Supporting Information

2,5,8,11-Tetraboronic Ester Perylenediimides: a Next Generation Building Block for Dye-Stuff Synthesis

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Measurements and Methods

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 700 süectrometer, Bruker Avance 500 spectrometer and a Bruker Avance 250 spectrometer. Chemical shifts are denoted in δ unit (ppm), and were referenced to residual solvent. Mass spectra were recorded with a Finnigan MAT and VG Instruments ZAB 2-SE-FPD. UV/Vis spectra were recorded at room temperature on a Perkin-Elmer Lambda 900 spectrometer with toluene and dichloromethane as solvent. Fluorescence emission spectra were recorded on a J&M Tidas spectrometer. Elemental analyses were performed on an Elementar Vario EL.

The oxidation potentials of the dyes were determined by cyclovoltammetry on a EG&G Princeton Applied Research potentiostat, model 273. The measurements were performed in a solution of Bu_4NPF_6 (0.1 M) in dry dichloromethane: working electrode: inlaid platinum disk (1.5 mm diameter); counter electrode: platinum wire: reference electrode: silver wire. Internal calibration by ferrocene/ferrocenium (Fc/Fc+) measurements.

***N,N'*-Bis(1-ethylpropyl)-2,5,8,11-tetrakis[4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-y]perylene-3,4:9,10-tetracarboxylic acid diimide (2a)**

Compound **1a** (100 mg, 0.19 mmol) and bis(pinacolato)diboron (383 mg, 1.51 mmol) are mixed together and dissolved in 2 mL anhydrous mesitylene and 0.15 mL anhydrous pinacolone. Argon is bubbled through the solution for 30 minutes. $RuH_2(CO)(PPh_3)_3$ (87 mg, 0.09 mmol) is added to the mixture and the reaction is heated at 140°C for 24 hours. After cooling the system to room temperature, the solvent is evaporated and the desired compound purified by column chromatography (CH_2Cl_2/AcOEt 50/1). **2a** is obtained as an orange bright solid with 60% yield (117 mg, 0.11 mmol). ^{1}H NMR (250 MHz, CD_2Cl_2) δ 8.59 (s, 4H), 4.94 (tt, *J* = 9.2, 6.0 Hz, 2H), 2.33 – 2.10 (m, 4H), 2.04 – 1.84 (m, 4H), 1.51 (s, 48H), 0.92 (t, *J* = 7.4 Hz, 12H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 166.39 (s), 139.46 (s), 133.80 (s), 128.85 (s), 127.30 (s), 126.31 (s), 84.91 (s), 58.51 (s), 25.56 (s), 25.34 (s), 11.79 (s). FD/MS (8kV): m/z= 1033.33 (100%) [M+]. UV-Vis(in toluene): λ_{max}(ε[$M^{-1}cm^{-1}$]): 538 nm (7.30 X 10^4 $M^{-1}cm^{-1}$). Fluorescence (in toluene, λ_{ex}=538 nm): 548 nm. φ_F: 0.89. Elem. Anal.: theoretical: C: 67.34%; H: 7.21%; N: 2.71%; experimental: C: 67.29%; H: 7.40%; N: 2.96%.

***N,N'*-Bis(1-heptyloctyl)-2,5,8,11-tetrakis[4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-y]perylene-3,4:9,10-tetracarboxylic acid diimide (2b)**

Compound **1b** (100 mg, 0.12 mmol) and bis(pinacolato)diboron (250 mg, 0.99 mmol) are mixed together and dissolved in 2 mL anhydrous mesitylene and 0.15 mL anhydrous pinacolone. Argon is bubbled through the solution for 30 minutes. $RuH_2(CO)(PPh_3)_3$ (57 mg, 0.06 mmol) is added to the mixture and the reaction is heated at 140°C for 30 hours. After cooling the system to room temperature, the solvent is evaporated and the desired compound purified by column chromatography (CH_2Cl_2). **2b** is obtained as a red solid with 70% yield (113 mg, 0.09 mmol). ^{1}H NMR (250 MHz, CD_2Cl_2) δ 8.58 (s, 4H), 5.06 (s, 2H), 2.35 – 2.06 (m, 4H), 1.98 – 1.72 (m, 4H), 1.50 (s, 48H), 1.24 (s, 40H), 0.84 (t, *J* = 6.5 Hz, 12H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 166.27 (s), 139.25 (s), 133.80 (s), 128.82 (s), 127.57 (s), 127.30 (s), 126.29 (s), 84.90 (s), 55.19 (s), 32.83 (s), 32.45 (s), 30.03 (s), 29.76 (s), 27.37 (s), 25.38 (s), 23.22 (s), 14.43 (s). FD/MS (8kV): m/z= 1312.4 (100%) [M+]. UV-Vis(in toluene): λ_{max}(ε [$M^{-1}cm^{-1}$]): 538 nm (7.21 X 10^4 $M^{-1}cm^{-1}$). Fluorescence (in toluene, λ_{ex}=538 nm): 548 nm. φ_F: 0.83. Elem. Anal.: theoretical: C: 71.24%; H: 8.74%; N: 2.13%; experimental: C: 70.97%; H: 8.41%; N: 2.28%.

***N,N'*-Bis(1-heptyloctyl)- 2,5,8,11-tetrakis[p-benzonitril]perylene-3,4:9,10-tetracarboxylic acid diimide (3)**

Compound **2b** (100 mg, 0.08 mmol) and 4-bromo-benzonitrile (83 mg, 0.46 mmol) are mixed together and dissolved in 30 mL toluene and 0.3 mL ethanol. Potassium carbonate (252 mg, 1.83 mmol) is dissolved in 3 mL of water and added to the reaction mixture. After bubbling argon inside the solution for 30 minutes, $Pd(PPh_3)_4$ (53 mg, 0,05 mmol) is added. After bubbling argon in the reaction mixture for 30 minutes, the reaction is connected with a condenser and heated, under argon atmosphere for 14 hours at 80°C. After cooling the reaction mixture to room temperature, the solvent is evaporated and the desired compound purified by column chromatography (CH_2Cl_2). **3** is obtained as an orange solid with 70% yield (65 mg, 0.05 mmol). ^{1}H NMR (700 MHz, CD_2Cl_2) δ 8.37 (s, 4H), 7.80 (d, *J* = 8.1 Hz, 8H), 7.52 (d, *J* = 8.1 Hz, 8H), 4.86 – 4.80 (m, 2H), 1.99 – 1.91 (m, 4H), 1.63 (m, 4H), 1.28 – 1.14 (m, 40H), 0.84 (t, *J* = 7.1 Hz, 12H). ^{13}C NMR (176 MHz, CD_2Cl_2) δ 164.01 (s), 163.05 (s), 147.59 (s), 146.75 (s), 133.29 (s), 132.65 (s), 131.50 (s), 129.28 (s), 127.65 (s), 126.52 (s), 122.62 (s), 121.89 (s), 119.20 (s), 112.16 (s), 55.41 (s), 32.50 (s), 32.36 (s), 29.93 (s), 29.82 (s), 27.42 (s), 23.20 (s), 14.41 (s). FD/MS (8kV): m/z= 1216:3 (100%) [M+]. UV-Vis(in dichloromethane): λ_{max} (ε [$M^{-1}cm^{-1}$]): 528 nm (6.29 X 10^4 $M^{-1}cm^{-1}$). Fluorescence (in dichloromethane, λ_{ex}=528 nm): 542 nm. φ_F: 0.69. Elem. Anal.: theoretical: C: 81.02%; H: 6.80%; N: 6.91%; experimental: C: 81.21%; H: 6.78%; N: 6.61%.

***N,N'*-Bis(1-heptyloctyl)- 2,5,8,11-tetraiodo-perylene-3,4:9,10-tetracarboxylic acid diimide (4)**

Compound **2b** (100 mg, 0.08 mmol) is suspended in 50 mL of a 1/3 water/THF mixture. Chloramine-T (600 mg, 4.53 mmol) and sodium iodide (680 mg, 4.53 mmol) are added to the reaction, the vessel sealed and heated at 55°C for 12 hours without light. After cooling the reaction to room temperature, 10 mL of a saturated solution of sodium sulfite are added to the reaction. Successively the reaction mixture is thrown in 100 mL of water, the solid filtrated, dried and purified by column chromatography (1/1 PE/CH_2Cl_2). **4** is obtained as a red solid with 42% yield (42 mg, 0.03 mmol). ^{1}H NMR (700 MHz, CD_2Cl_2) δ 9.10 (s, 4H), 5.22 – 5.11 (m, 2H), 2.26 – 2.14 (m, 4H), 1.95 – 1.87 (m, 4H), 1.40 – 1.18 (m, 40H), 0.84 (t, *J* = 7.0 Hz, 12H). ^{13}C NMR (176 MHz, CD_2Cl_2) δ 161.27 (s), 139.06 (s), 138.60 (s), 132.38 (s), 131.73 (s), 126.28 (s), 124.09 (s), 56.56 (s), 32.76 (s), 32.38 (s), 30.04 (s), 29.80 (s), 27.52 (s), 23.22 (s), 14.43 (s). FD/MS (8kV): m/z= 1315.4 (100%) [M+]. UV-Vis(in dichloromethane): λ_{max}(ε[$M^{-1}cm^{-1}$]): 518 nm (7.23 X 10^4 $M^{-1}cm^{-1}$). Elem. Anal.: Elemental Analysis: theoretical: C: 49.33%; H: 5.06%; N: 2.13%; experimental: C: 49.68%; H: 5.01%; N: 2.24%.

***N,N'*-Bis(1-heptyloctyl)- 2,5,8,11-tetrakis[octylamino]perylene-3,4:9,10-tetracarboxylic acid diimide (5)**

Compound **4** (100 mg, 0.08 mmol) was suspended in 10 mL octylamine. The reaction mixture is heated under argon atmosphere for 3 hours. After cooling the reaction to room temperature, 50 mL of water are added and the precipitate filtrated and dried. **5** is obtained as a dark red solid with 96% yield (96 mg, 0.07 mmol). ^{1}H NMR (500 MHz, $C_2Cl_4D_2$, 373 K) δ 10.18 (s, 4H), 7.43 (s, 4H), 5.19 (m, 2H), 3.44 (d, *J* = 5.7 Hz, 8H), 2.16 (m, 4H), 1.84 – 1.70 (m, 12H), 1.45 (m, 8H), 1.23 (m, 72H), 0.78 (dd, *J* = 25.2, 6.6 Hz, 24H). ^{13}C NMR (126 MHz, $C_2Cl_4D_2$, 373 K) δ 166.66 (s), 153.67 (s), 135.55 (s), 134.74 (s), 110.78 (s), 103.77 (s), 99.76 (s), 53.48 (s), 43.14 (s), 32.69 (s), 31.81 (s), 31.75 (s), 29.67 (s), 29.60 (s), 29.37 (s), 29.17 (s), 29.15 (s), 27.36 (s), 27.13 (s), 22.55 (s), 22.52 (s), 13.91 (s). FD/MS (8kV): m/z= 1319.4 (100%) [M+]. UV-Vis(in dichloromethane): λ_{max}(ε[$M^{-1}cm^{-1}$]): 512 nm (5.42 X 10^4 $M^{-1}cm^{-1}$). Fluorescence (in dichlomethane, λ_{ex}=512 nm): 608 nm. φ_F: 0.05. Elem. Anal.: theoretical: C: 78.25%; H: 10.54%; N: 6.37%; experimental: C: 78.51%; H: 10.73%; N: 6.30%.

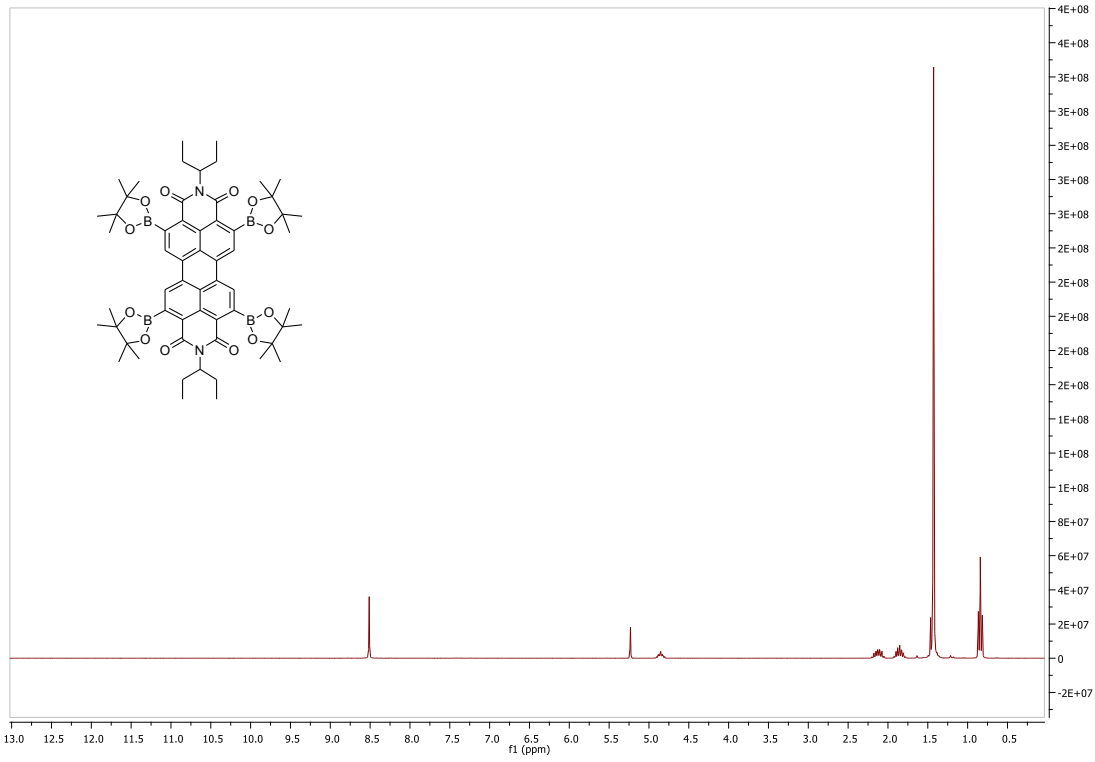

Figure 1: ^{1}H NMR of compound 2a in CD_2Cl_2

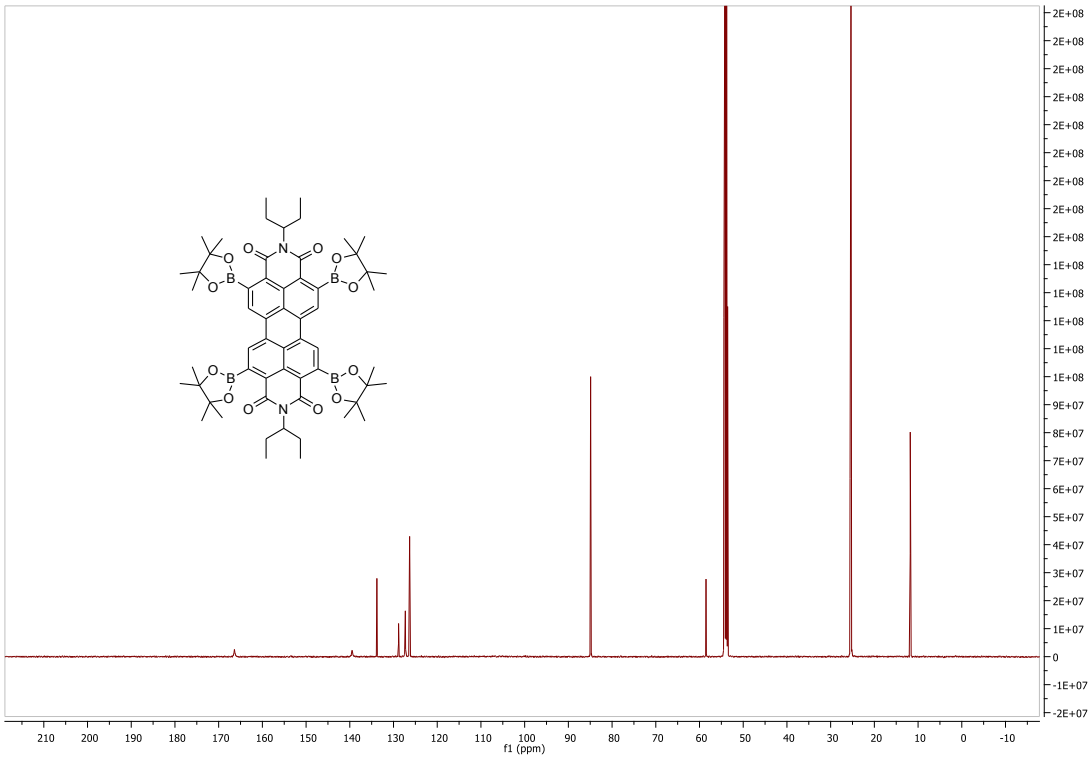

Figure 2: ^{13}C NMR of compound **2a** in CD_2Cl_2

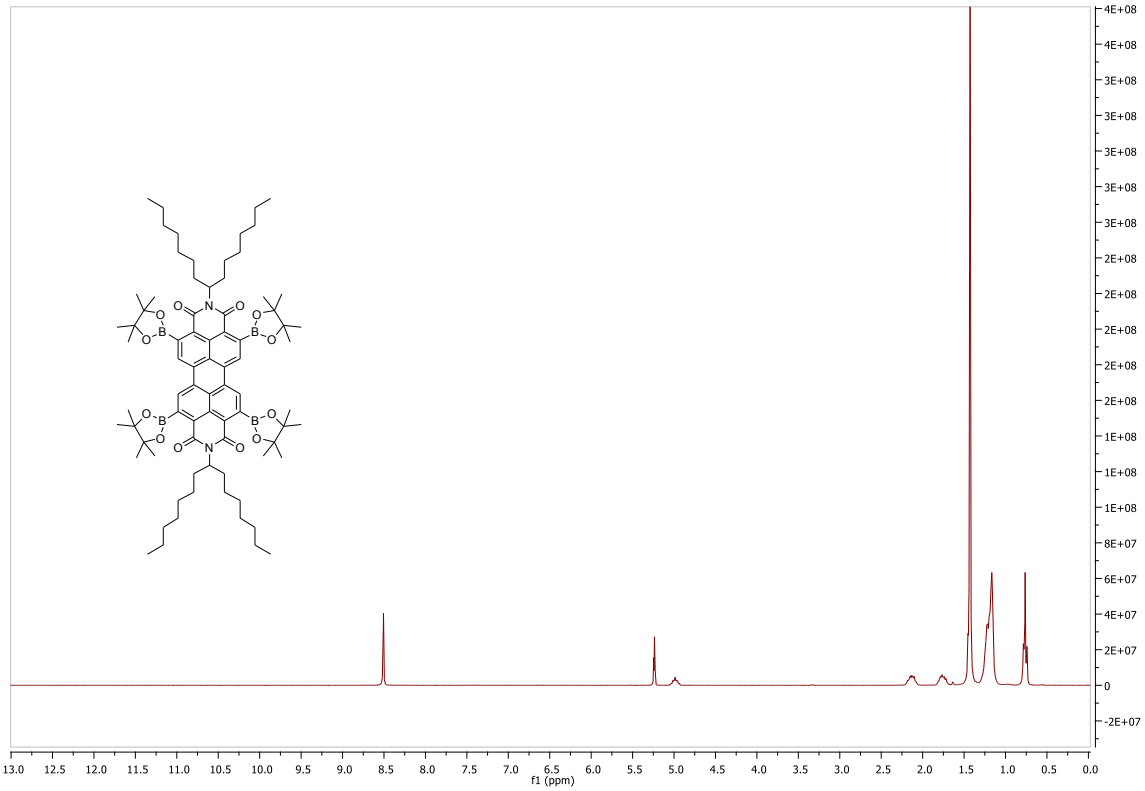

Figure 3: ^{1}H NMR of compound **2b** in CD_2Cl_2

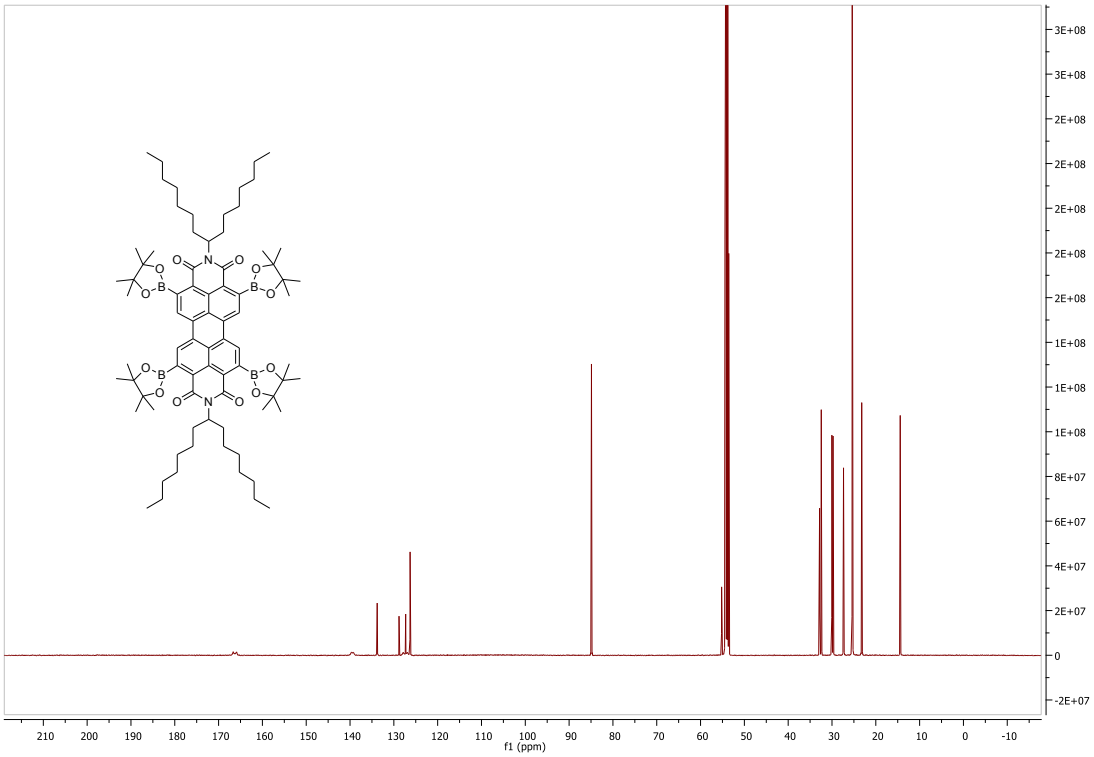

Figure 4: ^{13}C NMR of compound **2b** in CD_2Cl_2

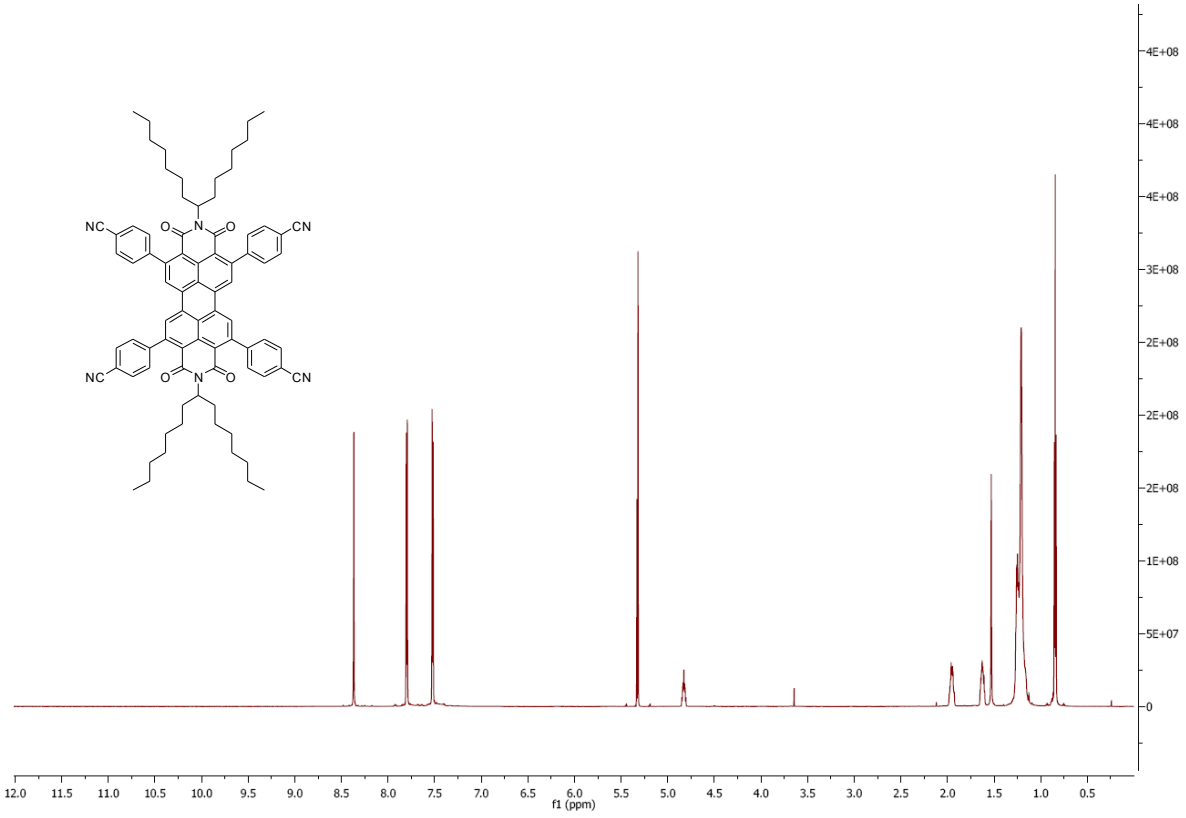

Figure 5: ^{1}H NMR of compound **3** in CD_2Cl_2.

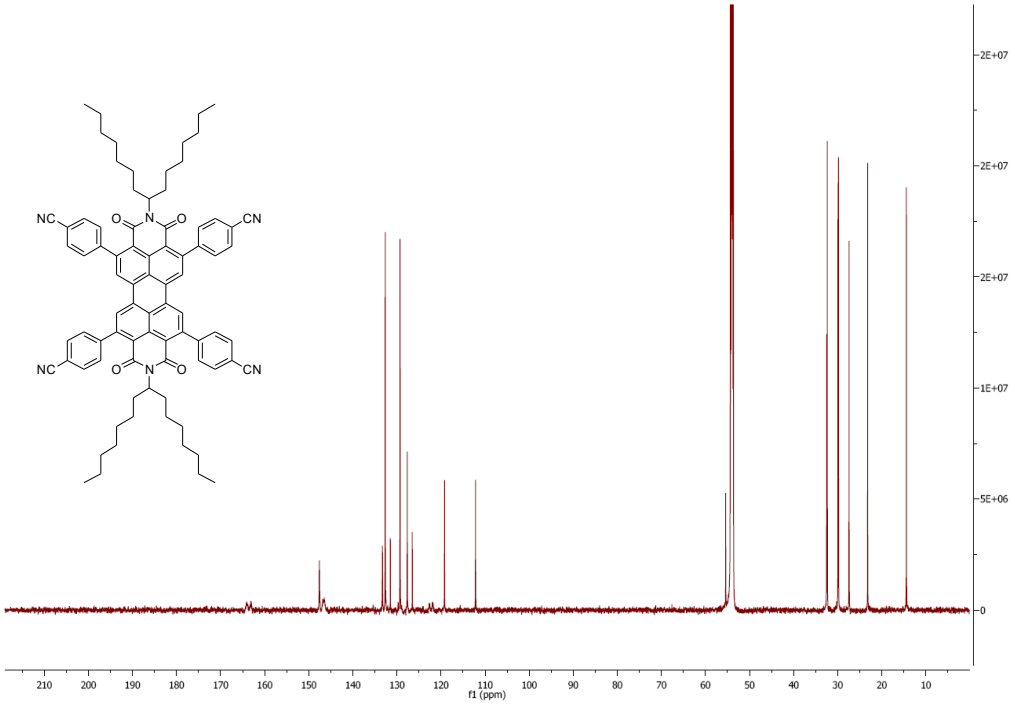

Figure 6: ^{13}C NMR of compound **3** in CD_2Cl_2

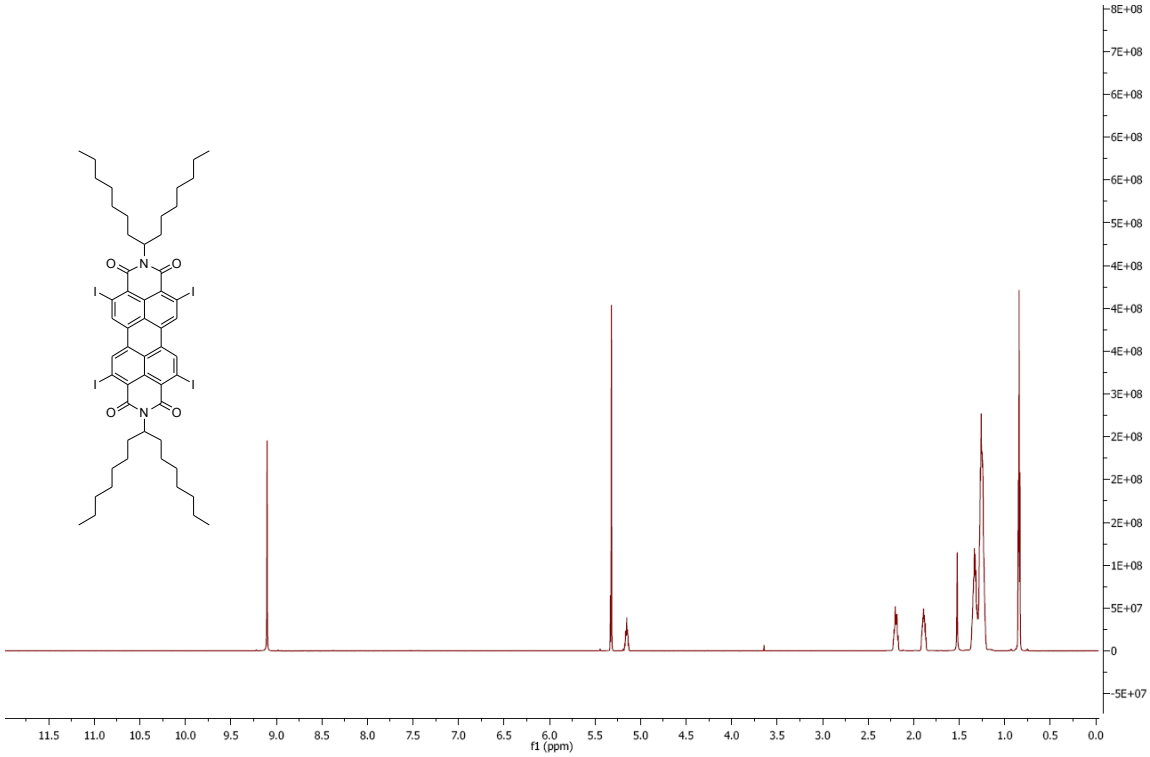

Figure 7: ^{1}H NMR of compound **4** in CD_2Cl_2.

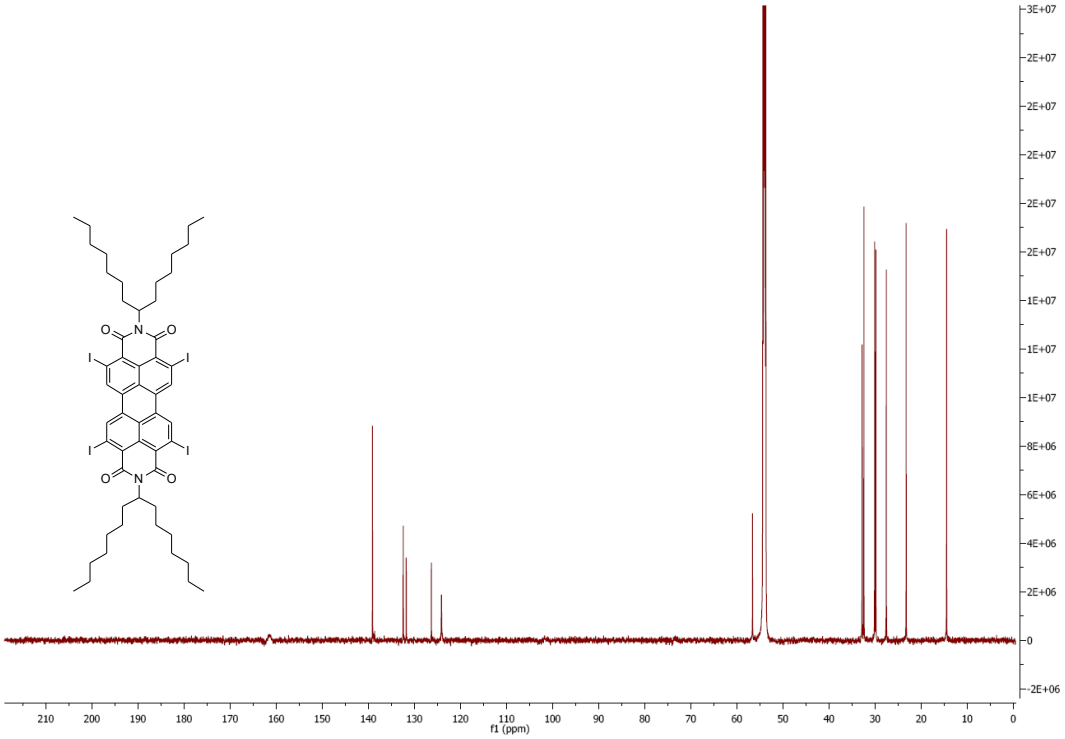

Figure 8: ^{13}C NMR of compound **4** in CD_2Cl_2

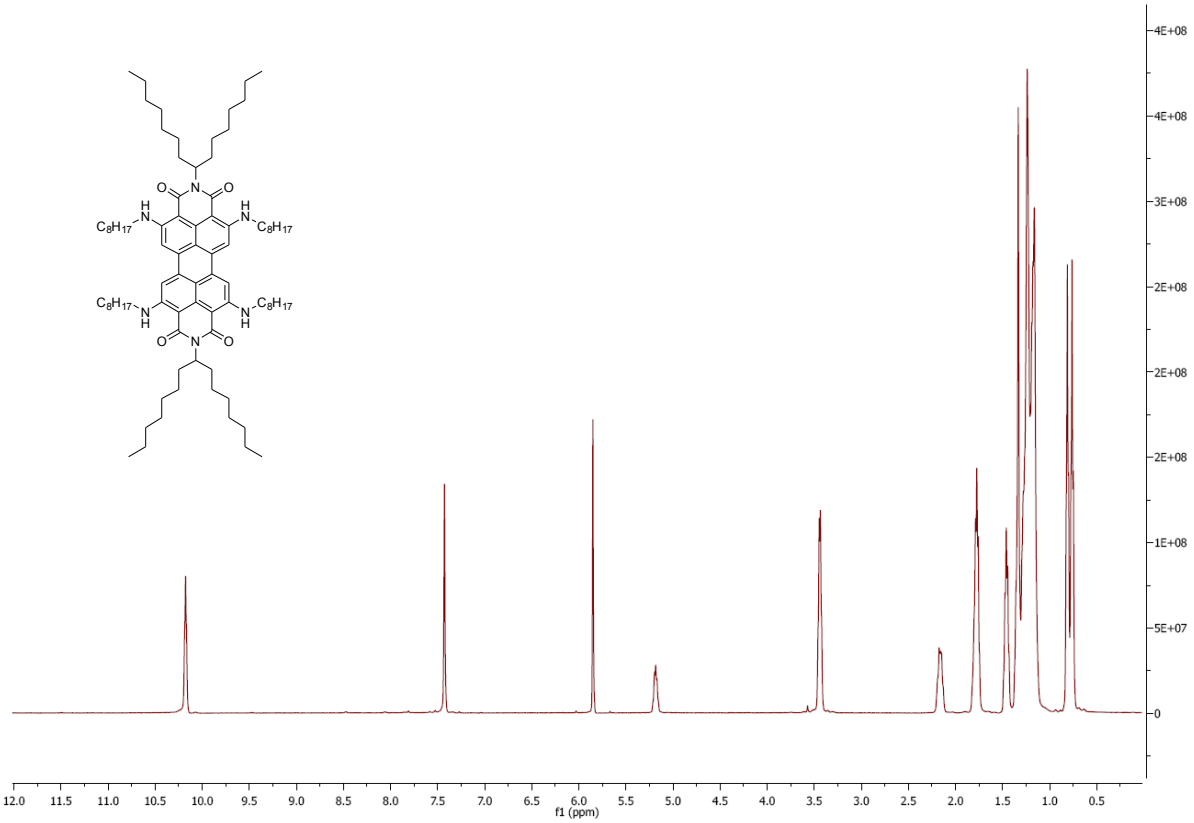

Figure 9: ^{1}H NMR of compound **5** in $C_2D_2Cl_4$.

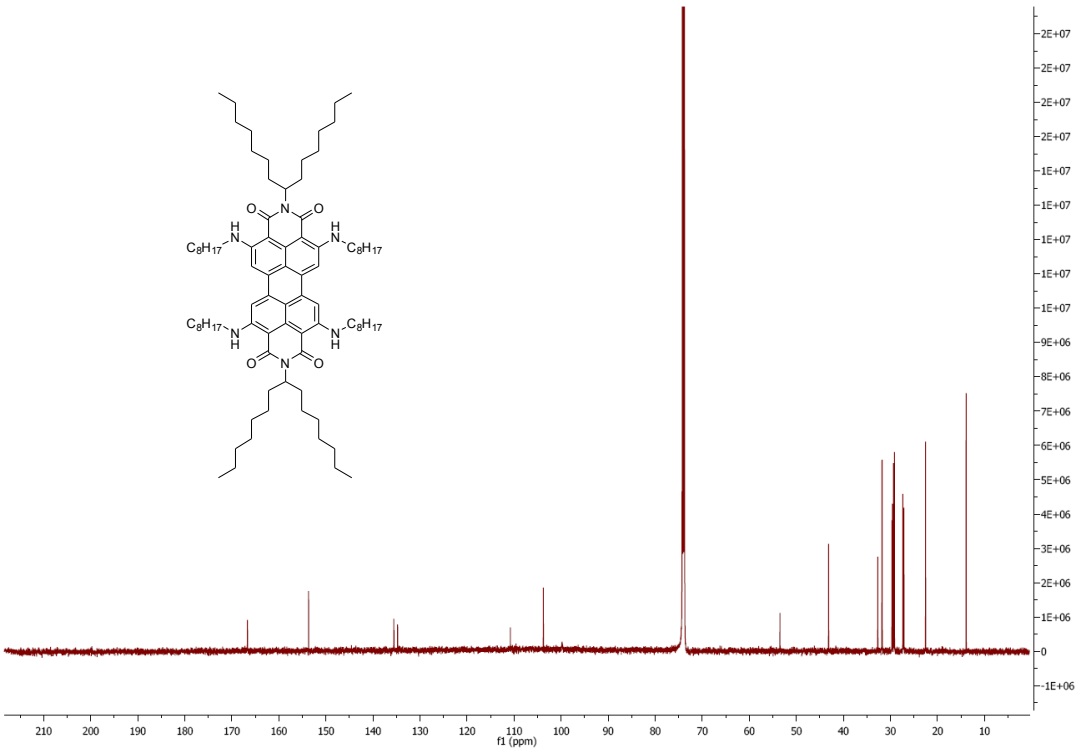

Figure 10: ^{13}C-NMR of compound **5** in $C_2D_2Cl_4$.

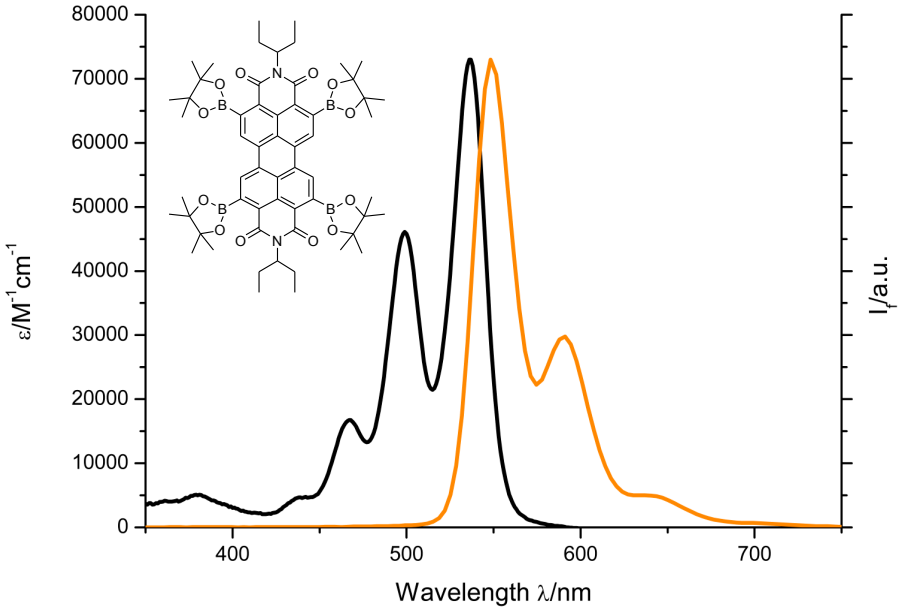

Figure 11: UV/vis absorption spectrum (black) and fluorescence spectrum (orange) in toluene of compound **2a**.

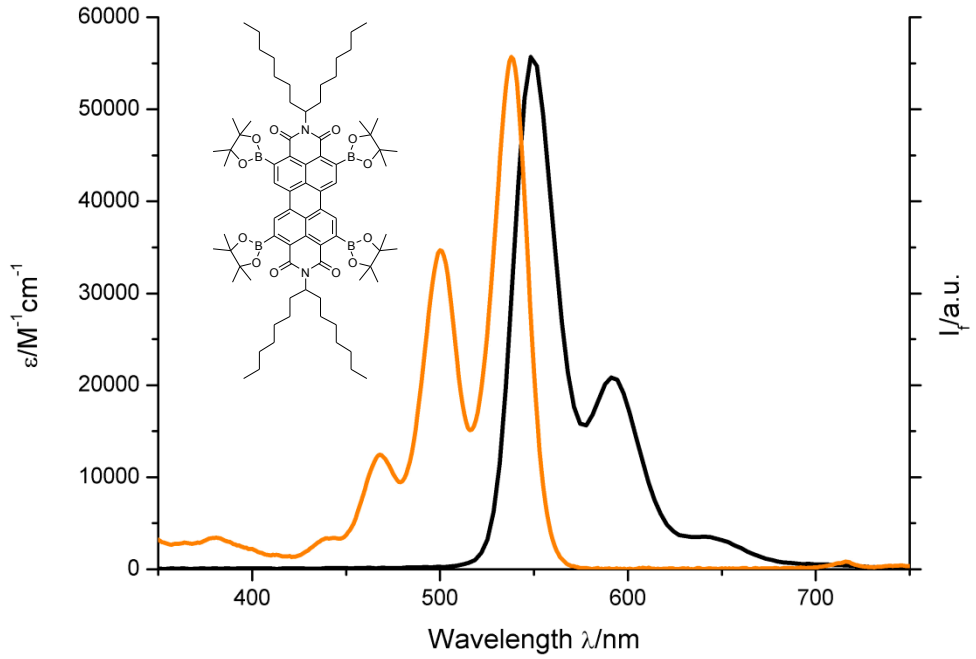

Figure 12. UV/vis absorption spectrum (orange) and fluorescence spectrum (black) in toluene of compound **2b**.

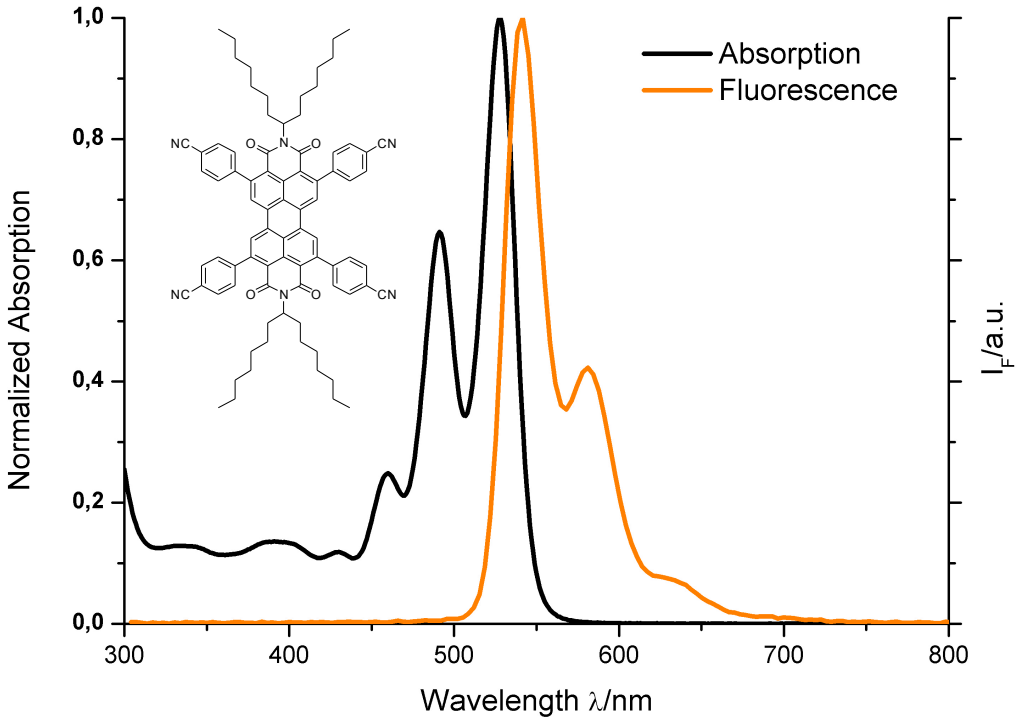

Figure 13: UV/vis absorption spectrum (black) and fluorescence spectrum (orange) in dichloromethane of compound **3**.

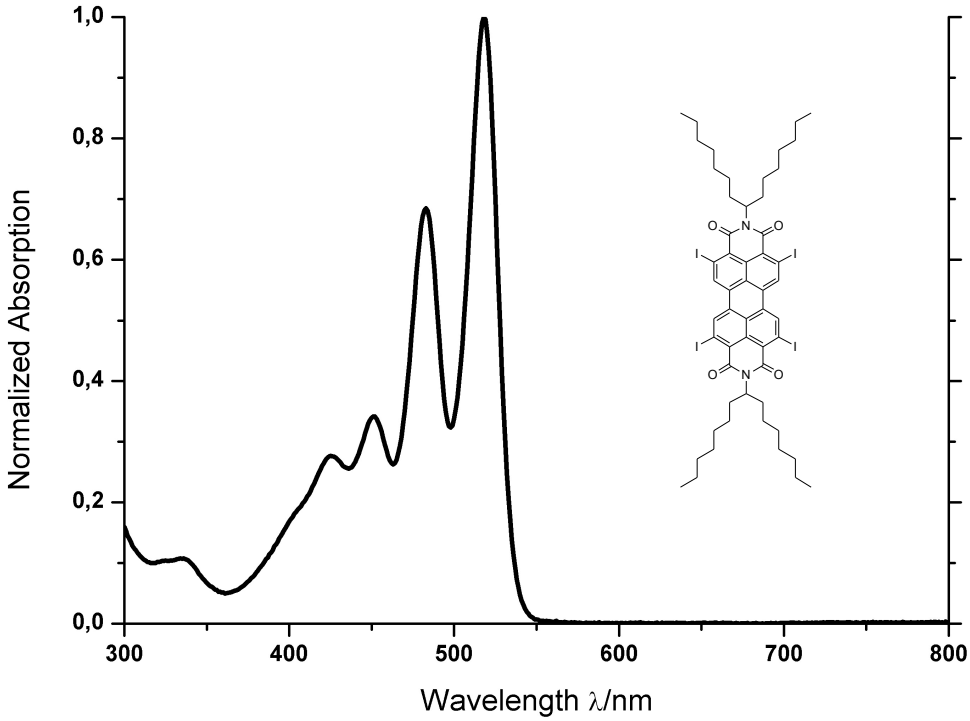

Figure 14: UV/vis absorption spectrum (black) in dichloromethane of compound **4**.

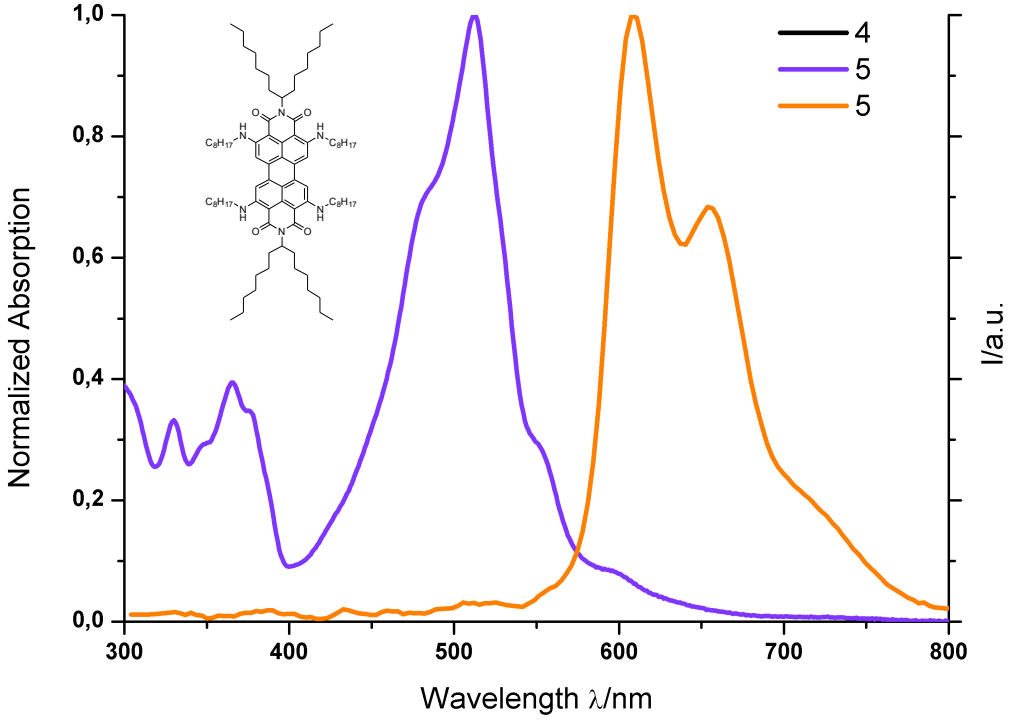

Figure 15: UV/vis absorption spectrum (violet) and fluorescence spectrum (orange) in dichloromethane of compound **5**.

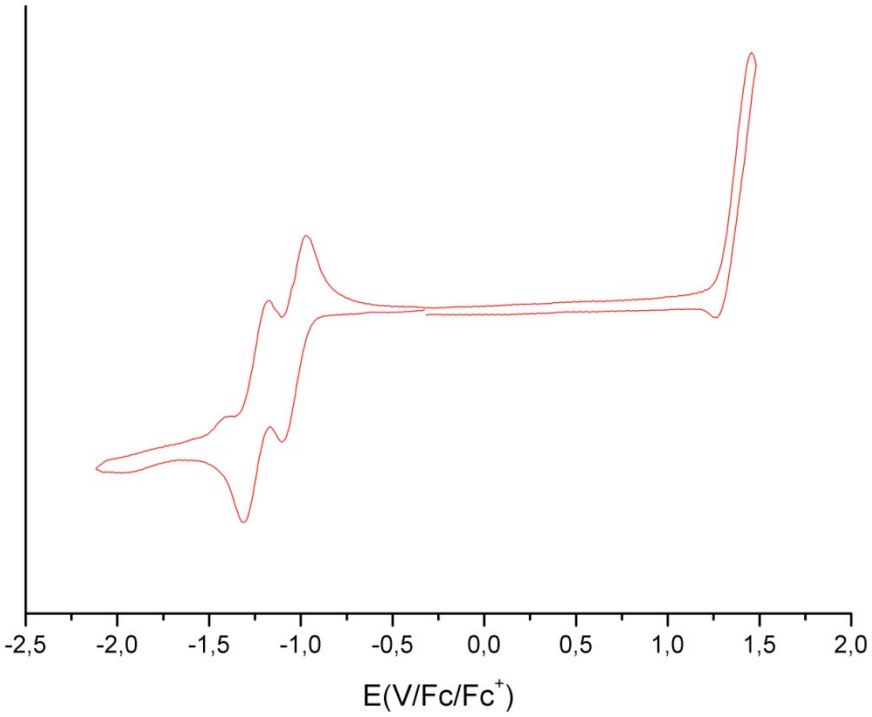

Figure 16 Cyclic Voltammograms of **2** in 0.1 M Bu_4NPF_6 CH_2Cl_2 solution, RT (100 mV/ sec)