

Supporting information for

Aggregation Behavior in Naphthalene-Appended Diketopyrrolopyrrole Derivatives and its Gas Adsorption Impact on Surface Potential

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1. Experimental Section

1.1 Synthesis

6-Bromo-2-octyloxynaphthalene (2): In a two-neck round bottom flask (100 mL), 6-bromo-2-naphthol (2 g, 8.96 mmol), 1-bromooctane (1.8 g, 9.32 mmol), KOH (0.55 g, 9.85 mmol) and NaI (0.09 g, 0.6 mmol) were dissolved in ethanol (50 mL) and the reaction mixture was refluxed for 24 h. The solution was concentrated in rotavapor; water was added and extracted by ethyl acetate followed by drying over anhydrous MgSO₄. The solvent was removed and the desired product was purified by column chromatography using hexane as an eluent (2.64 g, 88 % yield).

¹H NMR (400 MHz, CDCl₃): δ 7.90 (s, 1H), 7.63 (d, J = 9.0 Hz, 1H), 7.58 (d, J = 8.8 Hz, 1H), 7.48 (dd, J = 8.7, 1.8 Hz, 1H), 7.16 (dd, J = 9.0, 2.4 Hz, 1H), 7.08 (d, J = 2.1 Hz, 1H), 4.07 (t, J = 6.4 Hz, 2H), 1.87-1.80 (m, 2H), 1.56-1.45 (m, 2H), 1.40-1.30 (m, 8H), 0.88 (t, J = 4.2 Hz, 3H).

¹³C NMR (400 MHz, CDCl₃): δ 157.44, 133.12, 129.93, 129.52, 128.39, 128.32, 120.07, 116.86, 106.55, 68.13, 31.81, 29.36, 29.22, 26.09, 22.65, 14.07. Anal. Calcd for C₁₈H₂₃BrO: C, 64.48; H, 6.91; Br, 23.83; O, 4.77. Found: C 64.94, H 7.10.

2-Octyloxy-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolato)naphthalene (3) : A two necked round bottom flask was charged with 6-bromo-2-octyloxynaphthalene (2.0 g, 5.96 mmol), bis(pinacolato)diboron (1.66 g, 6.56 mmol), potassium acetate (1.75 g, 17.83 mmol), dichlorobis(triphenylphosphine)palladium(II) (0.258 g, 0.368 mmol) and dry 1,4-dioxane (30 mL) was then added and the mixture was bubbled with argon for 15 min. The reaction mixture was heated at 80 °C for 24 h, cooled to room temperature. Water (200 mL) was added and then extracted with ethyl acetate (50 mL × 3) and the combined organic layer was washed with 2N HCl (100 mL) and dried over anhydrous magnesium sulfate. The solvent was removed by rotary evaporation and the residue was passed through a flash silica gel column with 5-10% ethyl acetate/hexane (1.90 g, yield 85%). ¹H NMR (400 MHz, CDCl₃): δ 8.28 (s, 1H), 7.82-7.75 (m, 2H), 7.70 (d, J = 8 Hz, 1H), 7.14-7.11 (m, 2H), 4.07 (t, J = 6.4 Hz, 2H), 1.88-1.81 (m, 2H), 1.53-1.46 (m, 2H), 1.38 (s, 12H), 1.36-1.29 (m, 8H), 0.89 (t, J = 6.8 Hz, 3H). ¹³C NMR (400 MHz, CDCl₃): δ 158.10, 136.47, 135.97, 131.02, 130.16, 128.3, 125.84, 118.98, 106.42, 83.77, 68.04, 31.82, 29.38, 29.24, 26.12, 24.92, 22.66, 14.08. Anal. Calcd for C₂₄H₃₅BO₃: C, 75.39; H, 9.23; B, 2.83; O, 12.55. Found: C, 75.39; H, 9.00.

2,5-dihexyl-3,6-bis(4-(6-(octyloxy)naphthalen-2-yl)phenyl)pyrrolo[3,4-c]pyrrole1,4

(2H,5H)-dione (Naph-PDPP): 2-Octyloxy-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolato)naphthalene (0.56 g, 1.46 mmol), 3,6-bis(4-bromophenyl)-2,5-dihexylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (PDPP) (0.40 g, 0.651 mmol), Aliquat 336 (2 drops) 2 M aqueous K₂CO₃ (0.540 g, 3.91 mmol) toluene (30 mL) and water (1 mL) were placed together in a round bottom flask and purged with argon for 20 min. To this solution, Pd₂(dba)₃ (0.017 g, 0.018 mmol), (o-tolyl)₃P (0.02 g, 0.065 mmol) was added and the reaction mixture was heated at 110 °C for 72 h. Then the reaction mixture was poured into water (100 mL) and extracted with chloroform. The organic layer was washed with 2 N HCl (200 mL) then concentrated in rotavapor. The resulting product was purified by silica gel column chromatography using hexane: chloroform (1:1) as eluent (0.470 g, yield 75%). ¹H NMR (400 MHz, CDCl₃): δ 8.05 (s, 2H), 7.97 (d, J= 8.4 Hz, 4H), 7.88 (d, J= 8.4 Hz, 4H), 7.82 (d, J= 7.6Hz, 4H), 7.75 (d, J= 8.8 Hz, 2H), 7.20 (d, J= 8.8 2H), 7.17 (s, 2H), 4.10 (t, J = 6.8 Hz, 4H), 3.84 (t, J = 7.2 Hz, 4H), 1.90-1.83 (m, 4H), 1.70-1.67 (m, 4H), 1.54-1.48 (m, 4H), 1.41-1.25 (m, 28H), 0.90 (t, J= 6.4 Hz, 6H), 0.84 (t, J= 6Hz, 6H). ¹³C NMR (400 MHz, CDCl₃): δ 162.85, 157.64, 148.06, 143.82, 134.88, 134.28, 129.80, 129.28, 128.98, 127.45, 126.75, 125.97, 125.47, 127.79, 119.69, 68.11, 42.12, 31.25, 29.49, 29.38, 29.25, 26.44, 26.11, 22.66, 22.48, 14.10, 13.96. MALDI-MS: Found: m/z = 966.20 [M+H]⁺, Calcd for C₆₆H₈₀N₂O₄ [M]⁺= 965.35 Anal. Calcd for C₆₆H₈₀N₂O₄: C, 82.12; H, 8.35; N, 2.90; O, 6.63. Found: C, 81.82; H, 7.81; N, 3.1.

2,5-dihexyl-3,6-bis(5-(6(octyloxy)naphthalen-2-yl)thiophen-2-yl)pyrrolo[3,4-c]pyrrole-

1,4(2H,5H)-dione (Naph-TDPP): Naph-TDPP was synthesized by similar procedure. Since the solubility of Naph-TDPP was less it was purified by washing with hot methanol and acetone (0.5 g, yield 80%). ¹H NMR (400 MHz, CDCl₃): δ 9.00 (d, J= 4Hz, 2H), 8.06 (s, 2H), 7.80 (d, J= 8 Hz, 2H), 7.79-7.74 (m, 4H), 7.56 (d, J= 4Hz, 2H), 7.19 (d, J= 8, 2H), 7.12 (s, 2H), 4.16 (t, J = 5.6 Hz, 4H), 4.07 (t, J = 6.8 Hz, 4H), 1.87-1.78 (m, 8H), 1.51-1.48 (m, 8H), 1.37-1.25 (m, 24H), 0.93-0.88 (m, 12H). ¹³C NMR for Naph-TDPP was not able to record due to low solubility. MALDI-MS: Found: m/z = 976.77 [M]⁺, Calcd for C₆₂H₇₆N₂O₄S₂ [M]⁺: 976.52. Anal. Calcd for:

$C_{62}H_{76}N_2O_4S_2$: C, 76.19; H, 7.84; N, 2.87; O, 6.55; S, 6.56. Found: C, 75.67; H, 7.65; N, 3.0; S, 6.52.

2. Structural Characterization

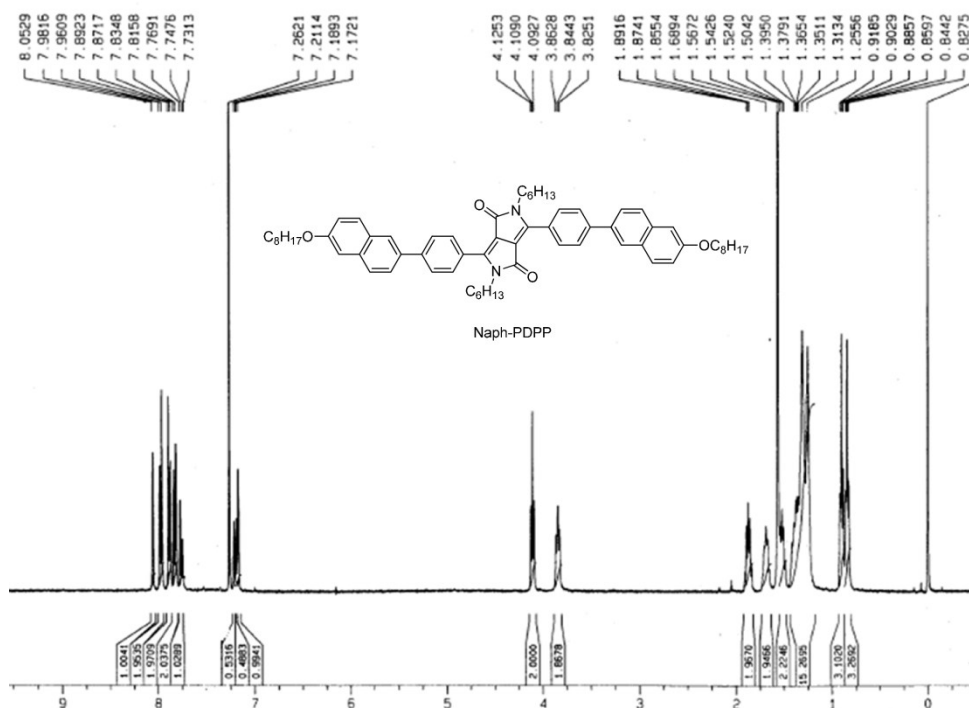


Figure S1 1H NMR (400 MHz) of Naph-PDPP in $CDCl_3$.

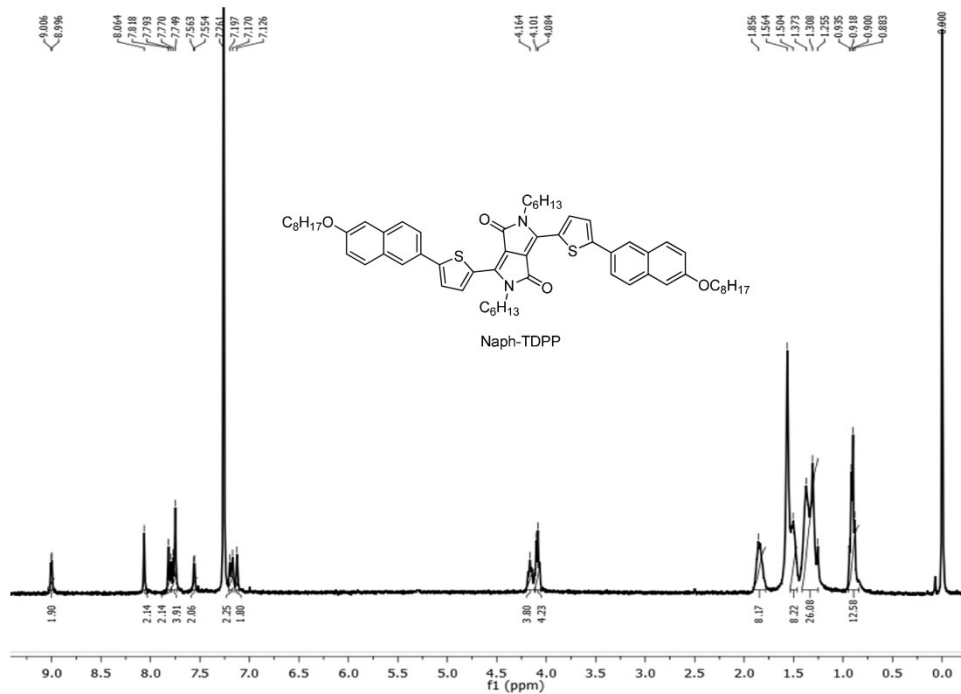


Figure S2 ¹H NMR (400 MHz) of Naph-TDPP in CDCl₃.

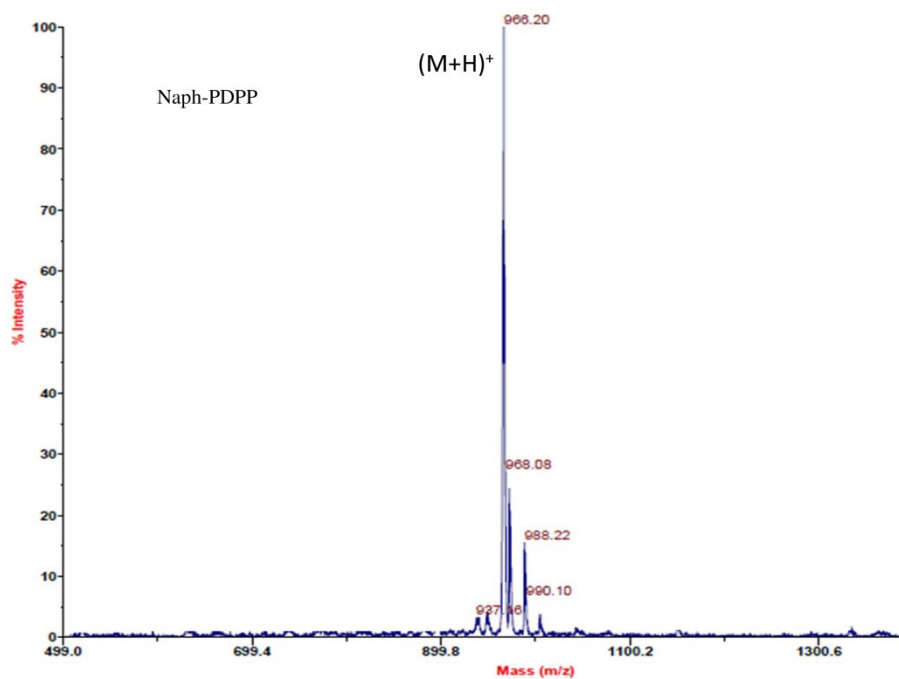


Figure S3 The HR-MS of Naph-PDPP.

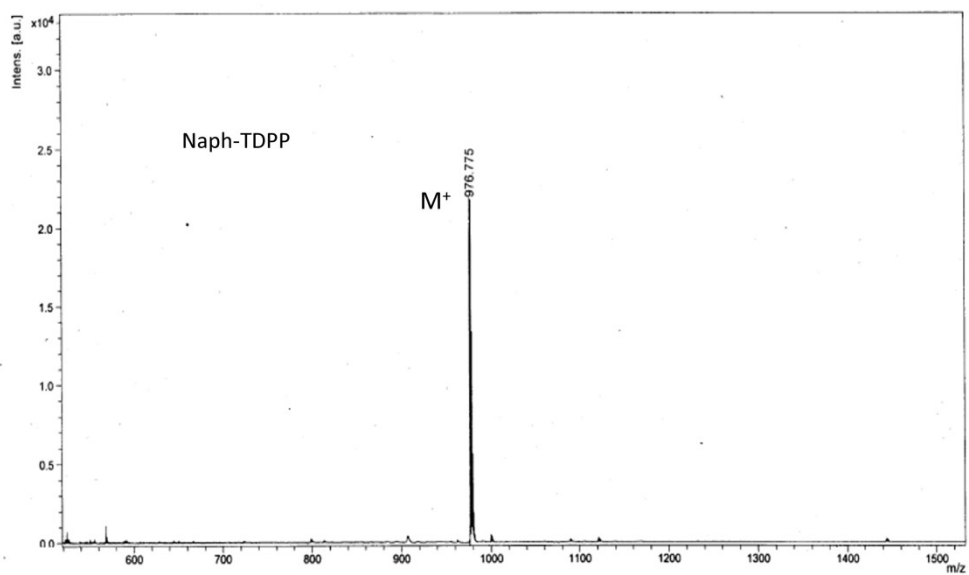


Figure S4 The HR-MS of Naph-TDPP.

3. Photophysical studies

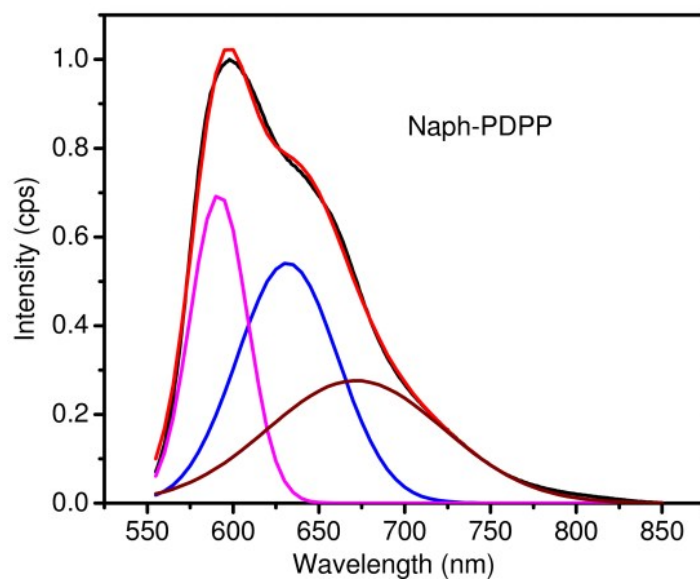


Figure S5 The de-convolution of the emission spectra of Naph-PDPP.

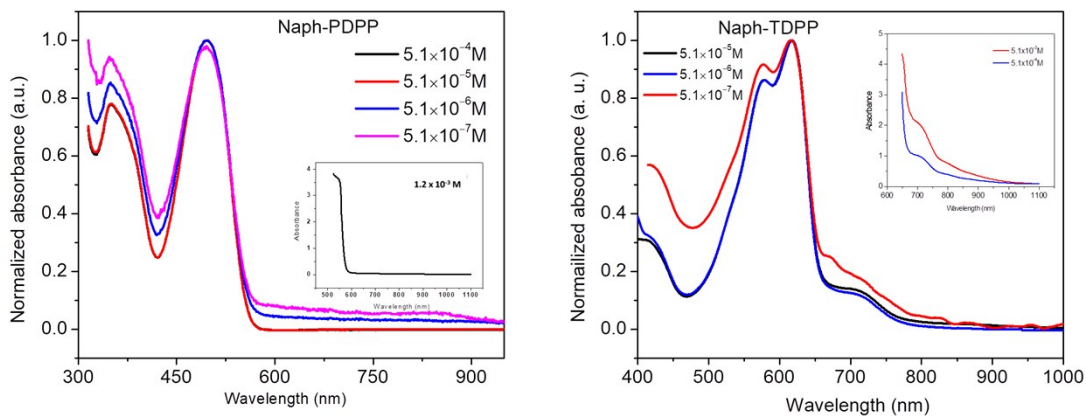


Figure S6 Concentration-dependent absorption spectra of Naph-PDPP and Naph-TDPP.

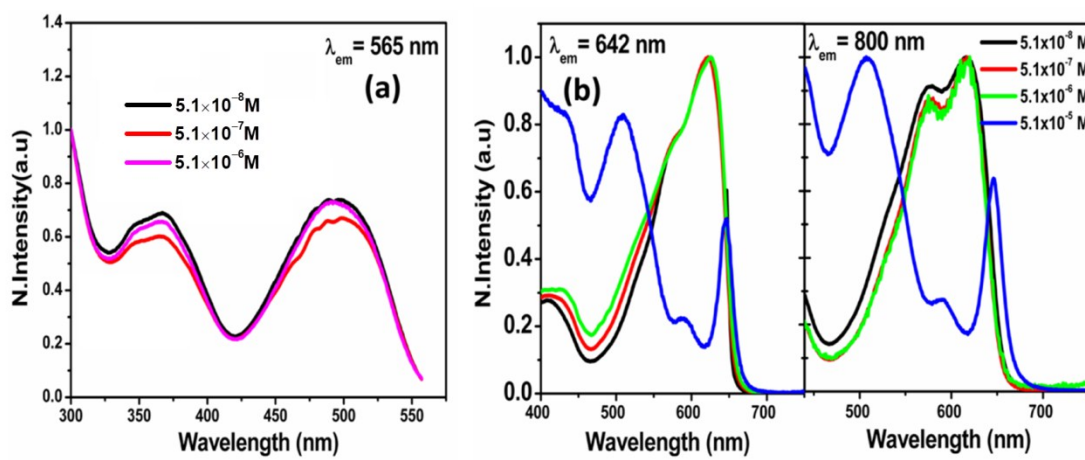


Figure S7 Excitation spectra of Naph-PDPP (a) and Naph-TDPP (b) at different concentrations.

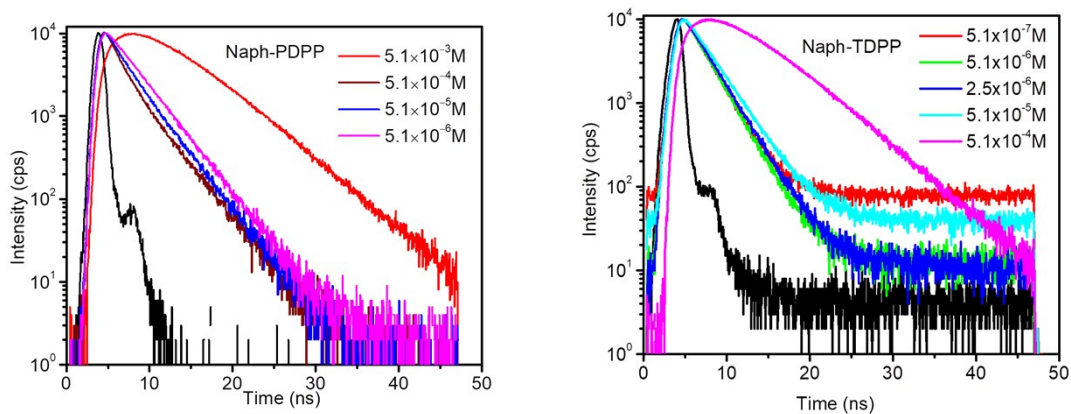


Figure S8 Fluorescence lifetime decay curve of Naph-PDPP and Naph-TDPP.

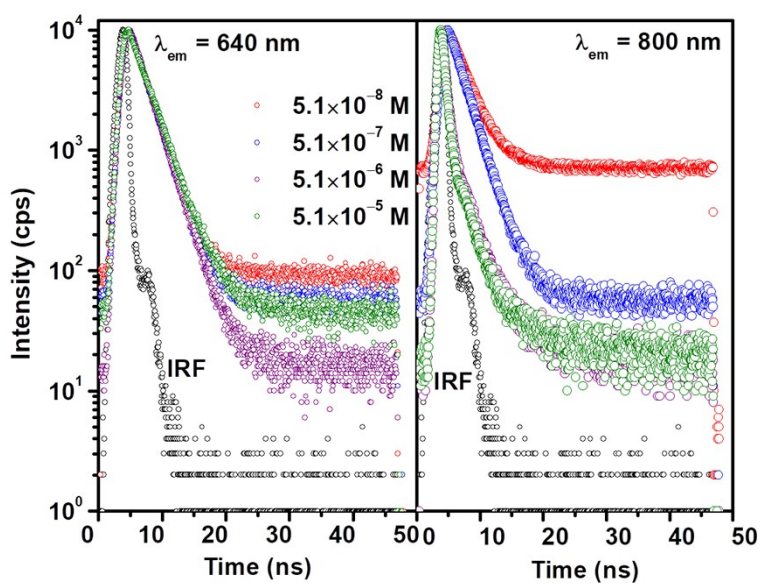


Figure S9 Fluorescence lifetime decay of Naph-TDPP at different concentrations and at different emission wavelengths.

4. Electrochemical study

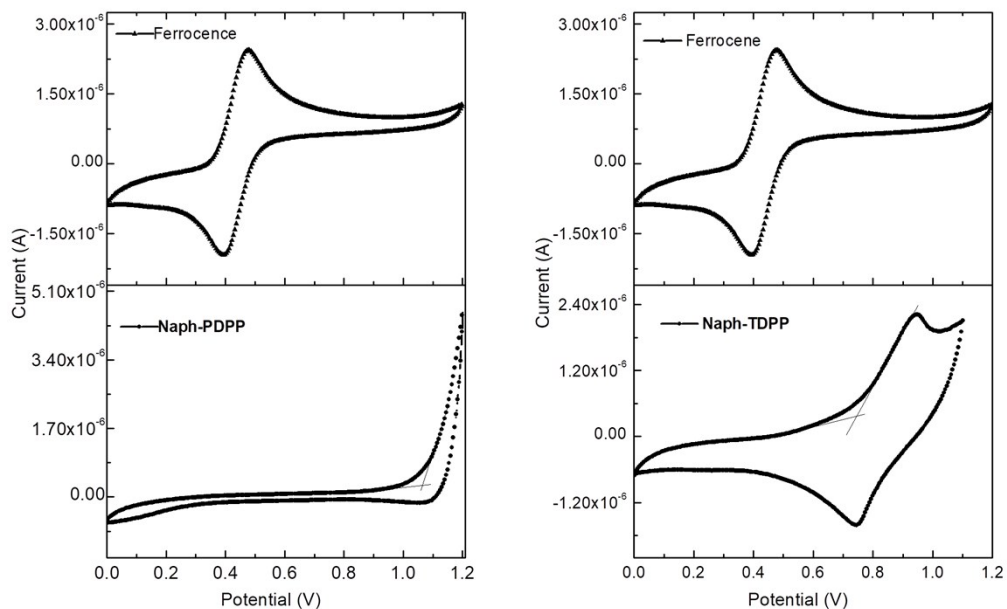


Figure S10 Cyclic voltammogram of Naph-PDPP and Naph-TDPP.

Table S1 Summary of optical and electrochemical properties

Compounds	Film		Solution		CV			
	λ_{abs} [nm]	λ_{em} [nm]	λ_{abs} [nm]	λ_{em} [nm]	E_{g} [eV]	$E_{\text{Ox}}^{\text{onset}}$ (V)	E_{HOMO} [eV]	LUMO [eV]
Naph-PDPP	552	598	498	566	2.1	1.06	-5.50	-3.40
Naph-TDPP	618	695	617	642	1.8	0.74	-5.18	-3.38

5. DFT and TD-DFT studies

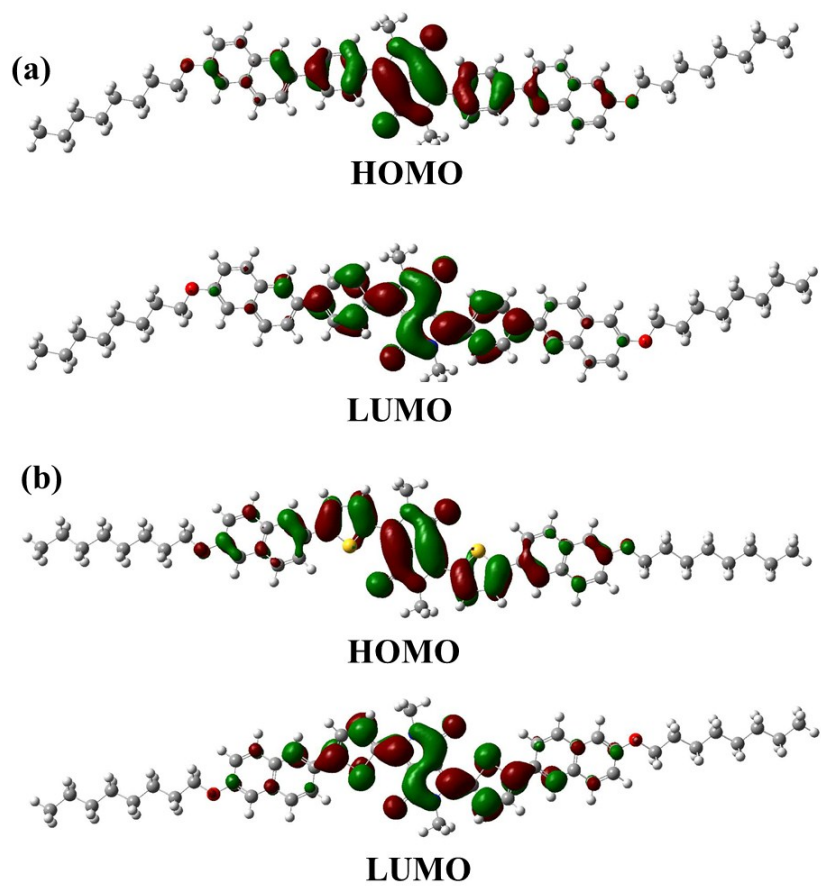
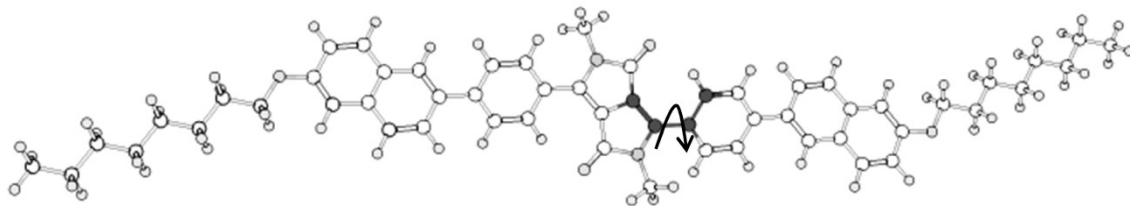
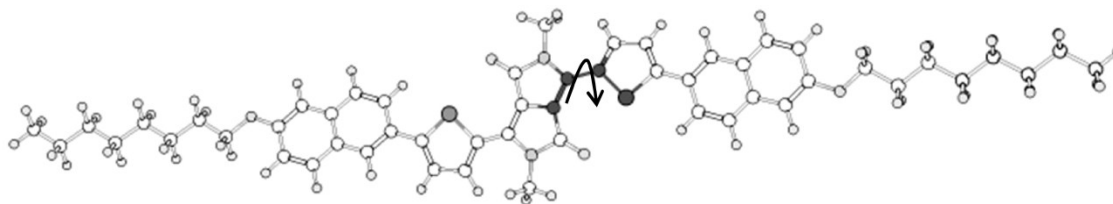


Figure S11 Electron density surface of Naph-PDPP (a) and Naph-TDPP.



(a) Torsion angle (23.95°)



(b) Torsion angle (10.27°)

Figure S12 Optimized geometry of (a) Naph-PDPP (b) Naph-TDPP.

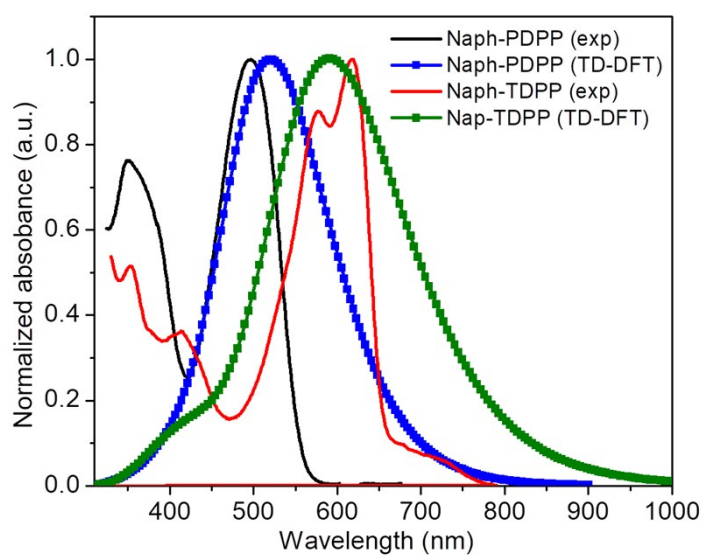


Figure S13 Comparison of UV-Visible spectra of Naph-PDPP and Naph-TDPP in solution (CHCl_3) with TD-DFT calculations.

Table S2. Summary of TD-DFT calculations

Compounds	Dominant Contribution (%)	Absorption (nm)	Energy (eV)	Oscillator strength (<i>f</i>)	Dipole Moment (D)
Naph-PDPP	H -> L (61.2%)	517.00	2.3752	1.2630	0.3123
	H-2 -> L (67.68%)	418.53	2.9624	0.1364	
	H-6 -> L (56.73%)	359.75	3.4464	0.0194	
	H-4 -> L (26.7%)				
Naph-TDPP	H -> L (60.7%)	594.75	2.0952	1.4832	0.5385
	H-2 -> L (66.33%)	439.44	2.8214	0.1841	
	H -> L+2 (16.5%)				
	H -> L+2 (66.28%)	384.25	3.2267	0.0736	

6. Thin film X-ray diffraction studies

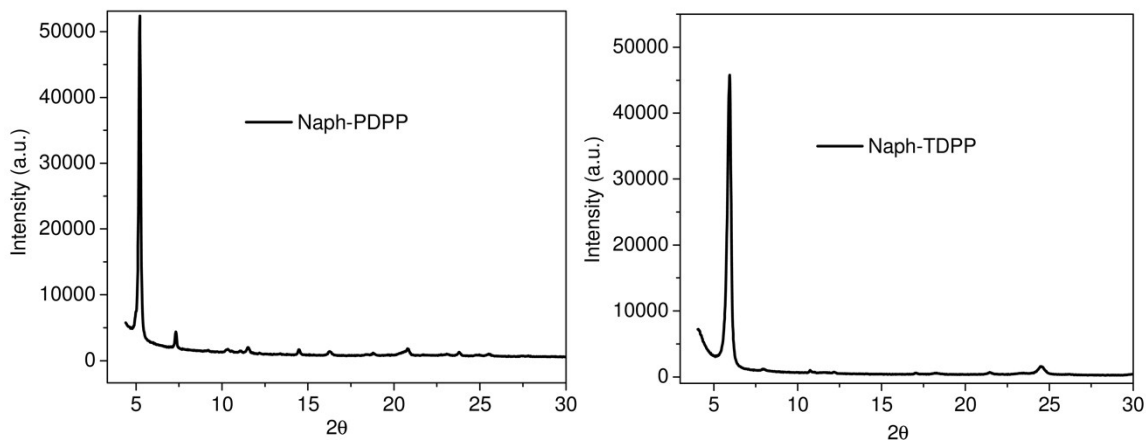


Figure S14 Thin film XRD of Naph-PDPP and Naph-TDPP.

7. Morphology

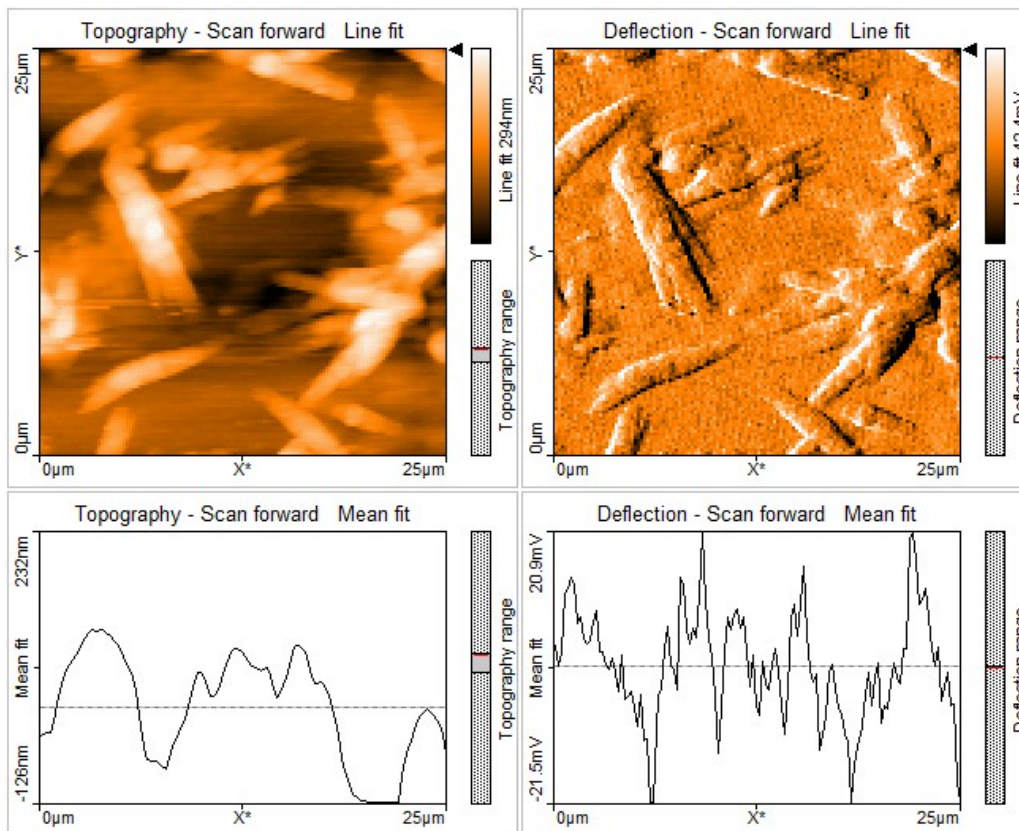


Figure S15 AFM images of Naph-PDPP.

8. DSC and TGA analysis

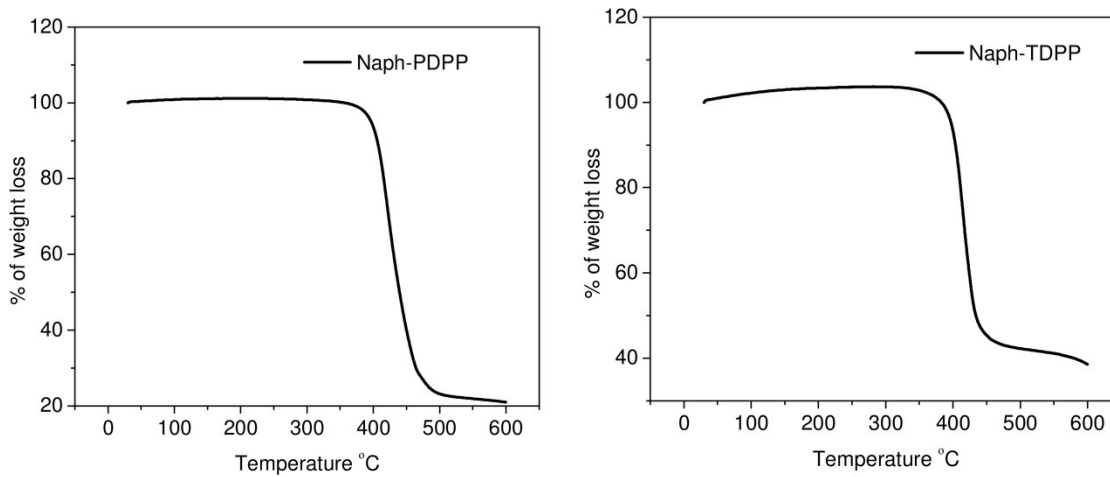


Figure S16 TGA of Naph-PDPP and Naph-TDPP.

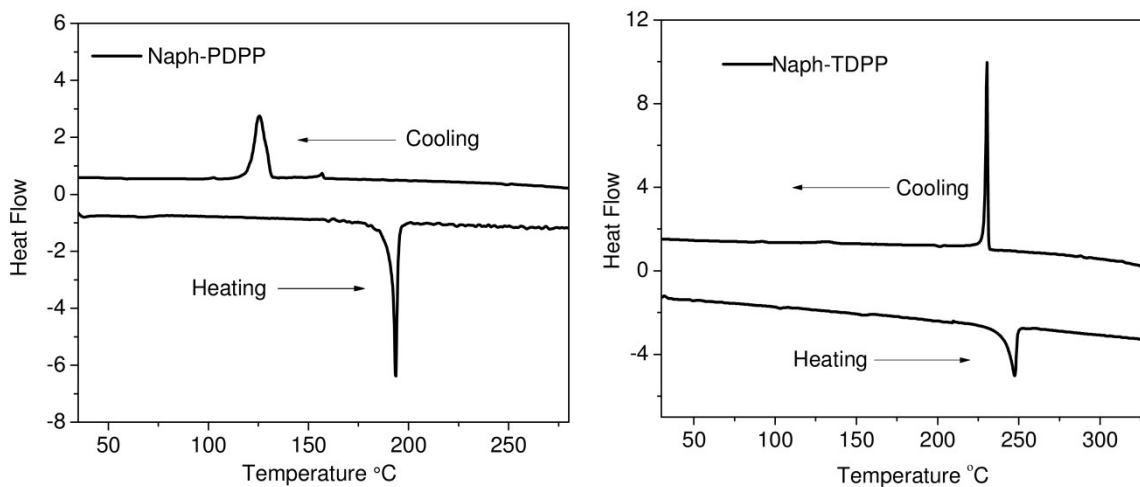


Figure S17 DSC of Naph-PDPP and Naph-TDPP.

9. Sample preparation for SKP measurements

First, the ITO substrate was cut into $1\text{ cm} \times 2\text{ cm}$ and cleaned with soap solution followed by millipore water, acetone, and ethanol at 55°C in ultrasonicator for 30 minutes. The Naph-PDPP and Naph-TDPP were dissolved in chloroform and drop-cast on the cleaned ITO substrate. The sample is allowed to dry at ambient temperature. All the experiments were carried out in the presence of Millipore water.

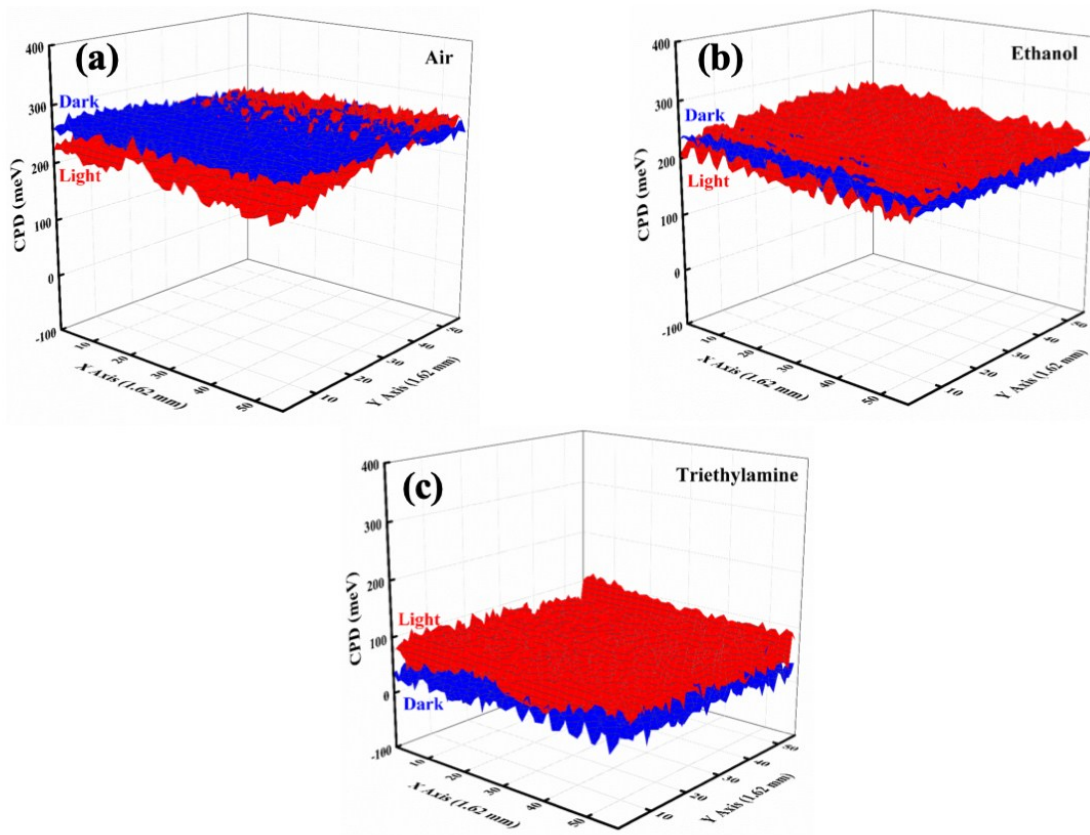


Figure S18 Raster scan of Naph-TDPP films in dark and light illumination: (a) Naph-TDPP film in ambient air, (b) Naph-TDPP film in ethanol and (c) Naph-TDPP film in triethylamine.