

Charge Delocalization in a Homologous Series of α,α' -Bis(dianisylamino)-Substituted Thiophene Monocations

Supporting Information

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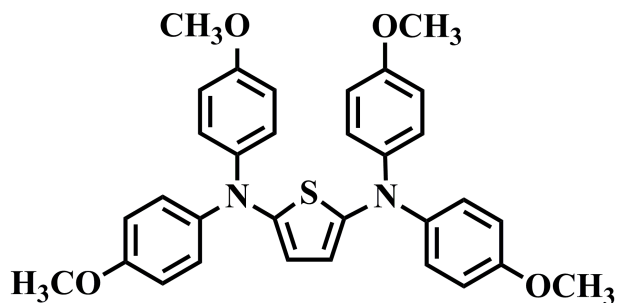
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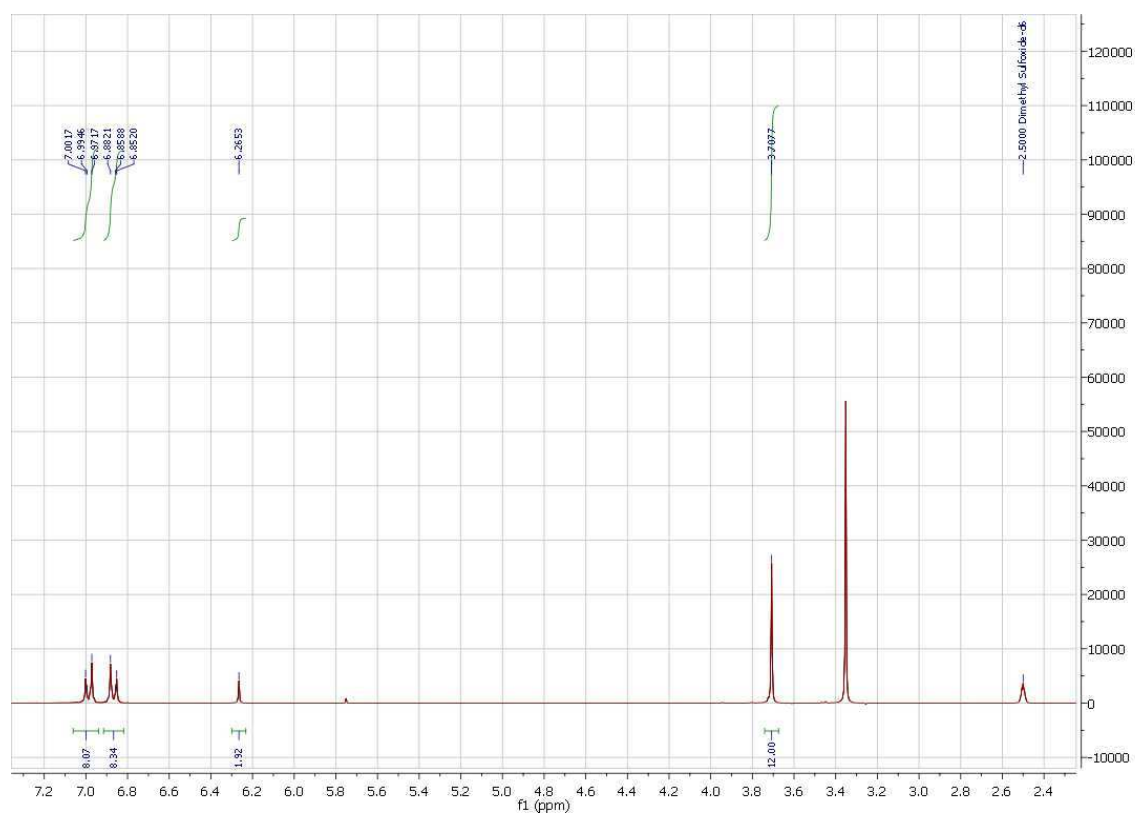
Bis[bis(4-methoxyphenyl)amino]-thiophene (1)



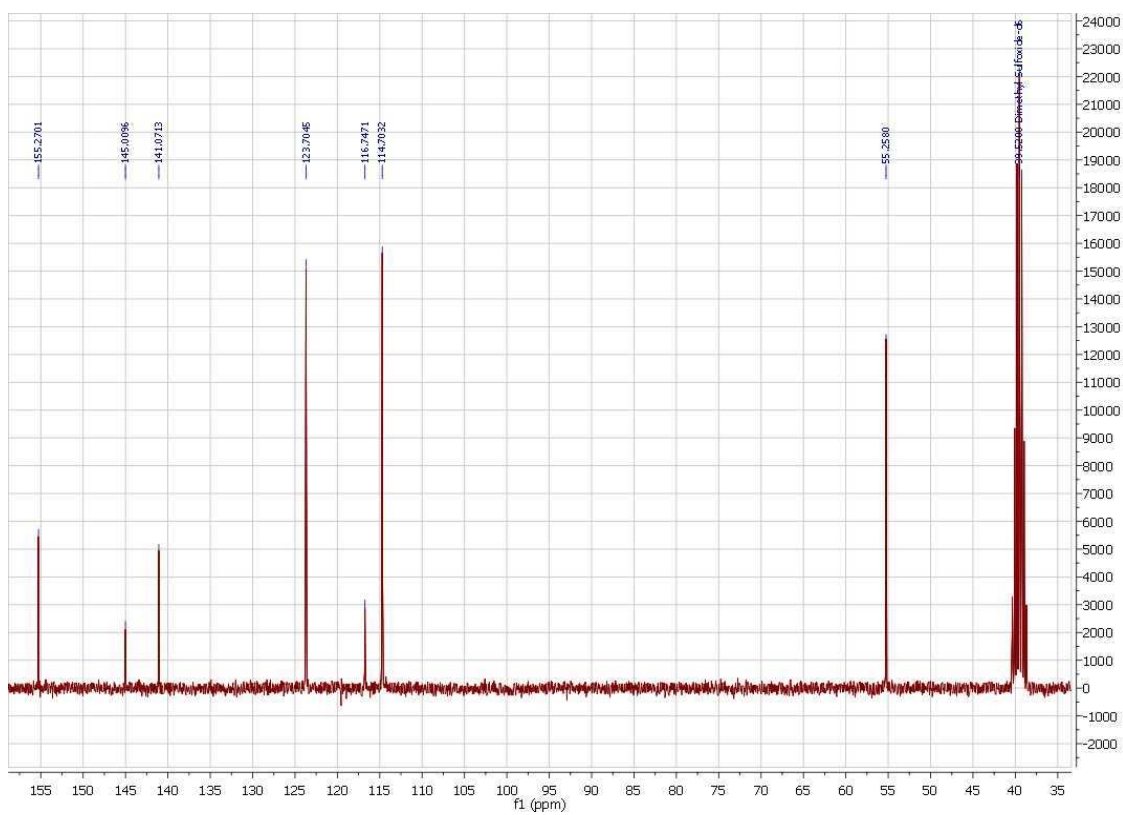
2,5-Dibromothiophene (100 μ L, 0.89 mmol), 4,4'-dimethoxydiphenylamine (449 mg, 1.96 mmol), Na-*t*BuO (1.68 g, 17.44 mmol), Pd(dba)₂ (25.5 mg, 5 mol-%) (dba = dibenzylideneacetone), tri-*tert*-butylphosphine tetrafluoroborate (12.0 mg, 5 mol-%) and 15 mL of dry toluene were placed in a flask under N₂. Then the reaction mixture was heated to 80 °C for 24 h. After the reaction mixture had been cooled to room temperature it was filtered over neutral alumina, and the latter was washed with CH₂Cl₂. After solvent removal, the crude product was purified by column chromatography on silica gel: First using a 3:1 mixture of pentane and ethyl acetate and then pure CH₂Cl₂ as the eluent. This gave the pure product as a yellow-orange oil which solidified after prolonged standing (163 mg, 303 μ mol, 34 %).

¹H-NMR (DMSO-d₆, 300 MHz): δ (ppm) 6.98 (m, 8H), 6.87 (m, 8H), 6.27 (s, 2H), 3.71 (s, 12H). ¹³C-NMR (DMSO-d₆, 75 MHz): δ (ppm) 55.26 (C-1), 114.70 (C-4), 116.75 (C-6/7), 123.70 (C-3), 141.07 (C-5), 145.01 (C-6/7), 155.27 (C-2). EI-MS calculated (m/z) for C₃₂H₃₀N₂O₄S: 538.1926; found: 538.1917. Elemental analysis calculated (%) for C₃₂H₃₀N₂O₄S: C 71.35; H 5.61; N 5.20; found: C 71.15; H 5.55; N 5.08.

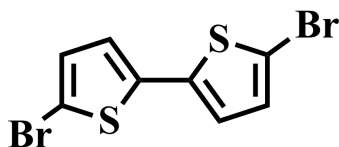
^1H -NMR of molecule **1** in DMSO- d_6 .



^{13}C -NMR of molecule **1** in DMSO- d_6 .

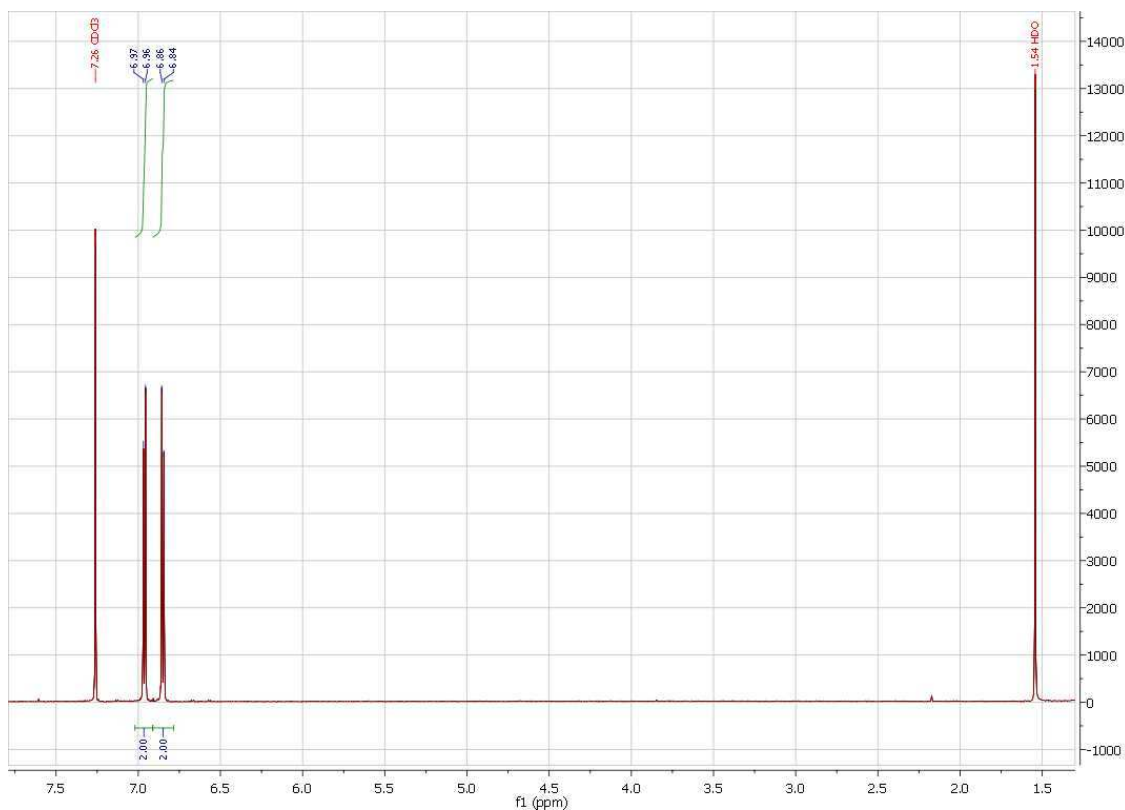


5,5'-Dibromo-2,2'-bithiophene

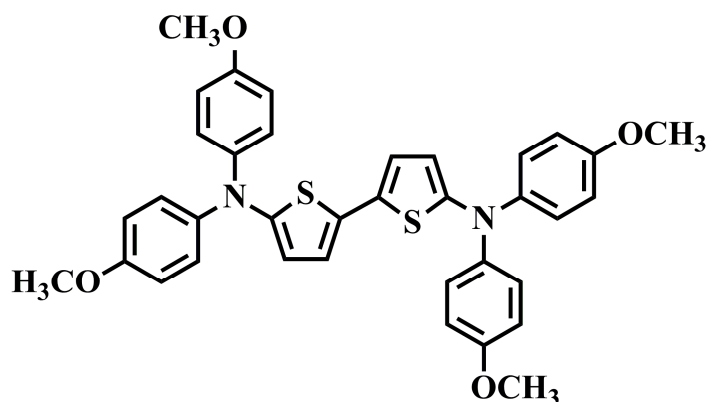


In a 3-necked flask under nitrogen 2,2'-bithiophene (200 mg, 1.2 mmol) was dissolved in dry DMF and cooled to 0° C. Then, N-bromosuccinimide (428 mg, 2.4 mmol) was added in small portions. The dark green solution was stirred over night at room temperature. Reaction was poured in 100 ml ice water and a precipitate was formed. The light beige precipitate was filtered and recrystallized from hot hexane. The product was isolated as light beige and shiny crystals in a yield of 360 mg (92%). (Synthetic protocol adapted from: Getmaneko, Y. A.; Twieg, R. T. *J. Org. Chem.* **2008**, 73, 830).

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ 6.84-6.86 (d, 2H, $J = 3.87$ Hz); δ 6.96-6.97 (d, 2H, $J = 3.85$ Hz).



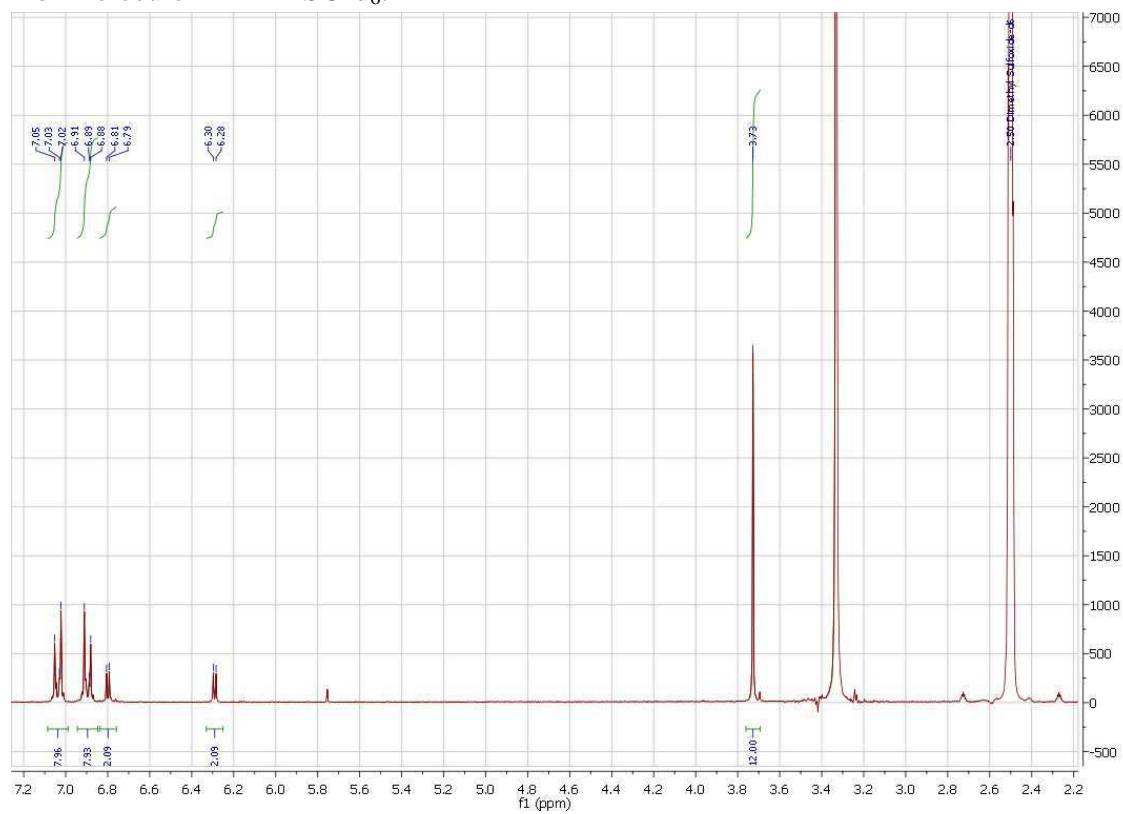
Bis[bis(4-methoxyphenyl)amino]-2,2'-bithiophene (2)



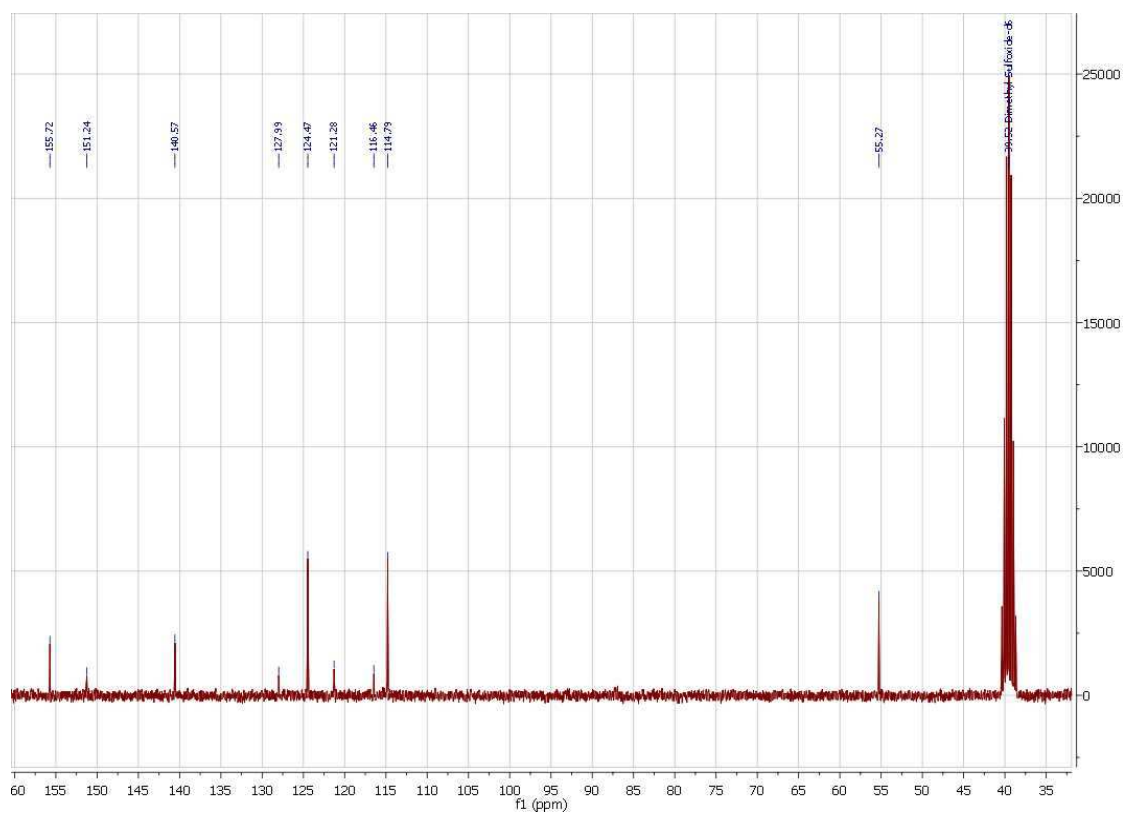
To a 2-necked flask under nitrogen Pd(dba)₂ (25 mg, 0.040 mmol) (dba = dibenzylideneacetone), 4, 4'-dimethoxydiphenylamine (400 mg, 1.75 mmol) and Na-*t*BuO (1.49 g, 15.5 mmol) in 15 ml dry toluene were added. After addition of 5,5'-dibromo-2,2'-bithiophene (256 mg, 0.79 mmol) the mixture was deoxygenated for 10 minutes and *Pt*Bu₃ (10% wt. solution in hexanes, 0.504 mmol, 1.5 mL) was added. The reaction mixture was heated to reflux for 24 hours. After the mixture had been cooled to room temperature it was passed through a pad of neutral alumina, eluting with 20% ethyl acetate in hexanes. The product was chromatographed twice [1st column: SiO₂, ethylacetate/hexane (1:9); 2nd column: SiO₂, dichloromethane/hexane (2:1)] to get the pure bright yellow compound (54.86 mg, 88 μmol, 11 %).

¹H-NMR (DMSO-d₆, 300 MHz): δ (ppm) 3.73 (s, 12H); 6.28 (s, 1H); 6.30 (s, 1H); 6.79 (s, 1H); 6.81 (s, 1H); 6.88-6.91 (m, 8H); 7.02-7.05 (m, 8H). ¹³C-NMR (DMSO-d₆, 75 MHz): δ (ppm) 55.27; 114.79; 116.46; 121.28; 124.47; 127.99; 140.57, 151.24; 155.72. EI-MS calculated (m/z) for C₃₆H₃₂N₂O₄S₂: 620.1803; found: 620.1797. Elemental analysis calculated (%) for C₃₆H₃₂N₂O₄S₂ · 1 H₂O: C 67.74; H 5.37; N 4.39; found: C 67.89; H 5.28; N 4.17.

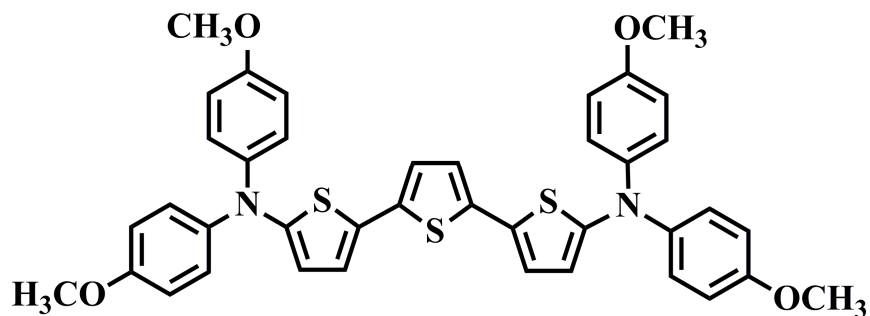
^1H -NMR of molecule **2** in DMSO-d_6 .



^{13}C -NMR of molecule **2** in DMSO-d_6 .



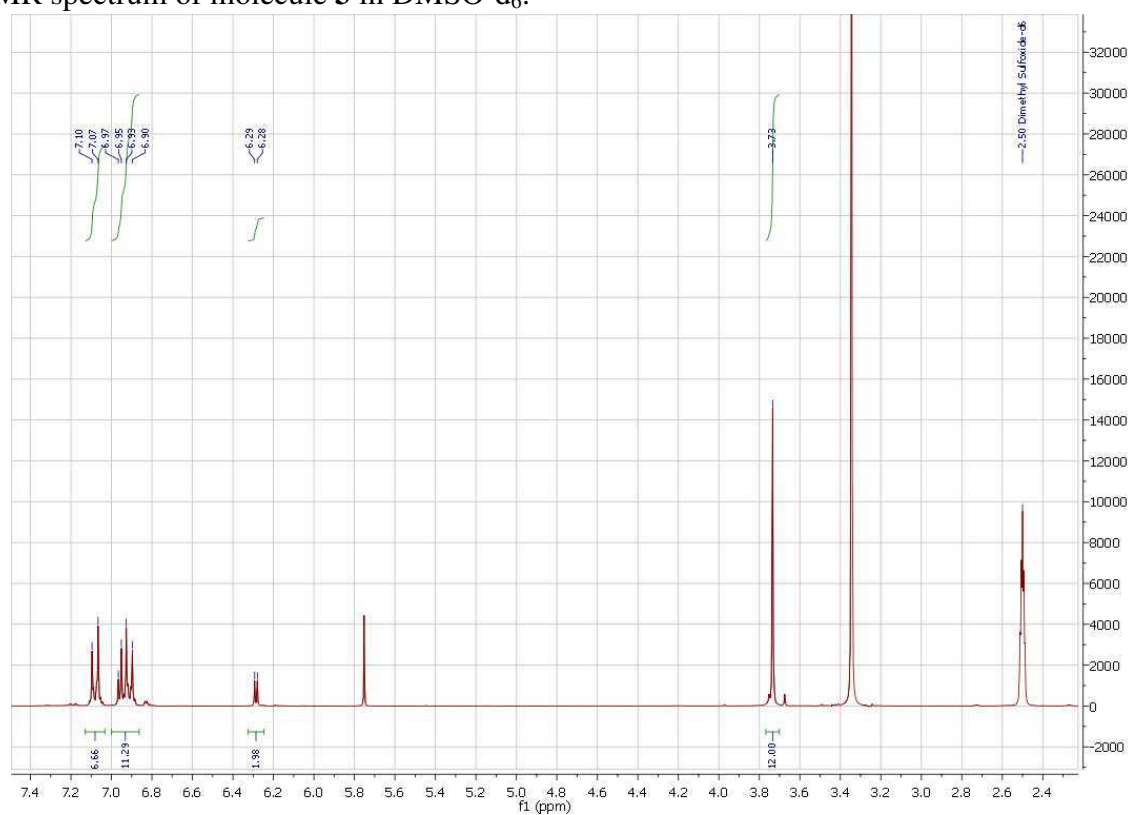
Bis[bis(4-methoxyphenyl)amino]-2,2':5',2''-terthiophene (3)



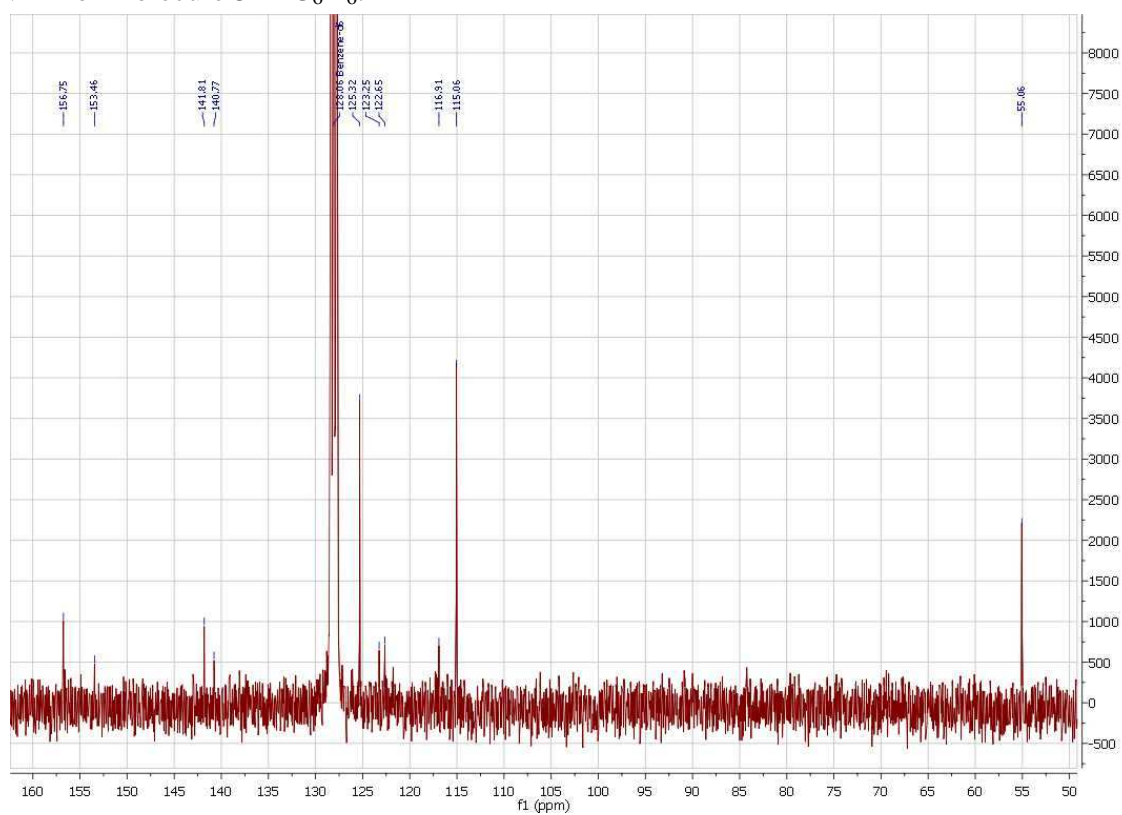
To a 2-necked flask under nitrogen $\text{Pd}(\text{dba})_2$ (0.025 g, 0.040 mmol), 4, 4'-dimethoxydiphenylamine (0.40 g, 1.75 mmol) and $\text{Na-}t\text{BuO}$ (1.49 g, 15.5 mmol) in 15 ml dry toluene were added. After addition of commercial 5,5''-dibromo-2,2':5',2''-terthiophene (321 mg, 0.79 mmol) the mixture was degassed for 10 minutes and PrBu_3 (10% wt. solution in hexanes, 0.504 mmol, 1.5 mL) was added. The reaction mixture was heated to reflux for 24 hours. After the mixture had been cooled to room temperature it was passed through a pad of neutral alumina, eluting with 20% ethyl acetate in hexanes. The product was chromatographed twice [1st column: SiO_2 , ethylacetate/hexane (1:9); 2nd column: SiO_2 , dichloromethane/hexane (2:1)] to get the pure orange compound (211 mg, 300 μmol , 38 %).

$^1\text{H-NMR}$ (DMSO-d_6 , 300 MHz): δ (ppm) 3.72 (s, 12H); 6.27-6.28 (d, 2H, 3.54 Hz); 6.88-6.95 (m, 12 H); 7.05-7.08 (m, 8H). $^{13}\text{C-NMR}$ (Benzene- d_6 , 75 MHz): δ (ppm) 55.06; 115.06; 116.91; 122.65; 123.25; 125.32; 140.77; 141.81; 153.46; 156.75. EI-MS calculated (m/z) for $\text{C}_{40}\text{H}_{34}\text{N}_2\text{O}_4\text{S}_3$: 702.1681; found: 702.1699. Elemental analysis calculated (%) for $\text{C}_{40}\text{H}_{34}\text{N}_2\text{O}_4\text{S}_3$: C 68.35; H 4.88; N 3.99; found: C 68.33; H 5.10; N 3.89.

^1H -NMR spectrum of molecule **3** in DMSO-d_6 .



^{13}C -NMR of molecule **3** in C_6D_6 .



Additional optical absorption spectra

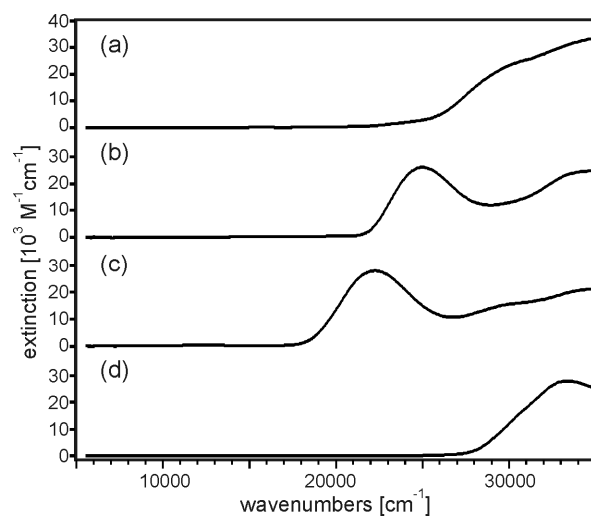


Figure S1. Optical absorption spectra (with molar extinction coefficients) of the four compounds from Scheme 1 in acetonitrile solution: (a) compound **1**; (b) compound **2**; (c) compound **3**; (d) compound **4**.

Numerical fit of cyclic voltammetry data of compound 3

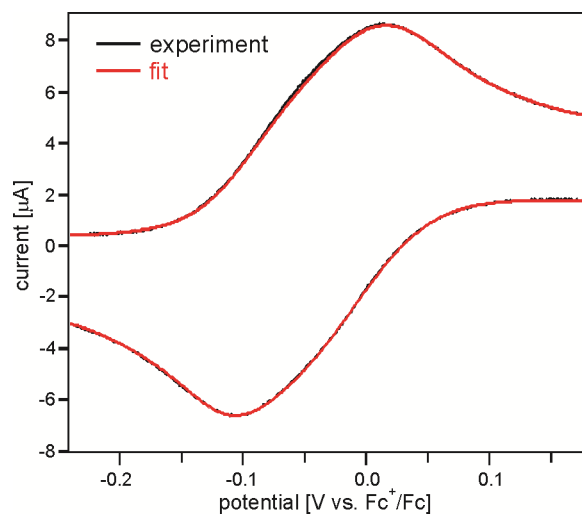


Figure S2. Extract from the cyclic voltammogram from Figure 1c (compound **3**) and numerical fit used to extract the potential splitting of 70 mV between the two triarylamine-based oxidations in this compound (fourth column of Table 1).