

Supporting Information for
NIR J-aggregates of Hydroazaheptacene Tetraimides

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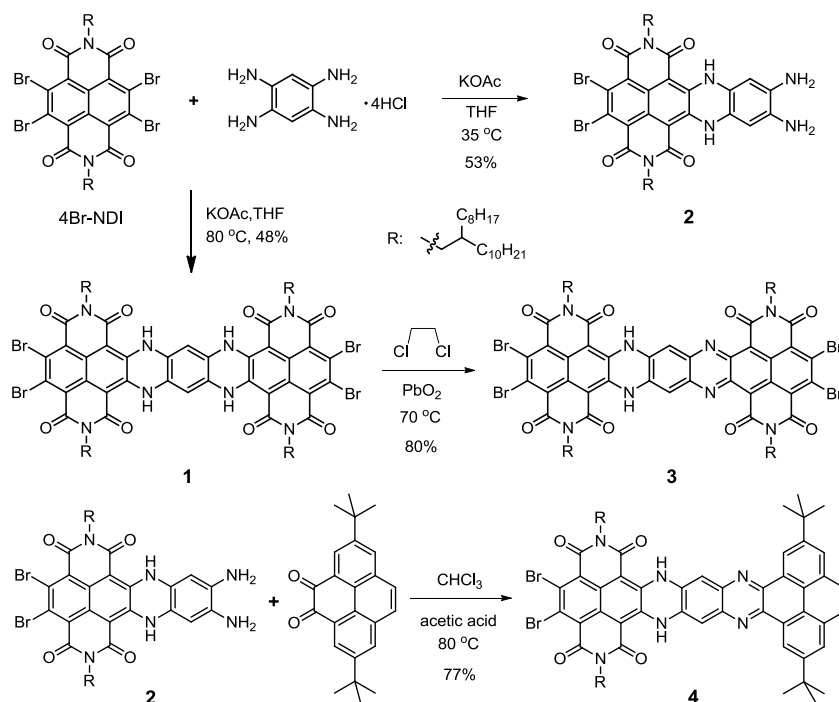
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I. Synthetic Procedures and Characterizations

General Methods. Chemicals were used as received unless otherwise indicated. All oxygen or moisture sensitive reactions were performed under nitrogen atmosphere using the standard Schlenk method. ^1H and ^{13}C NMR spectra were recorded on Mercury plus 300 (300 MHz), Bruker Avance 400 (400 MHz), or Bruker Avance 500 (600 MHz) using CDCl_3 as the solvent unless otherwise noted. Chemical shifts were reported in parts per million (ppm) with TMS (0 ppm) as the reference for ^1H NMR spectra and CDCl_3 (77.0 ppm) as reference for ^{13}C NMR spectra. MALDI-TOF mass spectra were recorded on a Bruker BIFLEX III time-of-flight (TOF) mass spectrometer using a 337 nm nitrogen laser as the matrix. ESI mass spectra were recorded on a Bruker Apex IV Fourier transformation mass spectrometer. Elemental analyses were performed using a German Vario EL III elemental analyzer.

Synthetic Procedures



Scheme S1. Syntheses of studied molecules.

1: A mixture of 4Br-NDI¹ (900 mg, 0.79 mmol), KOAc (352 mg, 3.6 mmol) and benzene-1,2,4,5-tetraamine (84 mg, 0.30 mmol) in THF (30 mL) was heated at 80 °C for 36 h under nitrogen atmosphere. Then the reaction mixture was diluted with dichloromethane (DCM, 50 ml) and washed with water for three times. The organic solution was dried over anhydrous Na_2SO_4 and then solvents were removed *in vacuo*. The crude product was purified with column

chromatography over silica gel, eluted with dichloromethane/petroleum ether (DCM/PE=1/2, v/v) to afford **1** as a dark green solid (302 mg, yield: 48%). ^1H NMR (CDCl_3 , 300 MHz) δ 13.00 (s, 4H), 6.23 (s, 2H), 4.09 (d, $J = 5.7$ Hz, 8H), 1.92-1.91 (m, 4H), 1.26-1.05 (m, 128H), 0.87-0.84 (m, 24H). ^{13}C NMR (CDCl_3 , 75 MHz) δ 164.7, 159.9, 139.8, 128.4, 126.3, 126.0, 121.6, 102.4, 95.9, 43.6, 36.3, 31.9, 31.7, 30.3, 29.7, 29.4, 26.5, 22.7, 14.2. MALDI-TOF MS: Calcd. for $\text{C}_{114}\text{H}_{170}\text{Br}_4\text{N}_8\text{O}_8$: 2100.0; Found: 2100.8. Elem. Anal.: Calcd. for $\text{C}_{114}\text{H}_{170}\text{Br}_4\text{N}_8\text{O}_8$: C, 65.19; H, 8.16; N, 5.34. Found: C, 65.32; H, 8.11; N, 5.06.

3: A mixture of **1** (50 mg, 0.024 mmol) and PbO_2 (500 mg, 3.1 mmol) in 1,2-dichloroethane (10 mL) was heated at 70°C for 1 h. Then PbO_2 solid was removed by filtration and the solvents were removed *in vacuo*. The crude product was purified with column chromatography over silica gel, eluted with DCM to afford **3** as a dark cyan solid (40 mg, yield: 80%). ^1H NMR (CDCl_3 , 300 MHz) δ 13.37 (s, 2H), 7.30 (s, 2H), 4.17 (d, $J = 6.6$ Hz, 8H), 2.11-1.96 (m, 4H), 1.60-1.24 (m, 128H), 0.88-0.82 (m, 24H). ^{13}C NMR (CDCl_3 , 75 MHz) δ 165.0, 161.1, 159.63, 159.56, 145.1, 139.4, 136.3, 136.0, 133.7, 130.6, 126.4, 126.3, 123.7, 122.9, 119.4, 110.0, 100.4, 46.3, 45.9, 36.6, 31.95, 31.94, 31.8, 30.4, 30.33, 30.28, 30.1, 29.80, 29.78, 29.76, 29.7, 29.6, 29.5, 29.44, 29.40, 26.52, 26.49, 22.70, 22.66, 14.10. HR-ESI MS: Calcd. for $\text{C}_{114}\text{H}_{169}\text{Br}_4\text{N}_8\text{O}_8$ ($\text{M}+\text{H}^+$): 2098.9789; Found: 2098.9736. Elem. Anal.: Calcd. for $\text{C}_{114}\text{H}_{168}\text{Br}_4\text{N}_8\text{O}_8$: C, 65.26; H, 8.07; N, 5.34. Found: C, 65.20; H, 7.82; N, 5.14.

2: A mixture of 4Br-NDI^I (125 mg, 0.11 mmol), KOAc (120 mg, 1.2 mmol) and benzene-1,2,4,5-tetraamine (29 mg, 0.10 mmol) in THF (15 mL) was heated at 35°C for 12 h. Then the reaction mixture was diluted with DCM (50 mL), and washed with water for three times. The organic solution was dried over anhydrous Na_2SO_4 and then solvents were removed *in vacuo*. The crude product was purified with column chromatography over silica gel, eluted with DCM/MeOH (30/1, v/v) to afford **2** as a green solid (59 mg, yield: 53%). ^1H NMR (CDCl_3 , 300 MHz) δ 13.20 (s, 2H), 6.05 (s, 2H), 4.19 (d, $J = 7.5$ Hz, 4H), 3.59 (s, 4H), 1.93 (br, 2H), 1.23-1.16 (m, 64H), 0.88-0.82 (m, 12H). ^{13}C NMR (CDCl_3 , 75 MHz) δ 164.0, 160.4, 140.2, 135.5, 127.7, 124.9, 120.3, 119.8, 103.2, 93.3, 44.7, 36.2, 31.9, 31.7, 30.2, 29.7, 29.63, 29.59, 29.4, 29.3, 26.5, 22.6, 14.0. ESI MS: Calcd. for $\text{C}_{60}\text{H}_{90}\text{Br}_2\text{N}_6\text{O}_4$: 1118.5; Found: 1118.5. Elem. Anal.: Calcd. for $\text{C}_{60}\text{H}_{90}\text{Br}_2\text{N}_6\text{O}_4$: C, 64.39; H, 8.11; N, 7.51. Found: C, 64.42; H, 8.03; N, 7.39.

4: A mixture of **2** (66 mg, 0.059 mmol), 2,7-di(*tert*-butyl)pyrene-4,5-dione (24 mg, 0.070 mmol)

in CHCl_3 (3 ml) and HOAc (3 mL) was heated at 80°C for 30 min. Then the reaction mixture was diluted with DCM, and washed with water for three times. The organic solution was dried over anhydrous Na_2SO_4 and then solvents were removed *in vacuo*. The crude product was purified with column chromatography over silica gel, eluted with DCM/PE (3/2, v/v) to afford **4** as a green solid (65 mg, yield: 77%). ^1H NMR (CDCl_3 , 300 MHz) δ 12.30 (s, 2H), 9.03 (s, 2H), 7.73 (s, 2H), 7.08 (s, 2H), 6.09 (s, br, 2H), 3.99 (s, br, 4H), 1.66 (s, br, 2H), 1.42 (s, 18H), 1.28-1.24 (m, 64H), 0.87-0.83 (m, 12H). ^{13}C NMR (CDCl_3 , 75 MHz) δ 143.5, 133.1, 132.7, 131.8, 130.0, 128.7, 127.9, 127.4, 126.5, 126.0, 125.2, 123.0, 121.6, 92.4, 91.0, 89.8, 39.3, 31.93, 31.91, 31.55, 30.3, 29.78, 29.75, 29.72, 29.69, 29.40, 29.36, 27.0, 22.7, 14.2, 14.1. MALDI-TOF MS: Calcd. for $\text{C}_{84}\text{H}_{110}\text{Br}_2\text{N}_6\text{O}_4$: 1426.7; Found: 1427.4. Elem. Anal.: Calcd. for $\text{C}_{84}\text{H}_{110}\text{Br}_2\text{N}_6\text{O}_4$: C, 70.67; H, 7.77; N, 5.89. Found: C, 70.91; H, 7.89; N, 5.76.

II. Absorption and Emission Spectra

UV-vis-IR absorption spectra of the compounds were recorded on a Hitachi U-4100 spectrophotometer using 1-cm quartz cell. The emission spectra of compound **1** and **3** in n-hexane and film, as well as that of **1** in CHCl_3 , were recorded on a Nanolog FL3-2iHR fluorescence spectrometer with an InGaAs detector. The emission spectra of **3** and **4** in CHCl_3 and those of **4** in n-hexane and thin film were recorded on a Perkin Elmer LS55 Luminescence Spectrometer. Due to the limitation of detector sensitivity range, the spectrum of **3** in CHCl_3 was collected up to 900 nm. The emission spectra shown in Figures 2 and 4 were corrected using the correction curves provided by the instruments, and the corresponding uncorrected spectra are displayed in Fig. S9. Solvents DCM, CHCl_3 and n-hexane were distilled over CaH_2 prior to use.

The emission quantum yield of **1** in CHCl_3 was determined at 5.0×10^{-7} M using IR-140 in ethanol ($\Phi_{\text{fl}}=0.167$; excited at 720 nm) as the standard.² The apparent emission quantum yield of J-aggregated **1** in hexane was estimated likely with a relatively large error bar, due to the lack of suitable standard absorbing and emitting at >900 nm. Molecule IR-140 ($\lambda_{\text{em}}=843$ nm) was the closest choice, but neither its absorption nor emission perfectly match those of aggregated **1**. The Φ value of IR-140 was assumed not to change significantly when excited at different wavelengths, and the measurement was carried out by exciting at 775 nm. Moreover, due to the very small Stokes shift and intense absorption of J-band around 900 nm, the Φ measurement was carried out

at a very low concentration of 2.5×10^{-7} M, when the optical density (OD) at the excitation wavelength was near the instrument detection limit, while OD at 905 nm was still slightly >0.1 . Minor self-absorption was inevitable. The emission quantum yield of **4** in CHCl_3 was measured using Nanolog FL3-2iHR fluorescence spectrometer with an integrating sphere system.

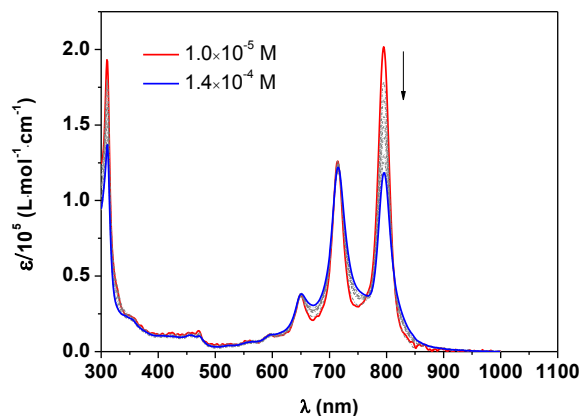


Figure S1. Varied-concentration absorptions of **1** in CHCl_3 (arrows indicate the direction of change at increased concentrations).

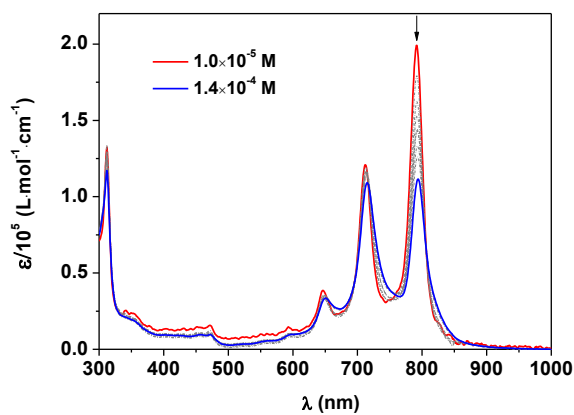


Figure S2. Varied-concentration absorptions of **1** in toluene (arrows indicate the direction of change at increased concentrations).

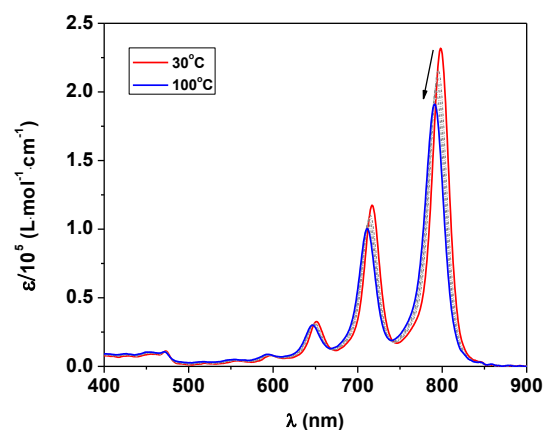


Figure S3. Absorptions of **1** in 1-chlorobenzene (5.0×10^{-6} M) at varied temperatures between 30 °C (red line) and 100 °C (blue solid). Arrows indicate the direction of change at increased temperature.

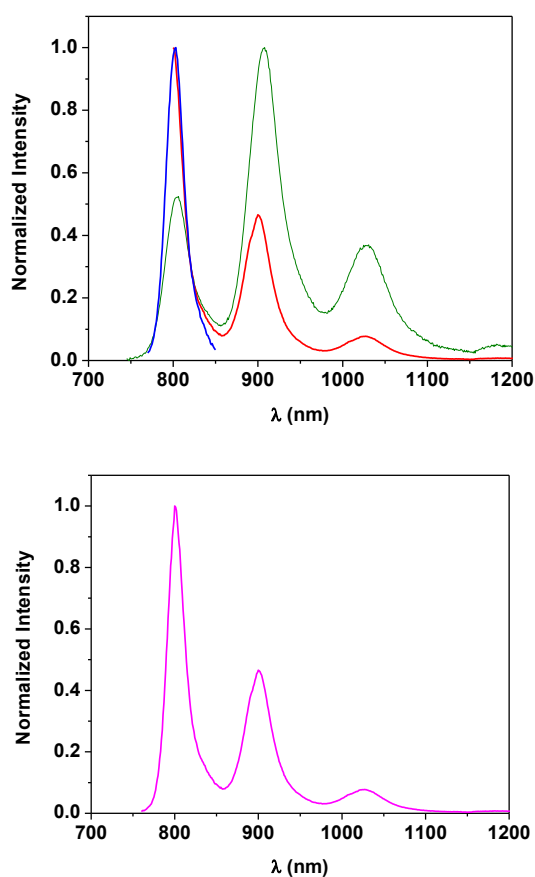


Figure S4. Normalized emission spectra (1.0×10^{-6} M, excited at 720 nm) of **1** in CHCl_3 . Due to the detection sensitivity limit of the InGaAs detector on Nanolog FL3-2iHR spectrometer, the uncorrected (green) and corrected (red) spectra show different intensity for 0-0 and 0-1 bands. The instrument correction only works in the range of ≥ 800 nm, so the corrected spectrum (red line) begins at 800 nm. Partial emission spectrum (blue line, corrected) was also recorded from Perkin Elmer LS55 Luminescence Spectrometer. The complete, corrected emission spectrum shown in the inset of Figure 2 (reproduced here as the purple line) was an overlay of partial blue line (< 801 nm, i.e., the left side of the 0-0 peak) and red line (≥ 801 nm, i.e., the right side of the 0-0 peak).

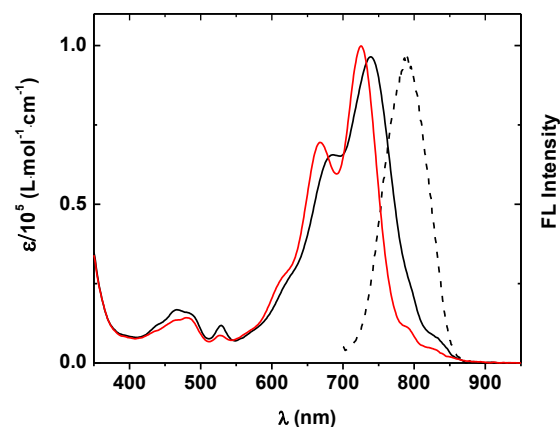


Figure S5. Absorption (solid, 1.0×10^{-5} M) and emission (dashed, 5.0×10^{-7} M excited at 680 nm) spectra of **3** in chloroform (black) and toluene (red).

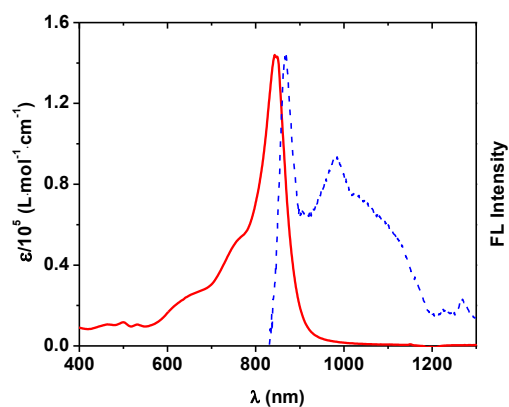


Figure S6. Absorption (solid, 1.0×10^{-5} M) and emission (dashed, 4.0×10^{-6} M excited at 750 nm) spectra of aggregated **3** in n-hexane.

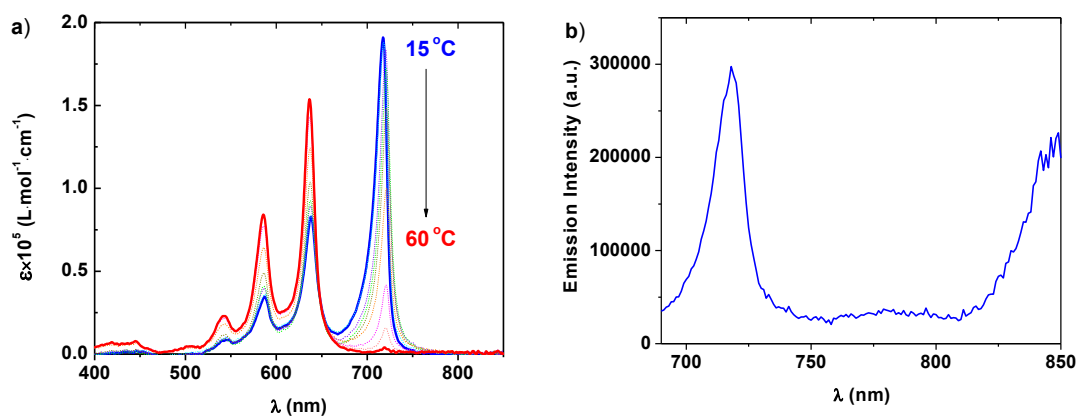


Figure S7. a) Absorptions of **4** in octane (2.0×10^{-6} M) at varied temperatures between 15 (blue solid) and 60 °C (red solid); b) emission spectrum of **4** in n-hexane (1.0×10^{-6} M, excited at 660 nm).

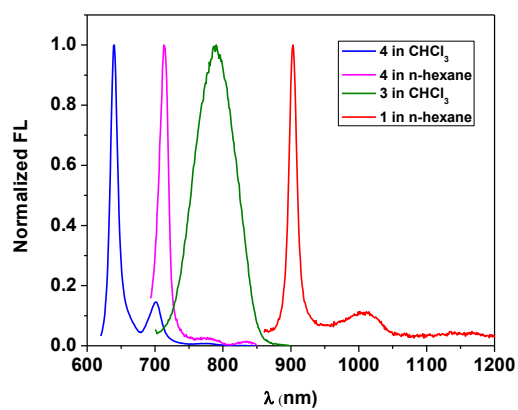


Figure S8. Normalized, uncorrected emission spectra. Red line: **1** in n-hexane; green line: **3** in CHCl_3 ; purple line: **4** in n-hexane; blue line: **4** in CHCl_3 .

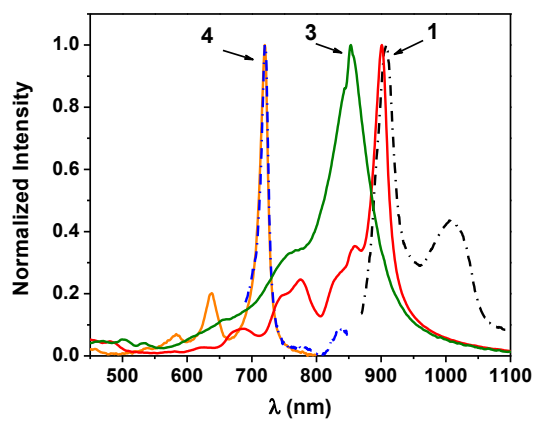


Figure S9. Normalized absorption (solid) and emission (dash dot) spectra of **1**, **3**, and **4** in thin films.

III. Electrochemical Characterizations

Cyclic voltammetry was performed using BASI Epsilon workstation and the measurements were carried out in dichloromethane containing 0.1 M n-Bu₄NPF₆ as the supporting electrolyte. Glassy carbon electrode was used as a working electrode and a platinum sheet as a counter electrode. All potentials were recorded versus Ag/AgCl as a reference electrode, and ferrocene/ferrocenium as an external reference. CH₂Cl₂ was freshly distilled over CaH₂ prior to use. The redox potential of Fc/Fc⁺ is assumed to be -4.8 eV below the vacuum level.^{3,4} The LUMO levels of **1** and **2** were estimated from the half-wave potentials of the reduction peaks. The half-wave potential of oxidation peak of Fc was measured to be 0.48 V against Ag/AgCl.

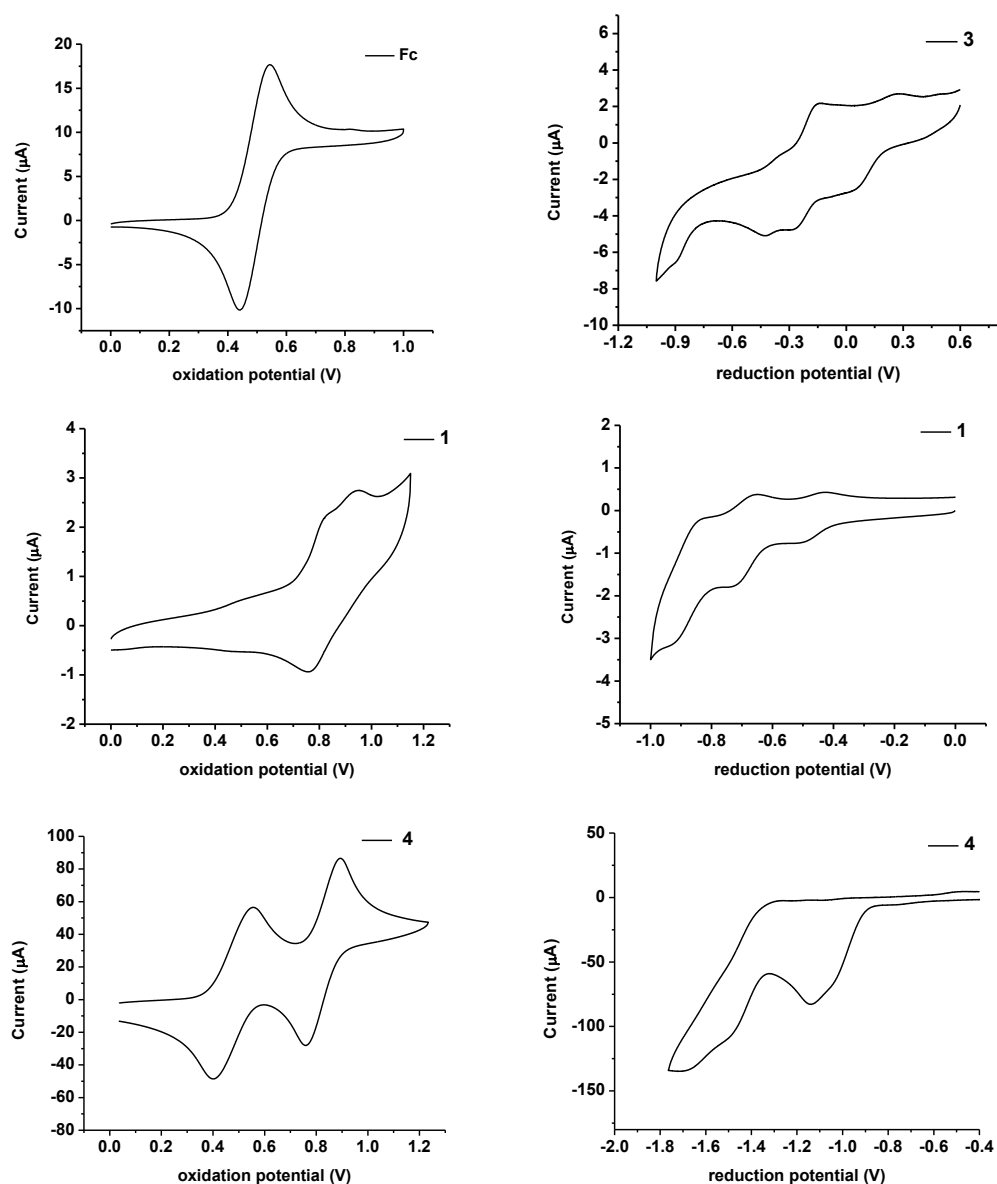


Figure S10. CVs of ferrocene, **1**, **3** and **4**.

IV. DFT and TD-DFT Calculations

The geometry the molecules was optimized with Density Functional Theory (DFT) using B3LYP hybrid functional⁵ with a basis set limited to 6-31g(d,p). Molecular orbital shapes and energies were obtained at optimized geometries. TD-DFT calculations were performed at optimized geometries with theory level at B3LYP/6-31g(d,p). Quantum-chemical calculations were performed with the Gaussian03 package⁶ and the orbital pictures were prepared using Gaussview⁷. All long alkyl substituents were replaced with methyl groups in calculations.

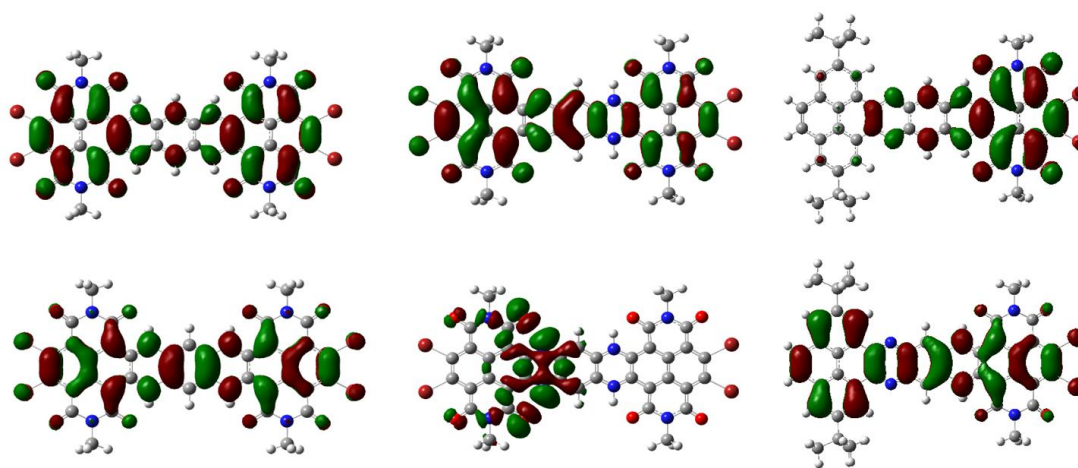


Figure S11. DFT calculated LUMO (top) and HOMO (bottom) of **1** (left), **3** (middle) and **4** (right).

V. References

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Copies of ^1H and ^{13}C NMR Spectra

