

Supporting Information

A four-state capacitance molecular switch based on a redox active tetrathiafulvalene self-assembled monolayer

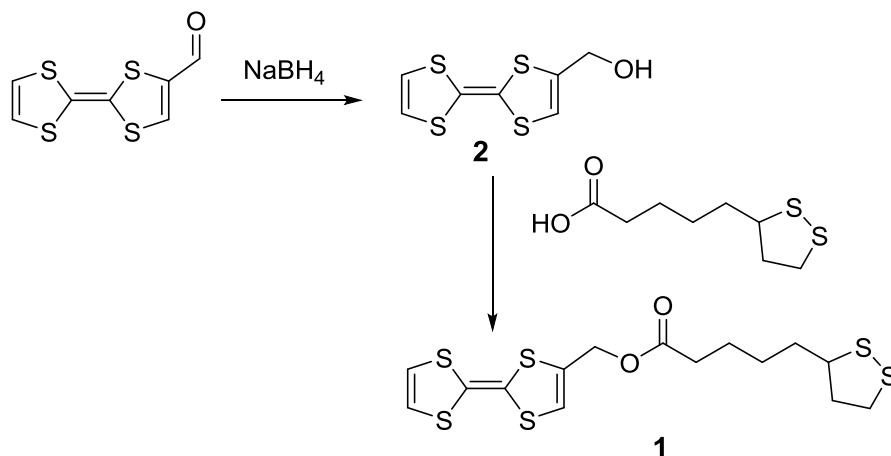
E. Marchante^a, M.S. Maglione^a, N. Crivillers^a, C. Rovira^a and M. Mas-Torrent^{a,*}

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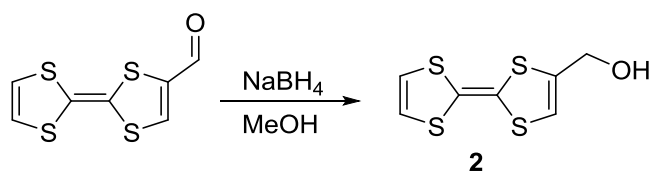
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Synthesis of TTF molecule (1)

TTF **1** was synthesized according to the following scheme:



Synthesis of [2,2'-bi(1,3-dithiolyliene)]-4-ylmethanol¹ (2)



To a solution of 2-formyltetrathiafulvalene (500 mg, 2.15 mmol) in MeOH (20 mL), it was added NaBH_4 (89 mg, 2.36 mmol). The solution was stirred during 30 minutes. CH_2Cl_2 was then added and the mixture was washed with brine and water. The organic phase was isolated, dried over MgSO_4 and concentrated under reduced pressure. The yellow solid thus obtained was purified by column chromatography (silica gel) using CH_2Cl_2 . Compound **2** was obtained in a 96% yield.

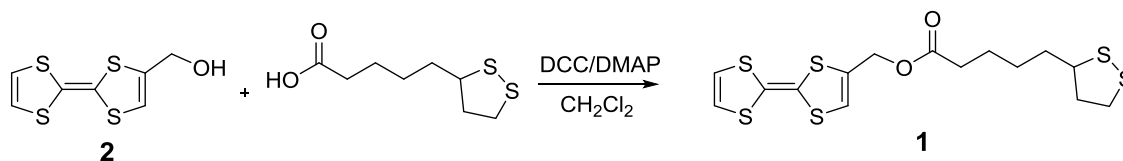
IR: (ν/cm^{-1}): 3290; 3057; 2925; 2857; 1542; 1456; 1114; 109; 1016; 793; 767; 648; 628.

¹H NMR (250 MHz CD_2Cl_2): δ = 6.35 (s, 2H); 6.24 (s, 1H); 4.37 (s, 2H) 1.96 (s, 1H).

¹³C NMR (400 MHz CD_2Cl_2): δ = 137.43; 119.54; 119.47; 115.50; 111.50; 109.86; 60.96.

LDI-TOF (m/z): calculated: 234.3; experimental: 233.9 ($[\text{M}^+]$).

Synthesis of [2,2'-bi(1,3-dithiolyliene)]-4-ylmethyl 5-(1,2-dithiolan-3-yl)pentanoate² (1)



¹ J. Gran, J. Orduna, S. Uriel A.J. Moore, M.R. Bryce, S. Wegener, D.S. Yufit, J.A.K. Howard *Synthesis*, **1994**, 489-493

² G. Cooke, F. Duclairoir, V. Rotello, M. J. Stoddart *Tetrahedron Letters* **2000**, 41, 8163-8166. M. A. Herranz, L. Yu, N. Martín, L. Echegoyen *J. Org. Chem.* **2003**, 68, 8379-8385

To 40 mL of CH₂Cl₂ previously filtered through basic alumina, compound **2** (290 mg, 1.23 mmol) and thioctic acid (305 mg, 1.48 mmol) were added. The mixture was stirred under N₂ at 0°C during 15 minutes. A solution of DCC (379 mg, 1.84 mmol) and DMAP (45 mg, 0.37 mmol) in 10 mL of CH₂Cl₂ was added and the mixture was kept stirring for 15 minutes at 0° C. The solution was then allowed to reach room temperature and was left under stirring for another 24 h. The reaction mixture was then washed with water, the organic layer was dried under MgSO₄ and the solvent was evaporated under reduced pressure. The crude of the reaction was purified by silica column chromatography using CH₂Cl₂ as eluent and compound **1** was obtained with a 90% yield.

IR: (v/cm⁻¹): 3062; 2925; 2824; 1728; 1578; 1518; 1456; 1389; 1151; 1125; 661; 570.

¹H NMR (400 MHz, CD₂Cl₂): δ= 6.36(s, 1H)-6.35 (s, 2H); 4.81 (s, 2H) 3.60-3.54 (m, 1H); 3.20-3.07 (m, 2H); 2.49-2.41 (m, 1H); 2.36 (t, J=7.3 Hz, 2H); 1.94-1.86 (m, 1H) 1.74-1.61 (m, 4H); 1.51-1.41 (m 2H).

¹³C NMR (500 MHz CD₂Cl₂): δ=172.81; 131.41; 119.19; 119.16; 119.08, 111.55; 109.05; 60.58; 56.38; 40.23; 38.55; 34.56; 33.73; 28.65; 24.60.

LDI-TOF (m/z): calculated: 422.6; experimental: 421.9 ([M⁺]).

Experimental methodologies

Materials and reagents. HPLC solvents, dichloromethane, acetone, absolute ethanol, isopropanol, tetrahydrofuran and acetonitrile were supplied by Teknokroma. Lithium perchlorate (LiClO₄) was purchased from Aldrich and used as received. Gold (111) substrates consisting of 300 nm Au on mica were purchased from Georg Albert PVD-Beschichtungen.

2-formyltetrathiafulvalene was purchased from TCI Chemicals, while NaBH₄ and thioctic acid were bought from Sigma-Aldrich. All the reagents were used without further purification.

Experimental procedures and apparatus

Self-assembled monolayers preparation. The substrates were first rinsed with dichloromethane, acetone and ethanol and dried under nitrogen stream. Then, these substrates were cleaned in a UV ozone chamber for 20 minutes and afterwards immediately immersed in ethanol for at least 20 minutes, rinsed with ethanol and isopropanol and dried under N₂ stream. Subsequently, the substrates were immediately immersed in 1mM solution of **1** in tetrahydrofuran for 72h. SAM formation was carried out under light exclusion and under nitrogen atmosphere.

XPS Measurements. X-ray photoelectron spectroscopy measurements were performed with a Phoibos 150 analyzer (SPECS GmbH, Berlin, Germany) in ultra-high vacuum conditions (base pressure 5x10⁻¹⁰ mbar) with a monochromatic aluminium K α X-ray source (1486.74eV). The energy resolution measured by the FWHM of the Ag 3d_{5/2} peak for a sputtered silver foil was 0.6 eV. The spot size was 3.5 mm by 0.5 mm.

ToF-SIMS Measurements. Time of flight secondary ions mass spectrometry measurements were performed with a TOF-SIMS5 using the following specific conditions of analysis: primary gun energy of 25 KV; extractor energy of 10 KV; an emission current 1.00 μ A; employing Bi³⁺ with an intensity of the primary ions of 0.26 pA. The experiments were performed under vacuum at 2.3 E-9 mbar. The spot size was 250 x 250 μ m with a resolution of 128 x 128 pixels, collecting above of 1 E12 of ionic intensity per spectrum.

Cyclic Voltammetry measurements. Cyclic voltammetry experiments were performed using a Novocontrol modular equipment system which consists on an Alpha-AN impedance analyzer with a POT/GAL 30V/2A electrochemical interface. A conventional three electrode set-up was employed using the modified gold substrate as the working electrode, a platinum wire as counter electrode and a silver wire as quasi-reference electrode. We have used a homemade electrochemical cell with a control active area of the functionalized substrate (i.e. working electrode) of 0.5 cm². A degasificated solution of LiClO₄ 0.1 M in acetonitrile was used as electrolyte (after bubbling N₂ for 20 min).

Electrochemical Impedance Spectroscopy (EIS) measurements: The impedance measurements were obtained at four different DC potentials, and were superimposed on a sinusoidal potential modulation of ± 5 mV (V_{rms}). The resulting current was recorded over a frequency domain of 200 KHz to 500 mHz. Ninety points, equally spaced on a logarithmic scale, were acquired per decade increment in frequency. All experiments were performed at room temperature and under environmental conditions.

Switching Measurements. The AC impedance switching process was recorded at 1Hz. A low AC voltage of 5 mV was superimposed at four different applied DC bias (10, 250, 450 and 620 mV). These cycling experiments were performed by pre-biasing the sample at the corresponding DC voltage for each state during 3 seconds.

Supporting information figures:

Table S1. Summary of the binding energies observed in the high-resolution XPS characterization of the TTF SAM

Binding energy (eV)	Atom	Type of bond
532.2	O1s	C-O
333.3	O1s	C=O
284.8	C1s	C-C
285.7	C1s	C=C
288.9	C1s	O-C=O
161.9	S2p _{3/2}	S-Au
163.1	S2p _{1/2}	S-Au
163.6	S2p _{3/2}	C-S-C
164.7	S2p _{1/2}	C-S-C

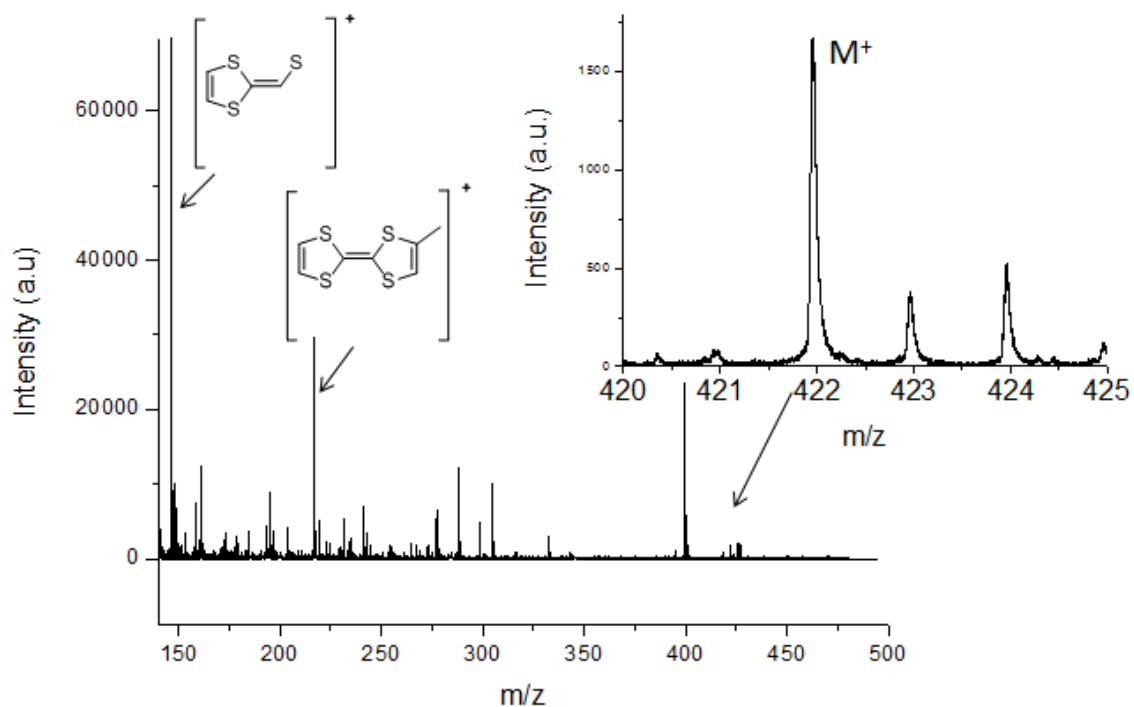


Figure S1. ToF-SIMS spectrum for TTF SAM.

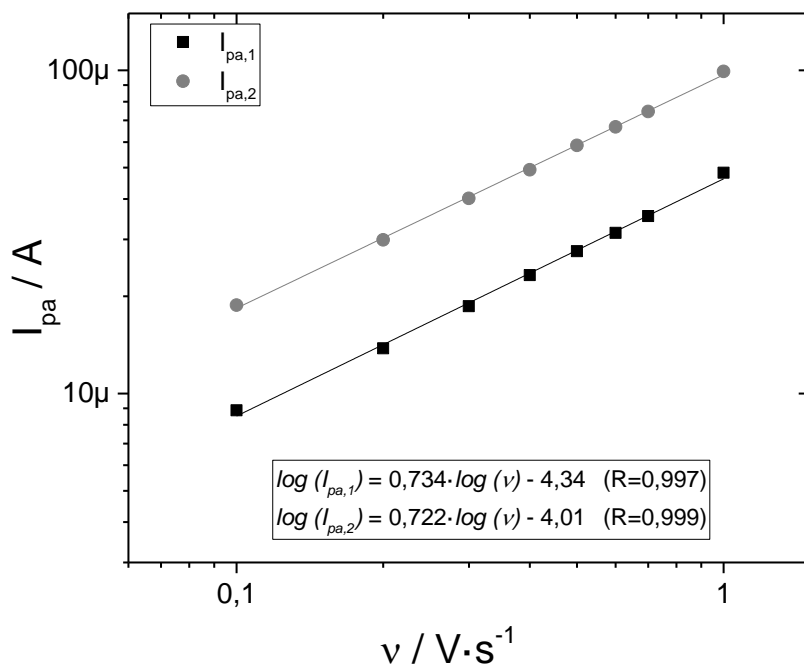


Figure S2. Linear relationship of the current peak (I_{pa}) vs the scan rate (v) for the two redox processes observed in the TTF SAM on gold.

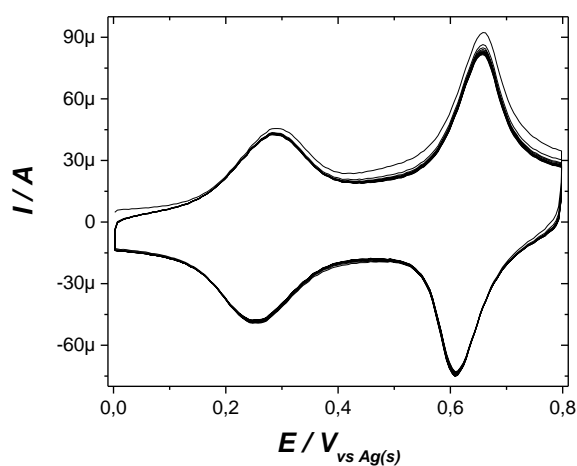


Figure S3. CV of the TTF SAM in LiClO_4 0.1M in acetonitrile, at 1V/s, during 10 cycles.

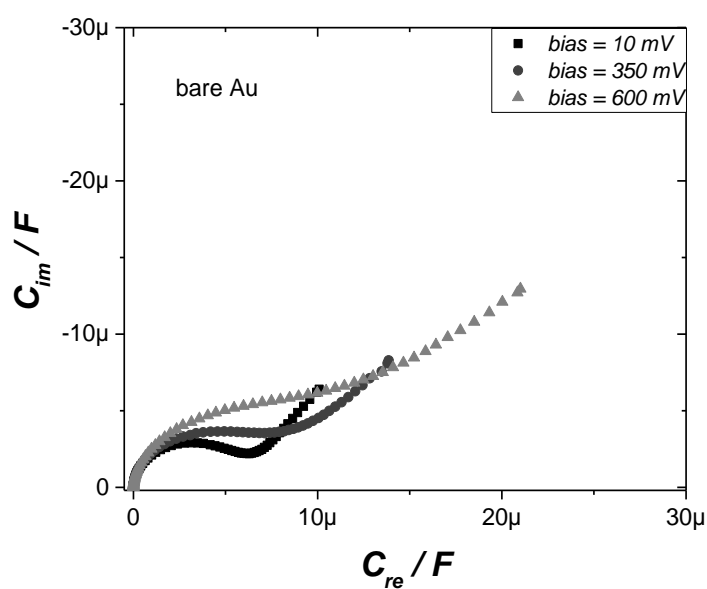


Figure S4. Capacitance Cole-Cole plot of the unmodified Au substrate in LiClO_4 0.1 M in acetonitrile at three DC voltages (10 mV, 350 mV and 600 mV).

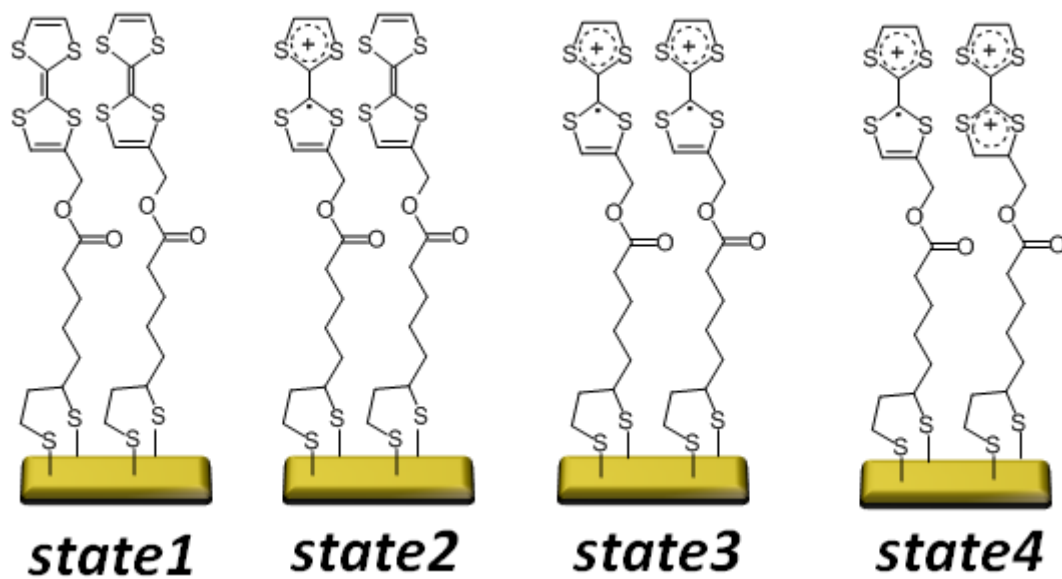


Figure S5. Scheme of the TTF-SAM states at the four different DC bias applied: 10 mV (state 1), 250 mV (state 2), 450 mV (state 3), and 620 mV (state 4).

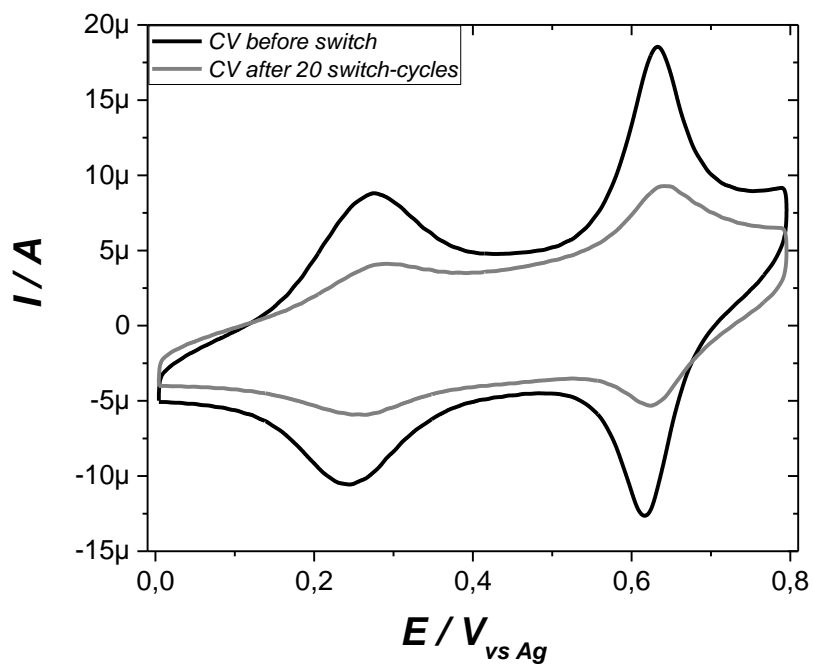


Figure S6. CV of the TTF SAM in LiClO₄ 0.1M in acetonitrile before and after the 20 switching cycles performed by EIS.

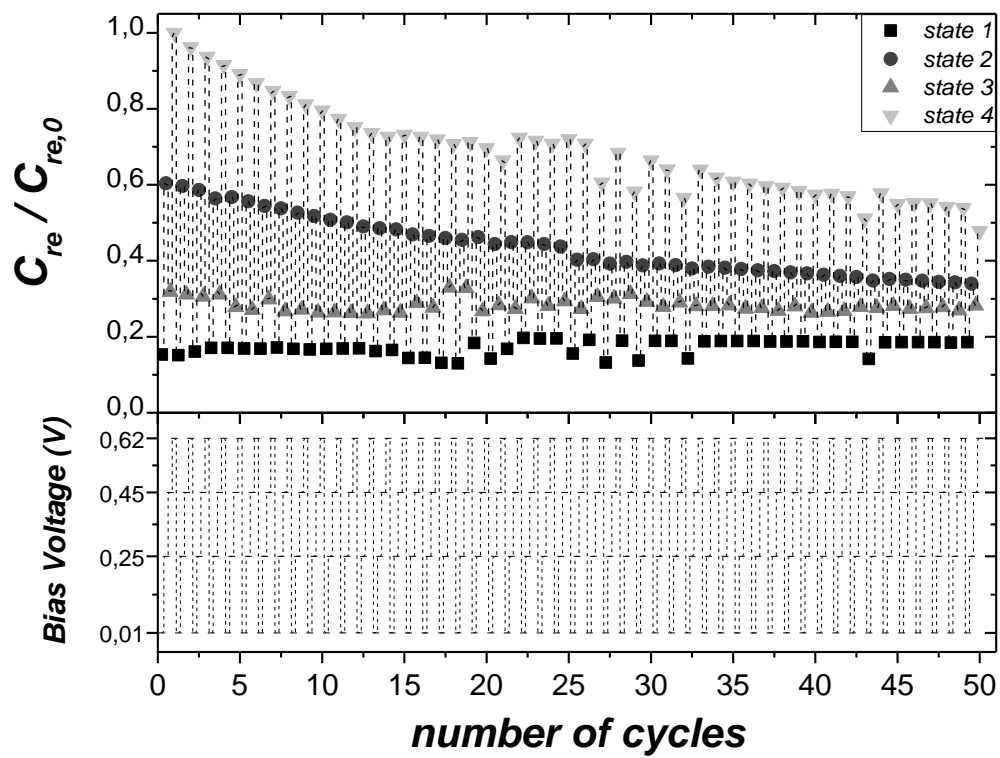


Figure S7. Relative capacitance values of a TTF-SAM during 50 switching cycles.