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Ternary Organic Solar Cells with 16.88 % Efficiency Enabled with a Twisted Perylenediimide Derivative To Enhance Open-circuit voltage

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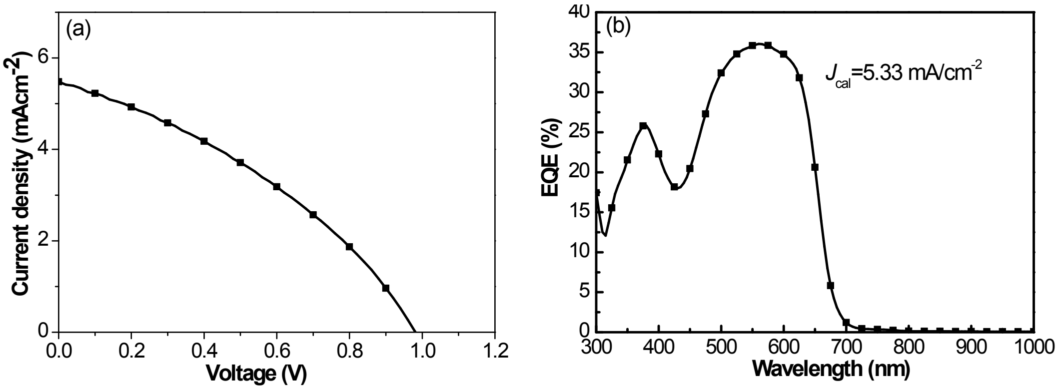


Figure S1. (a) *J–V* characteristics and (b) *EQE* of PM6:**Cor-T-PDI**(1:1.2) based OSCs.

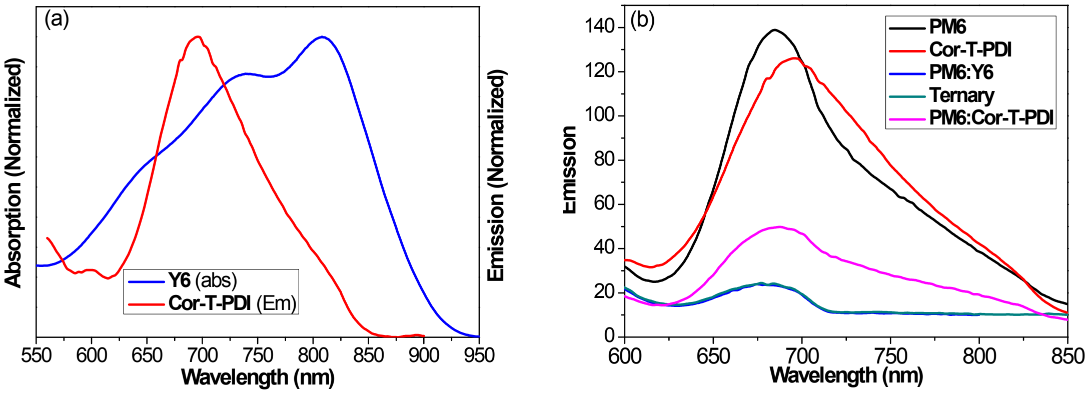


Figure S2. (a) The absorption spectra of **Y6** and the emission spectra of **Cor-T-PDI** in solid films. (b) The emission spectra for pure **PM6**, **Cor-T-PDI** and different blend films (excited at 500 nm).

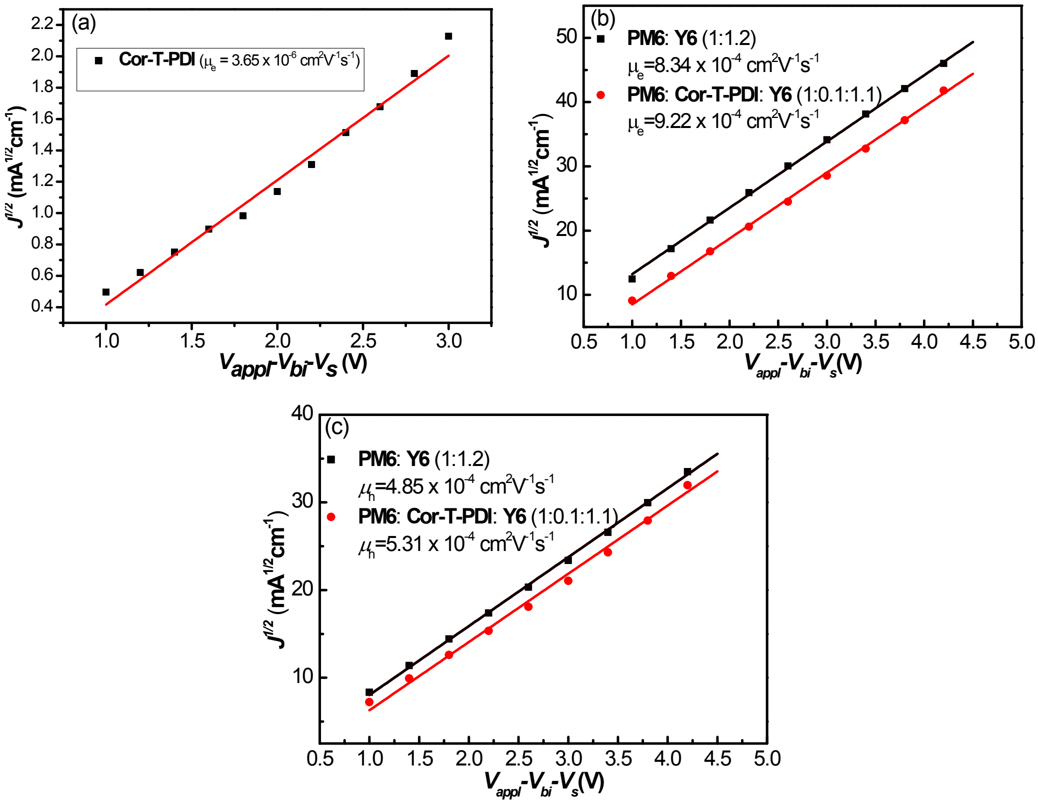
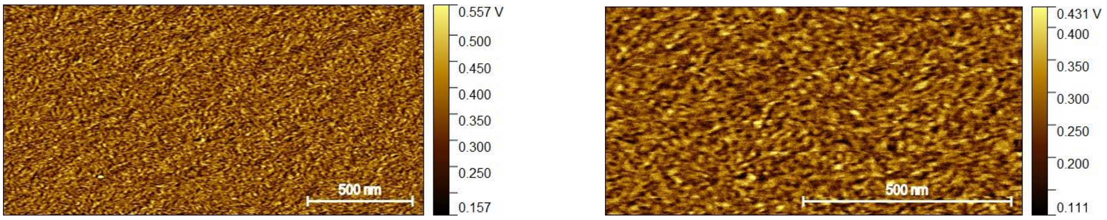
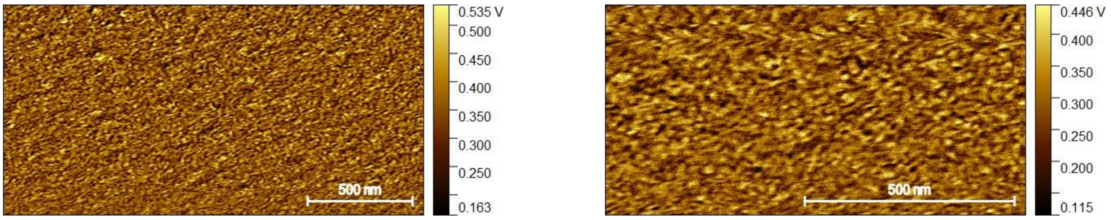


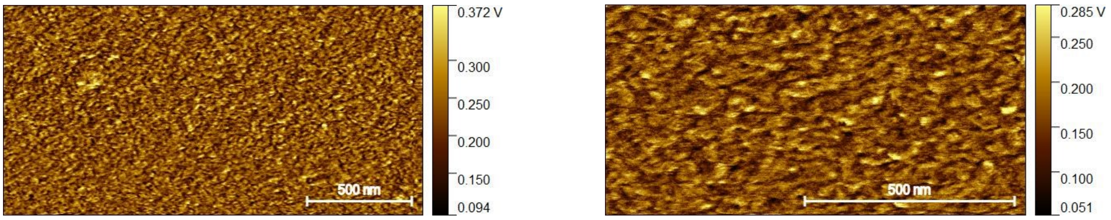
Figure S3. SCLC *J-V* plots of (a) electron for pure **Cor-T-PDI**, (b) electron and (c) hole mobilities for PM6:Y6 (1 : 1.20) binary blend and PM6: **Cor-T-PDI** :Y6(1 : 0.1 : 1.10) ternary blend, respectively.



PM6:Y6 (1:1.20) blend



PM6:Y6: **Cor-T-PDI** (1:1.10: 0.10) blend



PM6:**Cor-T-PDI** (1:1.20) blend

Figure S4. AFM images for different blends.

Experimental

1. Materials.

All reagents were obtained from commercial suppliers and used as received. Toluene was dried over sodium/ benzophenone and freshly distilled prior to use. Triethylamine was dried over solid KOH.

2. Measurements and Instruments.

NMR spectra were recorded on a Bruker DPX 400 (^{1}H NMR 400, 500 MHz) spectrometer. The mass spectra were obtained using an Ion-Spec 4.7 T HiRes MALDI instrument. UV absorption spectra were obtained using a Scinco S-3150 UV/vis spectrophotometer. The electrochemical cyclic voltammogram was obtained using a

CHI 660C electrochemical workstation with Pt disk, Pt plate, and standard calomel electrode (SCE) as working electrode, counter electrode, and reference electrode, respectively, in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) CH_2Cl_2 solution or CH_3CN solution. DFT calculation. Geometry optimizations were carried out by the density functional theory (DFT) method at the B3LYP/6-31G level. All the calculations were performed using Gaussian 09 program.

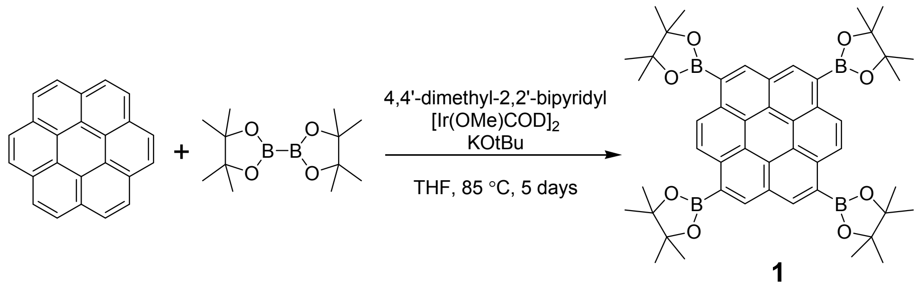
3. Device Fabrication and Characterization.

The devices were fabricated with a structure of ITO/PEDOT: PSS /active layer/PFN-Br/Ag. The glass substrates with pre-patterned indium tin oxide (ITO) were cleaned by sonication in detergent, deionized water, acetone and isopropanol for 15 min successively. After drying, the substrates were treated in an ultraviolet-ozone chamber for 15 min. Then a PEDOT: PSS layer (40 nm) was deposited through spin-coating from a PEDOT: PSS aqueous solution (Baytron P VP AI 4083 from H. C. Starck) at 3500 rpm and dried subsequently at 150 °C for 15 min in air. Then the device was transferred to a nitrogen glove box, where the active blend layer of PM6: **Cor-T-PDI**: Y6 was spin-coated from its chloroform solution (the concentration of PM6 in solution is 7.5 mg mL^{-1}) with additives (0.5 % (V/V) 1-chloronaphthalene (CN) onto the PEDOT: PSS layer. The thickness of the active layer was about 120 nm for these devices, respectively. Then methanol solution of PFN-Br at a concentration of 0.5 mg mL^{-1} was deposited atop the active layer at 3000 rpm for 30 s. Finally, top Ag electrode was deposited in vacuum onto the cathode buffer layer at a pressure of ca. 5.0×10^{-5} Pa.

4. Morphology Characterizations

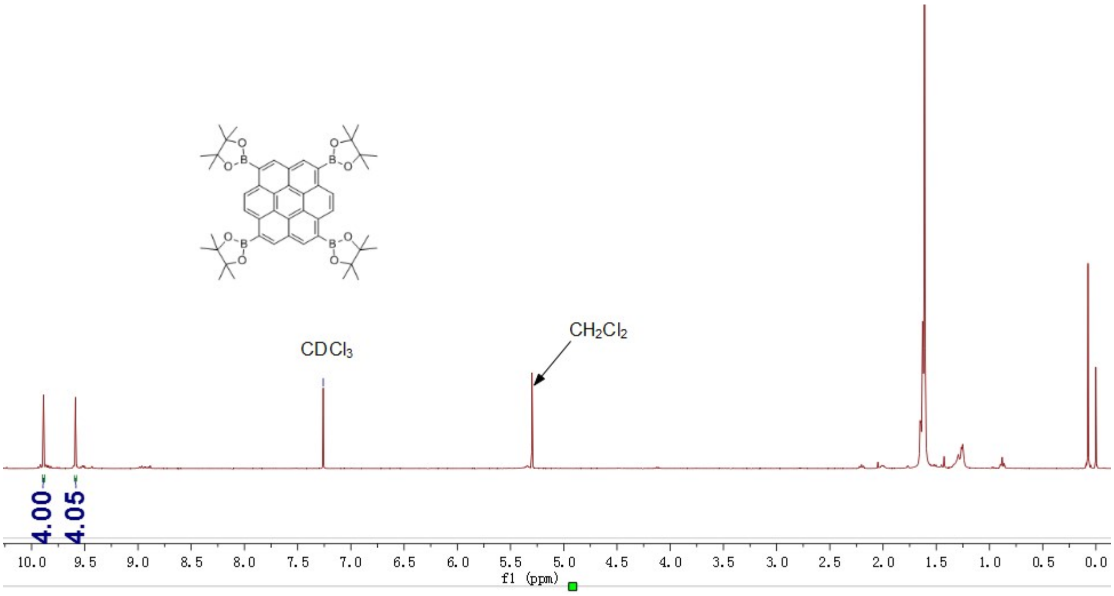
The grazing incident wide-angle X-ray scattering (GIWAXS) and the grazing incident small-angle X-ray scattering (GISAXS) measurements were carried out with a Xeuss 2.0 SAXS/WAXS laboratory beamline using a Cu X-ray source (8.05 keV, 1.54 Å) and a Pilatus3R 300K detector. The incident angle is 0.2°.

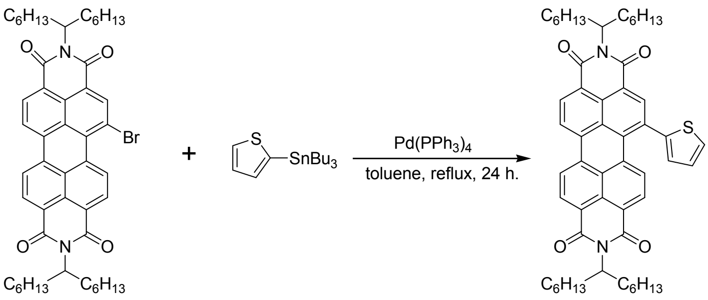
5. Synthetic procedures:



Compound **1**: A 15 mL glass pressure vessel equipped with a magnetic stirring bar and a silicon rubber septum was flushed with nitrogen and charged with $[Ir(OMe)COD]_2$ (106 mg, 0.16 mmol), 4,4'-dimethyl-2,2'-bipyridyl (60 mg, 0.32 mmol), B_2pin_2 (1.4 g, 5.6 mmol), and KtOBu(10 mg, 0.08 mmol). THF (1 mL) was added by syringe, and the mixture was heated at 50 °C for 10 min. Coronene (240 mg, 0.80 mmol) was added, and the reaction mixture was heated at 85 °C in an oil bath for 5 days. The mixture was removed from the oil bath, cooled, opened to the air, and diluted with dichloromethane (5 mL). The reaction was quenched by the drop wise addition of 10% aqueous HCl (2 mL). The layers were separated, and the aqueous layer was thoroughly extracted with dichloromethane. The solvent was evaporated under reduced pressure on rotary evaporator, then separated by column chromatography (hexanes : ethyl acetate 95:5 to 90:10) to afford pure 1,4,7,10-*tetrakis*(Bpin)coronene as yellow powder (300 mg, 46%). ^1H NMR (400 MHz, $CDCl_3$)

δ 9.89 (s, 4H), 9.59 (s, 4H), 1.61 (s, 48H). MALDI-TOF-MS: m/z calculated for $C_{48}H_{56}B_4O_8$: 804.4 m/z found 804.6.





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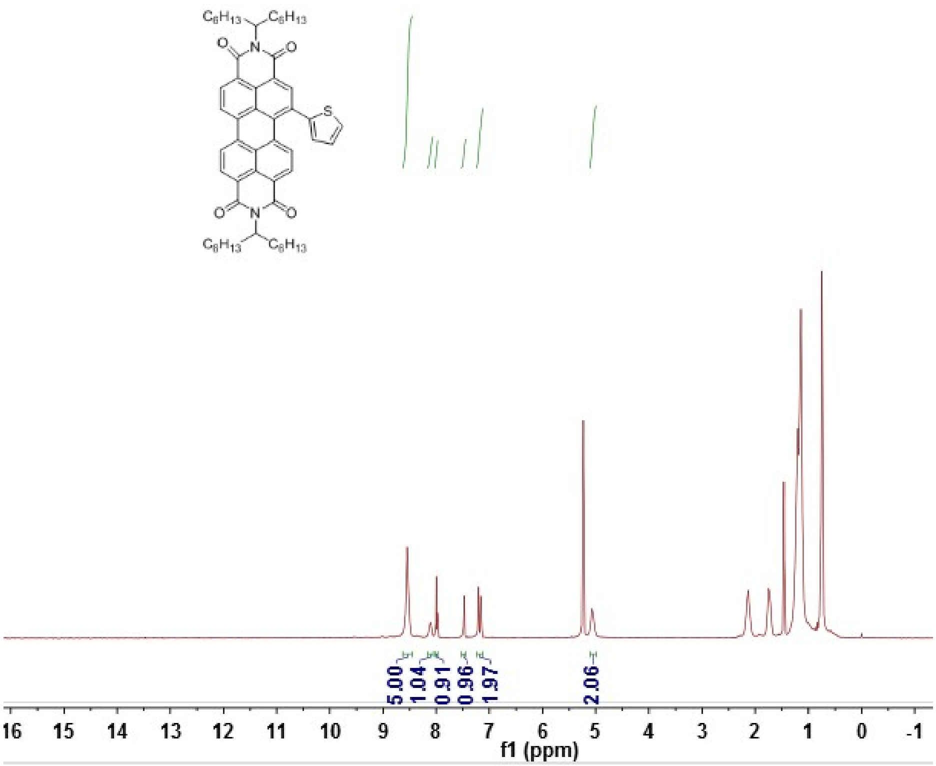
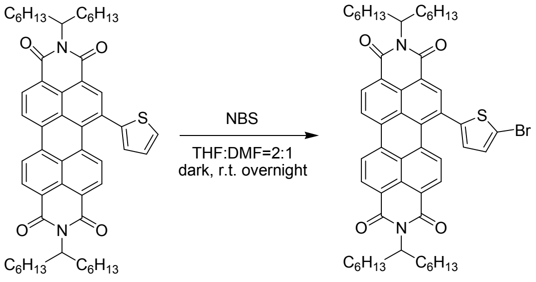
Compound **2**: A solution of PDI-Br (1.45 g, 1.73 mmol), 2-(Tributylstannyl)thiophene (648 mg, 1.73mmol), and $Pd(PPh_3)_4$ (20 mg, 0.173mmol) in dry toluene (30 mL) was deoxygenated with the nitrogen gas for about 5 min and the reaction was heated to 110 ºC for 24 h. After cooling, the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica, dichloromethane) to yield a red solid(1.1 g, 75.8 %). ^1H NMR (400 MHz, CD_2Cl_2): δ 8.63-8.45 (d, 5H), 8.16-8.06 (s, 1 H), 8.02-7.97 (d, 1H), 7.53-7.44 (m, 1H), 7.24-7.12 (m, 2H), 5.11-4.99

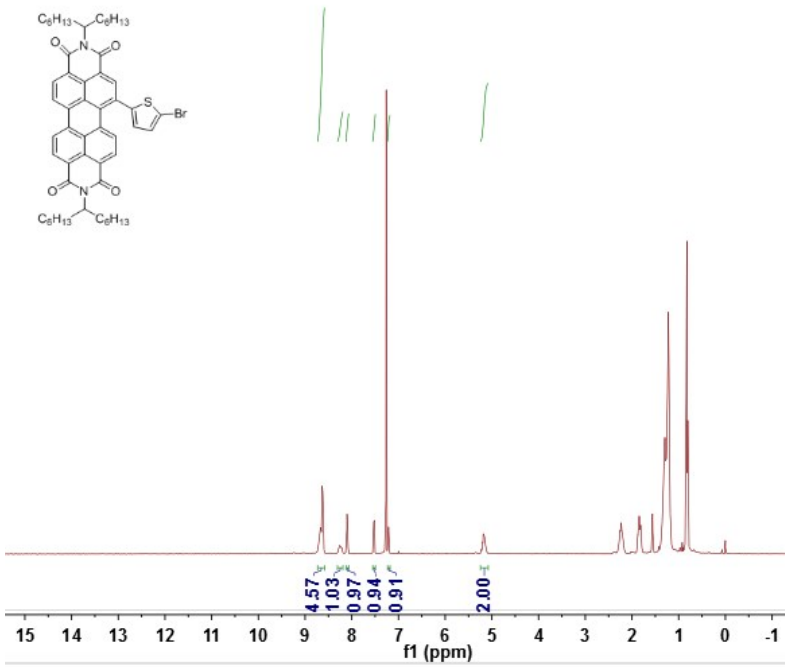
(m, 2H). MALDI-TOF-MS: m/z calculated for $C_{54}H_{64}N_2O_4S$: 836.4 m/z found 836.0.

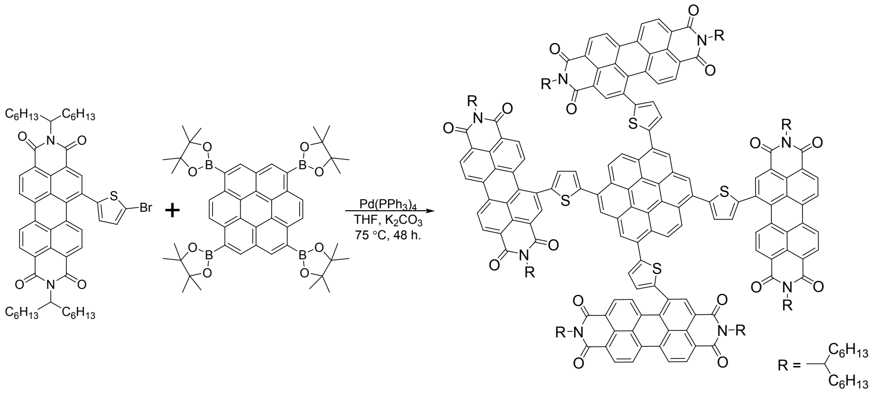




2 **3**

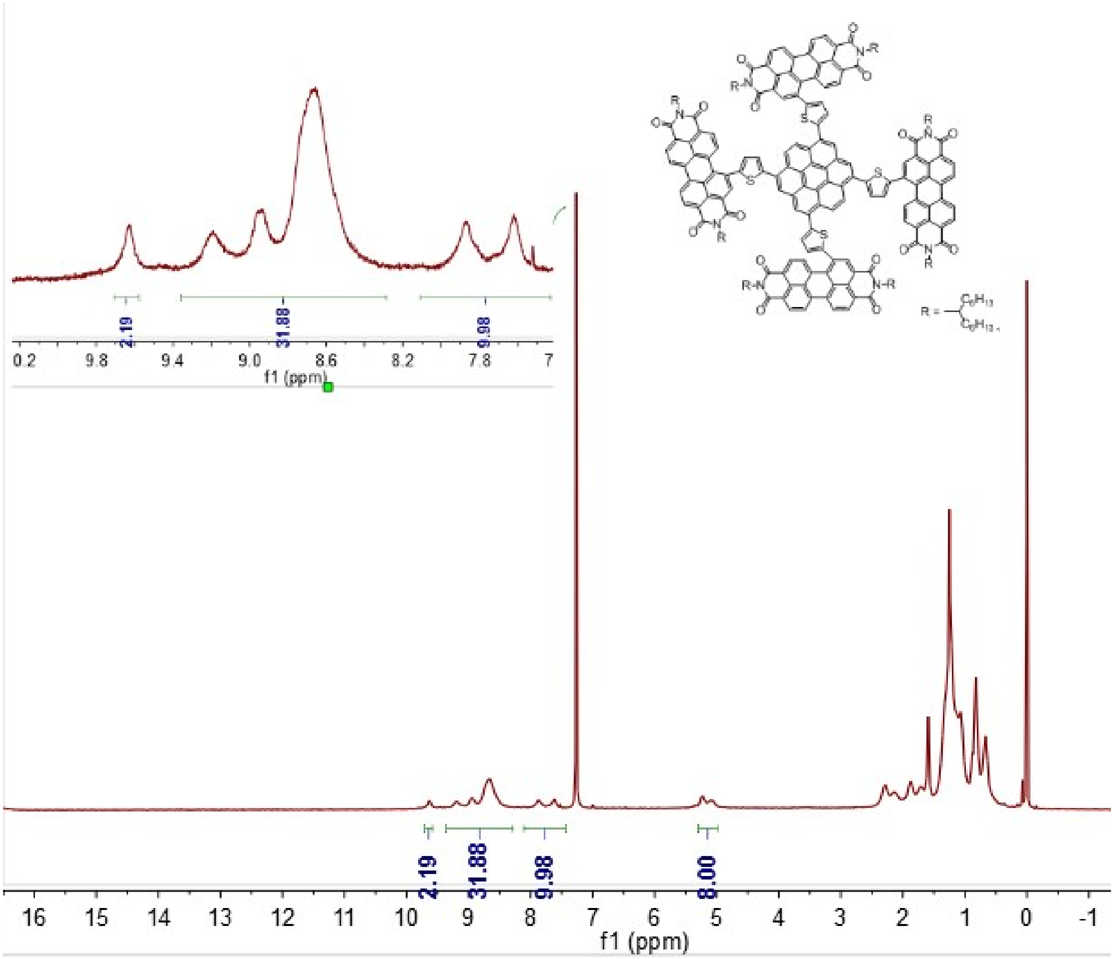
Compound **3**: To a solution of **2** (837 mg, 1.0 mmol) in THF/DMF (2:1, 100 ml) was added N-bromosuccinimide (190 mg, 1.1 mmol). This mixture was stirred overnight in the absence of light at room temperature, then pour into water. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica, dichloromethane) to yield a red solid(820 mg, 89.5 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73-8.57 (d, 5H), 8.31-8.19 (s, 1 H), 8.13-8.07 (d, 1H), 7.55-7.49 (m, 1H), 7.24-7.18 (m, 1H), 5.25-5.08 (m, 2H).

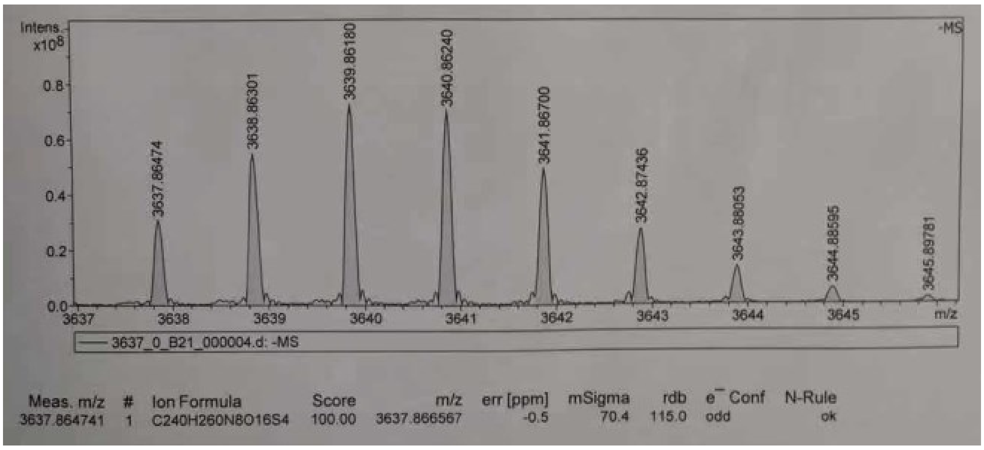




COR-T-PDI: To a 50 ml three-necked, round-bottomed flask, compound **1** (40 mg, 0.05mmol), **3** (318 mg, 0.3mmol), Pd(PPh$_3$)$_4$ (23 mg, 0.02 mmol) was added. The flask was connected to Schlenk line and evacuated air and refilled with the nitrogen. 20 mL of THF and 4 mL K$_2$CO$_3$ solution(2M) was firstly degassed and added into above flask. This resulted mixture was stirred and refluxed for 48 hour. The reaction mixture was then cooled to rt and extracted with diethyl ether for three times. The organic layer was combined, washed with brine, dried over Na$_2$SO$_4$, and concentrated in vacuum. The residue was purified by flash column chromatography (Hexane :

Chloroform = 1:3) to get the product as red solid (41 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.71-9.58 (s, 2H), 9.36-8.29 (m, 32H),8.11-7.43 (m, 10H), 5.30-4.99 (m, 8H). MALDI-TOF-MS: m/z calculated for $C_{240}H_{260}N_8O_{16}S_4$: 3637.8 m/z found 3639.9. HRMS(MALDI): calcd for $C_{240}H_{260}N_8O_{16}S_4$: 3637.8660; found: 3637.8647.





Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
3637.864741	1	C240H260N8O16S4	100.00	3637.866567	-0.5	70.4	115.0	odd	ok

The high-resolution MALDI-TOF mass for **Cor-T-PDI**.