

Supporting Information for

Aromaticity in Tropone-Containing Polythiophene

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1. General

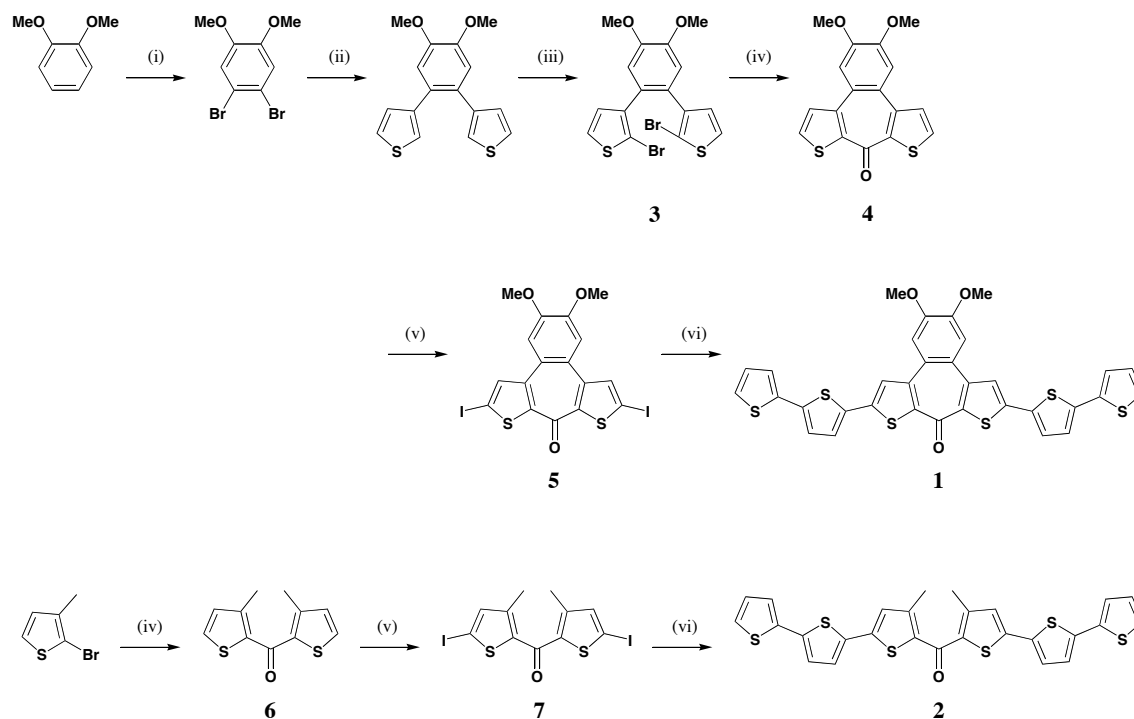
All air and water sensitive synthetic manipulations were performed under an argon atmosphere using standard Schlenk techniques. The intermediate 1,2-Bis(2-bromo-3-thienyl)-4,5-dimethoxybenzene (**3** in Scheme S1) was prepared by a similar procedure reported previously.¹ Tri-*n*-butylstannyl-2-2'-bithiophene was prepared by lithiation of 2-2'-bithiophene and trapping with *n*-Bu₃SnCl.² Ether was passed through activated alumina columns prior to storage in dry air-free vessels. All other solvents and chemicals were of reagent grade and used as received. Column chromatography was performed using ultra pure silica gel (SILIYCYCLE, 40~63 μm). NMR spectra were obtained on Bruker Advance 400 spectrometer, and all chemical shifts are referenced to residual CHCl₃ (77.23 ppm for ¹³C) or (CH₃)₄Si (0 ppm for ¹H). IR spectra were obtained on NEXUS 870 ATR-FT-IR spectrometer. High-resolution mass spectra were obtained at the MIT Department of Chemistry Instrumentation Facility (DCIF) on a Bruker Daltonics APEX II3 Tesla FT-ICR-MS. Melting point was measured with MEL-TEMP instrument. UV-Vis-NIR absorption spectra were obtained on an Agilent 8453 diode array spectrophotometer.

All electrochemical measurements were made with an AUTOLAB PGSTAT 20 potentiostat (Eco Chemie) using a quasi-internal Ag wire reference electrode (BioAnalytical Systems) submersed in 0.01 M AgNO₃/0.1 M *n*-Bu₄NPF₆ in anhydrous MeCN. Typical CVs were recorded using platinum button electrodes or indium tin oxide (ITO) coated glass electrodes as the working electrode and a platinum coil counter electrode. The ferrocene/ferrocenium (Fc/Fc⁺) redox couple was used as an external reference. Spectroelectrochemistry was performed under ambient laboratory conditions on polymer films electrodeposited onto ITO coated glass electrodes. The films were placed in a quartz cuvette in the path of the light source along with counter and reference electrodes as used above. In-situ conductivity measurements were carried out by using 5 μm interdigitated microelectrodes as working electrodes. Films were grown on interdigitated microelectrodes for conductivity studies by applying a cyclic potential. Once grown, the films were then placed in monomer-free electrolyte. Conductivity measurements were typically carried out at a scan rate of 5 mV/s with a 40 mV offset potential between the two working electrodes. Film thickness was determined with a Veeco Dektak 6M STYLUS PROFILER. The conductivity (σ) was then calculated by the following equation, where *i_D* is the drain current, *V_D* is the offset potential, and *T* is the polymer thickness; with a 5 μm gap, *D*; *n* = 99 gaps; and 0.5 cm electrode length, *L*. We also corrected the value with poly(3-methylthiophene) as 60 Scm⁻¹.

$$\sigma = (i_D/V_D)(D/n T L)$$

Films for in situ EPR studies were prepared on a platinum wire electrode, using a platinum wire counter electrode and an Ag/Ag⁺ reference electrode. The polymer-deposited working electrode was then transferred to a quartz EPR-electrochemistry cell (Wilma Glass) containing 0.1 M *n*-Bu₄NPF₆ CH₂Cl₂ electrolyte solution. Spectra were obtained using a Bruker Model EMX Electron Paramagnetic Resonance Spectrometer operating at the X-band with 100 kHz field modulation at room temperature. The maximum EPR signal intensity was followed as a function of oxidation potential while scanning the polymer through a complete cycle at 7.15 mV/s.

2. Syntheses of monomers



Scheme S1. Syntheses of **1** and **2**: (i) Br₂ in CH₂Cl₂ at 0°C, (ii) 3-thienylbromic acid, Na₂CO₃, Pd(PPh₃)₄ in toluene/ethanol/water mixture at 90°C, (iii) Br₂ in CH₂Cl₂ at 0°C, (iv) *n*-butyllithium then dimethylcarbamyl chloride in ether at -78°C, (v) PhI(CF₃COO)₂, I₂ in CH₂Cl₂ at r.t. (vi) tributylstannyl-2-2'-bithiophene, Pd(PPh₃)₄ in DMF at 90°C.

Synthesis of compound **4**³

To a solution of compound **3** (2.0 g, 4.3 mmol) in dry ether (500 mL) was added a 1.6 M of *n*-butyllithium solution in hexane (5.4 mL, 8.6 mmol) at -78°C under argon atmosphere. The reaction mixture was warmed to 0°C and stirred for 3 hours, then cooled to -78°C again, and dimethylaminocarbamyl chloride (400 µL, 4.3 mmol) was added. The mixture was warmed to r.t. and stirred for 15 h. The solvent was evaporated and the product was dissolved in CH₂Cl₂. The solution was washed with NaCl aq. and dried over MgSO₄. The crude product was purified through column chromatography (silica gel, CHCl₃) to give compound **4** as a yellow powder (900 mg, 64%). M.p. 241-243°C. ¹H-NMR (400 MHz, CDCl₃, TMS) δ: 4.04 (s, 6H), 7.55 (s, 2H), 7.77 (d, *J* = 5.4 Hz, 2H), 7.81 (d, *J* = 5.4 Hz, 2H). ¹³C-NMR (100 MHz, CDCl₃, TMS) δ: 56.2, 111.8, 125.9, 129.2, 132.9, 140.9, 141.3, 149.3, 175.6. ATR-FTIR ν /cm⁻¹: 1552, 1525, 1263, 1100, 1048. HR-MS calcd. for C₁₇H₁₃O₃S₂ 329.0301 [M+H]⁺; found 329.0316.

Synthesis of compound **5**

To a solution of compound **4** (700 mg, 2.1 mmol) in CH₂Cl₂ (200 mL), I₂ (1.0 g, 3.9 mmol) and PhI(CF₃COO)₂ (1.7 g, 4.0 mmol) were added portionwise with stirring for 80 h under argon atmosphere while shielding from light. The reaction mixture was washed with aq. Na₂S₂O₃ and aq. NaCl and dried over MgSO₄. Insoluble material was filtered off and the filtrate was evaporated. The product was purified through column chromatography (silica gel, CHCl₃) to give compound **5** as yellow powder (470 mg, 38%). M.p. 294-296°C. ¹H-NMR (400 MHz, CDCl₃, TMS) δ: 4.09 (s, 6H), 7.72 (s, 2H), 7.95

(s, 2H). ^{13}C -NMR (100 MHz, CDCl_3 , TMS) δ : 56.5, 114.3, 124.9, 138.0, 142.0, 142.3, 147.9, 149.2, 175.8. ATR-FTIR ν/cm^{-1} : 1606, 1572, 1555, 1522, 1405, 1377, 1261, 1211, 1094, 1055. HR-MS calcd. for $\text{C}_{17}\text{H}_{11}\text{I}_2\text{O}_3\text{S}_2$ 580.8234 $[\text{M}+\text{H}]^+$; found 580.8259.

Synthesis of compound 1

The mixture of compound **5** (250 mg, 0.43 mmol), 2-(tributylstannyl)bithiophene (590 mg, 1.29 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (40 mg, 0.035 mmol) in dry DMF (20 mL) was stirred for 5 h at 90°C under argon atmosphere. After cooling the reaction mixture, toluene (200 mL) was added and the solution was washed with aq. NaCl. The organic layer was dried over MgSO_4 and insoluble material was filtered off. The filtrate was evaporated and the product was purified through column chromatography (silica gel, CHCl_3). Yellow product was further reprecipitated from CHCl_3 with Hexane to give compound **1** as yellow powder (200 mg, 72%). M.p. $278\text{--}279^\circ\text{C}$. ^1H -NMR (400 MHz, CDCl_3 , TMS) δ : 3.44 (s, 6H), 6.89 (d, $J = 3.6$ Hz, 2H), 7.04 (dd, $J = 5.2, 3.6$ Hz, 2H), 7.11 (s, 2H), 7.13 (d, $J = 3.6$ Hz, 2H), 7.17 (dd, $J = 3.6, 1.2$ Hz, 2H), 7.25 (dd, $J = 5.2, 1.2$ Hz, 2H), 7.80 (s, 2H). ^{13}C -NMR (100 MHz, CDCl_3 , TMS) δ : 55.1, 113.8, 124.1, 124.2, 124.7, 124.9, 128.0, 128.1, 132.2, 136.1, 136.7, 137.8, 138.1, 139.8, 143.8, 147.2, 177.0. ATR-FTIR ν/cm^{-1} : 1587, 1555, 1513, 1383, 1281, 1212, 1143, 1101. HR-MS calcd. for $\text{C}_{33}\text{H}_{21}\text{O}_3\text{S}_6$ 656.9809 $[\text{M}+\text{H}]^+$; found 656.9786. UV-vis. (CH_2Cl_2) λ/nm (ϵ): 247 (45900), 329 (42700), 411 (8100).

Synthesis of compound 6

Compound **6** was obtained as light brown oil by a method similar to the synthesis of compound **4** using 2-bromo-3-methylthiophene (72%). ^1H -NMR (400 MHz, CDCl_3 , TMS) δ : 2.50 (s, 6H), 6.98 (d, $J = 5.0$ Hz, 2H), 7.45 (d, $J = 5.0$ Hz, 2H). ^{13}C -NMR (100 MHz, CDCl_3 , TMS) δ : 16.5, 130.0, 132.0, 145.3, 149.2, 182.4. ATR-FTIR: ν/cm^{-1} : 1611, 1516, 1400, 1256. HR-MS calcd. for $\text{C}_{11}\text{H}_{11}\text{OS}_2$ 223.0246 $[\text{M}+\text{H}]^+$; found 223.0246.

Synthesis of compound 7

Compound **7** was obtained as white powder by a method similar to the synthesis of compound **5** using compound **6**. (68%). M.p. $121\text{--}123^\circ\text{C}$. ^1H -NMR (400 MHz, CDCl_3 , TMS) δ : 2.45 (s, 6H), 7.15 (s, 2H). ^{13}C -NMR (100 MHz, CDCl_3 , TMS) δ : 16.14, 141.4, 141.9, 146.9, 149.2, 178.8. ATR-FTIR: ν/cm^{-1} : 1611, 1517, 1389, 1372, 1244. HR-MS calcd. for $\text{C}_{17}\text{H}_9\text{I}_2\text{OS}_2$ 474.8179 $[\text{M}+\text{H}]^+$; found 474.8164.

Synthesis of compound 2

Compound **2** was obtained as orange powder by a method similar to the synthesis of compound **1** using compound **7**. (75%). M.p. $174\text{--}176^\circ\text{C}$. ^1H -NMR (400 MHz, CDCl_3 , TMS) δ : 2.51 (s, 6H), 7.04 (dd, $J = 4.8, 3.6$ Hz, 2H), 7.06 (s, 2H), 7.11 (d, $J = 4.0$ Hz, 2H), 7.20–7.21 (m, 4H), 7.25 (dd, 2H). ^{13}C -NMR (100 MHz, CDCl_3 , TMS) δ : 16.8, 124.4, 124.7, 125.2, 126.1, 128.2, 134.0, 135.0, 136.9, 138.2, 141.3, 146.5, 149.2, 180.7. ATR-FTIR: ν/cm^{-1} : 1594, 1456, 1406, 1378, 1272. HR-MS calcd. for $\text{C}_{27}\text{H}_{19}\text{OS}_6$ 550.9755 $[\text{M}+\text{H}]^+$; found 550.9758. UV-vis. (CH_2Cl_2) λ/nm (ϵ): 418 (43500).

References for the syntheses

- 1) (a) Tovar, J. D.; Swager, T. M. *Adv. Mater.*, **2001**, *13*, 1775. (b) Tovar, J. D.; Rose, A.; Swager, T. M. *J. Am. Chem. Soc.*, **2002**, *124*, 7762.
- 2) Apperloo, J. J.; Janssen, R. A. J.; Malenfant, P. R. L.; Groenendaal, L.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2000**, *122*, 7042.
- 3) Lucas, P.; Mehdi, N. E.; Ho, H. A.; Bélanger, D.; Breau, L. *Synthesis*, **2000**, 1253.

3. NMR spectra of monomers

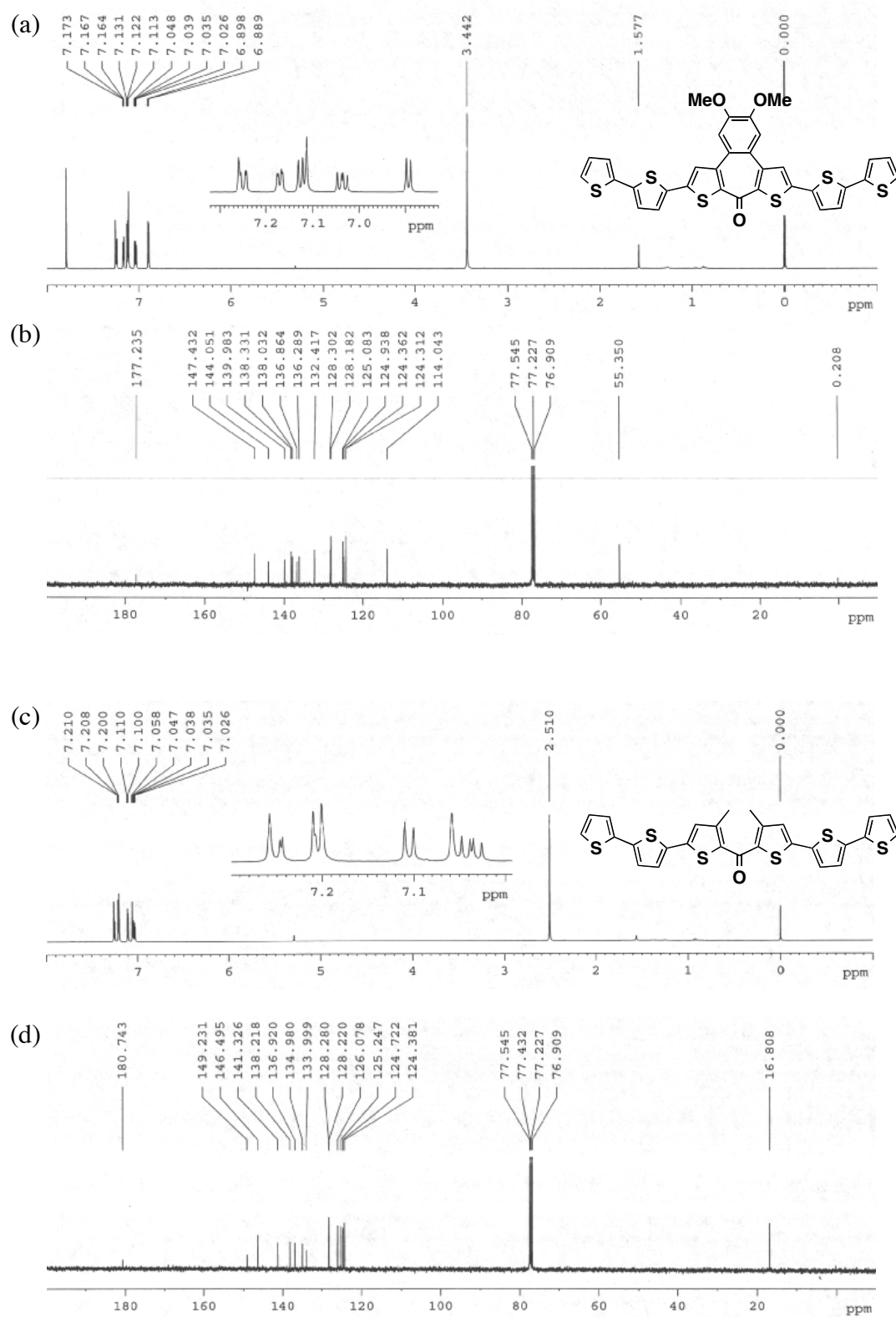


Figure S1 ¹H- (a, c) and ¹³C-NMR (b, d) spectra of monomer **1** (top) and **2** (bottom).

4. Crystal data and structure refinement for 4

Empirical formula	$C_{17}H_{12}O_3S_2$	
Formula weight	328.39	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 11.2885(5) Å	$\alpha = 90^\circ$.
	b = 14.1230(6) Å	$\beta = 90^\circ$.
	c = 17.4374(7) Å	$\gamma = 90^\circ$.
Volume	2780.0(2) Å ³	
Z	8	
Density (calculated)	1.569 Mg/m ³	
Absorption coefficient	0.393 mm ⁻¹	
F(000)	1360	
Crystal size	0.40 x 0.35 x 0.25 mm ³	
Theta range for data collection	2.34 to 29.57°.	
Index ranges	-15 ≤ h ≤ 15, -19 ≤ k ≤ 19, -24 ≤ l ≤ 24	
Reflections collected	51274	
Independent reflections	3892 [R(int) = 0.0265]	
Completeness to theta = 29.57°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9082 and 0.8587	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3892 / 0 / 201	
Goodness-of-fit on F ²	1.046	
Final R indices [I > 2σ(I)]	R1 = 0.0312, wR2 = 0.0841	
R indices (all data)	R1 = 0.0332, wR2 = 0.0861	
Largest diff. peak and hole	0.518 and -0.273 e.Å ⁻³	

5. Electrochemical polymerization

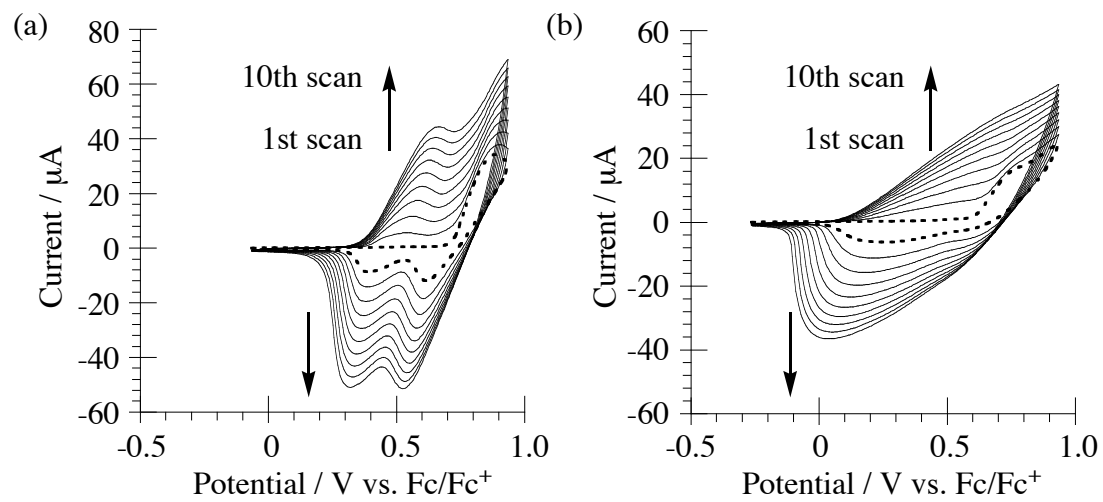


Figure S2. Electrochemical polymerization of **1** (a) and **2** (b) on Pt button electrode in CH_2Cl_2 with 0.1 M TBAPF₆ as a supporting electrolyte. Dotted lines represent the first scans.

6. Scan rate dependence of polymer films

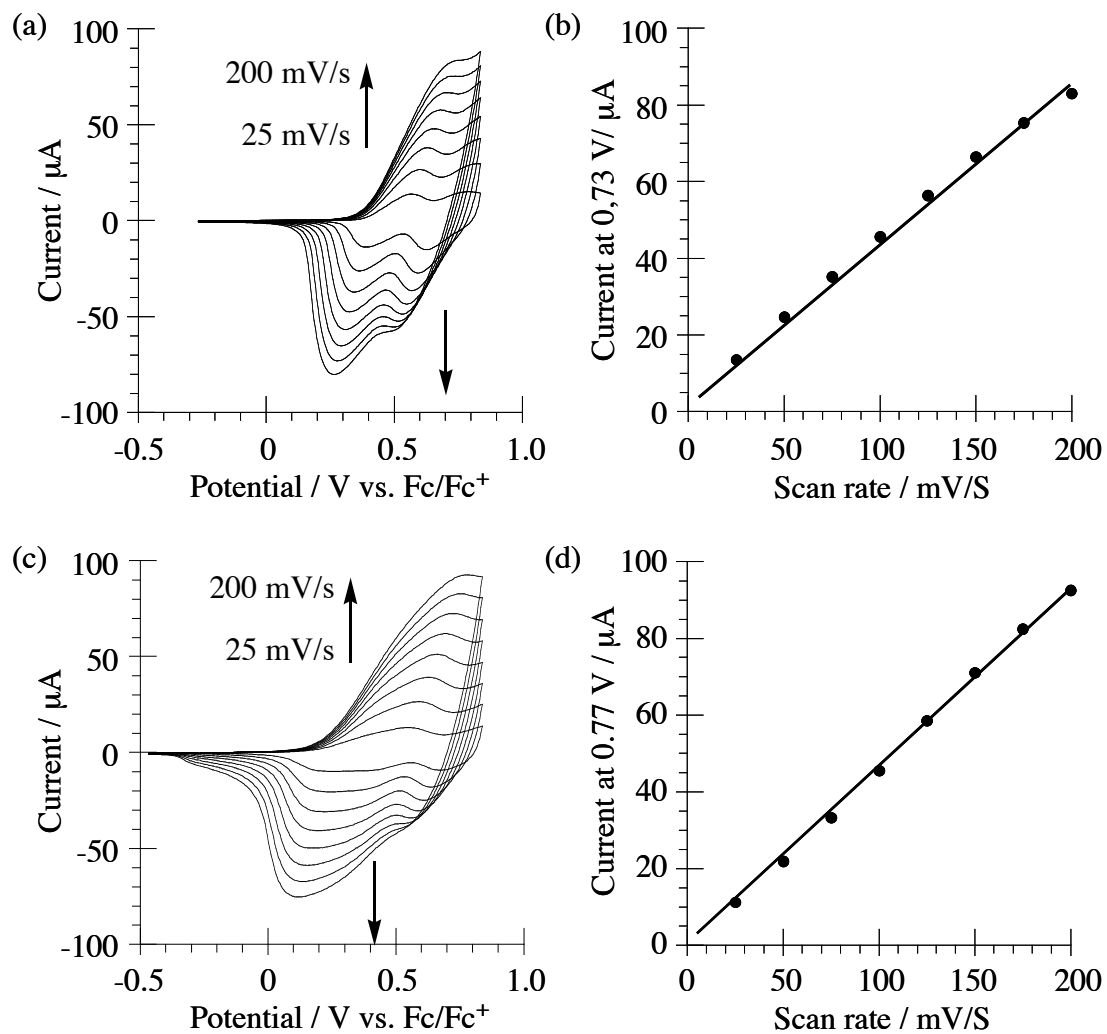


Figure S3. CVs of poly(1) (a) and poly(2) (b) at different scan rates and dependences of scan rate on CV current of poly(1) (c) and poly(2) (d).

7. Spectroelectrochemistry of polymer films

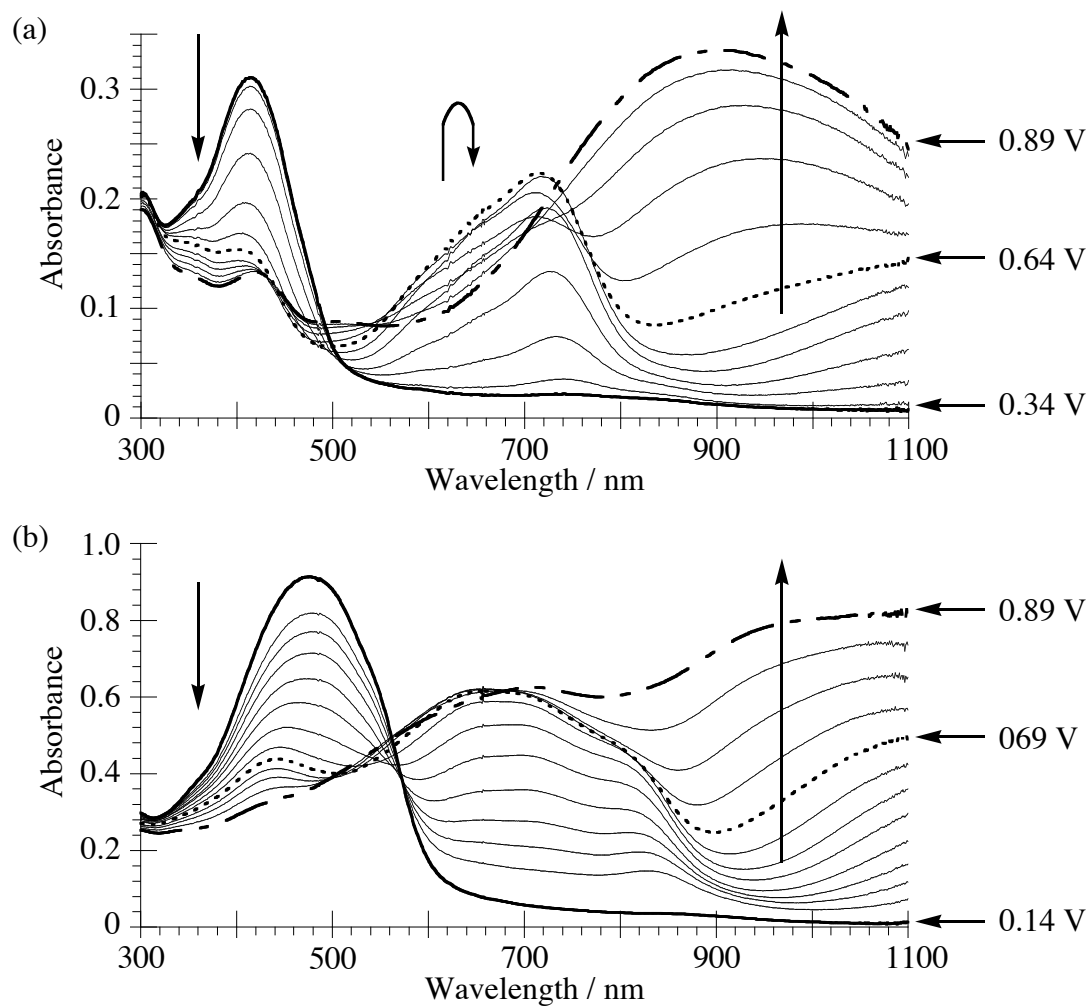


Figure S4. Spectroelectrochemistry of poly(1) (a) and poly(2) (b): Potentials are shown vs. Fc/Fc^+ .

8. In-situ EPR measurements

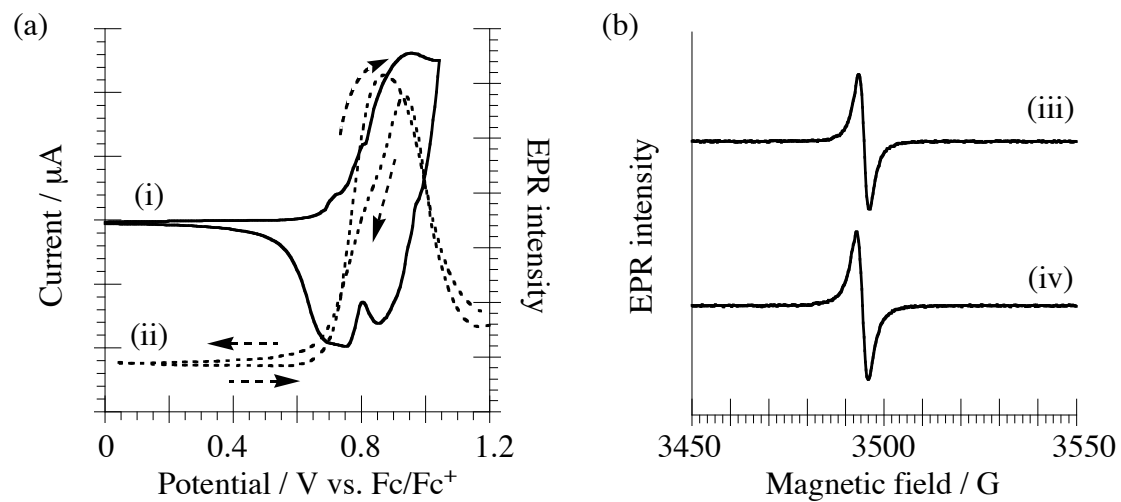


Figure S5. (a) CV (i) and in situ EPR profile (ii) of poly(**1**) in the absence of TFA, and (b) EPR spectra of oxidized poly(**1**) without (iii) and with 500 mM of TFA (iv).