

**Electronic Supplementary Information**  
*for*

**A Polymer Acceptor Containing B←N Unit for 14% Efficiency All Polymer Solar  
Cells**

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Wang*

**Contents**

- 1. Experimental details**
- 2. OSCs device and SCLC device fabrications and measurements**
- 3. Synthesis and characterizations**
- 4. Thermal properties**
- 5. Absorption and emission properties**
- 6. Molecular packing**
- 7. Morphology analysis**
- 8. Charge carrier mobilities**
- 9. Femtosecond-resolved absorption measurement**
- 10. <sup>1</sup>H NMR spectra**
- 11. Molecular weights and molecular weight distribution**
- 12. Reference**

## 1. Experimental details

$^1\text{H}$  NMR spectra of polymers were measured with a Bruker AV-400 in  $\text{C}_2\text{D}_2\text{Cl}_4$  at  $110\text{ }^\circ\text{C}$ . The molecular weight of the polymer was determined by gel permeation chromatography (GPC) on a PL-GPC 220-type at the room temperature. tetrahydrofuran (THF) was used as the eluent and monodisperse polystyrene was used as the standard. UV-vis absorption spectra and fluorescence spectra were measured with a Shimadzu UV-3600 spectrometer and a Hitachi F-4500 spectrometer, respectively, in spectral grade solvents. Thermal analyses were performed on a Perkin-Elmer 7 instrument under nitrogen flow at a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$ . Atomic force microscopy (AFM) was performed with a SPA300HV (Seiko Instruments, Inc., Japan) in tapping mode. The thickness of various layers was measured with a Dektak 6M Stylus Profile. Transmission electron microscopy (TEM) was performed on JEM-1400 (JEOLLtd., Japan) at an acceleration voltage of 120 kV. Two-dimensional grazing-incidence wide angle X-ray scattering (2D-GIWAXS) was measured at Shanghai Synchrotron Radiation Facility (SSRF) on beam line BL14B1 ( $\lambda = 0.124\text{ nm}$ ) with a MarCCD area detector at incidence angle of  $0.16^\circ$ . Samples were prepared on Si substrates using identical blend solutions as those used in devices. Femtosecond transient visible absorption spectroscopies were carried out by using an Astrella (Coherent Corporation, USA) Ti:sapphire regenerative amplifier, the spectra were measured using a Helios Fire TA spectrometer with an 8 ns delay stage. TA measurements were performed using low excitation fluences of  $1.9\text{ }\mu\text{J cm}^{-2}$  at 630 nm to avoid nonlinear photophysics. Cyclic voltammetry (CV) was performed on an CHI660a electrochemical workstation using  $\text{Bu}_4\text{NClO}_4$  (0.1 M) in acetonitrile as electrolyte solution and ferrocene as an internal reference at a scan rate of  $100\text{ mV s}^{-1}$ . The CV cell consisted of a glassy carbon electrode, a Pt wire counter electrode, and a standard calomel reference electrode. The polymer was casted on the working electrode for measurements. The redox potentials were calibrated with ferrocene as an internal standard. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the materials were estimated by the equations:  $E_{\text{HOMO/LUMO}} = -(4.80 + E_{\text{onset}}^{\text{ox}}/E_{\text{onset}}^{\text{red}})$ .

## 2. OSCs device and SCLC device fabrications and measurements

*All-Polymer Photovoltaic Devices:* Indium tin oxide (ITO) glass substrates were cleaned by sequential ultrasonication in detergent, deionized water, acetone, and isopropyl alcohol, followed by dried at 120 °C for 30 min and treated with UV-ozone for 25 min. Then PEDOT:PSS (Baytron PVP Al 4083) was spin-coated on the ITO glass substrates at 5000 rpm for 40 s to give a thickness of 40 nm, followed by baking at 120 °C for 30 min. The substrates were transferred to a nitrogen-filled glove box. The PM6:acceptor blends (1:1.3 weight ratio) were dissolved in chloroform (the total concentration of blend solutions was 16 mg mL<sup>-1</sup> for all blends, where 1.8% vol 1-chloronaaphthalene was added as additive). The blend solution was spin-cast at 4000 rpm for 60 s. The active layers of PM6:PBN25 and PM6:PBN25-CC blends were annealed at 110 °C for 10 min. PDI functionalized with amino N-oxide (PDINO) in methanol (the concentration of solution was 1.0 mg mL<sup>-1</sup>) was spin-cast at 3000 rpm for 30 s on active layer. Finally, the device was transferred to a vacuum chamber, Al (100 nm) was deposited by thermal evaporation at the pressure of about  $2 \times 10^{-4}$  Pa. An aperture with an area of 2 mm<sup>2</sup> was used to accurately measure the device performance. The current density-voltage (*J-V*) curves of the PSC devices were measured using a computer-controlled Keithley 2400 source meter under 100 mW cm<sup>-2</sup> AM 1.5G simulated solar light illumination provided by a XES-40S2-CE Class Solar Simulator (Japan, SAN-EI Electric Co., Ltd.). The EQE spectrum was measured using a Solar Cell Spectral Response Measurement System QE-R3011 (Enlitech Co., Ltd.). The light intensity at each wavelength was calibrated using a calibrated monosilicon diode.

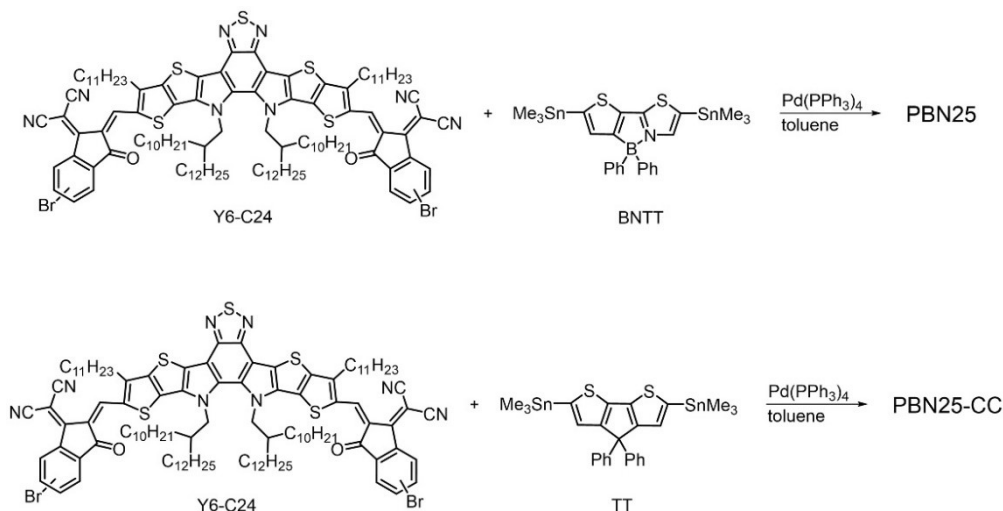
*Hole-Only and Electron-Only Devices:* The hole mobilities of the neat films were measured using the space-charge-limited current (SCLC) method. The electron-only device structure is ITO/PEIE/Active layer/Ca/Al and the hole-only device structure is ITO/PEDOT:PSS/Active layer/MoO<sub>3</sub>/Al. The current-voltage curves in the range of 0-10 V were recorded using a computer-controlled Keithley 2400 source meter, and the results were fitted to a space-charge limited function:  $J = \frac{9}{8} \epsilon_r \epsilon_0 \mu \frac{V^2}{L^3} \exp\left(0.89\beta \frac{\sqrt{V}}{\sqrt{L}}\right)$

Where *J* is the current density,  $\epsilon_0$  is permittivity of free space,  $\epsilon_r$  is the relative

permittivity (assumed to be 3),  $\mu$  is the zero-field mobility,  $V$  is the potential across the device ( $V = V_{\text{applied}} - V_{\text{bi}} - V_{\text{series}}$ ),  $L$  is the thickness of active layer, and  $\beta$  is the field-activation factor. The series and contact resistance of the device (10-15  $\Omega$ ) were measured using blank device of ITO/PEIE/Ca/Al or ITO/PEDOT:PSS/MoO<sub>3</sub>/Al.

### 3. Syntheses and characterizations

Synthetic route of the two polymers PBN25 and PBN25-CC are shown in Scheme S1. All reactions were performed under argon atmosphere. Commercially available solvents and reagents were used without further purification unless otherwise mentioned. Toluene, *n*-hexane, THF and CHCl<sub>3</sub> were dried using sodium or calcium hydroxide and distilled before used. The three monomers Y6-C24, BNTT and TT were synthesized according to the previous reports.<sup>1-3</sup>



**Scheme S1.** Synthetic route of the two polymers PBN25 and PBN25-CC.

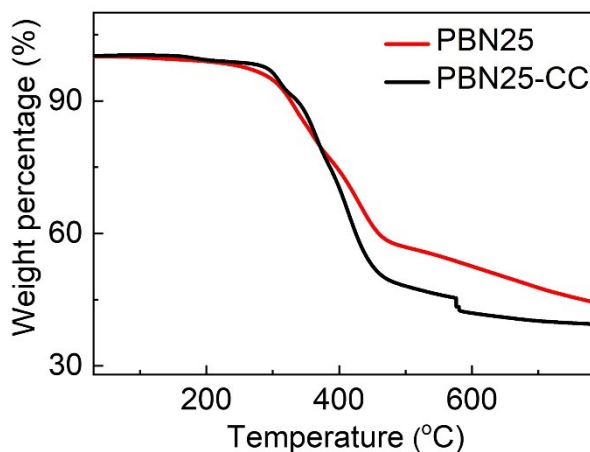
**Polymer PBN25:** Y6-C24 (198.2 mg, 0.098 mmol), BNTT (49.6 mg, 0.076 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (2.1 mg, 0.0018 mmol) were placed in a two-necked flask under argon and then dried toluene (14.0 mL) was added. The mixture was stirred at 110 °C for 1 h. After cooled, the reaction mixture was poured to methanol and the precipitate was collected. The obtained dark solid was purified by sequential Soxhlet extraction in acetone, hexane and CHCl<sub>3</sub>. The CHCl<sub>3</sub> fraction was concentrated and poured to methanol. Finally, the precipitate was collected and dried in vacuum overnight. Yield: 151.0 mg (91%). <sup>1</sup>H NMR (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>)  $\delta$  9.34-9.18 (m, 1.7H), 9.13-8.92 (m, 1H), 8.88-8.62 (m, 0.3H), 8.25-7.85 (m, 3H), 7.73-7.60 (m, 1H), 7.53-7.32 (m, 6H),

4.89 (d,  $J = 1.0$  Hz, 4H), 3.47-3.27 (m, 4H), 2.21 (dd,  $J = 13.6, 10.0$  Hz, 2H), 2.06 (dd,  $J = 6.2, 5.3$  Hz, 4H), 1.67 (dd,  $J = 13.2, 6.8$  Hz, 4H), 1.46-0.86 (m, 126H).

**Polymer PBN25-CC:** Y6-C24 (86.5 mg, 0.043 mmol), TT (21.6 mg, 0.033 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (1.0 mg, 0.0008 mmol) were placed in a two-necked flask under argon and then dried toluene (6.0 mL) was added. The mixture was stirred at 110 °C for 1 h. After cooled, the reaction mixture was poured to methanol and the precipitate was collected. The obtained dark solid was purified by sequential Soxhlet extraction in acetone, hexane and CHCl<sub>3</sub>. The CHCl<sub>3</sub> fraction was concentrated and poured to methanol. Finally, the precipitate was collected and dried in vacuum overnight. Yield: 51.0 mg (73%). <sup>1</sup>H NMR (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>) δ 9.36-8.61 (m, 2H), 8.38-7.81 (m, 3H), 7.57-7.42 (m, 2H), 7.44-7.18 (m, 4H), 4.90 (d,  $J = 4.1$  Hz, 4H), 3.43-3.32 (m, 4H), 2.21 (t,  $J = 11.3$  Hz, 2H), 2.07 (dd,  $J = 14.4, 7.8$  Hz, 4H), 1.67 (dd,  $J = 17.2, 11.3$  Hz, 4H), 1.47-1.05 (m, 112H), 1.05-0.88 (m, 16H).

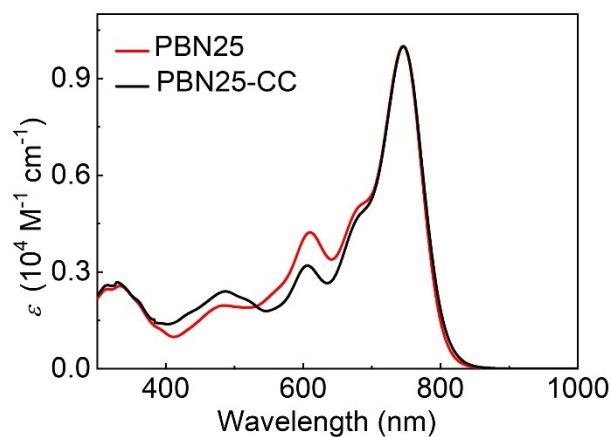
#### 4. Thermal properties

The thermal properties of the two polymers were investigated by thermogravimetric analysis (TGA) in N<sub>2</sub> flow. PBN25 and PBN25-CC show good thermal stabilities with thermal decomposition temperatures ( $T_d$ ) of 298 °C and 307 °C, respectively.

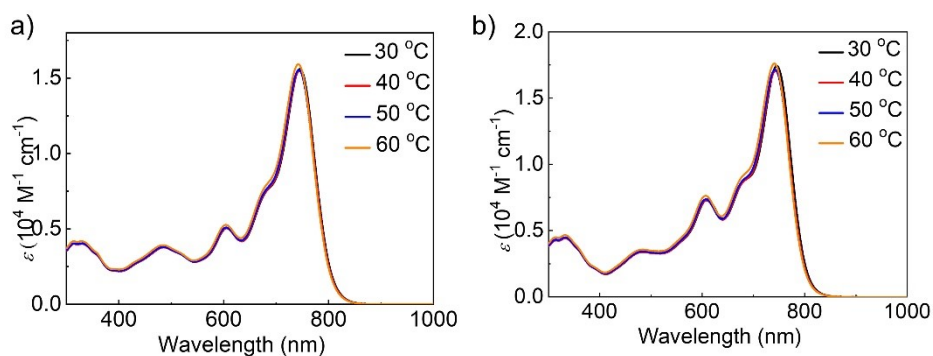


**Figure. S1** TGA plots of PBN25 and PBN25-CC under N<sub>2</sub> atmosphere

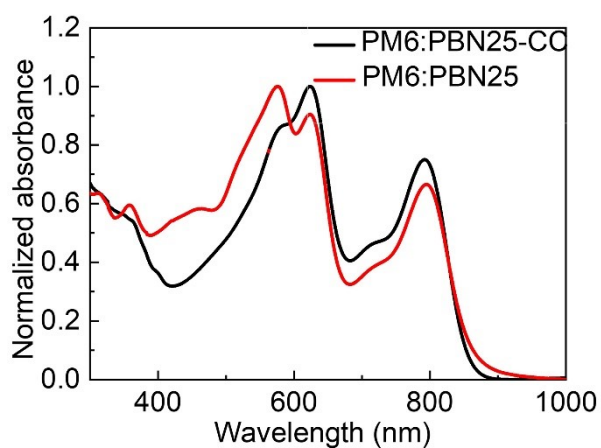
## 5. Absorption and emission properties



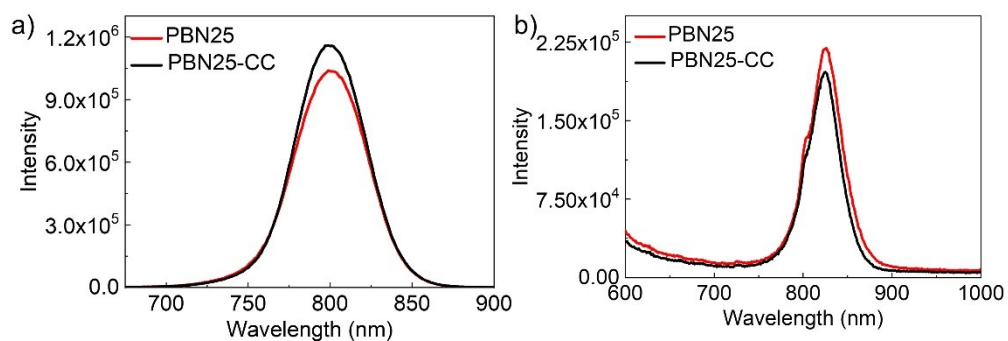
**Figure S2.** UV/Vis absorption spectra of PBN25 and PBN25-CC in chloroform solution.



**Figure S3.** Temperature-dependent UV-vis absorption spectra of PBN25 (a) and PBN25-CC (b) in chloroform solution.

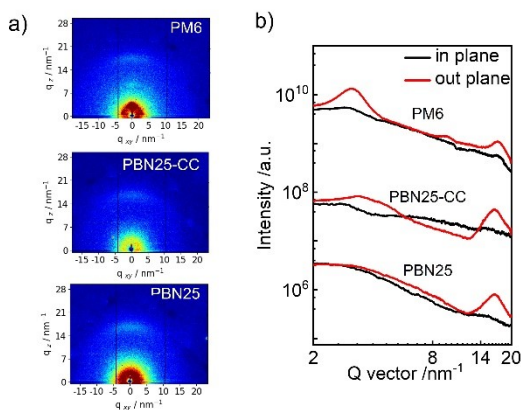


**Figure S4.** The normalized absorption spectra in film of the blends of PM6 and PBN25 or PBN25-CC.

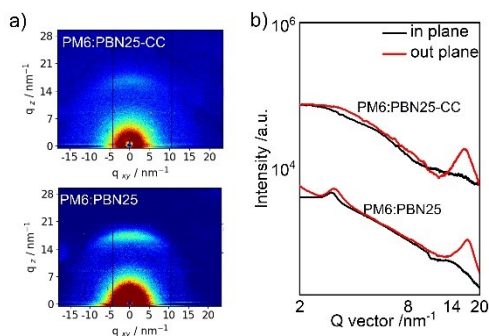


**Figure S5.** Fluorescence spectra of PBN25 and PBN25-CC in solution (a) and in thin film (b).

## 6. Molecular packing



**Figure. S6** a) 2D-GIWAXS patterns and b) the corresponding in-plane and out-of-plane linecuts of the neat film of PM6, PBN25 and PBN25-CC

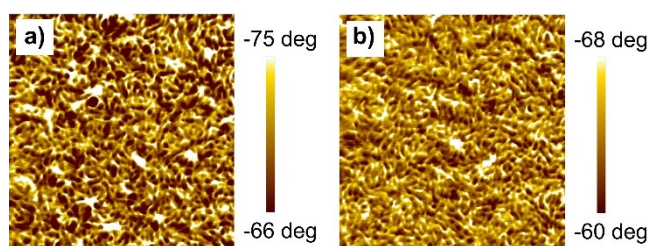


**Figure. S7** a) 2D-GIWAXS patterns and b) the corresponding in-plane and out-of-plane linecuts of the PM6:PBN25 and PM6:PBN25-CC active layers.

**Table S1.** Characteristics of the 2D-GIWAXS patterns.

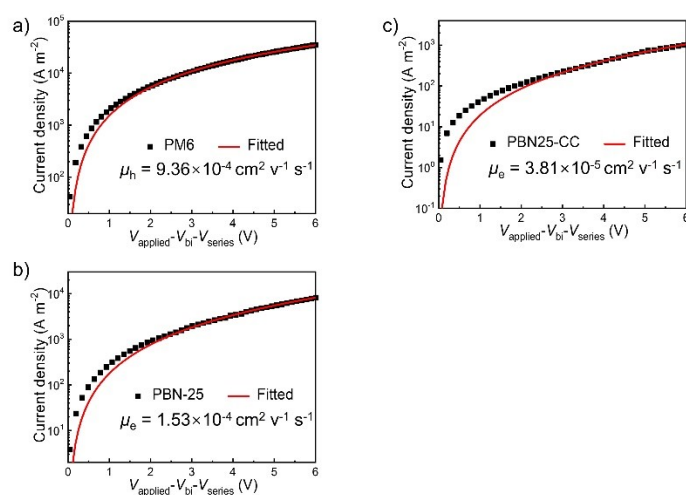
Films	Directions	100				010			
		Location [Å <sup>-1</sup> ]	d-spacing [Å]	FWHM [Å <sup>-1</sup> ]	CL [Å]	Location [Å <sup>-1</sup> ]	d-spacing [Å]	FWHM [Å <sup>-1</sup> ]	CL [Å]
PM6	Out-of- plane	0.31	20.27	0.092	62	1.71	3.67	0.193	30
	In-plane	0.32	19.45	0.162	35	1.72	3.65	0.157	36
PBN25-CC	Out-of- plane					1.65	3.81	0.496	11
	In-plane								
PBN25	Out-of- plane					1.65	3.81	0.322	18
	In-plane								
PM6:PBN25-CC	Out-of- plane					1.67	3.76	0.460	12
	In-plane								
PM6:PBN25	Out-of- plane	0.31	20.20	0.051	111	1.71	3.67	0.279	21
	In-plane	0.30	20.60	0.068	83				

## 7. Morphology analysis



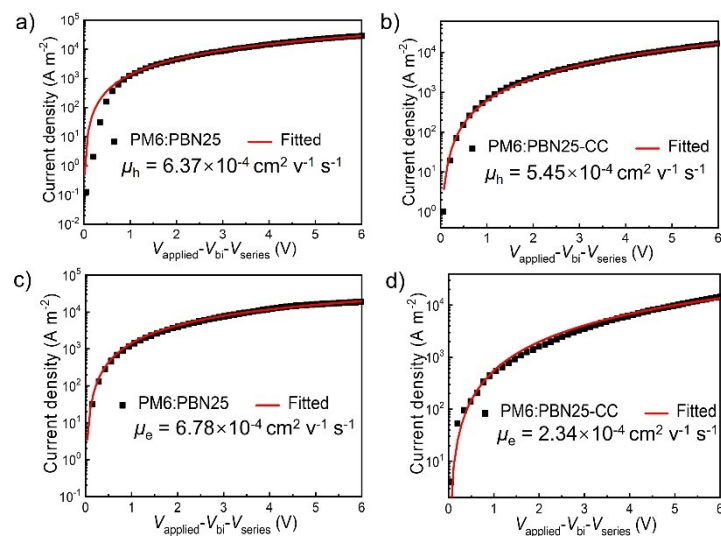
**Figure S8.** AFM phase images of the PM6:PBN25 (a) and PM6:PBN25-CC (b) blend films.

## 8. Charge carrier mobilities



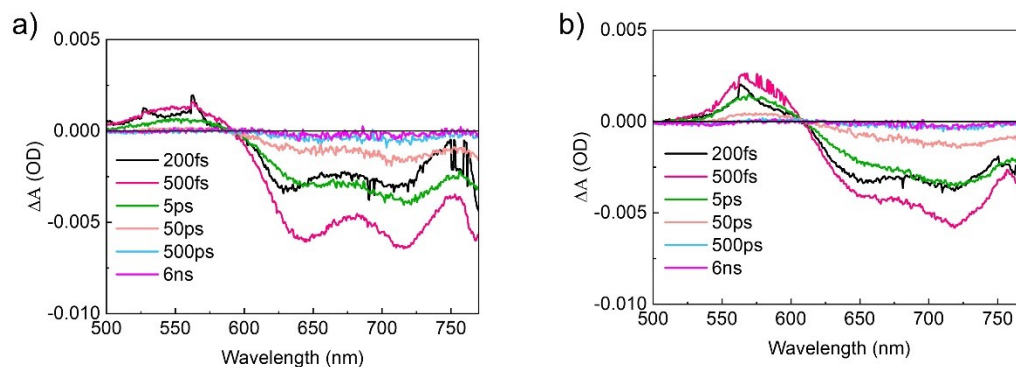
**Figure S9.**  $J$ - $V$  curves and SCLC fittings of the hole-only device of PM6 (a) and of the electron-only devices of PBN25 (b) and PBN25-CC (c).



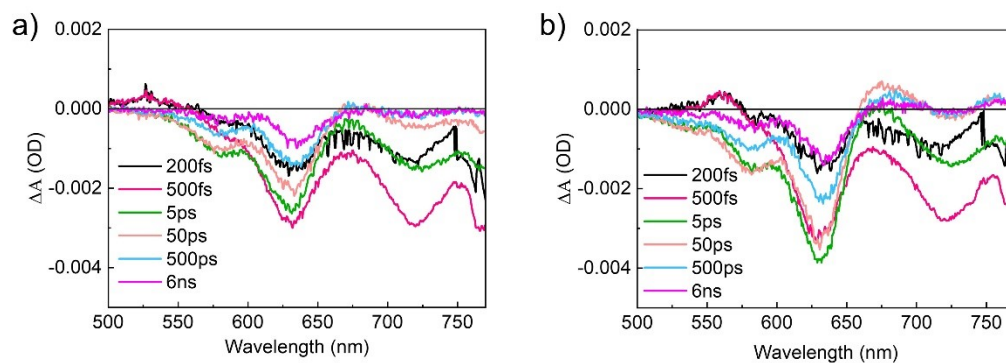


**Figure S10.**  $J$ - $V$  curves and SCLC fittings of the hole-only device of (a) PM6: PBN25 and (b) PM6: PBN25-CC blend films and of electron-only devices of (c) PM6: PBN25 and (d) PM6: PBN25-CC blend films.

## 9. Femtosecond-resolved absorption measurement



**Figure S11.** The femtosecond time-resolved (excited by 800 nm) TA spectra of a) PBN25-CC and b) PBN25 neat films.



**Figure S12.** The femtosecond time-resolved (excited by 800 nm) TA spectra of a)

PM6:PBN25-CC and b) PM6:PBN25 blend films.

### 10. $^1\text{H}$ NMR spectra

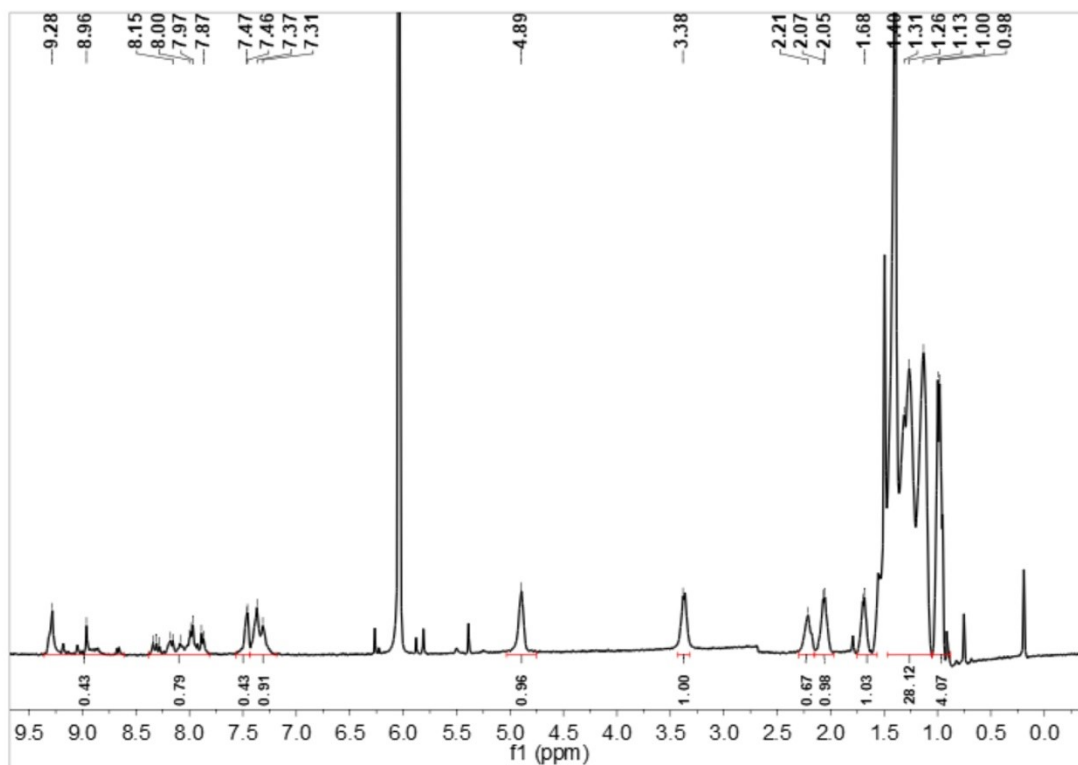


Figure S13.  $^1\text{H}$  NMR spectra of PBN25-CC.

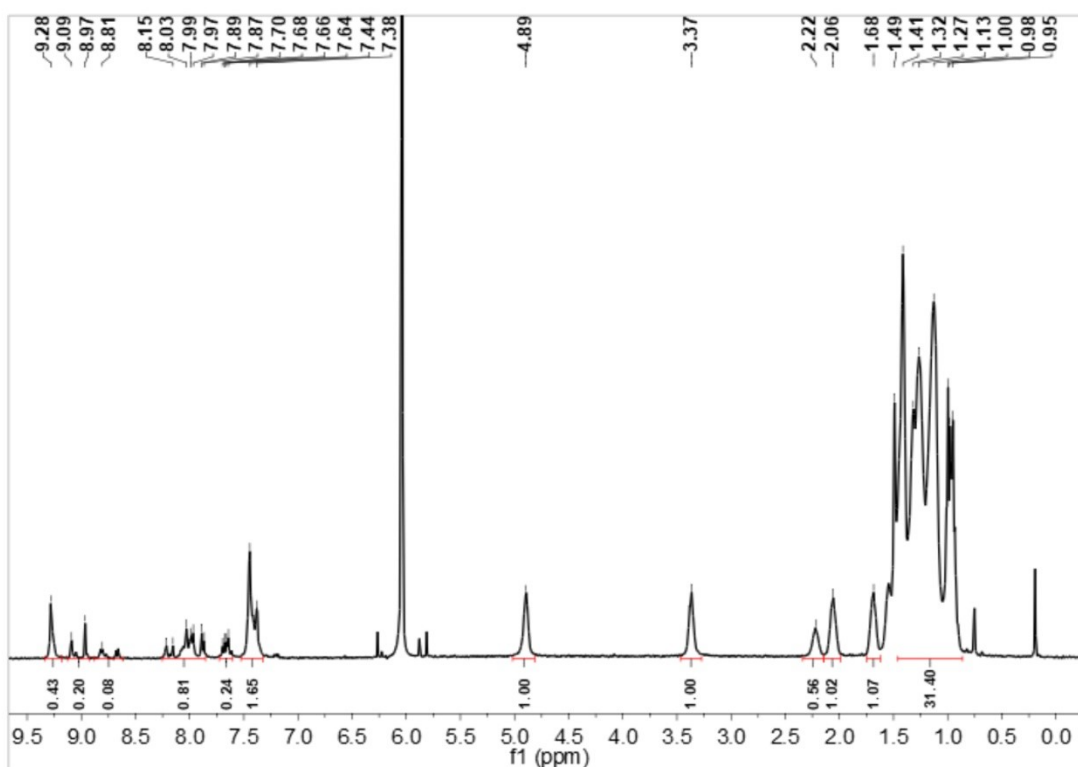
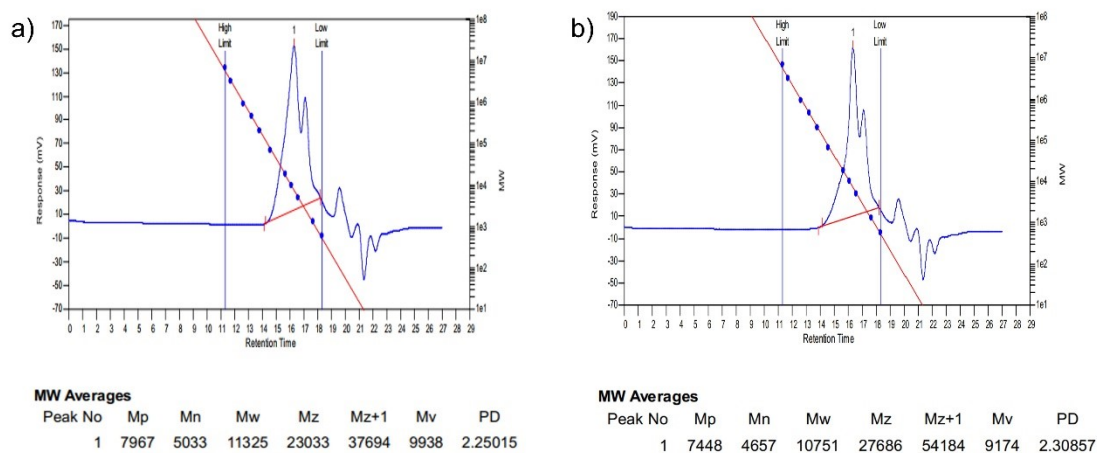


Figure S14.  $^1\text{H}$  NMR spectra of PBN25.

## 11. Molecular weights and molecular weight distribution



**Figure S15.** Gel permeation chromatography (GPC) elution curves of PBN25 a) and PBN25-CC b) with tetrahydrofuran as the eluent at room temperature.

## 12. Reference

- 1 T. Jia, J. Zhang, W. Zhong, Y. Liang, K. Zhang, S. Dong, L. Ying, F. Liu, X. Wang, F. Huang and Y. Cao, *Nano Energy*, **2020**, *72*, 104718.
- 2 R. Zhao, B. Lin, J. Feng, C. Dou, Z. Ding, W. Ma, J. Liu and L. Wang, *Macromolecules*, **2019**, *52*, 7081-7088.
- 3 L. Zhao, H. Sun, X. Liu, C. Liu, H. Shan, J. Xia, Z. Xu, F. Chen, Z.-K. Chen and W. Huang, *Chem. Asian J.*, **2017**, *12*, 2052-2056.