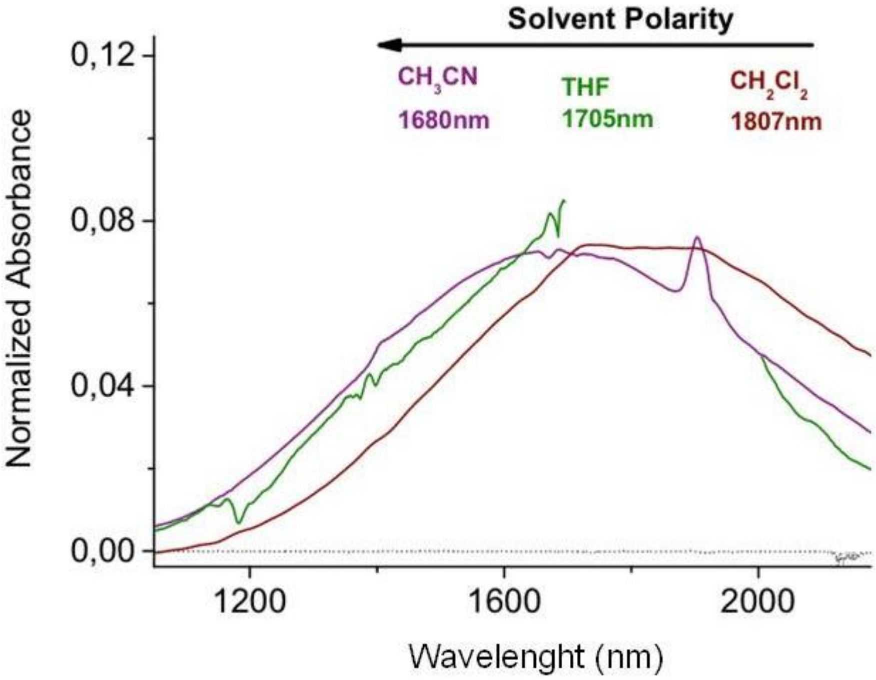

Figure S4. Vis-NIR spectra of the radical-cation of **2** in different solvents showing the dependence of the charge transfer band position with the solvent polarity.

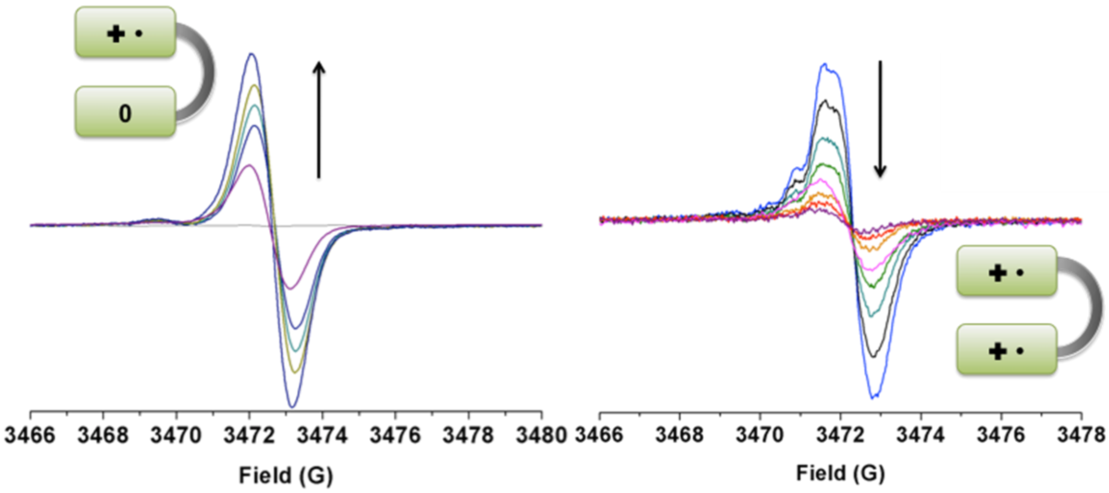

Figure S5. EPR spectra collected along time while electrochemically oxidizing a solution of **2** in 0.1 M TBAHFP in CH_3CN, applying a voltage of +0.9 V (left) and +1.3V (right). Pt wires were used as working and counter electrodes and Ag/AgCl as reference electrode.

Additional Characterization Data of the SAM-4

contact angle of S-4 73º

X-ray photoelectron spectroscopy of S-4 : S 2p 163,61 eV, Si 2p 102,81 ev and C1s 296,74 eV

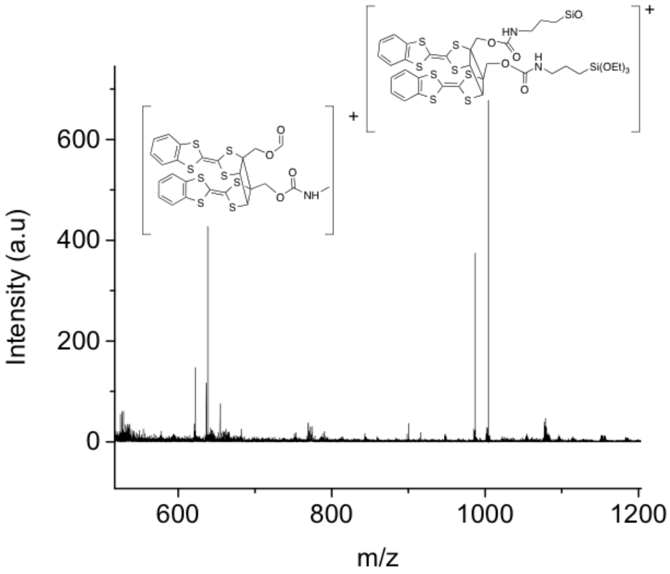

Figure S6. ToF-SIMS spectra of SAM **S-4**

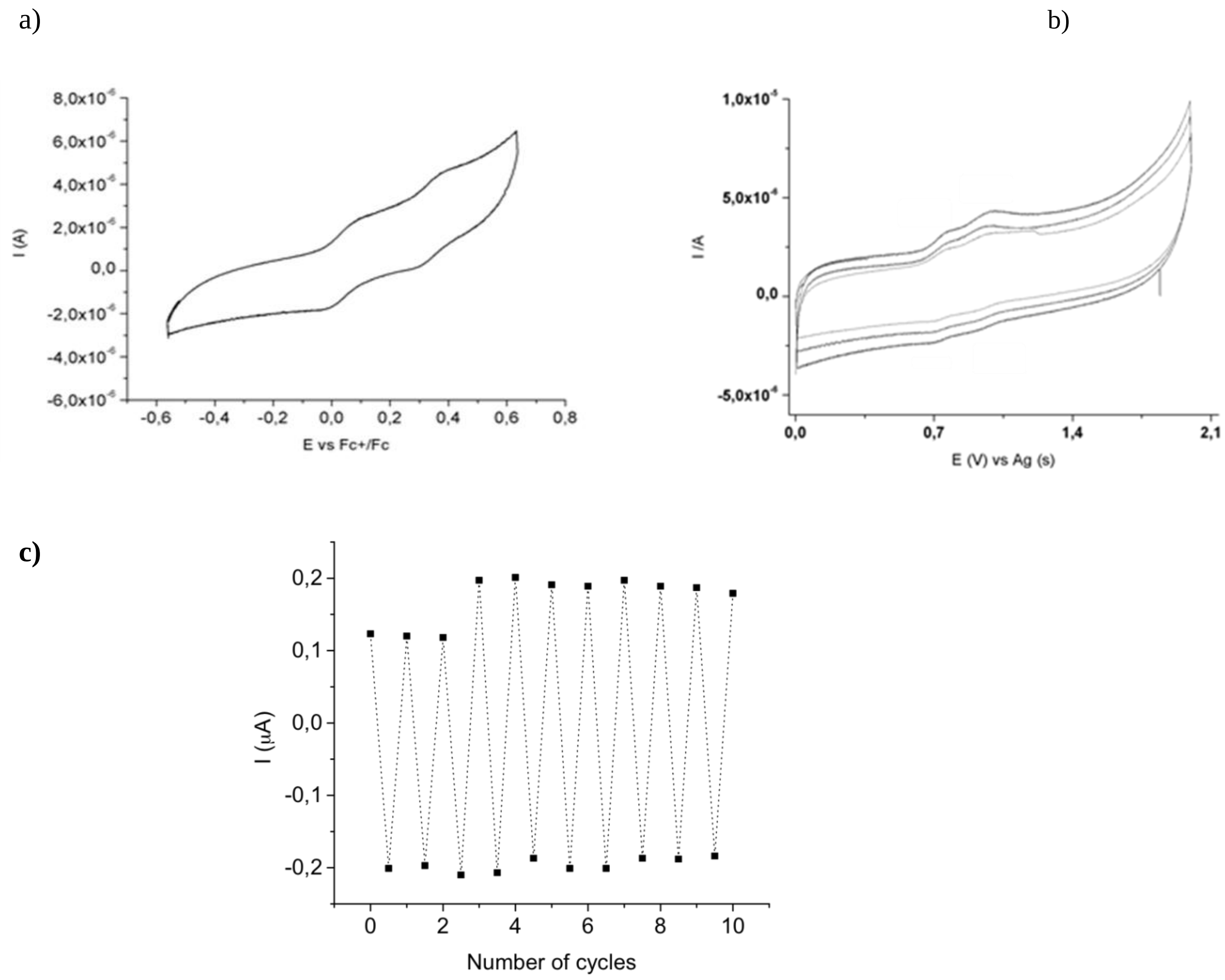

Figure S7. a) Cyclic voltammogram of **4** (0.1 M TBAHFP in CH_2Cl_2, Pt wires as working and counter electrodes, Ag/AgCl as reference electrode). b) CV response using **S-4** as working electrode versus $Ag_{(s)}$, and Pt wire as counter-electrode in 0.02 M TBAHFP in acetonitrile. The different cycles correspond to scan rates of (from lower to higher current intensity) 0.05, 0.1, and 0.15 V/s. c) Plot of the current intensity versus the number of cycles at scan rate 0.10 V/s using **S-4** as electrode. After 2 cycles of conditioning, the switching behavior proved to be highly reversible.

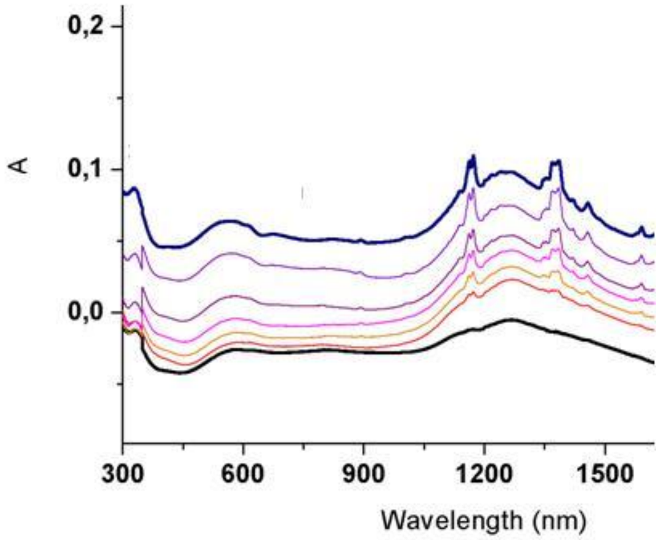

Figure S8. Evolution of Vis-NIR absorbance spectra of **S4** with time on adding $FeClO_4$ as oxidant.

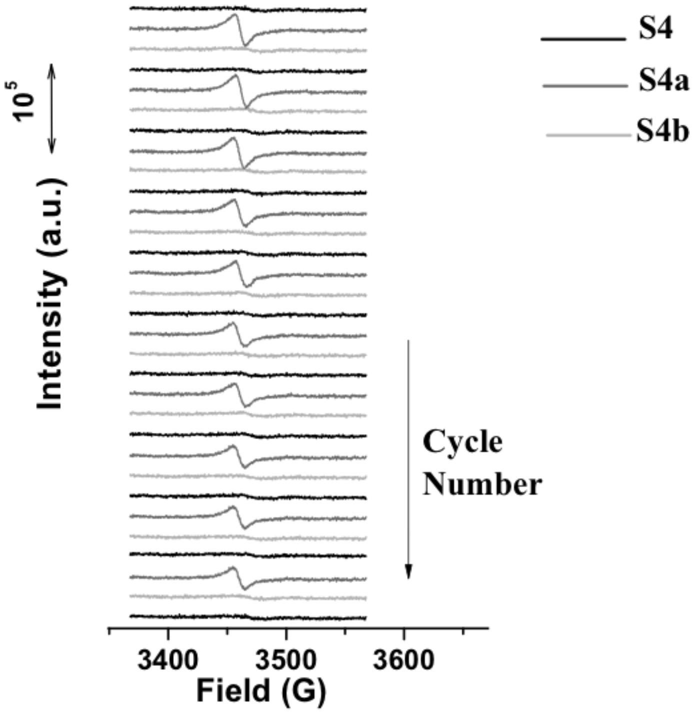

Figure S9. Ten switching cycles (-0.2, +0.9 and +1.5 V, versus $Ag_{(s)}$) of SAM **S-4** monitored by the EPR.

References

[1] pp. SMART (Bruker, 2005).

[2] pp. SAINT (Bruker, 2005).

[3] pp. SADABS (Bruker, 2005).

[4] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Cryst.* 1999, **32**, 115.

[5] G. M. Sheldrick, SHELX97 - Programs for Crystal Structure Analysis (Release 97-2), Institut fur Anorganische Chemie der Universitat, Tammanstrasse 4, D-3400 Gorringen, Alemannha, 2008.

[6] L. J. Farrugia, *J. Appl. Cryst*. 1999, **32**, 837.