

Diazapentacene Derivatives: Synthesis, Properties, and Structures.

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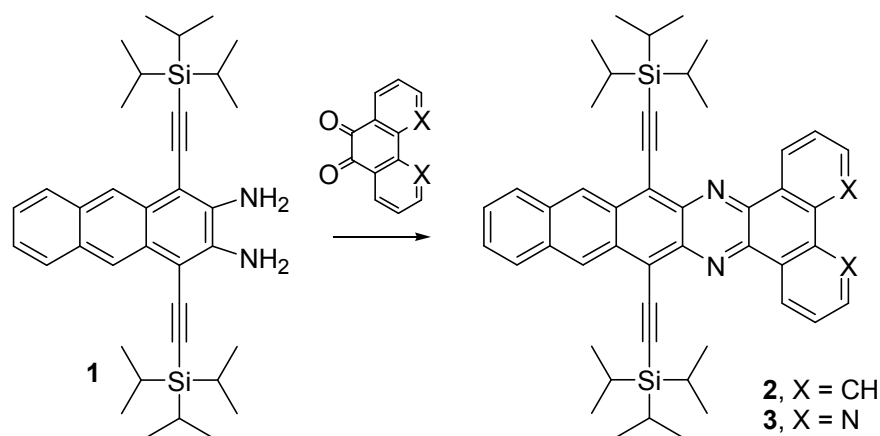
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Synthesis

All reagents and solvents were obtained from commercial suppliers and used without further purification except for tetrahydrofuran (THF) that had been distilled over sodium/benzophenone. 1,4-Bis((triisopropylsilyl)ethynyl)anthracene-2,3-diamine (**1**)^{1,2} was synthesized according to the literature. ¹H-NMR (300 MHz) and ¹³C-NMR (75 MHz) spectra were recorded on a Bruker DRX-300 spectrometer at room temperature. Infrared spectra were recorded on a Thermo Scientific Nicolet iS5 FT-IR spectrometer with ATR accessory. Absorption spectra were recorded on a Hitachi U-4100. Emission spectra were recorded on a Hitachi F-7000 fluorescence spectrophotometer. High resolution mass spectrometry were recorded on a MAT 95 XP mass spectrometer. Melting points were determined with a melting point apparatus MEL-TEMP (Thermo Scientific) and are uncorrected. X-ray intensity data were collected at 120(10) K using a SuperNova, Dual, Cu at zero, Atlas diffractometer (Cu K α radiation, $\lambda = 1.54184$ Å). Cyclic voltammetry (CV) measurements were carried out on a CHI 760E Electrochemical workstation (Shanghai, China).



Synthesis of **2**: To the mixture of **1** (0.500 g, 0.879 mmol) in CH₃COOH (20.0 mL) was added phenanthrene-9,10-dione (0.201 g, 0.965 mmol, 1.10 equivalent) at r.t. The resultant mixture was

heated at 100 °C for 2.5 hours. The mixture was cooled down to r.t. and was added to 200 mL of H₂O. The mixture was then filtered and the precipitate was washed with H₂O (3x200mL), CH₃OH (3x100mL), and dried. The dark-green product **2** (0.321g, 49%) was obtained after column chromatography on silica gel using a Hex:CH₂Cl₂ (5:1, v/v) solvent mixture. m. p. = 342-344 °C. IR (ATR): 2939, 2889, 2862, 2134, 1602, 1449, 1354 cm⁻¹. ¹H-NMR (300 MHz, CDCl₃): δ = 9.59-9.56 (dd, *J* = 8.0 Hz, *J* = 1.4 Hz, 2H), 9.49 (s, 2H), 8.50-8.48 (d, *J* = 8.0 Hz, 2H), 8.10-8.07 (dd, *J* = 6.5 Hz, *J* = 3.2 Hz, 2H), 7.81-7.78 (dt, *J* = 7.2 Hz, *J* = 1.4 Hz, 2H), 7.72-7.69 (t, *J* = 7.2 Hz, 2H), 7.56-7.53 (dd, *J* = 6.6 Hz, *J* = 3.2 Hz, 2H), 1.45-1.42 ppm (m, 42H). ¹³C-NMR (75 MHz, CDCl₃): δ = 144.21, 139.97, 132.81, 132.72, 132.21, 131.18, 130.59, 128.66, 127.96, 127.44, 126.78, 126.58, 123.01, 120.44, 107.92, 103.68, 19.01, 11.80 ppm. HRMS (EI, 70ev): *m/z* [M]⁺ calcd for C₅₀H₅₆N₂Si₂: 740.3977u, found: 740.3960u.

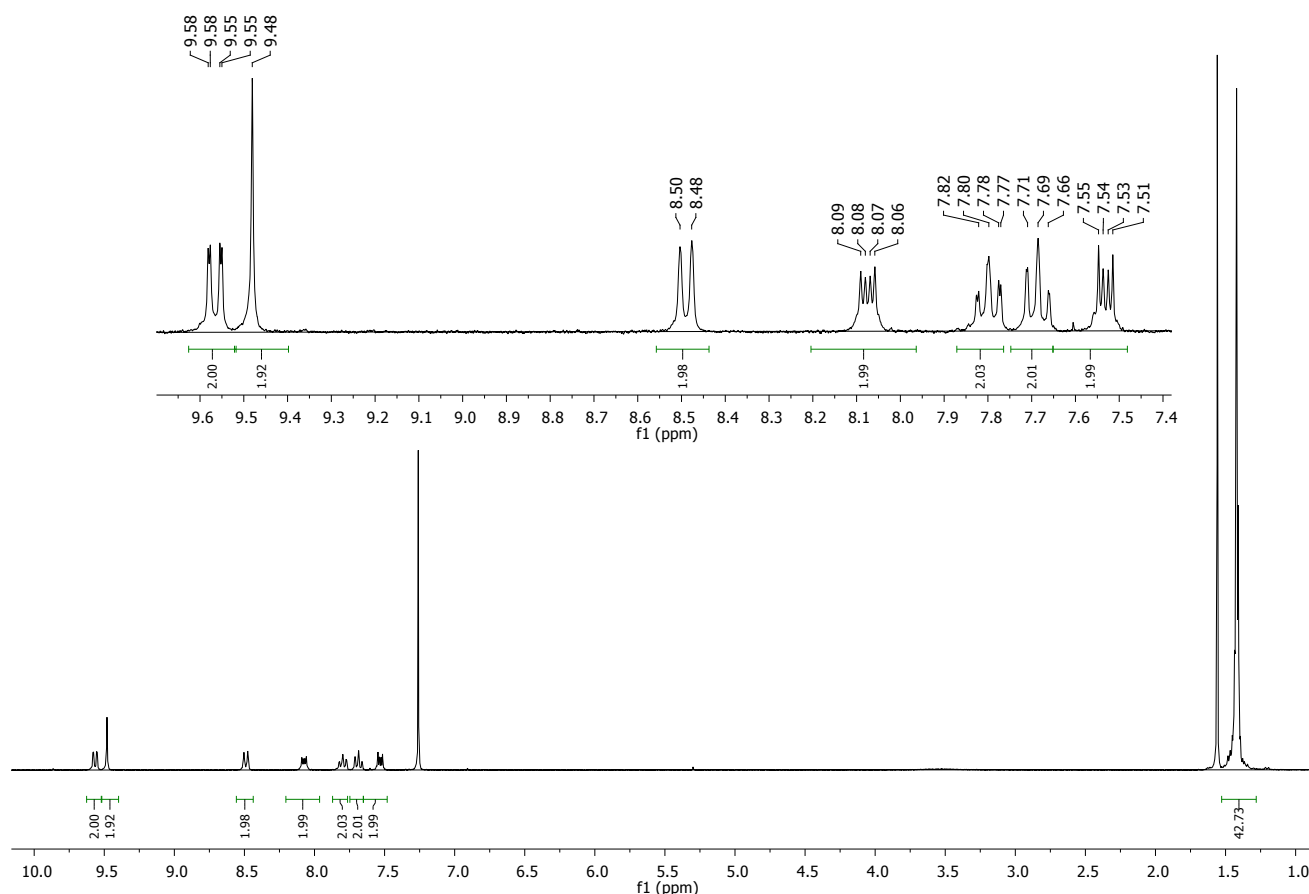


Figure S1. ¹H-NMR (300 MHz) spectrum of **2** in CDCl₃ at 300 K.

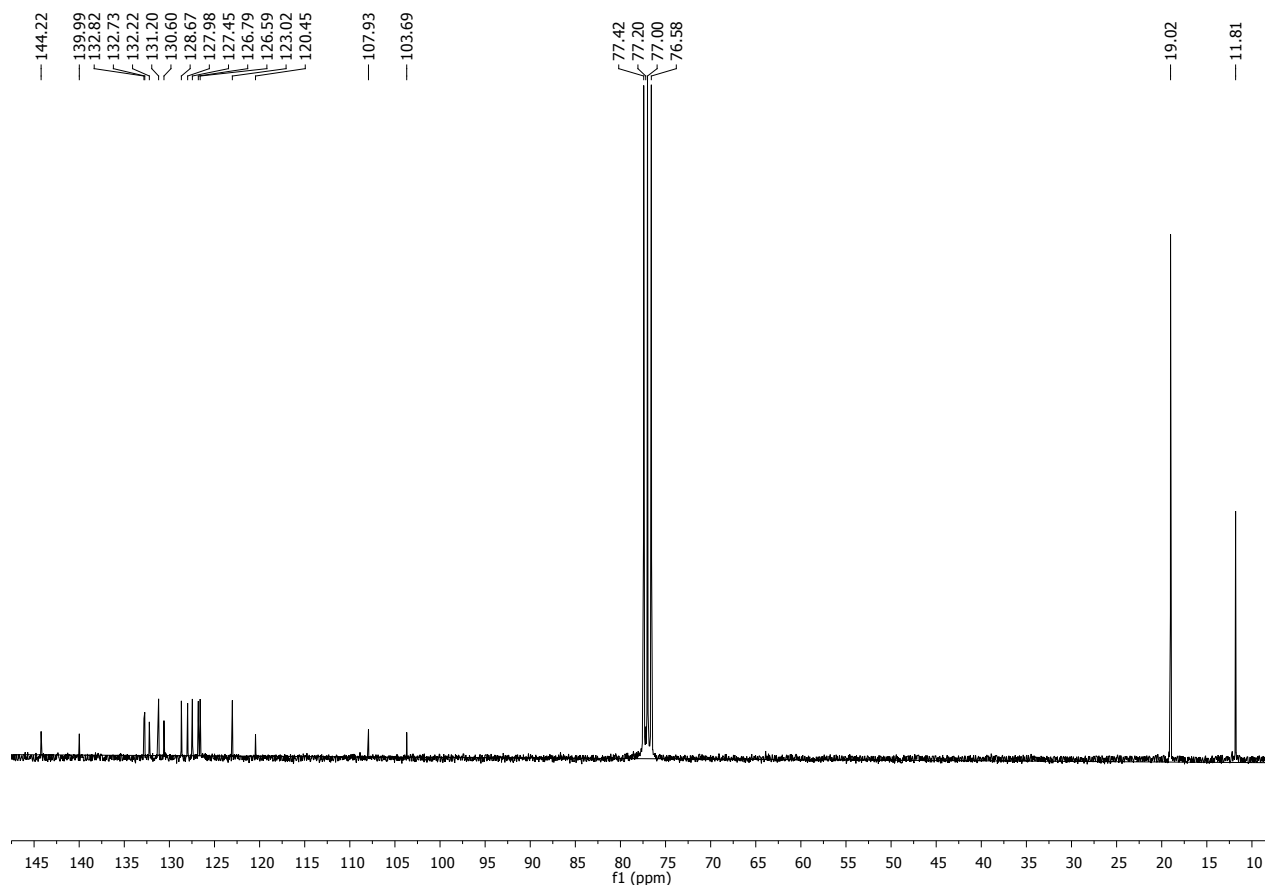


Figure S2. ^{13}C -NMR (75 MHz) spectrum of **2** in CDCl_3 at 300 K.

Synthesis of **3**: To the mixture of **1** (0.500 g, 0.879 mmol) in CH_3COOH (25.0 mL) was added 1,10-phenanthroline-5,6-dione (0.203 g, 0.966 mmol, 1.10 equivalent) at r.t. The resultant mixture was heated at 100 °C for 2.5 hours. The mixture was cooled down to r.t. and was added to 200 mL of H_2O . The mixture was then filtered and the precipitate was washed with H_2O (3x200mL), CH_3OH (3x100mL), and dried. The dark-green product **3** (0.430g, 66%) was obtained after column chromatography on silica gel using a CH_2Cl_2 :ethyl acetate (1:1, v/v) solvent mixture. m. p. = 350-352 °C. IR (ATR): 2941, 2863, 2128, 1587, 1460, 1354 cm^{-1} . ^1H -NMR (300 MHz, CDCl_3): δ = 9.78-9.75 (dd, J = 8.1 Hz, J = 1.8 Hz, 2H), 9.51 (s, 2H), 9.26-9.24 (dd, J = 4.5 Hz, J = 1.8 Hz, 2H), 8.11-8.07 (dd, J = 6.5 Hz, J = 3.3 Hz, 2H), 7.77-7.73 (dd, J = 8.1 Hz, J = 4.5 Hz, 2H), 7.58-7.55 (dd, J = 6.7 Hz, J = 3.3 Hz, 2H), 1.44-1.42 ppm (m, 42H). ^{13}C -NMR (75 MHz, CDCl_3): δ = 153.07, 149.37, 142.70, 139.76, 134.47, 133.04, 132.40, 128.67, 128.00, 126.99, 124.20, 120.98, 108.81, 103.31, 19.00, 11.75 ppm. HRMS (EI, 70ev): m/z [M] $^+$ calcd for $\text{C}_{48}\text{H}_{54}\text{N}_4\text{Si}_2$: 742.3882u, found: 742.3895u.

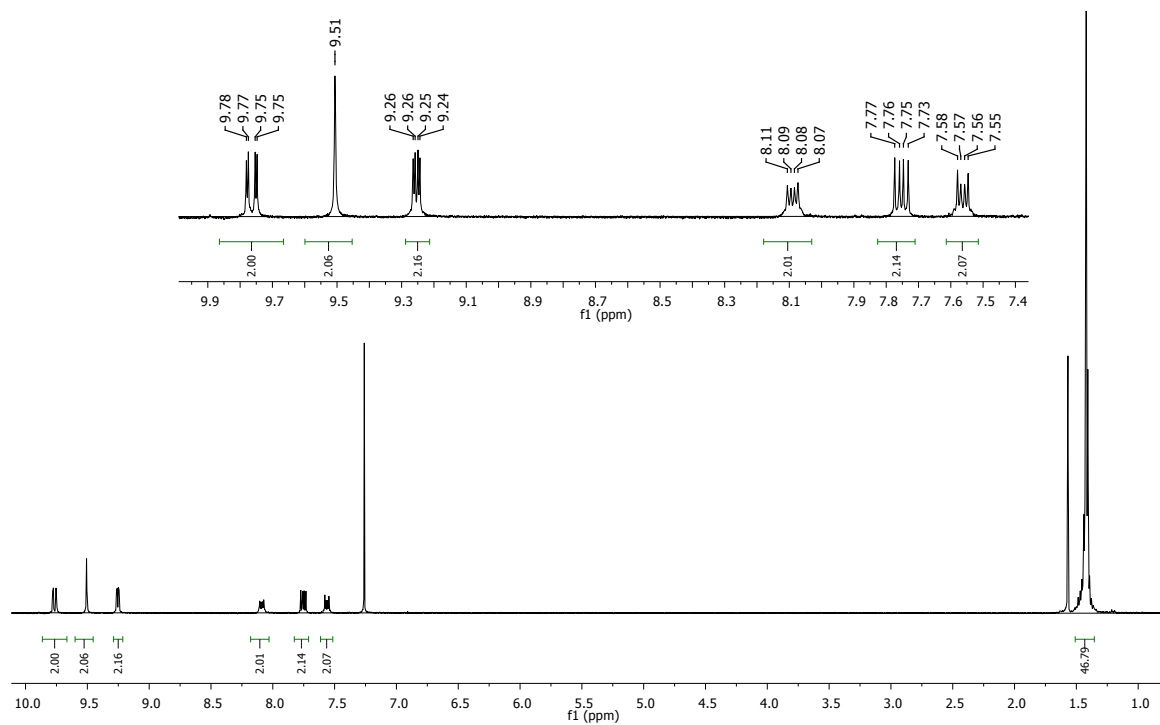


Figure S3. $^1\text{H-NMR}$ (300 MHz) spectrum of **3** in CDCl_3 at 300 K.

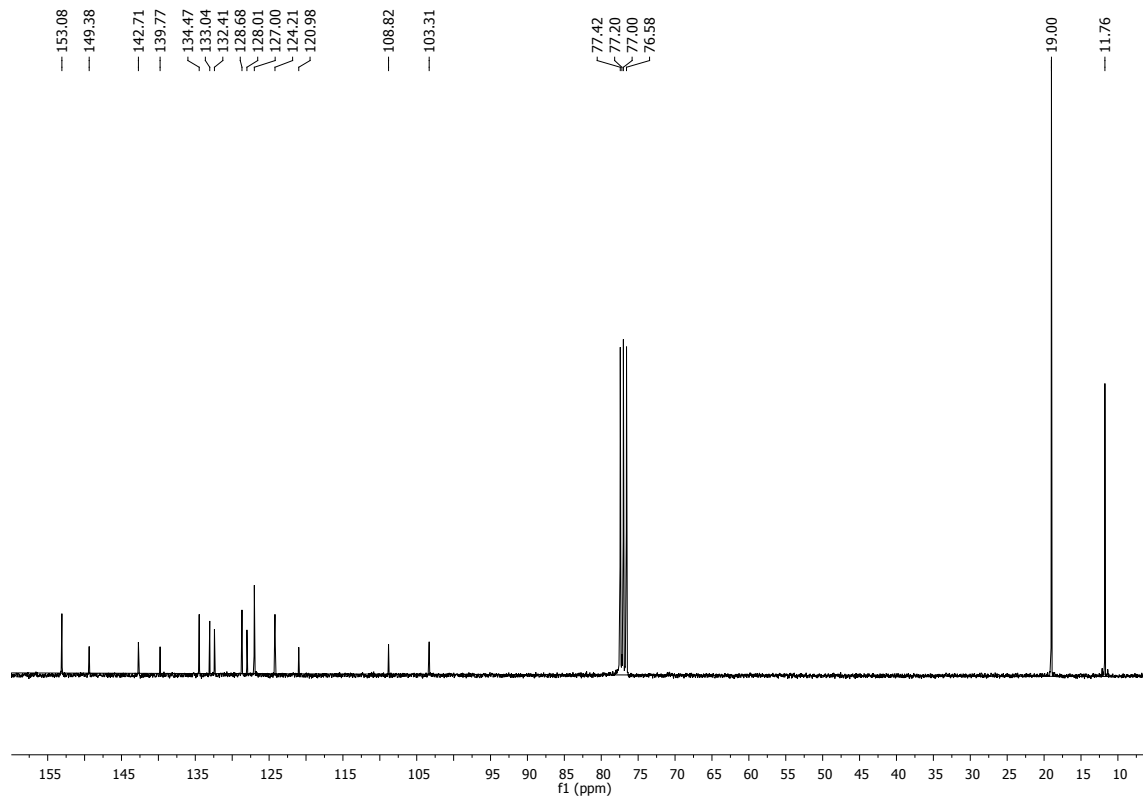


Figure S4. $^{13}\text{C-NMR}$ (75 MHz) spectrum of **3** in CDCl_3 at 300 K.

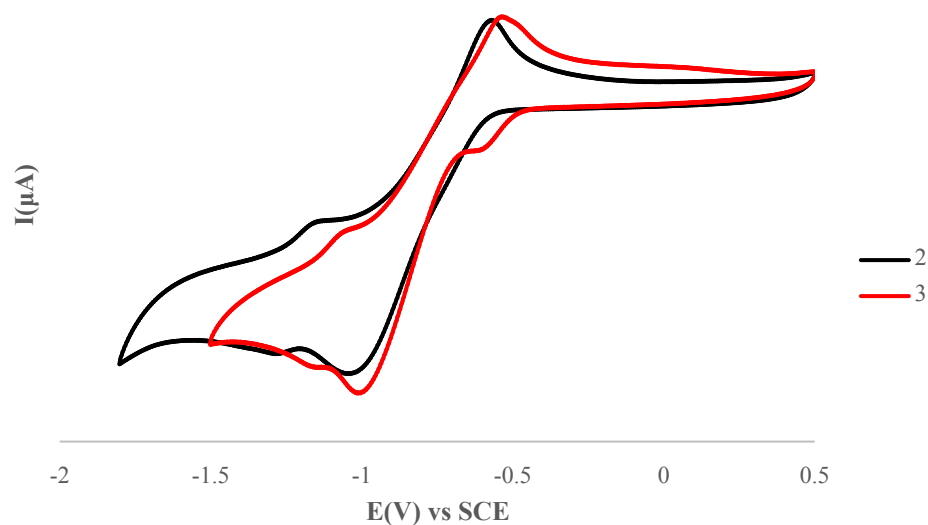


Figure S5. Cyclic voltammetry of **2** and **3** (0.4×10^{-3} M) on a glassy carbon electrode in CH_2Cl_2 + 0.1 M $n\text{-Bu}_4\text{NBF}_4$ at room temperature, scan at $v = 200$ mV/s. A glassy carbon electrode as the working electrode, a Pt wire as a counter electrode and a saturated calomel electrode (SCE) as a reference.

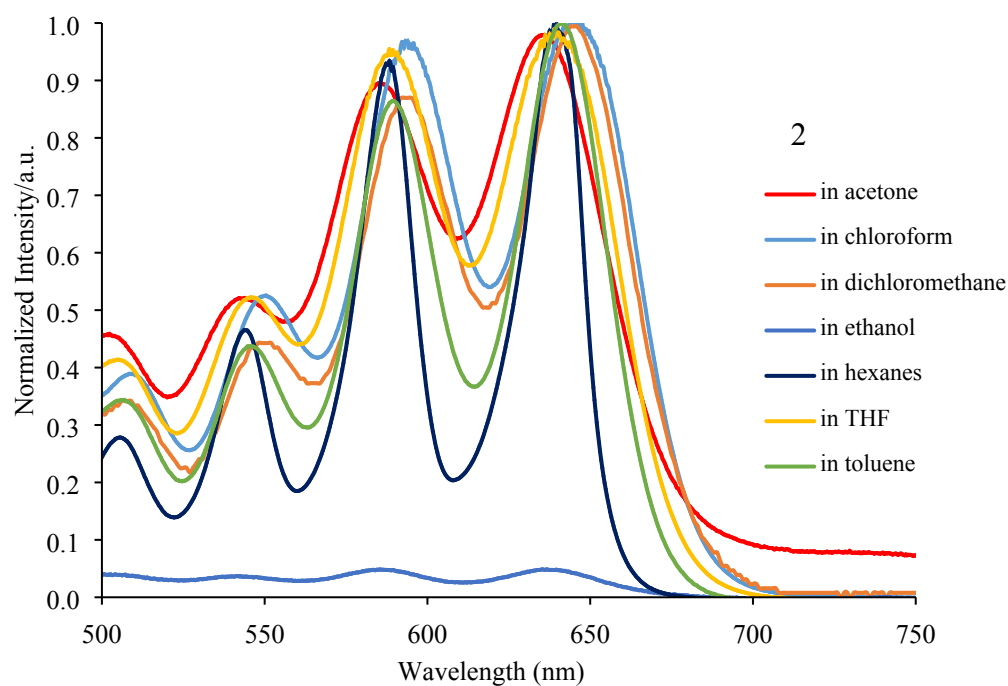


Figure S6. Normalized UV-vis absorption spectra of **2** in different solvents.

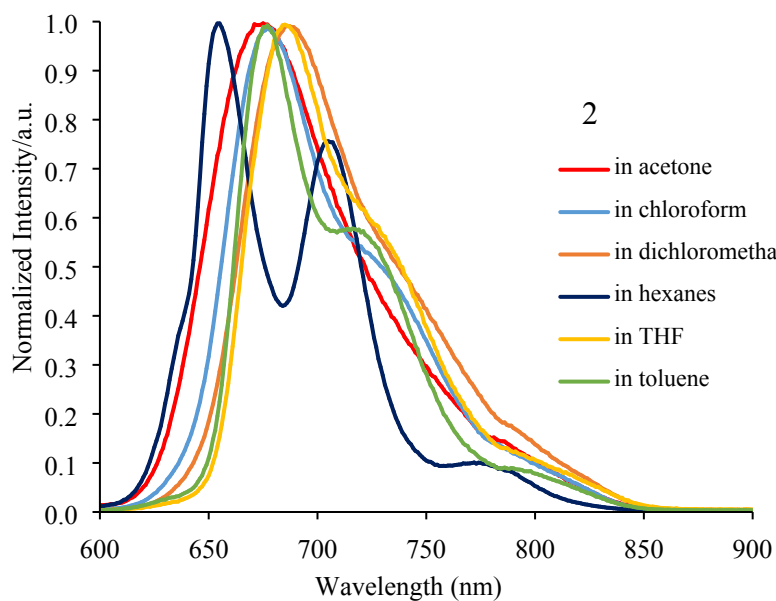


Figure S7. Normalized emission spectra of **2** in different solvents (excitation wavelength: 590nm).

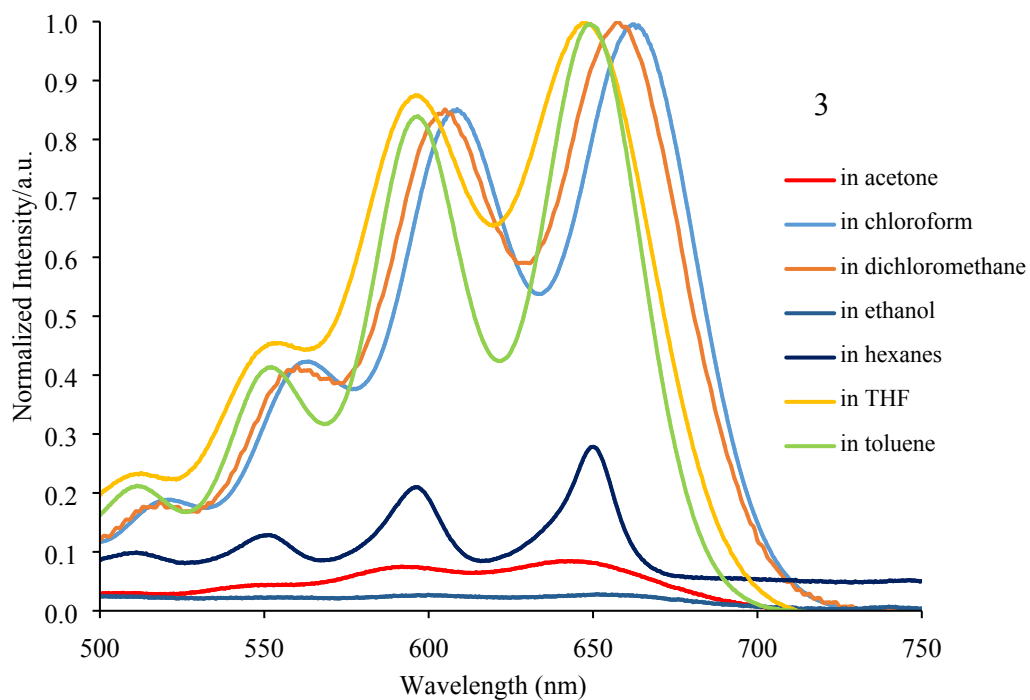


Figure S8. Normalized UV-vis absorption spectra of **3** in different solvents.

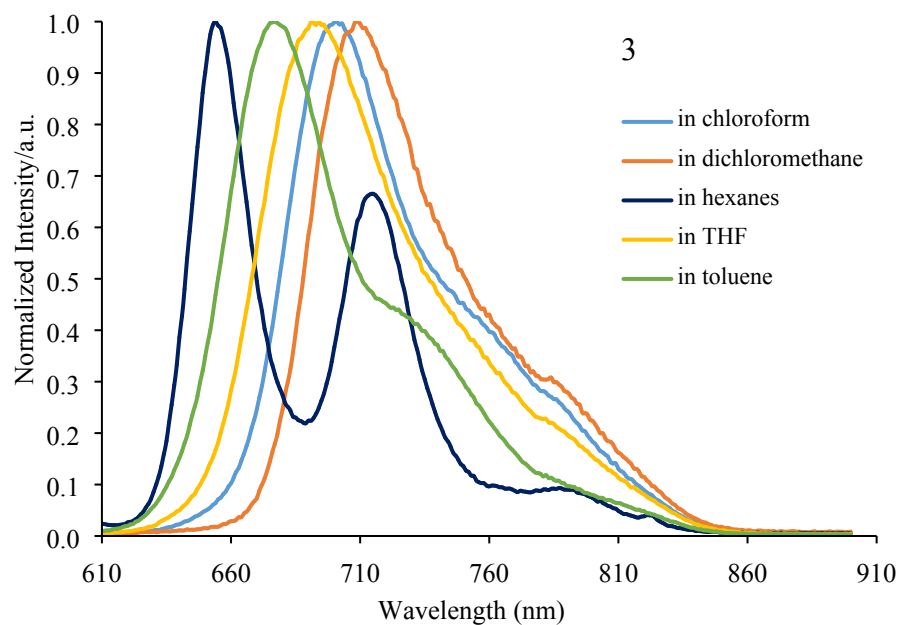


Figure S9. Normalized emission spectra of **3** in different solvents (excitation wavelength: 600nm).

References:

1. Appleton, A. L.; Brombosz, S. M.; Bralow, S.; Sears, J. S.; Bredas, J.-L.; Marder, S. R.; Bunz, U. H. F. *Nat. Commun.* **2010**, *1*, 91.
2. Appleton, A. L.; Miao, S.; Brombosz, S. M.; Berger, N. J.; Barlow, S.; Marder, S. R.; Lawrence, B. M.; Hardcastle, K. I.; Bunz, U. H. F. *Org. Lett.* **2009**, *11*, 5222-5225.