Supporting Information

Tetrathiafulvalene-based molecular nanowires

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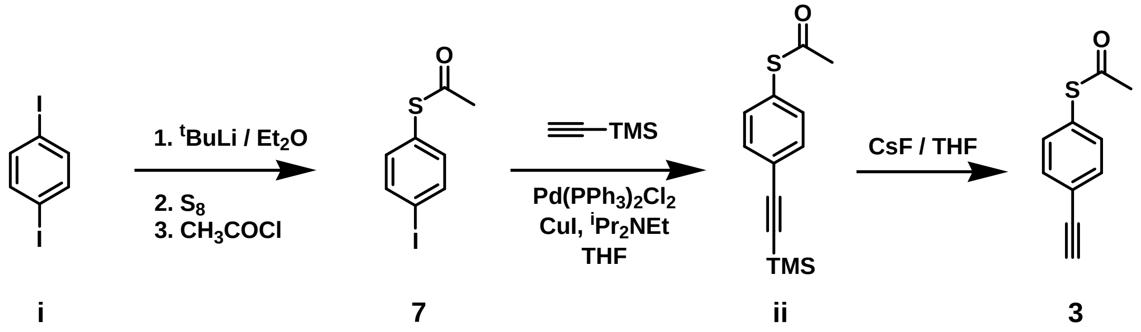
Synthesis and Structural Characterization of Molecular Wire 4

General. All solvents were dried and distilled according to standard procedures. Reagents were used as purchased. All air-sensitive reactions were carried out under an argon atmosphere. Flash chromatography was performed using silica gel (Merck, kiesegel 60, 230-240 mesh o Scharlau 60, 230-240 mesh). Analytical thin layer chromatography (TLC) was performed using aluminum coated Merck Kieselgel 60 F254 plates. An Agilent 1100 Series LC Module (HPLC) system, equipped with a diode array detector, was used to determine the purity of the molecular wire **4**. A semipreparative SiO_2 column (column dimensions: 25 cm × 10 mm; flow rate: 1.0 mL min^{-1}; injection volume: 20 μL; mobile phase: CH_2Cl_2) was employed. The retention time (t_R) and the peak area (PA) reported were determined at a wavelength of 285 nm. Melting points were determined on a Gallenkamp apparatus. NMR spectra were recorded with Bruker AC-200, Bruker Avance DPX-300, or a Bruker Avance AV-500 spectrometers. Coupling constants (*J*) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet. IR spectra were recorded on a Perkin-Elmer 257. UV-Vis spectra were recorded in a Varian Cary 50 spectrophotometer by using $CHCl_3$ as solvent. Mass spectra by electronic impact (EI) were recorded on a HP1100MSD spectrometer. Electrochemical measurements were performed on an Autolab PGStat 30 equipment using a three electrode configuration system. The measurements were carried out using CH_3CN, CH_2Cl_2 or THF solutions 0.1 M in tetrabutylammonium perchlorate ($TBAClO_4$). A glassy carbon electrode (3 mm diameter) was used as the working electrode, and a platinum wire and an $Ag/AgNO_3$ electrode were employed as the counter and the reference electrode, respectively. Both the counter and the reference electrodes were directly immersed in the electrolyte solution. The surface of the working electrode was polished with commercial alumina prior to use. Solutions were stirred and deaerated by bubbling argon for a few minutes prior to each voltametric measurements. Unless otherwise specify the scan rate was 100 mV/s.

Mixture of *cis* and *trans* Diiodotetrathiafulvalene (2). To a solution of tetrathiafulvalene (1g, 4.89 mmol) in 10 mL of diethyl ether cooled at -78 ºC, LDA was added (2 M in hexane, 9.78 mL, 19.56 mmol) and the mixture was stirred for 1 h. Subsequently, perfluorohexyl iodide (4.25 mL, 19.57 mmol) was added and the reaction was left to reach r.t. overnight and then was quenched with water. The mixture was extracted twice with dichloromethane and the combined organic layers were washed with brine and dried over magnesium sulphate. The solvent was removed under vacuum and the residue obtained was purified by flash chromatography (SiO_2, hexane) to yield 1.44 g (65%) of compound **2**. Compound **2** has already been reported (see: Wang, C. S.; Ellern, A.; Khodorkovsky, V.; Bernstein, J.; Becker, J. I.; J. *Chem. Soc. Chem. Commun.* **1994**, *8*, 983).



***S*-4-Iodophenyl thioacetate (7).** To a solution of 1,4-diiodobenzene (i) (4.95 g, 17.5 mmol) in dry ether (150 mL), cooled at -78 °C, was added dropwise *tert*-butyllithium (1.7 M in hexane, 19.5 mL, 33 mmol). The solution was stirred at this temperature for 10 min. Hence the solution is allowed to warm up, and sulfur is added (800 mg, 3.1 mmol), as soon as the temperature reached -10 °C. The reaction was kept at 0 °C for 30 min. and then cooled again at -78 °C before the addition of acetyl chloride in one portion (1.6 mL, 22.5 mmol). The solution was allowed to reach room temperature overnight. After hydrolysis with water, the mixture was extracted with dichloromethane. The organic layers were washed with a dilute solution of sodium hydrogenocarbonate and dried over magnesium sulfate. The crude product was purified by silica gel flash chromatography (eluent, hexane:dichloromethane 8:2) affording 1.44 g of a white solid. Yield: 30%. Compound **7** has already been reported (see: (a) Pearson, D. L.; Tour, J. M. *J. Org. Chem.* **1997**, *62*, 1376; (b) Hortholary, C.; Coudret, C. *J. Org. Chem.* **2003**, *68*, 2167 and (c) Mayor, M.; Weber, H. B.; Reichert, J.; Elbing, M.; Von Hänisch, C.; Beckmann, D.; Fischer, M. *Angew. Chem. Int. Ed.* **2003**, *42*, 5834).

***S*-(4-Trimethylsilylethynyl)phenyl thioacetate (ii).** To a solution of **7** (0.80 g, 2.88 mmol) in THF (5 mL) were added trimethylsilyl acetylene (0.41 g, 4.32 mmol) and *N*,*N*-diisopropylethylamine (1.00 mL). The catalyst bis(triphenylphosphine)palladium

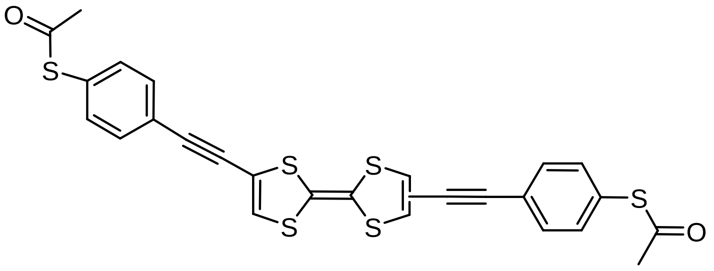
(II) chloride (0.1 g, 0.14 mmol) and copper iodide (0.028 g, 0.14 mmol) were added, and the reaction was allowed to stir for 1 day. The reaction was quenched with water, the aqueous layer was extracted with ether, and the organic extracts were washed with brine. The ether layers were dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residue was purified by silica gel flash chromatography (first using hexane and then slowly increasing the polarity to hexane:dichloromethane 9:1) to provide 0.60 g (84%) of the title product **ii** as an off-white solid. Compound **ii** has already been reported (see: Pearson, D. L.; Tour, J. M. *J. Org. Chem.* **1997**, *62*, 1376).

***S*-4-Ethynylphenyl thioacetate (3).** To a solution of **ii** (0.15 g, 0.60 mmol) in THF (15 mL) at r.t. was added CsF (0.092 g, 0.60 mmol) and stirred overnight. The reaction was passed through a silica gel plug to remove the solid impurities. Subsequently, the reaction was quenched with water, the aqueous layer extracted with dichloromethane, and the organic layers dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residue was purified by silica gel flash chromatography (hexane:Et_2O 98:2) to provide 0.044 g (42%) of **3**. Compound **3** has already been reported (see: Pearson, D. L.; Tour, J. M. *J. Org. Chem.* **1997**, *62*, 1376).

Mixture of *cis* and *trans* Bis-(trimethylsilylethynyl)tetrathiafulvalene (5). To a solution of **2** (0.40 g, 0.88 mmol) in THF (25 mL) were added trimethylsilyl acetylene (0.26 g, 2.63 mmol) and the catalysts tetrakis(triphenylphosphine)palladium (0.1 g, 0.09 mmol) and copper iodide (0.017 g, 0.09 mmol). *N,N*-diisopropylethylamine (3.40 mL) was added, and the reaction was allowed to stir 4 h. at 75 ºC. The reaction was left to cool and dichloromethane was added. Then the reaction mixture was washed with a satured solution of ammonium chloride, water and brine and dried over magnesium sulfate. The solvent was removed, and the residue was purified by silica gel flash chromatography (hexane:dichloromethane 99:1) to provide 0.347 g (88%) of **5**. FTIR (KBr, cm^{-1}): 3071, 2956, 2897, 2144, 1249, 1129, 856, 839, 765, 696; ^1H NMR ($CDCl_3$, 300 MHz), δ: 6.52 (s, 2H), 0.21 (s, 18H); ^{13}C NMR ($CDCl_3$, 75 MHz), δ: 125.40, 125.10, 115.79, 100.12, 94.78, -0.20; MS (EI) *m/z*, (%I): 396 [M^+, 13], 381 (5), 355 (5), 156 (3), 85 (24), 49 (88); elemental analysis: calcd. for $C_{16}H_{20}Si_2S_4$ (%): C 48.44, H 5.08; found: C 48.38, H 5.00.

Mixture of *cis* and *trans* Bis-(ethynyl)tetrathiafulvalene (6). To a solution of **5** (0.175 g, 0.44 mmol) in a 1:1 mixture of THF/MeOH (12 mL) potassium carbonate was added and the reaction was stirred for 1.5 h. Then, water was added and the aqueous layer was extracted with dichloromethane. The organic layer was dried over magnesium sulfate and the solvent was removed. The residue (100% yield) was dissolved in THF and used, before decomposition, for the following synthetic step. ^{1}H NMR ($CDCl_3$, 300 MHz), δ: 6.53 (s, 2H), 3.00 (s, 2H).

Mixture of *cis* and *trans* Bis-[4-(acetylthia)phenylethynyl]tetrathiafulvalene (4).



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Route A

To a solution of **6** (0.11 g, 0.44 mmol) in THF (5 mL) were added **7** (0.245 g, 0.88 mmol) and the catalysts bis(triphenylphosphine)palladium (II) chloride (0.031 g, 0.044 mmol) and copper iodide (0.009 g, 0.044 mmol). *N,N*-diisopropylethylamine (0.20 mL) was added, and the reaction was allowed to stir overnight. The solvent was removed under reduced pressure, and the residue was purified by silica gel flash chromatography (hexane:Et_2O 9:1 to 8:2) to provide 0.056 g (23%) of compound **4** as a dark red solid.

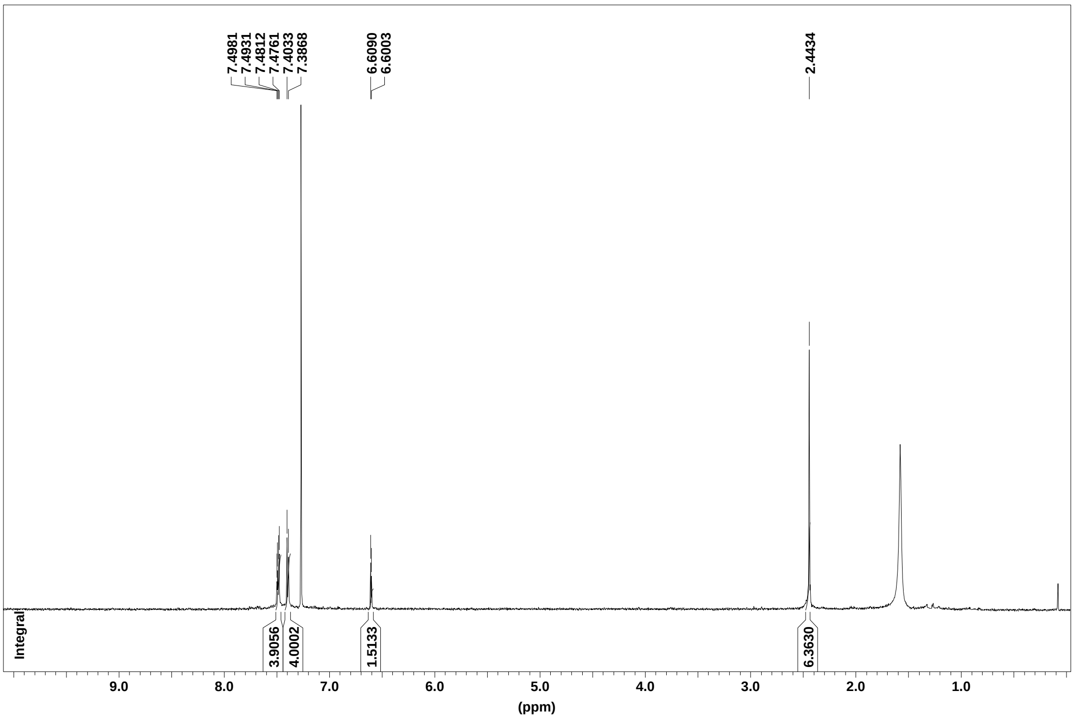
Route B

To a solution of **2** (0.10 g, 0.22 mmol) in THF (5 mL) were added **3** (0.41 g, 4.32 mmol) and the catalysts bis(triphenylphosphine)palladium (II) chloride (0.015 g, 0.02 mmol) and copper iodide (0.004 g, 0.02mmol). *N,N*-diisopropylethylamine (0.20 mL) was added, and the reaction was allowed to stir overnight. The solvent was removed under reduced pressure, and the residue was purified by silica gel flash chromatography (hexane:Et_2O 9:1 to 8:2) to provide 0.065 g (47%) of compound **4** as a dark red solid.

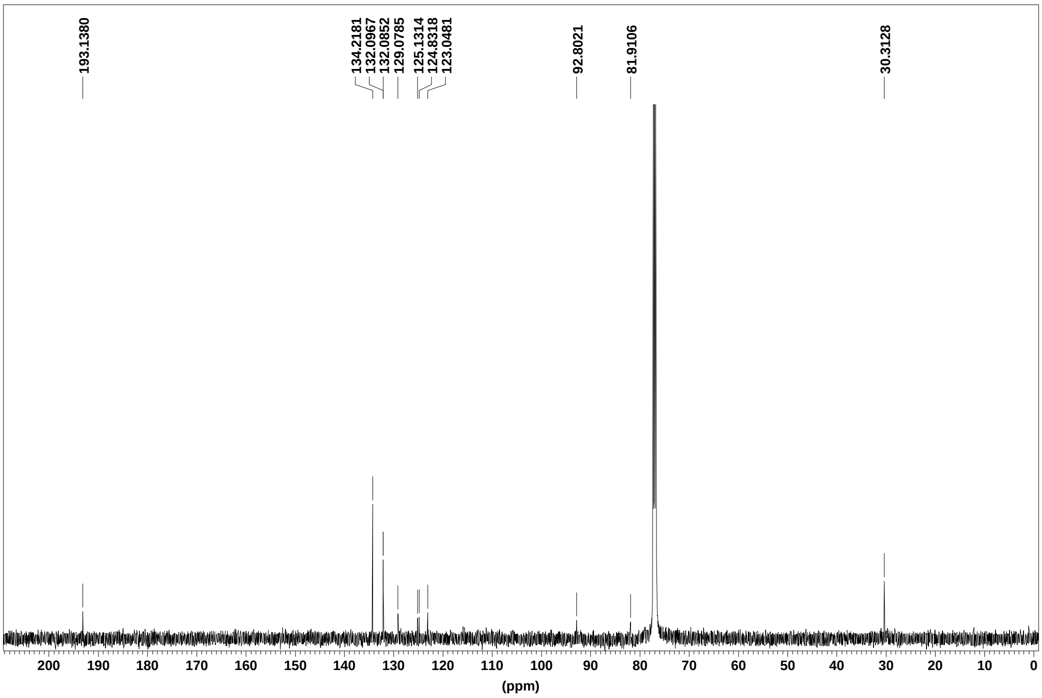
mp. 194-196 °C.

FTIR (KBr, cm^{-1}): 2922, 2852, 2240, 2190, 1734, 1701, 1481, 1437, 1121, 1092, 825, 542.

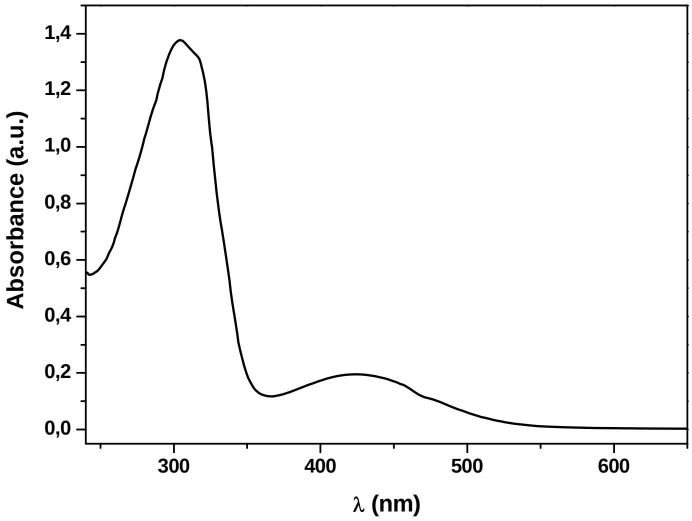
^{1}H NMR ($CDCl_3$, 500 MHz), δ: 7.49 (d, 4H, *J* = 8.5 Hz), 7.39 (d, 4H, *J* = 8.5 Hz), 6.61 (s, 1H), 6.60 (s, 1H), 2.44 (s, 6H)



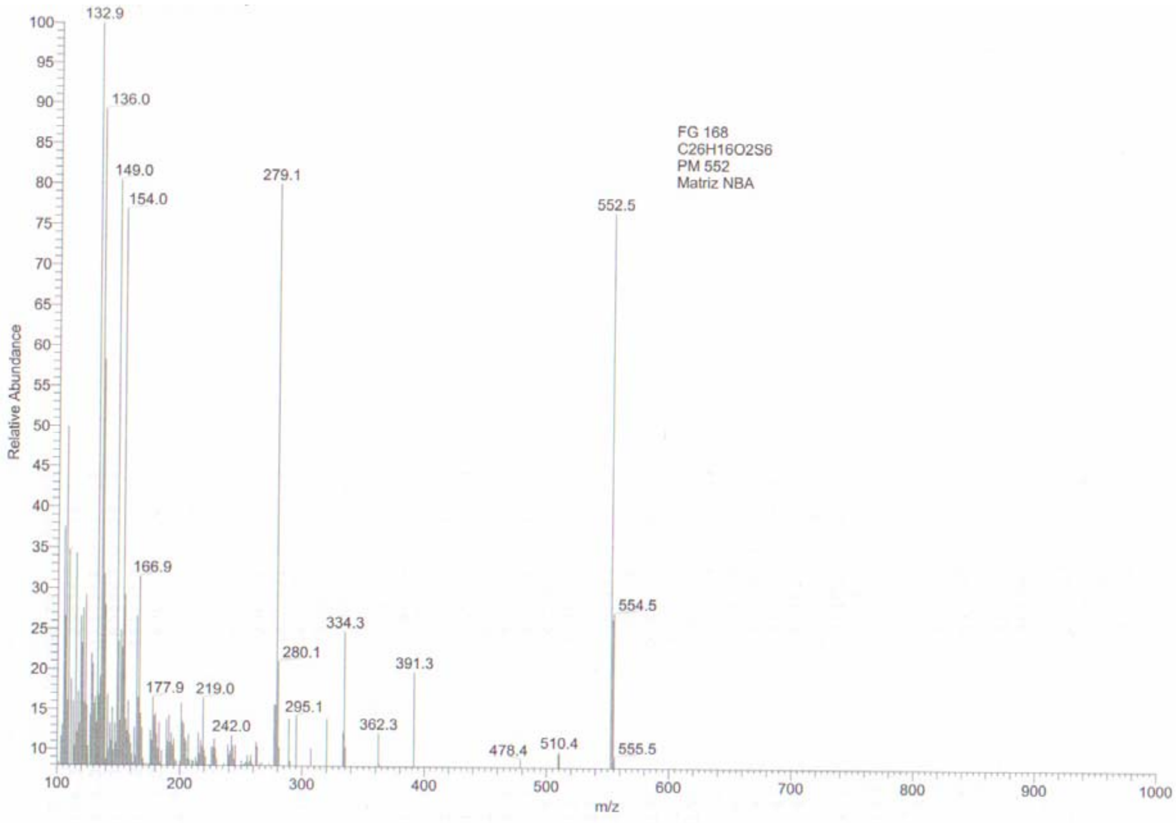
^{13}C NMR ($CDCl_3$, 125 MHz), δ: 193.1, 134.2, 132.1, 132.0, 129.1, 125.1, 124.8, 123.1, 92.8, 81.9, 30.3.



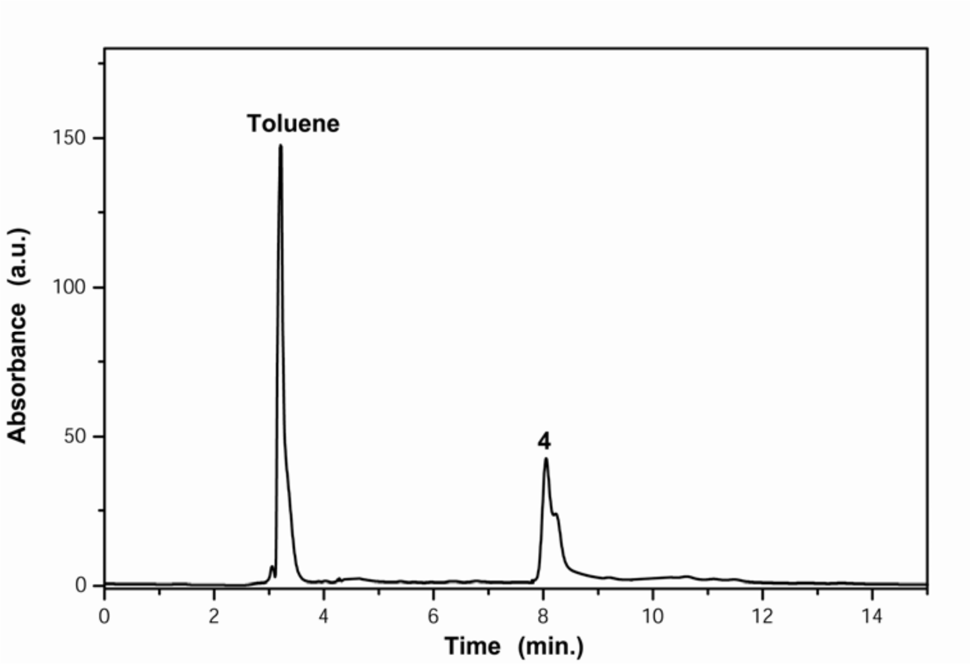
UV-vis ($CHCl_3$) λ_{max} (log ε): 303 (1.37), 427 (0.19) nm.



MS (FAB) *m/z* (%I): 552 [M^+, 76].



HPLC (analytical) $t_R = 8.35$ min, PA = 95% (mixture)



Electrochemistry

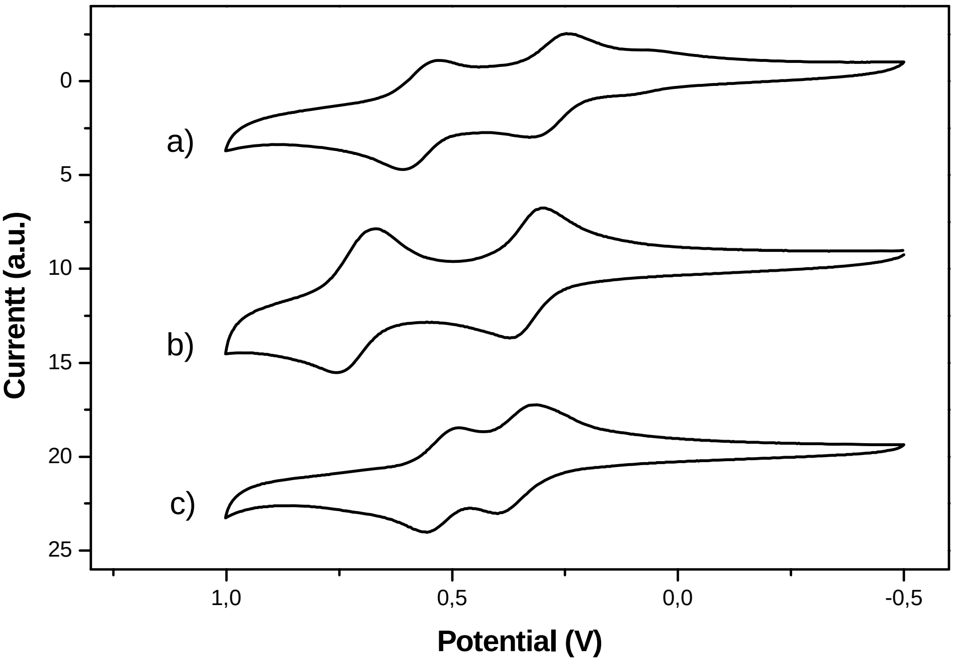


Figure S1. Cyclic voltammograms of **4** in CH_3CN (a), CH_2Cl_2 (b), and THF (c) solutions containing 0.1 M $TBAClO_4$ as supporting electrolyte. The voltammograms were recorded at 0.1 V/s using GC as working electrode, Pt wire as the counter electrode and $Ag/AgNO_3$ (CH_3CN) as the reference electrode.

The thermodynamic stability of a cation-radical can be determined from the difference in potenials of the corresponding cation-radical and dication species, using the equation: $\Delta E = E^2_{1/2,\,ox} - E^1_{1/2,\,ox} = 0.059 \log K$, where K is the disproportionation constant in the equilibium:[1]

$$2D^{\bullet +} \rightleftharpoons D + D^{2+}$$

For the CVs of **4**, the increase in solvent polarity leads to a decrease in K: log K = 6.49 (CH_2Cl_2); 4.71 (CH_3CN); 2.69 (THF). These values show that the radical species are thermodinamically less stable in polar solvents. This trend is also observed for the parent TTF (see Table S1)

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[1] B. S. Jensen, U. D. Parker, *J. Am. Chem. Soc.*, 1975, **97**, 5211.

Table S1. Cyclic voltammetry data for the redox switch **4** and the **TTF** molecule used as reference.[a]

Compound	**$E^1_{1/2, ox}$ (mV)**	**$E^2_{1/2, ox}$ (mV)**	**Solvent**	**ΔE^b (mV)**	**log K^d**	**SE**
TTF	+53 (ΔE^c = 65 mV)	+432 (ΔE^c = 69 mV)	CH_3CN	379	6.42	$TBAClO_4$
TTF	+126 (ΔE^c = 74 mV)	+524 (ΔE^c = 115 mV)	CH_2Cl_2	398	6.74	$TBAClO_4$
TTF	+148 (ΔE^c = 90 mV)	+400 (ΔE^c = 85 mV)	THF	252	4.27	$TBAClO_4$
TTF	+102 (ΔE^c = 66 mV)	+484 (ΔE^c = 64 mV)	CH_3CN	382	6.47	$TBAPF_6$
TTF	+222 (ΔE^c = 66 mV)	+681 (ΔE^c = 110 mV)	CH_2Cl_2	459	7.78	$TBAPF_6$
TTF	+198 (ΔE^c = 64 mV)	+484 (ΔE^c = 64 mV)	THF	286	4.85	$TBAPF_6$
4	+288 (ΔE^c = 83 mV)	+566 (ΔE^c = 81 mV)	CH_3CN	278	4.71	$TBAClO_4$
4	+331 (ΔE^c = 61 mV)	+714 (ΔE^c = 71 mV)	CH_2Cl_2	383	6.49	$TBAClO_4$
4	+365 (ΔE^c = 91 mV)	+524 (ΔE^c = 76 mV)	THF	159	2.69	$TBAClO_4$
4	+317 (ΔE^c = 83 mV)	+620 (ΔE^c = 93 mV)	CH_3CN	303	5.13	$TBAPF_6$
4	+392 (ΔE^c = 61 mV)	+856 (ΔE^c = 80 mV)	CH_2Cl_2	464	7.86	$TBAPF_6$
4	+407 (ΔE^c = 56 mV)	+622 (ΔE^c = 66 mV)	THF	215	3.64	$TBAPF_6$

[a] GC working electrode, Ag/$AgNO_3$ (CH_3CN) reference electrode, Pt Counter, SE = supporting electrolyte 0.1 M; [b] $\Delta E = E^2_{1/2, ox} - E^1_{1/2, ox}$; [c] $\Delta E = E_{anodic\ peak} - E_{cathodic\ peak}$; [d] log $K = \Delta E^b/0.059$.