Supporting Information for

Pyrene and Diketopyrrolopyrrole-based Oligomers Synthesized via Direct Arylation for OSC Applications

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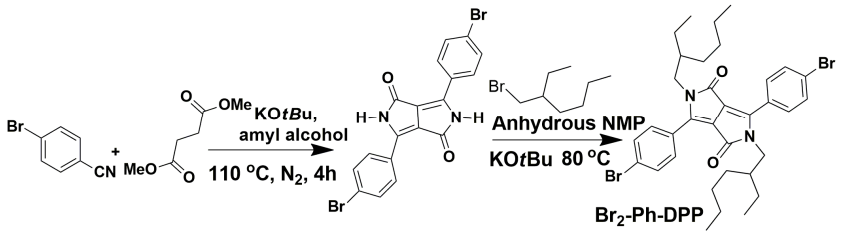
Contents

1. Synthesis of starting DPPs [1, 2]

1) Br_2-Ph-DPP

The synthetic route of **Br_2-Ph-DPP** is shown in Scheme S1. Potassium *tert*-butylate (5.61 g, 35.7 mmol) was added to a round flask with N_2 protection. Then a solution of 4-bromo-phenylcarbonitrile (7.28 g, 40 mmol) in 34 mL *t*-amyl alcohol was injected by a syringe one portion. The mixture was warmed up to 100-110 ^oC, and a solution of dimethyl succinate (2.34 g, 16 mmol) in *t*-amyl alcohol (10 mL) was dropped slowly in 1 h. When the addition was completed, the reaction was kept at the same temperature for about 1 h, and then the byproduct of methanol was distilled off and the reaction was kept for 4 h. Then the mixture was cooled to 65 ^oC, diluted with 50 mL of methanol, and neutralized with acetic acid and refluxed for another 10 min. Then the suspension was filtered, and the red filter cake was washed by hot methanol and water twice each and dried in vacuum to get coarse 1,4-diketo-3,6-bis(4-bromophenyl)pyrrolo[3,4-*c*]pyrrole and could be used directly to next step without further purification (7.30 g, yield 80%).

7.30 g (16 mmol) of 1,4-diketo-3,6-bis(4-bromophenyl)pyrrolo[3,4-*c*]pyrrole and 3.6 g (32 mmol) of potassium *tert*-butoxide were suspended in dry N-methyl-2-pyrrolidone (NMP) and vigorously stirred at 80 ^oC for 30 min, and then 19 g (99 mmol) of 2-ethylhexyl bromide was added dropwise over a period of 90 min. After 20 h, the reaction mixture was diluted with 100 mL of toluene and washed with water and brine several times. The organic phase was dried over magnesium sulfate and concentrated using a rotary evaporator. The crude product was purified by column chromatography on silica using CH_2Cl_2 and petroleum ether as the solvent. Thus, 4.3 g (40%) of bright orange needles were obtained. ^1H NMR (500 MHz, $CDCl_3$) δ 7.65 (s, 8H), 4.12 – 3.94 (m, 4H), 1.46 (s, 2H), 1.07 (m, 16H), 0.88 (ddd, *J* = 20.0, 13.0, 7.5 Hz, 12H).



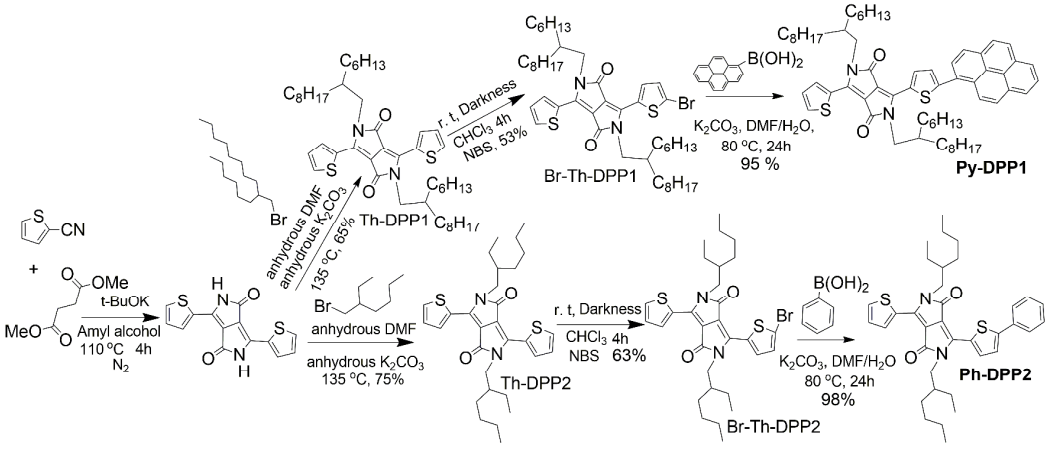
Scheme S1. Synthetic route of **Br_2-Ph-DPP**

2) Py-DPP1

The synthetic route of **Py-DPP1** is shown in Scheme S2. **Th-DPP 1** shown in

Scheme S2 was synthesized according to previous reports. The bromination of Th-DPP 1 with 1 equiv. N-bromosuccinimide (NBS) led to formation of mono-bromo-DPP, **Br-Th-DPP1**. Typically, N-bromosuccinimide (0.85 g, 4.76 mmol) was added in portions to a solution of **Th-DPP 1** (3.5 g, 4.76 mmol) in $CHCl_3$ (50 mL) in a two-necked flask at 5 ^oC. The mixture was warmed to room temperature and stirred overnight. CH_2Cl_2 was added and then the solution was washed with brine. The organic phase was dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. The crude product was purified chromatographically (silica gel; CH_2Cl_2-petroleum ether, 2: 1, v/v) to yield **Br-Th-DPP1** as a red solid (1.71 g, 53%). ^1H NMR (300 MHz, $CDCl_3$) δ 8.87 (d, J = 3.9 Hz, 1H), 8.59 (d, J = 4.2 Hz, 1H), 7.64 (d, J = 5.1 Hz, 1H), 7.28 – 7.18 (m, 2H), 4.02–3.92 (m, 4H), 1.89(m, 2H), 1.30–1.21 (m, 48H), 0.91–0.83 (m, 12H).

The above synthesized **Br-Th-DPP1** (171 mg, 2 mmol), pyren-1-ylboronic acid (760 mg, 3 mmol), K_2CO_3 (420 mg, 3 mmol) were dissolved in 10 mL of DMF followed by adding 1 mL H_2O and $Pd(PPh_3)_4$ (70 mg, 0.06 mmol) was stirred for 24 h at 80 °C under nitrogen atmosphere. Then the reaction mixture was washed by NaCl solution to remove the high boiling point solvent DMF, followed by extraction using CH_2Cl_2. Removal of the CH_2Cl_2 by rotary evaporator afforded the crude products, which were then purified by column chromatography on silica gel using the mixtures of CH_2Cl_2 and petroleum ether (v/v, 2:1) as eluent and gave the **Py-DPP1 as a** purple-black solid. (**Py-DPP1**, 178 mg, 95%). ^1H NMR (300 MHz, $CDCl_3$) δ 9.13 (d, J = 4.2 Hz, 1H), 8.90 (dd, J = 3.9, 1.1 Hz, 1H), 8.55 (d, J = 9.3 Hz, 1H), 8.31 – 7.91 (m, 8H), 7.71 – 7.50 (m, 2H), 4.21 – 3.91 (m, 4H).



Scheme S2. Synthetic route of **Py-DPP1** and **Ph-DPP2**

3) Ph-DPP2

The synthetic route of **Ph-DPP2** is shown in Scheme S2. The synthetic procedure of **Ph-DPP2** was similar to the above **Py-DPP1**, except that the alkyl bromide 2-hexyldecyl bromide was change to 2-ethylhexyl bromide.

Br-Th-DPP2 (red solid, yield 63%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.90 (d, J = 3.9 Hz, 1H), 8.64 (d, J = 4.2 Hz, 1H), 7.65 (d, J = 5.1 Hz, 1H), 7.29 – 7.18 (m, 2H), 4.03–3.92 (m, 4H), 1.84(m, 2H), 1.38–1.23 (m, 16H), 0.91–0.83 (m, 12H).

Ph-DPP2 (dark red solid, yield 98%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.97 (d, J = 4.0Hz, 1H), 8.89 (d, J = 3.5 Hz, 1H), 7.68 (d, J = 7.5 Hz, 2H), 7.62 (d, J = 5.0 Hz, 1H), 7.42 (ddd, 4H), 7.30 – 7.27 (m, 1H), 4.16 – 3.89 (m, 4H), 1.93 (d, J = 5.5 Hz, 2H), 1.37 – 1.25 (m, 16H), 0.88 (ddd, 12H).

REFERENCES

(1) Liu, S-Y.; Li, H-Y.; Shi, M-M.; Jiang, H.; Hu, X-L.; Li, W-Q.; Fu, L.; Chen, H-Z. *Macromolecules* **2012**, *45*, 9004.

(2) Liu, S-Y.; Shi, M.; Huang, J.; Jin, Z.; Hu, X..; Pan, J.; Li, H.; Jen, A. K.-Y.; Chen, H. Z. *J. Mater. Chem. A* **2013**, *1*, 2795.

2. ^{1}H & ^{13}C NMR and MALDI-TOF MS spectra (Figures S1-S9)

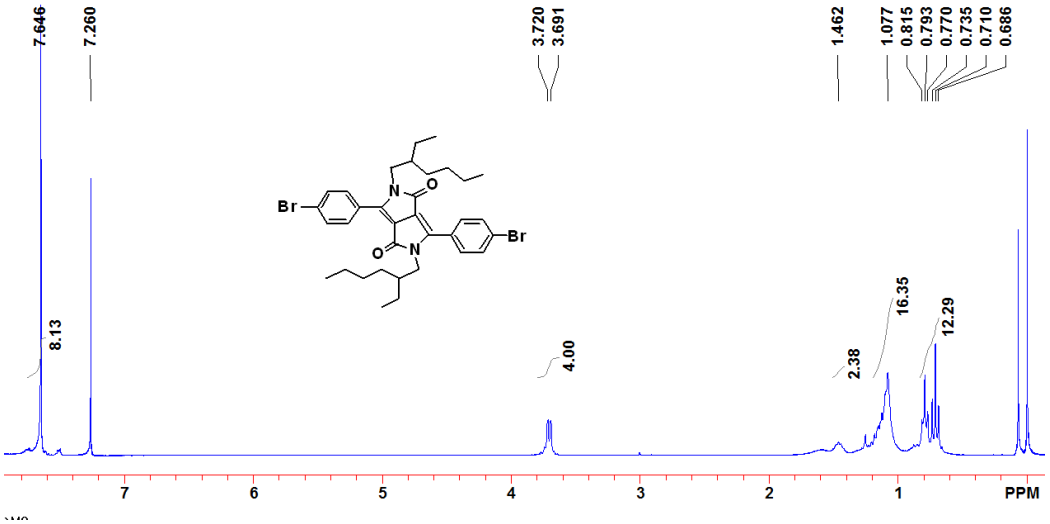


Figure S1. ^{1}H NMR of Br_2-Ph-DPP.

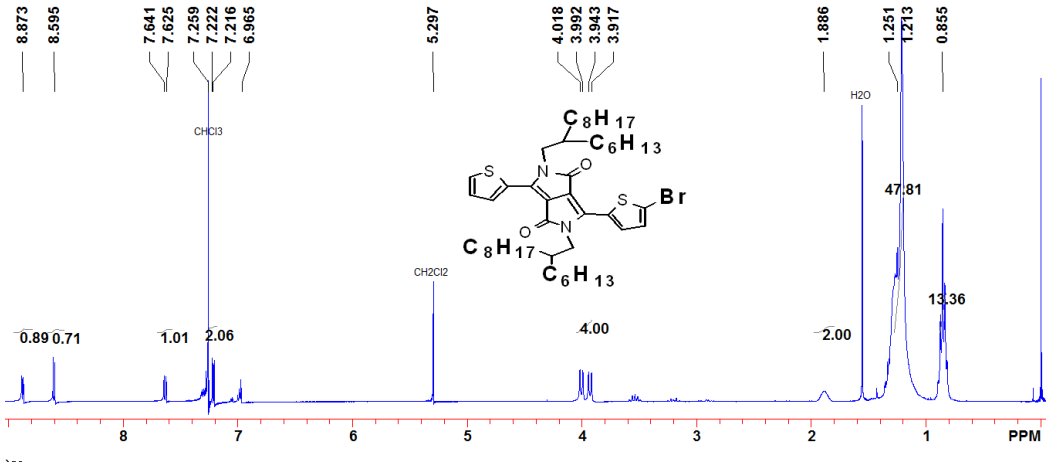


Figure S2. ^{1}H NMR of mono-bromo-DPP1

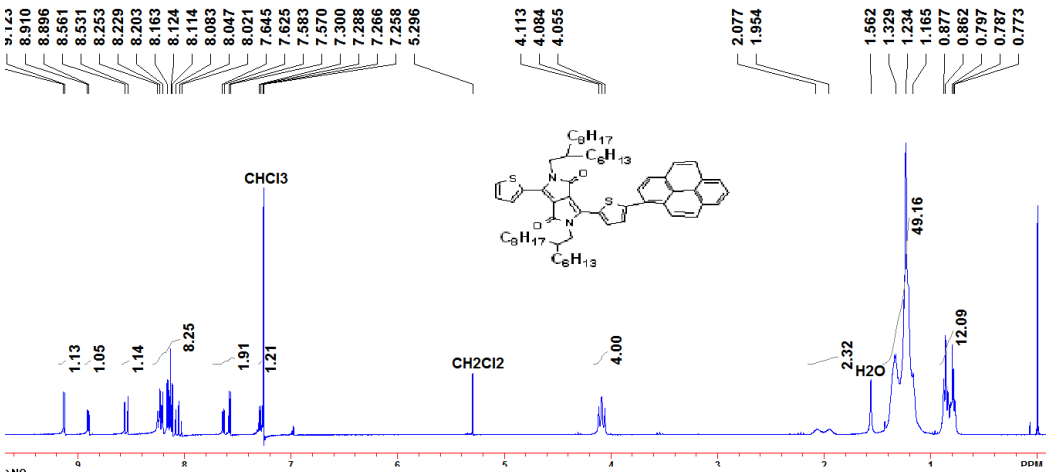


Figure S3. ^{1}H NMR of **Py-DPP1**.

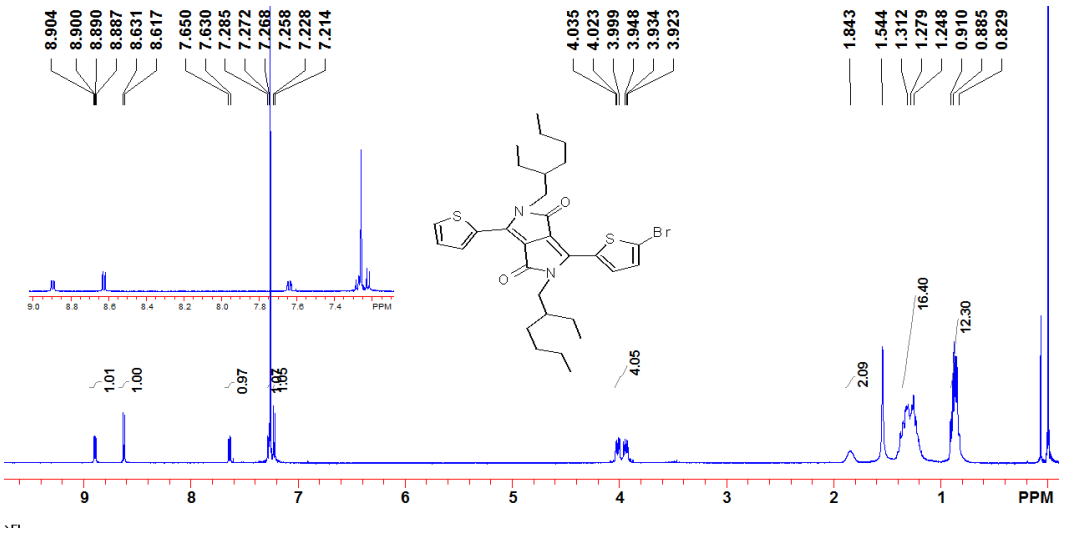


Figure S4. ^{1}H NMR of mono-bromo-DPP2.

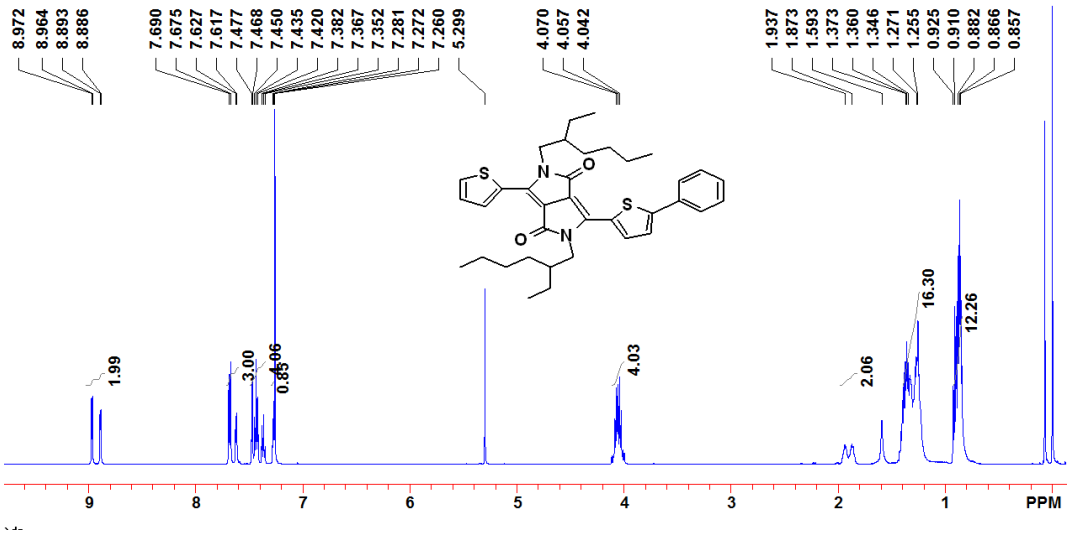


Figure S5. ^{1}H NMR of **Ph-DPP2**.

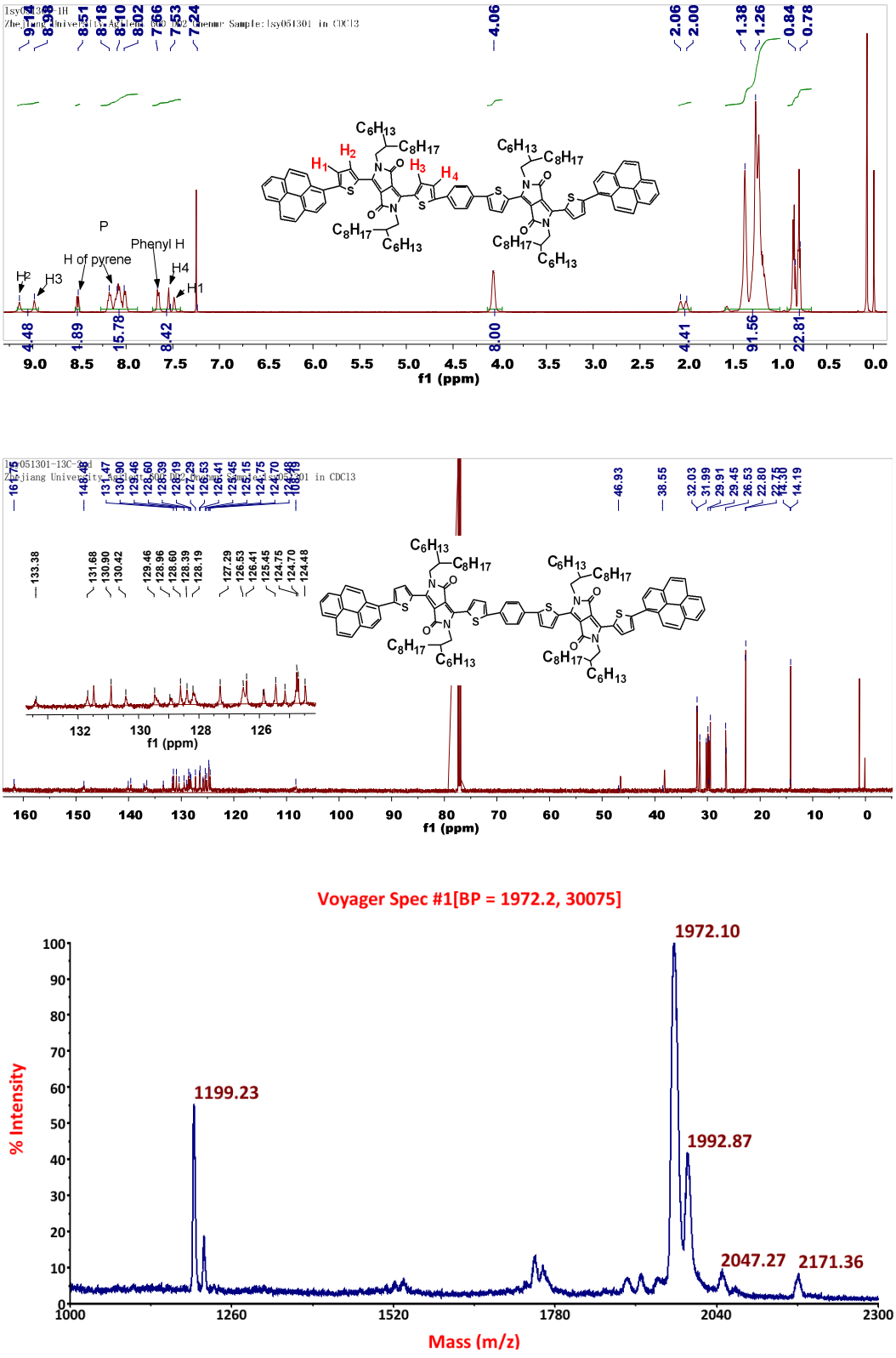
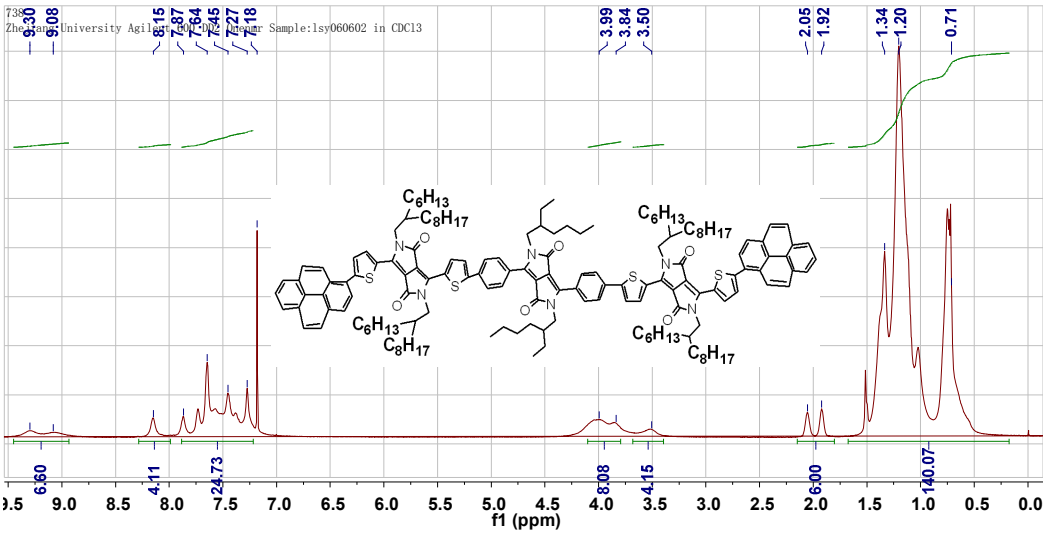
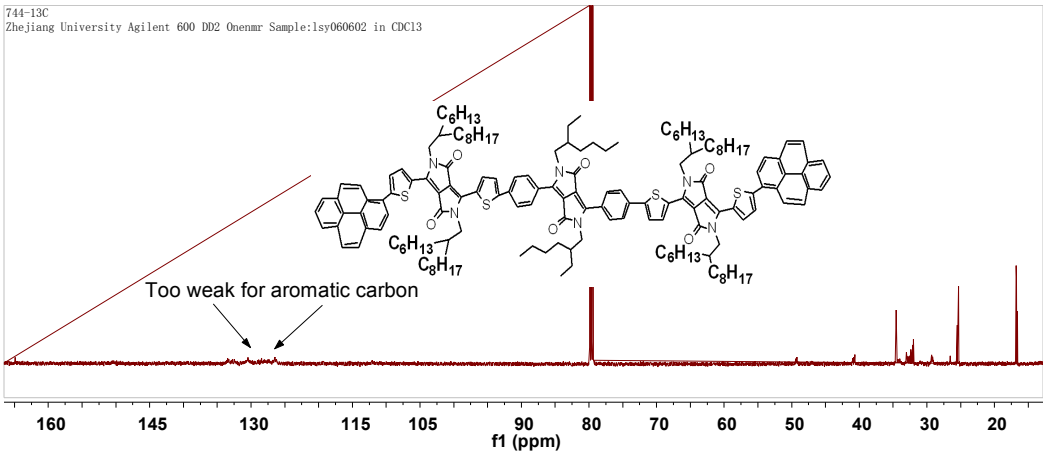


Figure S6. ^{1}H &^{13}C NMR and MALDI-TOF MS of **$Py_2PhTh_4(DPP)_2$ (SM 1)**.





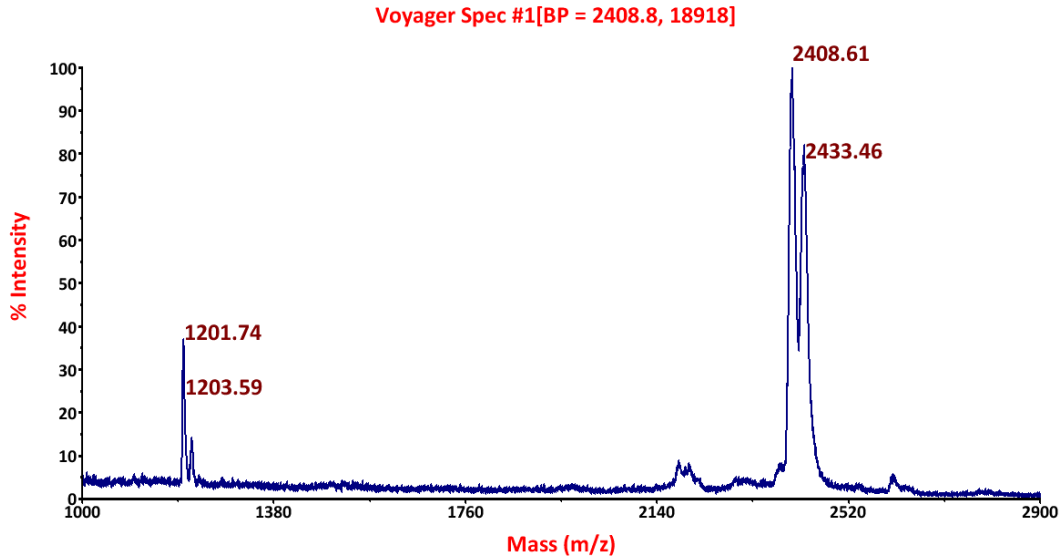
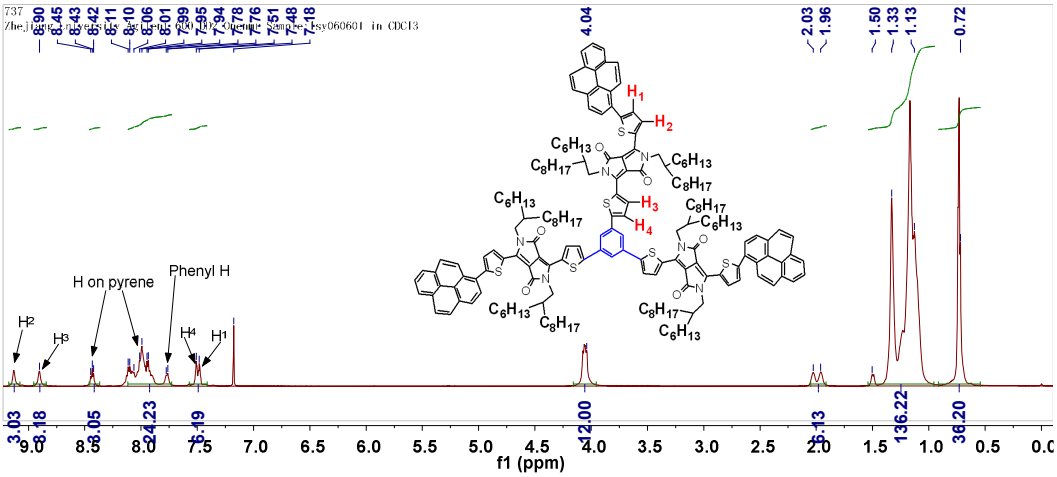
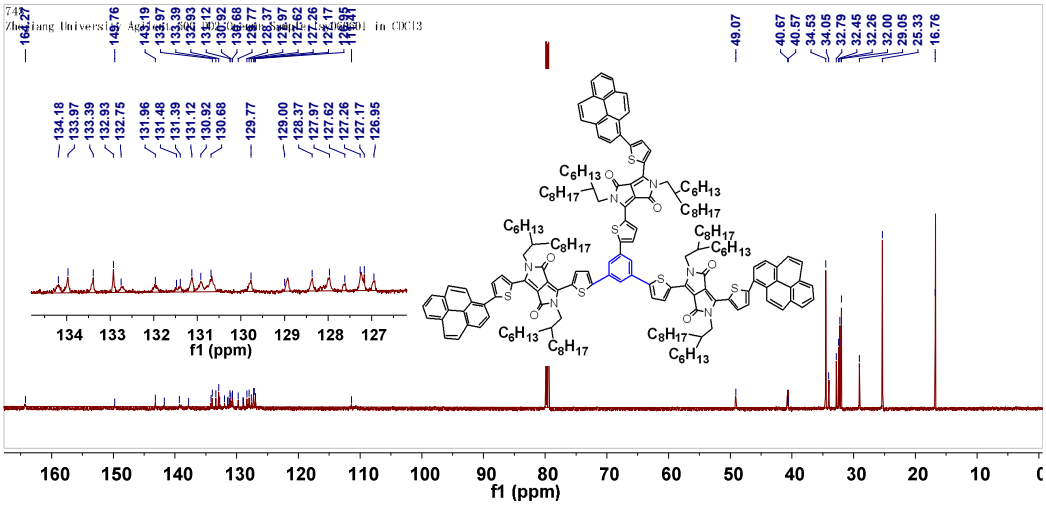


Figure S7. ^{1}H &^{13}C NMR and MALDI-TOF MS of **$Py_2Ph_2Th_4(DPP)_3$** (**SM 2**).





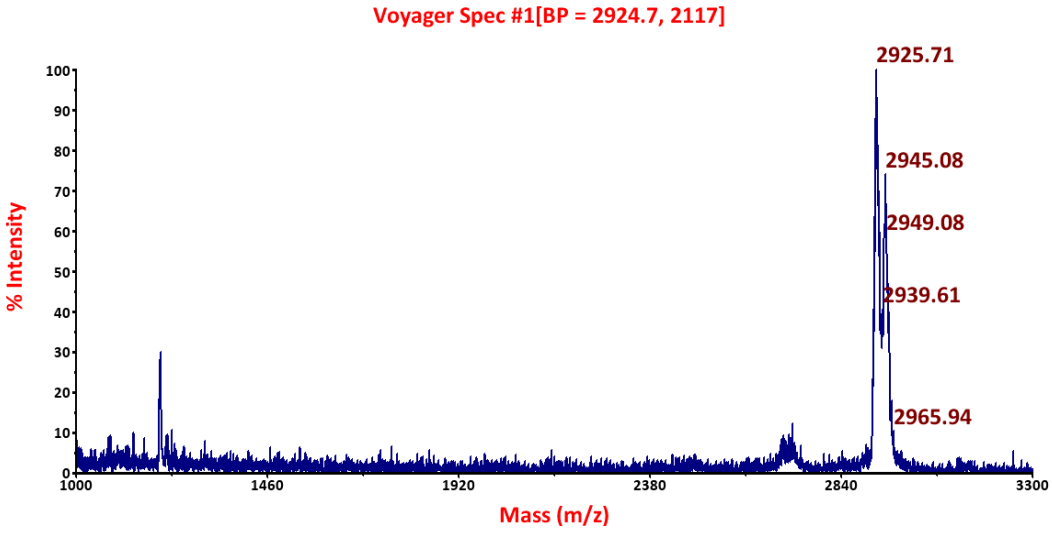
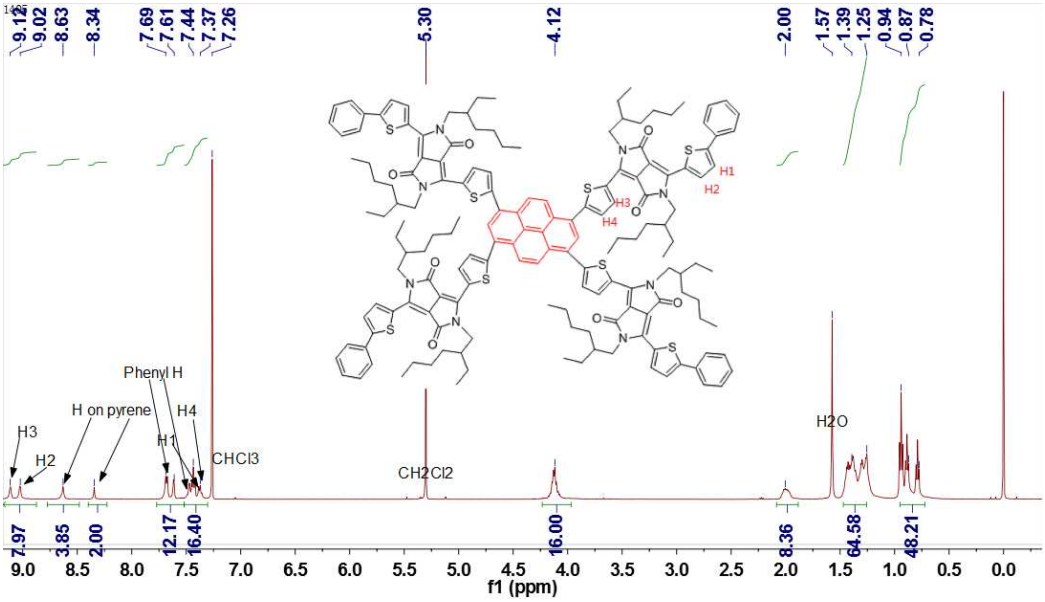
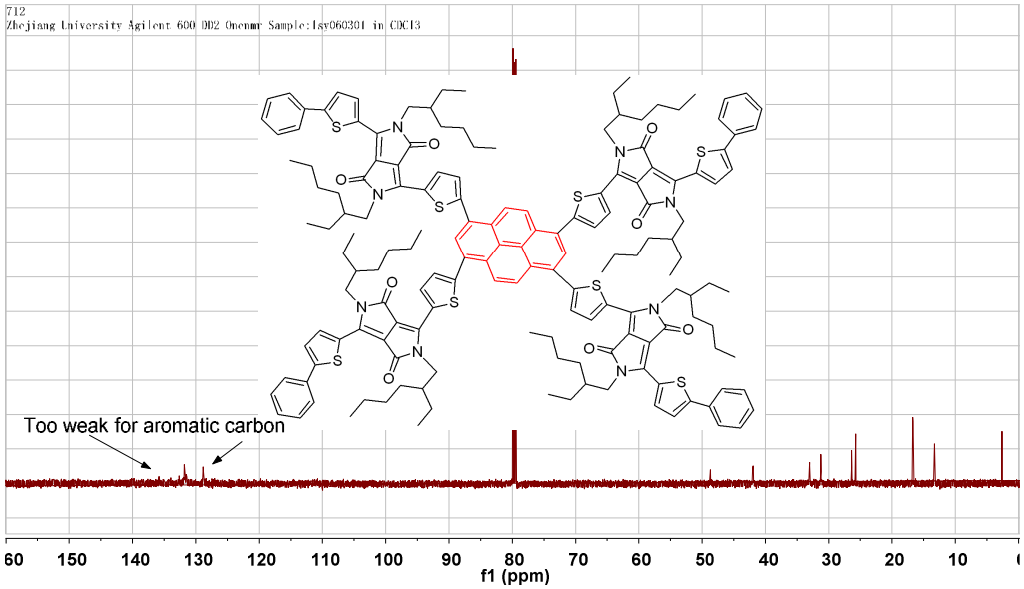


Figure S8. ^{1}H &^{13}C NMR and MALDI-TOF MS of **$Py_3PhTh_6(DPP)_3$ (SM 3)**.





Voyager Spec #1[BP = 2622.3, 18543]

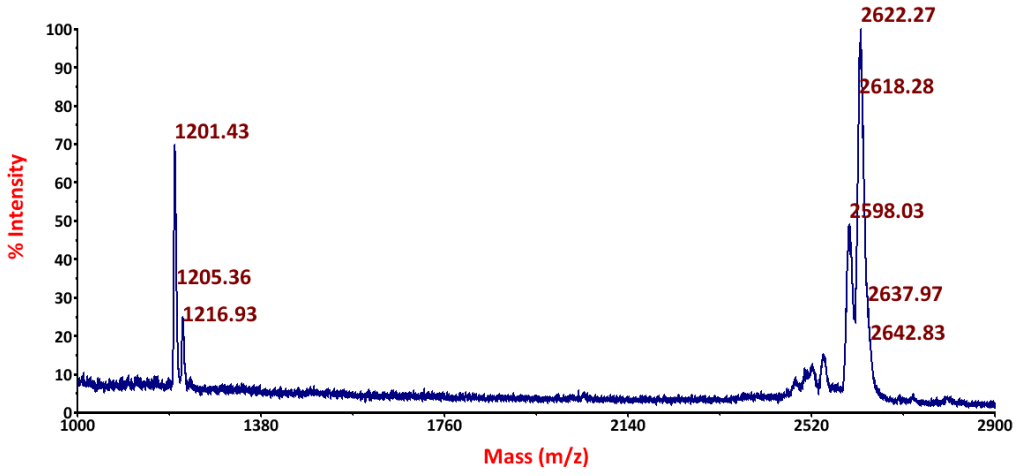
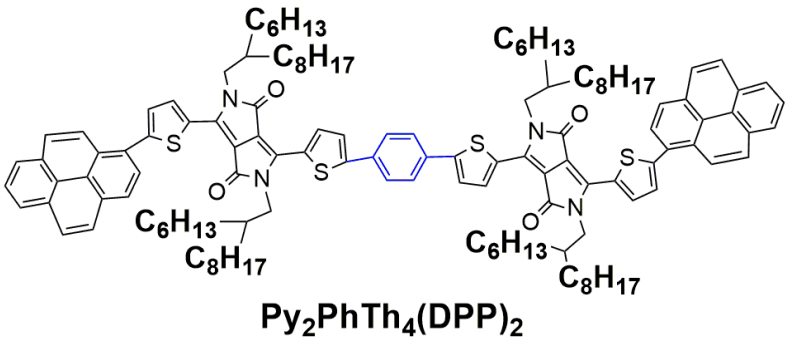


Figure S9. ^{1}H &^{13}C NMR and MALDI-TOF MS of **$PyPh_4Th_8(DPP)_4$ (SM 4)**.

3. HOMO and LUMO orbits of SMs 1-4 obtained by DFT (Figures S10-S13)

SM 1



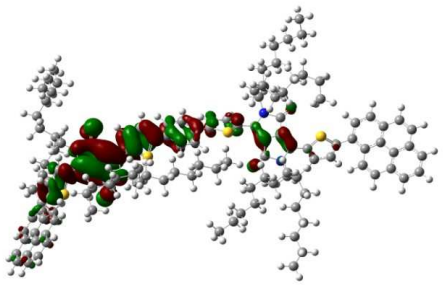
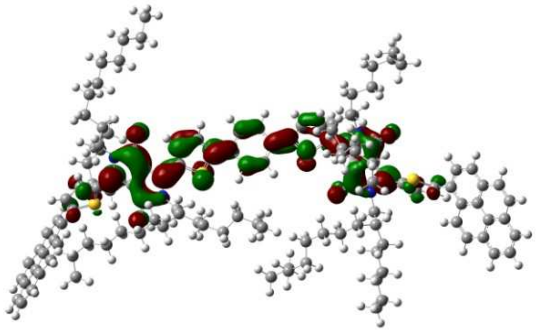
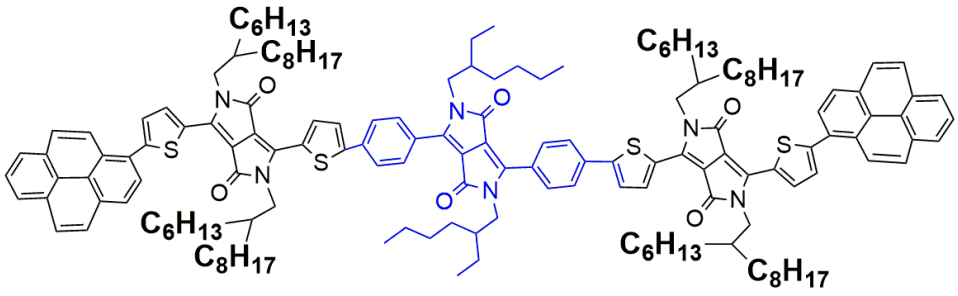
HOMO=-5.04ev	LUMO=-2.58ev
 LUMO- HOMO=2.46ev	

Figure S10. HOMO and LUMO orbits of **SM 1**obtained by theoretical calculations.

SM 2



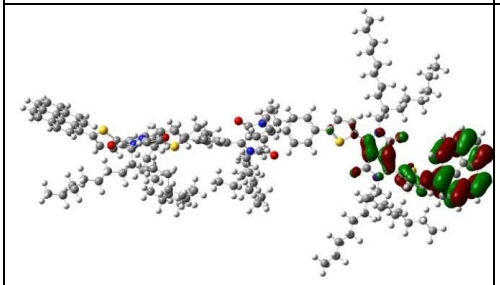
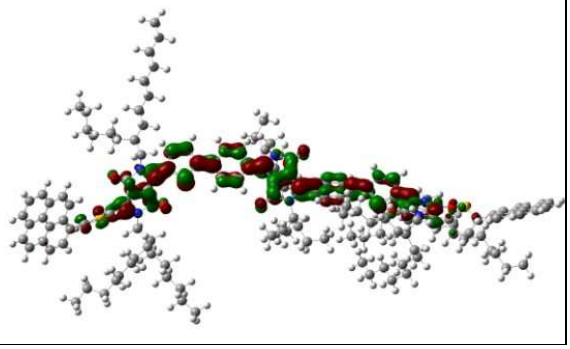
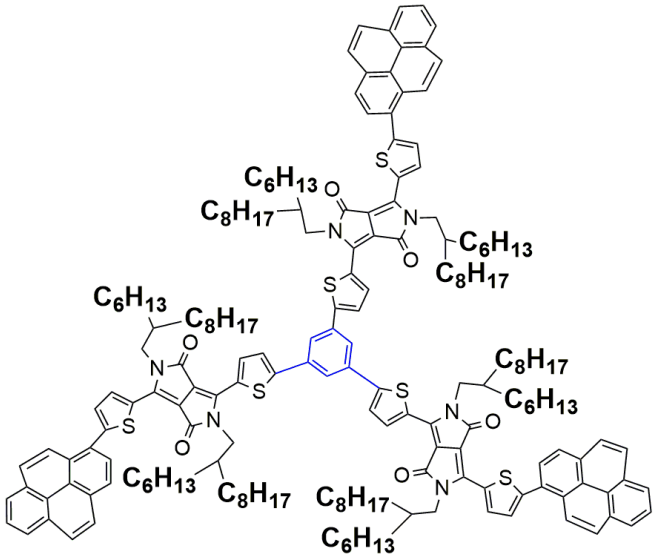
HOMO= -5.07ev	LUMO= -2.69ev
 LUMO- HOMO=2.38ev	

Figure S11. HOMO and LUMO orbits of **SM 2** obtained by theoretical calculations.

SM 3



$Py_3PhTh_6(DPP)_3$

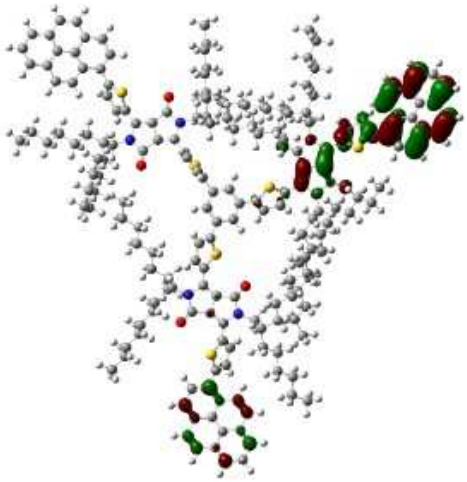
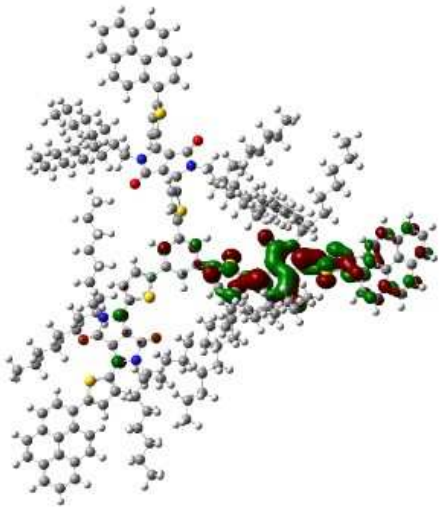
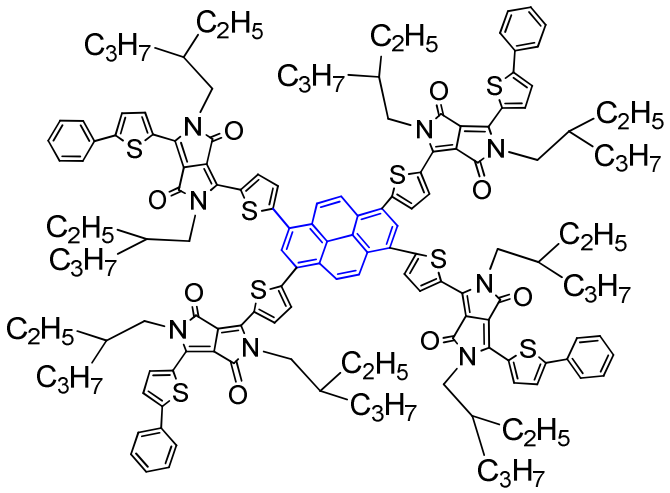
HOMO=- 5.17ev	LUMO=- 2.50ev
 LUMO- HOMO=2.67ev	

Figure S12. HOMO and LUMO orbits of **SM 3** obtained by theoretical calculations.

SM 4



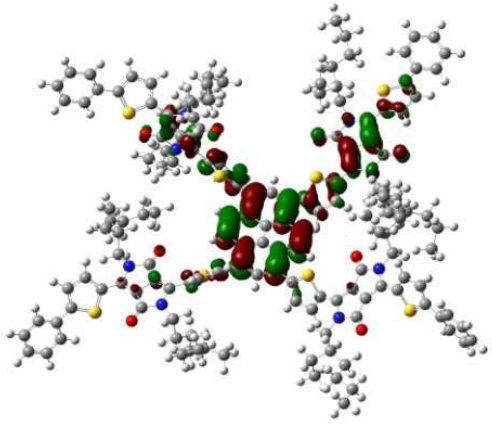
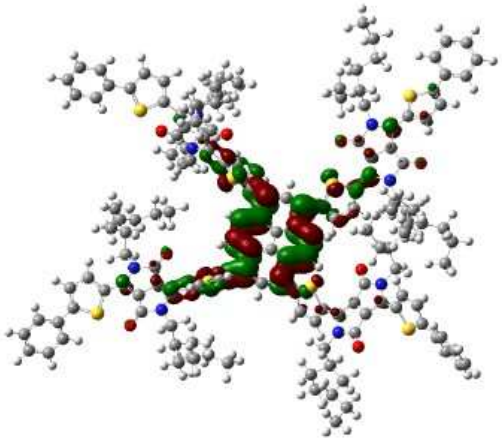
HOMO= -5.18ev	LUMO=-2.65ev
 LUMO- HOMO=2.53ev	

Figure S13. HOMO and LUMO orbits of **SM 4** obtained by theoretical calculations.

4. DSC curves of SMs 1-4 (Figures S14-S17)

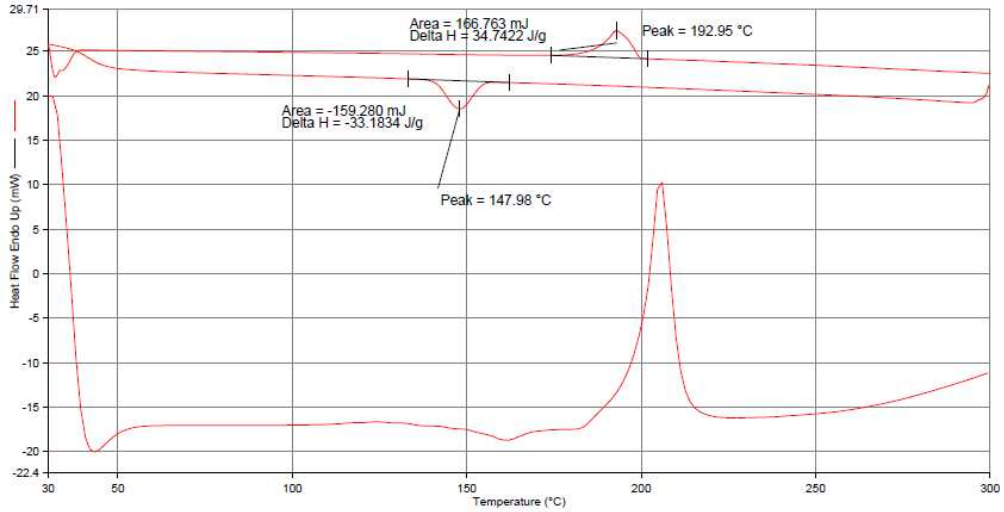


Figure S14. DSC curve of **SM 1**.

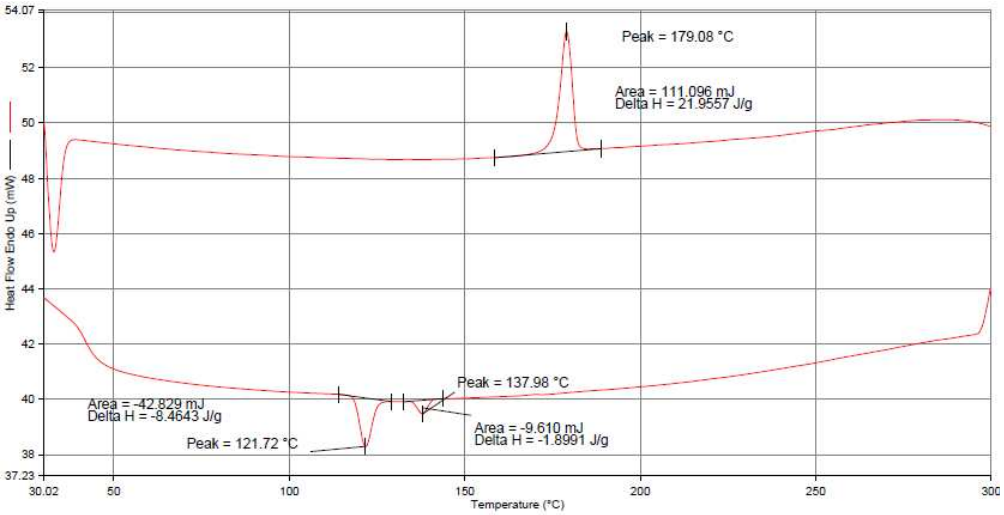


Figure S15. DSC curve of **SM 2**.

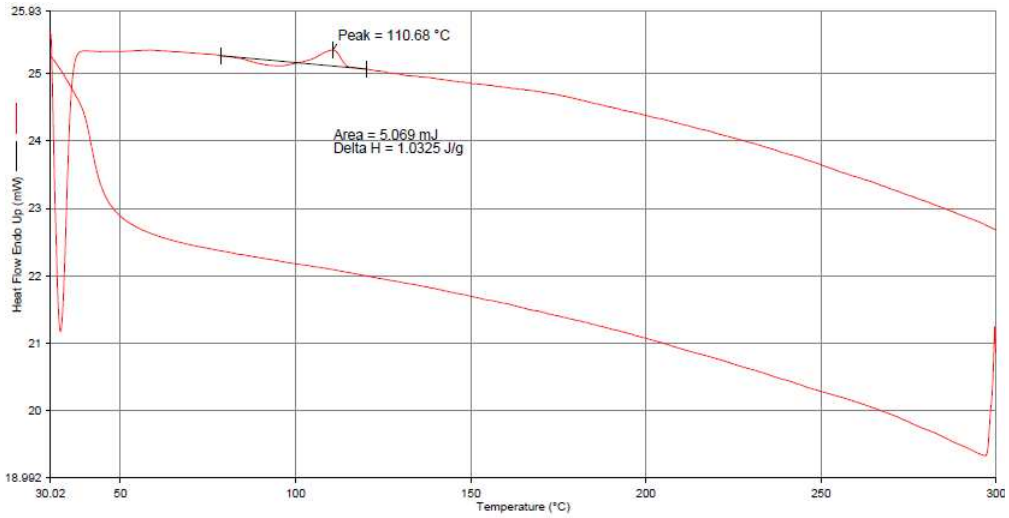


Figure S16. DSC curve of **SM 3**.

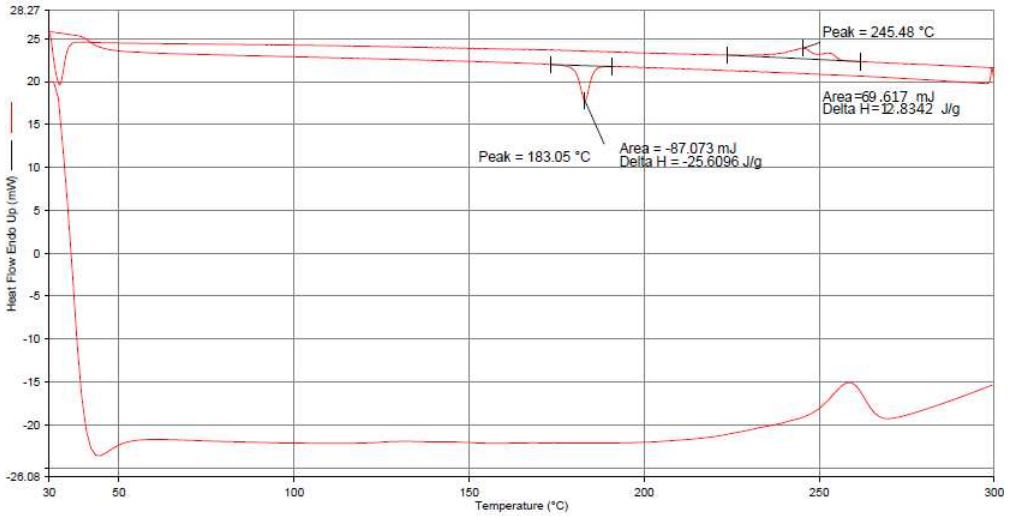


Figure S17. DSC curve of **SM 4**.