

# Efficient Design and Structural Modifications for Tuning the Photoelectric Properties of Small-Molecule Acceptors in Organic Solar Cells

Xiaodong He,<sup>a</sup> Lunxiang Yin,<sup>a</sup> Yanqin Li\*<sup>a</sup>

<sup>a</sup>*School of Chemistry, Dalian University of Technology, Dalian, 116024, China.*

*Fax: 86-411-84986040; Tel: 86-411-84986040;*

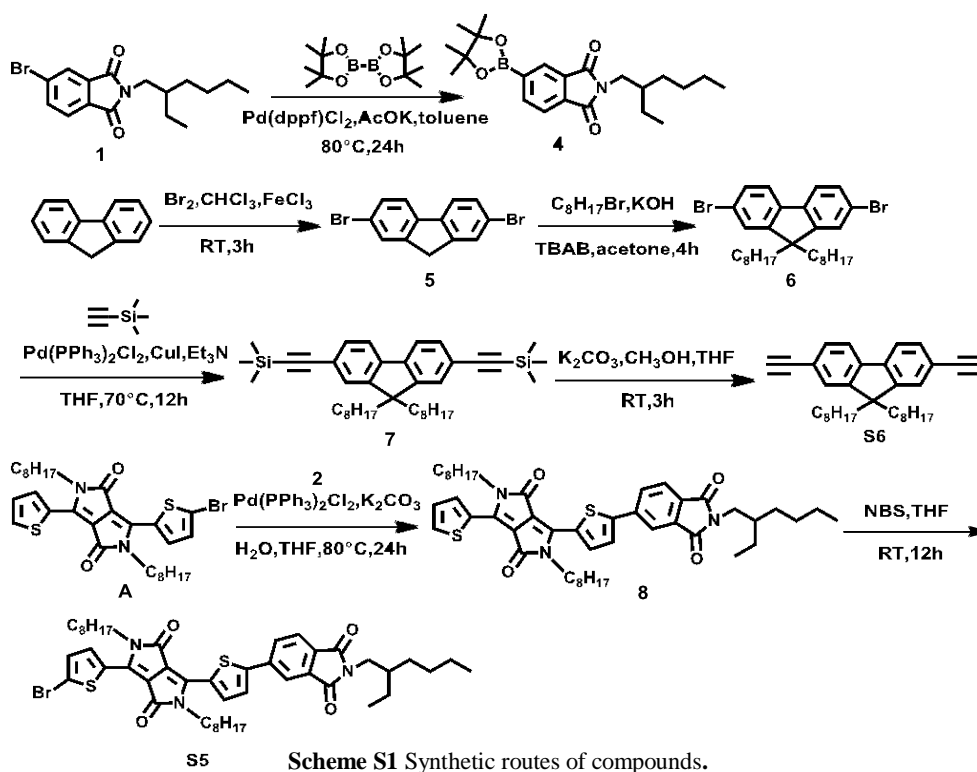
*E-mail: liyanqin@dlut.edu.cn*

## Supporting information

### Table of contents

1. Synthetic procedures.....	S2
2. <sup>1</sup> H-NMR and <sup>13</sup> C-NMR spectra.....	S4
3. DSC curve.....	S13
4. XRD curve.....	S14
5. TD-DFT calculated electronic transitions.....	S15
4. <i>J-V</i> characteristics of photovoltaic devices.....	S15
5. References.....	S16

## 1. Synthetic procedures



S5 Scheme S1 Synthetic routes of compounds.

### 2-(2-ethylhexyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-isoindole-1,3(2*H*)-dione(**4**)

A solution of compound **1** (1.00 g, 3.05 mmol), bis(pinacolato)diborane (0.85 g, 3.36 mmol), Pd(dppf)Cl<sub>2</sub> (67 mg, 0.092 mmol) and potassium acetate (0.90 g, 9.15 mmol) in 30 ml distilled toluene was stirred at 100 °C under nitrogen atmosphere for 24 h. The cooled solution was diluted with 30 ml water and extracted with dichloromethane (3 × 30 ml). The organic phase was dried over anhydrous sodium sulfate and then the solvent was evaporated under reduced pressure. The residue was purified by silica column chromatography eluting with petroleum ether/ethyl acetate (5:1, v/v), affording a pale yellow liquid (**4**) (1.06 g, 91%). <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>, ppm): δ 8.20 (s, 1H), 8.07 (d, *J* = 7.5 Hz, 1H), 7.74 (d, *J* = 7.3 Hz, 1H), 3.51 (d, *J* = 7.3 Hz, 2H), 1.79-1.74 (m, 1H), 1.28 (s, 12H), 1.24-1.16 (m, 8H), 0.84-0.79 (m, 6H).

**2,7-Dibromo-9*H*-fluorene(**5**)**.<sup>1</sup> Fluorene (10 g, 60 mmol) and FeCl<sub>3</sub> (0.15 g, 0.90 mmol) were dissolved in 50 ml chloroform, then a solution of Br<sub>2</sub> (6.46 mL, 126 mmol) in chloroform (20 mL) was added dropwise at 0 °C, and the resulted mixture was stirred for 2 h at room temperature. The mixture was neutralized using saturated aqueous sodium hydrogen sulfite and extracted with dichloromethane (3 × 20 ml). Then, the organic layer was dried over anhydrous sodium sulfate and the solvent was evaporated under reduced pressure. A white solid compound (**5**) was obtained in a yield of 99% without further purification (19.20 g).

**2,7-Dibromo-9,9-dioctyl-9*H*-fluorene(**6**)**.<sup>1</sup> Compound **5** (3.24 g, 10 mmol), tetrabutyl ammonium bromide (0.32 g, 1 mmol) and KOH (1.12 g, 20 mmol) were dissolved in 40 ml acetone. After adding 1-bromooctane (4.0 ml, 23 mmol) in the mixture, the reaction solution was refluxed at 57 °C for 4 h. The reaction solution was cooled down, then the precipitate was filtered off and filtrate was collected.

After removing the solvent under reduced pressure, the residue was purified by silica column chromatography eluting with petroleum ether to obtain a colourless liquid (**6**) (4.73 g, 86%). <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>, ppm): δ 7.51 (d, *J* = 8.2 Hz, 2H), 7.47-7.42 (m, 4H), 1.93-1.88 (m, 4H), 1.22-1.03 (m, 20H), 0.83 (t, *J* = 7.2 Hz, 6H), 0.59-0.56 (m, 4H).

**9,9-Dioctyl-2,7-bis[2-(trimethylsilyl)ethynyl]-9H-fluorene(7).**<sup>2</sup> Under nitrogen atmosphere, compound **6** (3.00 g, 5.47 mmol), trimethylsilyl acetylene (1.70 ml, 12 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.19 g, 0.27 mmol) and CuI (0.10 g, 0.54 mmol) were added in a 100 ml three-neck flask, and then triethylamine (20 ml) and freshly distilled tetrahydrofuran (20 ml) were injected into the reaction mixture. The mixture was refluxed at 70 °C for 24 h. The reaction solution was cooled down and poured into 20 ml water. After being extracted with dichloromethane (3 × 20 ml), the organic layer was dried over anhydrous sodium sulfate, then the solvent was removed under reduced pressure. The residue was purified by silica column chromatography using petroleum ether/ dichloromethane (40:1, v/v) as the eluent to give a yellow liquid (**7**) (1.96 g, 61%). <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>, ppm): δ 7.58 (d, *J* = 7.8 Hz, 2H), 7.45 (dd, *J* = 7.8, 1.2 Hz, 2H), 7.41 (s, 2H), 1.96 – 1.89 (m, 4H), 1.22 – 1.00 (m, 20H), 0.82 (t, *J* = 7.2 Hz, 6H), 0.54-0.53 (m, 4H), 0.28 (s, 18H).

**2,7-Diethynyl-9,9-dioctyl-9H-fluorene (S6).**<sup>2</sup> To a solution of compound **7** (1.64 g, 2.81 mmol) in tetrahydrofuran (15 ml) and methanol (15 ml), K<sub>2</sub>CO<sub>3</sub> (3.88 g, 28.1 mmol) was added and the mixture was stirred at 25 °C for 4 h. Then the precipitate was filtered off and filtrate was collected. After removing the solvent under reduced pressure, the residue was purified by silica column chromatography eluting with petroleum ether/ dichloromethane (20:1, v/v) to obtain a yellow liquid (S6) (1.10 g, 90%). <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>, ppm): δ 7.62 (d, *J* = 7.8 Hz, 2H), 7.48 (dd, *J* = 7.8, 1.2 Hz, 2H), 7.46 (s, 2H), 3.14 (s, 2H), 1.95-1.91 (m, 4H), 1.21-1.03 (m, 20H), 0.83 (t, *J* = 7.1 Hz, 6H), 0.58-0.53 (m, 4H).

**5-(5-(2,5-dioctyl-3,6-dioxo-4-(thiophen-2-yl)-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)thiophen-2-yl)-2-(2-ethylhexyl)isoindoline-1,3-dione(8)** Compound A<sup>3</sup> (0.20 g, 0.33 mmol) and compound **4** (0.14 g, 0.36 mmol) were placed in a dry three-neck flask (50 ml) with Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (24 mg, 0.033 mmol) and K<sub>2</sub>CO<sub>3</sub> (0.91g, 6.60 mol). Deionized water (3.3 ml) and freshly distilled tetrahydrofuran (20 ml) were injected into the reaction mixture, and the mixture was stirred at 80 °C for 24 h under nitrogen atmosphere. After being cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica column chromatography eluting with petroleum ether/ dichloromethane (1:4, v/v) to obtain a purple solid (**8**) (0.20 g, 78%). M.p.:202-204°C; <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>, ppm): δ 8.97 (dd, *J* = 3.9, 1.1 Hz, 1H), 8.93 (d, *J* = 4.2 Hz, 1H), 8.12 (d, *J* = 1.1 Hz, 1H), 7.99 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.67 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.63 (d, *J* = 4.2 Hz, 1H), 7.30 (dd, *J* = 5.0, 3.9 Hz, 1H), 4.09 (m, 4H), 3.61 (d, *J* = 7.2 Hz, 2H), 1.88 – 1.84 (m, 1H), 1.77 (m, 4H), 1.37 – 1.25 (m, 28H), 0.93 – 0.85 (m, 12H).

**5-(5-(4-(5-bromothiophen-2-yl)-2,5-dioctyl-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)thiophen-2-yl)-2-(2-ethylhexyl)isoindoline-1,3-dione (S5)** N-bromobutanamide (0.05 g, 0.27 mmol) dissolved in chloroform (10 ml) was added dropwise in the dark to a solution of compound **8** (0.20 g, 0.26 mmol) in tetrahydrofuran (10 mL) at 0 °C. Then, the mixture was stirred at room temperature for 12 h. Afterwards, the reaction solution was poured into 20 ml water and extracted with chloroform (3 × 20 ml). The combined organic layer was dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the residue was recrystallized from petroleum ether to afford an atropurpureus solid (S5) (0.21 g, 95%) M.p.:233-234°C; <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>, ppm): δ 8.94 (d, *J* = 4.2 Hz, 1H), 8.72 (d, *J* = 4.2 Hz, 1H), 8.12 (s, 1H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.88 (d, *J* = 7.8 Hz,

1H), 7.63 (d,  $J = 4.1$  Hz, 1H), 7.25 (d,  $J = 1.4$  Hz, 1H), 4.14 – 4.08 (m, 2H), 4.04 – 3.98 (m, 2H), 3.61 (d,  $J = 7.3$  Hz, 2H), 1.88 – 1.82 (m, 1H), 1.75 (m, 4H), 1.40 – 1.19 (m, 28H), 0.95 – 0.85 (m, 12H).

## 2. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra

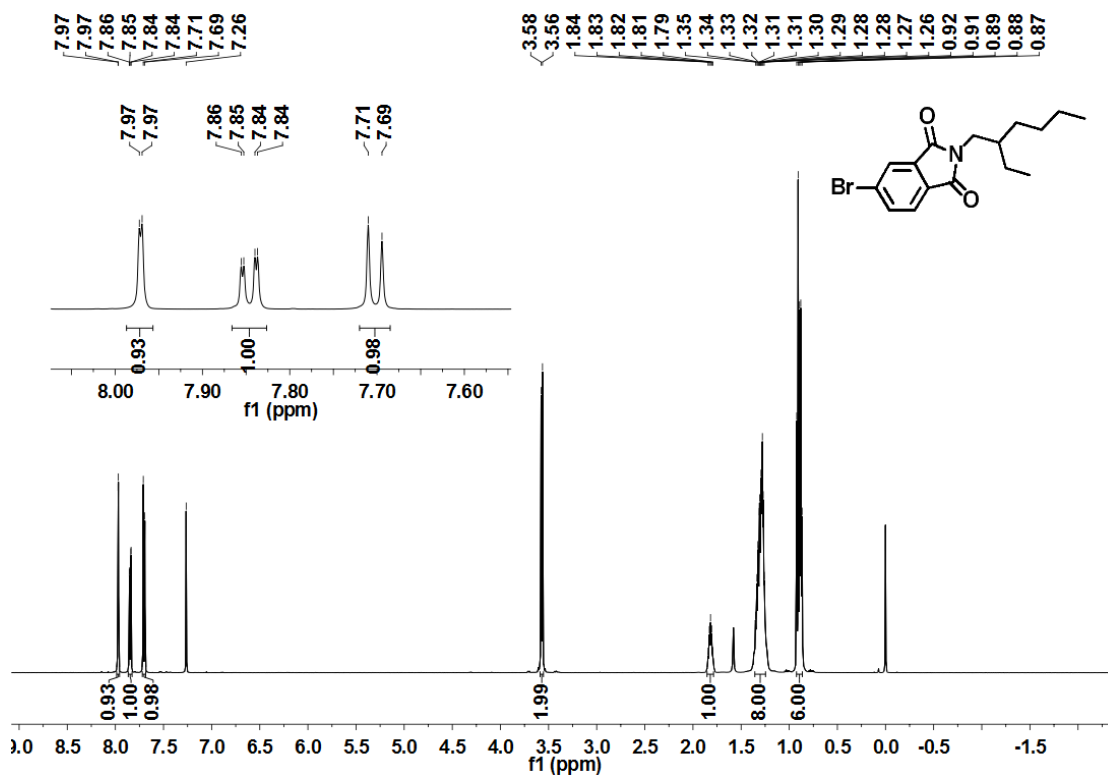


Fig. S1  $^1\text{H-NMR}$  spectra of compound 1

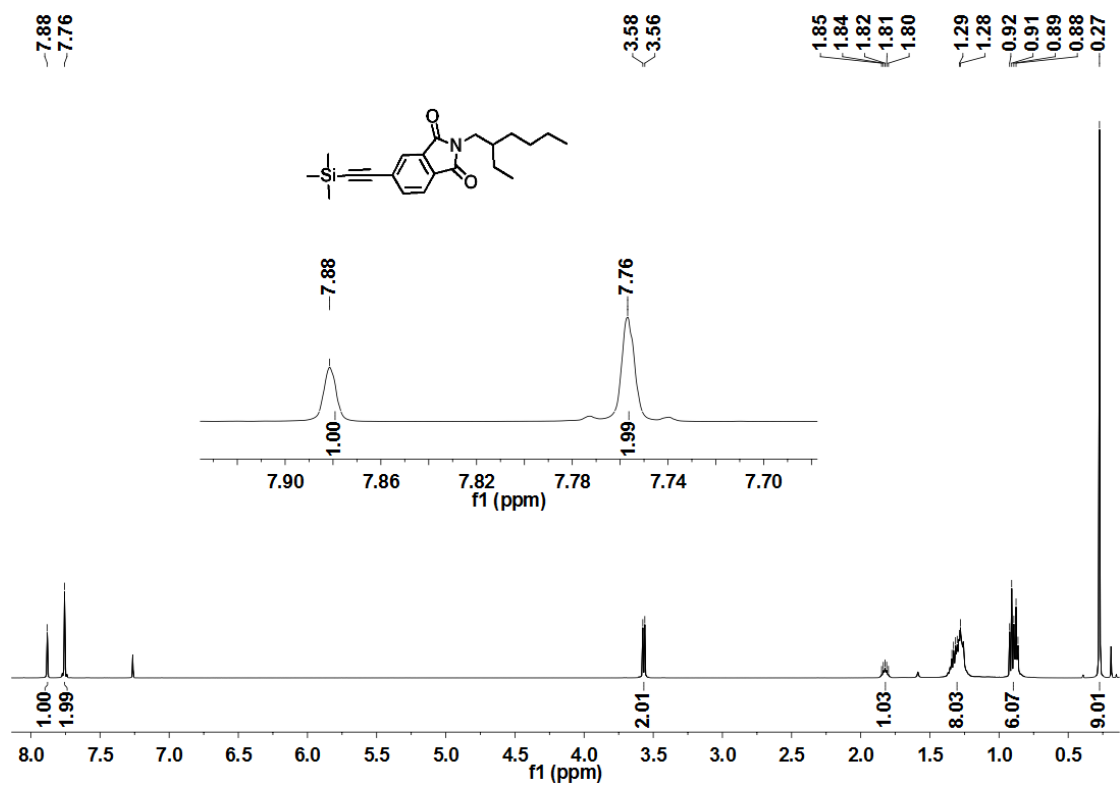


Fig. S2 <sup>1</sup>H-NMR spectra of compound 2

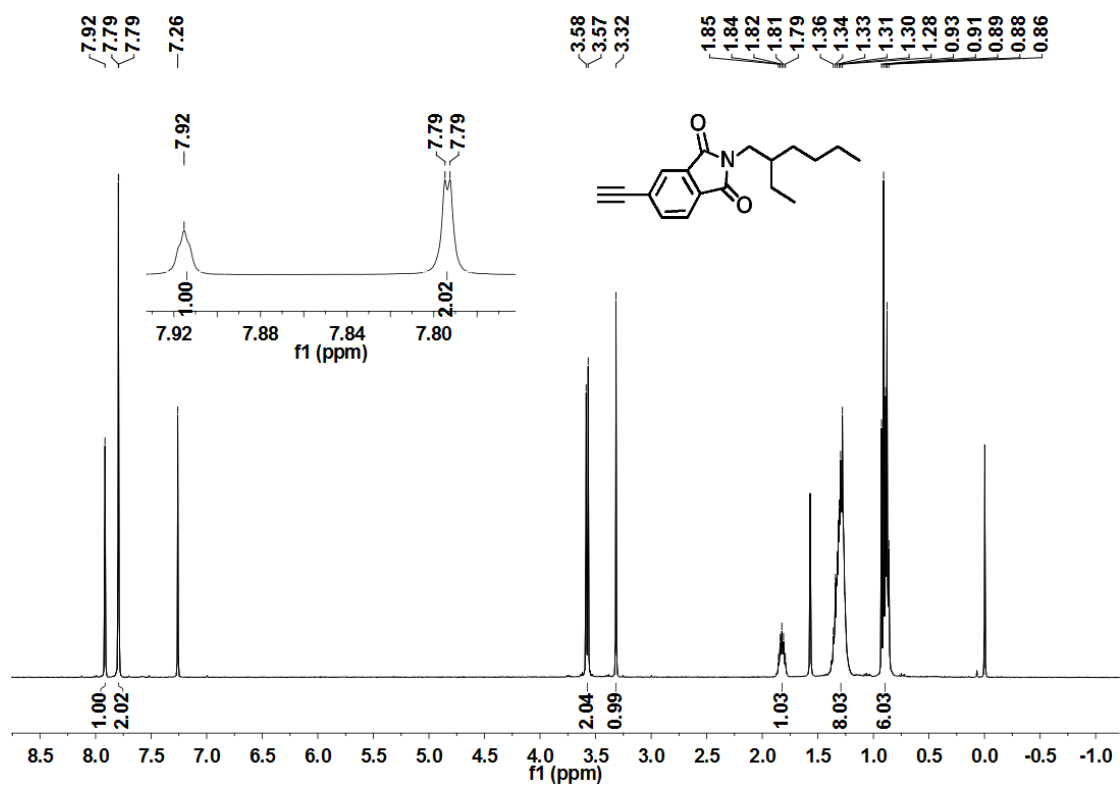


Fig. S3 <sup>1</sup>H-NMR spectra of compound 3

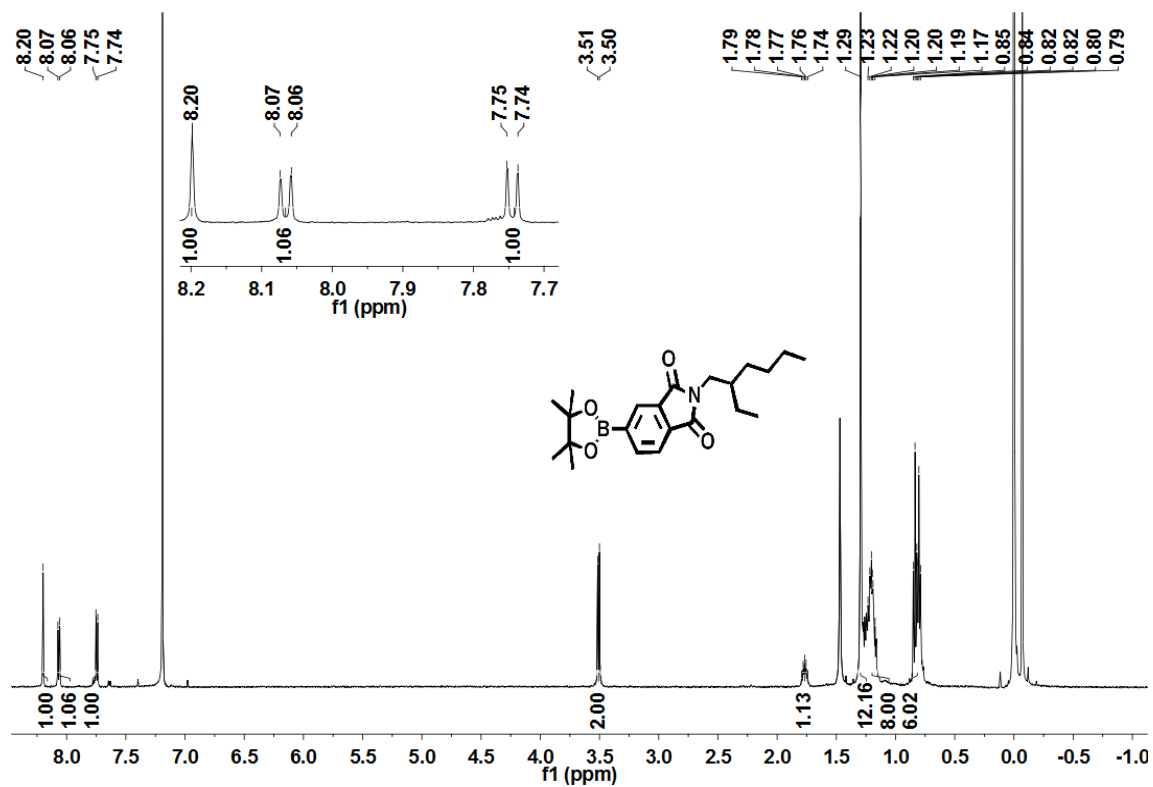


Fig. S4  $^1\text{H-NMR}$  spectra of compound 4

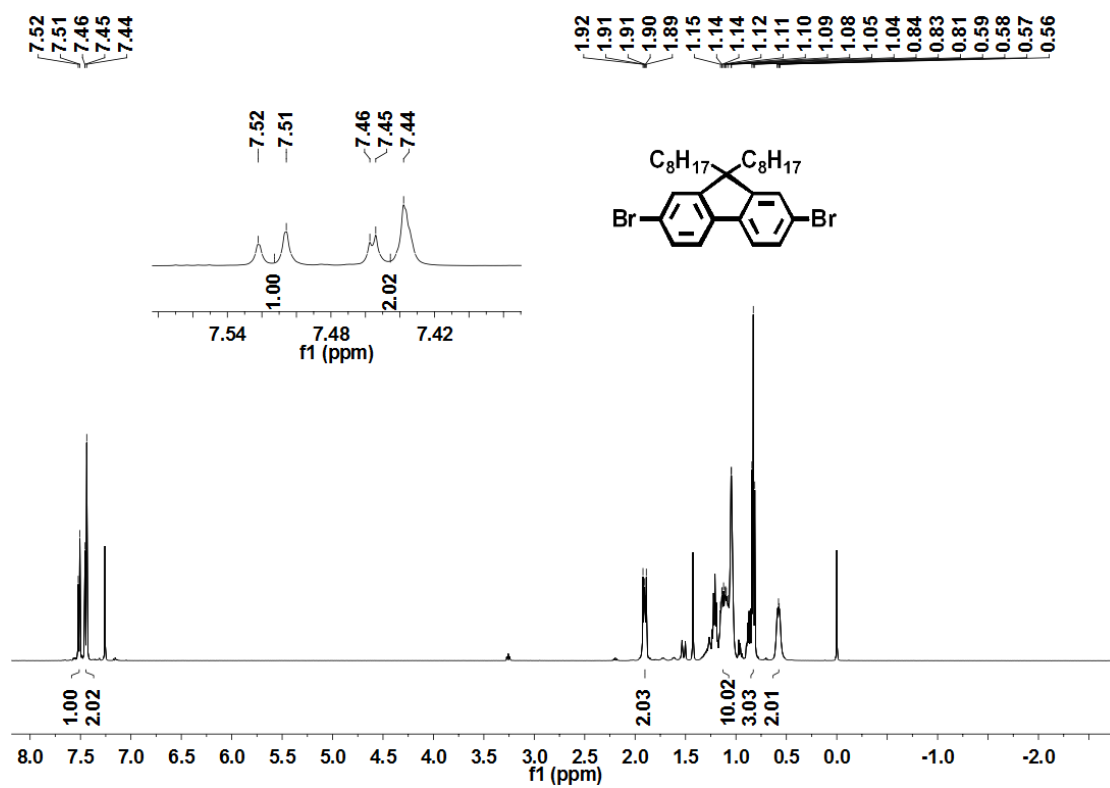


Fig. S5  $^1\text{H-NMR}$  spectra of compound 6

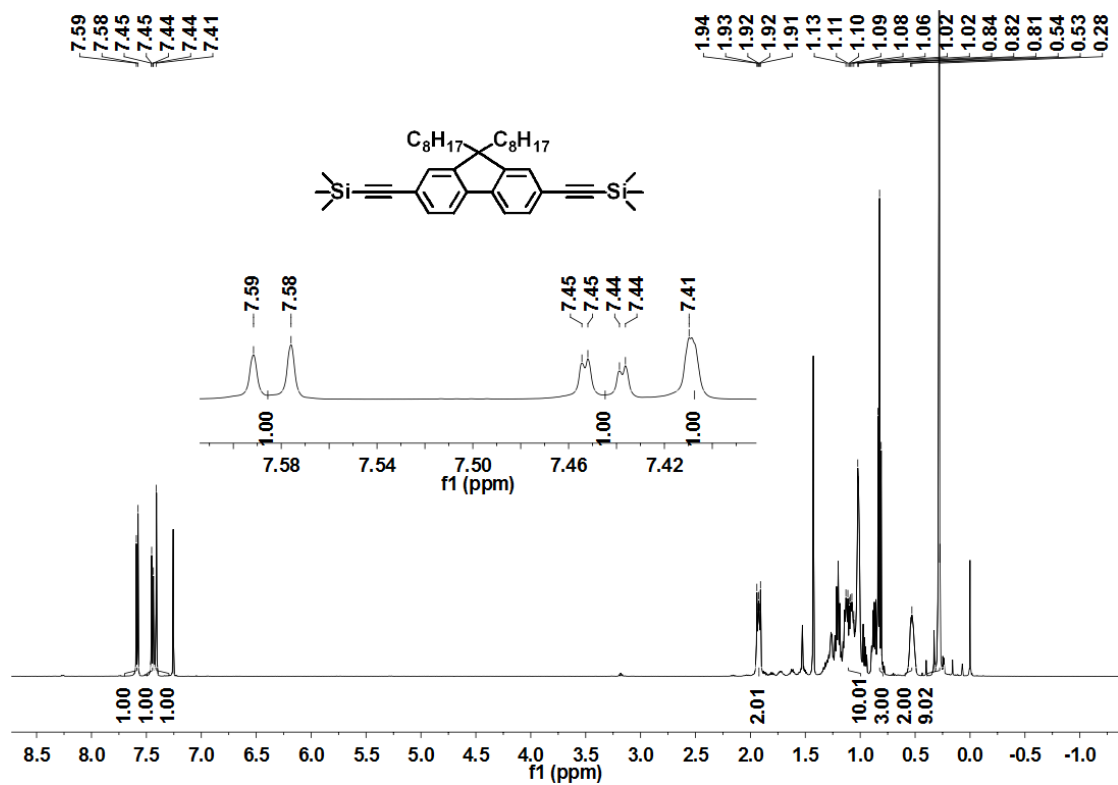


Fig. S6 <sup>1</sup>H-NMR spectra of compound 7

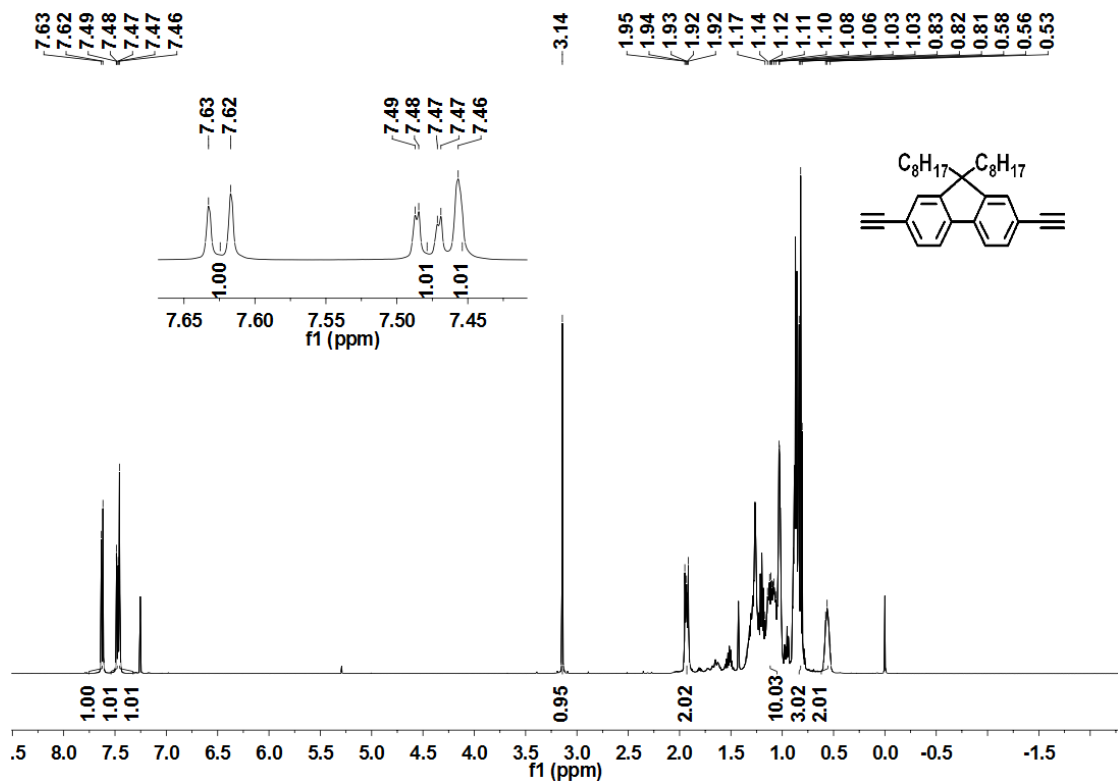


Fig. S7 <sup>1</sup>H-NMR spectra of compound S6

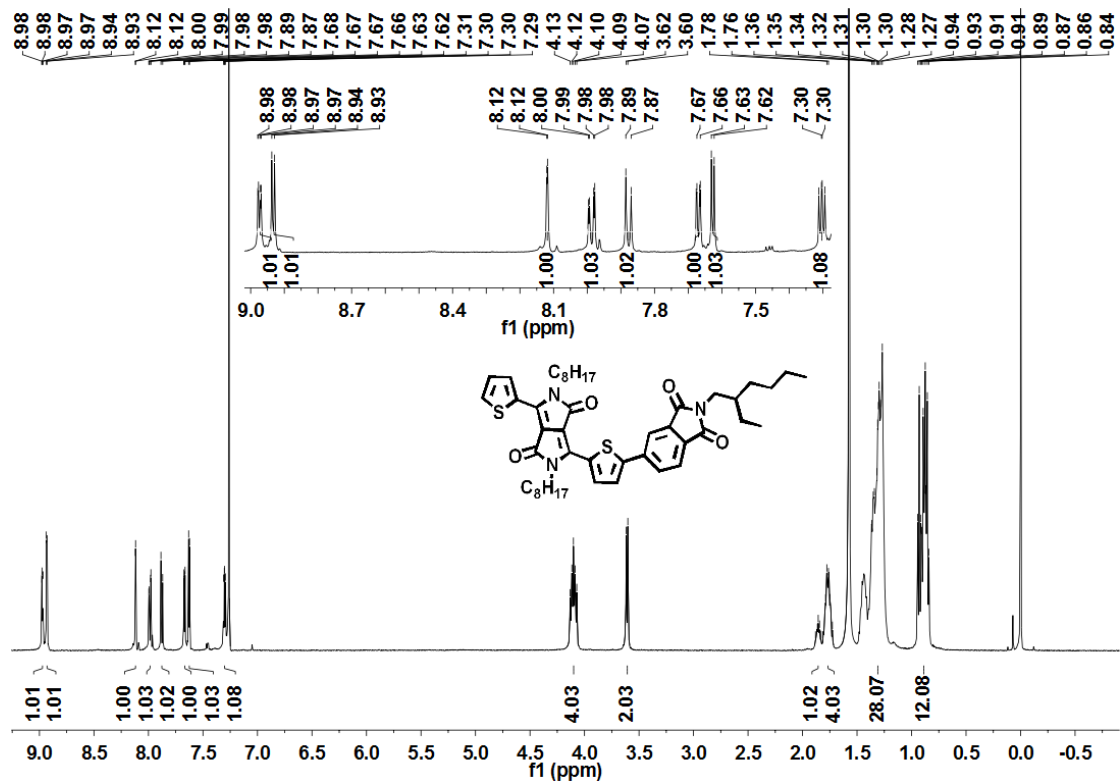


Fig. S8  $^1\text{H-NMR}$  spectra of compound 8

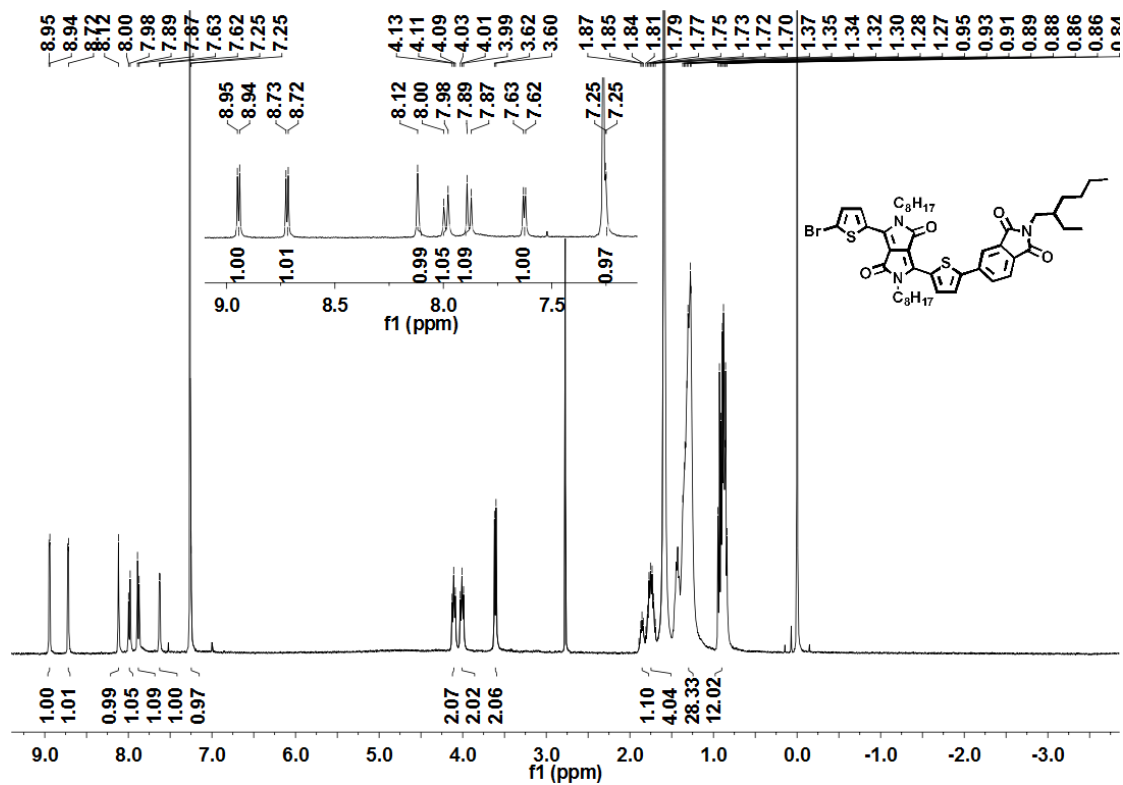


Fig. S9  $^1\text{H-NMR}$  spectra of compound S5



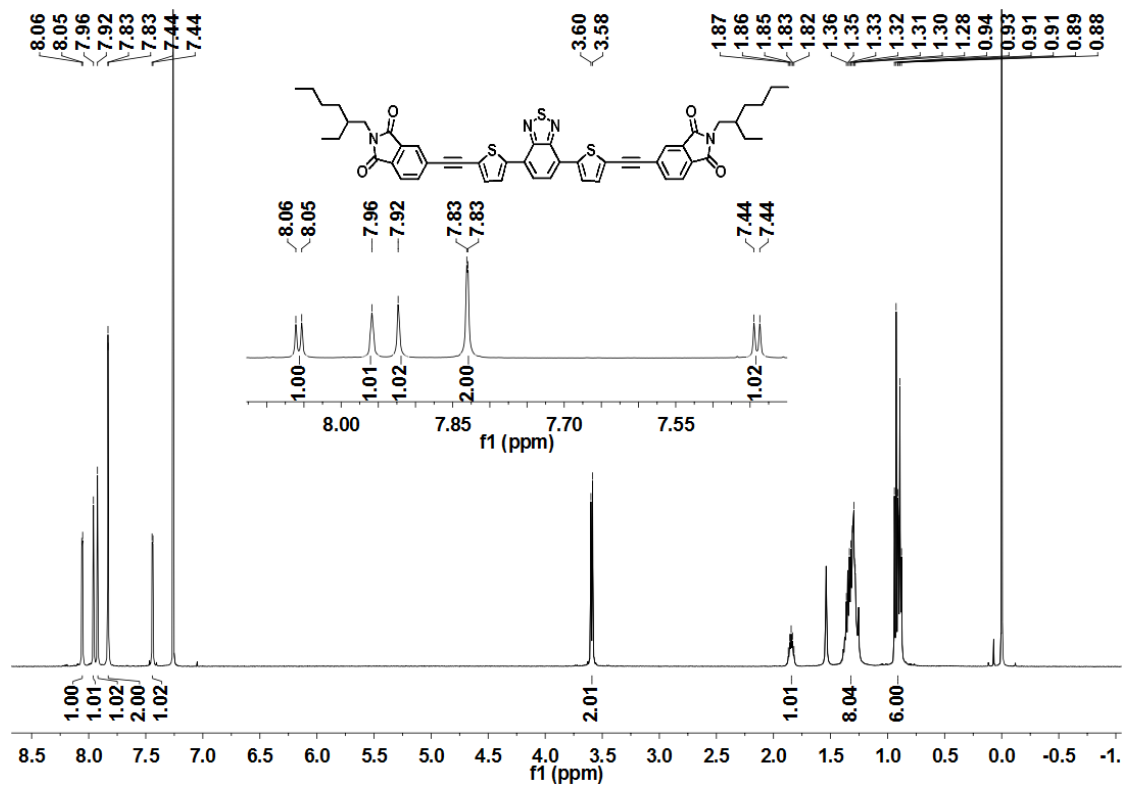


Fig. S10 <sup>1</sup>H-NMR spectra of compound (PIAT)<sub>2</sub>BT

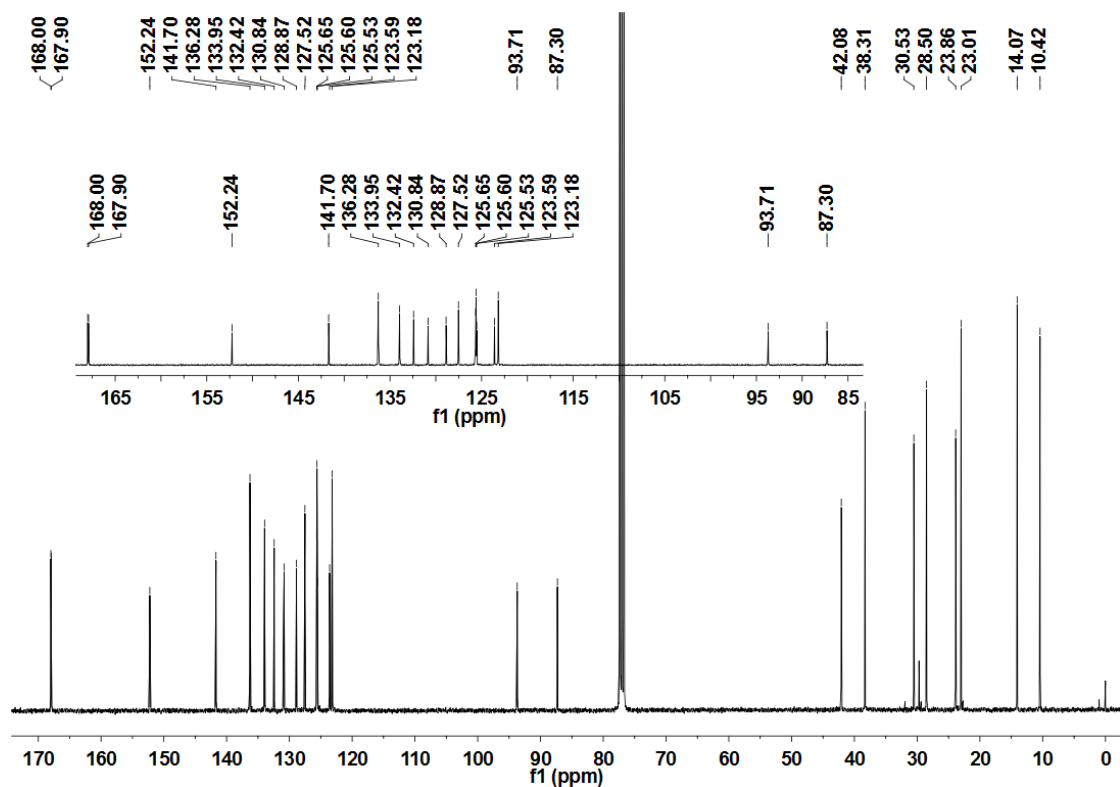


Fig. S11 <sup>13</sup>C-NMR spectra of compound (PIAT)<sub>2</sub>BT

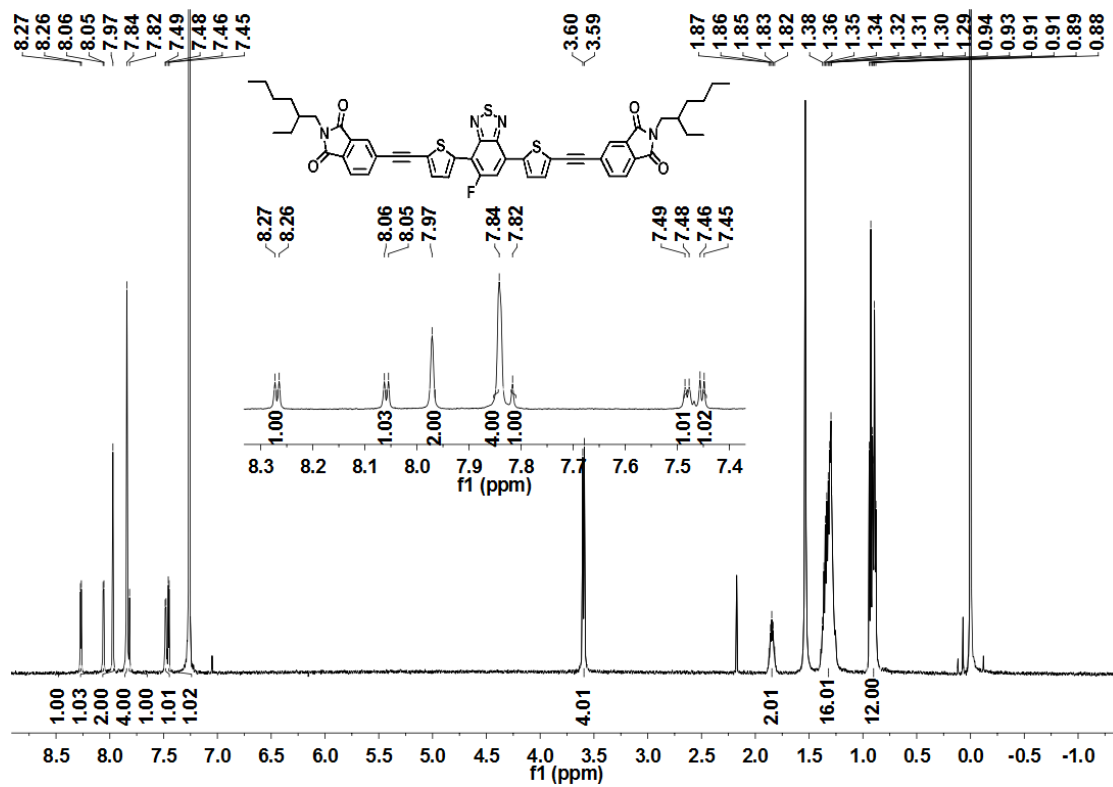


Fig. S12 <sup>1</sup>H-NMR spectra of compound (PIAT)<sub>2</sub>fBT

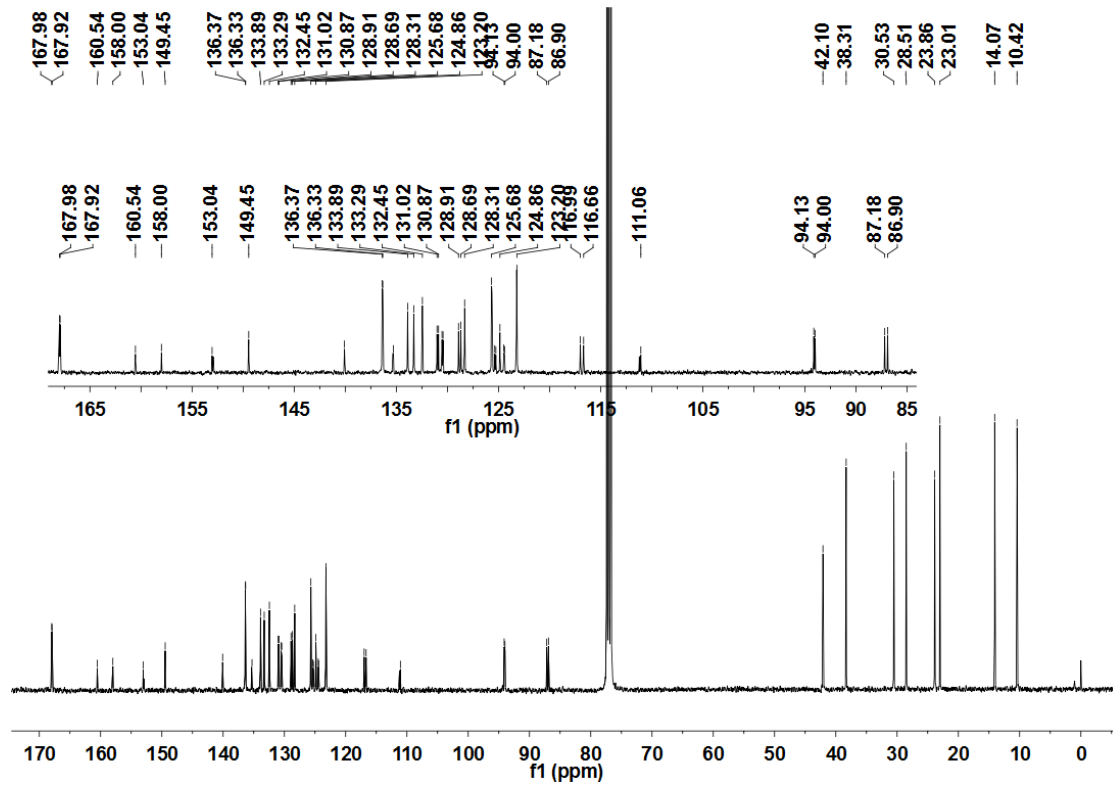


Fig. S13 <sup>13</sup>C-NMR spectra of compound (PIAT)<sub>2</sub>fBT

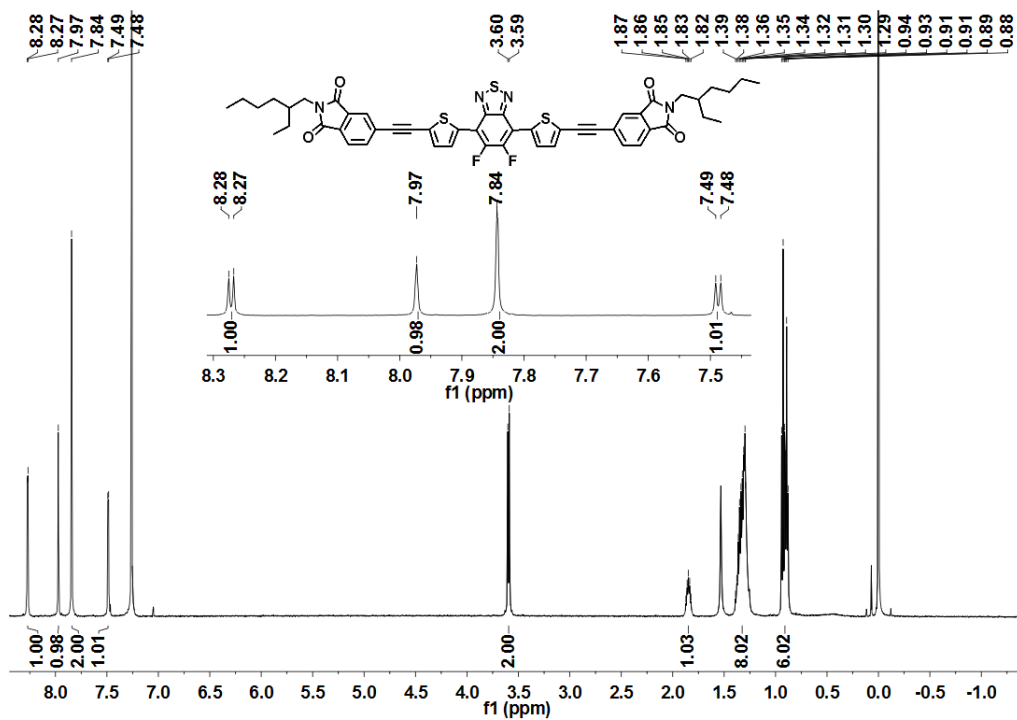


Fig. S14 <sup>1</sup>H-NMR spectra of compound (PIAT)<sub>2</sub>dfBT

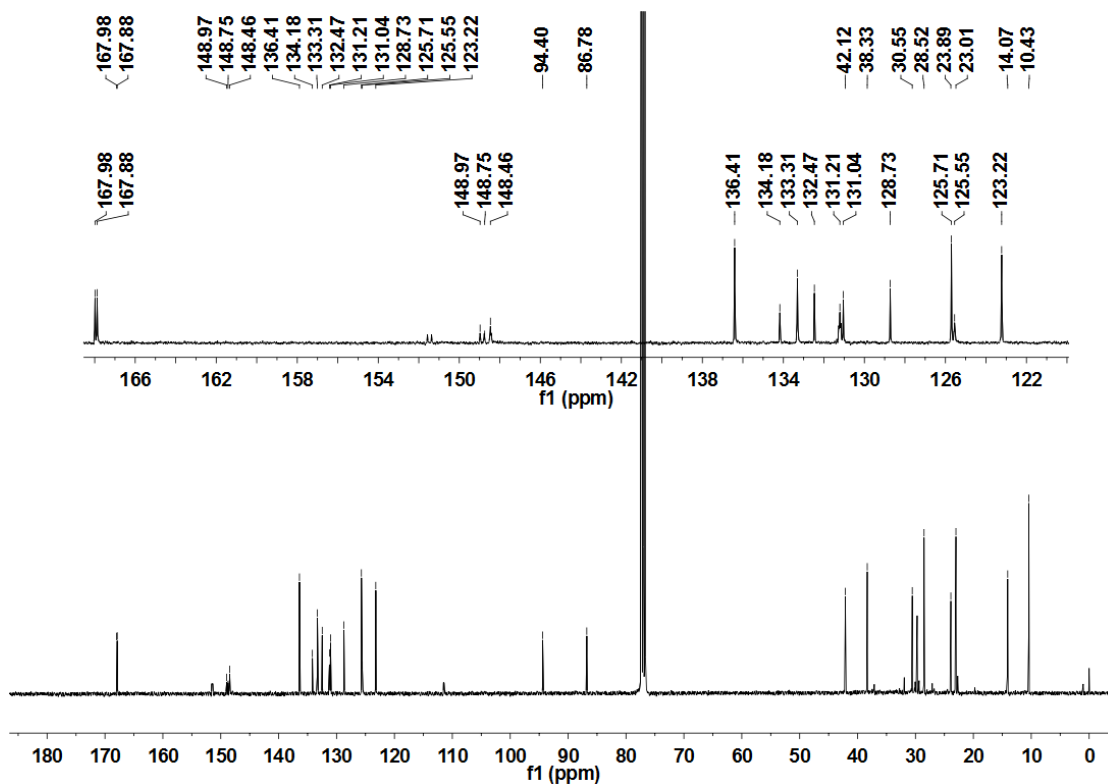


Fig. S15 <sup>13</sup>C-NMR spectra of compound (PIAT)<sub>2</sub>dfBT

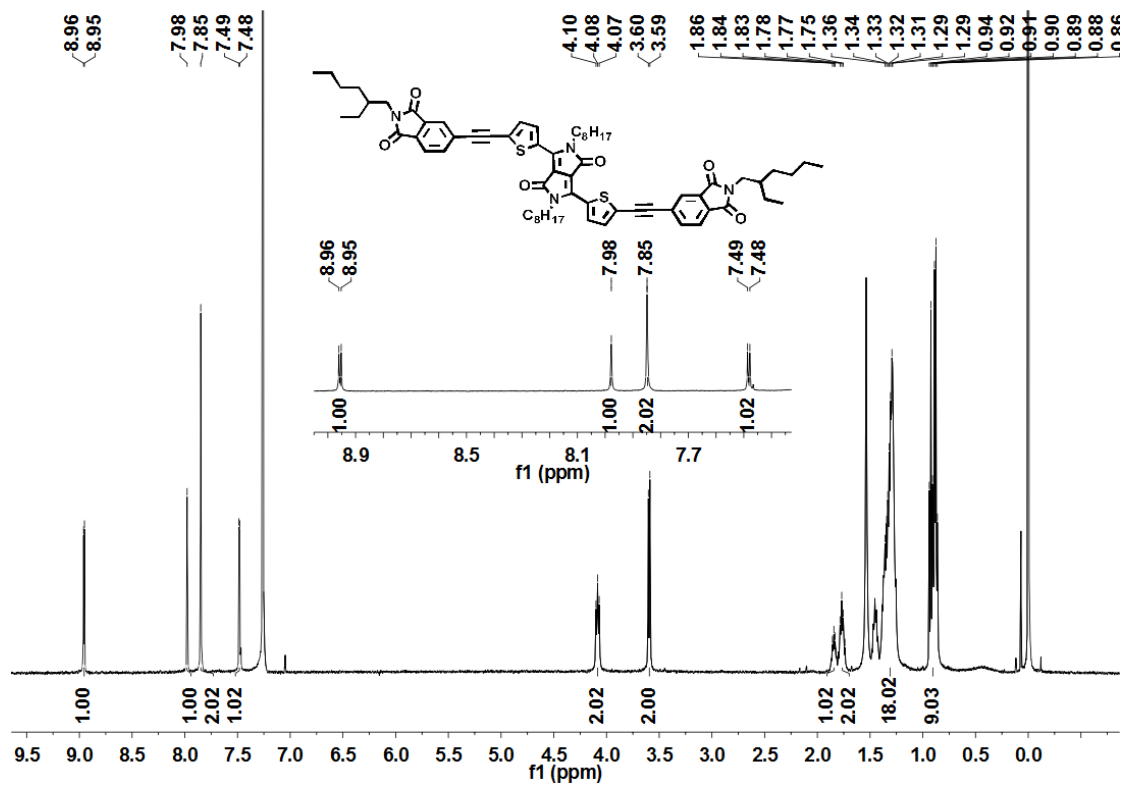


Fig. S16 <sup>1</sup>H-NMR spectra of compound (PIAT)<sub>2</sub>DPP

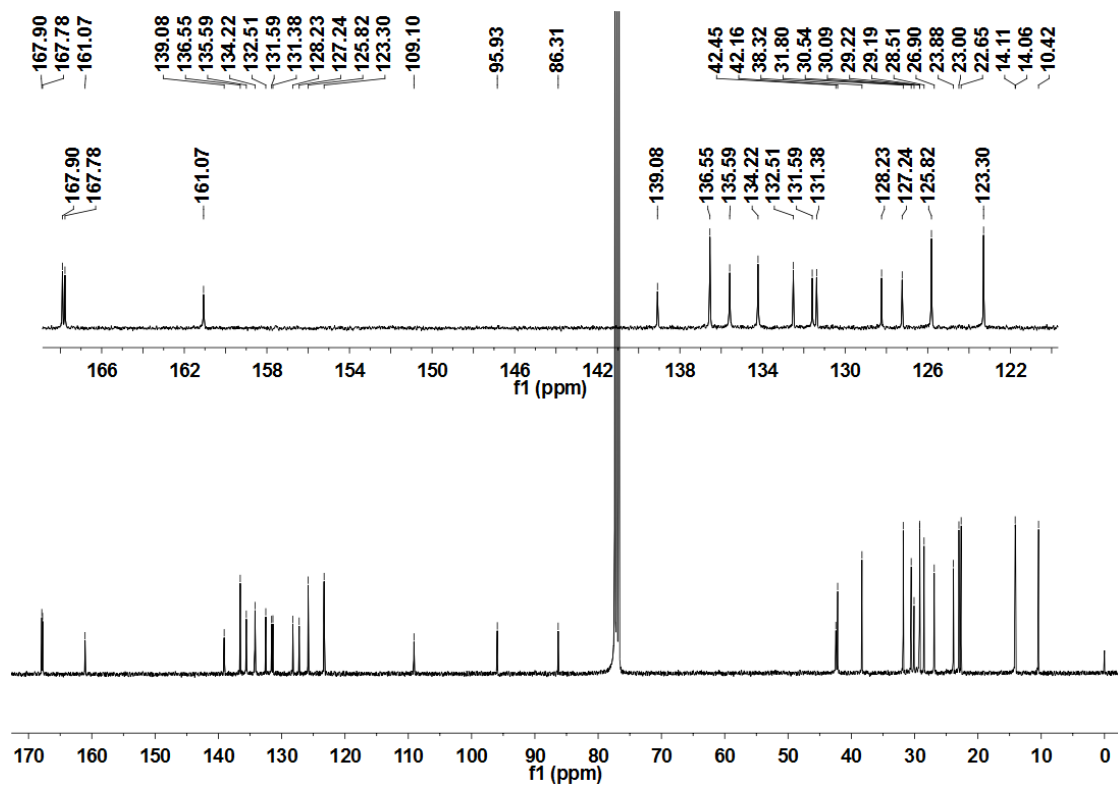


Fig. S17 <sup>13</sup>C-NMR spectra of compound (PIAT)<sub>2</sub>DPP

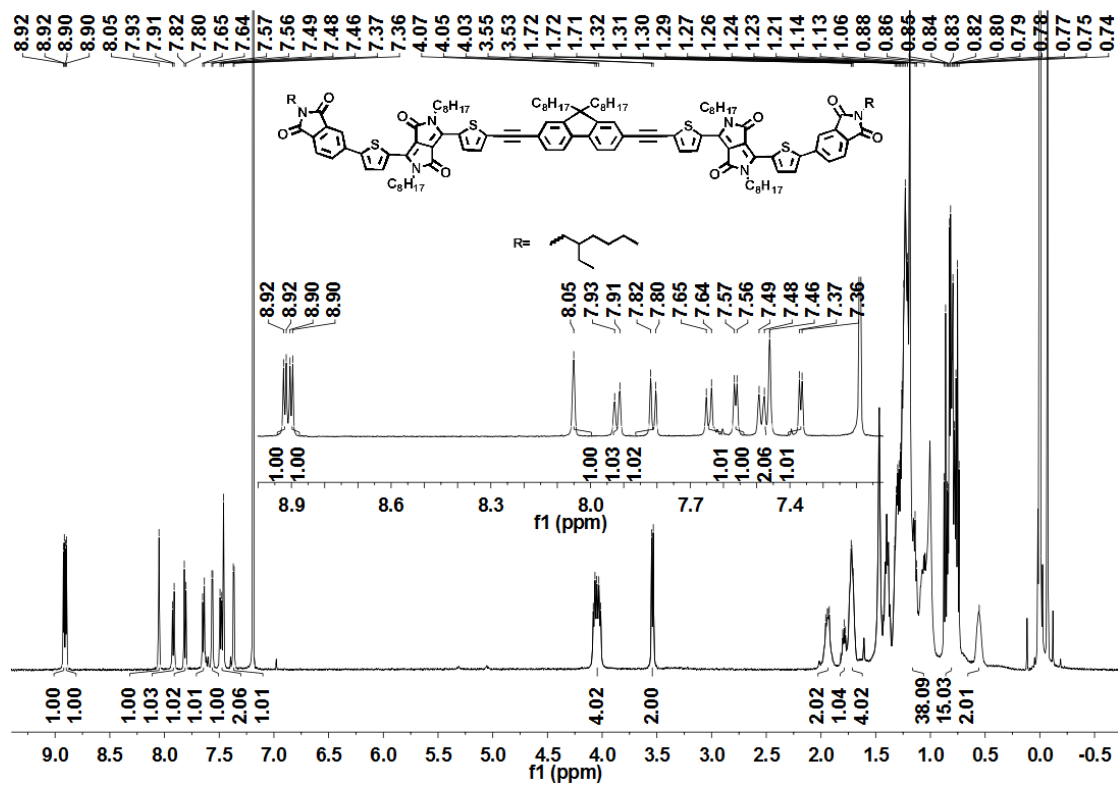


Fig. S18  $^1H$ -NMR spectra of compound FADPPPI

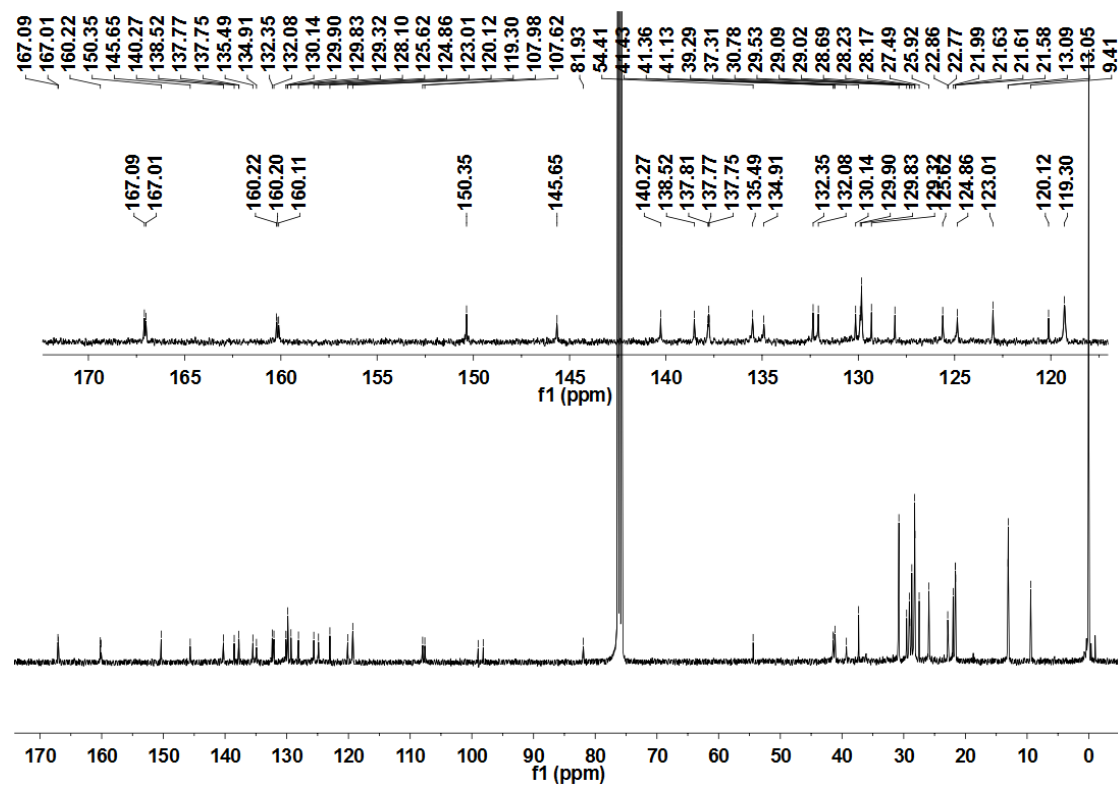


Fig. S19  $^{13}C$ -NMR spectra of compound FADPPPI

### 3. DSC curves

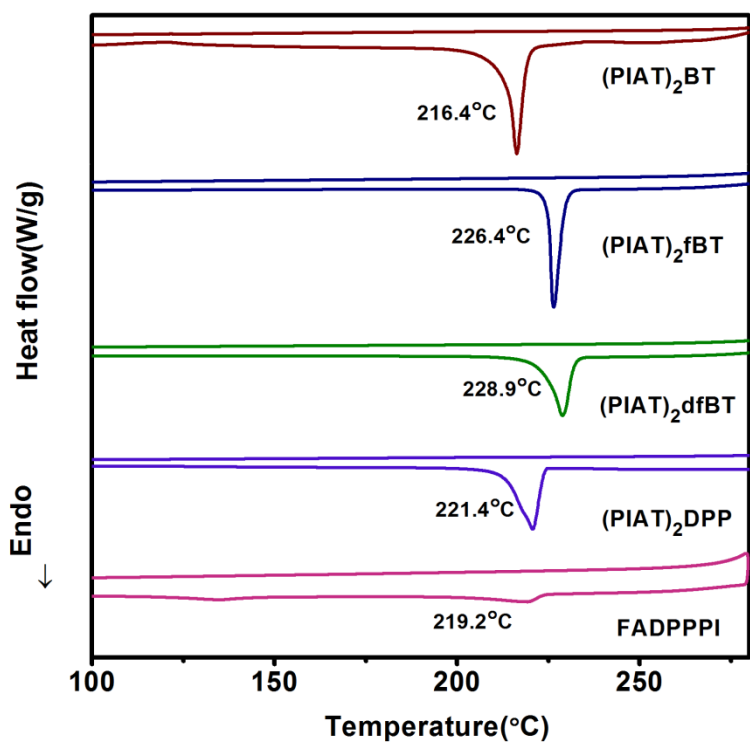


Fig.S20 DSC curves of five compounds

#### 4. XRD patterns

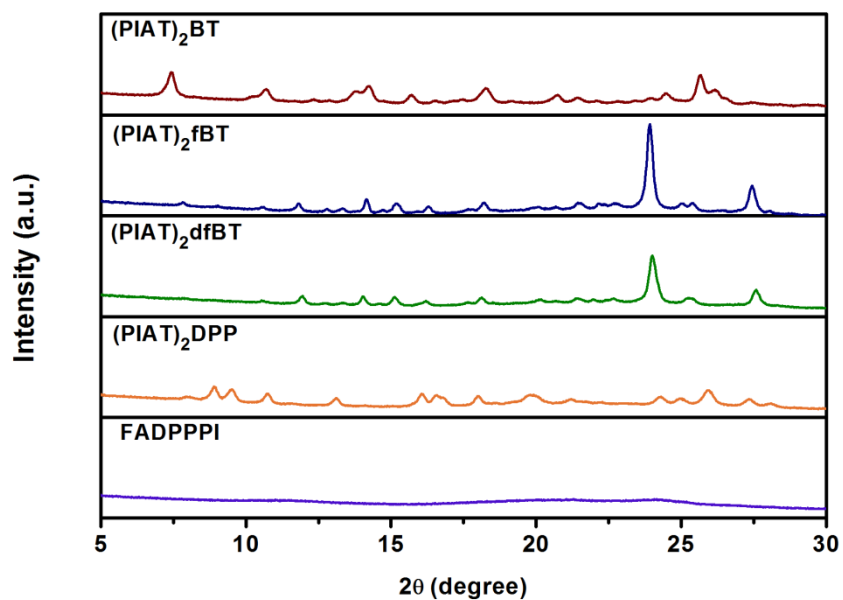


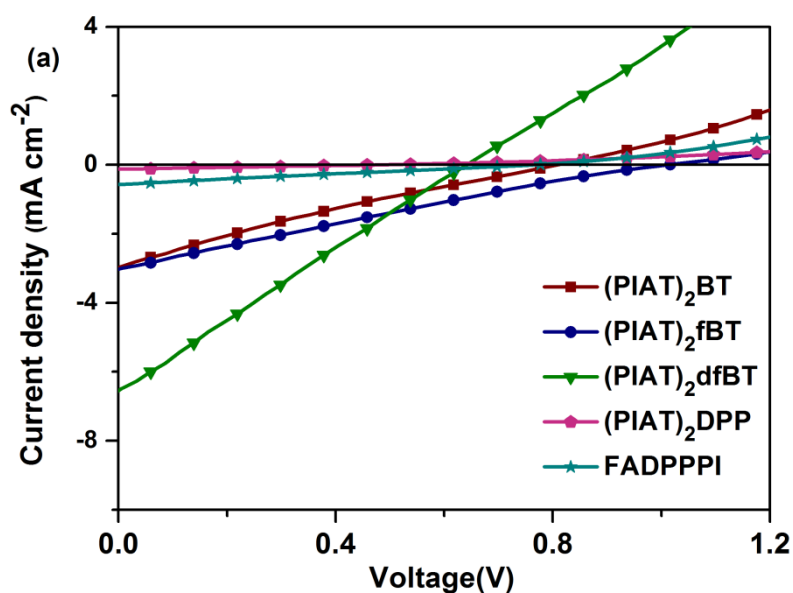
Fig.S21 XRD patterns of five compounds

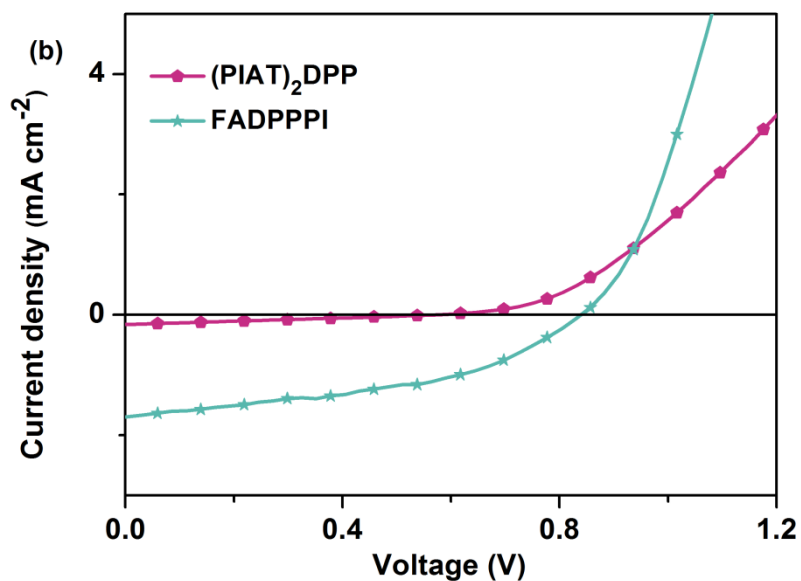
## 5. TD-DFT calculated electronic transitions

Table S1 TD-DFT calculated electronic transitions of five compounds

Compound	State	$E^{\text{opt}}$ (eV)	$\lambda$ (nm)	f	Composition
<b>(PIAT)<sub>2</sub>BT</b>	S1	2.04	609.2	1.47	HOMO → LUMO (70%)
	S3	2.72	456.1	0.59	HOMO → LUMO+2 (69%)
	S4	2.85	435.7	0.22	HOMO → LUMO+1 (54%)
	S5	3.32	372.3	0.63	HOMO → LUMO+3 (68%)
<b>(PIAT)<sub>2</sub>fBT</b>	S1	2.02	613.0	1.39	HOMO → LUMO (70%)
	S3	2.73	454.5	0.72	HOMO → LUMO+2 (51%)
	S4	2.87	432.0	0.24	HOMO → LUMO+2 (46%)
	S5	3.33	372.5	0.56	HOMO → LUMO+3 (66%)
<b>(PIAT)<sub>2</sub>dfBT</b>	S1	2.06	602.2	1.39	HOMO → LUMO (70%)
	S3	2.77	447.9	0.84	HOMO → LUMO+2 (68%)
	S5	3.36	368.6	0.52	HOMO → LUMO+3 (65%)
<b>(PIAT)<sub>2</sub>DPP</b>	S1	1.89	656.9	1.82	HOMO → LUMO (71%)
	S5	2.98	416.6	0.72	HOMO-2 → LUMO (67%)
	S10	3.51	353.3	0.43	HOMO-1 → LUMO+1 (59%)
<b>FADPPPI</b>	S1	1.76	703.7	3.23	HOMO → LUMO (70%)
	S4	2.02	613.6	0.75	HOMO-1 → LUMO+1 (69%)
	S18	3.18	389.4	0.55	HOMO-3 → LUMO+1 (44%)

## 6. J-V characteristics of photovoltaic devices





**Fig.S22** *J-V* characteristics of photovoltaic devices employing a configuration of (a). ITO/PEDOT:PSS/P3HT : NSMAs/Al under an illumination of AM 1.5G, 100 mWcm<sup>-2</sup>; (b) ITO/PEDOT:PSS/DPP-based molecules : PC<sub>61</sub>BM /Al under an illumination of AM 1.5G, 100 mWcm<sup>-2</sup>.

**Table S2** The photovoltaic properties of the OSCs based on (PIAT)<sub>2</sub>DPP : PC<sub>61</sub>BM and FADPPPI : PC<sub>61</sub>BM

Compound	D : A	V <sub>oc</sub> (V)	J <sub>sc</sub> (mAcm <sup>-2</sup> )	FF	PCE (%)
(PIAT) <sub>2</sub> DPP	1:2	0.57	0.16	0.22	0.02
FADPPPI	1:3	0.84	1.70	0.44	0.63

## 7. References

1. Suman, V. Gupta, A. Bagui, S. Singh, *Adv. Funct. Mater.*, 2017, **27**, 1603820.
2. W. Xu, S. Liu, X. Zhao, N. Zhao, Z. Liu, H. Xu, H. Liang, Q. Zhao, X. Yu, W. Huang, *Chem. Eur. J.*, 2013, 19, 621-629.
3. H. Gao, Y. Li, L. Wang, C. Ji, Y. Wang, W. Tian, X. Yang, L. Yin, *Chem. Commun.*, 2014, 50, 10251-10254.