*Supporting Information for*

# Photophysical, Electrochemical and Solid State Properties of Diketopyrrolopyrrole-based Molecular Materials: Importance of Donor Group

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## Synthesis of DPP Derivatives:

**Synthesis of PDPP-Hex:** 3,6-diphenylpyrrolo[3,4-c]pyrrole-1,4(*2H,5H*)-dione (PDPP) (0.21 g, 0.73 mmol) was dissolved in 30:15 mL of NMP/DMF mixture and stirred for 30 min in inert atmosphere. Then *t*-BuOK (0.19 g, 1.7 mmol) was added to it and heated at 90 °C for 1 h followed by dropwise addition of 1-bromohexane (0.42 mg, 2.56 mmol) dissolved in DMF. The reaction was allowed to continue for next 20 h at 125°C. The reaction was quenched by addition of water. NMP/DMF solvent mixture was distilled out. The compound was eluted by hexane/ethyl acetate in column chromatography (yield: 64%). $^{1}$H NMR (400 MHz, $CDCl_3$, ppm): δ 7.79-7.82 (m, 4H), 7.55-7.5 (m, 6H), 3.75-3.72 (t, 4H), 1.62-1.53 (m, 4H),1.26-1.16 (m, 12H), 0.83-0.8 (t, 6H). $^{13}$C NMR (101 MHz, $CDCl_3$, ppm): δ 162.74, 148.53, 131.10, 128.9, 128.71, 128.33, 41.92, 31.21, 29.71, 29.41, 26.39, 22.46, 13.94. Elemental Analysis: Calc. (%): ($C_{30}H_{36}N_2O_2$): C, 78.91; H, 7.95; N, 6.13 Found (%): C, 79.16; H, 8.03; N, 5.9. (ESI-MS) calculated for $C_{30}H_{36}N_2O_2$ $(M)^+$: m/z: 457.5

**Synthesis of TDPP-Hex:** 3,6-di(thiophen-2-yl)-pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (TDPP) (0.5gm, 1.66 mmol) and potassium carbonate (0.81gm, 5.83 mmol) were taken in DMF (20 mL), heated at 90 °C for 1h. Then slowly 1-bromohexane was added to the reaction mixture and temperature was raised to 125 °C and continued for next 20 h. Later DMF was distilled out, washed with water and extracted in $CH_2Cl_2$. The organic layer was passed through $Na_2SO_4$ and concentrated. The crude product was purified by column chromatography (yield: 78%). $^{1}$H NMR (400 MHz, $CDCl_3$, ppm): δ 8.93 (d, J = 3.9 Hz, 2H), 7.64 (d, J= 5.1 Hz, 2H), 7.29 (d, J = 4.9, 4.0 Hz, 2H), 4.12−4.01 (m, 4H), 1.80−1.69 (m, 4H), 1.48−1.37 (m, 4H), 1.36−1.26 (m, 8H), 0.88 (t, J = 7.0 Hz, 6H). $^{13}$C NMR (101 MHz, $CDCl_3$, ppm): δ 161.38, 140.03, 135.22, 130.63, 129.80, 128.59, 107.73, 42.22, 31.40, 29.91, 26.53, 22.53, 13.98. Elemental Analysis: ($C_{26}H_{32}N_2O_2S_2$): Calc. (%): C, 66.63; H, 6.88; N, 5.98; S, 13.68 Found (%): C, 65.43; H, 6.43; N, 5.71; S, 12.54. (ESI-MS) calculated for $C_{26}H_{32}N_2O_2S_2$ $(M)^+$: m/z: 469.4

**Synthesis of SeDPP-Hex:**2,5-dihexyl-3,6-di(selenophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(*2H,5H*)-dione (SeDPP) (0.5 g, 1.27 mmol) and potassium carbonate (0.6 g, 4.44 mmol) were taken in a round-bottomed flask in 30 mL of DMF. It was heated at 90 °C for 1 h. Then 1-bromohexane was added drop wise to the reaction mixture and temperature was raised to 125 °C and stirred for 20 h in argon atmosphere. Water was added to quench the reaction. Solvent was distilled off and product was purified by column chromatography using hexane/ethyl acetate as eluent. (yield 45%). $^{1}$H NMR (400 MHz, $CDCl_3$, ppm) δ 8.87 (d, J = 3.9 Hz, 2H), 8.40 (d, J= 5.1 Hz, 2H), 7.50 (d, J = 4.9, 4.0 Hz, 2H), 4.01 (t, 4H), 1.75 (m, 4H),

1.45−1.38 (m, 4H), 1.36−1.25 (m, 8H), 0.88 (t, J = 7.0 Hz, 6H). $^{13}$C NMR (101 MHz, $CDCl_3$, ppm): δ 161.56, 141.08, 137.18, 136.52, 133.96, 131.00, 107.84, 42.19, 31.49, 30.00, 29.71, 26.61, 22.56, 14.00 ppm. (ESI-MS) calculated for $C_{26}H_{32}N_2O_2Se_2$ $(M)^+$: m/z: 565.2

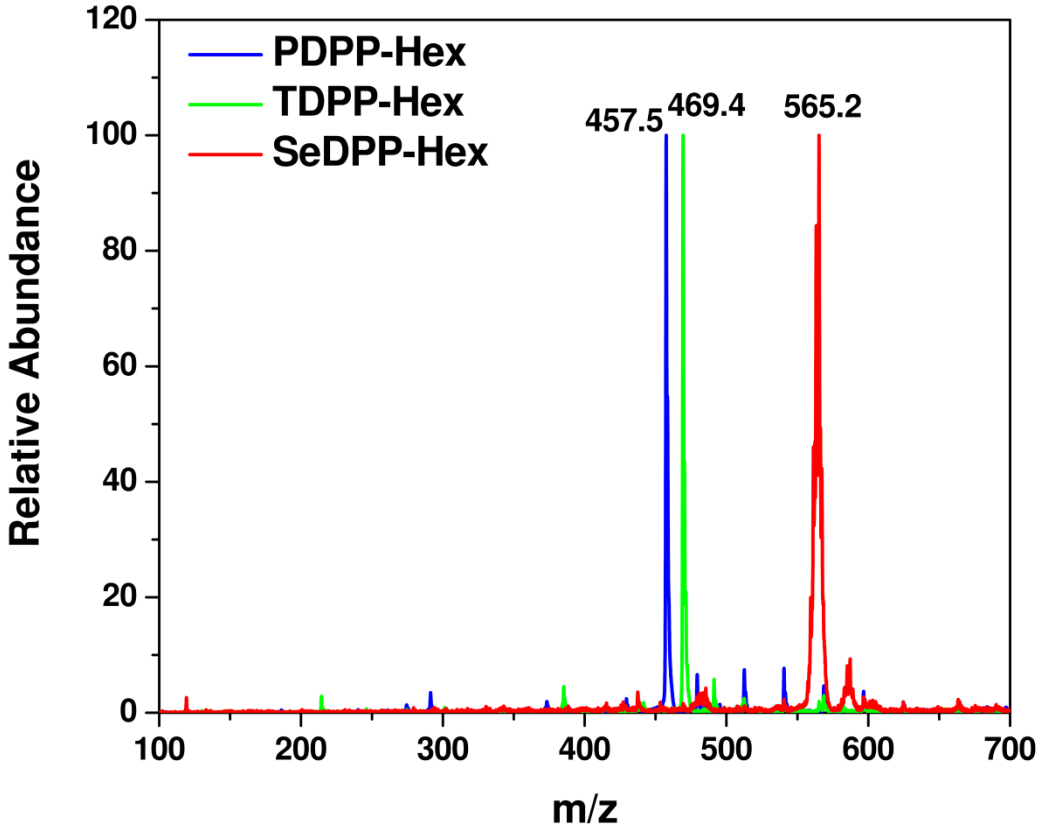



**Figure S1.** ESI Mass spectra of three DPP derivatives.

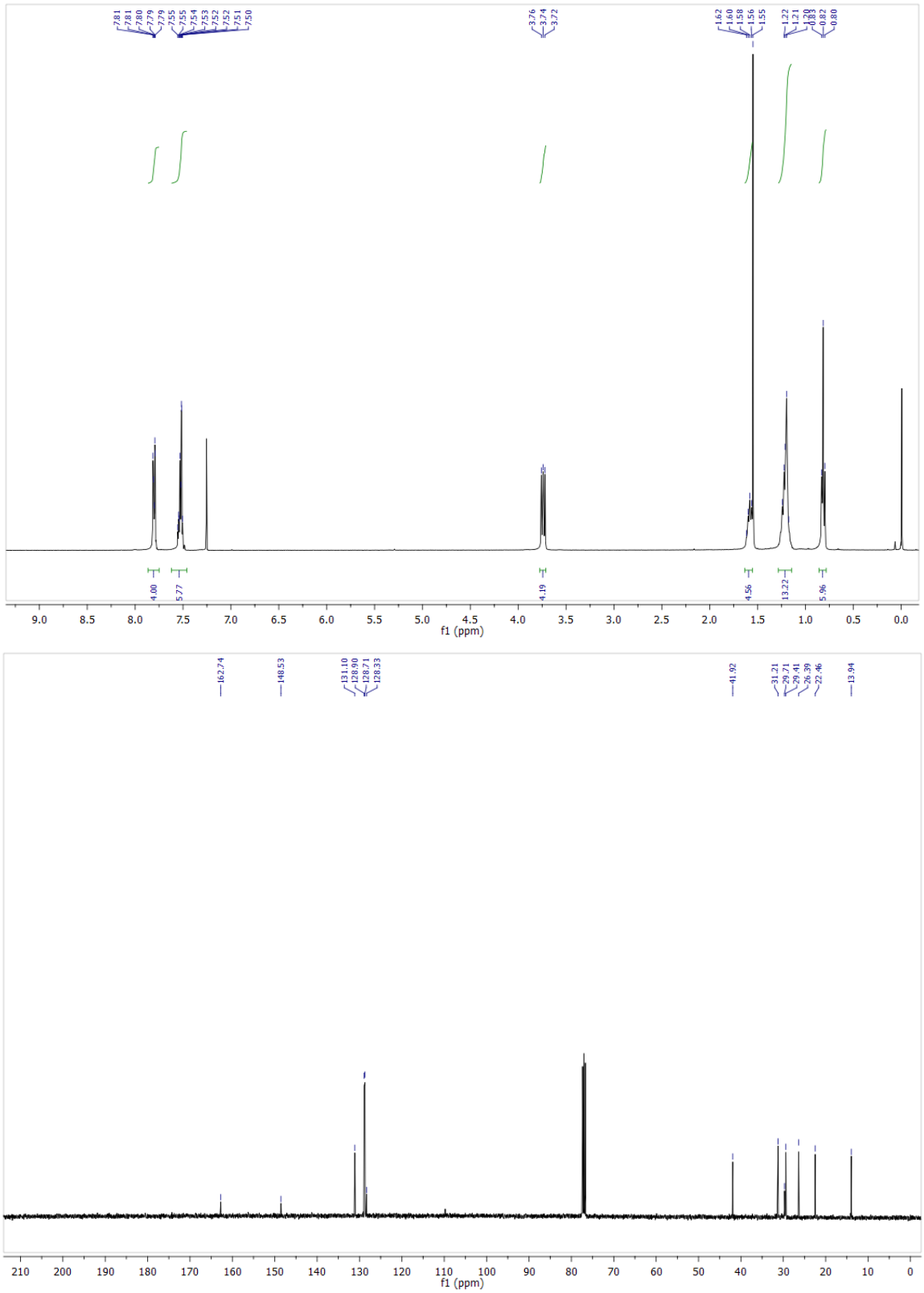



**Figure S2.** $^{1}H$ and $^{13}C$ NMR spectra of PDPP-Hex.

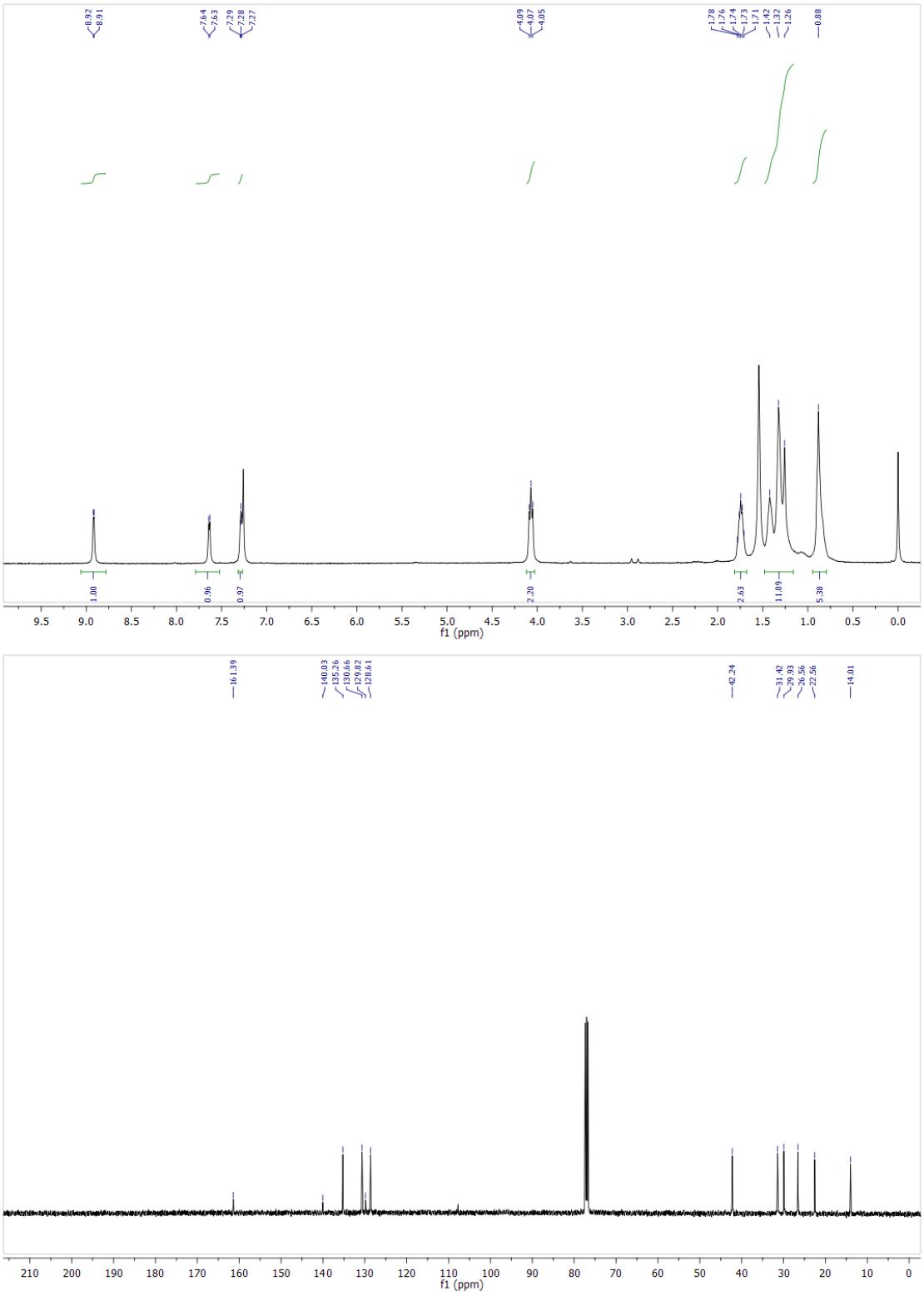



**Figure S3.** $^{1}H$ and $^{13}C$ NMR spectra of TDPP-Hex.

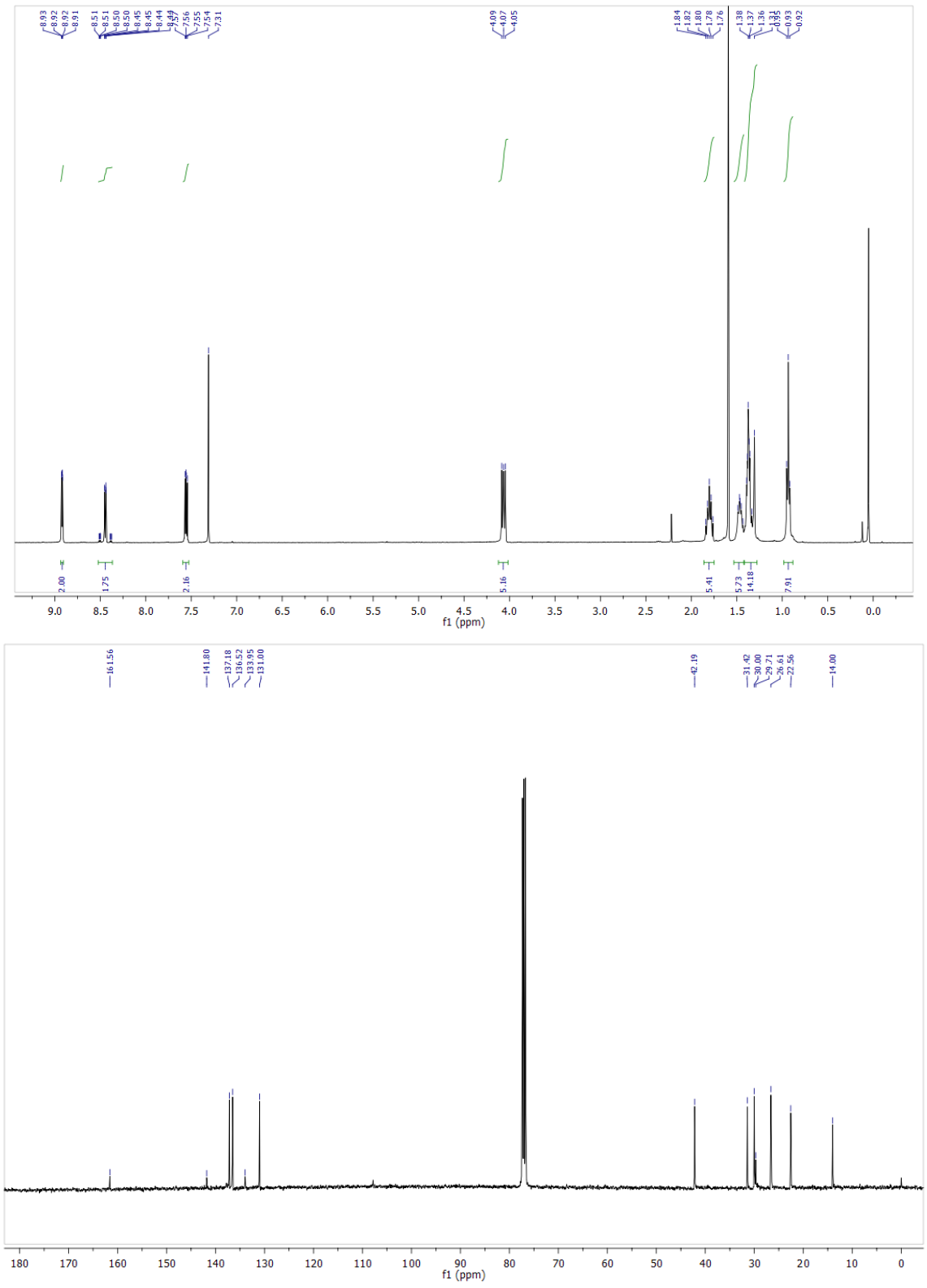



**Figure S4.** $^{1}H$ and $^{13}C$ NMR spectra of SeDPP-Hex.

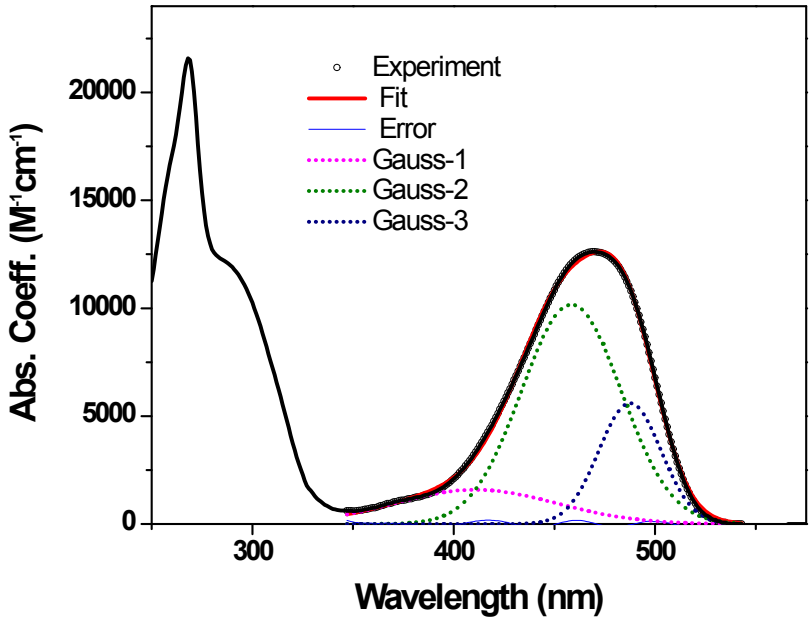



**Figure S5.** Absorption spectra overlapped with deconvoluted low energy band of PDPP-Hex.

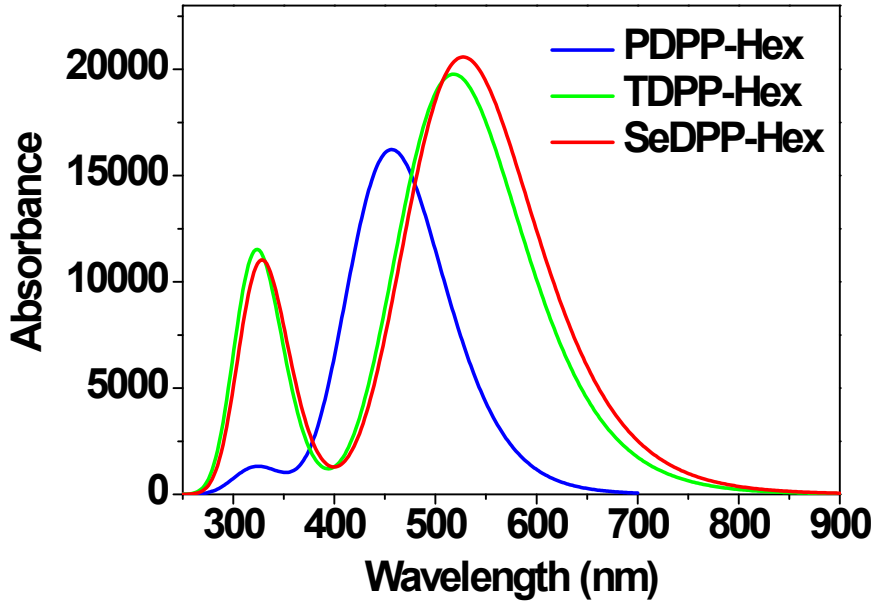



**Figure S6.** TD-DFT simulated absorption spectra of three DPP molecules.

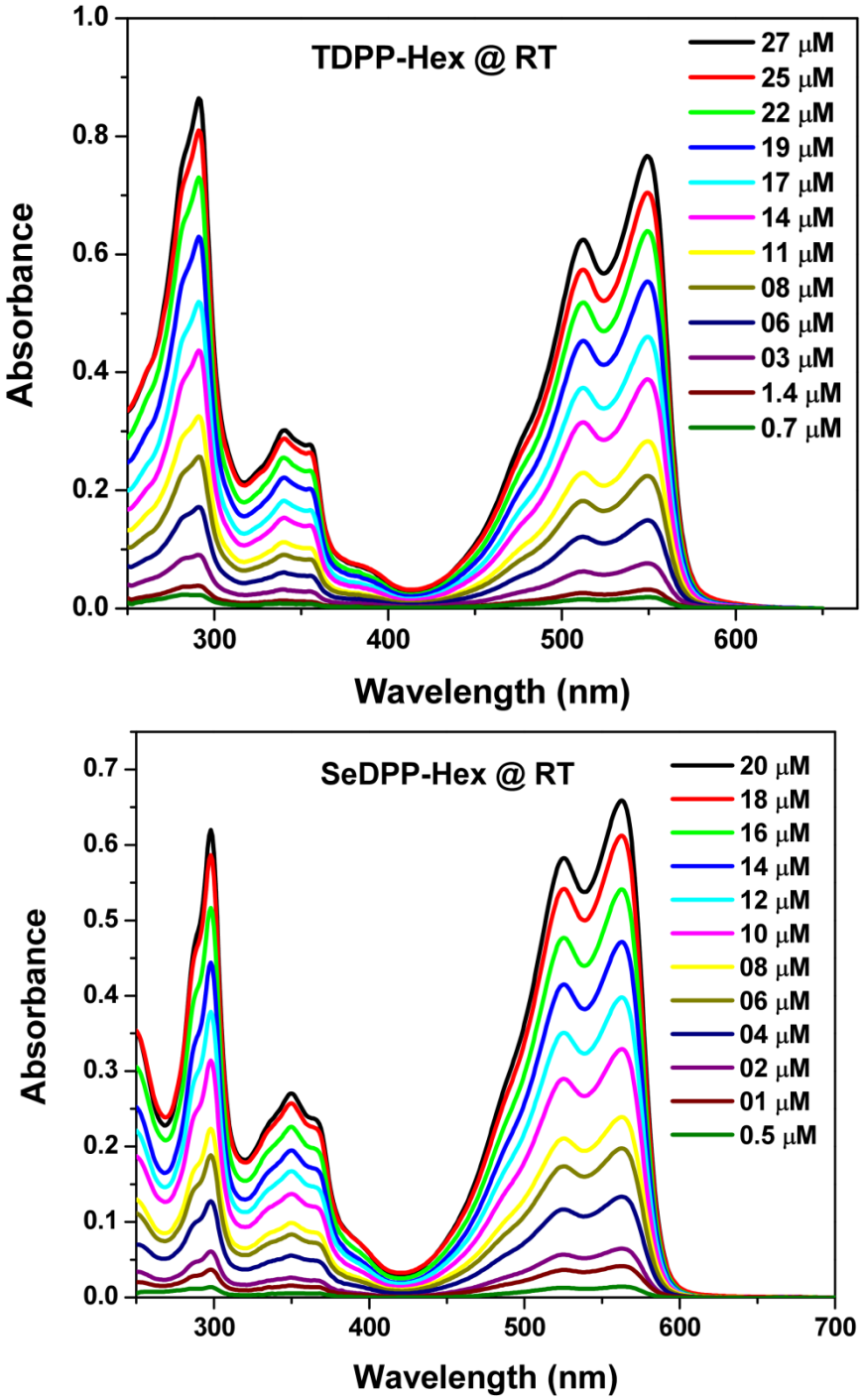



**Figure S7:** Room temperature concentration dependent absorption spectra of TDPP-Hex and SeDPP-Hex.

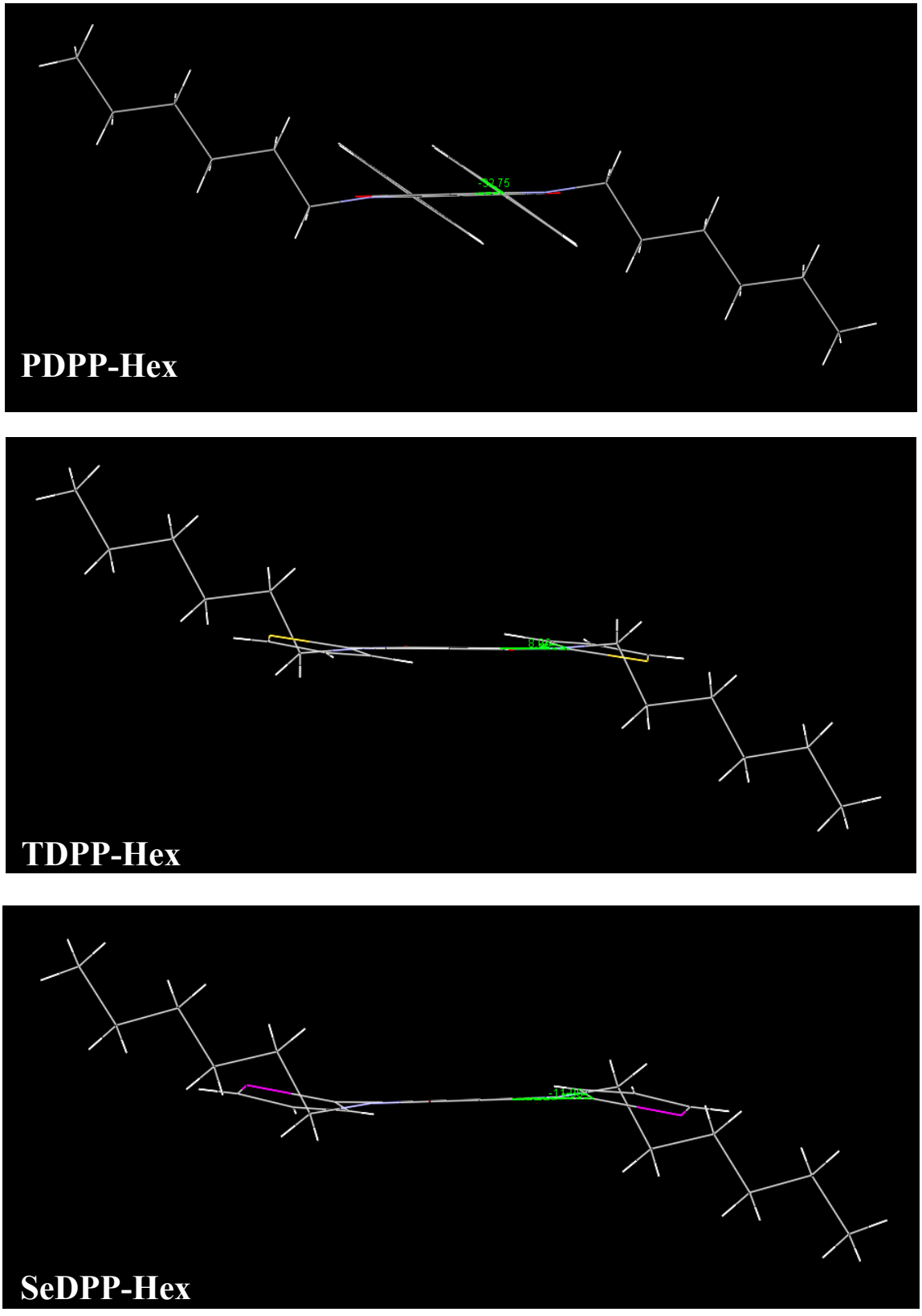
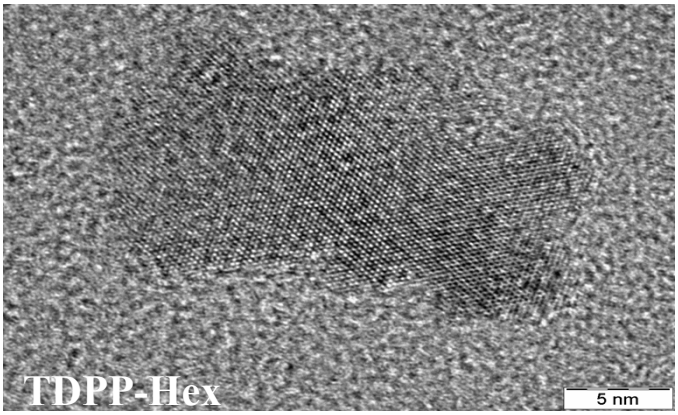
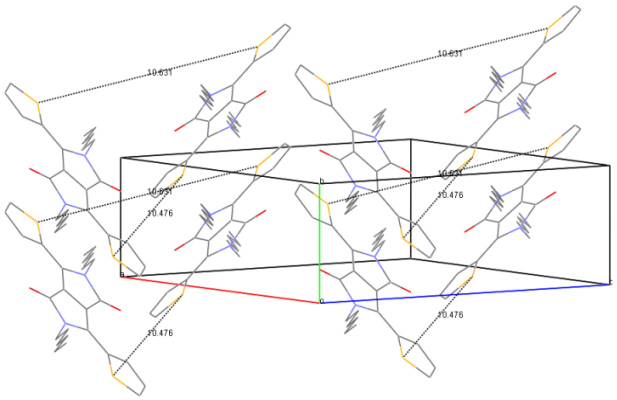
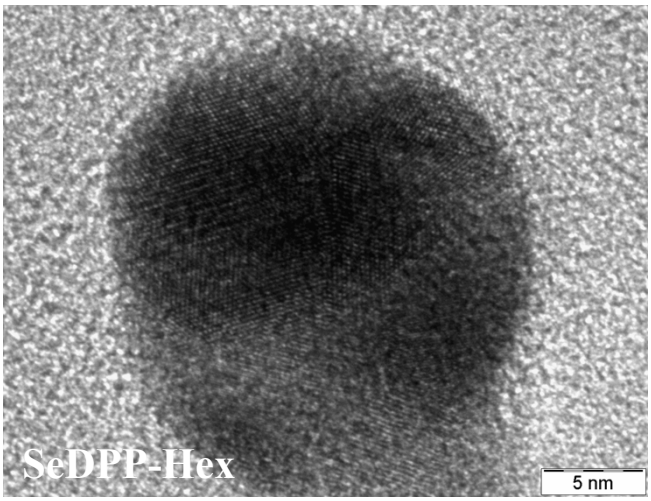



**Figure S8:** Torsional angle of three DPP derivatives.





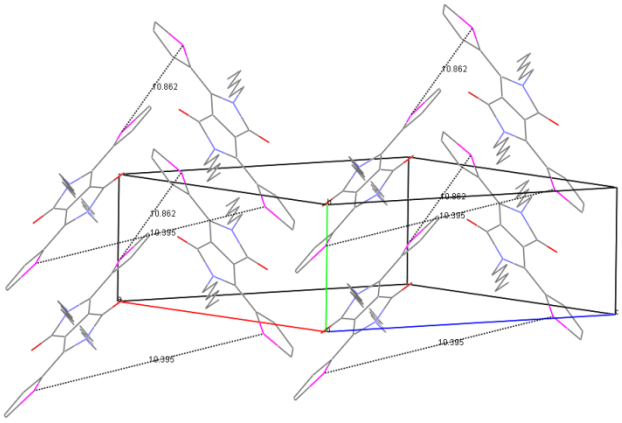



**Figure S9:** HRTEM image of the nanostructure observed from two DPP derivatives with plausible packing diagram.

**Table S1:** Summary of bond length and torsion data of DPP derivatives varied with different donor units.

| | **Inter-ring C-C (Å)** | **C-N (Å)** | **C-X (X=S, Se) (Å)** | **Torsion (°)** |
|---|---|---|---|---|
| **PDPP-Hex** | 1.46 | 1.39, 1.42 | - | 33 |
| **TDPP-Hex** | 1.43 | 1.39,1.41 | 1.69, 1.72 | 9 |
| **SeDPP-Hex** | 1.44 | 1.38, 1.41 | 1.84, 1.88 | 12 |

**Table S2**: Summary of the '*d*' spacing calculated from HR-TEM image of three DPP molecules.

| | PDPP-Hex | TDPP-Hex | SeDPP-Hex |
|---|---|---|---|
| 'd' spacings (Å) | 9.7,10.1, 10.4, 11, 11.8 | 10.1, 10.7 | 10.1, 11.0 |