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SUPPORTING INFORMATION

Tunable spectroscopic and electrochemical properties of conjugated *push-push*, *push-pull* and *pull-pull* thiopheno azomethines

*Stéphane Dufresne, Marie Bourgeaux, and W. G. Skene**

Département de Chimie, Pavillon JA Bombardier, Université de Montréal, CP 6128, succ. Centre-ville, Montréal, Québec, CANADA, H3C 3J7,

w.skene@umontreal.ca

Experimental Section

Materials and general experimental. All reagents were commercially available from Aldrich and were used as received unless otherwise stated. Anhydrous and deareated solvents were obtained via a Glass Contour solvent purification system. Isopropanol was dried over activated molecular sieves and stored under nitrogen. ^{1}H-NMR spectra were recorded on a Bruker 400 spectrometer with the appropriate deuterated solvents.

Spectroscopic Measurements

Absorption measurements were done on a Cary-500 spectrometer and fluorescence studies were carried out on an Edinburgh Instruments FLS-920 fluorimeter after deareating the samples thoroughly with nitrogen for 20 minutes. Fluorescence quantum yields were measured at 10^{-5} M by exciting the corresponding compounds at 303 nm in anhydrous spectroscopic grade acetonitrile and compared to bithiophene ($\phi_{303\,nm}$ = 0.013)[1] excited at the same wavelength. The actinometer absorbencies, and those of the compounds, were matched at the excitation wavelength to within 5%. The phosphorescence measurements were done on a Cary Eclipse in a 1:4 methanol/ethanol glass matrix at 77 K, exciting at the compound's absorption maximum. The triplet-triplet absorption spectra were measured in anhydrous acetonitrile using a Luzchem mini-LFP system excited at 266 nm from the forth harmonic of a Continuum YAG:Nd Sure-lite laser. The triplet quantum yields were measured by optically matching samples within 5 % at 266 nm with benzophenone, whose triplet growth was monitored at 525 nm (Φ_T = 1) and was used the actinometer reference.[2] Phosphorescence quantum yields were

determined by comparing optically matched samples relative to fluorenone ($\Phi_{phosphorescence}$ = 0.06 in ethanol) at 77 K.[3]

Electrochemical Measurements

Cyclic voltammetric measurements were performed on a Bio Analytical Systems EC Epsilon potentiostat with a scan rate varying from 100 to 1000 mV/s. Measurements for determining the HOMO energy levels form the oxidation potential were done using a scan rate of 100 mV/s. The compounds of study were dissolved in anhydrous and deareated dichloromethane at 10^{-5} M with 0.1 M NBu_4PF_6. A glassy carbon electrode and a platinum electrode were employed as working and auxiliary electrodes, respectively. A saturated Ag/AgCl electrode was used as the reference electrode. Ferrocene was added to the samples after the measurements and was used as an internal reference.

Synthetic Details

2,5-Diamino-thiophene-3,4-dicarboxylic acid diethyl ester (1). The optimized procedure is based on similar reports.[4] Sulfur (4.53 g, 0.14 mol) and triethylamine (7.09 mL, 0.05 mol) were stirred in DMF (15 mL) in a 250 mL three necked flask whereupon the solution turned red in color within 30 min of stirring at room temperature. Ethylcyanoacetate (20.4 mL, 0.19 mol) diluted in DMF (5 mL) was subsequently added drop-wise over 30 minutes resulting in the deepening of the color. The opaque solution was allowed to stir under ambient condition for three days after which the solvent was

removed under vacuum leaving a brown solid. The solid was loaded onto a silica column and eluted with a hexanes gradient up to 35 % ethylacetate. The procedure was repeated a second time to obtain the title compound (2.15 g, 9 %) as gold flaky crystals. M.p.: 155-156°C. ^{1}H-NMR (acetone-d_6): δ = 6.15 (s, 4H), 4.17 (q, 4H, J = 7.1 Hz), 1.25 (t, 6H, J = 7.0 Hz). ^{13}C-NMR (DMSO-d_6): δ = 165.6, 148.9, 104.5, 60.4, 14.8. EI-MS: m/z 258.1 ([M]+, 80 %), 212 ([M-C_2H_5O]+, 100%), Anal. calc. for $C_{10}H_{14}N_2O_4S$ (258.30): C 46.50, H 5.46, N 10.85, O 24.74, S 12.41, found: C 45.89, H 5.10, N 10.47, S 12.01.

5-Diethylaminothiophene-2-carbaldehyde (2). In a 100 mL round flask was added 5-bromothiophene-2-carboxaldehyde (1.37 mL, 11.5 mmol) in distilled water (15 mL). Diethylamine (12 mL, 11.5 mmol) was added slowly and then, the mixture was refluxed for 6 days. The resulting oil was extracted with ethyl acetate and was then purified by chromatography with hexanes/ethylacetate (90 %/ 10% v/v) up to hexanes/ethylacetate (70 % / 30% v/v) to afford the product as a brownish oil (1.13 g, 54 %). ^{1}H-NMR (acetone-d_6): δ = 9.46 (s, 1H), 7.56 (d, 1H, J = 4.4 Hz), 6.07 (d, 1H, J = 4.4 Hz), 3.49 (q, 4H, J = 7.1 Hz), 1.23 (t, 6H, J = 7.1 Hz). ^{13}C-NMR (acetone-d_6): δ = 179.2, 166.0, 140.8, 125.9, 102.8, 47.6, 11.8. HRMS(+) calculated for $[C_9H_{13}NOS+H]^+$: 184.07906, found: 184.07913.

2-Amino-thiophene-3-carbonitrile (3). To a solution of 1,4-dihydroxy-dithiol (12.12 g, 78 mmol) and malenonitrile (10.52 g, 156 mmol) in DMF (55 mL) at 0°C was slowly added 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (12 mL, 94 mmol). The solution was stirred for 8 hours at 60 °C. The reaction mixture was then hydrolysed with 0.4 M acetic

acid (120 mL), extracted with ether, and dried over $MgSO_4$. The solvent was removed and the crude product was purified by recrystallization in ethylacetate / dichloromethane (70 % / 30 % v/v) to give a light yellow solid (11.2 g, 57 %). M.p.: 97-99 °C. ^{1}H-NMR ($CDCl_3$): δ = 6.73 (d, 1H, J = 5.8 Hz), 6.35 (d, 1H, J = 5.8 Hz). ^{13}C-NMR ($CDCl_3$): δ = 163.3, 125.6, 115.3, 110.3, 88.4. HRMS(+) calculated for $[C_5H_5N_2S+H]^+$: 125.01679, found: 125.0172.

5-Methyl-thiophene-2-carbaldehyde (4). Phosphorous chloride (2 mL, 20 mmol) was added in anhydrous DMF (10 mL) at 0°C. After 20 minutes, 2-methyl-thiophene (0.5 mL, 5 mmol) was slowly added to the solution. The flask was carefully heated at 50 °C for 3 hours and the mixture was poured with stirring into a beaker containing crushed-ice (10 g). The aqueous layer was extracted with ethylacetate (7 times), while the organic layers were combined, then dried over anhydrous magnesium sulphate, and finally concentrated. The crude mixture was purified by chromatography (SiO_2) eluted with hexanes/ethylacetate (50 % / 50 % v/v). The product was isolated as a yellow oil (160 mg, 25 %). ^{1}H-NMR ($CDCl_3$): δ = 9.85 (s, 1H), 7.78 (d, 1H, J = 3.7 Hz), 7.03 (d, 1H, J = 3.7 Hz), 2.58 (s, 3H). ^{13}C-NMR ($CDCl_3$): = 184.0, 152.4, 143.8, 139.2, 128.9, 16.6. HRMS(+) calculated for $[C_6H_6S+H]$+: 127.02121, found: 127.02137.

2-Amino-5-[(thiophen-2-ylmethylene)-amino]-thiophene-3,4-dicarboxylic acid diethyl ester (5). In a 50 mL round bottom flask was added **1** (50 mg, 0.19 mmol) in absolute ethanol (20 mL) to which was added 2-thiophene carboxaldehyde (24 mg, 0.21 mmol) and a catalytic amount of trifluoroacetic acid (TFA). The mixture was refluxed

for 20 hours under normal atmosphere. Complete removal of the solvent led to an orange solid which was purified by flash chromatography (SiO_2) and eluted with hexanes/ethylacetate (80 % / 20 %). The product was isolated as an orange solid (81 %). M.p.: 114-116 °C. ^{1}H-NMR (acetone-d_6): δ = 8.24 (s, 1H), 7.63 (d, 1H, J = 5.0Hz), 7.52 (dd, 1H, J = 3.7 Hz and J = 0.7 Hz), 7.48 (s, 2H), 7.14 (dd, 1H, J = 5.0 Hz and 3.7 Hz), 4.32 (q, 2H, J = 7.2 Hz), 4.19 (q, 2H, J = 7.1 Hz), 1.37 (t, 3H, J = 7.1 Hz), 1.26 (t, 3H, J = 7.1 Hz). ^{13}C-NMR (acetone-d_6): δ = 165.0, 164.3, 161.1, 161.0, 146.1, 143.2, 132.8, 132.1, 130.5, 128.4, 101.8, 61.0, 60.0, 14.3, 14.1. HRMS(+) calculated for $[C_{15}H_{16}O_4N_2S_2+H]^+$: 353.06242, found: 353.06251.

2-Amino-5-[(5-nitro-thiophen-2-ylmethylene)-amino]-thiophene-3,4-dicarboxylic acid diethyl ester (6). In a 50 mL round bottom flask, **1** (30 mg, 0.12 mmol) was dissolved in isopropanol (20 mL). To this, was added with vigorous stirring, 5-nitro-2-thiophene carboxaldehyde (91 mg, 0.58 mmol) and catalytic TFA followed by refluxing for 30 minutes. The title compound was isolated as a dark black-purple powder (87 %) by flash chromatography (SiO_2) eluted with hexanes/ethylacetate (90 % / 10 % v/v) up to hexanes/ethylacetate (50% / 50 % v/v). M.p.: 194-196 °C. ^{1}H-NMR (acetone-d_6): δ = 8.21 (s, 1H), 8.00 (d, 1H, J = 4.4 Hz), 7.74 (s, 2H), 7.50 (d, 1H, J = 4.4 Hz), 4.37 (q, 2H, J = 7.1 Hz), 4.22 (q, 2H, J = 7.1 Hz), 1.40 (t, 3H, J = 7.1 Hz), 1.27 (t, 3H, J= 7.1 Hz). ^{13}C-NMR (acetone-d_6): δ = 164.6, 164.1, 162.8, 162.7, 152.7, 149.7, 143.7, 134.3, 131.4, 130.1, 129.7, 61.4, 60.3, 14.3, 14.0. HRMS(+) calculated for $[C_{15}H_{16}O_6N_3S_2+H]^+$: 398.04750, found: 398.04794.

2-Amino-5-[(5-diethylamino-thiophen-2-ylmethylene)-amino]-thiophene-3,4-dicarboxylic acid diethyl ester (7). In a 50 mL round bottom flask was added **1** (67 mg, 0.26 mmol) dissolved in 20 mL of anhydrous toluene to which was subsequently added 1,4-diazabicyclo[2.2.2]octane (DABCO) (32 mg, 0.29 mmol), $TiCl_4$ 1.0 M solution in toluene (286 μL, 0.29 mmol) at 0 ^oC and then **2** (52 mg, 0.29 mmol) was added. The mixture was then refluxed for two hours after which the solvent was removed. Purification by flash chromatography (SiO_2) with hexanes/ethylacetate (90 % / 10 % v/v) and increased up to hexanes/ethylacetate (50 % / 50 % v/v) yielded the title product as a yellow-orange solid (67 %). M. decomp.: 95 °C. ^{1}H-NMR (acetone-d_6): δ = 7.96 (s, 1H), 7.23 (s, 2H), 7.21 (d, 1H, J = 4.4 Hz), 5.93 (d, 1H, J = 4.2 Hz), 4.27 (q, 2H, J = 7.2 Hz), 4.17 (q, 2H, J = 7.1 Hz), 3.43 (q, 4H, J = 7.1 Hz), 1.35 (t, 3H, J = 7.1 Hz), 1.24 (t, 3H, J = 7.1 Hz), 1.21 (t, 6H, J = 7.1 Hz). ^{13}C-NMR (acetone-d_6): δ = 164.5, 162.3, 159.3, 159.3, 146.9, 135.7, 135.5, 125.5, 124.5, 102.2, 101.7, 60.7, 59.7, 47.3, 14.2, 14.1, 12.0. HRMS(+) calculated for $[C_{19}H_{25}O_4N_3S_2+H]^+$: 424.13592, found: 424.13520.

Diethyl-2-((5-methylthiophen-2-yl)methyleneamino)-5-aminothiophene-3,4-dicarboxylate (8). **1** (30 mg, 0.12 mmol) and **4** (16 mg, 0.13 mmol) were mixed in anhydrous isopropanol with a catalytic amount of TFA and refluxed for 20 hours. The reaction was then purified by flash chromatography eluted with hexanes/ethylacetate (90 % / 10 % v/v) up to hexanes/ethylacetate (60 % / 40 % v/v) to afford the product as an orange viscous oil (30 mg, 70 %). ^{1}H-NMR (acetone-d_6): δ = 8.15 (s, 1H), 7.45 (s, 2H), 7.33 (d, 1H, ^3J = 3.6 Hz), 6.84 (dd, 1H, J = 3.7 Hz and 1.0 Hz), 4.33 (q, 2H, J = 7.2 Hz), 4.21 (q, 2H, J = 7.2 Hz), 2.51 (s, 3H), 1.39 (t, 3H, J = 7.2 Hz), 1.28 (t, 3H, J = 7.1 Hz).

^{13}C-NMR (acetone-d_6): δ = 165.0, 164.4, 160.8, 146.3, 145.7, 141.1, 139.7, 136.7, 132.6, 129.8, 127.0, 60.9, 59.9, 15.3, 14.3, 14.1. HRMS(+) calculated for $[C_{16}H_{18}N_2O_4S_2+H]^+$: 367.07807, found: 367.07862.

2-[(Thiophen-2-ylmethylene)-amino]-thiophene-3-carbonitrile (9). **3** (50 mg, 0.40 mmol) and thiophene-2-carboxaldehyde (54 mg, 0.48 mmol) were mixed in anhydrous isopropanol with a catalytic amount of TFA and then refluxed for 20 hours. The reaction was then purified by flash chromatography eluted with hexanes/ethylacetate (90 % / 10 % v/v) up to hexanes/ethylacetate (60 % / 40 % v/v) to afford the product as an orange solid (61 mg, 70 %). M.p.: 58-60 °C. ^{1}H-NMR (acetone-d_6): δ = 8.49 (s, 1H), 7.90 (d, 1H, J = 5.0 Hz), 7.82 (dd, 1H, ^3J = 3.7 Hz and 1.0 Hz), 7.42 (d, 1H, J = 5.7 Hz), 7.26 (d, 1H, J = 5.6 Hz), 7.26 (dd, 1H, J = 4.8 Hz and J = 3.5 Hz). ^{13}C-NMR (acetone-d_6): δ = 163.4, 155.4, 141.8, 136.2, 133.9, 129.0, 128.1, 122.5, 114.6, 105.8. HRMS(+) calculated for $[C_{10}H_6N_2S_2+H]^+$: 219.00452, found: 219.00514.

2-[(5-Nitro-thiophen-2-ylmethylene)-amino]-thiophene-3-carbonitrile (10). **3** (30 mg, 0.24 mmol) and 5-nitro-thiophene-2-carboxaldehyde (41 mg, 0.26 mmol) were mixed in anhydrous isopropanol with catalytic TFA and refluxed for 28 hours. The reaction was then purified by flash chromatography eluted with hexanes/ethylacetate (90 % / 10 %) up to hexanes/ethylacetate (70 % / 30 %) to afford the compound as an orange powder (45 mg, 71 %). M.p.: 192°-194°C. ^{1}H-NMR (acetone-d_6): δ = 8.98 (s, 1H), 8.12 (d, 1H, J = 4.3 Hz), 7.85 (d, 1H, J = 4.3 Hz), 7.61 (d, 1H, J = 5.7 Hz), 7.38 (d, 1H, J = 5.7 Hz). ^{13}C-NMR (acetone-d_6): δ = 161.2, 154.3, 147.3, 133.7, 130.0, 128.6, 125.9, 125.1,

109.5, 108.5. HRMS(+) calculated for $[C_{10}H_5O_2N_3S_2+H]^+$: 263.98959, found: 263.99006.

2-[(5-Diethylamino-thiophen-2-ylmethylene)-amino]-thiophene-3-carbonitrile (11). In a 50 mL round bottom flask was added **3** (30 mg, 0.24 mmol) in 20 mL anhydrous isopropanol to which was added **2** (48 mg, 0.26 mmol) and a catalytic amount of TFA. The mixture was refluxed for 3 hours. Complete removal of the solvent afforded an orange oil which was purified by flash chromatography (SiO_2) eluted with hexanes/ethylacetate (90 % / 10 % v/v) up to hexanes/ethylacetate (65 % / 35 % v/v). The product was isolated as an orange viscous oil (44 mg, 63 %). ^{1}H-NMR (acetone-d_6): δ = 8.44 (s, 1H), 7.54 (d, 1H, J = 4.5 Hz), 7.09 (s, 2H), 6.13 (d, 1H, J = 4.5 Hz), 3.54 (q, 4H, J = 7.1 Hz), 1.27 (t, 6H, J = 7.1 Hz). ^{13}C-NMR (acetone-d_6): δ = 166.1, 153.2, 141.2, 131.9, 127.9, 123.3, 118.8, 116.0, 104.5, 101.5, 48.2, 12.4. HRMS(+) calculated for $[C_{14}H_{15}N_3S_2+H]^+$: 290.07802, found: 290.07887.

2-((5-Methylthiophen-2-yl)methyleneamino)thiophene-3-carbonitrile (12). In anhydrous isopropanol was added **3** (30 mg, 0.24 mmol) and **4** (30 mg, 0.24 mmol) with a catalytic amount of TFA and then refluxed for 20 hours. The reaction was purified by flash chromatography eluted with hexanes/ethylacetate (90 % / 10 % v/v) up to hexanes/ethylacetate (60 % / 40 % v/v) to afford an orange oil (47 mg, 85%). ^{1}H-NMR (acetone-d_6): δ = 8.79 (s, 1H), 7.65 (d, 1H, J = 3.7 Hz), 7.39 (d, 1H, ^3J = 5.7 Hz), 7.27 (d, 1H, J = 5.7 Hz), 6.99 (dd, 1H, J = 3.7 Hz), 2.60 (s, 3H). ^{13}C-NMR (acetone-d_6):

δ =163.7, 155.1, 149.7, 139.8, 136.9, 128.0, 127.8, 122.0, 114.6, 105.3, 15.5. HRMS(+) calculated for $[C_{11}H_8N_2S_2+H]^+$: 233.02017, found: 233.02054.

2-((5-formylthiophen-2-yl)methyleneamino)thiophene-3-carbonitrile (13). 2,5-thiophene dicarboxaldehyde (60 mg, 0.42 mmol) and **3** (26 mg, 0.21 mmol) were dissolved in anhydrous isopropanol with a catalytic amount of TFA and then refluxed for 15 hours. The reaction was precipitated twice from ethylacetate/hexanes to give a light orange solid (20 mg, 39 %). M.p.: 214-217 °C. ^{1}H-NMR (acetone-d_6): δ = 10.07 (s, 1H), 9.00 (s, 1H), 8.07 (d, 1H, *J* = 3.9 Hz), 7.95 (d, 1H, *J* = 3.9 Hz), 7.56 (d, 1H, *J* = 5.7 Hz), 7.35 (d, 1H, *J* = 5.6 Hz). ^{13}C-NMR (acetone-d_6): δ = 184.4, 161.9, 154.8, 148.6, 147.8, 137.3, 135.5, 128.5, 124.3, 114.2, 107.7. HRMS(+) calculated for $[C_{11}H_6N_2OS_2+H]^+$: 246.99943, found: 246.99979.

2,5-Bis-[(thiophen-2-ylmethylene)-amino]-thiophene-3,4-dicarboxylic acid diethyl ester (14). **1** (100 mg, 0.4 mmol) and 2-thiophene carboxaldehyde (198.8 mg, 1.6 mmol) were refluxed in anhydrous isopropanol (10 ml), which turned from orange then red in color within 125 hours under nitrogen. The solution was then concentrated under vacuum to near dryness. The crude product was loaded onto a silica column and eluted with hexanes/ethylacetate (85 % / 15 % v/v) up to hexanes/ethylacetate (75 % / 25 %) to give a red solid (65 mg, 36 %). M.p.: 125-126 °C. ^{1}H-NMR (acetone-d_6): δ = 8.75 (s, 2H), 7.85 (d, 2H, *J* = 5.0 Hz), 7.76 (d, 2H, *J* = 3.7 Hz), 7.26 (dd, 2H, *J* = 5.2 and 3.7 Hz), 4.32 (q, 4H, *J* = 7.2 Hz), 1.37 (t, 6H, *J* = 7.2 Hz). ^{13}C-NMR (acetone-d_6): δ = 163.0,

153.6, 149.2, 142.4, 135.1, 133.2, 128.9, 127.5, 61.2, 14.2. HRMS(+) calculated for $[C_{20}H_{18}O_4N_2S_3+H]^+$: 447.05015, found: 447.04921.

Diethyl-2,5-bis((5-nitrothiophen-2-yl)methyleneamino)thiophene-3,4-dicarboxylate (15). 5-Nitrothiophene-2-carbaldehyde (40 mg, 0.25 mmol) was dissolved in anhydrous toluene at 0 °C with DABCO (29 mg, 0.25 mmol) and the slow addition of $TiCl_4$ 1.0 M solution in toluene (255 µL, 0.25 mmol). **1** (33 mg, 0.13 mmol) was added and the mixture was then refluxed for 4 hours. The title compound was isolated as a purple-grey solid after flash chromatography with hexanes/ethylacetate (90 % / 10 % v/v) up to hexanes/ethylacetate (60 % / 40 % v/v) (26 mg, 38 %). M.p.: 255-257 °C. ^{1}H-NMR (acetone-d_6): δ = 8.84 (s, 2H), 8.10 (d, 2H, *J* = 4.5 Hz), 7.80 (d, 2H, *J* = 4.4 Hz), 4.37 (q, 4H, *J* = 7.1 Hz), 1.39 (t, 6H, *J* = 7.1 Hz). ^{13}C-NMR (acetone-d_6): δ = 164.8, 163.3, 156.2, 147.0, 137.5, 131.3, 130.0, 127.8, 60.6, 14.4. HRMS(+) calculated for $[C_{20}H_{16}O_8N_4S_3+H]^+$: 563.10872, found: 537.01931.

Diethyl-2,5-bis((5-(diethylamino)thiophen-2-yl)methyleneamino) thiophene-3,4-dicarboxylate (16). **2** (50 mg, 0.27 mmol) was dissolved with DABCO (31 mg, 0.27 mmol) in anhydrous toluene (25 mL) at 0 °C and the slow addition of $TiCl_4$ 1.0 M solution in toluene (273 µL, 0.27 mmol). **1** (32 mg, 0.12 mmol) was added and then refluxed for 3 hours. The solvent was removed and the product isolated as a purple-grey solid after purification by flash chromatography with hexanes/ethylacetate (90 % / 10 % v/v) up to hexanes/ethylacetate (50 % / 50 % v/v) (64 mg, 88 %). M. decomp.: 86 °C. ^{1}H-NMR (acetone-d_6): δ = 8.26 (s, 2H), 7.39 (d, 2H, *J* = 4.4 Hz), 6.05 (d, 2H, *J* = 4.4

Hz), 4.24 (q, 4H, *J* =7.1 Hz), 3.49 (q, 8H, *J* =7.1 Hz), 1.34 (t, 6H, *J* = 7.1Hz), 1.25 (t, 12H, *J* = 7.1Hz). ^{13}C-NMR (acetone-d_6): δ = 164.2, 163.8, 150.6, 149.1, 138.4, 124.3, 124.2, 103.3, 60.5, 47.6, 14.2, 12.0. HRMS(+) calculated for $[C_{28}H_{36}O_4N_4S_3+H]^+$: 589.19714, found: 589.19778.

2-[(5-Nitro-thiophen-2-ylmethylene)-amino]-5-[(thiophen-2-ylmethylene)-amino]-thiophene-3,4-dicarboxylic acid diethyl ester (17). 5-Nitrothiophene-2-carbaldehyde (9 mg, 0.06 mmol) was dissolved in anhydrous toluene under nitrogen at 0 °C with DABCO (7 mg, 0.06 mmol), $TiCl_4$ 1.0 M solution in toluene (59 μL, 0.06 mmol) was slowly added follow by **14** (12 mg, 0.03 mmol). The mixture was refluxed for 6 hours, after which the solution was evaporated and the product was isolated as a red powder (7 mg, 48 %) after purification by flash chromatography eluted with hexanes/ethylacetate (90 % / 10 % v/v) up to hexanes/ethylacetate (60 % / 40 % v/v). M.p.: 220-222 °C. ^{1}H-NMR (acetone-d_6): δ = 8.81 (s, 1H), 8.79 (s, 1H), 8.10 (d, 1H, *J* = 3.2 Hz), 7.91 (d, 1H, *J* = 4.1 Hz), 7.81 (d, 1H, *J* = 2.9 Hz), 7.78 (d, 1H, *J* = 4.6 Hz), 7.29 (dd, 1H, *J* = 2.7 Hz and 3.8 Hz), 4.38 (q, 2H, *J* = 5.3 Hz), 4.32 (q, 2H, *J* = 5.3 Hz), 1.41 (t, 3H, *J* = 5.3 Hz), 1.36 (t, 3H, *J* = 5.3 Hz). ^{13}C-NMR (acetone-d_6): δ = 176.9, 174.2, 169.1, 166.5, 155.1, 151.7, 146.6, 142.2, 140.9, 136.1, 135.9, 134.0, 132.7, 130.0, 129.0, 127.5, 61.5, 61.3, 14.2, 14.0. HRMS(+) calculated for $[C_{20}H_{17}O_6N_3S_3+H]^+$: 492.03522, found: 492.03561.

2-[(5-Diethylamino-thiophen-2-ylmethylene)-amino]-5-[(5-nitro-thiophen-2-ylmethylene)-amino]-thiophene-3,4-dicarboxylic acid diethyl ester (18). 5-Nitrothiophene-2-carbaldehyde (23 mg, 0.15 mmol) was dissolved in anhydrous toluene

under nitrogen at 0 °C with DABCO (16 mg, 0.15 mmol), $TiCl_4$ 1.0 M solution in toluene (146 μL, 0.15 mmol) followed by **7** (56 mg, 0.13 mmol). The solution was then refluxed for 7 hours. The product was obtained as a purple-grey powder (53 mg, 72 %) after purification by flash chromatography eluted with hexanes/ethylacetate (90 % / 10 % v/v) up to hexanes/ethylacetate (50 % / 50 % v/v). M. decomp.: 170 °C. ^{1}H-NMR (acetone-d_6): δ = 8.55 (s, 1H), 8.36 (s, 1H), 8.06 (d, 1H, *J* = 4.3 Hz), 7.66 (d, 1H, *J* = 4.4 Hz), 7.55 (d, 1H, *J* = 4.6 Hz), 6.19 (d, 1H, *J* = 4.6 Hz), 4.36 (q, 2H, *J* = 7.3 Hz), 4.25 (q, 2H, *J* = 7.1 Hz), 3.55 (q, 4H, *J* = 7.5 Hz), 1.39 (t, 3H, *J* = 7.1 Hz), 1.34 (t, 3H, *J* = 7.2 Hz), 1.28 (t, 6H, *J* = 7.1 Hz). ^{13}C-NMR (acetone-d_6): δ = 173.0, 167.5, 164.1, 162.9, 149.7, 143.7, 132.9, 131.6, 131.3, 130.2, 130.1, 129.7, 129.1, 127.6, 114.0, 104.9, 61.4, 60.2, 39.2, 14.2, 13.8, 10.8. HRMS(+) calculated for $[C_{24}H_{26}O_6N_4S_3+H]^+$: 563.10872, found: 563.10838.

Diethyl-2,5-bis((5-methylthiophen-2-yl)methyleneamino)thiophene-3,4-dicarboxylate (19). **4** (52 mg, 0.41 mmol) was dissolved in anhydrous toluene under nitrogen at 0 °C with DABCO (260 mg, 2.32 mmol), $TiCl_4$ 1.0 M solution in toluene (580 μL, 0.58 mmol) and **1** (30 mg, 0.12 mmol). The solution was then refluxed for 2 hours. The product was obtained as a red viscous oil (15 mg, 26%) after filtration and washing with acetone and then with hexanes. ^{1}H-NMR (acetone-d_6): δ = 8.60 (s, 2H), 7.55 (d, 2H, *J* = 3.5 Hz), 6.95 (d, 2H, *J* = 3.6 Hz), 4.30 (q, 4H, *J* = 7.2 Hz), 2.56 (s, 6H), 1.36 (t, 6H, *J* = 7.2 Hz). ^{13}C-NMR (acetone-d_6): δ = 163.1, 153.2, 149.2, 148.8, 140.4, 135.7, 127.6, 127.1, 61.1, 15.5, 14.1. HRMS(+) calculated for $[C_{22}H_{22}N_2O_4S_3+H]^+$: 475.08145, found: 475.08065.

(13E)-N-((5-((E)-(3-Cyanothiophen-2-ylimino)methyl)thiophen-2-yl)methylene)-3-cyanothiophen-2-amine (20). 2,5-Thiophene dicarboxaldehyde (30 mg, 0.21 mmol) was dissolved along with **3** (134 mg, 1.07 mmol) in *n*-butanol in a 50 mL round bottom flask. The resulting solution was refluxed for 48 hours after which the product precipitated from solution. It was then filtered and washed with cold absolute ethanol to yield the title compound as a dark brown powder (58 mg, 77 %). M.p.: 244°-246°C. ^{1}H-NMR (acetone-d_6): δ = 8.96 (s, 2H), 7.91 (s, 2H), 7.53 (d, 2H, ^{3}J = 5.7Hz), 7.34 (d, 2H, ^{3}J = 5.6Hz). ^{13}C-NMR (acetone-d_6): δ = 154.7, 147.0, 140.8, 136.1, 128.4, 123.9, 117.3, 107.3. HRMS(+) calculated for $[C_{16}H_9N_4S_3 + H]^+$: 352.9984, found: 352.9994.

N-((Thiophen-2-yl)methylene)butan-1-amine (21). In a 50 mL round bottom flask was added 2-thiophene carboxaldehyde (100 mg, 0.89 mmol) diluted in *n*-butylamine (72 mg, 0.98 mmol). The reaction was mixed at room temperature for 4 hours after which the excess *n*-butylamine was removed under vacuum to give the pure product as a clear liquid (144 mg, 93 %). ^{1}H-NMR (acetone-d_6): δ = 8.42 (s, 1H), 7.51 (d, 1H, J = 5.0 Hz), 7.38 (d, 1H, J = 3.1 Hz), 7.11 (dd, 1H, J = 4.9 Hz and 3.2 Hz), 3.55 (t, 2H, J = 6.8 Hz), 1.64 (m(5), 2H, J = 7.0 Hz), 1.39 (m(6), 2H, J = 7.5 Hz), 0.95 (t, 3H, J = 7.4 Hz). ^{13}C-NMR (acetone-d_6): δ = 154.1, 143.7, 130.6, 129.0, 127.7, 61.0, 33.5, 20.8, 14.0. HRMS(+) calculated for $[C_9H_{13}NS+H]^+$: 168.08415, found: 168.08410.

N-((5-((Butylimino)methyl)thiophen-2-yl)methylene)butan-1-amine (22). In a 50 mL round bottom flask was added 2,5-thiophene dicarboxaldehyde (100 mg, 0.71 mmol) dissolved in *n*-butylamine (1 mL, 10.1 mmol). The reaction was stirred at room

temperature for 20 hours. The excess *n*-butylamine was removed under vacuum to give the pure product as a light yellow solid (160 mg, 90%). M.p.: 34-35 °C. ^{1}H-NMR (acetone-d_6): δ = 8.41 (s, 2H), 7.36 (s, 2H), 3.56 (t, 4H, J = 6.7 Hz), 1.62 (m(5), 4H, J = 7.7 Hz), 1.39 (m(6), 4H, J = 7.6 Hz), 0.93 (t, 6H, J = 7.4 Hz). ^{13}C-NMR (acetone-d_6): δ = 154.4, 145.5, 130.6, 60.8, 33.3, 20.6, 13.6. HRMS(+) calculated for $[C_{14}H_{22}N_2S+H]^+$: 251.15765, found: 251.15882.

Absorption and Emission Spectra

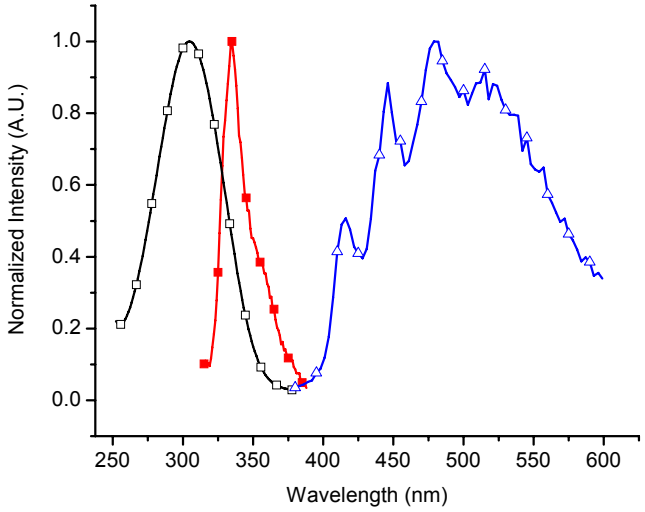

Figure 1. Normalized absorption (open squares), fluorescence (closed squares), and phosphorescence (open triangles) spectra of **1** in acetonitrile.

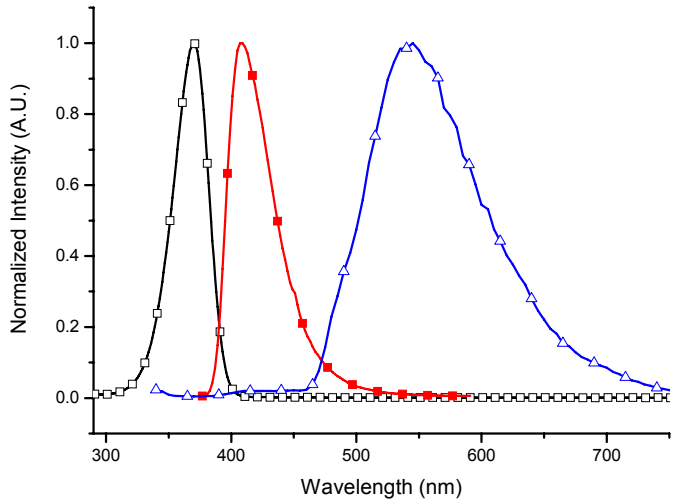

Figure 2. Normalized absorption (open squares), fluorescence (closed squares), and phosphorescence (open triangles) spectra of **2** in acetonitrile.

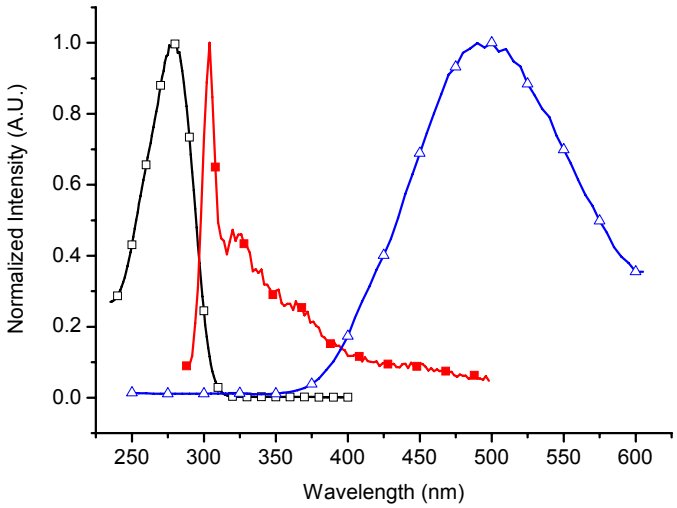

Figure 3. Normalized absorption (open squares), fluorescence (closed squares), and phosphorescence (open triangles) spectra of **3** in acetonitrile.

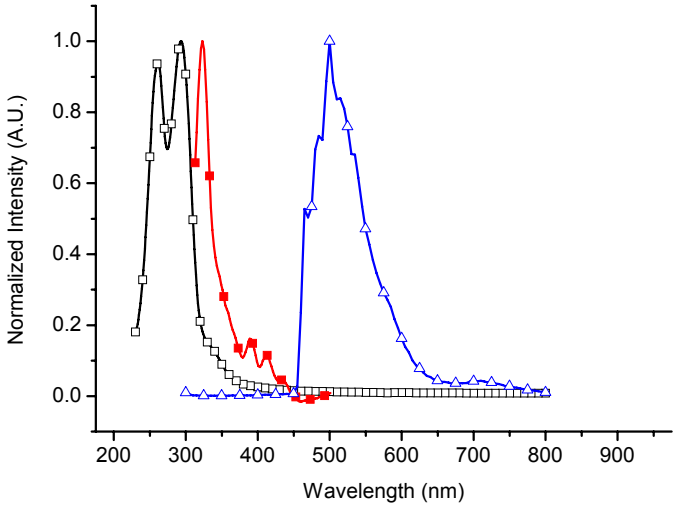

Figure 4. Normalized absorption (open squares), fluorescence (closed squares), and phosphorescence (open triangles) spectra of **4** in acetonitrile.

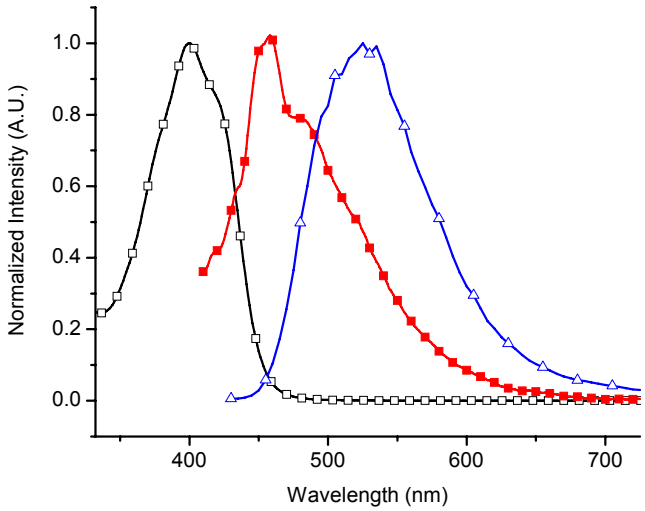

Figure 5. Normalized absorption (open squares), fluorescence (closed squares), and phosphorescence (open triangles) spectra of **5** in acetonitrile.

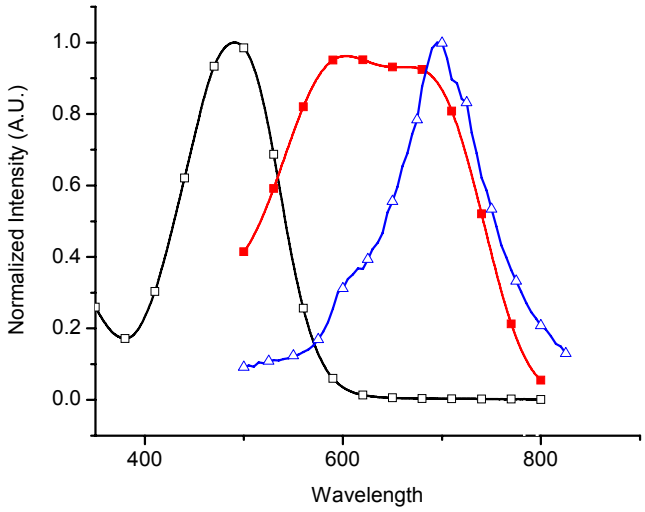

Figure 6. Normalized absorption (open squares), fluorescence (closed squares), and phosphorescence (open triangles) spectra of **6** in acetonitrile.

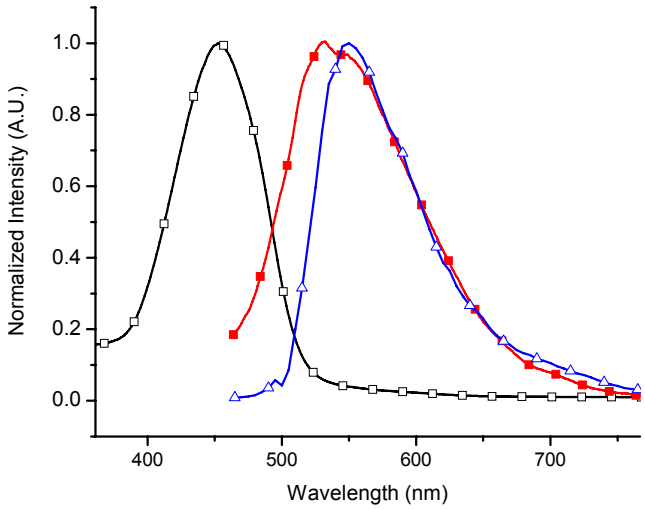

Figure 7. Normalized absorption (open squares), fluorescence (closed squares), and phosphorescence (open triangles) spectra of **7** in acetonitrile.

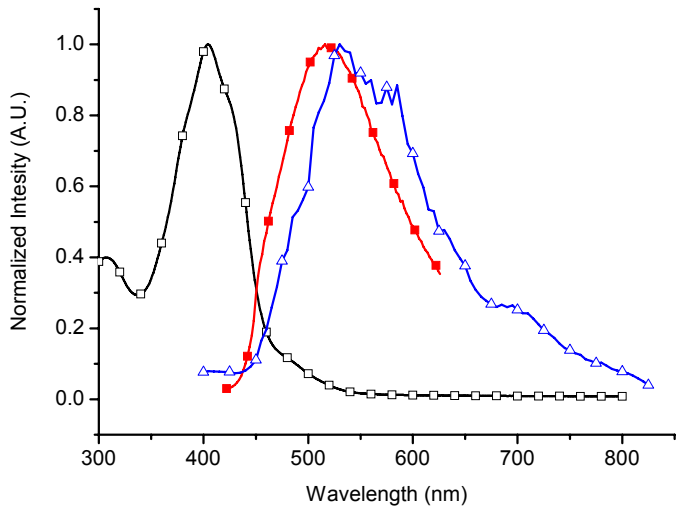

Figure 8. Normalized absorption (open squares), fluorescence (closed squares), and phosphorescence (open triangles) spectra of **8** in acetonitrile.

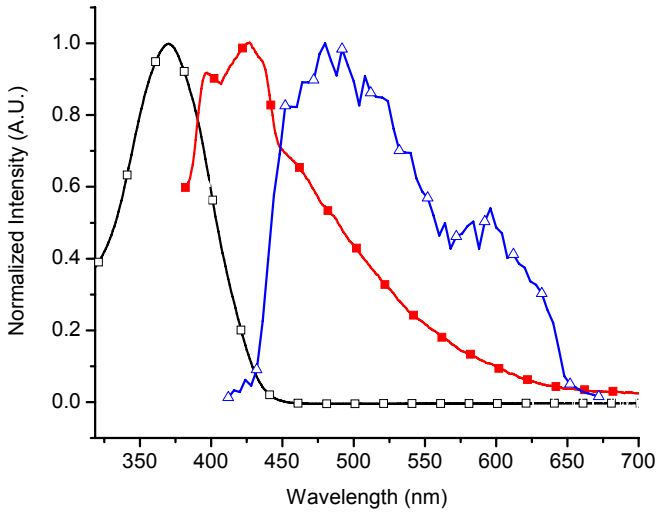

Figure 9. Normalized absorption (open squares), fluorescence (closed squares), and phosphorescence (open triangles) spectra of **9** in acetonitrile.

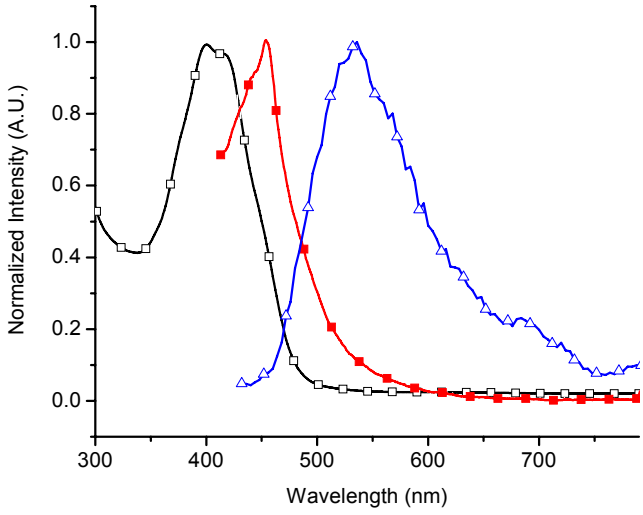

Figure 10. Normalized absorption (open squares), fluorescence (closed squares), and phosphorescence (open triangles) spectra of **10** in acetonitrile.

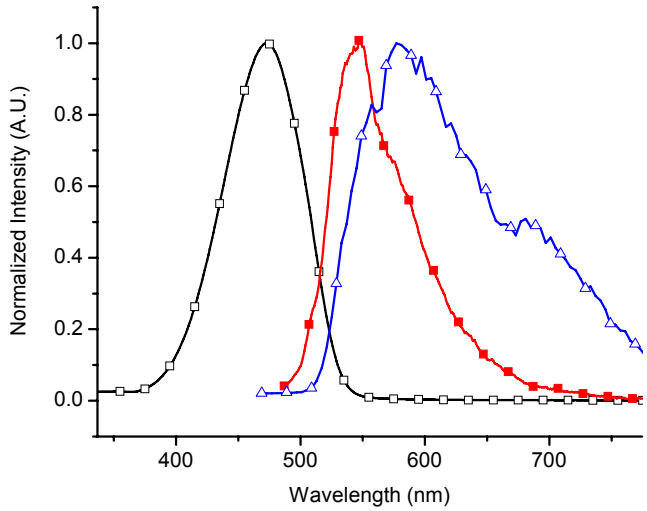

Figure 11. Normalized absorption (open squares), fluorescence (closed squares), and phosphorescence (open triangles) spectra of **11** in acetonitrile.

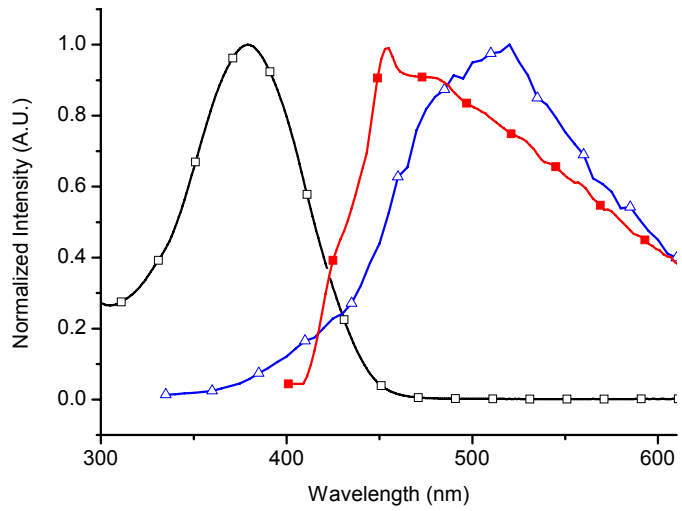

Figure 12. Normalized absorption (open squares), fluorescence (closed squares), and phosphorescence (open triangles) spectra of **12** in acetonitrile.

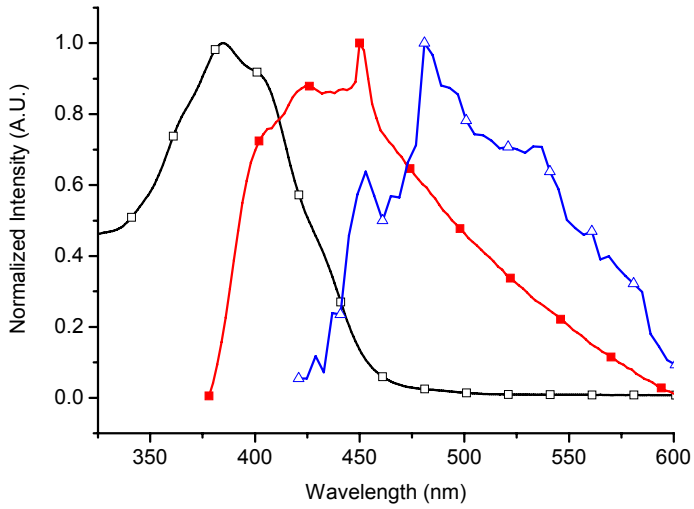

Figure 13. Normalized absorption (open squares), fluorescence (closed squares), and phosphorescence (open triangles) spectra of **13** in acetonitrile.

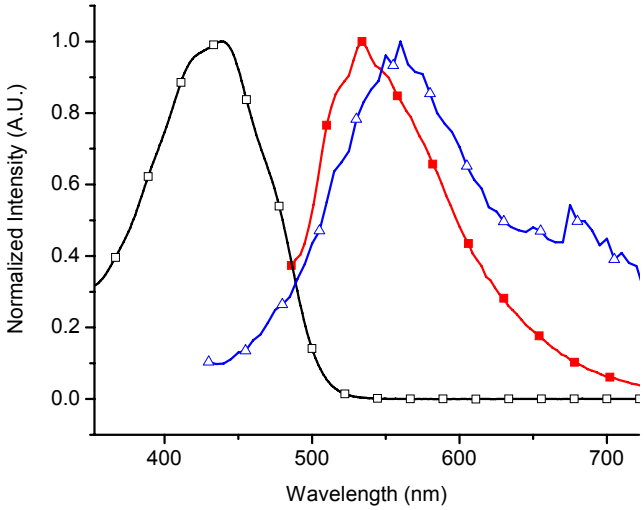

Figure 14. Normalized absorption (open squares), fluorescence (closed squares), and phosphorescence (open triangles) spectra of **14** in acetonitrile.

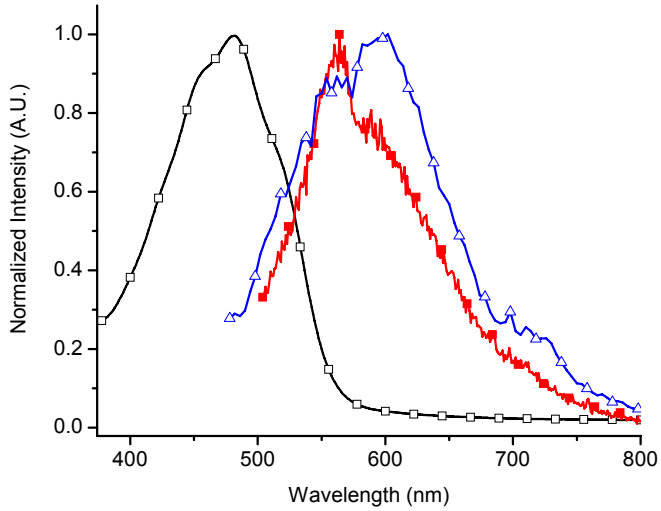

Figure 15. Normalized absorption (open squares), fluorescence (closed squares), and phosphorescence (open triangles) spectra of **15** in acetonitrile.

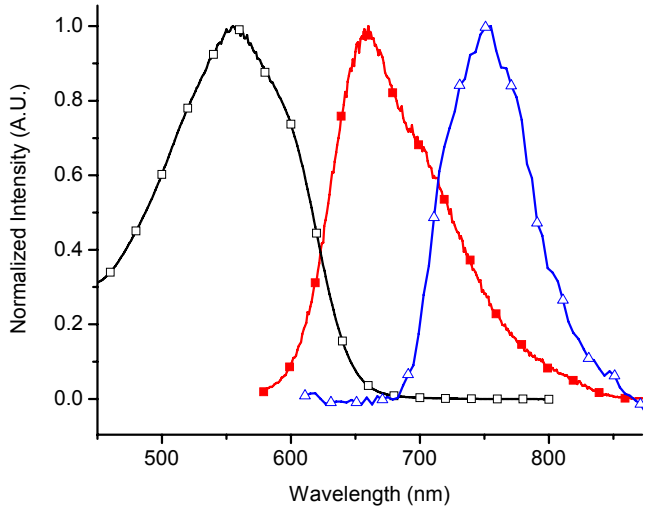

Figure 16. Normalized absorption (open squares), fluorescence (closed squares), and phosphorescence (open triangles) spectra of **16** in acetonitrile.

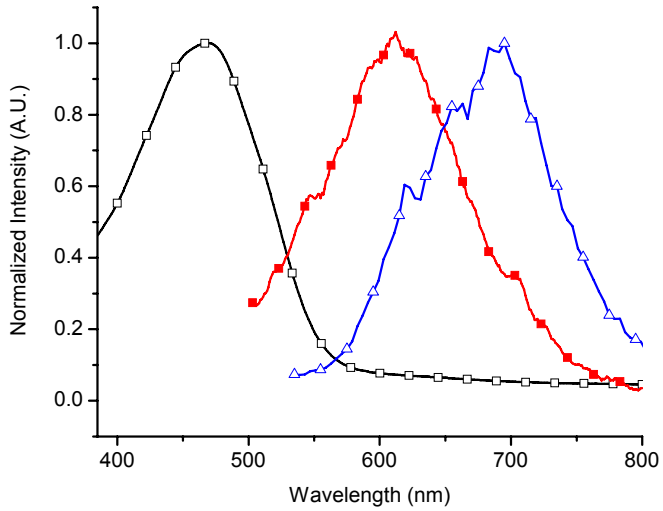

Figure 17. Normalized absorption (open squares), fluorescence (closed squares), and phosphorescence (open triangles) spectra of **17** in acetonitrile.

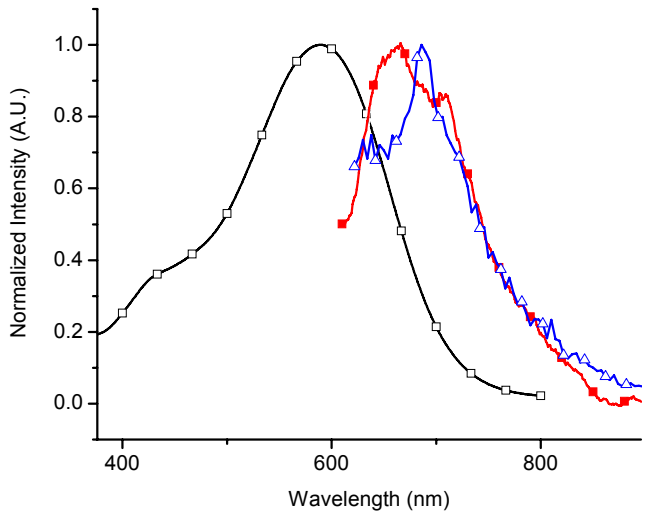

Figure 18. Normalized absorption (open squares), fluorescence (closed squares), and phosphorescence (open triangles) spectra of **18** in acetonitrile.

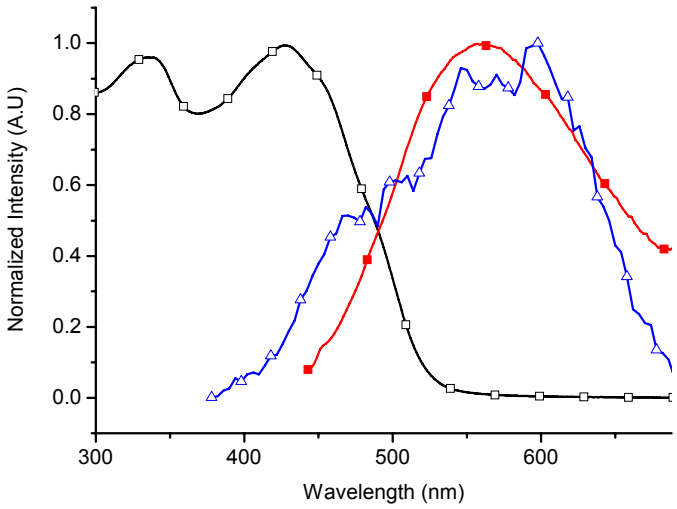

Figure 19. Normalized absorption (open squares), fluorescence (closed squares), and phosphorescence (open triangles) spectra of **19** in acetonitrile.

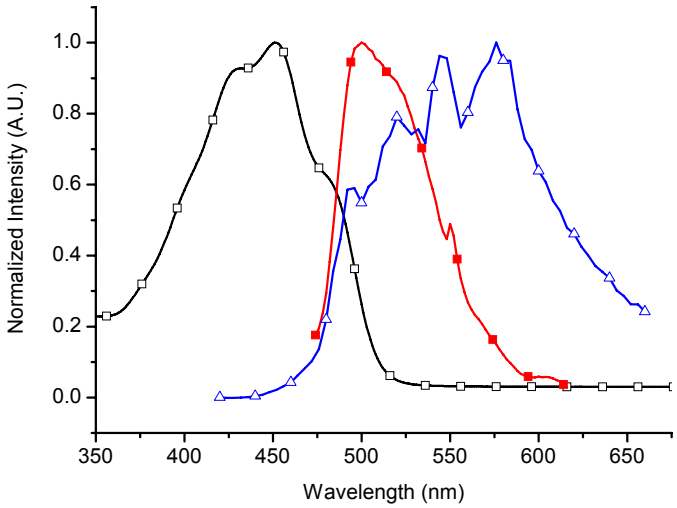

Figure 20. Normalized absorption (open squares), fluorescence (closed squares), and phosphorescence (open triangles) spectra of **20** in acetonitrile.

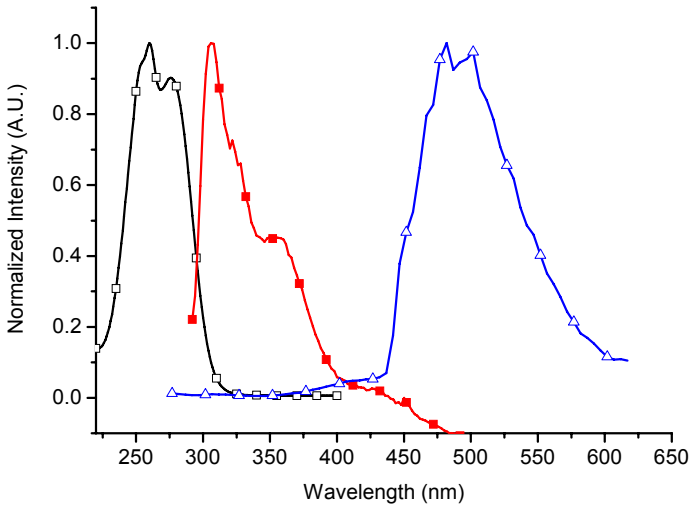

Figure 21. Normalized absorption (open squares), fluorescence (closed squares), and phosphorescence (open triangles) spectra of **21** in acetonitrile.

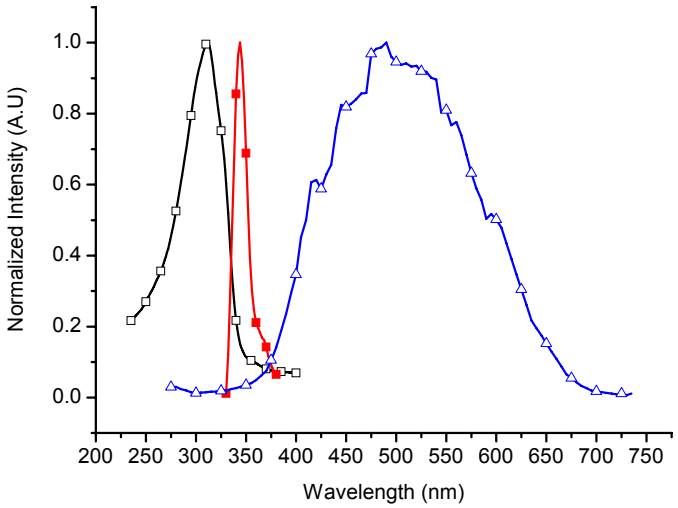

Figure 22. Normalized absorption (open squares), fluorescence (closed squares), and phosphorescence (open triangles) spectra of **22** in acetonitrile.

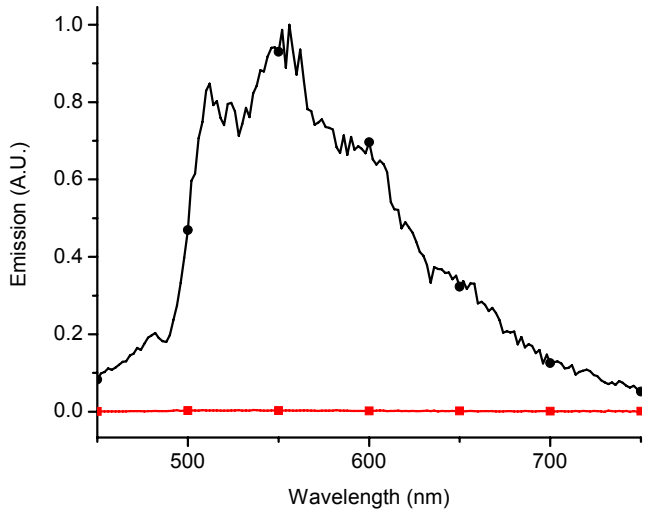

Figure 23. Emission spectra of **14** at 77 K (closed circles) relative to room temperature (closed squares).

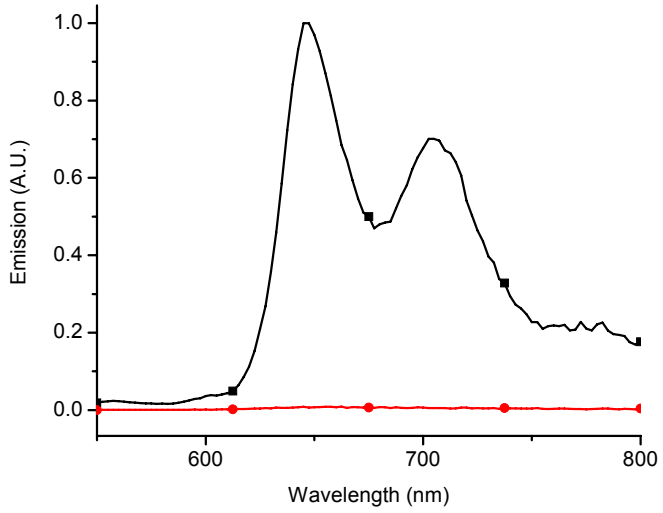

Figure 24. Emission spectra of **15** at 77 K (closed circles) relative to room temperature (closed squares).

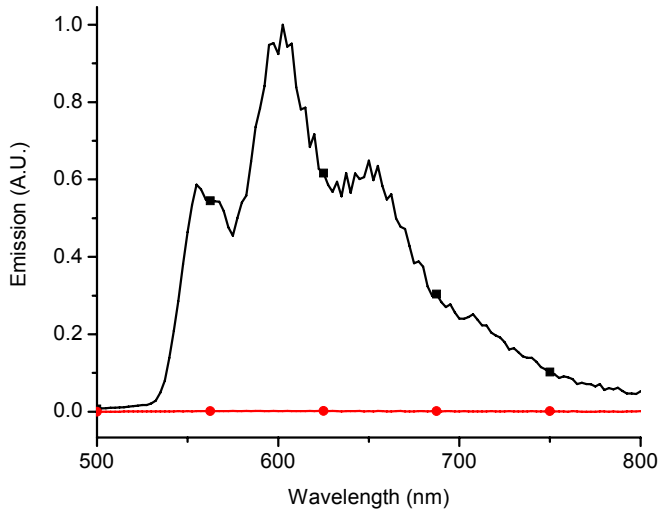

Figure 25. Emission spectra of **16** at 77 K (closed circles) relative to room temperature (closed squares).

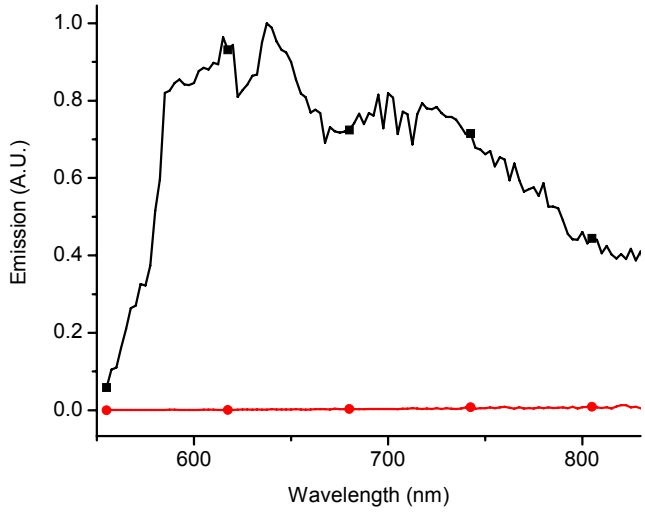

Figure 26. Emission spectra of **18** at 77 K (closed circles) relative to room temperature (closed squares).

Cyclic voltammetry

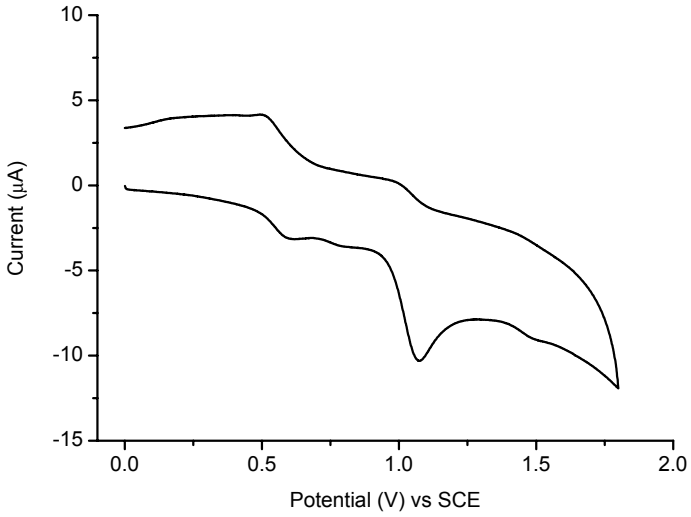

Figure 27. Cyclic voltammogram of **1** in anhydrous and deaerated dichloromethane.

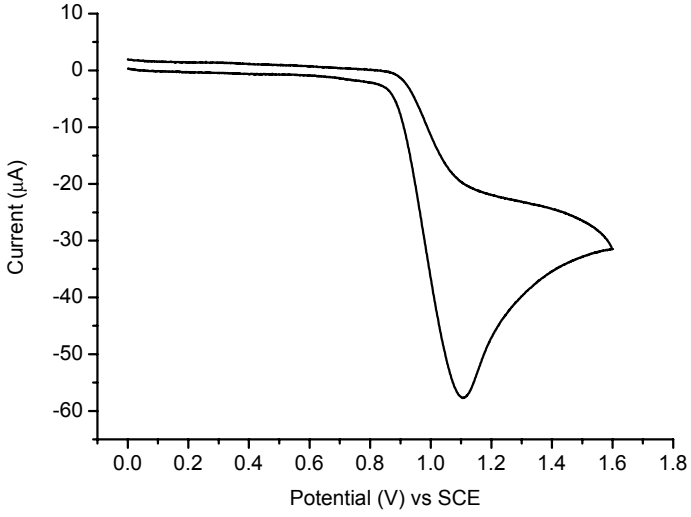

Figure 28. Cyclic voltammogram of **2** in anhydrous and deaerated dichloromethane.

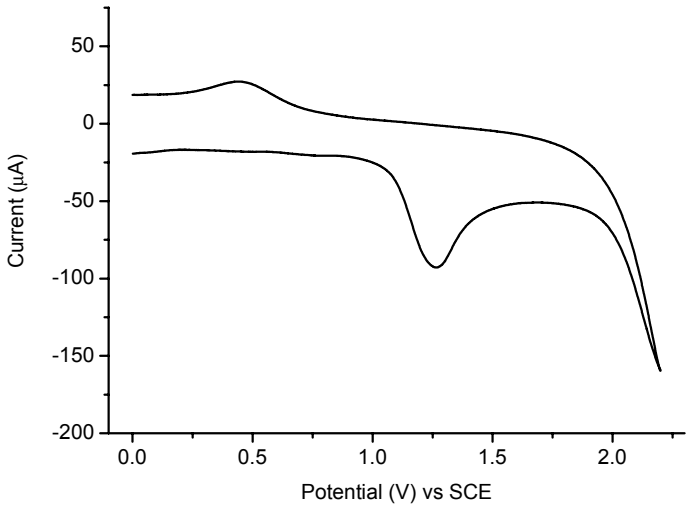

Figure 29. Cyclic voltammogram of **3** in anhydrous and deaerated dichloromethane.

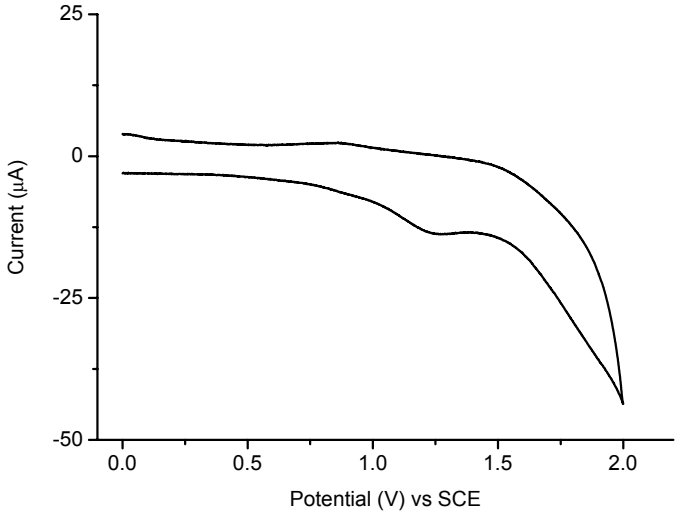

Figure 30. Cyclic voltammogram of **4** in anhydrous and deaerated dichloromethane.

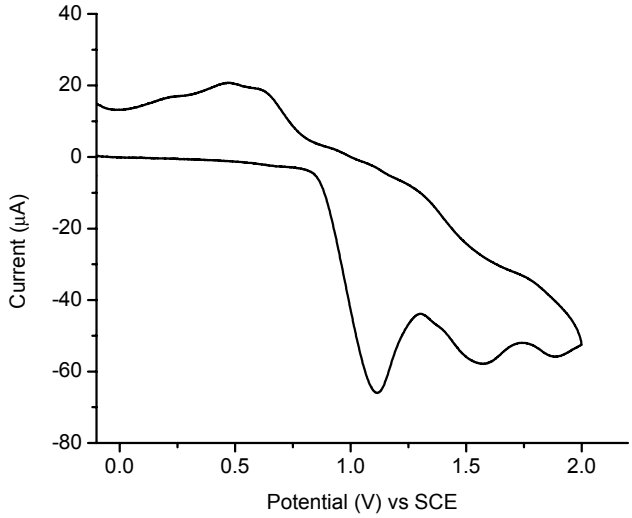

Figure 31. Cyclic voltammogram of **5** in anhydrous and deaerated dichloromethane.

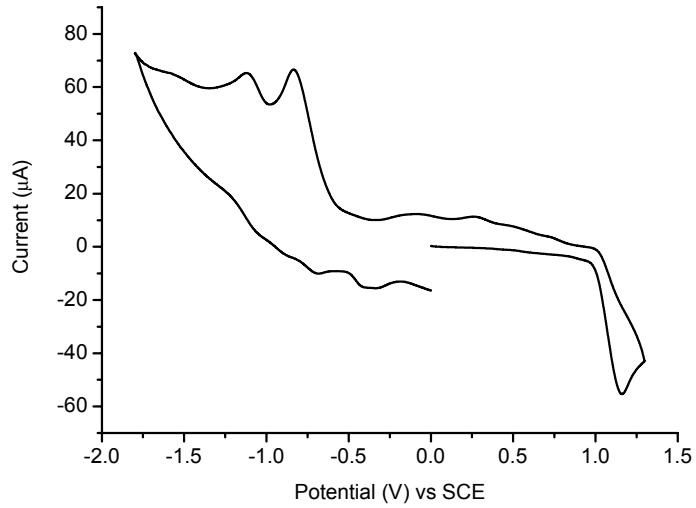

Figure 32. Cyclic voltammogram of **6** in anhydrous and deaerated dichloromethane.

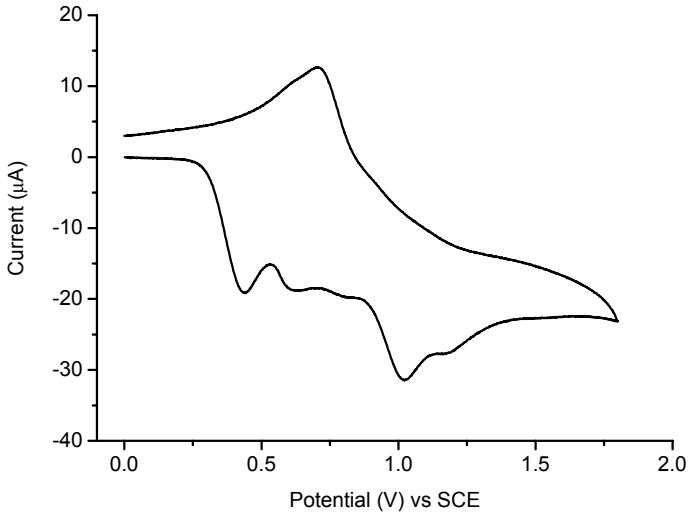

Figure 33. Cyclic voltammogram of **7** in anhydrous and deaerated dichloromethane.

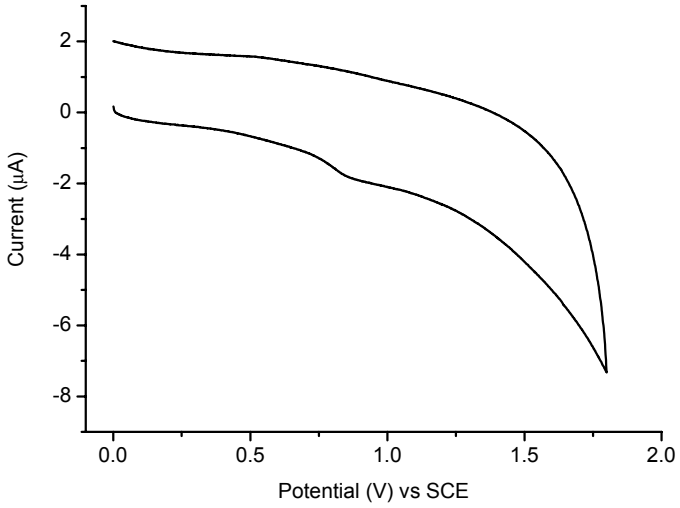

Figure 34. Cyclic voltammogram of **8** in anhydrous and deaerated dichloromethane.

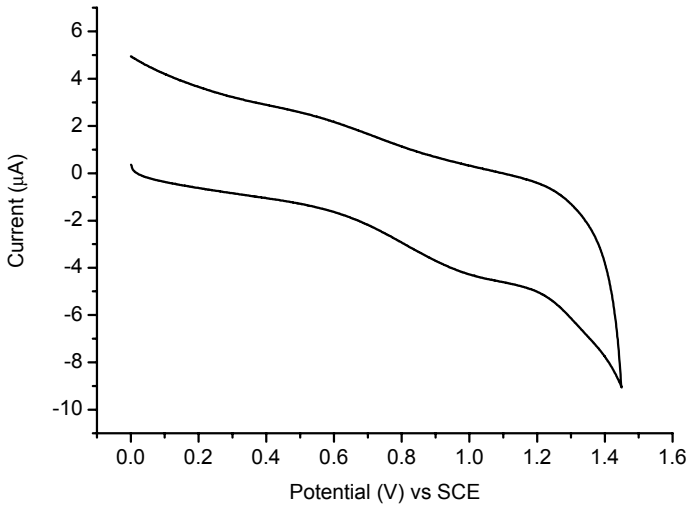

Figure 35. Cyclic voltammogram of **9** in anhydrous and deaerated dichloromethane.

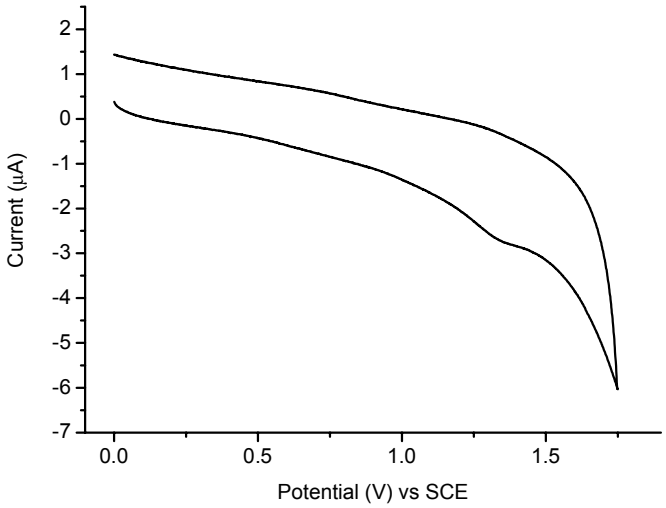

Figure 36. Cyclic voltammogram of **10** in anhydrous and deaerated dichloromethane.

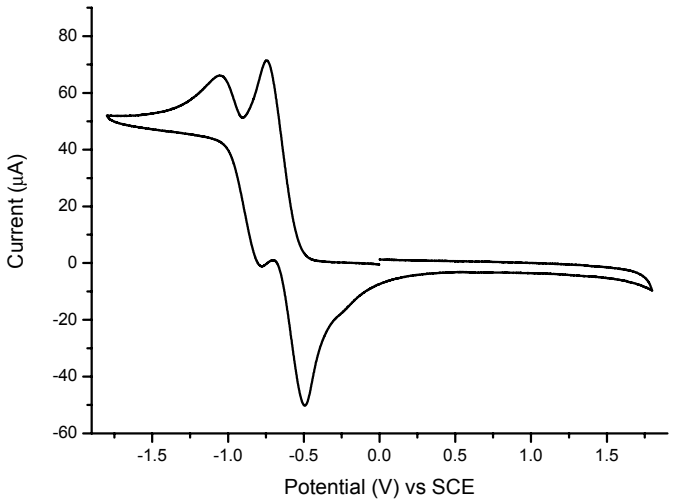

Figure 37. Cyclic voltammogram of **10** in anhydrous and deaerated dichloromethane.

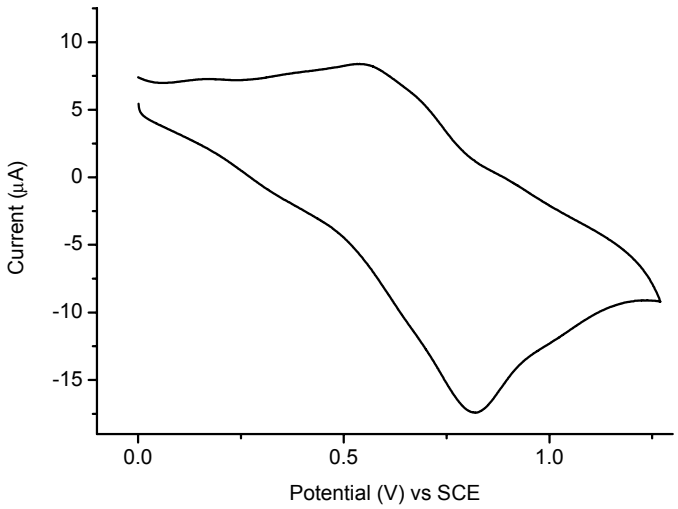

Figure 38. Cyclic voltammogram of **11** in anhydrous and deaerated dichloromethane.

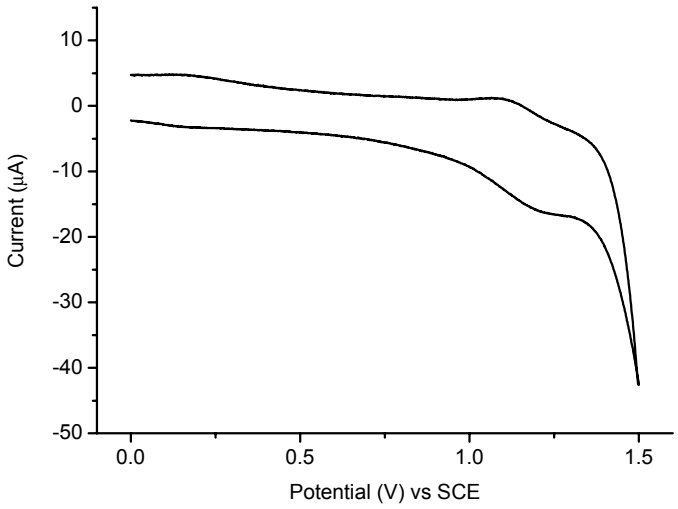

Figure 39. Cyclic voltammogram of **12** in anhydrous and deaerated dichloromethane.

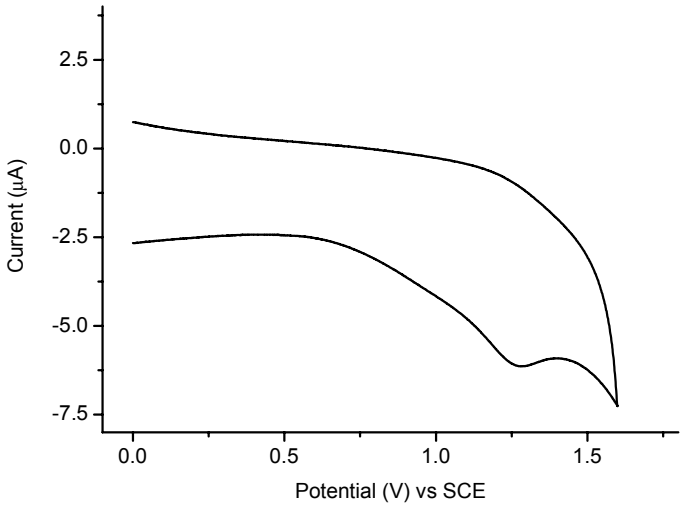

Figure 40. Cyclic voltammogram of **13** in anhydrous and deaerated dichloromethane.

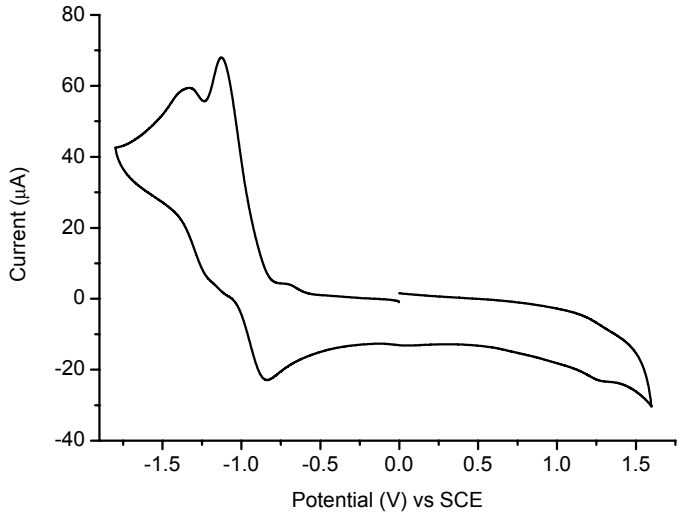

Figure 41. Cyclic voltammogram of **13** in anhydrous and deaerated dichloromethane.

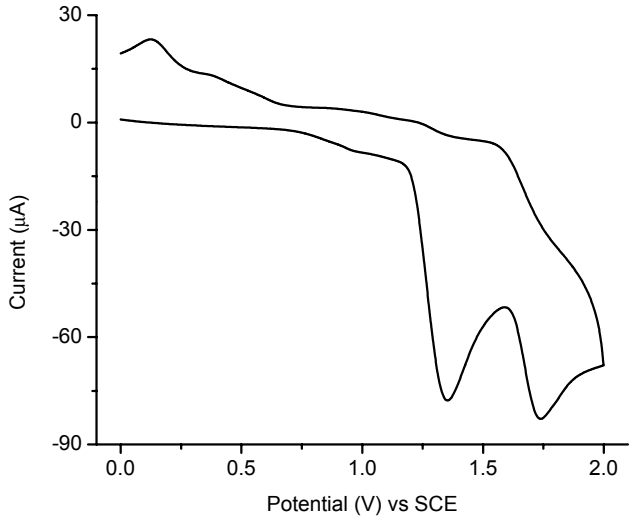

Figure 42. Cyclic voltammogram of **14** in anhydrous and deaerated dichloromethane.

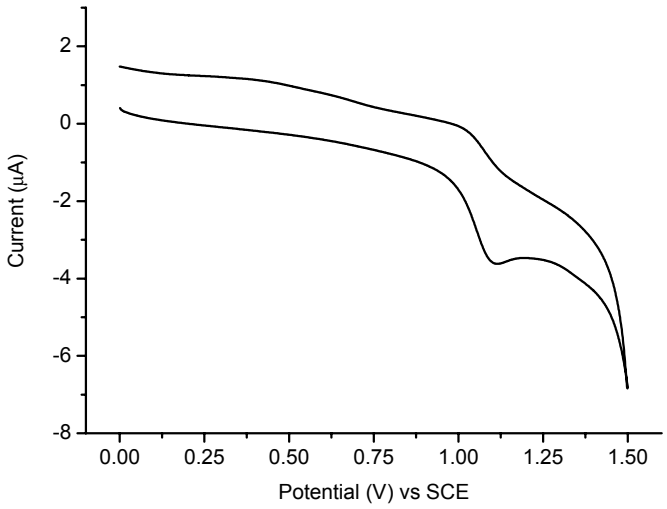

Figure 43. Cyclic voltammogram of **15** in anhydrous and deaerated dichloromethane.

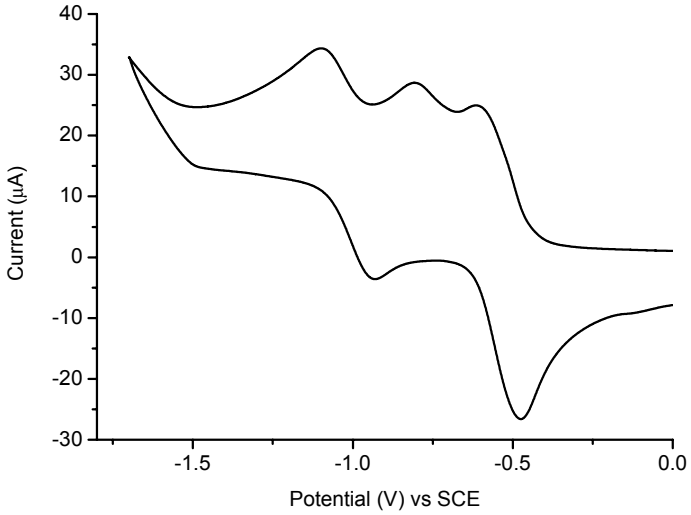

Figure 44. Cyclic voltammogram of **15** in anhydrous and deaerated dichloromethane.

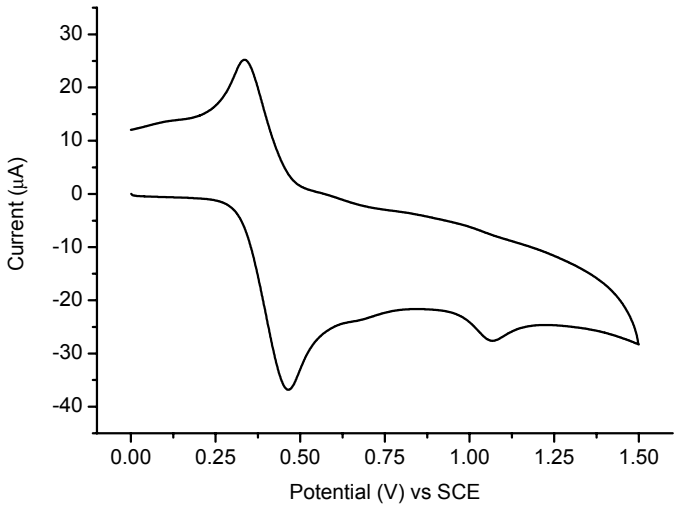

Figure 45. Cyclic voltammogram of **16** in anhydrous and deaerated dichloromethane.

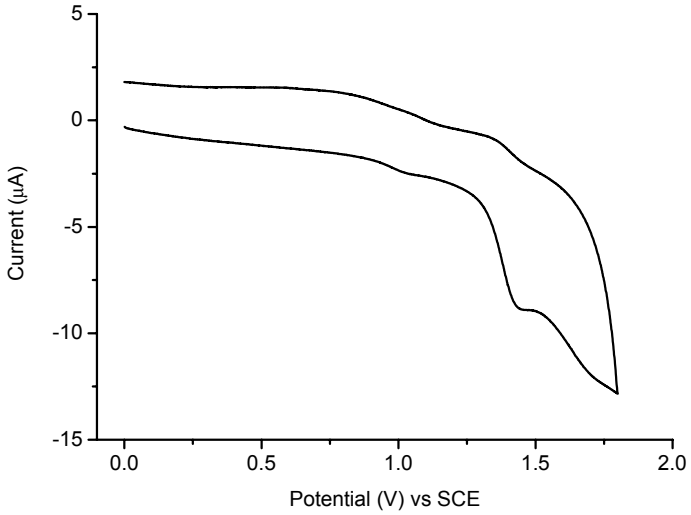

Figure 46. Cyclic voltammogram of **17** in anhydrous and deaerated dichloromethane.

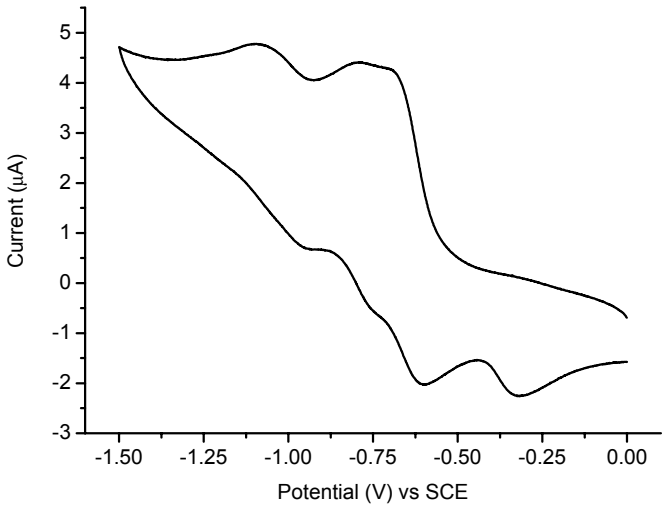

Figure 47. Cyclic voltammogram of **17** in anhydrous and deaerated dichloromethane.

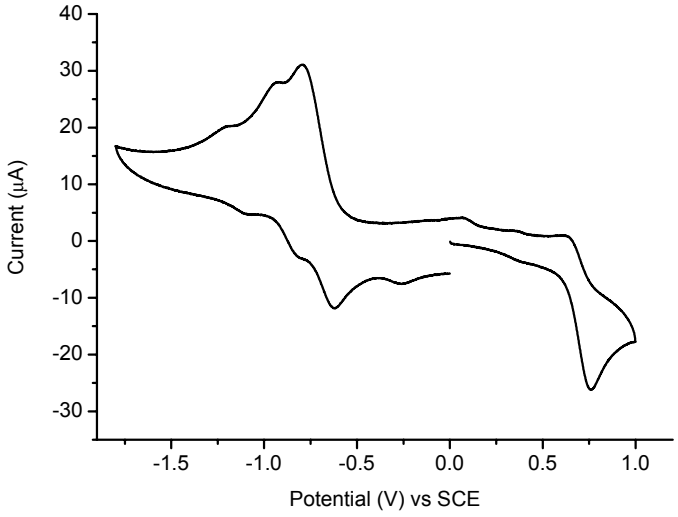

Figure 48. Cyclic voltammogram of **18** in anhydrous and deaerated dichloromethane.

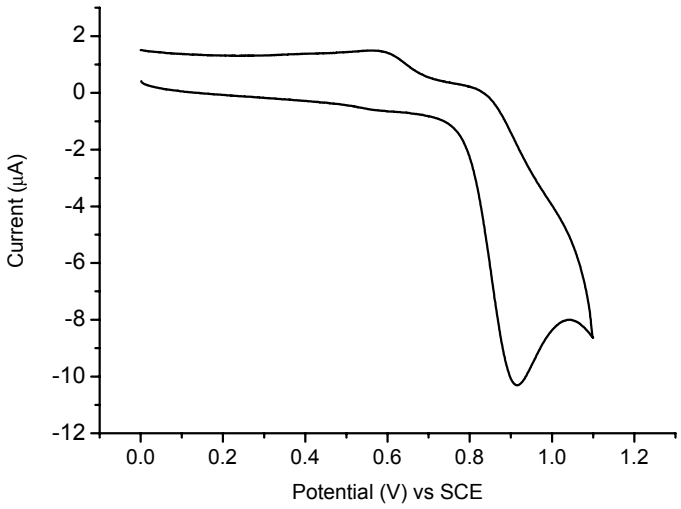

Figure 49. Cyclic voltammogram of **19** in anhydrous and deaerated dichloromethane.

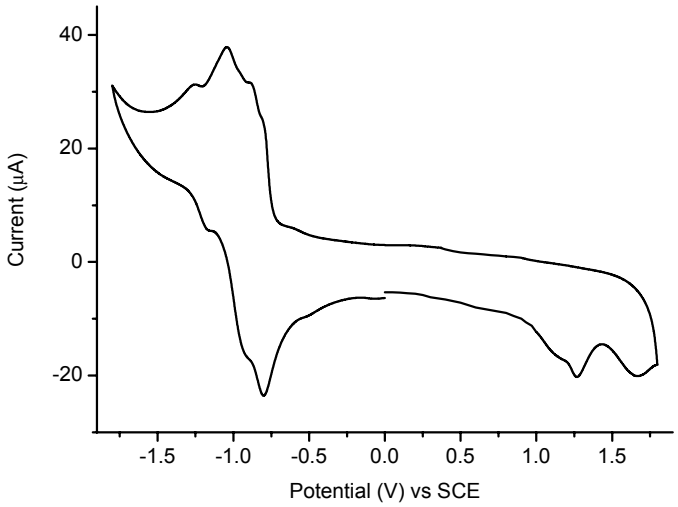

Figure 50. Cyclic voltammogram of **20** in anhydrous and deaerated dichloromethane.

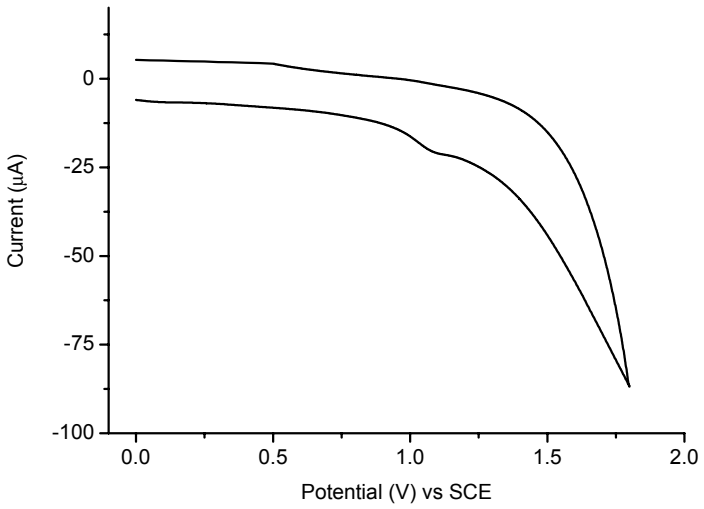

Figure 51 Cyclic voltammogram of **21** in anhydrous and deaerated dichloromethane.

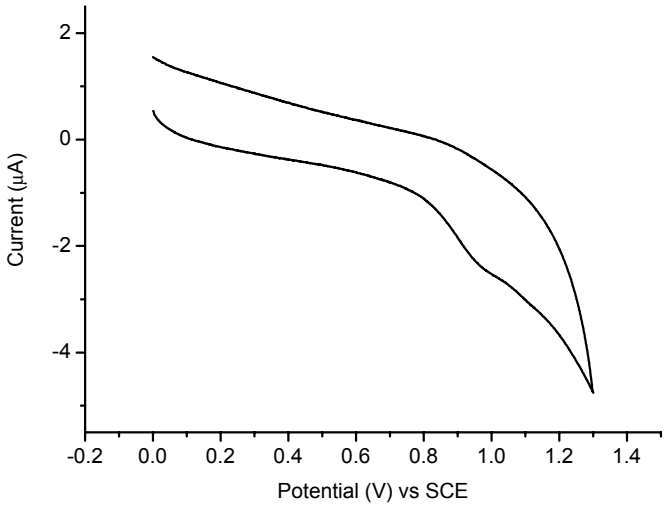

Figure 52. Cyclic voltammogram of **22** in anhydrous and deaerated dichloromethane.

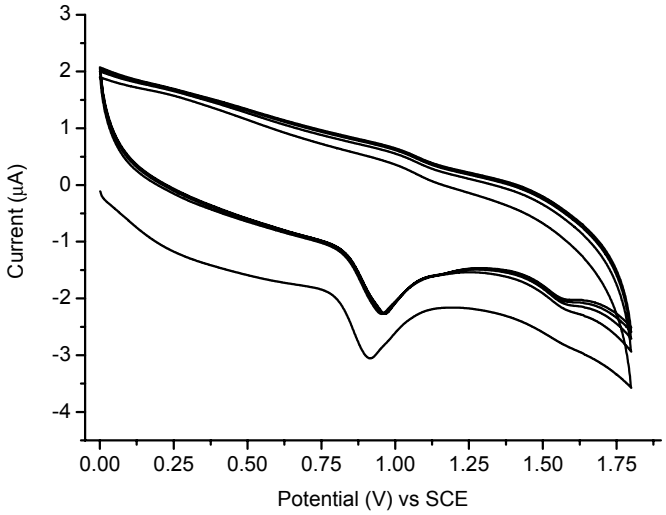

Figure 53. Repeated cyclic voltammogram of **2** leading to oxidative coupling.

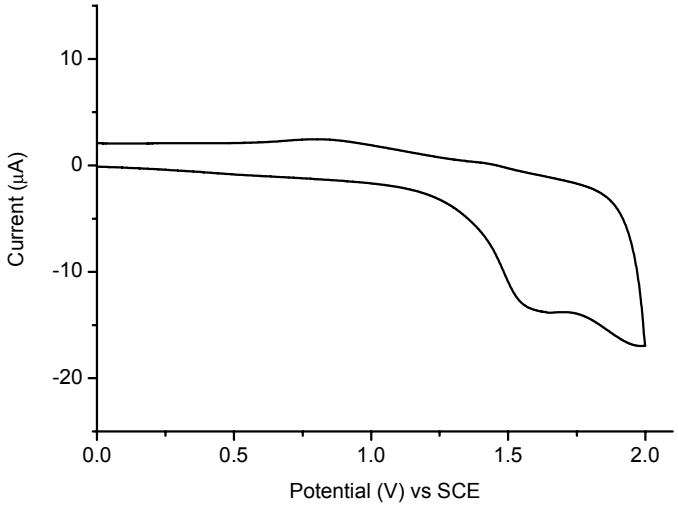

Figure 54. Cyclic voltammogram of the dimer obtained by oxidative coupling from **5**.

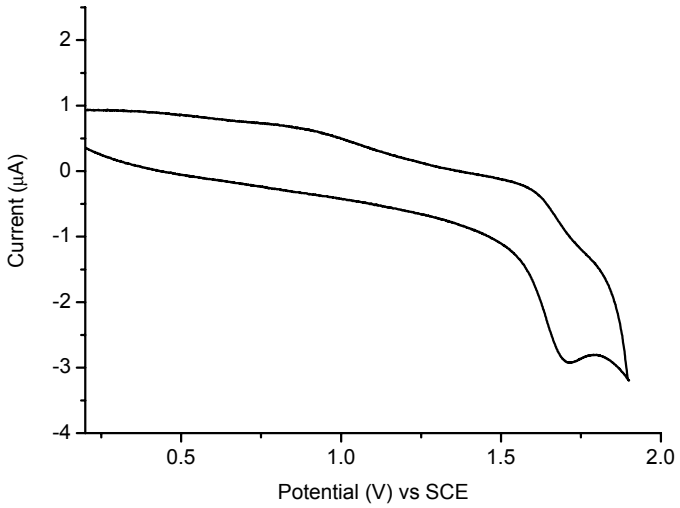

Figure 55. Cyclic voltammogram of the dimer obtained by oxidative coupling from **9**.

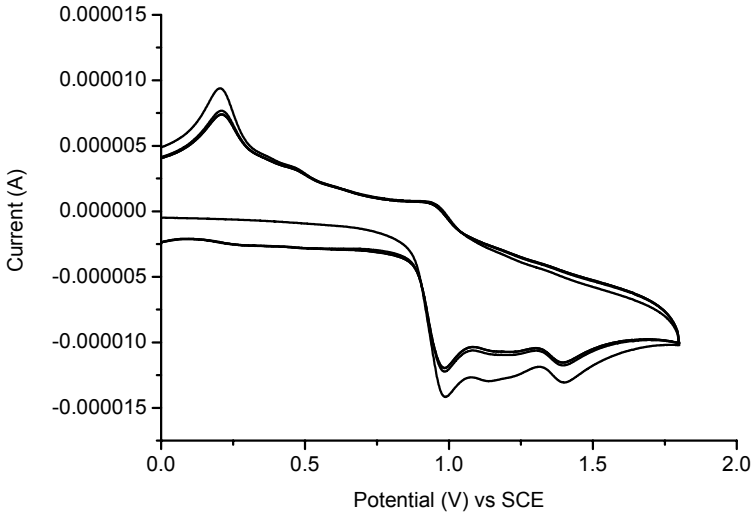

Figure 56. Repeated cyclic voltammogram of **14** leading to oxidative coupling.

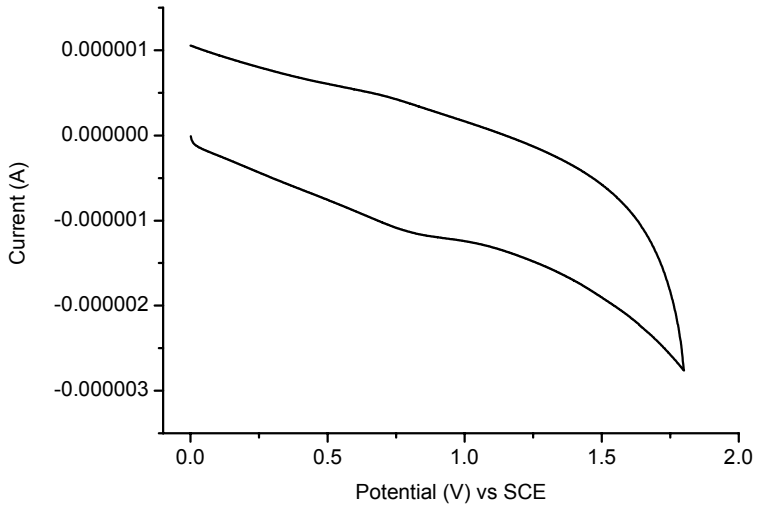

Figure 57. Cyclic voltammogram of the polymer obtained by oxidative coupling from **14**.

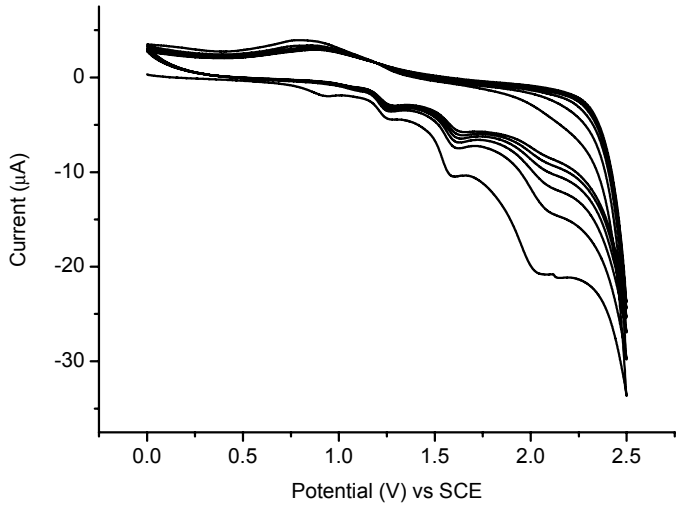

Figure 58. Repeated cyclic voltammogram of **17** leading to oxidative coupling.

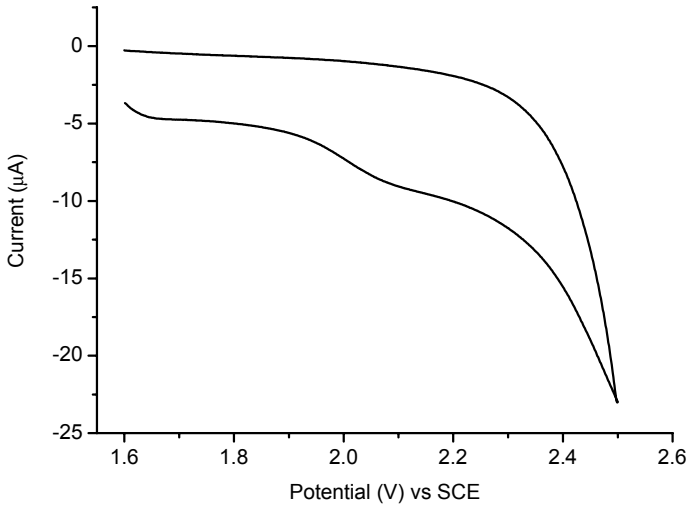

Figure 59. Cyclic voltammogram of the dimer made by oxidative coupling from **17**.

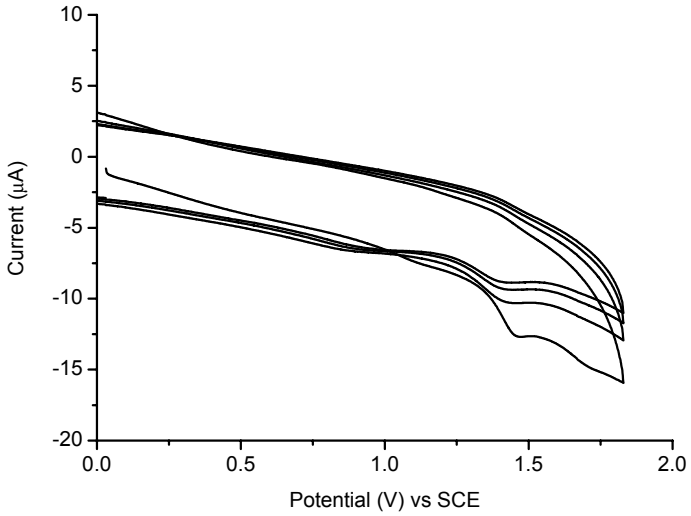

Figure 60. Repeated cyclic voltammogram of **21** leading to oxidative coupling.

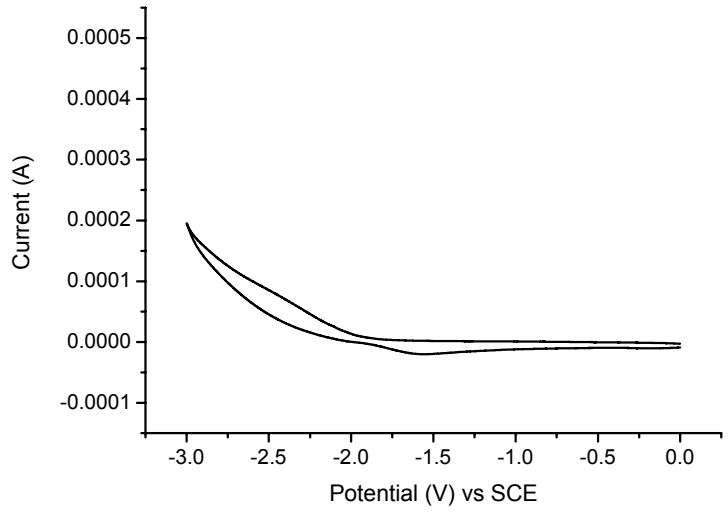

Figure 61. Reduction analysis of **14** in deaerated and anhydrous DMF.

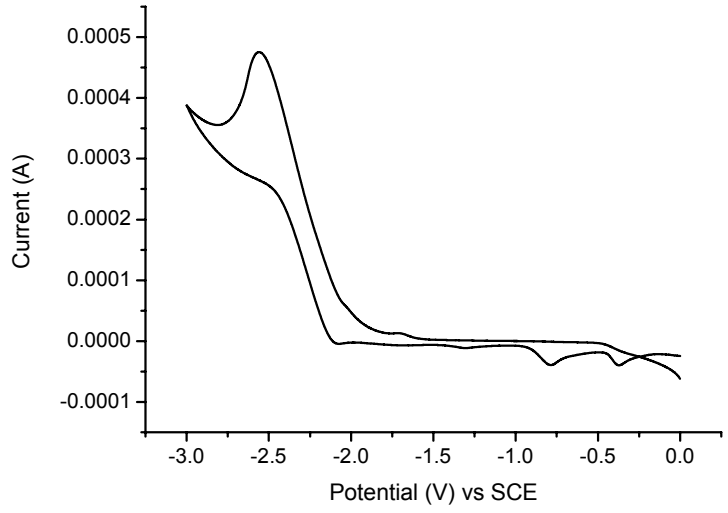

Figure 62. Reduction analysis of **21** in anhydrous and deaerated DMF.

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