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SUPPLEMENTARY INFORMATION

Thienylene vinylene dimerization: From solution to self-assembled monolayer on gold

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1. Chemicals and Instrumentation

SAM preparation

Au substrates were prepared by deposition of ca. 5 nm of chromium followed by ca. 100 nm of gold onto a glass substrate through a shadow mask (MECACHIMIQUE/France) using physical vapor deposition system (PVD ME300 PLASSYS/France) and were used immediately after (No electrochemical post-treatment was undergone after completion).

SAMs were prepared on fresh Au substrates (0.2 cm^2) by immersing for 15 min in 1 mM solution of TV-SS in dichloromethane at 293 K

Cyclic voltammetry and Spectroelectochemistry

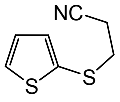
Electrochemistry and time-resolved spectroelectrochemistry in solution were performed using the already described home self-made cell (F. Gaillard and E. Levillain, *J. Electroanal. Chem.,* 1995, **398**, 77–87.)

Electrochemical measurements were carried out using a platinum wire counter electrode and a silver wire as a quasi-reference electrode with a Biologic SP-150 potentiostat driven by the EC-Lab software including ohmic drop compensation. Experiments were recorded in dry HPLC-grade dichloromethane with tetrabutylammoniumhexafluorophosphate (Bu_4NPF_6, electrochemical grade, Fluka) as supporting electrolyte. All solutions were prepared and transferred into the spectroelectrochemical cell in a glove box containing dry, oxygen-free (<1 ppm) argon, at room temperature.

In order to use commercially available thermostated cell holders, the spectroelectrochemical cell dedicated to SAMs is dimensionally close to the conventional quartz cuvette (outer dimensions = 12.5 mm × 12.5 mm × 45 mm). The inner part of the cuvette (Hellma® Analytics) has been specially redesigned, in order to insert, parallel to the quartz windows, a home self-made interdigitated three Au electrode with high precision. Spectrophotometric measurements were carried out in direct reflexing mode on the working electrode (i.e. Pt or Au) with a homemade bench composed of different Princeton Instruments modules (light sources, fibers, monochromators, spectroscopy camera and software). The connection between the light source, the cell and the spectrophotometer is ensured through a “Y-shaped” optical fiber bundle: 18 fibers guide the light to the cell, and 19 fibers collect the reflected light from the cell to visible (320–1080 nm/maximum acquisition frequency 2 MHz) and IR (900–1700 nm/maximum acquisition frequency 8 MHz) CCD detectors. The sensitivity of the spectroscopic measurement (<3 e− at 100 kHz and <13 e− at 2 MHz between 320 and 1080 nm; 400 e− (high gain) and 5000 électrons (low gain) between 900 nm and 1700 nm) allows performing a spectroelectrochemistry experiment under the usual conditions of electrochemistry.

2 Experimental procedure and characterization data

2-(2-cyanoethylsulfanyl)thiophene (1)



1

A solution of n-BuLi (27.5 mL, 2.5 M in hexane, 1.1 equiv.) was added dropwise to a solution of 2-bromothiophene (6.2 mL, 64 mmol) in 50 mL of dry ether under inert atmosphere (N_2) at -78°C. The reaction mixture was stirred for 30 min, and then 2.2 g of sulfur (1.05 equiv..)

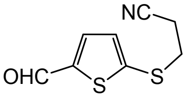
were added at -78°C. Once the sulfur was dissolved, the reaction mixture was warmed to room temperature and stirred for 20 min. After cooling at 0°C, 3-bromopropionitrile (6.32 mL, 1.2 equiv.) was added and the reaction mixture was stirred for 1 h at RT. An aqueous solution of HCl 0.5 M (80 mL) was added. The mixture was extracted with 3 x 10 mL of dichloromethane and the organic phase was washed with water and dried over $MgSO_4$. The excess of 3-bromopropionitrile was removed by distillation in a Kugelrohr (1 mbar, 78°C). The desired compound **1** was obtained as a yellow oil with a 52% yield (5.7 g) after purification by column chromatography using a 1:1 mixture of dichloromethane and Petroleum Ether as an eluent.

RMN ^{1}H ($CDCl_3$): δ (ppm)= 7.43 (dd, 1H, ^3J=5.4 Hz, ^4J=1.2 Hz), 7.21 (dd, 1H, ^3J=3.5 Hz, ^4J=1.2 Hz), 7.02 (dd, 1H, ^3J=5.4 Hz, ^4J=3.5 Hz), 2.96 (t, 2H, ^3J=7.2 Hz), 2.60 (t, 2H, ^3J=7.2 Hz)
RMN ^{13}C ($CDCl_3$): δ (ppm) =135.8, 131.0, 130.9, 127.9, 117.8, 33.7, 18.2

MS EI m/z: 169 (M^+, 40), 129 (25), 115 (75), 71 (100), 45 (90), 39 (38), 27 (55)
HRMS (CI^+ isobutane): MH^+ calculated: 170.0093; found:170.0094.

This compound is also commercially available (CAS registry number: 57713-42-5).

5-formyl-(2-cyanoethylsulfanyl)thiophene (2)



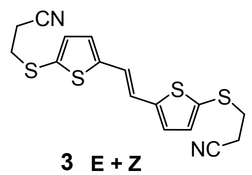
2

In a three-neck round-bottom flask fitted with a dropping funnel and under inert atmosphere, was introduced **1** (1g, 5.9 mmol), in 15 mL of 1,2-dichloroethane. Anhydrous DMF (0.95 mL, 2 equiv.) was added to the reaction mixture. After cooling to 0°C, $POCl_3$ (1.1 equiv., 0.61 mL) was added dropwise to the reaction mixture *via* a syringue. Once the reaction warmed to room temperature, the reaction mixture was heated at reflux and stirred during 2 h (the evolution of the reaction was followed on TLC). After the reaction mixture was cooled to room temperature, 40 mL of sodium acetate were added and stirred overnight. The mixture was extracted with 4 x 35 mL of dichloromethane and the organic phase was washed with water (2 x 100 mL) and dried over $MgSO_4$. The desired compound **2** was obtained as an orange oil in a 56% yield (655 mg) after purification by column chomatography using dichloromethane as eluent.

NMR ^{1}H ($CDCl_3$): δ (ppm)= 9.82 (s, 1H), 7.66 (d, 1H, ^3J=3.9 Hz), 7.22 (d, 1H, ^3J=3.6 Hz), 3.18 (t, 2H, ^3J=6.9 Hz), 2.71 (t, 2H, ^3J=6.9Hz)
NMR ^{13}C ($CDCl_3$): δ (ppm) = 181.9, 145.7, 144.8, 136.8, 132.9, 117.4, 32.7, 18.3

MS EI m/z: 197 (M^+, 100), 157.1 (60), 143 (25), 115 (25), 45 (40)
HRMS (CI^+ isobutane): MH^+ calculated: 198.0042; found: 198.0045.

(E+Z) 1,2 - bis[2-(2-cyanoethylsulfanyl)thienyl]ethylene (3)

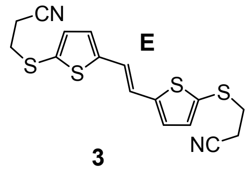


3 E + Z

In a three-neck round-bottom flask fitted with a dropping funnel and under inert atmosphere, a solution of 30 mL of anhydrous THF was cooled to 0°C. $TiCl_4$ (0.33 mL, 3 mmol) was then added to the solution and after 15 min of stirring at 0°C, 400 mg of Zinc (6 mmol) were added. The reaction mixture was heated to reflux for 1 h. Once the reaction mixture was warmed to room temperature, a solution of 370 mg of aldehyde **2** in 30 mL of anhydrous THF was added and the reaction was heated at reflux for 3 h. After cooling to room temperature, 50 mL of HCl 0.5 M were added. The mixture was extracted with 3 x 75 mL of dichloromethane and the organic phase was washed with water and dried over $MgSO_4$. After evaporation of the solvent *in vacuo* and purification by column chromatography using a 8:2 mixture of dichloromethane and Petroleum Ether as an eluent, the resulting yellow solid (233 mg, 63%) corresponds to a mixture of Z and E isomers of compound **3**.

NMR ^{1}H ($CDCl_3$): δ (ppm)= 7.10 (d, 2H, ^3J=3.6 Hz), 6.94 (d, 2H, ^3J=3.6 Hz), 6.91 (s, 1.85H, E isomer), 6.55 (s, 0.15H, Z isomer), 3.0 (t, 4H, ^3J=7.2 Hz), 2.65 (t, 4H, ^3J=7.2Hz)

(E)-1,2 - bis[2-(2-cyanoethylsulfanyl)thienyl]ethylene (3)



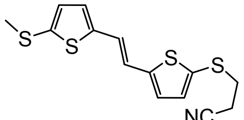
3

The pure isomer E was obtained by adding 10 mL of toluene and 5 mg of iodine to 10 mg of the mixture of E and Z isomers of **3**. The reaction mixture was heated to reflux overnight. Once cooled to room temperature, an aqueous solution of $Na_2S_2O_3$ 1 M was added and the solution was stirred for 20 min. The mixture was extracted with dichloromethane and the organic phase was washed with water and dried over $MgSO_4$. The desired compound (**3**, E isomer) was obtained as a yellow solid in a 90% yield (9 mg)

NMR ^{1}H ($CDCl_3$): δ (ppm)= 7.10 (d, 2H, ^3J=3.6 Hz), 6.94 (d, 2H, ^3J=3.6 Hz), 6.91 (s, 2H), 3.0 (t, 4H, ^3J=7.2 Hz), 2.65 (t, 4H, ^3J=7.2Hz)
NMR ^{13}C ($CDCl_3$): δ (ppm) = 147.1, 136.5, 130.7, 127.3, 122.2, 117.9, 33.8, 18.4

MS EI m/z: 362 (M^+)
HRMS (CI^+ isobutane): MH^+ calculated: 363.0113; found: 363.0115.

(E)-1-[2-(2-cyanoethylsulfanyl)thienyl]-2-[2-(methylthio)thienyl]ethylene (4)



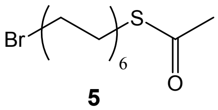
4

Under inert atmosphere, a degassed solution of cesium hydroxide (71 mg, 1.05 equiv.) in 5 mL of dry methanol, was added dropwise to the compound E-**3** (153 mg) in 25 mL of dry DMF. After 2 h of stirring at RT, 260 µL of iodomethane (10 equiv.) were added. The reaction mixture was stirred at room temperature overnight. The mixture was extracted with dichloromethane and the organic phase was washed with water and dried over $MgSO_4$. The desired compound **4** was obtained as a yellow solid in 62% yield (38 mg) after purification by column chomatography using dichloromethane as eluent.

NMR ^{1}H ($CDCl_3$): δ (ppm)= 7.09 (d, 1H, ^3J=3.9Hz), 6.90 (m, 5H), 2.99 (t, 2H, ^3J=7.2 Hz), 2.64 (t, 2H, ^3J=7.2Hz), 2.52 (s, 3H).
NMR ^{13}C ($CDCl_3$): δ (ppm) = 147.6, 143.7, 137.7, 136.6, 130.9, 129.9, 127.3, 126.7, 122.7, 120.7, 117.9, 33.8, 21.7, 18.4.

MS EI m/z: 323 (M^+)
HRMS (CI$^+$ isobutane): MH^+ calculated: 324.0004; found: 324.0002.

S-(12-bromododecyl) ethanethioate (5)



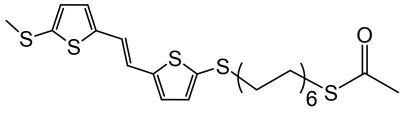
5

In a round-bottomed, three-necked flask, 9.36 g of 1,12-dibromododecane (29 mmol) and 830 mg of potassium thioacetate (0.25 equiv.) were dissolved in 100 mL of acetonitrile. The reaction mixture was heated to reflux for 24 h. The mixture was extracted with petroleum ether. The organic phase was washed and dried over $MgSO_4$ and then concentrated. The product was purified by column chromatography (using Hexane/dichloromethane, 6/1 as an eluent). The desired compound was obtained as a white powder (1.70g, 72%).

NMR ^{1}H ($CDCl_3$): δ (ppm) = 3.40 (t, 2H, ^3J=6.8Hz), 2.86 (t, 2H, ^3J=7.2Hz), 2.32 (s, 3H), 1.85 (q, 2H), 1.42 (m, 2H), 1.28 (m, 16H).
MS IE m/z: 323 (MH^+, 18), 281.5 (88), 264.5 (25), 248.5 (42), 201.5 (20)

This synthesis has already been described in the literature (S. Yokokawa, K. Tamada, E. Ito and M. Hara, J. *Phys. Chem. B*, 2003, **107**, 3544-3551.). The characterizations data are in accordance with the ones published.

(E)-1-[2-(dodecylethanethioate)thienyl]-2-[2-(methylthio)thienyl]ethylene (6)



6

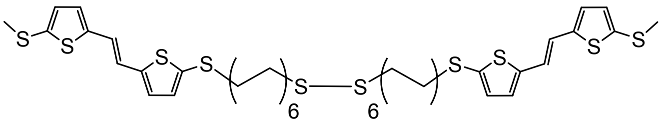
Under inert atmosphere , to a degassed solution of cesium hydroxide (26 mg, 1.05 equiv.) in 2 mL of anhydrous methanol, was added dropwise a solution of **4** (48 mg, 148 mmol) in 9 mL of anhydrous

DMF previously degassed. After 1 h under stirring at room temperature, a solution of **5** (95 mg, 2 equiv.) in 3 mL of anhydrous DMF previously degassed, was added drop wise. The reaction mixture was then stirred for one more hour at room temperature. The mixture was extracted with dichloromethane and the organic phase was washed with water, dried over $MgSO_4$, and then concentrated. The product was obtained by precipitation in hexane. After filtration, a yellow solid (57 mg, 76%) was obtained.

NMR ^{1}H ($CDCl_3$): δ (ppm) = 6.95 (d, 1H, ^{3}J=3.6Hz), 6.92 (d, 1H, ^{3}J=3.6Hz), 6.85 (dd, 4H), 2.83 (m, 4H), 2.51 (s, 3H), 2.32 (s, 3H), 1.60 (m, 4H), 1.25 (m, 16H).
NMR ^{13}C ($CDCl_3$): δ (ppm) = 196.2, 145.2, 144.3, 136.9, 134.8, 133.5, 131.1, 126.7, 126.6, 121.5, 121.4, 38.9, 29.7, 29.6, 29.5, 29.3, 21.8

MS (MALDI) m/z: 512 (M^+)
HRMS (FAB$^+$ Ar): M^+ calculated: 512.1370; found: 512.1367.

(E)-1-[2-(dodecylethanethioate)thienyl]-2-[2-(methylthio)thienyl]ethylene (TV-SS)



TV-SS

To a solution of **6** (44 mg, 0.9 µmol) in 10 mL of THF under inert atmosphere, was added dropwise a degassed solution of cesium hydroxide (17 mg, 1.05 equiv.) in anhydrous methanol (1.0 mL). The reaction mixture was stirred at room temperature for 45 min. The mixture was extracted with dichloromethane and the organic phase was washed with water and dried over $MgSO_4$, and then concentrated. The product was purified by column chromatography using dichloromethane as eluent. The desired compound was obtained as a yellow powder (56 mg, 70%).

NMR ^{1}H ($CDCl_3$): δ (ppm) = 6.95 (d, 2H, ^{3}J=3.6Hz), 6.92 (d, 2H, ^{3}J=3.9Hz), 6.86 (dd, 8H), 2.81 (t, 4H, ^{3}J=7.2Hz), 2,67 (t, 4H, ^{3}J=7.2Hz), 2.51 (s, 6H), 1.63 (m, 8H), 1.25 (m, 32H).
NMR ^{13}C ($CDCl_3$): δ (ppm) = 145.2, 144.3, 136.9, 134.8, 133.5, 131.1, 126.7, 126.6, 121.5, 121.4, 39.4, 38.9, 34.2, 29.7, 29.6, 21.8.

MS (MALDI) m/z: 938.5 (M^+)
HRMS (FAB$^+$ Ar) : MH^+ calculated : 938.2372 ; found :938.2377.

3 ^{1}H (300 MHz) and ^{13}C NMR (75 MHz) spectra

Figure S1. ^{1}H NMR spectra of 2 in $CDCl_3$

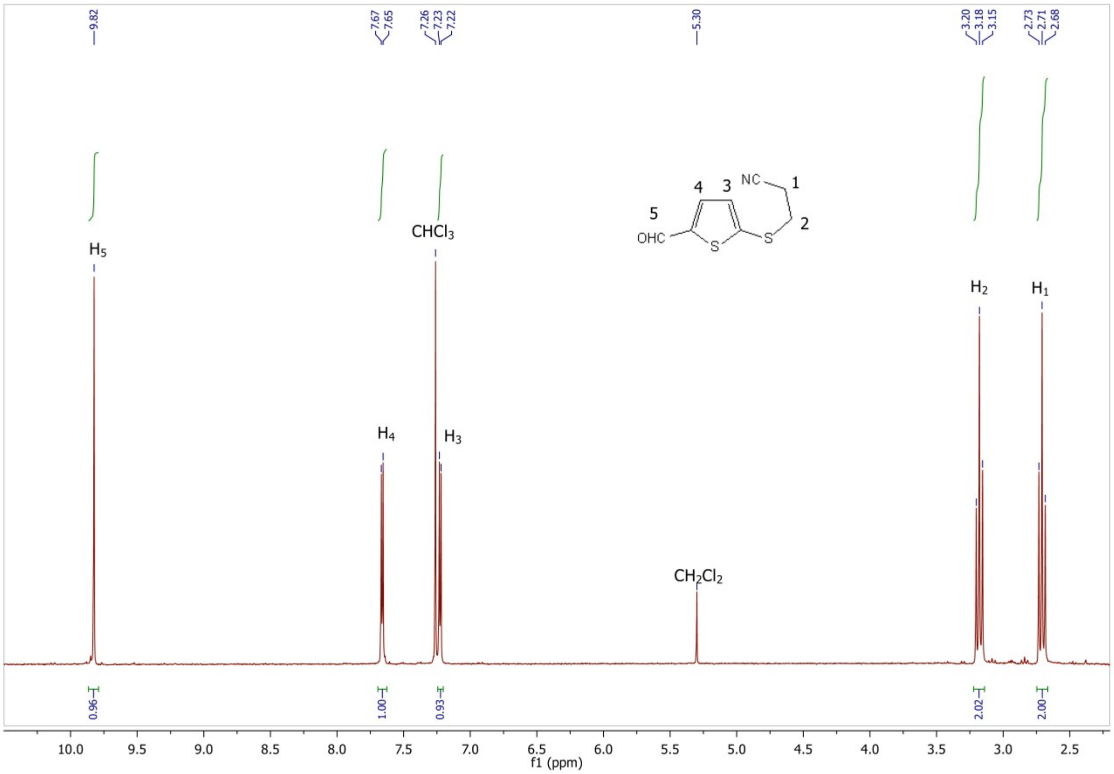


Figure S2. ^{13}C NMR spectra of 2 in $CDCl_3$

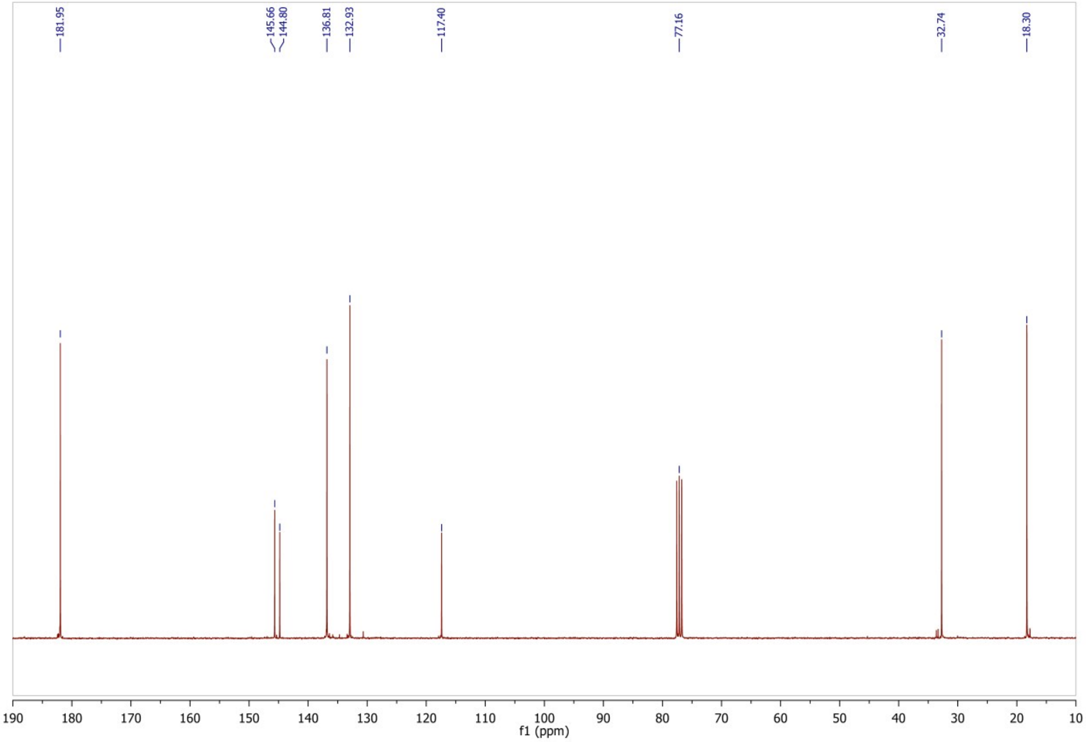


Figure S3. ^{1}H NMR spectra of 3 (Z+E) in $CDCl_3$

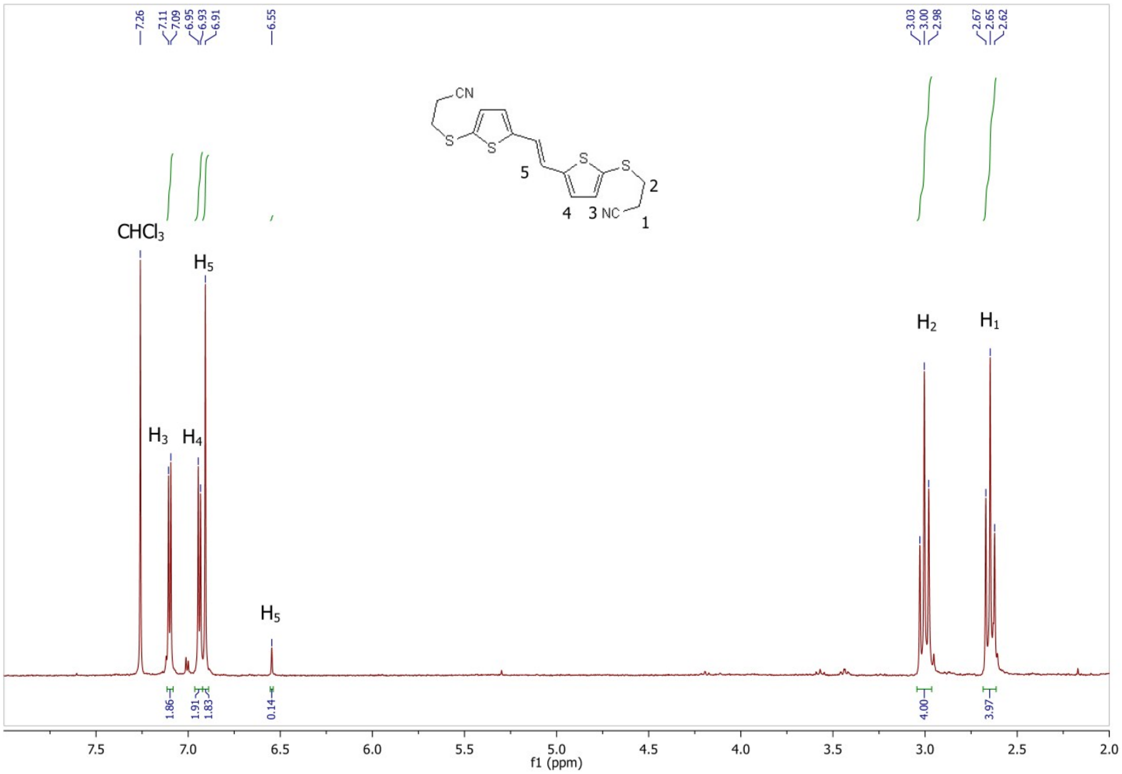


Figure S4. ^{1}H NMR spectra of 3 (E) in $CDCl_3$

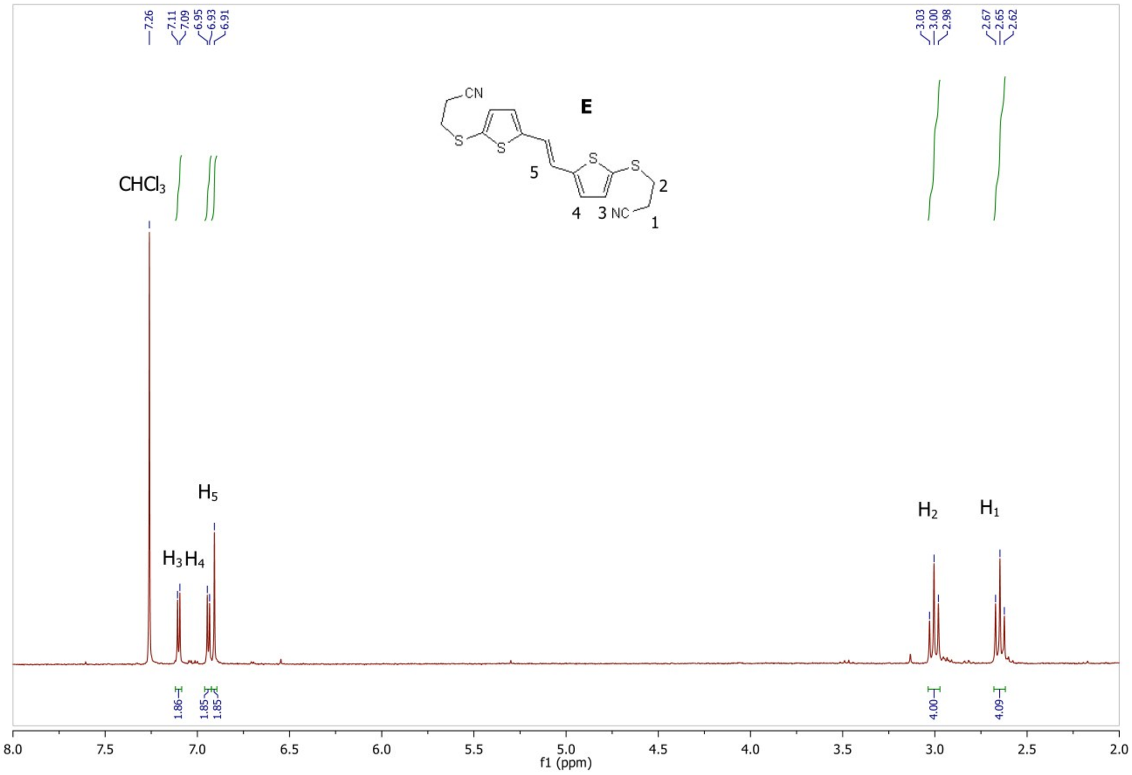


Figure S5. ^{13}C NMR spectra of 3 (E) in $CDCl_3$

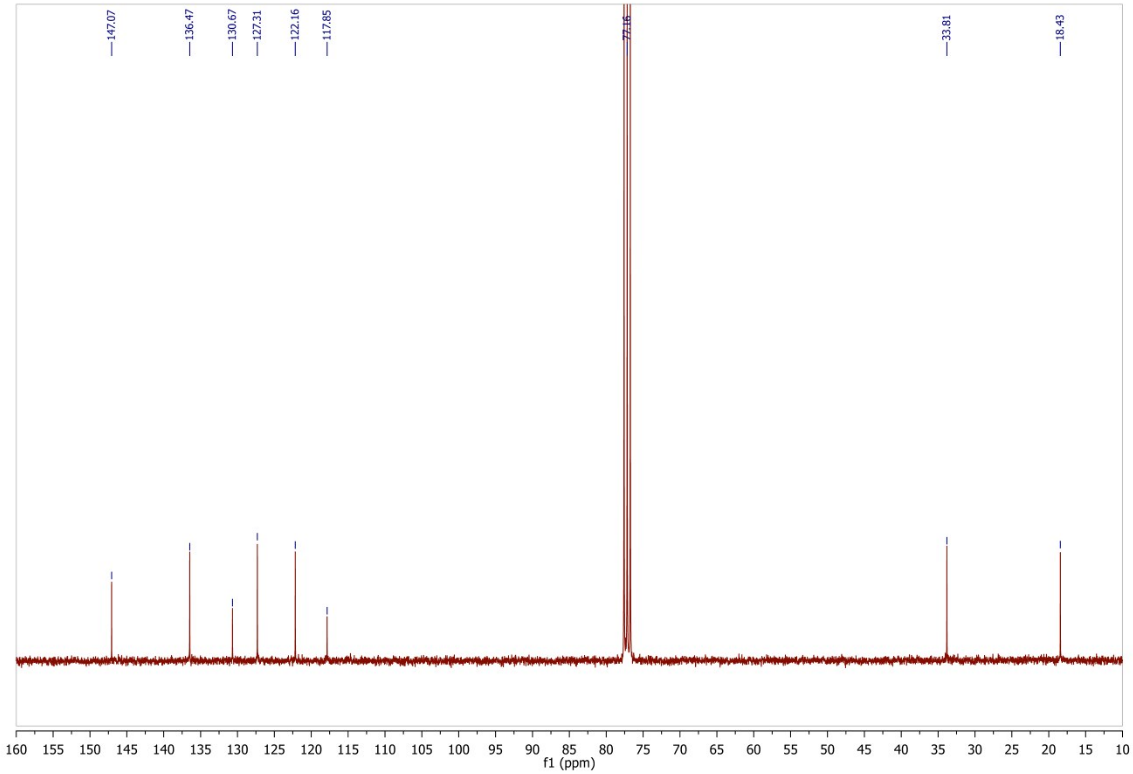


Figure S6. ^{1}H NMR spectra of 4 in $CDCl_3$

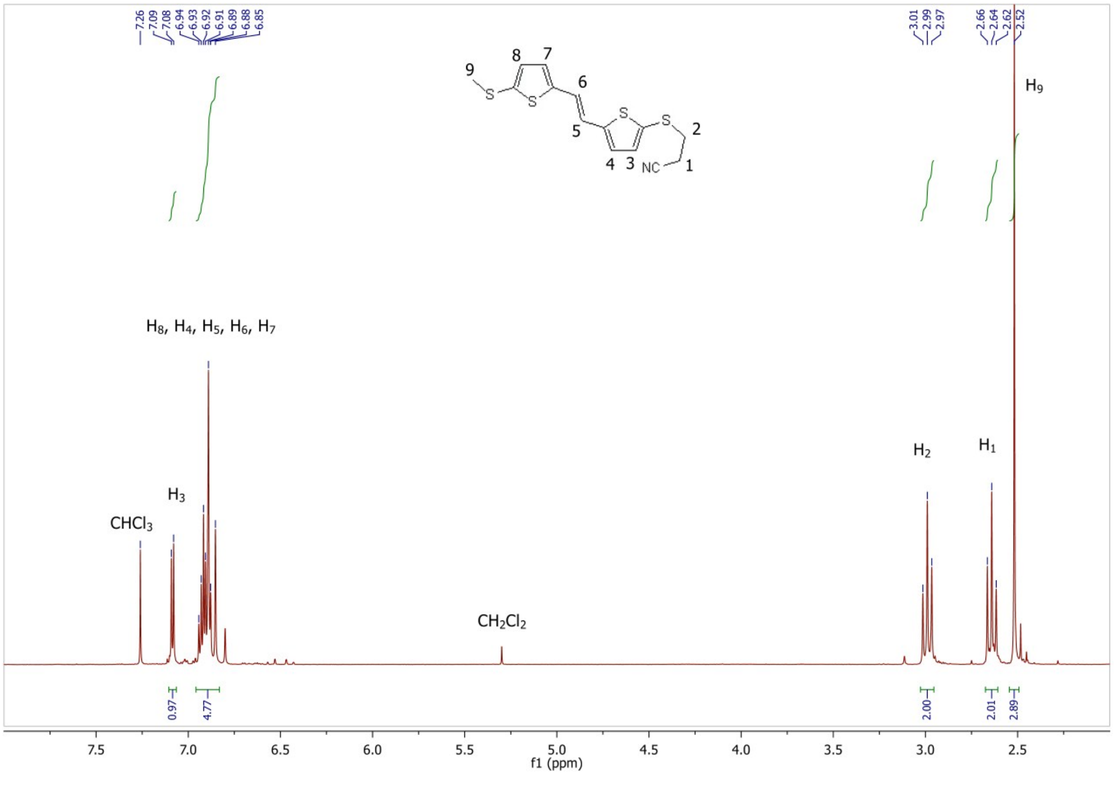


Figure S7. ^{13}C NMR spectra of 4 in $CDCl_3$

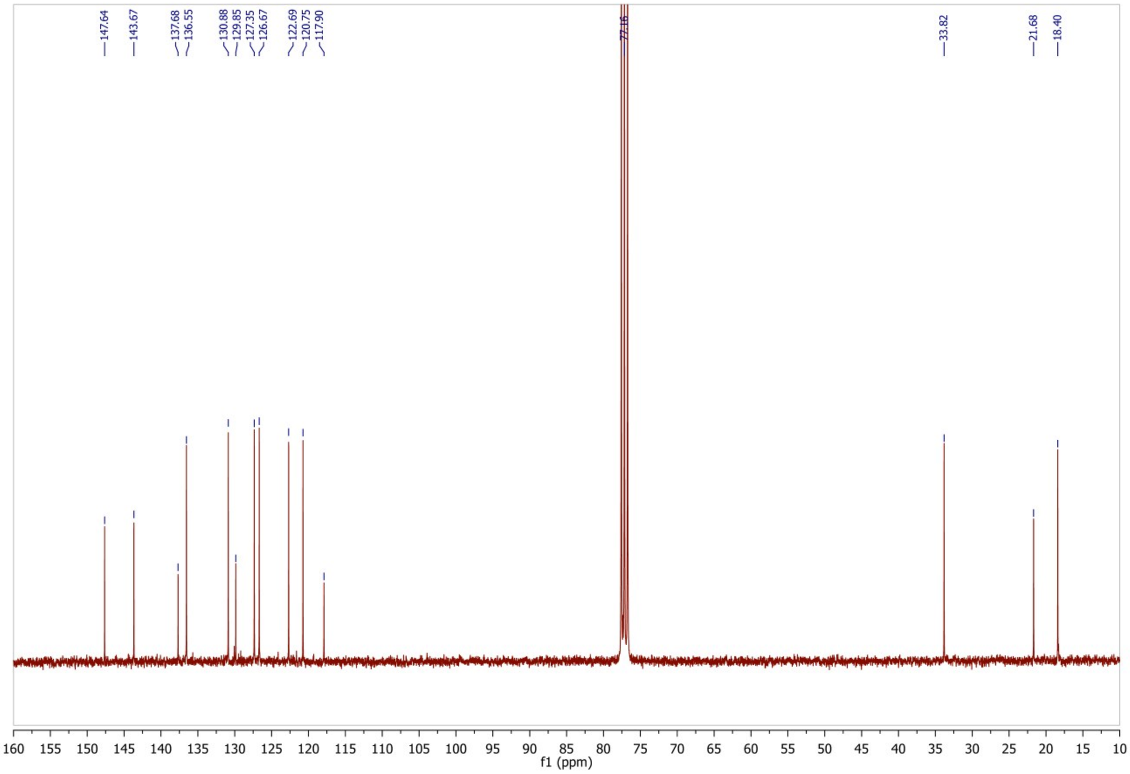


Figure S8. ^{1}H NMR spectra of 6 in $CDCl_3$

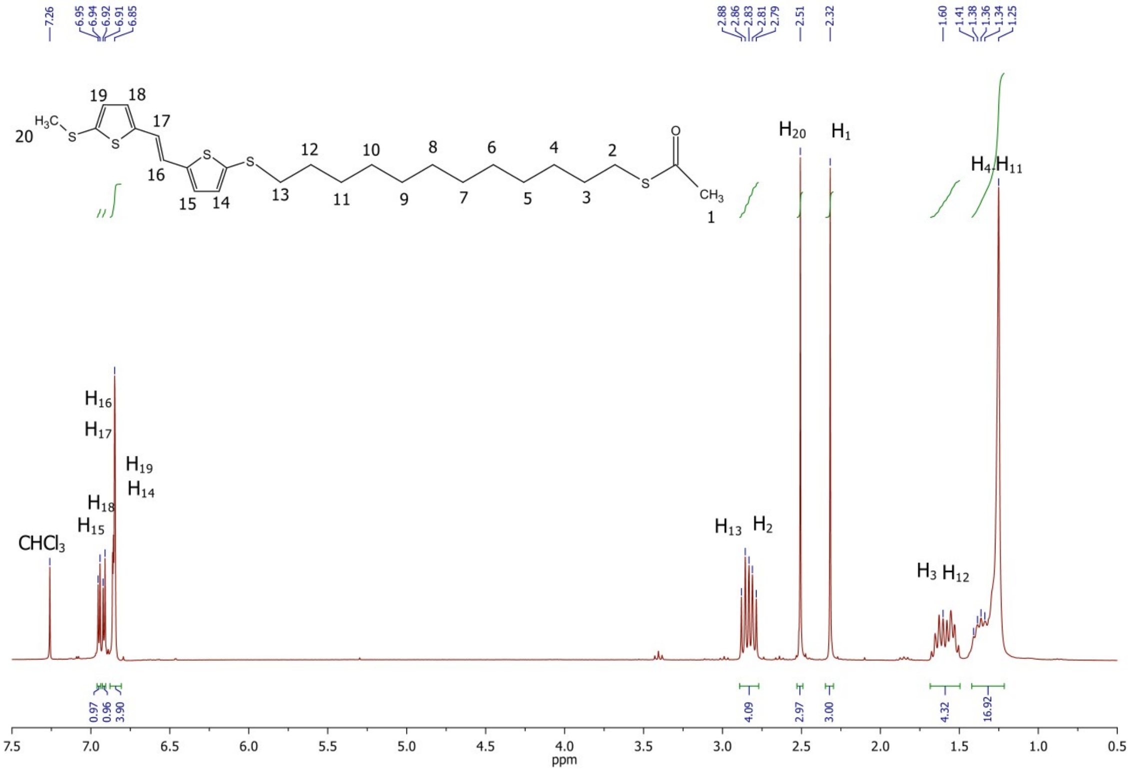


Figure S9. ^{13}C NMR spectra of 6 in CDCl$_3$

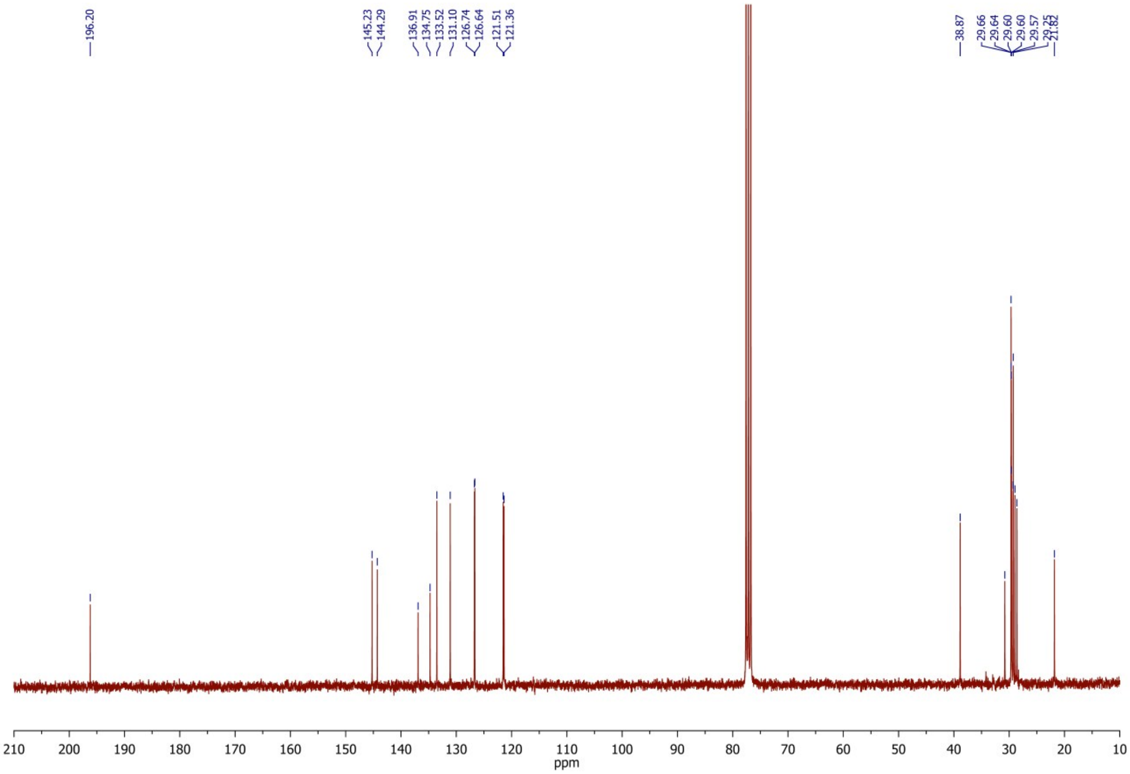


Figure S10. ^{1}H NMR spectra of TV-SS in CDCl$_3$

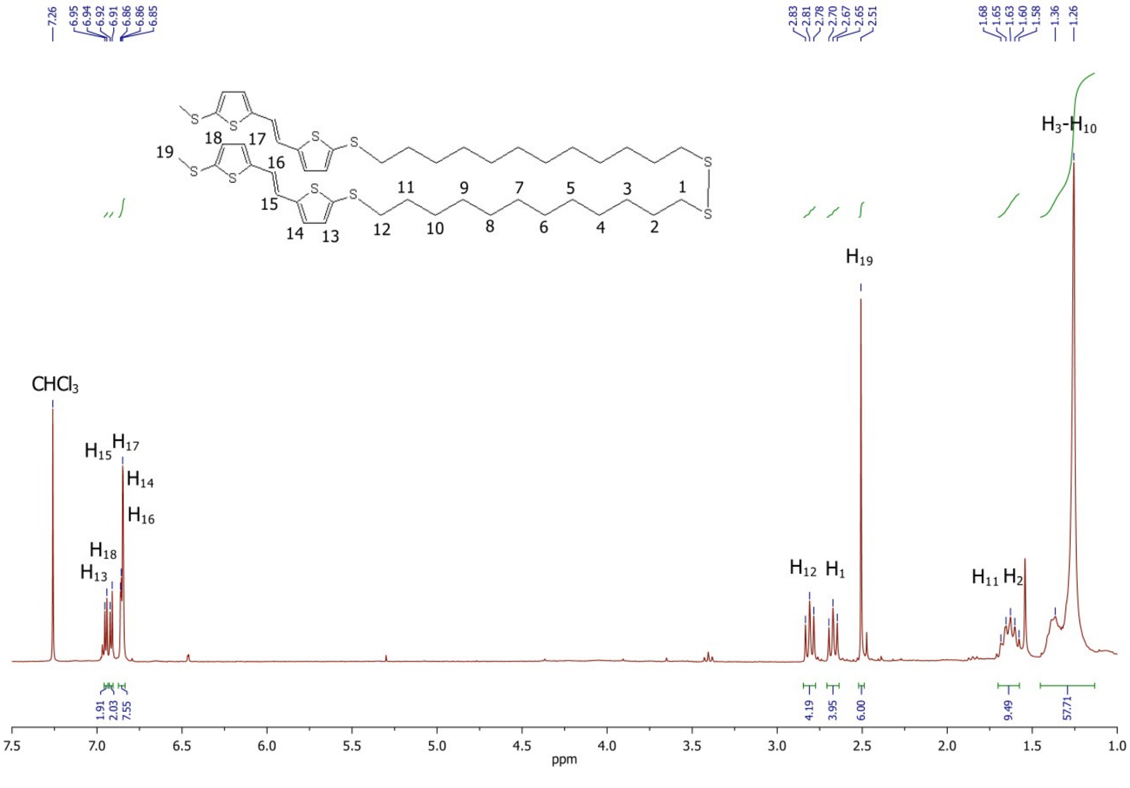
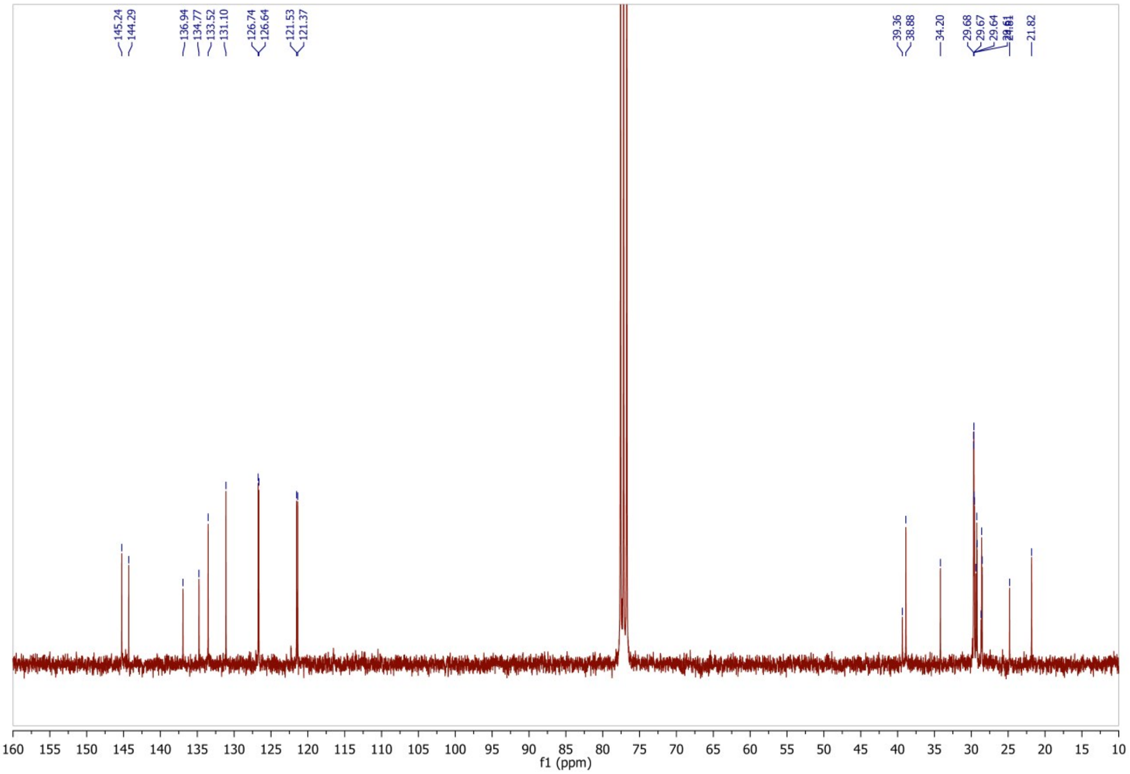


Figure S11. ^{13}C NMR spectra of TV-SS in $CDCl_3$



4 Cyclic voltammetry on TV-1 : Peak currents *vs.* $v^{1/2}$

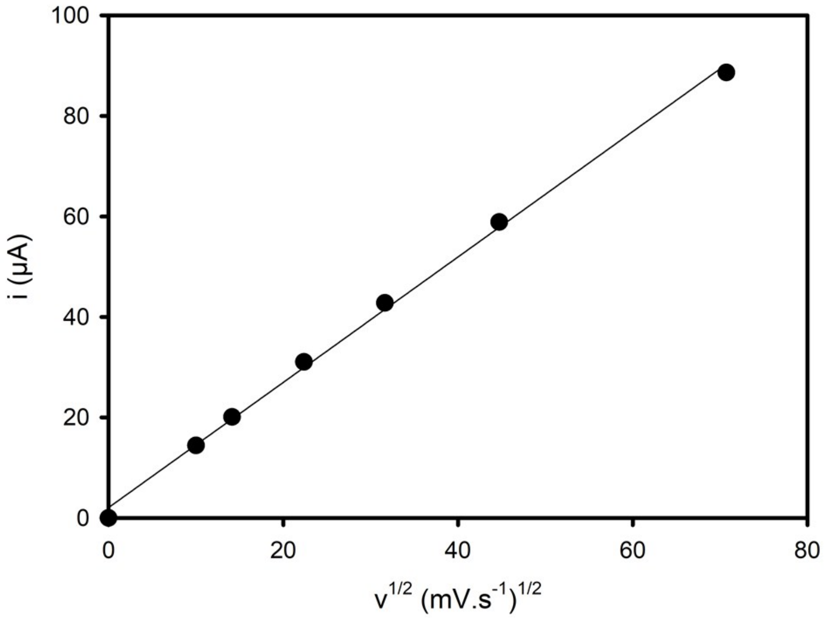


Figure S12. I_{peak2} *vs.* $v^{1/2}$ extracted from CVs of a 1 mM solution of TV-1 in 0.1 M Bu_4NPF_6/CH_2Cl_2 on a Pt working electrode (ϕ = 0.15 cm).