Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting information

A fully fused non-fullerene acceptor containing angular-shaped S,N-heteroacene and perylene diimide for additive-free organic solar cells

Zhaoning Li[a], Jungan Wang[a], Hongyan Huang[a], You Liu[a], Yikai Yun[a], Zhengchun Cheng[a], Shuli Liu[b], Zhucheng Ding[b], Baomin Zhao[b]*, Wei Huang[a,b,c]*

[a] *Key Laboratory of Flexible Electronics (KLOFE) & Institute of Advanced Materials (IAM), Jiangsu National synergetic Innovation Center for Advanced Materials (SICAM), Nanjing Tech University (NanjingTech), Nanjing 211816, China.*

[b] *Key Laboratory for Organic Electronics and Information Displays &Jiangsu Key Laboratory for Biosensors, Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing University of Posts and Telecommunications, 9 Wenyuan Road, Nanjing 210023, China.*

[c] *Shaanxi Institute of Flexible Electronics (SIFE) Northwestern Polytechnical University (NPU) Xi'an 710072, China.*

E-mail addresses: iambmzhao@njupt.edu.cn, iamwhuang@njtech.edu.cn.

Synthesis

According to our previous report, compound **1** was prepared via Cadogan annulation method in advance.

2,7-dibromo-9H-carbazole (1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.88 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 1.7 Hz, 2H), 7.36 (dd, J = 8.3, 1.7 Hz, 2H).

2,7-dibromo-9-dodecyl-9H-carbazole (2)

In a two-necked RBF (100 mL), to a solution of compound **1** (6 g, 18 mmol) in 40 mL of dry DMF was added anhydrous K_2CO_3 (4 g, 37.8 mmol). The mixture was degassed with N_2 flow for 20 min, and then 1-Bromododecane (4.98 g, 20.0 mmol) was added. The solution was stirred at 145 °C for 24 h under N_2 and then quenched with 30mL of water. The aqueous layer was extracted with dichloromethane three times. The organic fractions were dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The product was purified by column chromatography over silica gel (petroleum ether) to give compound **2** as a white solid (8.5 g, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 1.5 Hz, 2H), 7.35 (dd, *J* = 8.3, 1.6 Hz, 2H), 4.21 – 4.17 (t, *J* = 7.4 Hz, 2H), 1.85 – 1.80 (t, *J* = 9.5 Hz, 2H), 1.34 – 1.25 (m, 18H), 0.90 – 0.86 (t, *J* = 6.9 Hz, 3H).

2,7-dibromo-9-dodecyl-3,6-diiodo-9H-carbazole (3)

In a two-necked RBF (100 mL), a mixture of compound **2** (4.93 g, 10.0 mmol) and HOAC (100 mL) was heated to 80℃, and then KI (4.43 g, 26.7 mmol) and KIO_3 (2.85

g, 13.3 mmol) were added in one portion. The solution was stirred at 80°C for 12 h and allowed to cool to room temperature, the organic layer was washed with water (50 mL *2), brine (50 mL *2), then dried over anhydrous Na_2SO_4. After the solvent had been removed under reduced pressure, the residue was purified by recrystallization from alcohol to afford compound **3** as a white solid in a yield of 70.1% (5.20 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 2H), 7.68 (s, 2H), 4.16 – 4.12 (t, *J* = 7.2 Hz, 2H), 1.83 – 1.79 (m, 2H), 1.32 – 1.24 (m, 18H), 0.89 – 0.86 (t, *J* = 6.8 Hz, 3H).

4,4'-(2,7-dibromo-9-dodecyl-9H-carbazole-3,6-diyl)bis(2-methylbut-3-yn-2-ol) (4)

In a two-necked RBF (100 mL), compound **3** (4.172 g, 5.6 mmol), 3-methyl-1-butyn-3-ol (1.1 g, 13.44 mmol) were dissolved in THF (30 mL) and Et_3N (30 mL) .The mixture was degassed with N_2 flow for 20 min, CuI (20 mg, 0.1 mmol) and $Pd(PPh_3)_2Cl_2$ (150 mg, 0.14 mmol) was added under N_2 flow. The mixture was stirred at 90 °C under N_2 in dark for 36 h. Then the mixture was allowed to cool to room temperature and extracted with CH_2Cl_2 and dried with anhydrous Na_2SO_4. Pure product of 6 was obtained by column chromatography over silica gel (petroleum ether/ethyl acetate =1:2, v/v) to give compound **4** as a brown solid (2.92 g, yield of 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 2H), 7.58 (s, 2H), 4.18 – 4.11 (m, 2H), 2.11 (s, 2H), 2.05 – 1.93 (d, *J* = 47.0 Hz, 2H), 1.82 – 1.68 (m, 12H), 1.32 – 1.24 (m, 18H), 0.89 – 0.86 (t, *J* = 6.9 Hz, 3H).

10-dodecyl-10H-dithieno[2,3-b:3',2'-h]carbazole (DTC)

In two-necked RBF (100 mL), compound **4** (1.62 g, 3 mmol), sodium sulfide nonahydrate (2.88 g, 12.0mmol) and NMP (35 mL) were added, the mixture was then stirred at 190°C for 12 h. After being poured into 50mL of saturated aqueous ammonium chloride solution, the organic layer was washed with water (50 mL *2), brine (50 mL *2), then dried over anhydrous Na_2SO_4. And evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel with petroleum ether as eluent to afford **DTC** as a white solid in a yield of 62.9%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 2H), 7.79 (s, 2H), 7.48 (d, *J* = 5.7 Hz, 2H), 7.32 (d, *J* = 5.5 Hz, 2H), 4.32 (t, *J* = 7.5 Hz, 2H), 1.95 – 1.90 (m, 2H), 1.31 – 1.26 (m, 18H), 0.88 – 0.85 (m, 3H).

10-dodecyl-2,7-bis(tributylstannyl)-10H-dithieno[2,3-b:3',2'-h]carbazole (DTC-Sn)

In a 100 mL two-necked round bottom flask, **DTC** (3.14 g, 7 mmol) in dry THF (30 mL) was cooled to -78 ^{o}C under argon atmosphere. *n*-BuLi (2.4 M, 6 mL) was slowly added dropwise, and the temperature kept -78 ^{o}C. After addition the reaction mixture was stirred at room temperature for 2 h. Then, the mixture was cooled to -78 ^{o}C and tributylstannyl chloride (2.83 g, 14.2 mmol) was added. The reaction mixture was warmed to room temperature and stirred for 12 h. The THF was removed and the residue was extracted with dichloromethane. The organic layer was separated, dried over magnesium sulfate, and evaporated to give the product **DTC-Sn**. It was used directly without further purification.

2,9-di(undecan-6-yl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone (PDI-R)

PDI-R was synthesized in advance according to our previous report.

5-bromo-2,9-di(undecan-6-yl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone (PDI-Br)

In two-necked RBF (100 mL), **PDI-R** (1.32 g, 1.7 mmol) and bromine (18.66 g, 0.116 mol) in 60 mL of dichloromethane was stirred at 25 °C for 48 h. The excess of bromine was removed by air bubbling, and the solvent was removed under vacuum. The crude product was purified by silica gel column chromatography with chloroform as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (d, J = 8.2 Hz, 1H), 8.96 (s, 1H), 8.72 – 8.64 (m, 5H), 5.24 – 5.17 (m, 2H), 2.31 – 2.23 (m, 4H), 1.90 – 1.83 (m, 4H), 1.36 – 1.24 (m, 24H), 0.87 – 0.84 (t, J = 6.8 Hz, 12H).

DTC-PDI

In a 50 mL Schlenck tube, **DTC-Sn** (2.05 g, 2 mmol) and **PDI-Br** (217 mg, 0.24 mmol), (3.42 g, 4.4 mmol) were dissolved in toluene (25 mL) under N_2 atmosphere, the solution was flushed with N_2 for 10 min. Then $Pd_2(dba)_3$ (36 mg, 0.04 mmol) and P(o-tol)$_3$ (24 mg, 0.08 mmol) were added to the mixture. The mixture was heated to 100 ^{o}C and stirred for 24 h. After flushing with N_2 for 10 min, the reaction solution was heated to 100 ^{o}C for 24 h in dark and cooled to the room temperature, and extracted with dichloromethane. The crude product was obtained by rotary evaporation and purified by silica gel column chromatography with petroleum ether/dichloromethane as an eluent, affording the product **DTC-PDI** as the black solid with a yield of 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (d, *J* = 10.9 Hz, 1H), 8.73 – 8.65 (m, 10H), 8.49 (d, *J* = 8.2 Hz, 2H), 8.26 (s, 2H), 7.81 (s, 4H), 5.25 – 5.15 (m, 4H), 4.38 (t, *J* = 8.0 Hz, 2H), 2.31 – 2.21 (m, 8H), 2.07 – 2.03 (m, 2H), 1.89 – 1.86 (m, 8H), 1.56 – 1.51 (m, 2H), 1.40 – 1.29 (m, 64H), 0.88 – 0.83 (m, 27H). MALDI-TOF-MS m/z: [M] calcd for $C_{120}H_{137}N_5O_8S_2$, 1839.9909; found, 1840.4746 [M+].

FDTC-PDI

In a 50 mL Schlenck tube, **DTC-PDI** (0.92 g, 0.5 mmol) was dissolved in dry dichloromethane and methanesulfonic acid (v/v = 9:1), then DDQ (0.23 g, 1 mmol) was added into the mixture at 0 ^{o}C. The stirred reaction solution was allowed to warm to room temperature. After 6 h, it was poured into ice, the product was extracted with dichloromethane, and the organic extracts were dried and filtered. The residue was purified with dichloromethane-petroleum ether as an eluent by silica gel column chromatography, affording the product **FDTC-PDI** as the black solid with a yield of 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.54 – 8.12 (m, 16H), 5.44 – 5.31 (m, 2H), 4.73 – 4.59 (m, 2H), 4.33 – 4.22 (m, 2H), 2.63 – 1.85 (m, 20H), 1.35 – 0.24 (m, 91H). MALDI-TOF-MS m/z: [M] calcd for $C_{120}H_{133}N_5O_8S_2$, 1835.9596; found, 1836.4854 [M+].

Materials and instruments

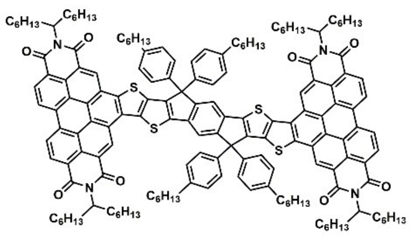
All the chemicals were purchased from J&K, Energy Chemical Inc, Sigma–Aldrich and directly used. ^{1}H NMR and ^{13}C NMR data were recorded a Bruker

Ultra Shield Plus AV400 spectrometer in deuterated chloroform ($CDCl_3$) solution at 298 K with tetramethylsilane (TMS; d = 0 ppm) as an internal standard (^1H NMR: 400 MHz, ^{13}C NMR:100 MHz). Matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) with anthracene-1,8,9-triol as matrix was carried out on a Bruker Autoflex III instrument. Thermogravimetry analysis (TGA, Rigaku TG-DTA 8120) was performed on a Mettler DSC823e thermal analyzer and a Rigaku TG-DTA 8120 thermal analyzer at a heating rate of 10 ^{o}C min^{-1} under N_2 atmosphere, respectively. UV–vis absorption spectrums were collected with a Shimadzu UV–1700 spectrometer. Cyclic voltammograms (CV) experiments of the two small acceptor molecules were executed with a CHI 620C electrochemical analyzer, and a gold disc with a diameter of 2 mm, a Pt wire and an Ag/Ag^+ electrode were used as the working electrode, counter electrode and reference electrode, respectively. Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, 0.1 M) in dry dichloromethane was used as the supporting electrolyte. The surface morphology was measured by tapping mode atomic force microscopy (AFM) (Thermo. Auto Probe C P Res).

BHJ organic solar cells fabrication and characterization

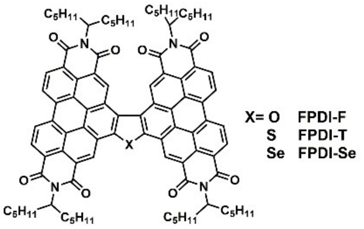
BHJ organic solar cells with an inverted configuration of ITO/ZnO/ polymer electron donor: small electron acceptor/MoO_3/Ag were fabricated by the following process. Patterned indium tin oxide (ITO) glass substrates were cleaned by sequential ultrasonic treatment in detergent, deionized water, acetone, and isopropanol, and then further treated with Jelight UV-ozone cleaner for 15 min. A thin layer of sol–gel ZnO was spin coating onto precleaned ITO glass substrates and then annealed at 180 °C for 15 min. After cooling to the room temperature, and the substrates were transferred into an argon-filled glove box. A blend solution of PTB7-Th and the small molecule acceptor in chlorobenzene was spin-coated onto the ZnO layer. Finally, a cathode made of MoO_3 and Ag layers were then thermally evaporated on the active layer at a pressure of 1.0×10^{-6} mbar via a shadow mask (active area 5 mm^2). The current density–voltage characteristics (*J*–*V*) of the photovoltaic cells were measured utilizing a Keithley 2400 digital source meter under a simulated AM 1.5G solar irradiation at 100 mW cm^2. External Quantum Efficiency (EQE) of solar cells were performed trough a certified Newport incident photon conversion efficiency (IPCE) measurement system.

Fully fused PDI derivatives for fullerene-free soalr cells with adding the solvent additive



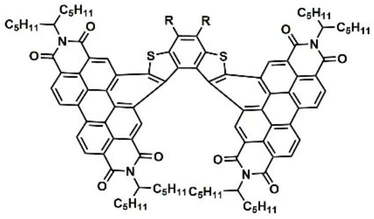
FITP

7.33% with 2% CN as the solvent additive



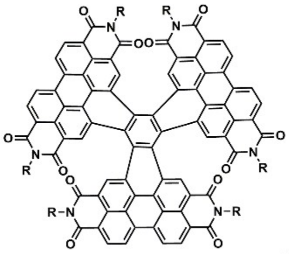
X= O FPDI-F
S FPDI-T
Se FPDI-Se

6.72% with 2% CN as the solvent additive



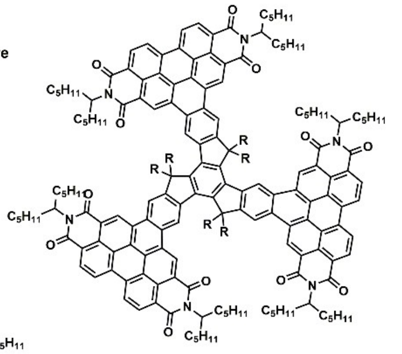
BPDI-2

3.24% without the solvent additive
4.44% with 2% CN as the additive
PTB7-Th as the donor material



TPH R = C_5H_{11} C_5H_{11}

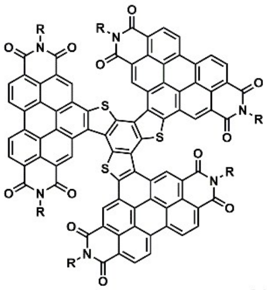
7.34 without the solvent additive
8.28% with 0.25% DIO as the solvent additives
PDBT-T1 as the donor material



R-PDI R = n-hexyl

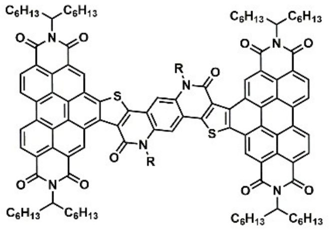
4.19% with 1% CN as the additive
PTB7-Th as the donor material

Fully fused PDI derivatives for fullerene-free solar cells without any solvent additive



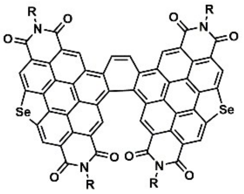
Fused-TriPDI R = C_5H_{11} C_5H_{11}

6.19% without the solvent additive
PTB7-Th as the donor material



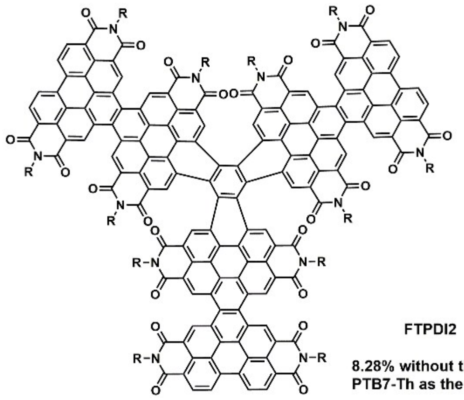
3 R = C_4H_9 C_6H_{13}

4.79% without the solvent additive
PTB7-Th as the donor material



TBDPDI-Se-C$_{11}$ R = C_5H_{11} C_5H_{11}

7.41% without the solvent additive
PBDB-T as the donor material



FTPDI2 R = C_6H_{13} C_6H_{13}

8.28% without the solvent additive
PTB7-Th as the donor material

Fig. S1 Typical fully fused PDI derivatives for fullerene-free solar cells.

TGA plots

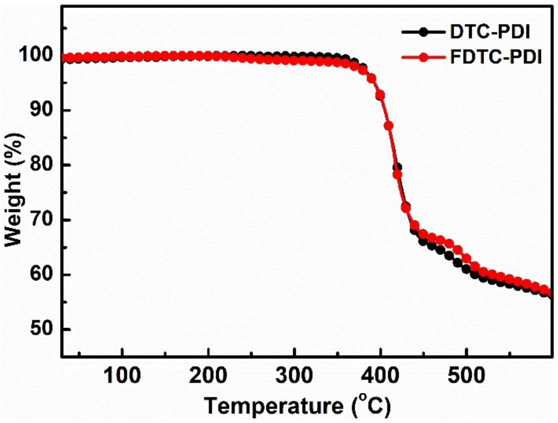


Fig. S2 TGA polts of **DTC-PDI** and **FDTC-PDI** at a heating rate of 10 °C min^{-1} under nitrogen atmosphere.

Devices optimization

Table S1. Device performance of the PSCs based on **PTB7-Th**:**acceptors** with different D/A ratio (from 1:0.8 to 1:2).

Blend	D/A (w/w)	J_{SC} (mA/cm^2)	V_{OC} (V)	*FF* (%)	PCE (%)
PTB7-Th:**DTC-PDI**	1:0.8	7.05	0.88	36.5	2.27
	1:1	7.18	0.89	37.1	2.45
	1:1.25	**7.23**	**0.88**	**37.4**	**2.38**
	1:1.5	7.17	0.91	39.3	2.55
PTB7-Th:**FDTC-PDI**	1:0.8	10.22	0.95	37.2	3.46
	1:1	10.48	0.94	37.8	3.75
	1:1.25	10.54	0.97	42.5	4.15
	1:1.5	**10.87**	**0.96**	**42.9**	**4.33**
	1:2	9.53	0.94	43.3	3.74

Table S2. Device performance of the organic solar cells based on **PTB7-Th**: **DTC-PDI** (w/w, 1:1.25) and **PTB7-Th**:**FDTC-PDI** (w/w, 1:1.5) with different thermal annealing temperature (from 80 to 150 °C).

Blend	Annealing Temp.(°C)	J_{SC} (mA/cm^2)	V_{OC} (V)	*FF* (%)	PCE (%)
PTB7-Th:**DTC-PDI**	**80**	**7.41**	**0.88**	**39.8**	**2.60**
	100	7.23	0.89	40.1	2.58
	150	7.47	0.87	36.4	2.36
PTB7-Th:**FDTC-PDI**	**80**	**11.72**	**0.96**	**43.6**	**4.78**
	100	11.37	0.96	44.7	4.62
	150	10.66	0.95	41.9	4.15

J–*V* plots of the hole-only and electron-only devices

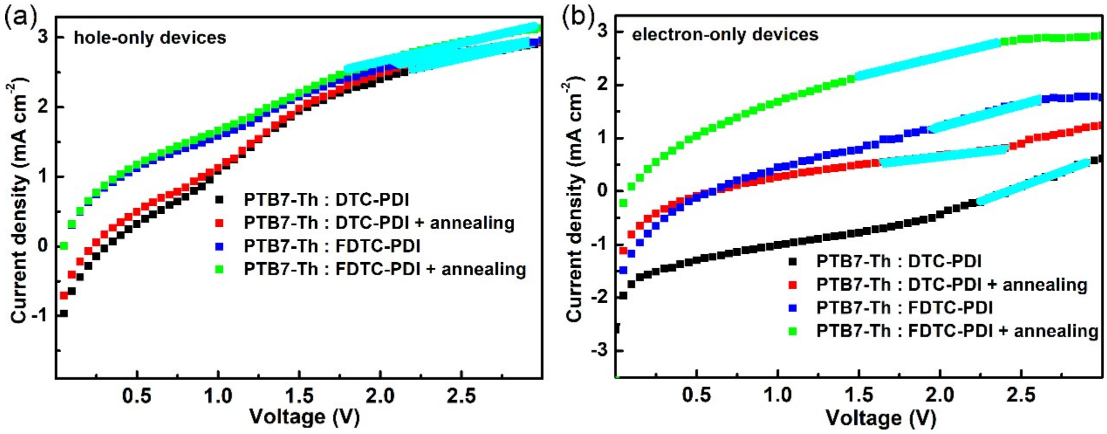


Fig. S3 Current density (*J*)–voltage (*V*) profiles of **PTB7-Th/DTC-PDI** or **FDTC-PDI** based devices with or without thermal annealing treatment. (a) the hole-only devices, (b) the electron-only devices.

NMR Spectrums

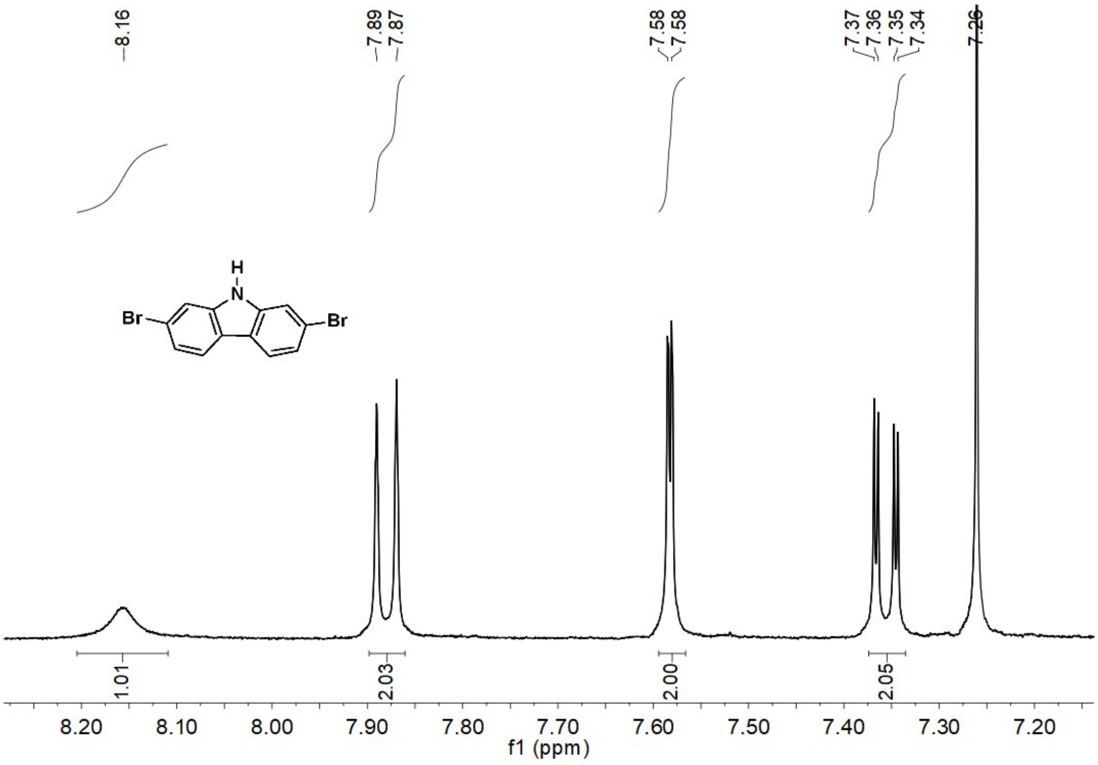


Fig. S4 ^{1}H NMR spectra of compound **1** in $CDCl_3$.

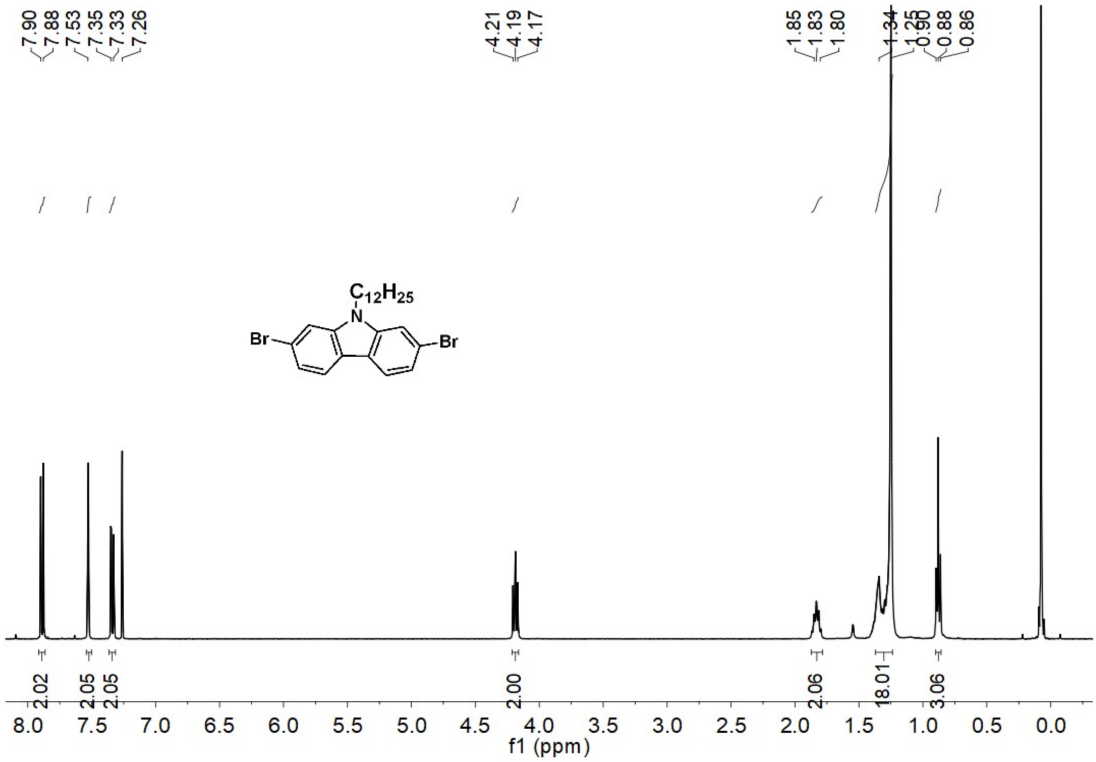


Fig. S5 ^{1}H NMR spectra of compound **2** in $CDCl_3$.

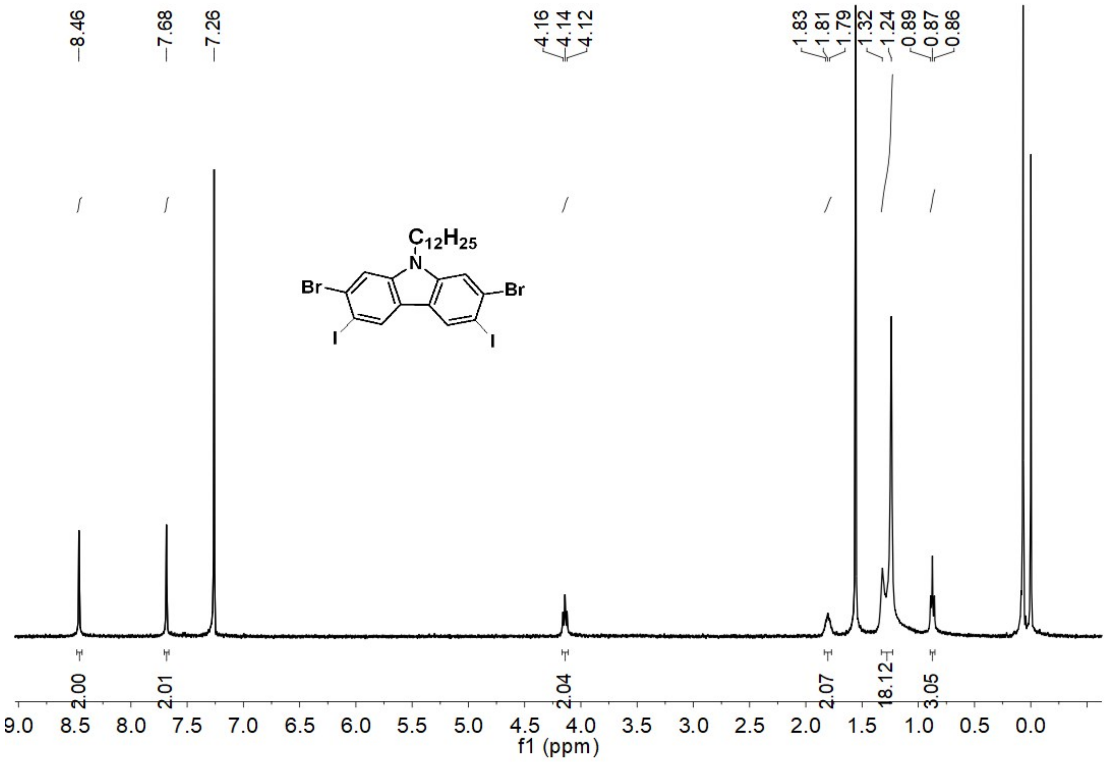


Fig. S6 ^{1}H NMR spectra of compound **3** in $CDCl_3$.

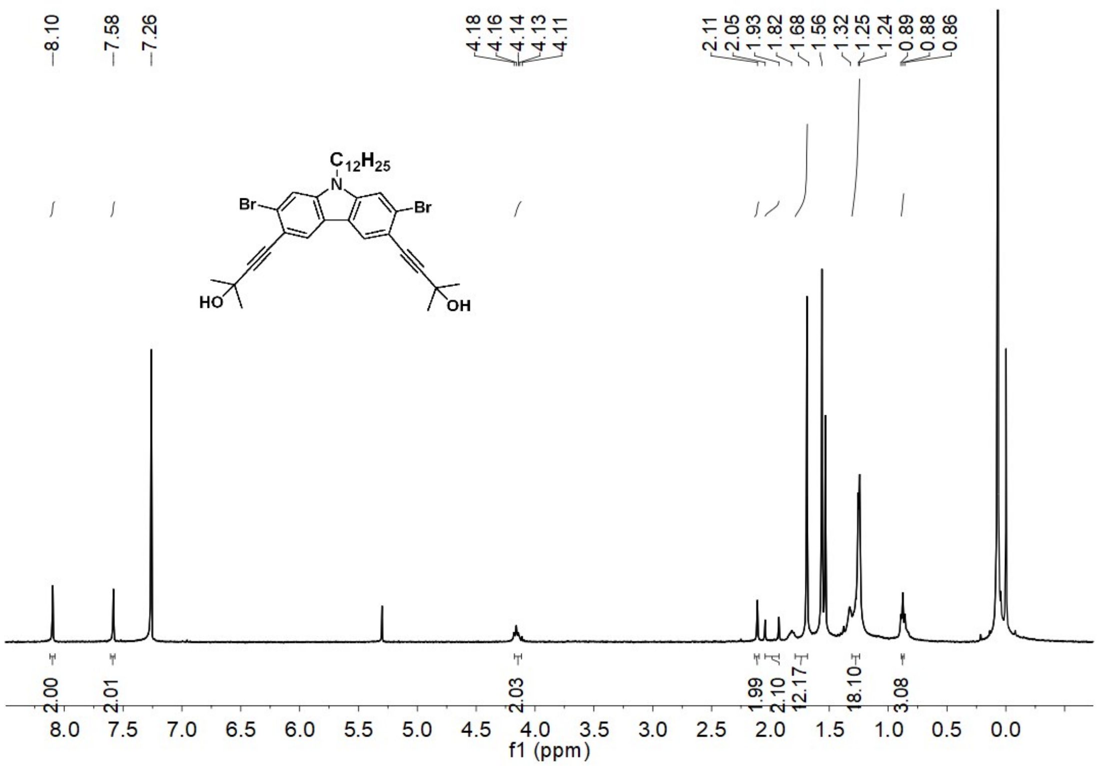


Fig. S7 ^{1}H NMR spectra of compound **4** in $CDCl_3$.

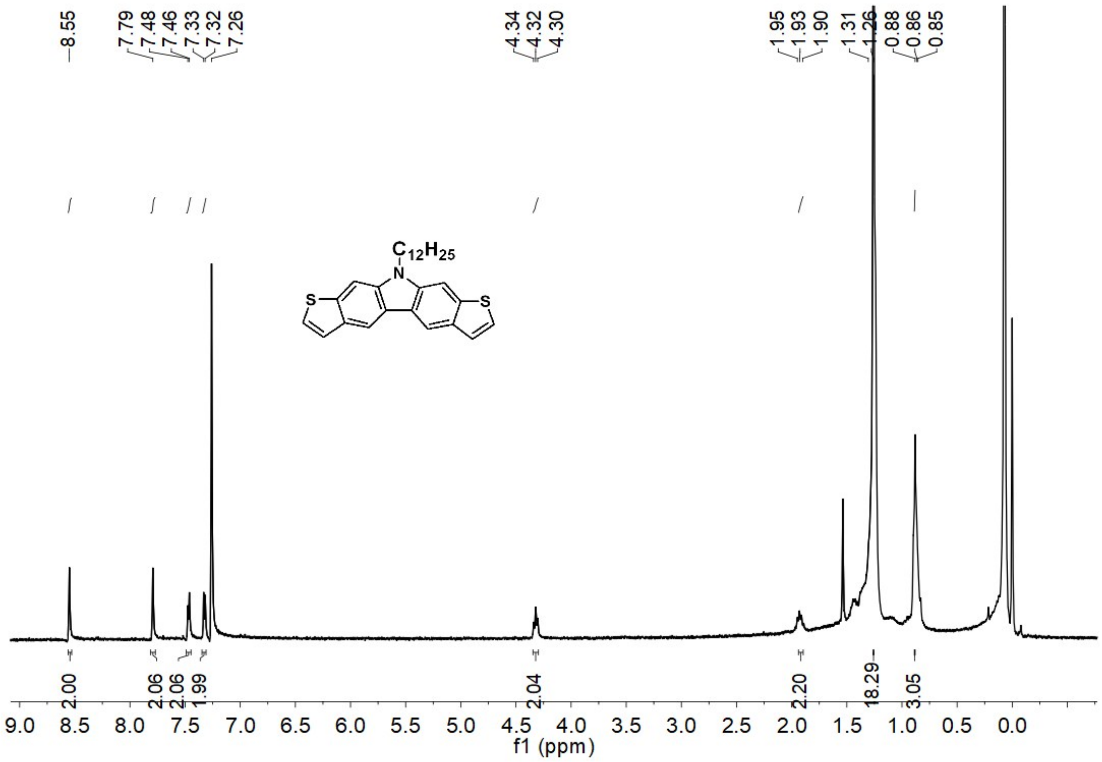


Fig. S8 ^{1}H NMR spectra of monomer **DTC** in $CDCl_3$.

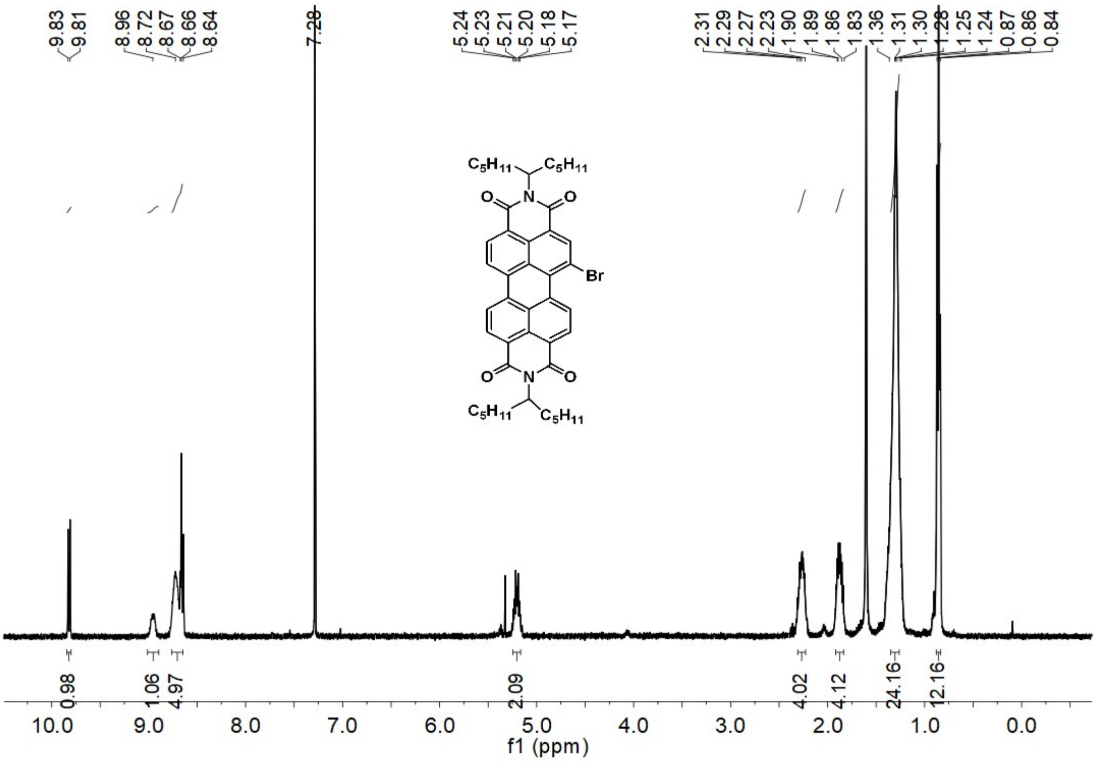


Fig. S9 ^{1}H NMR spectra of monomer **PDI-Br** in CDCl$_3$.

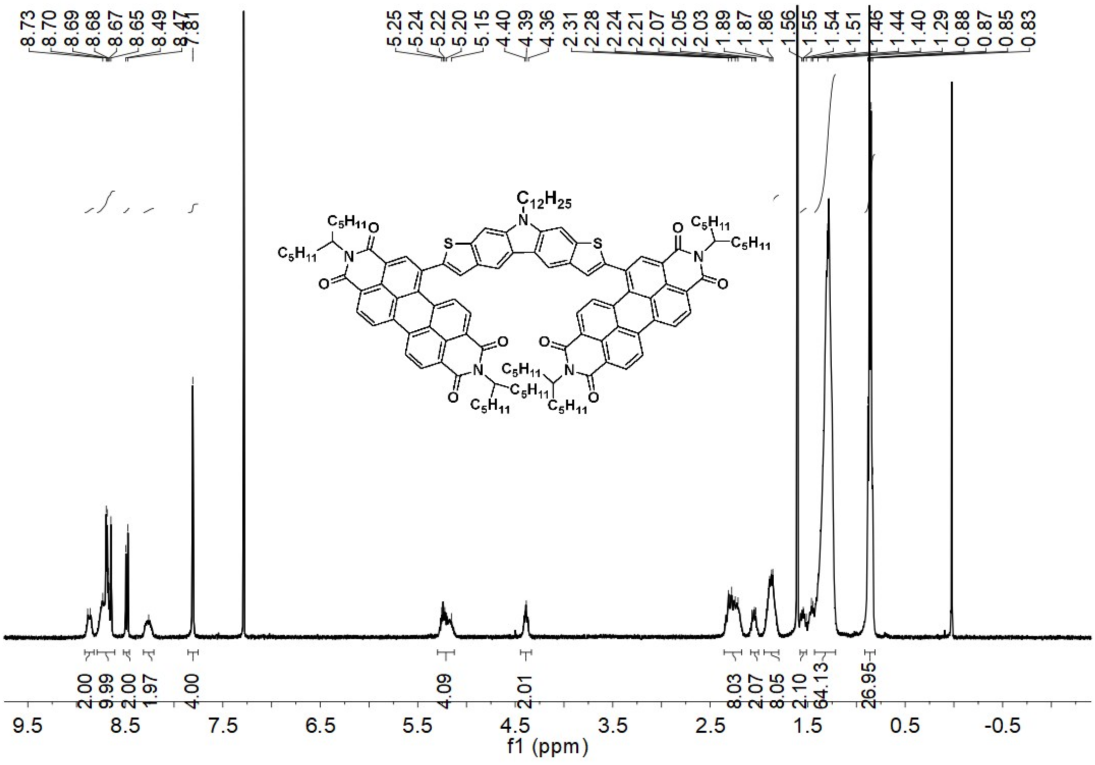


Fig. S10 ^{1}H NMR spectra of target compound **DTC-PDI** in CDCl$_3$.

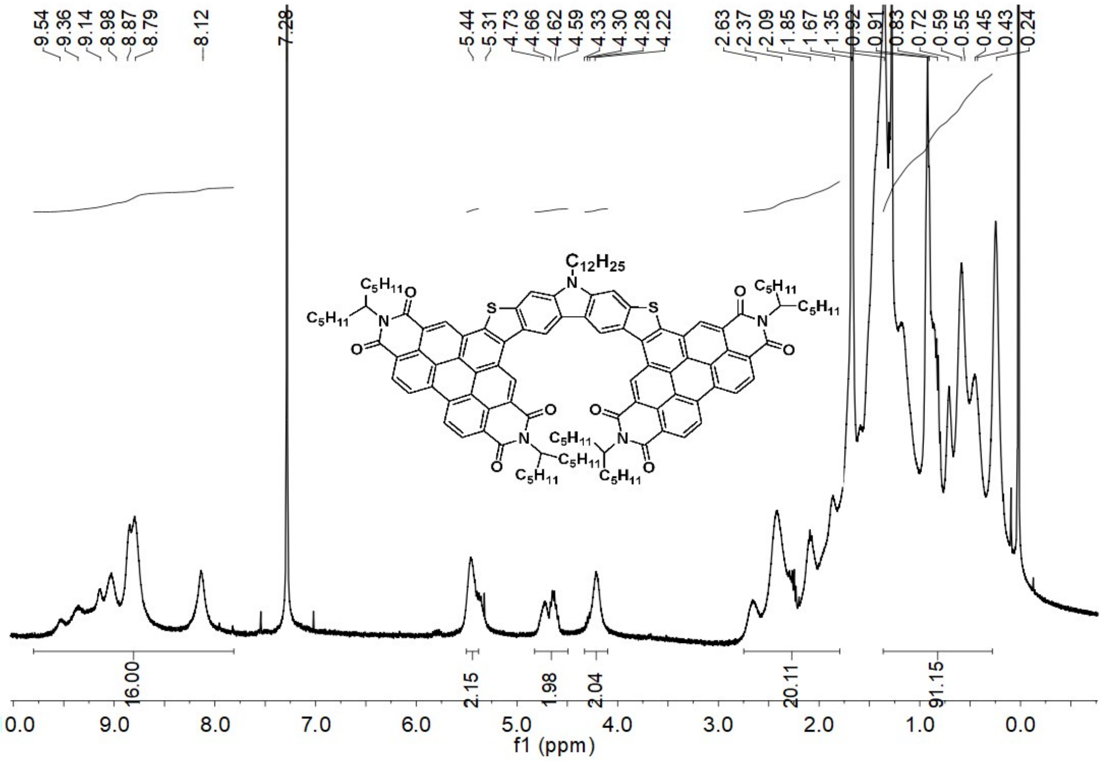


Fig. S11 ^{1}H NMR spectra of target compound **FDTC-PDI** in $CDCl_3$.

MS Spectrum

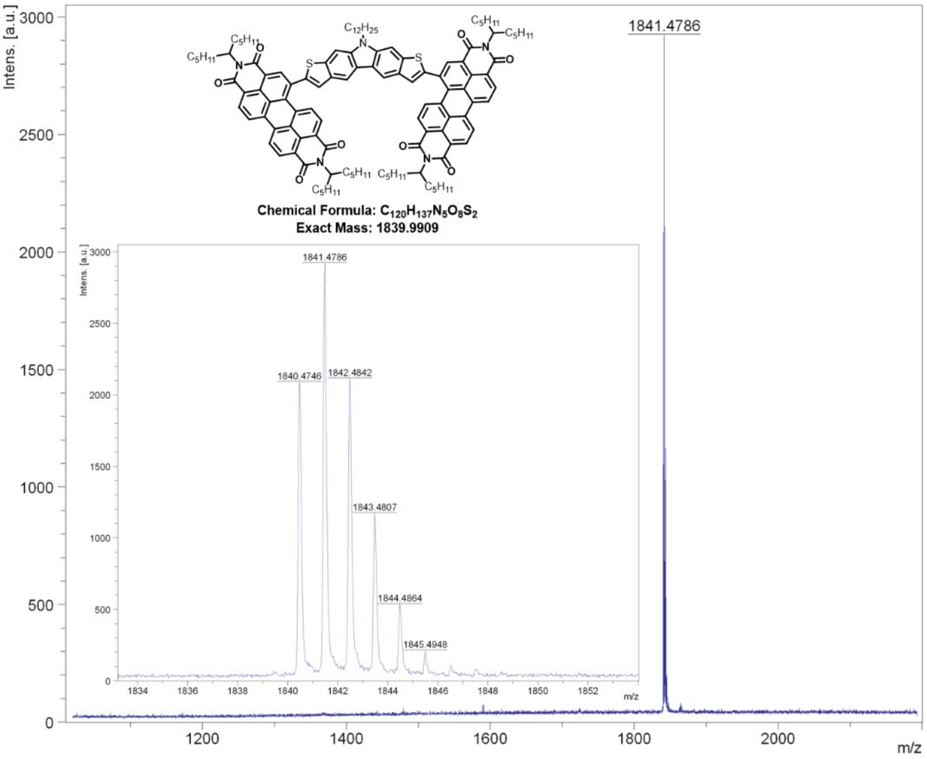


Fig. S12 MS spectrum of the target compound **DTC-PDI**.

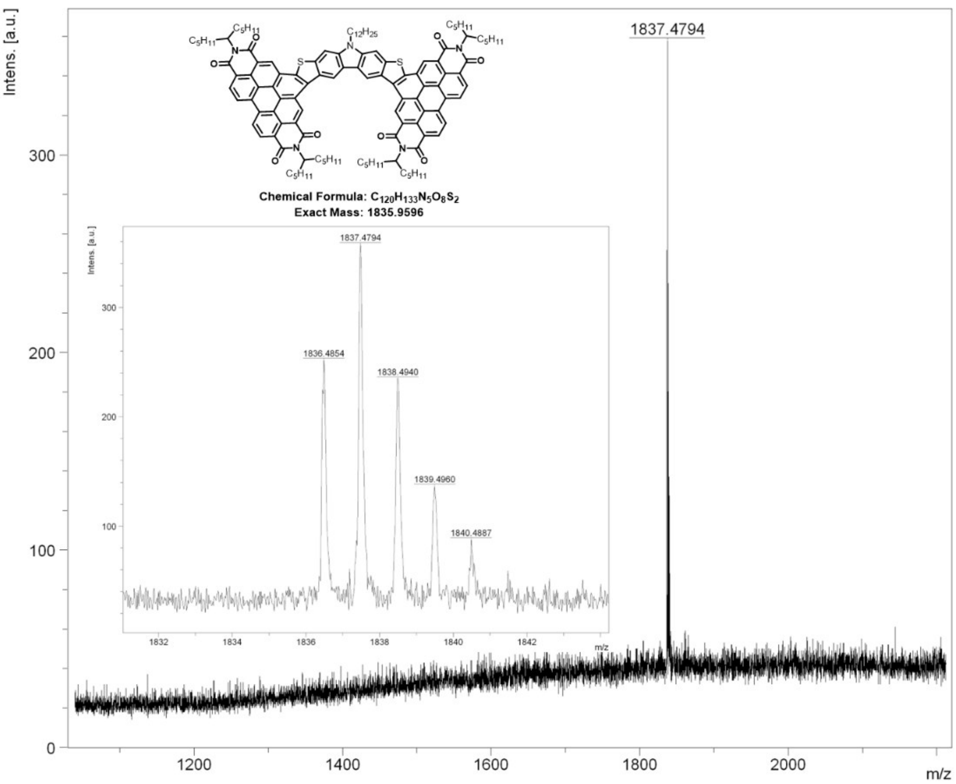


Fig. S13 MS spectrum of the target compound **FDTC-PDI**.

References

1 B. Zhao, B. Liu, R. Png, K. Zhang, K. Lim, J. Luo, J. Shao, P. Ho, C. Chi and J. Wu, *Chem. Mater.*, 2010, **22**, 435-449.

2 H. Huang, G. Jiao, S. Liu, Q. Li, X. Shi, N. Fu, L. Wang and W. Huang, *Chem. Commun.*, 2015, **51**, 15846-15849.

3 H. Huang, M. Qiu, Q. Li, S. Liu, X. Zhang, Z. Wang, N. Fu, B. Zhao, R. Yang and W. Huang, *J. Mater. Chem. C.*, 2016, **4**, 5448-5460.

4 X. Zhou, J. Lu, H. Huang, Y. Yun, Z. Li, F. You, B. Zhao, T. Qin, D. Gao and W. Huang, *Dyes. Pigments.*, 2019, **160**, 16-24.

5 F. You, X. Zhou, H. Huang, Y. Liu, S. Liu, J. Shao, B. Zhao, T. Qin and W. Huang, *New J. Chem.,* 2018, **42**, 15079-15087.