

## Electronic Supplementary Information

# A NIR Dye with High-performance N-type Semiconducting Property

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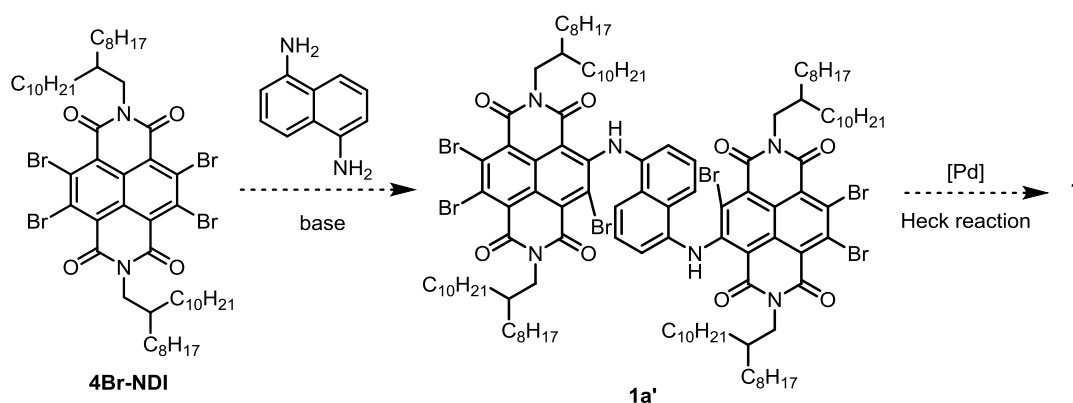
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## I. Synthetic Procedures and Characterizations

**General Methods.** Chemicals and solvents were purchased and used as received unless otherwise indicated. All oxygen and moisture sensitive reactions were performed under nitrogen atmosphere using the standard Schlenk method. Toluene and tetrahydrofuran (THF) were distilled over sodium and benzophenone.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Mercury plus 300, operating at 300 MHz ( $^1\text{H}$ ) and 75 MHz ( $^{13}\text{C}$ ), Bruker Avance 400, operating at 400 MHz ( $^1\text{H}$ ) and 101 MHz ( $^{13}\text{C}$ ), and Bruker-500, operating at 500 MHz ( $^1\text{H}$ ), using  $\text{CDCl}_3$  or  $\text{C}_2\text{D}_2\text{Cl}_4$  as the solvent. Chemical shifts are reported in parts per million (ppm) with TMS (0 ppm) as the reference for  $^1\text{H}$  NMR spectra and  $\text{CDCl}_3$  (77.04 ppm) as the reference for  $^{13}\text{C}$  NMR spectra. High-resolution ESI mass were recorded on a Bruker Apex IV Fourier transformation mass spectrometer. MALDI-TOF mass spectra were recorded on an MALDI-TOF/TOF Mass Spectrometer using CHCA as the matrix. Elemental analyses were performed using a German Vario EL III elemental analyzer. Atomic force microscopy studies were performed with a Nanoscope IIIa microscope.

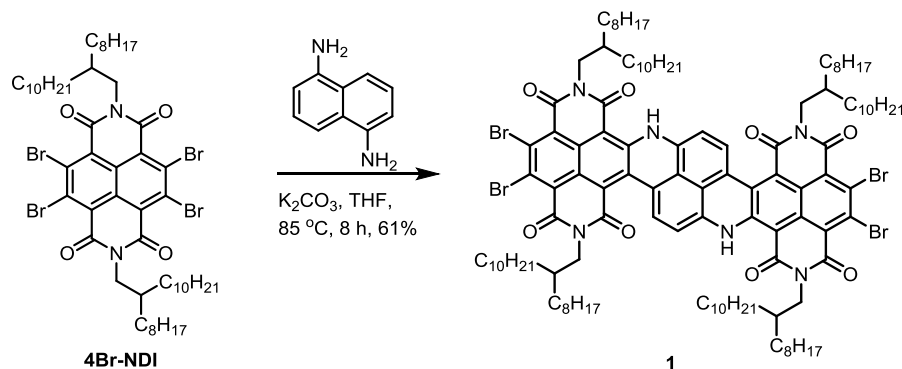
The absorption spectra were recorded on a Hitachi U-4100 spectrophotometer using 1 cm or 0.1 cm quartz cell. The emission spectra were recorded on NanoLog infrared fluorescence spectrometer. Cyclic voltammetry was performed using BASI Epsilon workstation and the measurements were carried out in chloroform containing 0.1 M  $n\text{-Bu}_4\text{NPF}_6$  as the supporting electrolyte. Glassy carbon electrode was used as a working electrode with a platinum sheet as a counter electrode. All potentials are reported vs.  $\text{Ag}/\text{AgCl}$  as the reference electrode, and ferrocene/ferrocenium was used as an external reference. The scan speed was  $100\text{ mV s}^{-1}$ . The potential of  $\text{Fc}^+/\text{Fc}$  is assumed to be  $-4.8\text{ eV}$  below the vacuum level.<sup>1,2</sup> The LUMO and HOMO levels were estimated from the onset potentials of the first reduction and first oxidation waves, respectively. The onset potential of oxidation peak of  $\text{Fc}^+/\text{Fc}$  was measured to be  $0.40\text{ V}$  against  $\text{Ag}/\text{AgCl}$ .



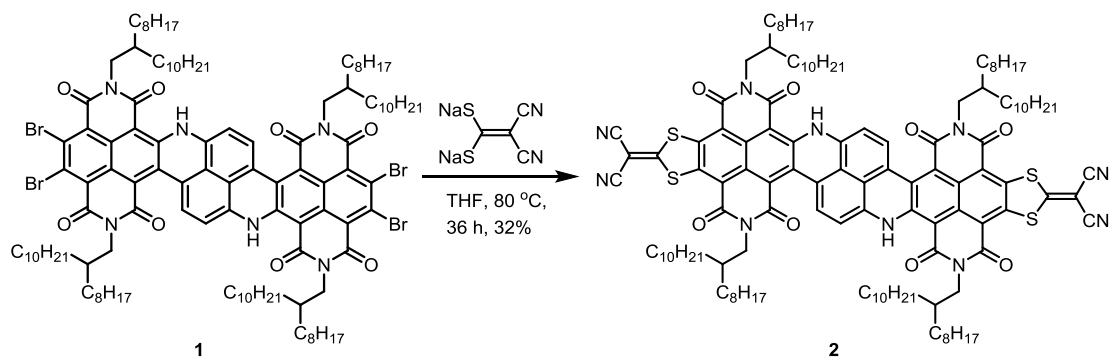
**Scheme S1.** Originally designed synthesis route of **1**.

### Synthetic procedures

**4Br-NDI** was synthesized according to the procedures reported in the literature.<sup>3</sup>

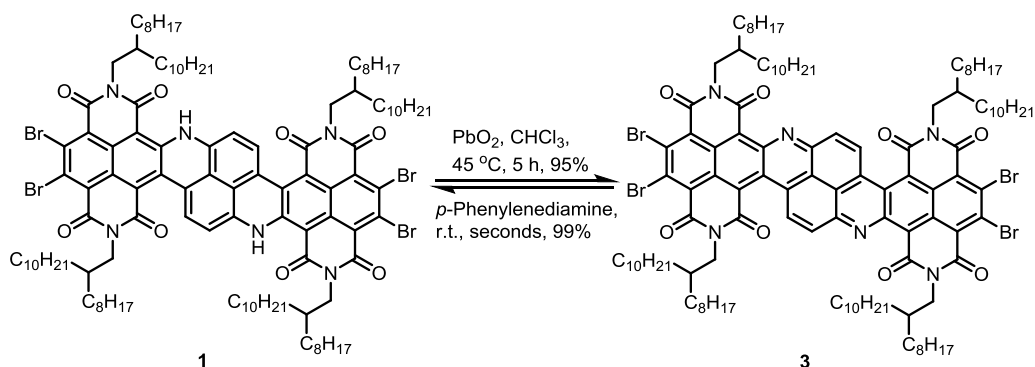


**1.** A Schlenk tube containing naphthalene-1,5-diamine (63 mg, 0.40 mmol), **4Br-NDI** (1.10 g, 1.20 mmol) and  $K_2CO_3$  (221 mg, 1.60 mmol) was evacuated and back-filled with nitrogen three times. After degassed THF (30 mL) was added via syringe, the tube was sealed under nitrogen atmosphere and heated at 85 °C for 8 h. After cooling to room temperature, the brown-green reaction mixture was diluted with petroleum ether (PE, 50 mL), washed with water (50 mL) for three times and then dried over anhydrous  $Na_2SO_4$ . Upon removal of solvents under reduced pressure, the residue was purified with silica gel column chromatography (PE/ $CH_2Cl_2$ , 4/1 to 1/2, v/v) to afford compound **1** (550 mg, 61%) as dark brown solid (decomposed at 284 °C in the air).  $^1H$  NMR (70 °C,  $C_2D_2Cl_4$ , 300 MHz, ppm):  $\delta$  13.78 (s, 2H), 7.75 (d,  $J = 8.4$  Hz, 2H), 6.84 (d,  $J = 8.3$  Hz, 2H), 4.05 (dd,  $J = 29.5, 5.7$  Hz, 8H), 1.91 (s, br, 4H), 1.17 (s, br, 128H), 0.78 (s, br, 24H).  $^{13}C$  NMR ( $CDCl_3$ , 101 MHz, ppm):  $\delta$  164.9, 163.5, 161.3, 159.9, 145.5, 136.8, 134.2, 132.8, 130.8, 127.8, 125.2, 124.9, 122.3, 121.3, 120.2, 119.8, 113.9, 98.2, 77.4, 77.0, 76.7, 53.4, 46.8, 45.6, 36.5, 36.3, 31.9, 31.8, 31.7, 30.2, 30.1, 30.1, 29.7, 29.7, 29.7, 29.4, 29.3, 26.6, 22.7, 14.1. MALDI-TOF MS: Calcd. for  $C_{118}H_{170}Br_4N_6O_8$  ( $M^+$ ): 2119.0; Found: 2119.4 (m/z). Elem. Anal.: Calcd. for  $C_{118}H_{170}Br_4N_6O_8$ : C, 66.84; H, 8.08; N, 3.96. Found: C, 67.12; H, 8.13; N, 3.89.



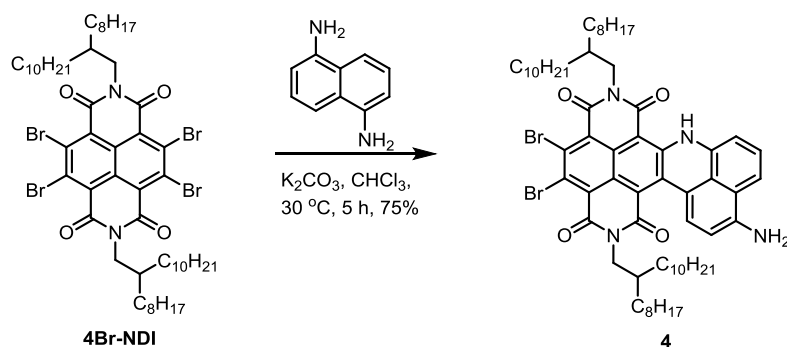
**2.** A Schlenk tube containing compound **1** (107 mg, 0.050 mmol) and sodium 1,1-dicyanoethylene-2,2-dithiolate (23 mg, 0.15 mmol) was evacuated and back-filled with nitrogen three times. After degassed THF (3 mL) was added, the tube was sealed under nitrogen atmosphere and heated at 80 °C for 36 h. After cooling to room temperature, the reaction mixture was diluted with  $CHCl_3$  (40 mL), washed with water (20 mL) for three times, and then dried over anhydrous  $Na_2SO_4$ . Upon removal of solvents under reduced pressure, the residue was purified with silica gel column chromatography (PE/ $CH_2Cl_2$ , 1/1, v/v) to afford compound **2** (41 mg, 32%) as a dark solid (decomposed at 332 °C in the air).  $^1H$  NMR (130 °C,  $C_2D_2Cl_4$ , 300 MHz, ppm):  $\delta$  13.64 (s, 2H), 7.96 (s, br, 2H), 6.94 (s, br, 2H), 4.11 (dd,  $J = 44.6, 7.1$  Hz, 6H), 1.98 (s, br, 4H),

1.63 – 0.98 (m, 128H), 0.77 (m, 24H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz, ppm):  $\delta$  182.2, 164.9, 163.1, 162.0, 161.5, 145.7, 142.0, 138.7, 137.0, 133.7, 131.4, 127.2, 125.6, 121.57, 120.35, 118.11, 117.08, 115.60, 114.70, 111.88, 98.47, 46.21, 45.67, 36.70, 36.5, 31.9, 31.7, 31.7, 30.3, 30.2, 29.8, 29.7, 29.4, 29.4, 26.6, 22.7, 14.1. MALDI-TOF MS: Calcd. for  $\text{C}_{126}\text{H}_{170}\text{N}_{10}\text{O}_8\text{S}_4$  ( $\text{M}^+$ ): 2080.2; Found: 2080.1 (m/z). Elem. Anal.: Calcd. for  $\text{C}_{126}\text{H}_{170}\text{N}_{10}\text{O}_8\text{S}_4$ : C, 72.72; H, 8.23; N, 6.73. Found: C, 72.93; H, 8.38; N, 6.46.

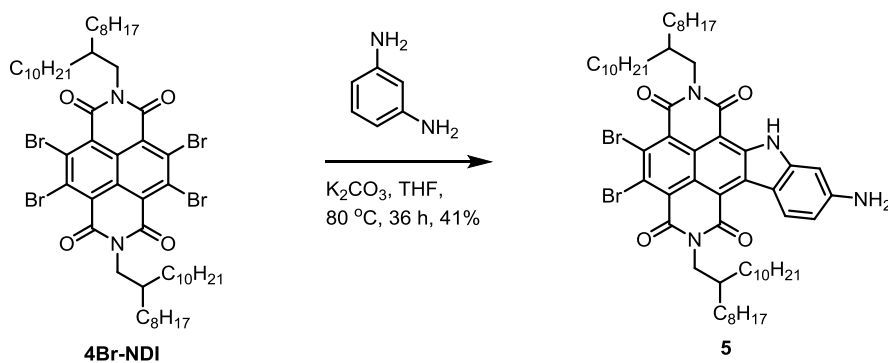


**3.** Compound **1** (50 mg, 0.025 mmol) was dissolved in  $\text{CHCl}_3$  (5 mL), and excess  $\text{PbO}_2$  was added to the solution. The mixture was heated at 45 °C for 5 h while TLC was conducted to monitor the reaction. After cooling to room temperature, the solid residue was filtered out. The filtrate was condensed under reduced pressure, and the residue was purified with flash silica gel column chromatography ( $\text{PE}/\text{CH}_2\text{Cl}_2$ , 3/1 to 1/3, v/v) to afford compound **3** (47 mg, 95%) as purple solid (decomposed at 203 °C in the air).  $^1\text{H}$  NMR (70 °C,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 300 MHz, ppm):  $\delta$  8.64 (br, 2H), 8.45 (br, 2H), 4.25 (br, 8H), 2.07 (s, br, 4H), 1.19 (m, 128H), 0.76 (m, 24H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz, ppm):  $\delta$  163.2, 161.3, 160.5, 159.6, 151.3, 151.2, 143.9, 142.1, 139.3, 138.0, 135.0, 133.2, 132.4, 130.4, 126.5, 125.6, 124.9, 124.0, 123.0, 121.7, 120.4, 115.5, 46.4, 36.7, 31.9, 30.2, 29.7, 29.3, 26.5, 22.7, 14.1. MALDI-TOF MS: Calcd. for  $\text{C}_{118}\text{H}_{168}\text{Br}_4\text{N}_6\text{O}_8$  ( $\text{M}^+$ ): 2117.0; Found: 2117.5 (m/z). Elem. Anal.: Calcd. for  $\text{C}_{118}\text{H}_{168}\text{Br}_4\text{N}_6\text{O}_8$ : C, 66.91; H, 7.99; N, 3.97. Found: C, 66.62; H, 7.97; N, 3.89.

**Reduction of 3 to 1.** Compound **3** (50 mg, 0.025 mmol, 1.0 eq.) was dissolved in  $\text{CHCl}_3$  (5 mL), and *p*-phenylenediamine (5 mg, 0.046 mmol, 1.8 eq.) was added to the solution. The purple mixture was converted to a yellow solution in a few seconds. The solvent was removed under reduced pressure and the solid was diluted with PE (20 ml). After washed with  $\text{MeOH}/\text{H}_2\text{O}$  (3/1, v/v) for several times to remove *p*-phenylenediamine and *p*-benzoquinone, the organic solution was dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After removal of the solvent under reduced pressure, the compound **1** was obtained in quantitatively yield.



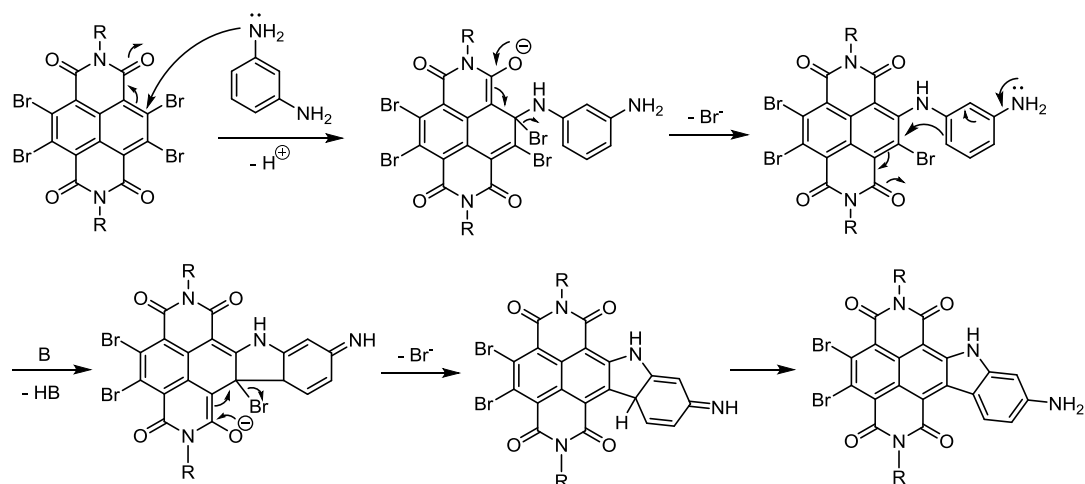
**4.** A Schlenk tube containing naphthalene-1,5-diamine (158 mg, 1.0 mmol), **4Br-NDI** (1.114 g, 1.0 mmol) and  $K_2CO_3$  (272 mg, 2.0 mmol) was evacuated and back-filled with nitrogen three times. After degassed  $CHCl_3$  (20 mL) was added via syringe, the tube was sealed and heated at 30 °C for 5 h. After cooling to room temperature, the green reaction mixture was diluted with PE (40 mL), washed with water (20 mL) for three times and then dried over anhydrous  $Na_2SO_4$ . Upon removal of solvents under reduced pressure, the residue was purified with silica gel column chromatography (PE/ $CH_2Cl_2$ =1/5, v/v) to afford compound **4** (830 mg, 75%) as green solid.  $^1H$  NMR ( $CDCl_3$ , 300 MHz, ppm):  $\delta$  13.38 (s, 1H), 7.66 (d,  $J = 8.4$  Hz, 1H), 7.15 (t,  $J = 7.5$  Hz, 1H), 7.02 (d,  $J = 7.9$  Hz, 1H), 6.76 (d,  $J = 7.0$  Hz, 1H), 6.02 (d,  $J = 8.1$  Hz, 1H), 4.93 (s, br, 2H), 4.09 (dd,  $J = 43.1, 6.8$  Hz, 4H), 1.93 (s, br, 2H), 1.23 (s, br, 64H), 0.92-0.82 (m, 12H).  $^{13}C$  NMR ( $CDCl_3$ , 75 MHz, ppm):  $\delta$  164.7, 164.1, 162.0, 160.4, 148.1, 146.8, 133.7, 133.5, 132.9, 129.7, 128.2, 126.0, 126.0, 125.3, 124.3, 123.6, 121.5, 120.2, 115.9, 115.5, 114.8, 113.0, 111.3, 95.7, 77.5, 77.0, 76.6, 46.4, 44.9, 36.6, 36.4, 31.9, 31.5, 30.2, 30.1, 29.7, 29.7, 29.6, 29.4, 29.3, 26.4, 26.3, 22.7, 14.1. HR ESI-MS: Calcd. for  $C_{64}H_{90}Br_2N_4O_4$  ( $M^+$ ): 1138.53084; Found: 1138.53102 (m/z).



**5.** A Schlenk tube containing *m*-phenylenediamine (5 mg, 0.046 mmol), **4Br-NDI** (52 mg, 0.046 mmol) and  $K_2CO_3$  (26 mg, 0.188 mmol) was evacuated and backfilled with nitrogen for three times. After degassed THF (4 mL) was added via syringe, the tube was sealed and heated at 80 °C for 36 h. After cooling to room temperature, the purple reaction mixture was diluted with petroleum ether (40 mL), washed with water (20 mL) for three times and then dried over anhydrous  $Na_2SO_4$ . Upon removal of solvents under reduced pressure, the residue was purified with silica gel column chromatography (PE/ $CH_2Cl_2$ , 4/1 to 1/2, v/v) to afford compound **5** (20 mg, 41%) as purple solid.  $^1H$  NMR ( $CDCl_3$ , 300 MHz, ppm):  $\delta$  10.92 (s, 1H), 9.05 (d,  $J = 7.5$  Hz, 1H), 6.53 (d,  $J = 7.5$  Hz, 1H), 6.48 (s, 1H), 4.40 (s, 1H), 4.29 – 4.22 (m, 4H), 2.06 (s, br, 2H), 1.00-1.50 (m, 64H), 0.70-0.99 (m, 12H).  $^{13}C$  NMR ( $CDCl_3$ , 101 MHz, ppm):  $\delta$  164.4, 162.8, 161.8, 161.5,

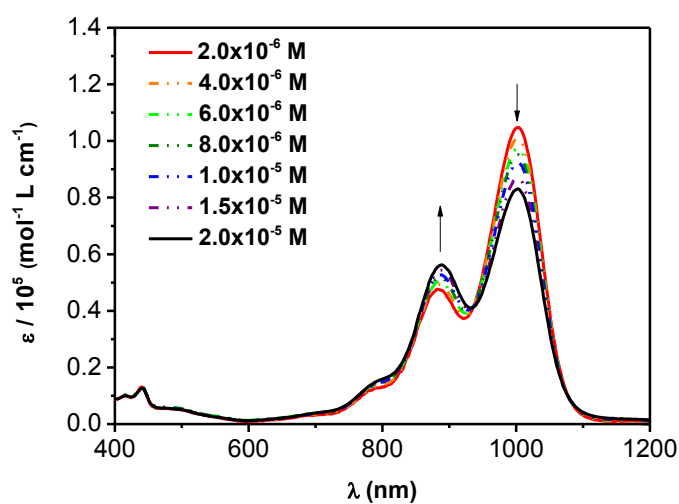
151.1, 147.0, 144.3, 132.1, 131.8, 130.9, 129.8, 125.7, 124.2, 123.6, 122.5, 115.8, 111.4, 110.5, 101.1, 95.2, 77.4, 77.0, 76.7, 45.7, 45.2, 36.6, 36.4, 31.9, 31.9, 31.8, 31.6, 30.2, 29.7, 29.7, 29.6, 29.4, 26.5, 26.4, 22.7, 14.1. HRESI FTMS: Calcd. for  $C_{60}H_{89}Br_2N_4O_4$  ( $M+H^+$ ): 1189.52301; Found: 1189.52379 ( $m/z$ ).

## II. Reaction Mechanisms

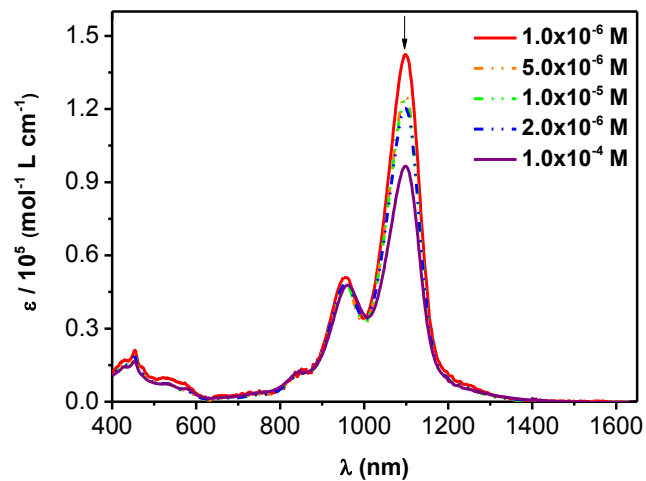


**Scheme S2.** Proposed mechanism of **5** ( $R = 2\text{-octyldodecyl}$ )

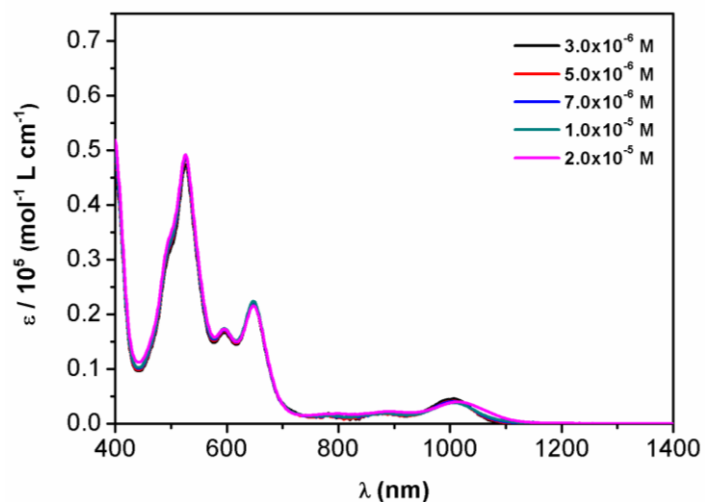
## III. Absorption and Emission Spectra



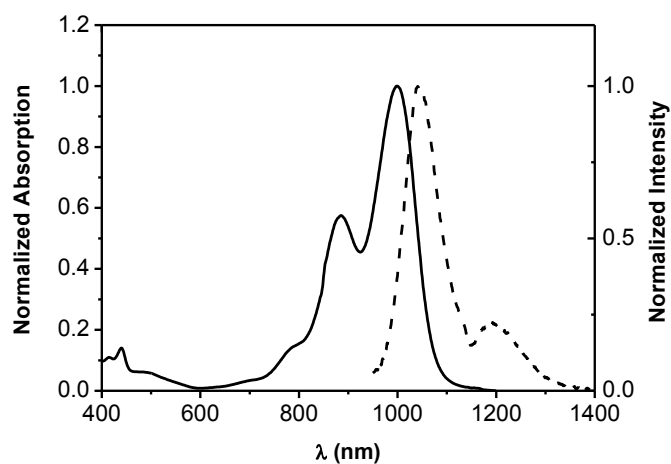
**Fig. S1** UV-vis-NIR spectra of **1** at varied concentrations in  $CHCl_3$  (arrows indicate the direction of change at increased concentration).



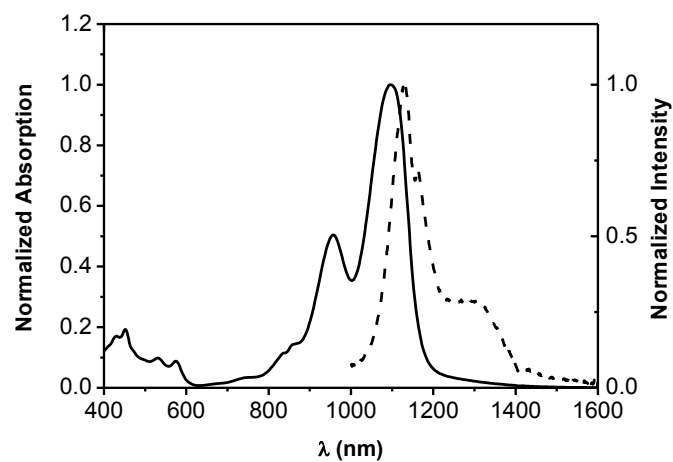
**Fig. S2** UV-vis-NIR spectra of **2** at varied concentrations in  $\text{CHCl}_3$  (arrow indicates the direction of change at increased concentration).



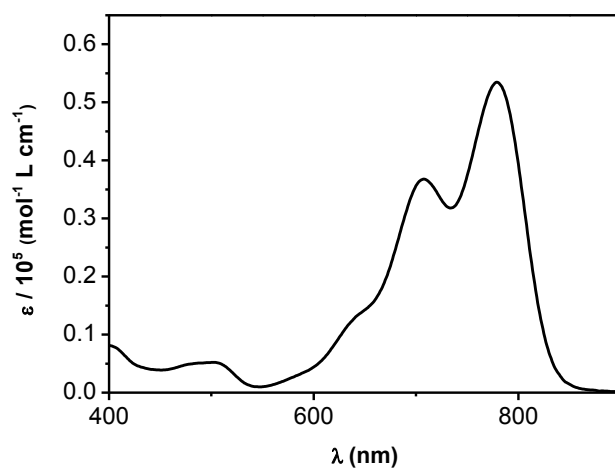
**Fig. S3** UV-vis-NIR spectra of **3** at varied concentrations in  $\text{CHCl}_3$ .



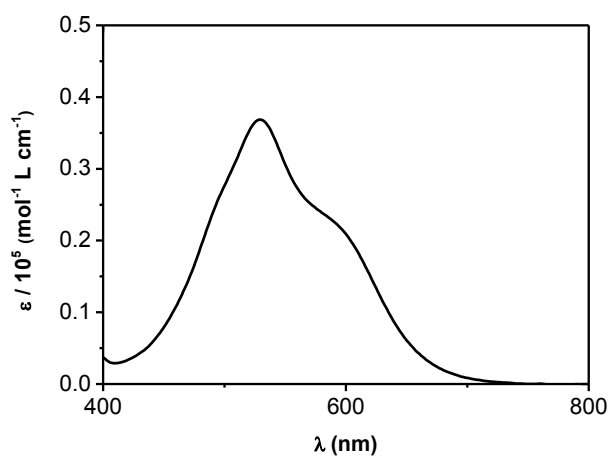
**Fig. S4** Normalized absorption and fluorescence spectra of **1** in  $\text{CHCl}_3$ .



**Fig. S5** Normalized absorption and fluorescence spectra of **2** in  $\text{CHCl}_3$ .



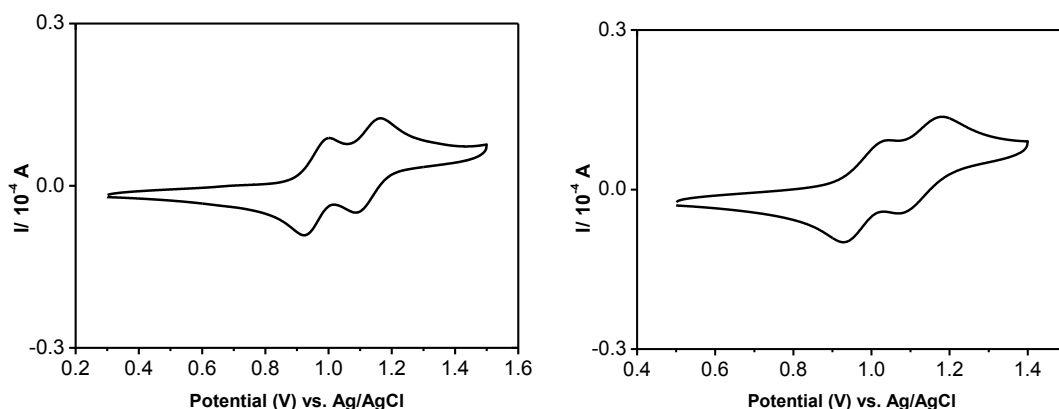
**Fig. S6** UV-vis-NIR absorption spectrum of **4** in  $\text{CHCl}_3$  ( $1.0 \times 10^{-5}$  M).



**Fig. S7** UV-vis absorption spectrum of **5** in  $\text{CHCl}_3$  ( $1.0 \times 10^{-5}$  M).

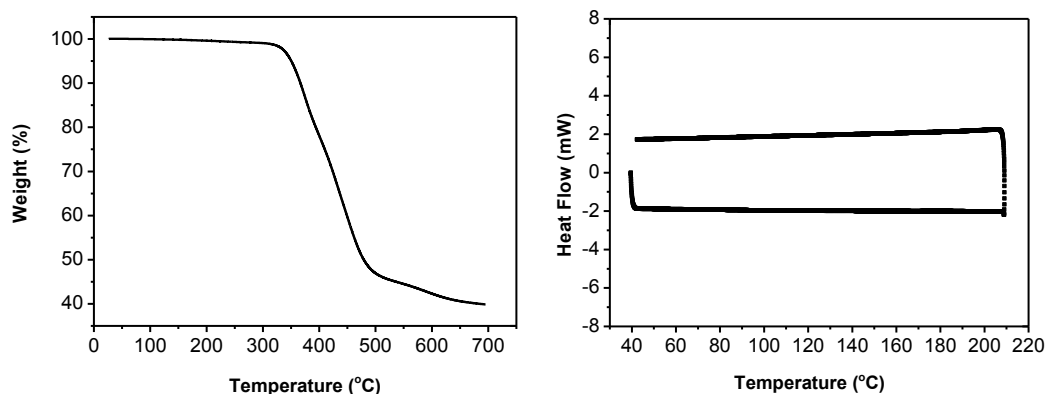
## IV. Electrochemical Characterizations





**Fig. S8** Oxidation waves of **1** (left) and **2** (right) in  $\text{CHCl}_3$ .

## V. Thermal Properties of **2**



**Fig. S9** TGA (left, 5% weight loss at 349 °C) and DSC (right) traces of **2**.

## VI. OFET Device Fabrication and Characterizations

Top-gate/bottom-contact OFET devices were fabricated on  $n^{++}\text{-Si/SiO}_2$  (300 nm) substrates. The gold source and drain bottom electrodes (with Ti as the adhesion layer) were patterned by photolithography on the  $\text{SiO}_2$  surface. The substrates were subjected to cleaning using ultrasonication in acetone, cleaning agent, deionized water (twice), and isopropanol. The cleaned substrates were dried under vacuum at 80 °C for 2 h. The substrates were transferred into a glove box. A thin film of semiconductive compound was deposited on the treated substrate by spin-coating a solution (10 mg/mL) in trichloroethylene at 1800 rpm for 60 s and annealed optionally, followed by thermal annealing at 100 °C, 120 °C, 150 °C, 180 °C, 200 °C, 220 °C, and 250 °C for 5 min. After the thin film deposition, a CYTOP solution (CTL809M:CT-solv180 = 3:1) was spin-coated onto the semiconducting layer at 2000 rpm for 60 s resulting in a dielectric layer of 500 nm thick. The CYTOP layer was then baked at 100 °C for 1 h. Gate electrodes comprising a layer of Al (50 nm) were then evaporated through a shadow mask onto the dielectric layer by thermal evaporation. The OFET devices had a channel length ( $L$ ) of 5  $\mu\text{m}$  and channel width ( $W$ ) of 100  $\mu\text{m}$ .

The characterizations of the OFETs were carried out in atmosphere (humidity 50-60 %) on a probe stage using a Keithley 4200 SCS as parameter analyzer. The carrier mobility,  $\mu$ , was calculated from the data in the saturated regime according to the equation  $I_{SD} = (W/2L)C_i\mu(V_G - V_T)^2$ , where  $I_{SD}$  is the drain current in the saturated regime.  $W$  and  $L$  are the semiconductor channel width and length, respectively.  $C_i$  ( $= 3.7$  nF) is the capacitance per unit area of the gate dielectric layer.  $V_G$  and  $V_T$  are the gate voltage and threshold voltage, respectively.  $V_G - V_T$  of the device was determined from the relationship between the square root of  $I_{SD}$  and  $V_G$  in the saturated regime.

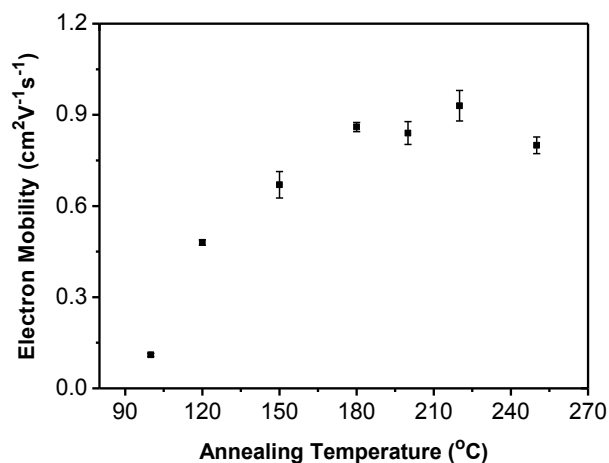


Fig. S10 Average electron mobility of 2 at various annealing temperatures.

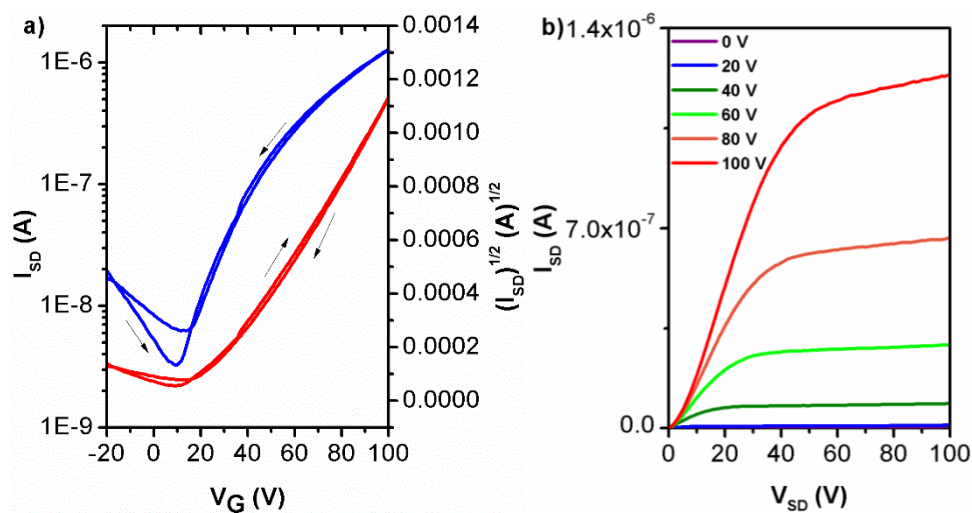
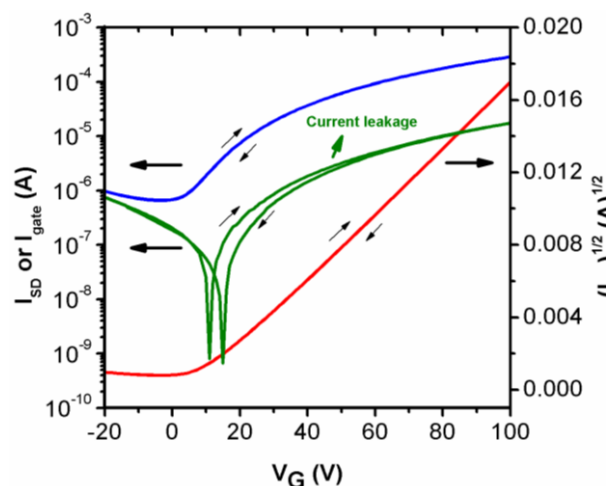


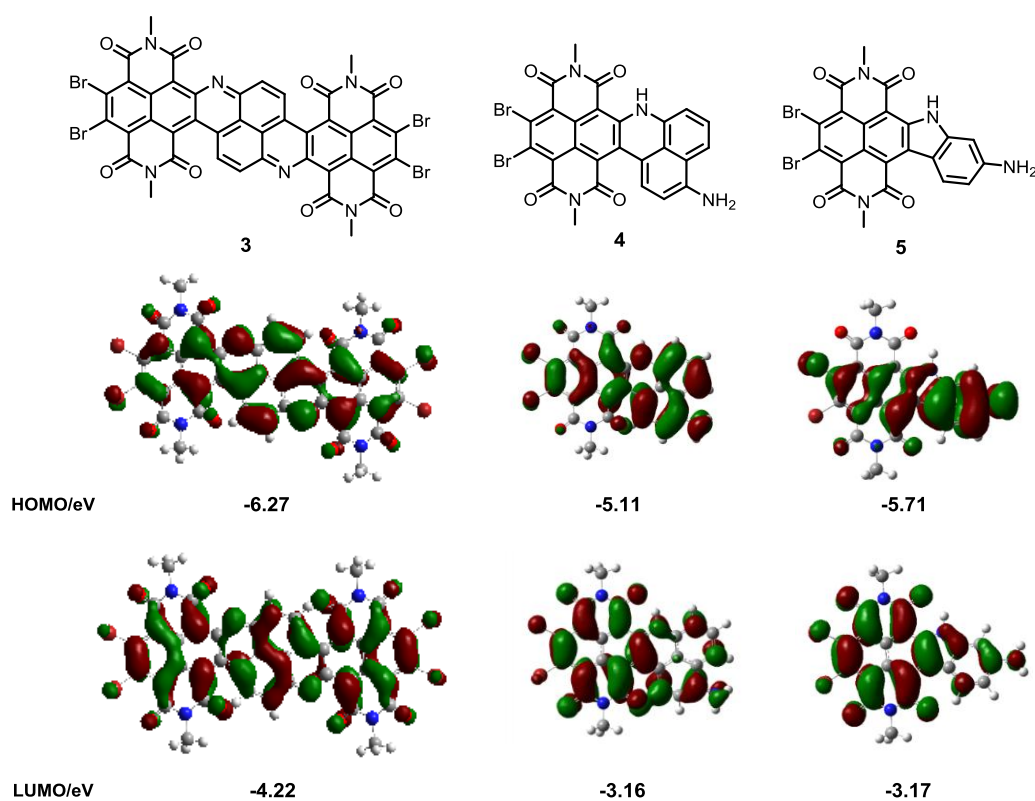
Fig. S11. (a) Transfer ( $V_{DS} = 100$  V) and (b) output profiles of 1 (annealed at 160 °C) in OFET.



**Fig. S12** Current leakage of **2** (annealed at 220 °C) in OFET ( $\mu_e = 0.96 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ ).

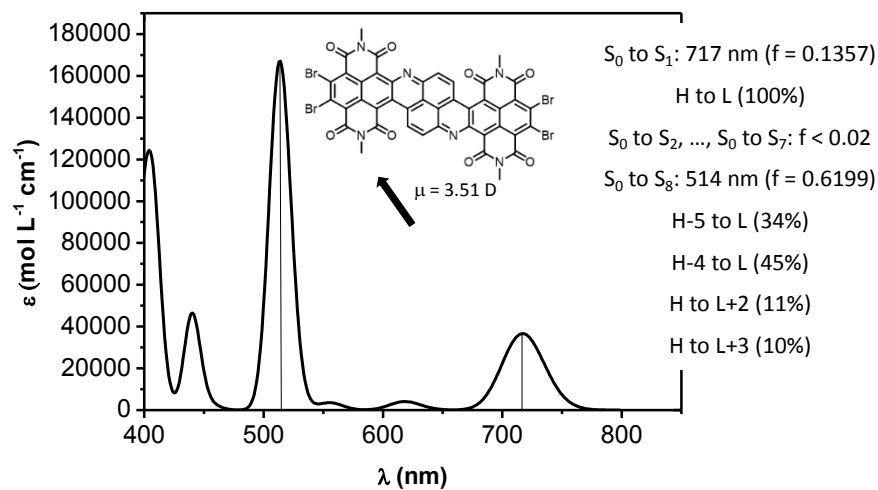
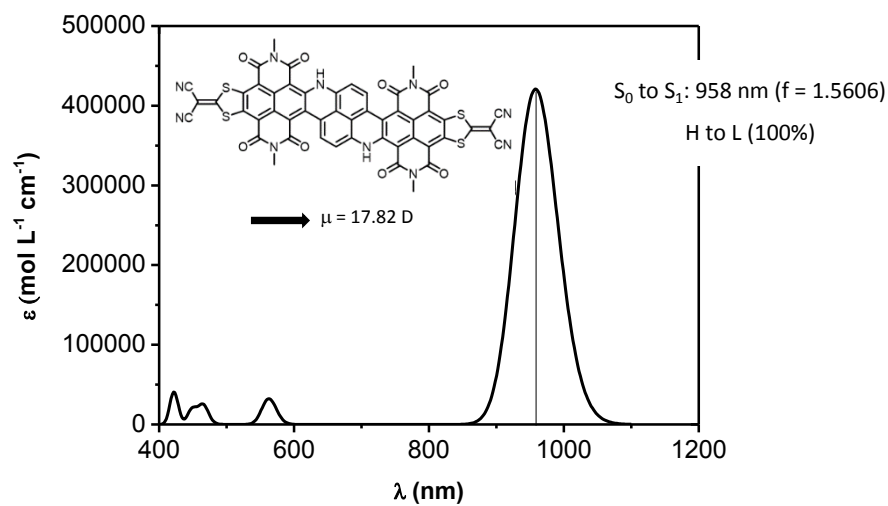
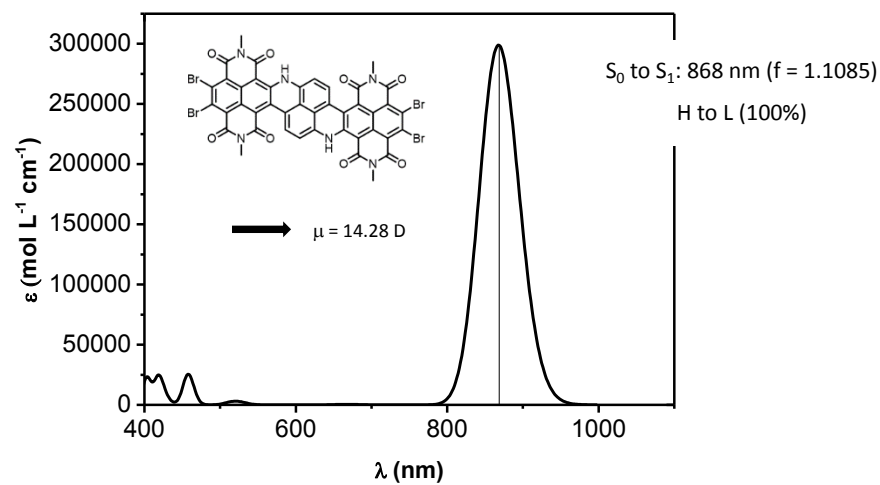
## VII. DFT and TD-DFT Calculations

The geometry of the molecules was optimized with Density Functional Theory (DFT) using B3LYP hybrid functional<sup>4</sup> 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 package<sup>5</sup> and the orbital pictures were prepared using Gaussview<sup>6</sup>. All long alkyl substituents were replaced with methyl groups in the calculations.



**Fig. S13** DFT calculated frontier orbitals (HOMO and LUMO) and energy levels of **3-5** using

B3LYP/6-31g (d, p)



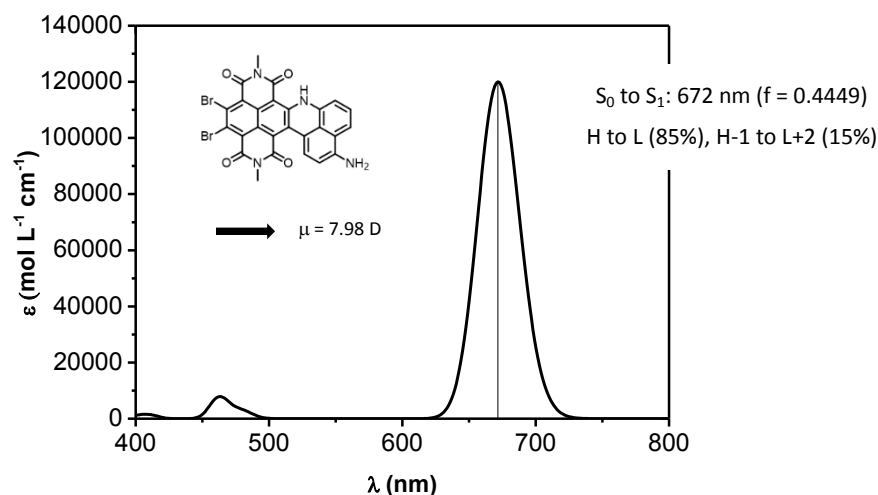


Fig. S14 TD-DFT calculation results of 1-4 (arrows indicate the direction of transition dipole moment).

## VIII. References

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# IX. Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra

