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

Supporting Information

N-annulated Perylene Diimide Derivatives as Non-Fullenence Acceptors for Solution-Processed Solar Cells with Open-Circuit Voltage up to 1.14 V

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The synthesis of 1-Pentylhexylamine, TPA-BPin and 5,7-bis(trimethylstannyl)-EDOT

1-Pentylhexylamine

In a 250 mL two neck round bottomed flask, ammonium acetate (20.06 g, 260.2 mmol) was dissolved in methanol (150 mL), then stirred at room temperature under N_2. After the ammonium acetate complete dissolved, inject 6-undecanone (5.03 g, 29.5 mmol) and the solution was stirred for 2 h before added $NaCNBH_3$ (1.12 g, 17.8 mmol). After 56 h, adding HCl solution (2 M, 4 mL) to quenched the reaction and then concentrated. The faint yellow grease was poured into water (100 mL) and the pH was adjusted to 10 with KOH. The mixture solution was extracted with ethyl acetate. The pale yellow oil was obtained by concentrating and directly used without any further purification.

TPA-BPin

In a 100 mLtwo-necked round bottom flask , Tris(4-bromophenyl)amine (2.90 g, 6 mmol), KOAc (2.94 g, 30 mmol), bis(pinacolato)diborane (5.33 g, 21 mmol) were added in DMF (30 mL). After degassing for 15 min, $Pd(dppf)_2Cl_2$ (0.5 g) was added. The reaction mixture was heat to 85 ^oC and stirred for 12 hr. After cool to room temperature, was extracted with CH_2Cl_2/H_2O. The organic solvent was removed, the crude product was obtained by rotary evaporation, and purified by silica gel column chromatography with petroleum ether/ CH_2Cl_2 as an eluent (2:1) to give product (111 mg, 52%).

5,7-bis(trimethylstannyl)-EDOT

In a 100 mL two-necked round bottom flask, 3,4-ethylenedioxythiophene (1.00 g, 7 mmol) and N,N,N',N',-tetramethylethylenediamine (TMEDA) (1.22 g, 7 mmol) in dry THF (15 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 again and tributylstannyl chloride (2.83 g, 14.2 mmol) was added. The reaction mixture was warmed to room temperature and stirred for 5 h. The THF was removed and the residue was extracted with CH_2Cl_2/H_2O. The pentane layer was separated, dried over magnesium sulfate, and evaporated to give the product 9 (3.43g, 68%). Although it contaminated with monostannylated product, this bisstannylated compound was used without further purification.

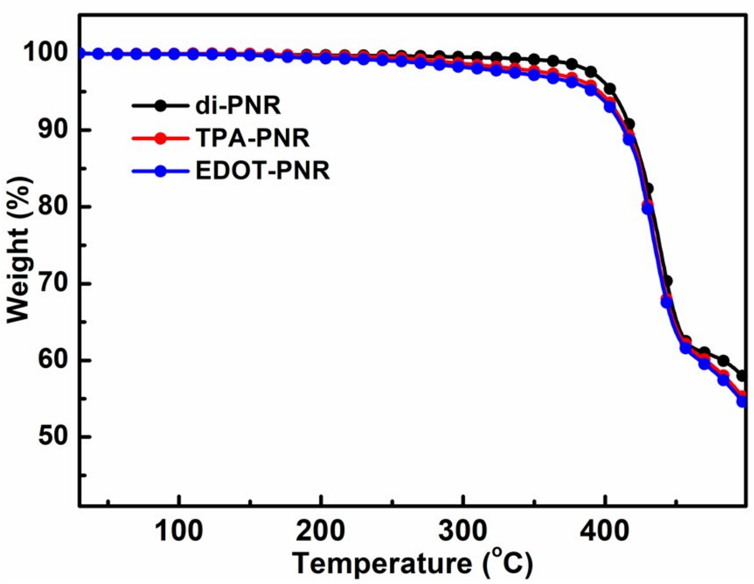

Fig. S1 TGA polts of di-PNR, TPA-PNR and EDOT-PNR at a heating rate of 10 °C min^{-1} under nitrogen atmosphere.

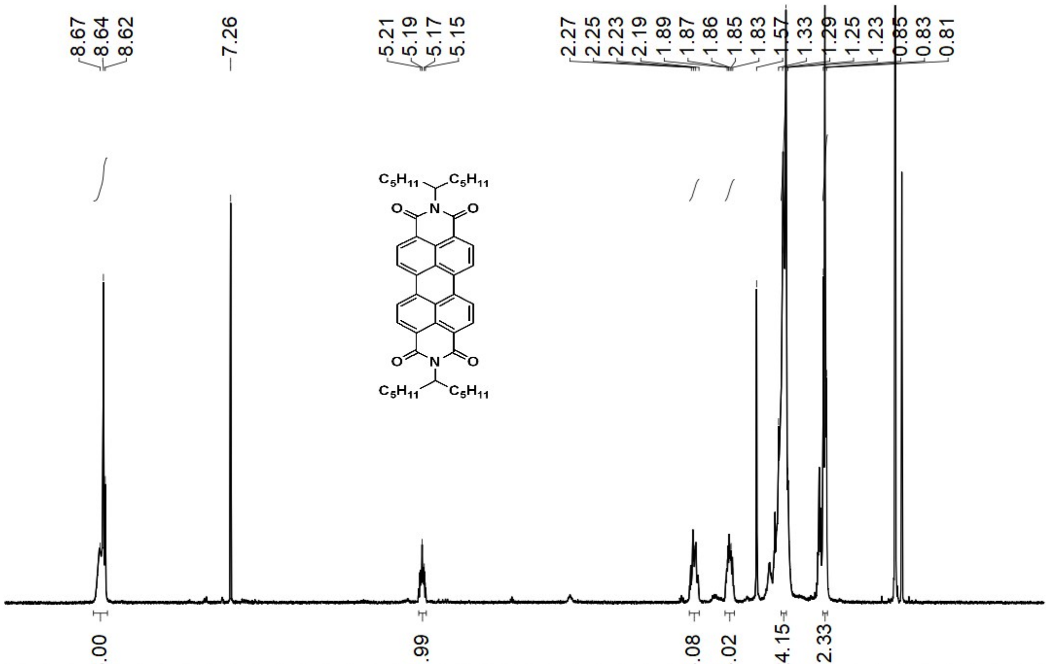

Figure S2. ^{1}H NMR spectrum of compound **1.**

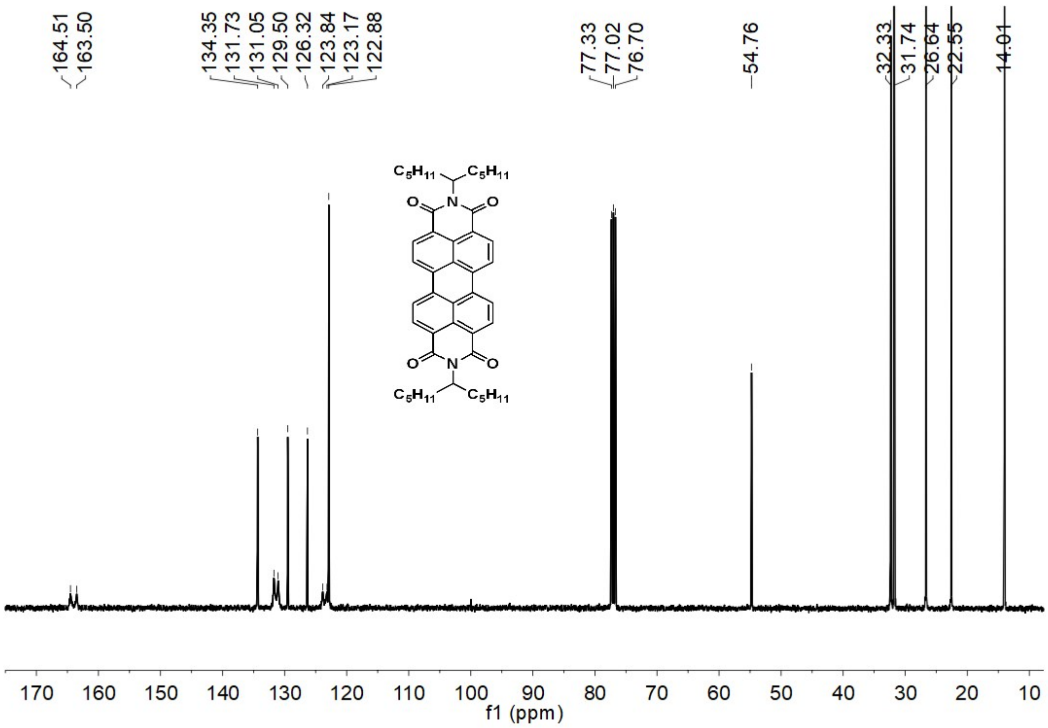

Figure S3. ^{13}C NMR spectrum of compound **1.**

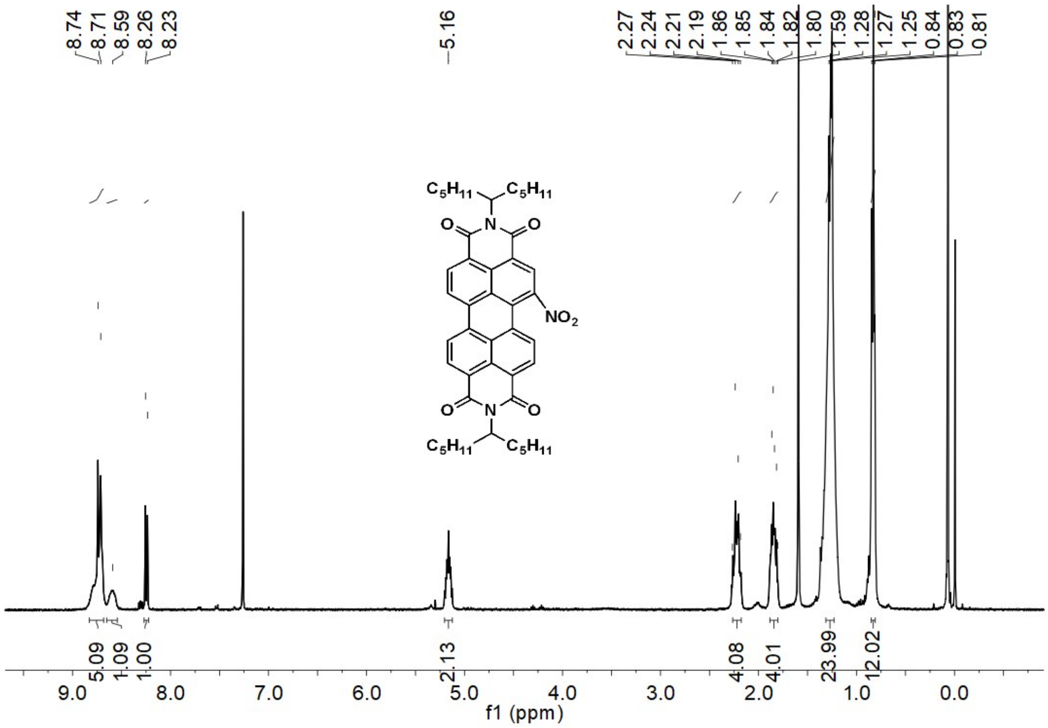

Figure S4. ^{1}H NMR spectrum of compound **2.**

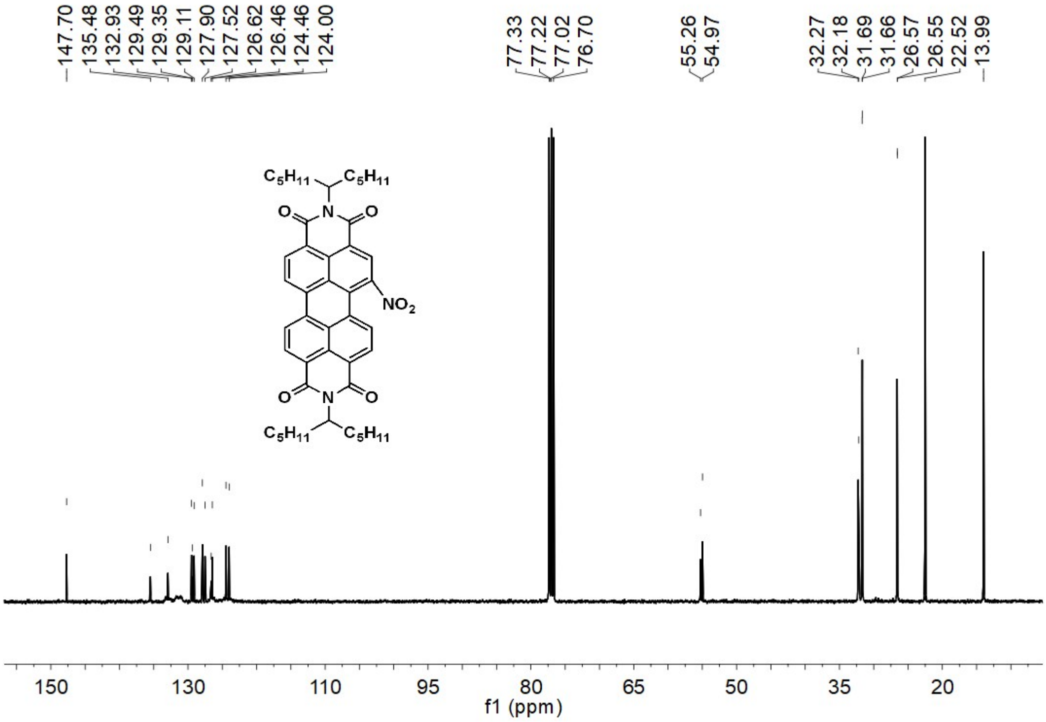

Figure S5. ^{13}C NMR spectrum of compound **2.**

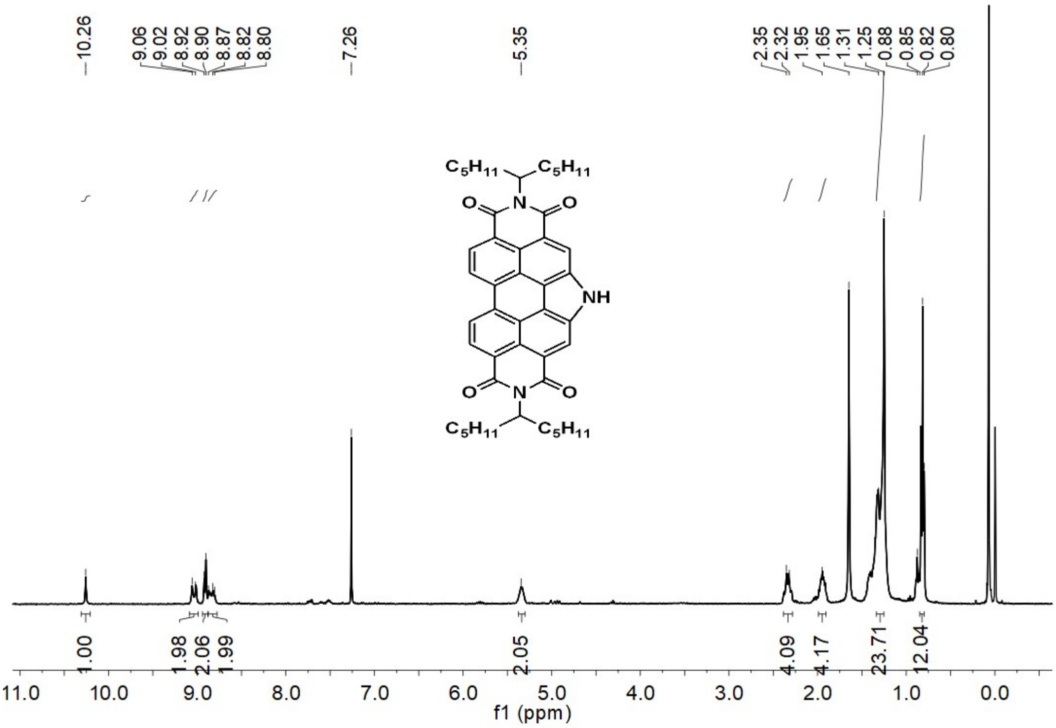

Figure S6. ^{1}H NMR spectrum of compound **3.**

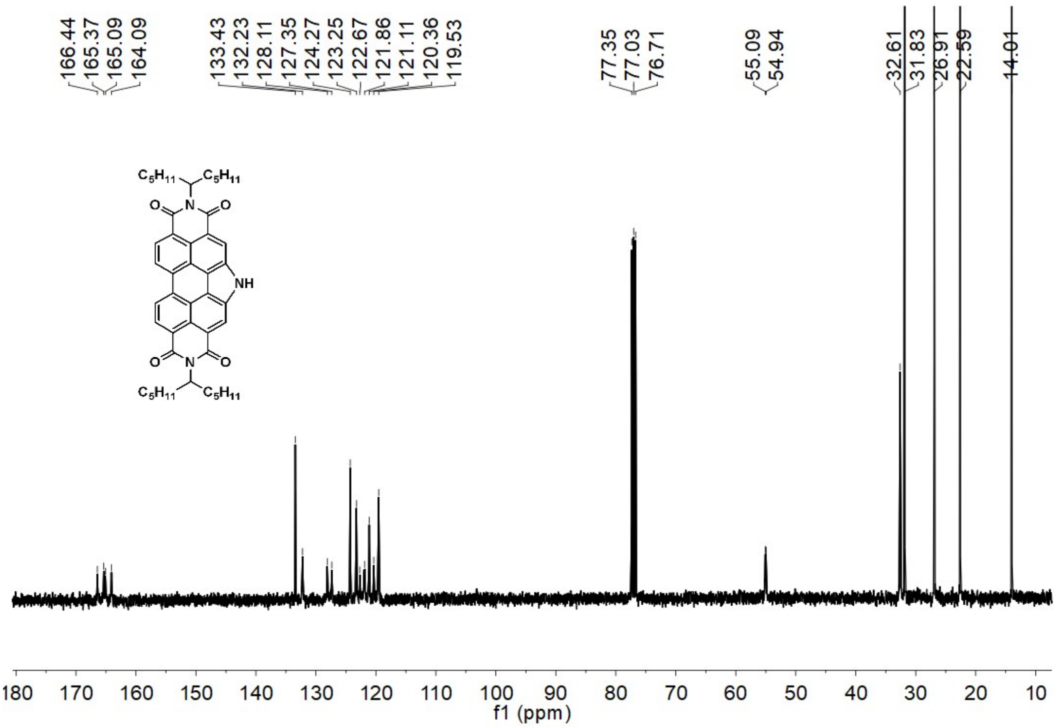

Figure S7. ^{13}C NMR spectrum of compound **3.**

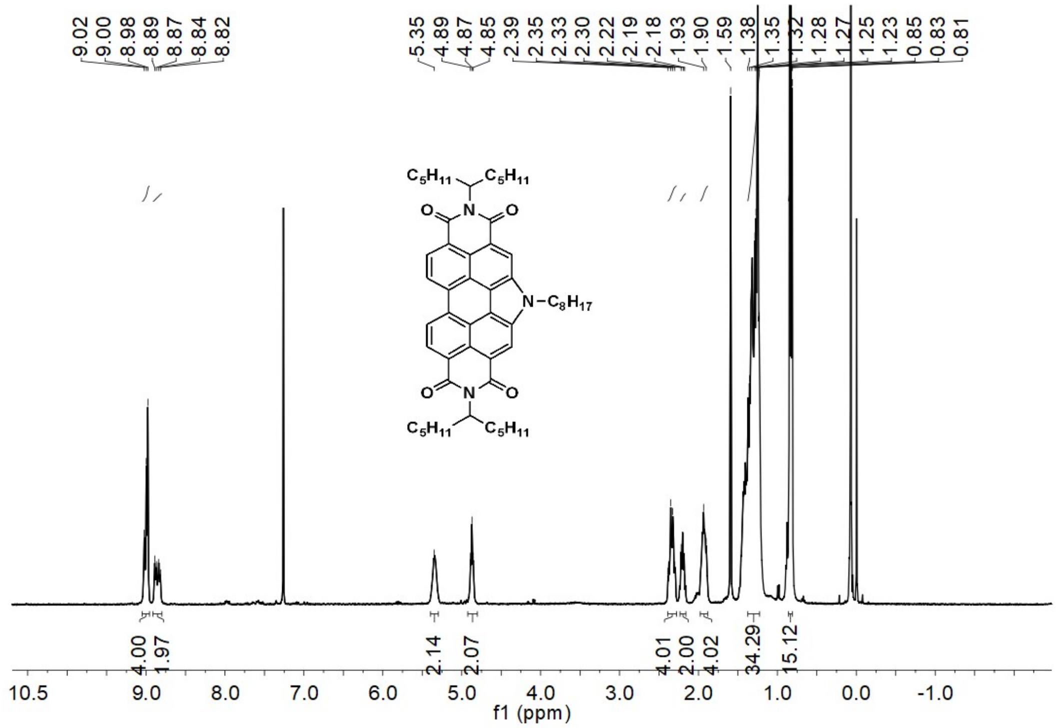

Figure S8. ^{1}H NMR spectrum of compound **PNR.**

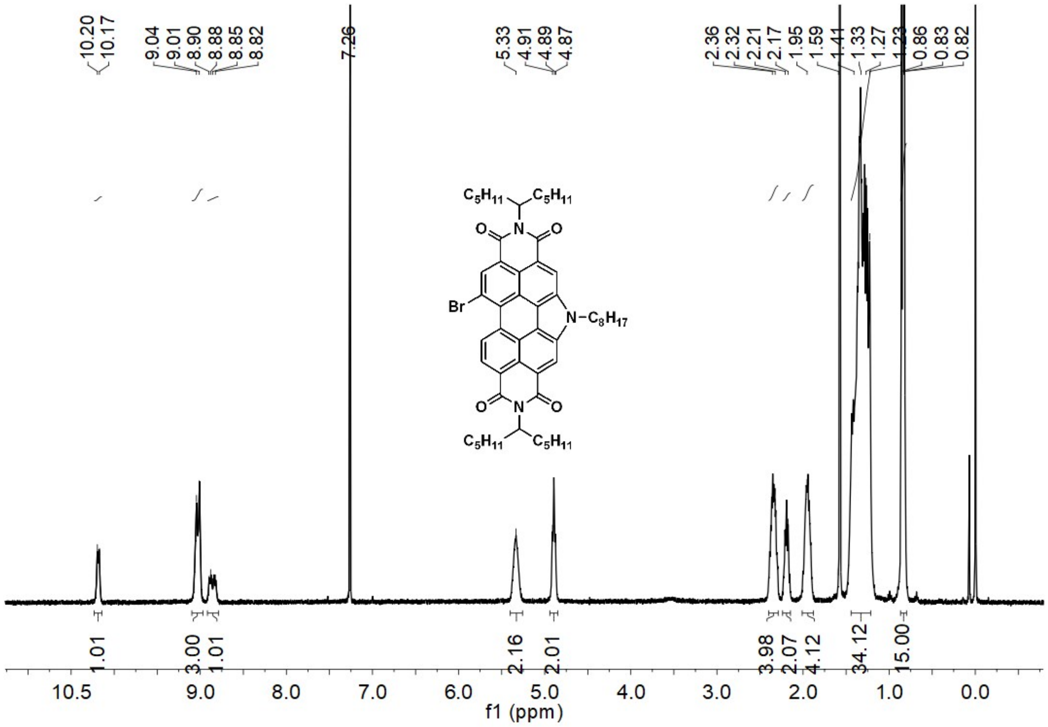

Figure S9. ^{1}H NMR spectrum of compound **PNR-Br.**

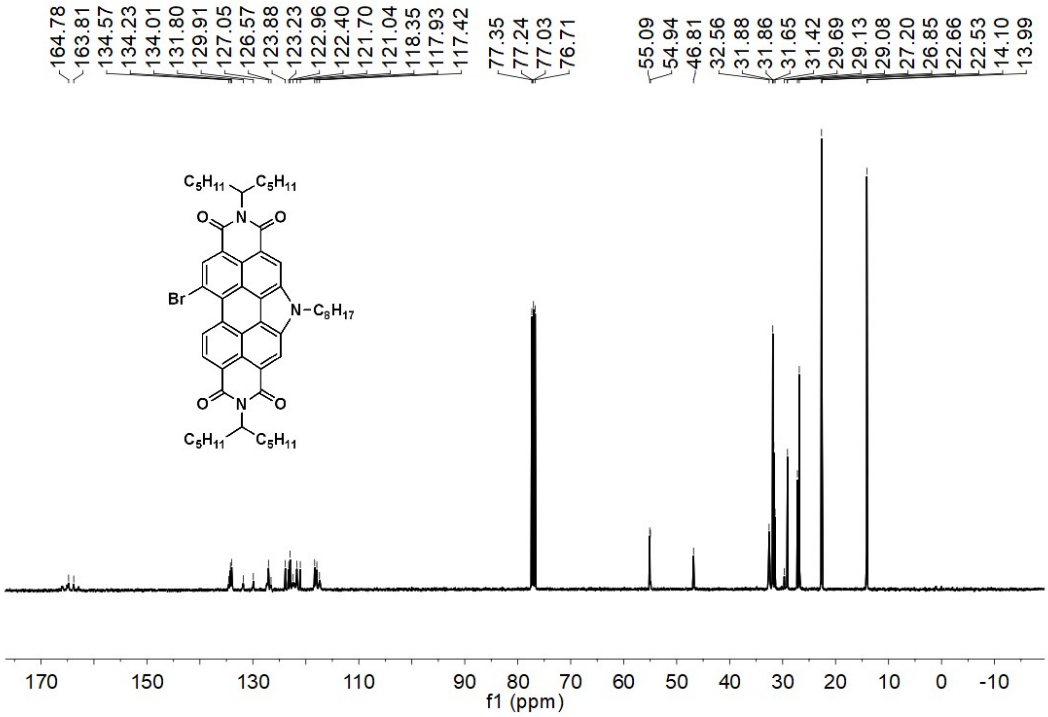

Figure S10. ^{13}C NMR spectrum of compound **PNR-Br.**

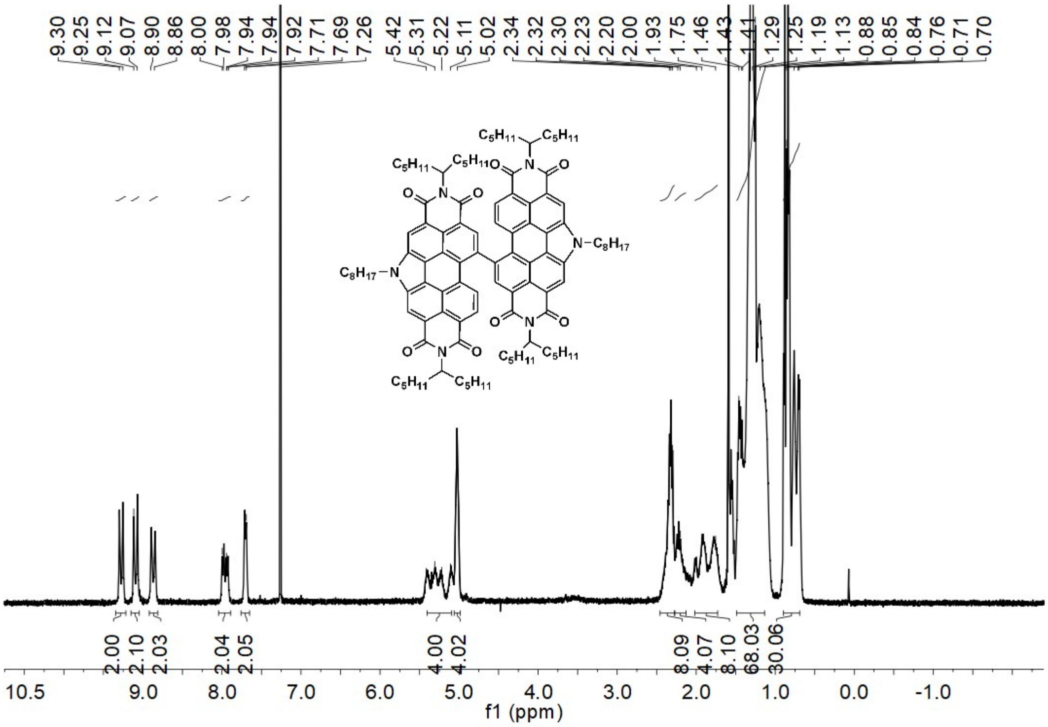

Figure S11. ^{1}H NMR spectrum of compound **di-PNR.**

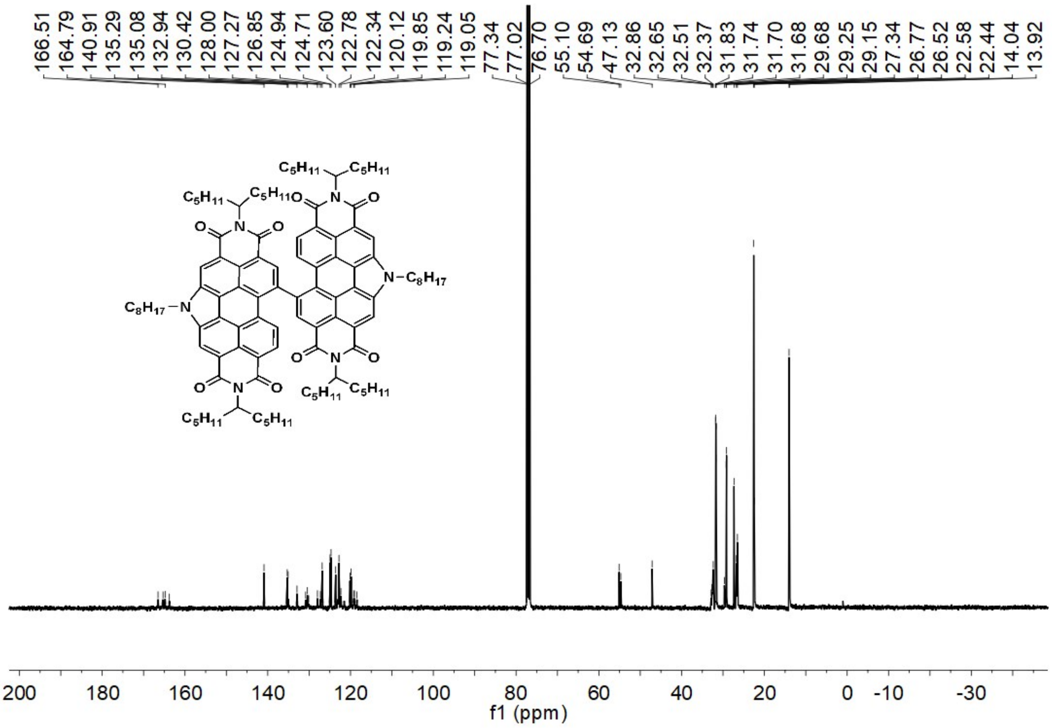

Figure S12. ^{13}C NMR spectrum of compound **di-PNR.**

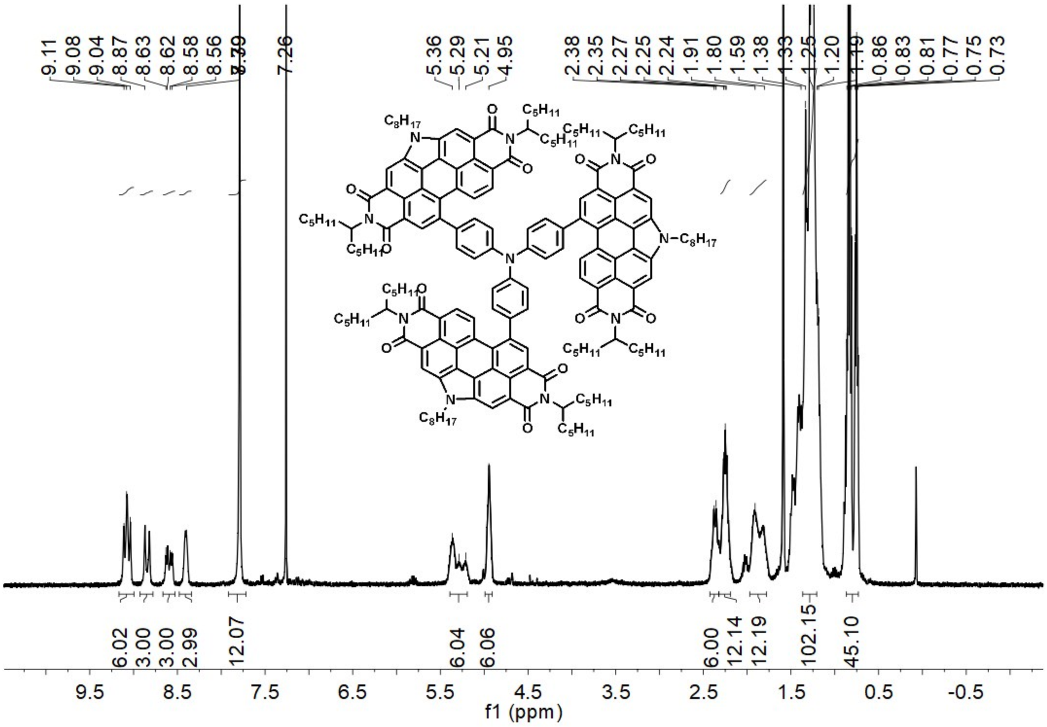

Figure S13. ^{1}H NMR spectrum of compound **TPA-PNR.**

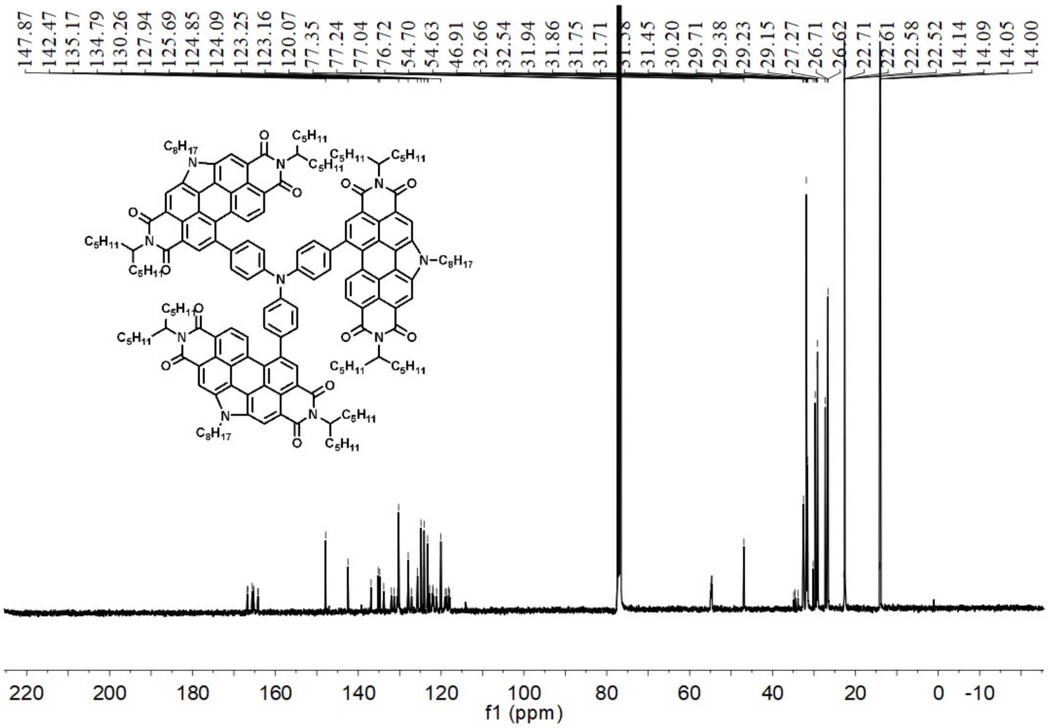

Figure S14. ^{13}C NMR spectrum of compound **TPA-PNR.**

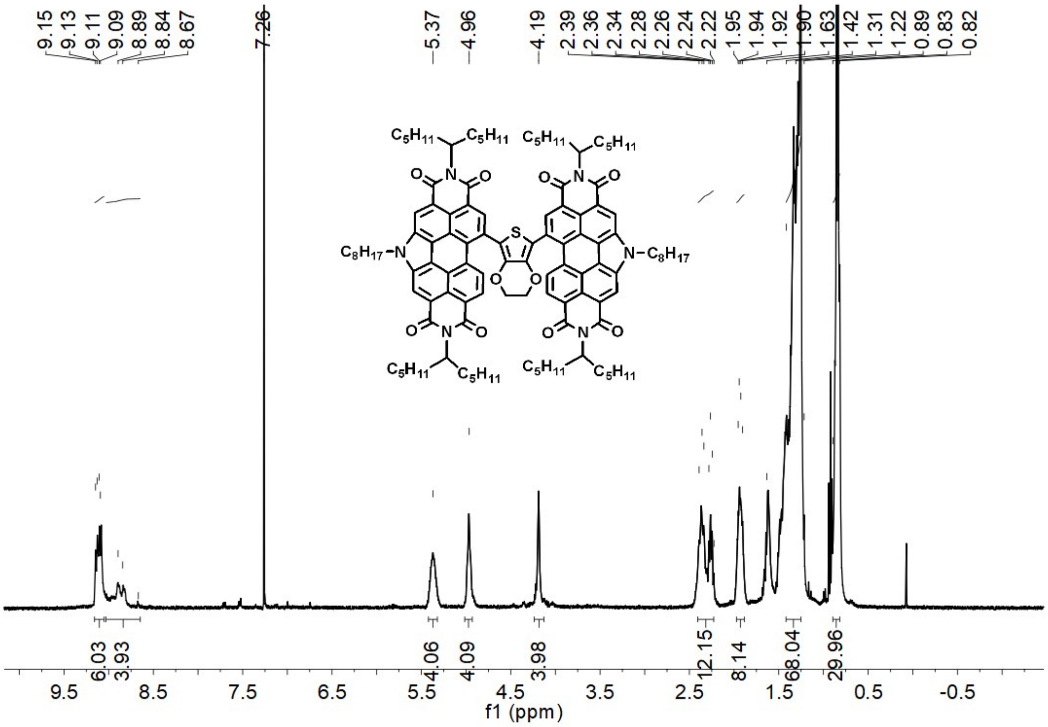

Figure S15. ^{1}H NMR spectrum of compound **EDOT-PNR.**

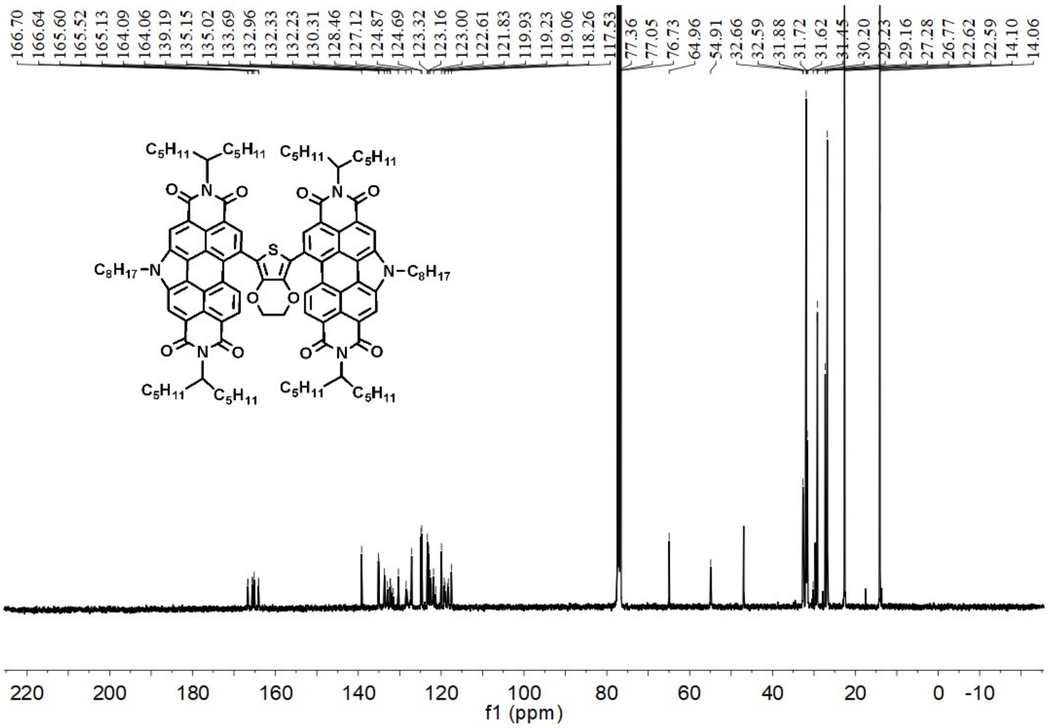

Figure S16. ^{13}C NMR spectrum of compound **EDOT-PNR.**

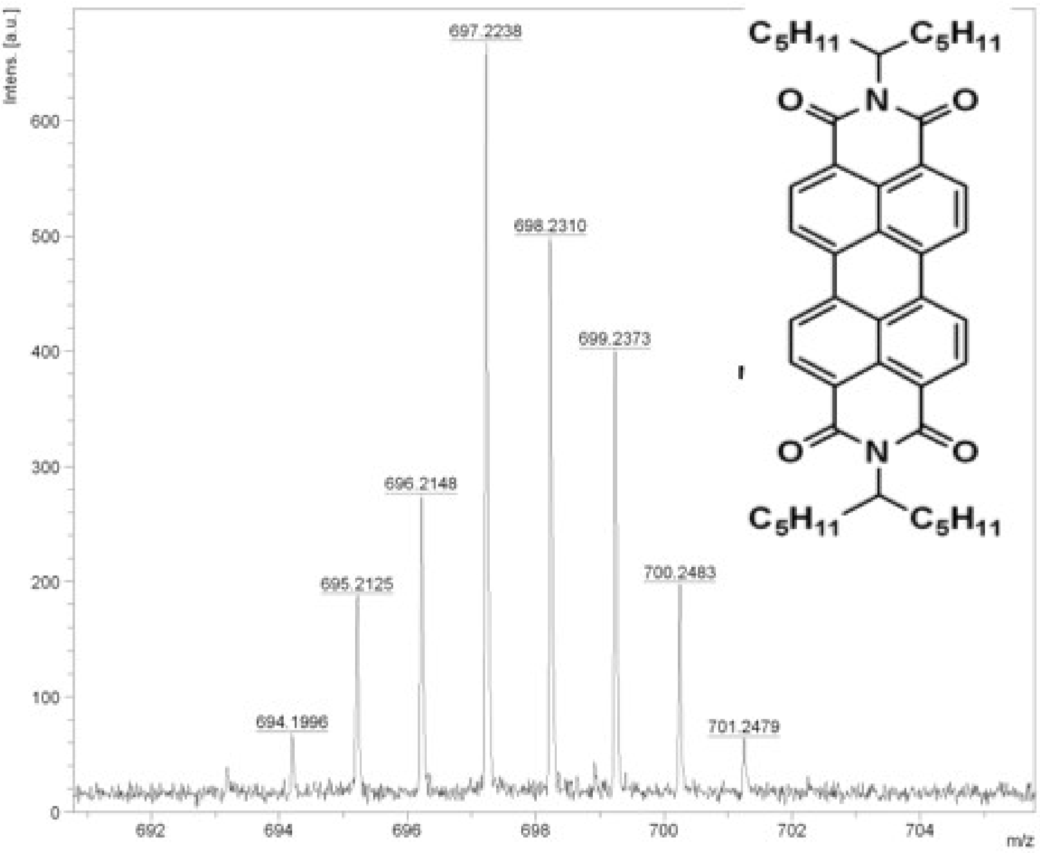

Figure S17. MALDI-TOF MS Spectrum of 1**.**

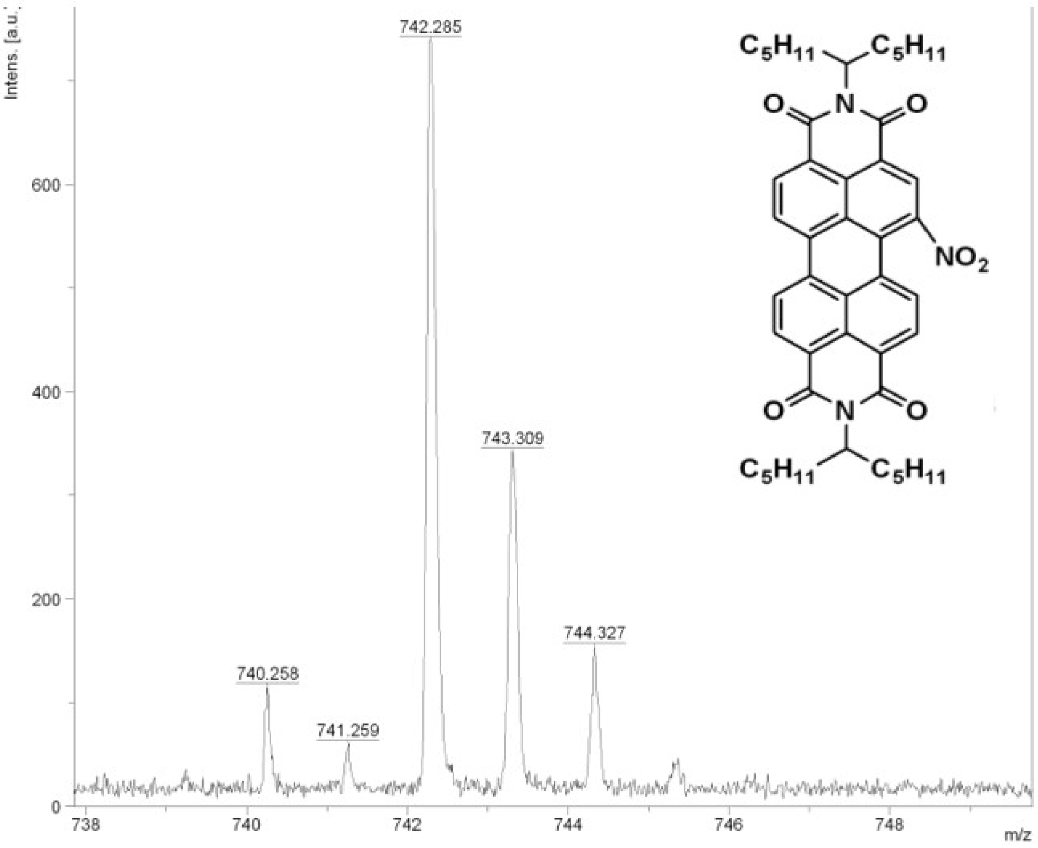

Figure S18. MALDI-TOF MS Spectrum of 2**.**

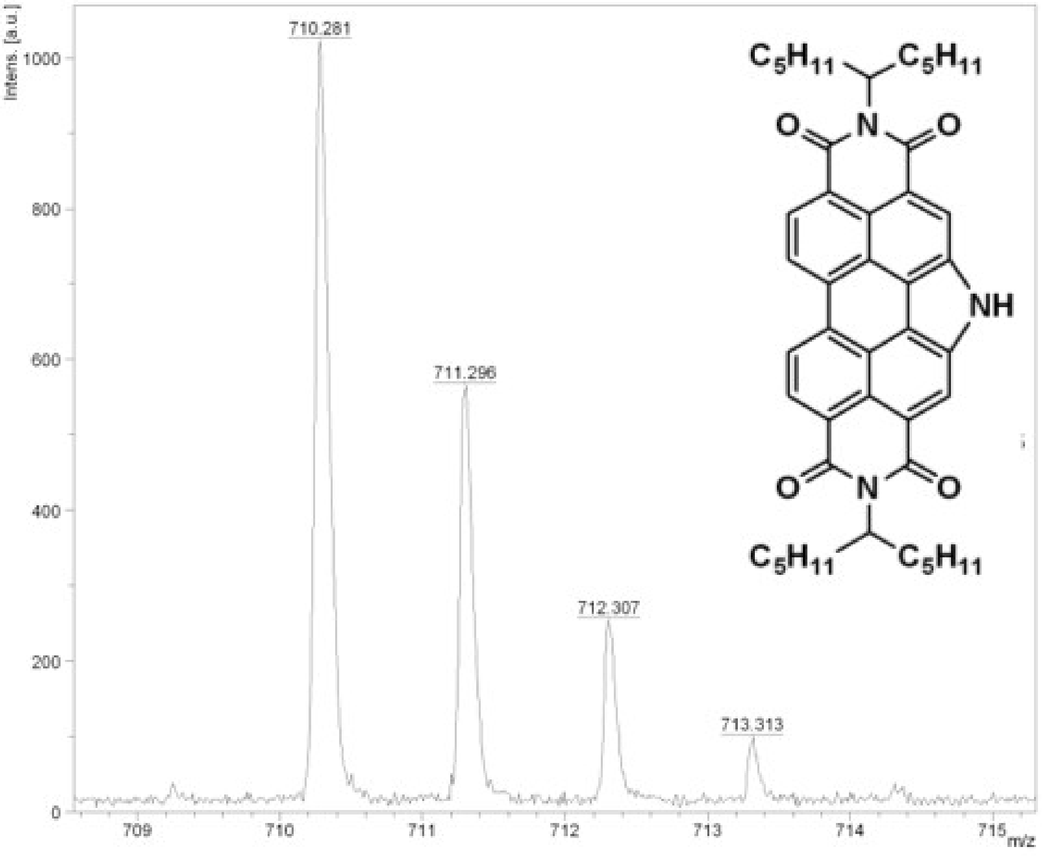

Figure S19. MALDI-TOF MS Spectrum of 3**.**

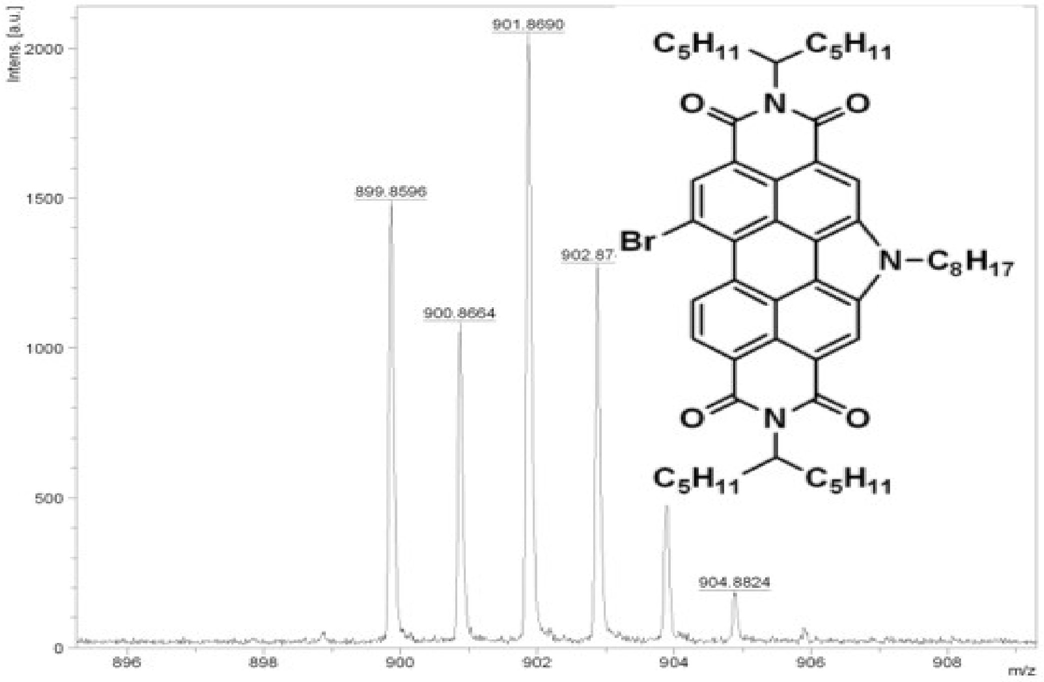

Figure S20. MALDI-TOF MS Spectrum of PNR-Br**.**

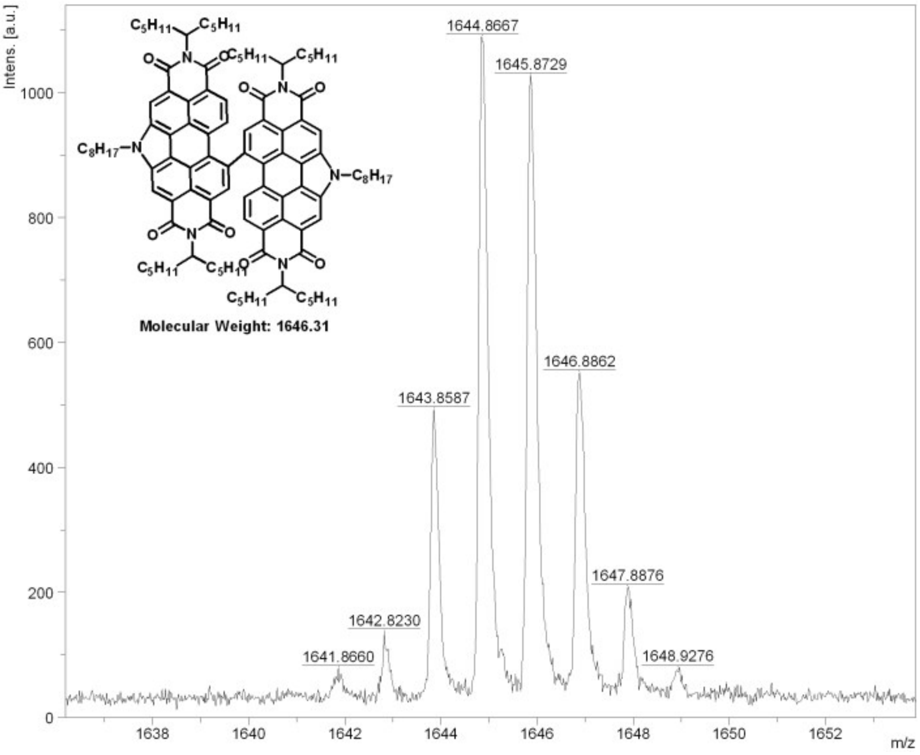

Figure S21. MALDI-TOF MS Spectrum of **di-PNR.**

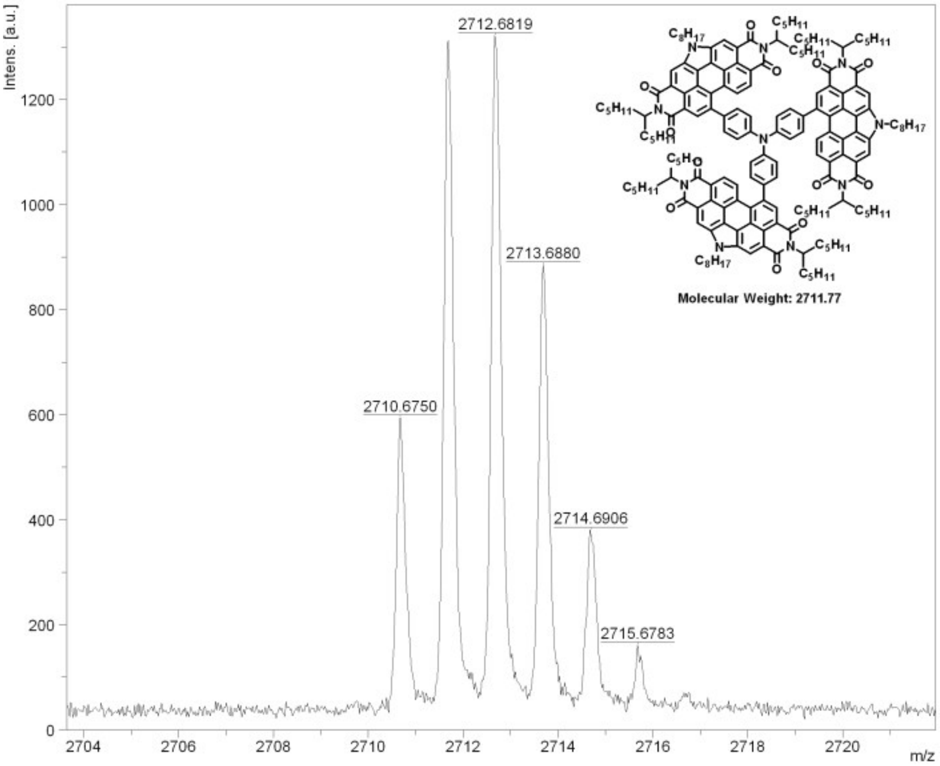

Figure S22. MALDI-TOF MS Spectrum of **TPA-PNR.**

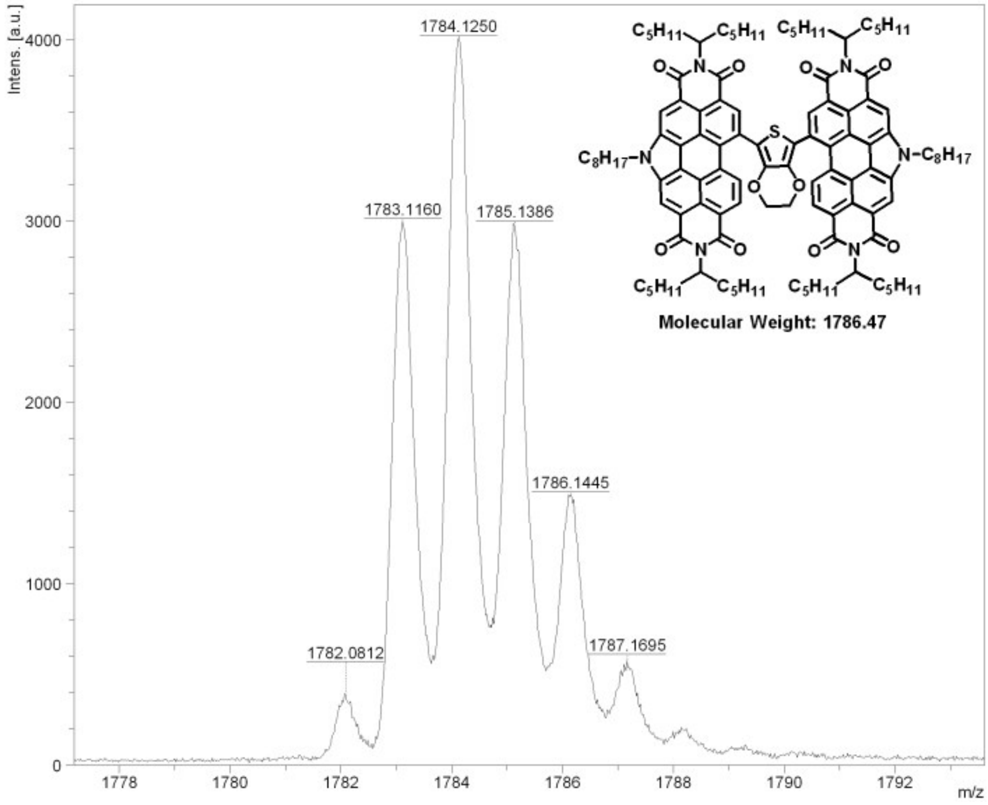

Figure S23. MALDI-TOF MS Spectrum of **EDOT-PNR.**

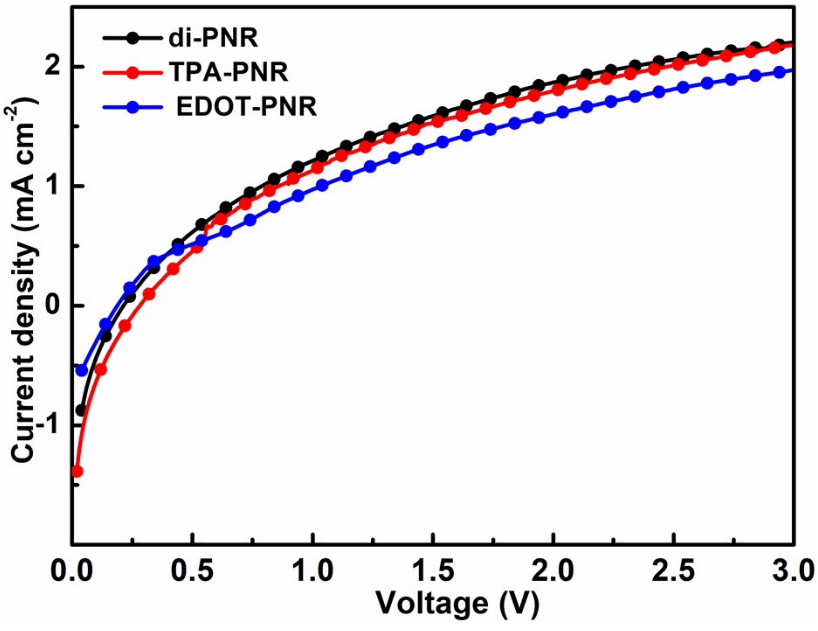

Figure S24. *J*–*V* plots of the electron mobilities of the pristine **di-PNR**, **TPA-PNR** and **EDOT-PNR.**

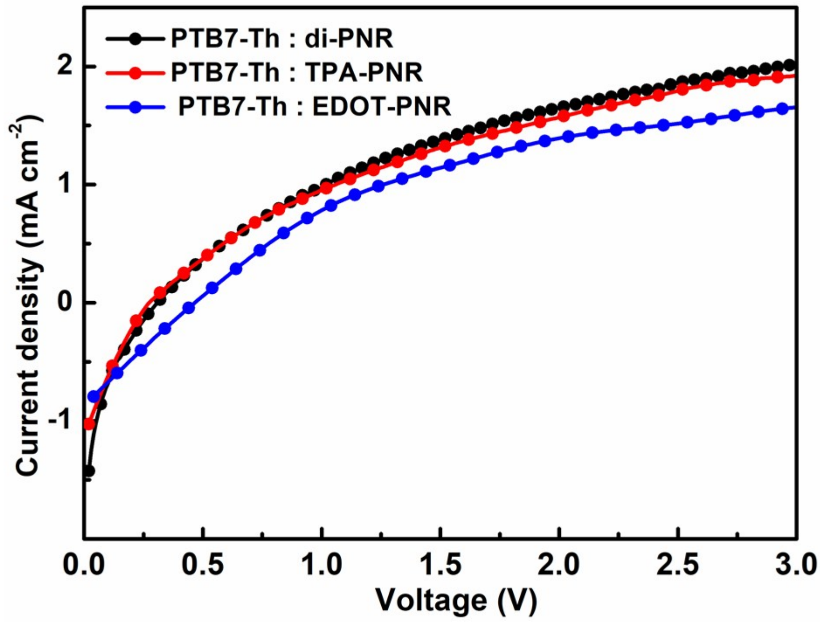

Figure S25. *J–V* plots of the electron-only devices based on **di-PNR**/PTB7-Th (1:1, w/w), **TPA-PNR**/PTB7-Th (1:1, w/w) and **EDOT-PNR**/PTB7-Th (1:1, w/w) under 0.25 v/v % DIO as the solvent additive.

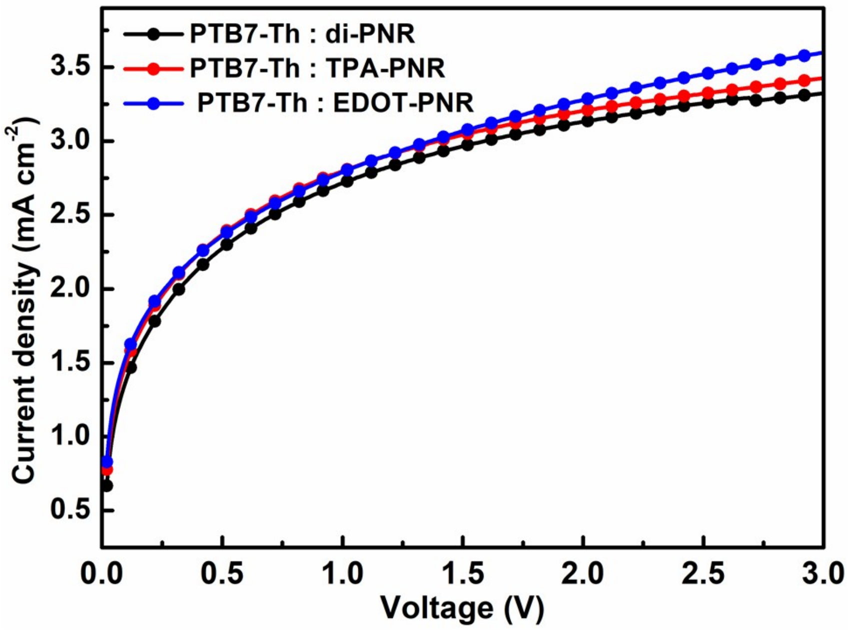

Figure S26 *J–V* plots of the hole-only devices based on **di-PNR**/PTB7-Th (1:1, w/w), **TPA-PNR**/PTB7-Th (1:1, w/w) and **EDOT-PNR**/PTB7-Th (1:1, w/w) under 0.25 v/v % DIO as the solvent additive.

References

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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.