

Supporting information

Synthesis, Cyclic Voltammetry and Photophysical Properties of a Bridged o-Phenylene Diamine-C₆₀ Dyad

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Experimental procedures and spectroscopic data of **3**, **4**, and **5**

Bismalonate **3**

To a solution of diol **2** (50 mg, 0.15 mmol) in dry dichloromethane (50 ml), methyl malonyl chloride (42 mg, 0.31 mmol) was added under nitrogen atmosphere. The mixture was stirred at room temperature for two hours.

Subsequently, the solution was washed with sodium bicarbonate solution and with water. Evaporation of the dried extract gave a slightly colored oil. Further purification was achieved by flash chromatography (toluene/triethylamine, 19/1).

Yield: **3**: 60 mg (0.11 mmol, 74%), colourless oil.

Spectroscopic data of 3:

¹H NMR (400 MHz, CDCl₃, 25°C): δ [ppm] = 2.39 (q, J = 6.4 Hz 4 H, CH₂), 3.46 (s, 4 H, CH₂), 3.69 (s, 6 H, CH₃), 4.24 (t, J = 6.4 Hz 4 H, CH₂), 4.63 (t, J = 6.4 Hz 4 H, CH₂), 7.49 (m, 4 H, CH), 8.23 (m, 4 H, CH);

¹³C NMR (100.50 MHz, CDCl₃, 25°C): δ [ppm] = 29.63 (2 C, CH₂), 41.40 (2 C, O=CCH₂C=O), 52.53 (2 C, CH₃), 62.56 (2 C, CH₂C=O), 71.78 (2 C, O-CH₂), 122.46 (4 C, CH), 125.02 (4 C, C), 125.46 (4 C, CH), 147.15 (2 C, C-O), 166.53 (2 C, C=O), 166.90 (2 C, C=O);

MS (FAB): m/z = 452 (M⁺);

IR (KBr): $\tilde{\nu}$ [cm⁻¹] = 3057, 2955, 2846, 2801, 1735, 1590, 1496, 1438, 1413, 1385, 1150, 1022, 957, 850, 754, 686, 666;

UV/Vis (CH₂Cl₂): λ_{max} (ε) [nm] = 239 (13600), 268 (6800).

O-phenylene diamine-C₆₀ dyad **4**

To a solution of C₆₀ (540 mg, 0.75 mmol) in dry toluene, bismalonate **3** (452 mg, 1.00 mmol), tetrabromomethane (662 mg, 2.00 mmol) and DBU (380 mg, 2.50 mmol) were added under nitrogen atmosphere. The solution was stirred at room temperature, while the progress of the reaction was monitored by TLC. After 16 hours the solution was filtered and the product was separated by flash chromatography (toluene/triethylamine, 19/1) followed by HPLC (gromsil amino phase, toluene). The product was washed with pentane and dried under vacuum.

Yield: **4**: 110 mg (0.09 mmol, 13%), red brownish solid.

Spectroscopic data of 4:

¹H NMR (400 MHz, CDCl₃, 25°C): δ [ppm] = 1.88 (m, 4 H, CH₂), 2.70 (s, 3 H, NCH₃), 2.80 (s, 3 H, NCH₃), 3.15 (t, 2 H, NCH₂), 3.31 (m, 2 H, NCH₂), 3.99 (s, 3 H, OCH₃), 4.04 (s, 3 H, OCH₃), 4.18 (m, 1 H, OCH₂), 4.27 (m, 1 H, OCH₂), 4.44 (m, 1 H, OCH₂), 4.63 (m, 1 H, OCH₂), 6.92 (m, 4 H, CH);

¹³C NMR (100.50 MHz, CDCl₃, 25°C): δ [ppm] = 25.35 (1 C, CH₂), 25.55 (1 C, CH₂), 39.36 (1 C, NCH₃), 40.08 (1 C, NCH₃), 50.22 (1 C, NCH₂), 50.44 (1 C, NCH₂), 51.37 (1 C, Bk-C), 53.85 (1 C, bridgehead-C), 53.92 (1 C, OCH₃), 53.98 (1 C, OCH₃), 65.87 (1 C, OCH₂), 66.00 (1 C, OCH₂), 70.35 (1 C, sp³-C₆₀-C), 71.50 (1 C, sp³-C₆₀-C), 71.61 (2 C, sp³-C₆₀-C), 119.44 (1 C, CH), 120.43 (1 C, CH), 121.85 (1 C, CH), 122.60 (1 C, CH), 138.64, 138.90, 139.63, 140.71, 141.27, 141.51, 141.66, 141.86, 141.93, 142.08, 142.33, 142.53, 143.06, 143.26, 143.45, 143.56, 143.70, 143.81, 143.85, 143.94, 144.03, 144.09, 144.31, 144.47, 144.60, 144.69, 144.76, 144.87,

144.93, 145.07, 145.18, 145.24, 145.33, 145.55, 145.73, 146.08, 146.13, 146.32, 146.44, 146.50, 146.74, 147.28, 148.44, (sp^2 C), 163.16, 163.78, 164.04 (C=O);

UV/Vis (CH_2Cl_2): λ_{max} (ϵ) [nm] = 252 (108000), 306 (41300), 396 (4200), 421 (2400), 478 (3000);

IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3053, 2950, 2844, 2796, 1749, 1494, 1433, 1384, 1266, 1237, 1212, 1102, 1061, 1024, 746, 708;

MS (FAB): m/z (%) = 1170 (M^+).

Hexaadduct **5**

To a solution of bisadduct **4** (35 mg, 0.03 mmol) in dry toluene (50 ml), dimethylantracene (62 mg, 0.3 mmol) was added under nitrogen atmosphere. The mixture was stirred for two hours. Subsequently, diethyl bromomalonate (72 mg, 0.3 mmol) and DBU (46 mg, 0.3 mmol) were added. The mixture was stirred at room temperature, while the progress of the reaction was monitored by TLC. After six days the solution was filtered and the product was separated by flash chromatography (toluene/triethylamine, 19:1). The product was washed with pentane and dried under vacuum.

Yield: 5: 16 mg (0.009 mmol, 30%), yellow solid.

Spectroscopic data of 5:

1H NMR (400 MHz, $CDCl_3$, 25°C): δ [ppm] = 1.34 (m, 24 H, CH_3), 1.69 (m, 2 H, CH_2), 1.82 (m, 2 H, CH_2), 2.65 (s, 3 H, NCH_3), 2.77 (s, 3 H, NCH_3), 3.20 (m, 4 H, CH_2), 3.84 (s, 3 H, OCH_3), 3.87 (s, 3 H, OCH_3), 4.10 (m, 2 H, OCH_2), 4.35 (m, 16 H, OCH_2), 4.44 (m, 2 H, OCH_2), 6.90 (m, 4 H, CH);

^{13}C NMR (100.50 MHz, $CDCl_3$, 25°C): δ [ppm] = 14.04 (8 C, CH_3), 25.03 (1 C, CH_2), 25.27 (1 C, CH_2), 39.13 (1 C, NCH_3), 39.77 (1 C, NCH_3), 45.34, 45.40, 45.46, 45.88 (Bk-C), 49.81 (1 C, NCH_2), 49.81 (1 C, NCH_2), 53.64 (1 C, OCH_3), 53.70 (1 C, OCH_3), 62.87 (8 C, OCH_2), 65.45 (1 C, OCH_2), 65.80 (1 C, OCH_2), 68.98, 69.06, 69.11, 69.17, 69.24, (sp^3 - C_{60} -C), 118.98 (1 C, CH), 120.47 (1 C, CH), 121.50 (1 C, CH), 122.43 (1 C, CH), 140.01, 140.24, 140.93, 140.96, 141.02, 141.10, 141.19, 141.28, 141.36, 141.60, 141.65, 141.91, 142.06, 143.53, 144.71, 144.79, 144.85, 145.00, 145.23, 145.50, 145.64, 145.70, 145.79, 145.90, 145.97, 146.02, 146.69 (sp^2 -C), 163.40, 163.69, 163.73, 163.78, 163.84, 164.28, 164.37, 164.67 (C=O);

MS (FAB): m/z (%) = 1800 (M^+H);

IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3060, 2980, 2937, 2906, 2871, 2851, 2801, 1746, 1446, 1368, 1265, 1221, 1079, 1019, 715;

UV/Vis (CH_2Cl_2): λ_{max} (ϵ) [nm] = 244 (94800), 272 (69900), 280 (72700), 316 (45100), 333 (35500).

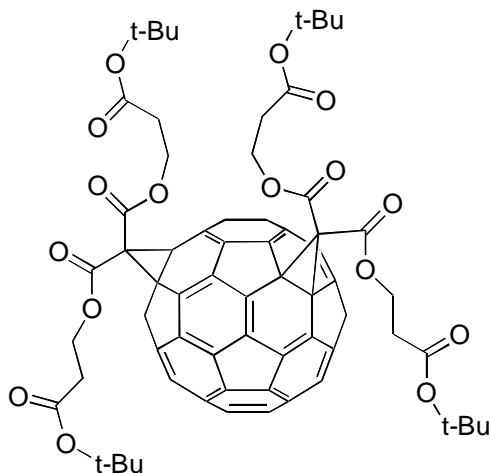


Figure 1. Equatorial bisadduct **6**

Cyclic voltammograms of C₆₀, **3**, **4**, **5** and **6**

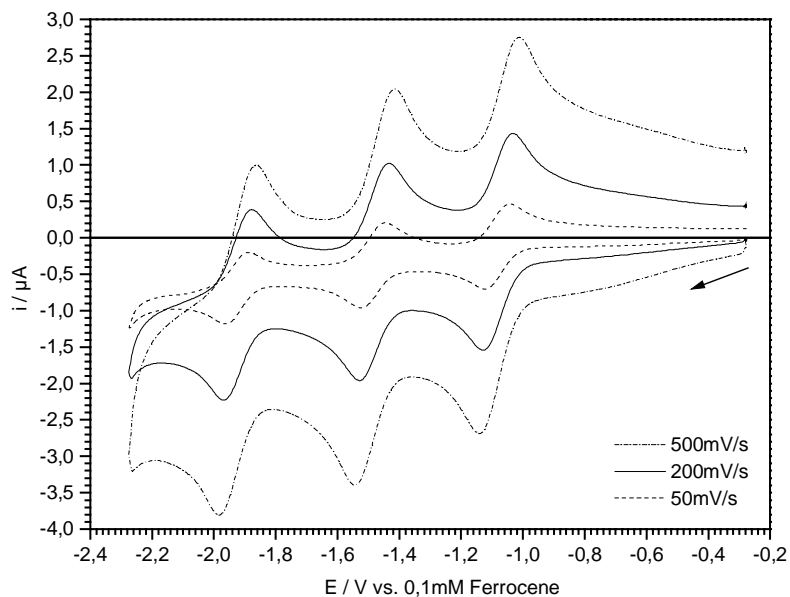


Figure 2. 0,1mM C₆₀ in 0,02M TBAPF₆ in CH₂Cl₂ working-electrode: glassy-carbon, diameter 2mm, counter-electrode: Pt
redox potentials: -1925mV, -1482mV, -1080mV.

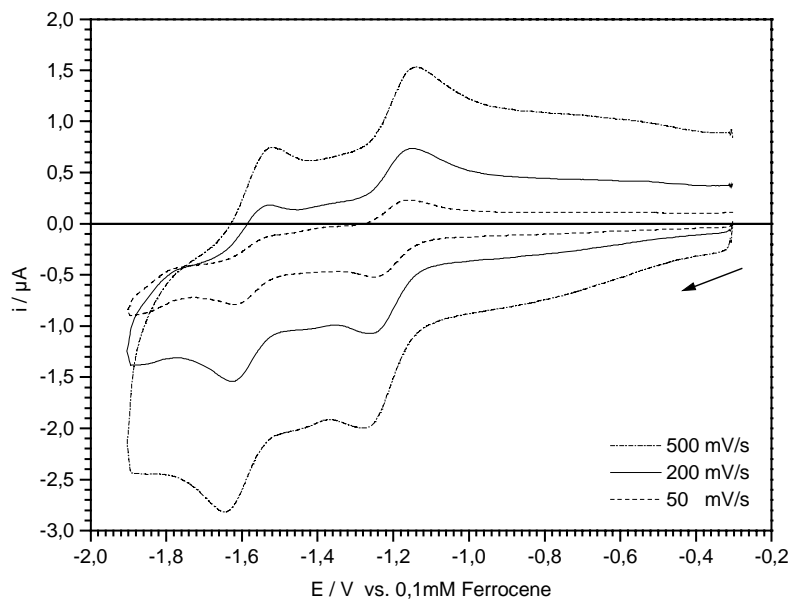


Figure 3. 0,1mM C₆₀-e-bisadduct **6** in 0,02M TBAPF₆ in CH₂Cl₂ working-electrode: glassy-carbon, diameter 2mm, counter-electrode: Pt
redox potentials: -1575mV, -1207mV.

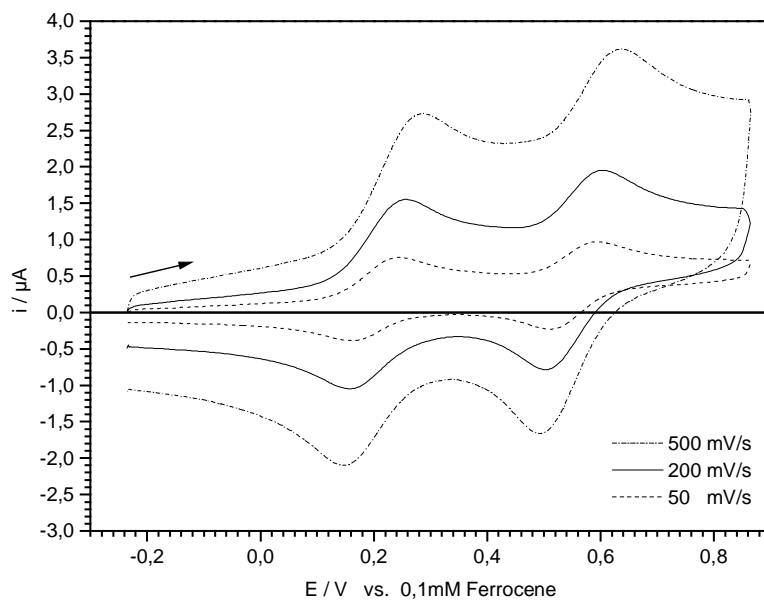


Figure 4. 0,1mM dimalonate **3** in 0,02M TBAPF₆ in CH₂Cl₂ working-electrode: glassy-carbon, diameter 2mm, counter-electrode: Pt redox potentials: +202mV, +557mV.

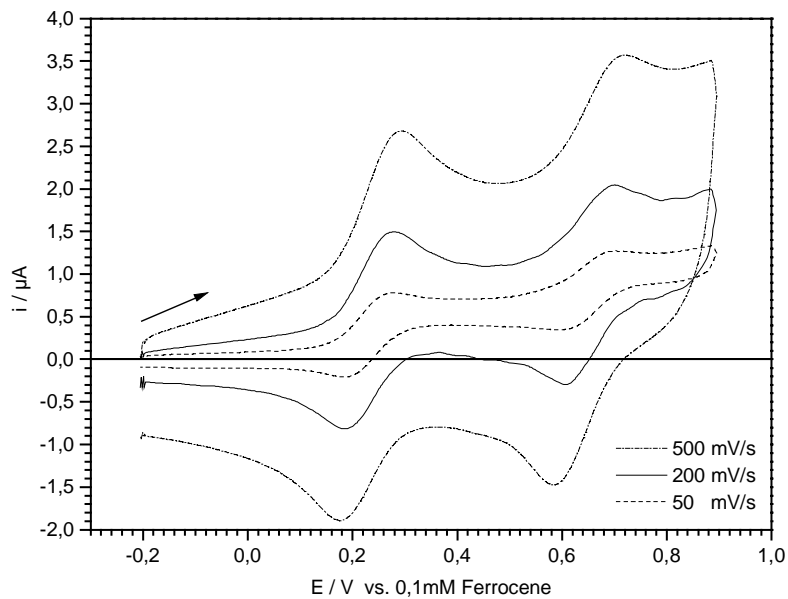


Figure 5. 0,1mM dyad **4** in 0,02M TBAPF₆ in CH₂Cl₂ working-electrode: glassycarbon, diameter 2mm, counter-electrode: Pt redox potentials: +232mV, +654mV.

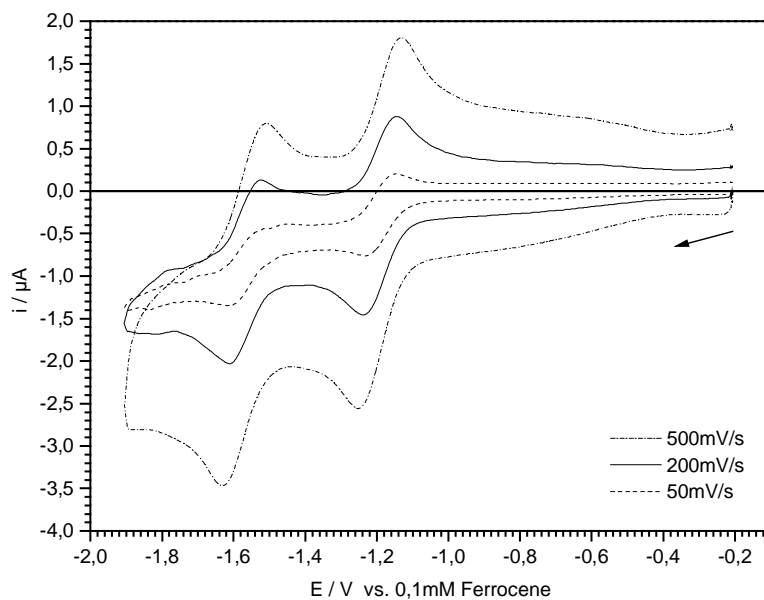


Figure 6. 0,1mM dyad **4** in 0,02M TBAPF₆ in CH₂Cl₂ working-electrode: glassy-carbon, diameter 2mm, counter-electrode: Pt redox-potentials: -1567mV, -1193mV.

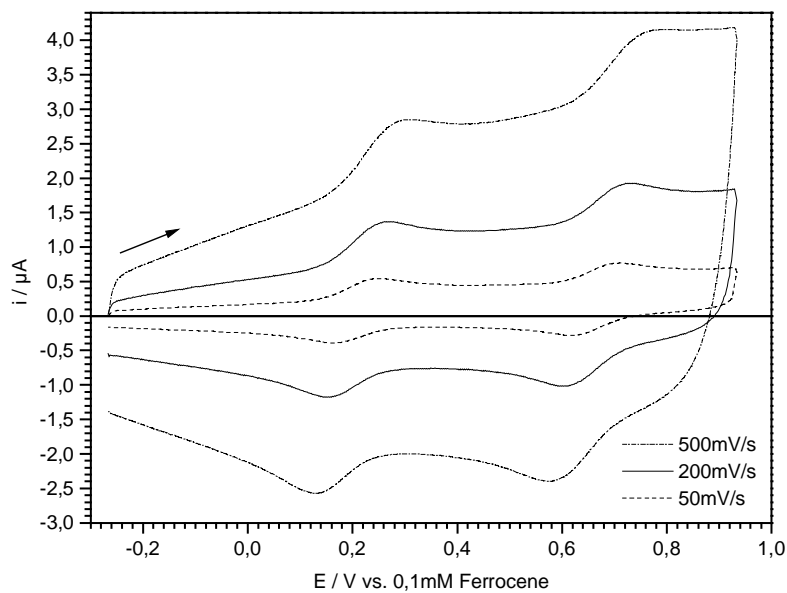


Figure 7. 0,1mM hexaadduct **5** in 0,02M TBAPF₆ in CH₂Cl₂ working-electrode: glassy-carbon, diameter 2mm, counter-electrode: Pt redox potentials: +209mV, +672mV.

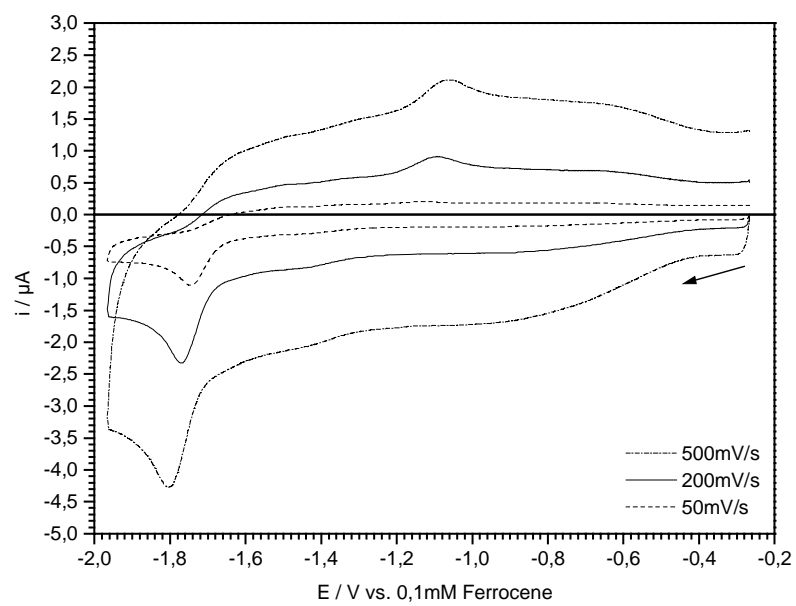


Figure 8. 0,1mM hexaadduct **5** in 0,02M TBAPF₆ in CH₂Cl₂ working-electrode: glassy-carbon, diameter 2mm, counter-electrode: Pt
cathodic peak-potential: -1770mV