

## Electronic Supplementary Information

for

### **A Polymer Acceptor Containing B←N Unit with Strong Fluorescence for Organic Photovoltaics.**

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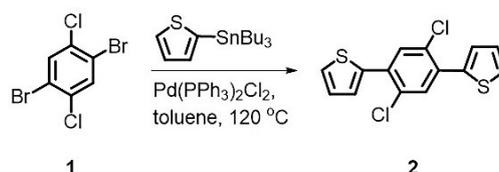
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## 1. Experimental details

**General.**  $^1\text{H}$ NMR spectra were measured with a Bruker AV-500 (500 MHz for  $^1\text{H}$ ) spectrometer in  $\text{CDCl}_3$  at 25 °C and 40 °C. The molecular weight of the polymer was determined by gel permeation chromatography (GPC) on a PL-GPC 220-type at the temperature of 150 °C. 1,2,4-Trichlorobenzene (TCB) was used as the eluent and monodisperse polystyrene was used as the standard. Thermal gravimetric analysis (TGA) was performed under an  $\text{N}_2$  flow at a heating rate of 10 °C/min with a Perkin-Elmer-TGA 7 system. The temperature of degradation ( $T_d$ ) was corresponding to a 5% weight loss. The grazing incident X-ray diffraction (GI-XRD) measurement was performed using a Bruker D8 Discover reflector. UV-vis absorption spectra were measured with a Shimadzu UV-3600 spectrometer. The absolute fluorescence quantum efficiency ( $\phi_F$ ) of the polymer in thin film and in solution was measured with a Hamamatsu Photonics C9920-2 instrument with an integrating sphere. Cyclic voltammetry (CV) was performed on an CHI660a electrochemical workstation using tetrabutylammonium hexafluorophosphate (0.1 M) in acetonitrile as electrolyte solution and ferrocene as an internal reference at a scan rate of 50  $\text{mV s}^{-1}$ . The CV cell consisted of a glassy carbon electrode, a Pt wire counter electrode, and a standard calomel reference electrode. The polymer was spin-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 the lowest unoccupied molecular orbital (LUMO) energy levels were estimated by the equations:  $E_{\text{HOMO/LUMO}} = -(4.80 + E_{\text{onset}}^{\text{ox}}/E_{\text{onset}}^{\text{red}})$  eV. The UV-vis absorption spectra of PBN-16 solution and thin film were measured with a Perkin-Elmer Lambda 35 UV-vis spectrometer. The surface morphologies of CD3:PBN-16 blend films were characterized using atomic force microscopy on a SPA 300HV with a SPI 3800N controller (Seiko Instruments, Inc., Japan) in tapping mode. A silicon micro cantilever (spring constant 2  $\text{N m}^{-1}$  and resonance frequency ca. 300 kHz, Olympus Co., Japan) with an etched conical tip was used for the scan. The transmission electron microscopy (TEM) measurement was performed on a JEOL JEM-1400 transmission electron microscope operating at 120 kV.

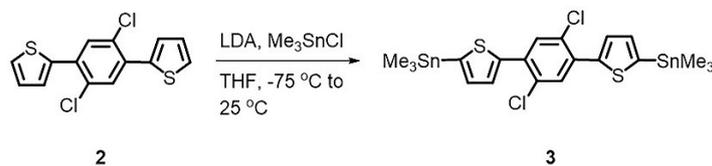
**Materials and reagents.** Commercially available solvents and reagents were used without further purification unless otherwise mentioned. Dry toluene, chloroform, dichloromethane, tetrahydrofuran, N,N-Dimethylformamide and triethylamine were distilled via standard methods. 1,4-dibromo-2,5-dichlorobenzene (**1**) and 5,5'-dibromo-N3,N3'-di-2-dodecylhexadecyl-[2,2'-bipyridine]-3,3'-diamine (**BNBP**) were prepared according to the literature methods.<sup>1</sup>

## 2. Syntheses and characterizations



### 2,2'-(2,5-dichloro-1,4-phenylene)dithiophene (**2**)

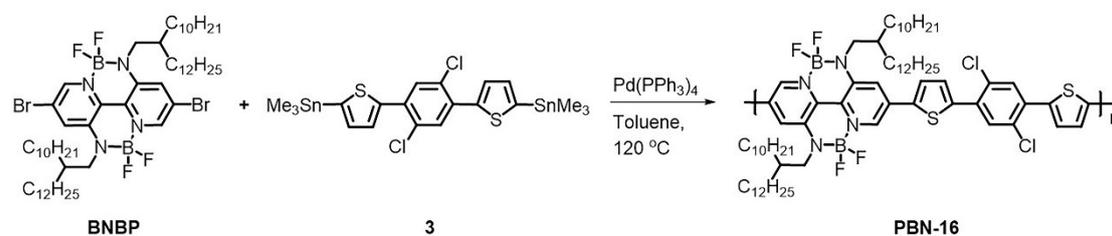
1,4-dibromo-2,5-dichlorobenzene (**1**) (2.28 g, 7.5 mmol), tributyl(thien-2-yl)stannane (8.39 g, 22.5 mmol) and bis(triphenylphosphine)palladium(II) dichloride (0.53 g, 0.75 mmol) were added to anhydrous toluene (40 ml) under argon atmosphere. The reaction mixture was stirred at 120 °C for 48 h. The solution was cooled to room temperature, poured to saturated KF solution and then extracted with dichloromethane (50 ml) for three times. The organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. The residual was purified by silica gel column chromatography (eluent: petroleum ether / chloroform = 10:1) to give **2** as a white solid (1.60 g, yielded 69%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C) δ 7.67 (s, 1H), 7.49 – 7.39 (m, 2H), 7.14 (s, 1H).



### ((2,5-dichloro-1,4-phenylene)bis(thiophene-5,2-diyl))bis(trimethylstannane) (**3**)

Under argon atmosphere, to a solution of 2,2'-(2,5-dichloro-1,4-phenylene)dithiophene (**2**) (0.78 g, 2.5 mmol) in anhydrous tetrahydrofuran (100 ml) at -78 °C was added dropwise lithium diisopropylamide (2 M solution in

tetrahydrofuran, 3.1 mL, 6.25 mmol) . The mixture was stirred at -78 °C for 3 hours and then trimethylstannyl chloride (1.345 g, 6.25 mmol) was added. After warmed to room temperature and stirred for extra 10 hours, the reaction mixture was quenched by the addition of water. The reaction mixture was extracted with diethyl ether, washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvents were evaporated and the crude product was recrystallized in ethanol to afford the product as a pale green needle-shaped crystal (0.98 mg, yielded 61%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C): δ 7.67 (s, 1H), 7.55 (d, J = 3.4 Hz, 1H), 7.21 (d, J = 3.4 Hz, 1H), 0.41 (s, 1H). Calcd for C<sub>20</sub>H<sub>24</sub>Cl<sub>2</sub>S<sub>2</sub>Sn<sub>2</sub>: C, 37.72; H, 3.80; S, 10.07. Found: C, 37.72; H, 3.80; S, 10.07.

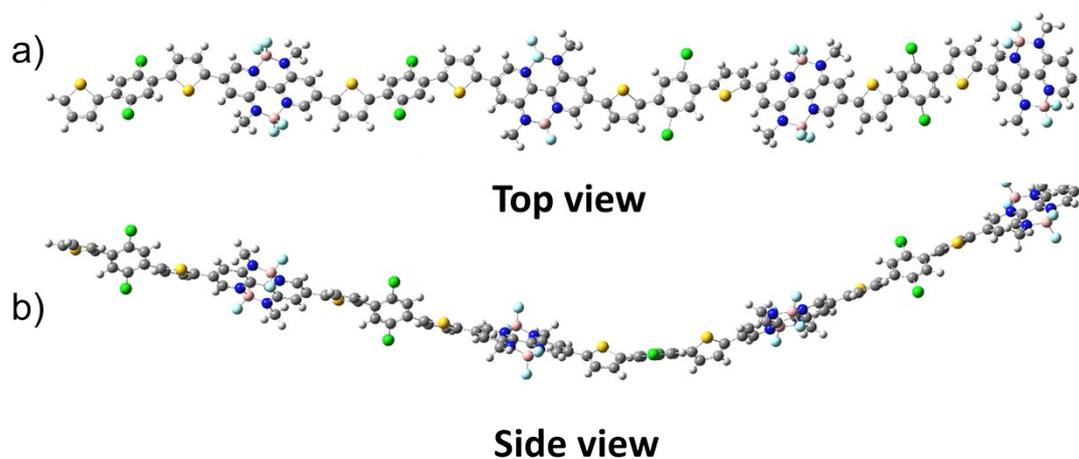


### Synthesis of polymer PBN-16

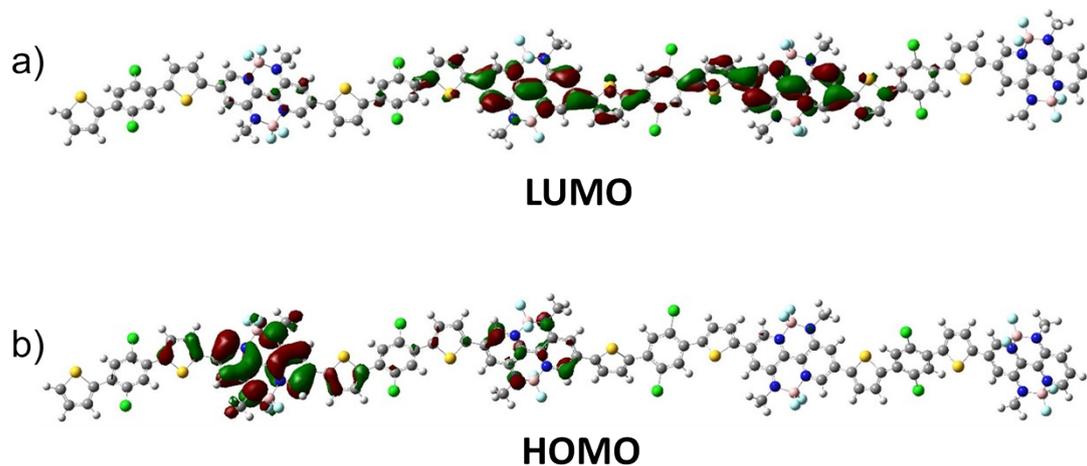
In a dry oxygen free two necked flask, the monomer BNBP (112.7 mg, 0.1 mmol), ((2,5-dichloro-1,4-phenylene)bis(thiophene-5,2-diyl))bis(trimethylstannane) (**3**) (64.69 mg, 0.1mmol) and tetrakis(triphenylphosphine) palladium(0) (1.2 mg, 0.001 mmol) was dissolved in anhydrous toluene (10 ml). The solution was stirred at 120 °C for 6 hours. After cooling to room temperature, the mixture was dispersed in methanol and the precipitate was collected. The polymer was purified by the Soxhlet extraction with acetone, hexane and chloroform. The polymer PBN-16 in the chloroform solution was collected and dried in a vacuum overnight. Yield: 125 mg (97%). GPC (TCB, polystyrene standard, 150 °C):  $M_n = 42.7\text{kDa}$ , PDI = 2.18. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 40 °C): δ 8.49 (s, 1H), 7.81 (s, 1H), 7.76 (s, 1H), 7.59 (s, 1H), 3.66 (s, 2H), 1.40 – 1.46 (br, 7H), 1.20 – 1.35(br, 34H), 0.88 (t, J = 6.5 Hz, 6H). Anal. Calcd for C<sub>72</sub>H<sub>108</sub>B<sub>2</sub>Cl<sub>2</sub>F<sub>4</sub>N<sub>4</sub>S<sub>2</sub>: C, 68.51; H, 8.62; N, 4.44; S, 5.08. Found: C, 68.26; H, 8.28; N, 4.06; S, 5.04.

### 3. DFT calculation results

All calculations were performed with the Gaussian 09 program. The geometry structure of PBN-16 was optimized by using DFT calculations (B3LYP/6-31G\*).

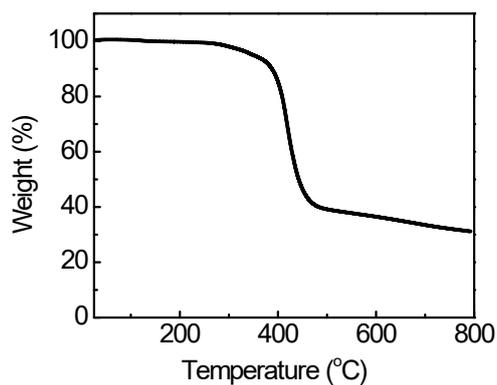


**Fig. S1** a) Top view and b) side view of the model compound (tetramer) of PBN-16.



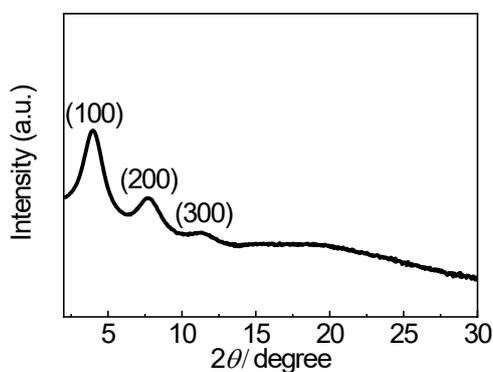
**Fig. S2** Kohn–Sham LUMO and HOMO of the model compound of PBN-16 based on calculations at the B3LYP/6-31G\* level.

#### 4. Thermalgravimetric Analysis



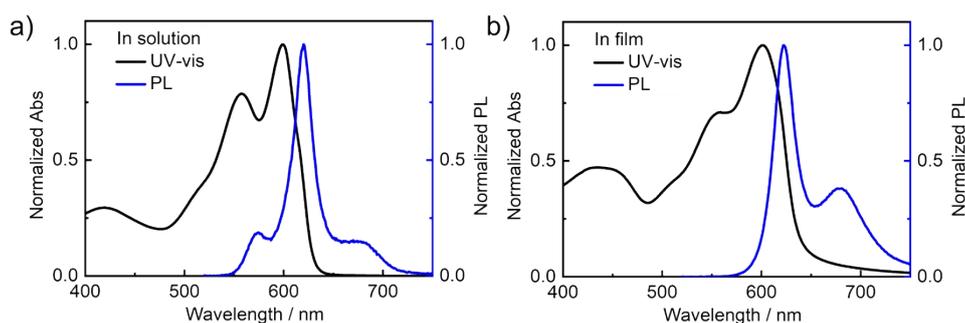
**Fig. S3** TGA plots of PBN-16 under N<sub>2</sub> atmosphere.

## 5. Molecular packing



**Fig. S4** The GI-XRD pattern of the PBN-16 thin film.

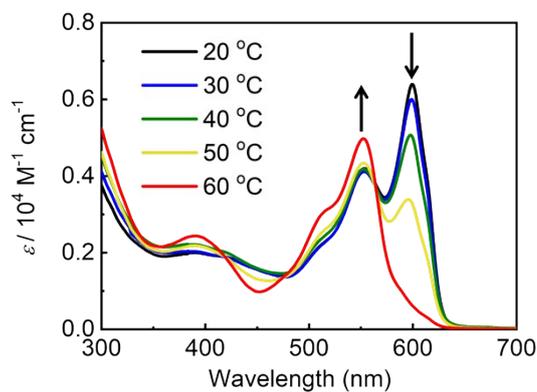
## 6. Stokes-shift



**Fig. S5** The UV/vis absorption (blackline) and fluorescence (blue line,  $\lambda_{\text{ex}}=365$  nm) spectra of PBN-16 in a) THF solution and b) thin film.

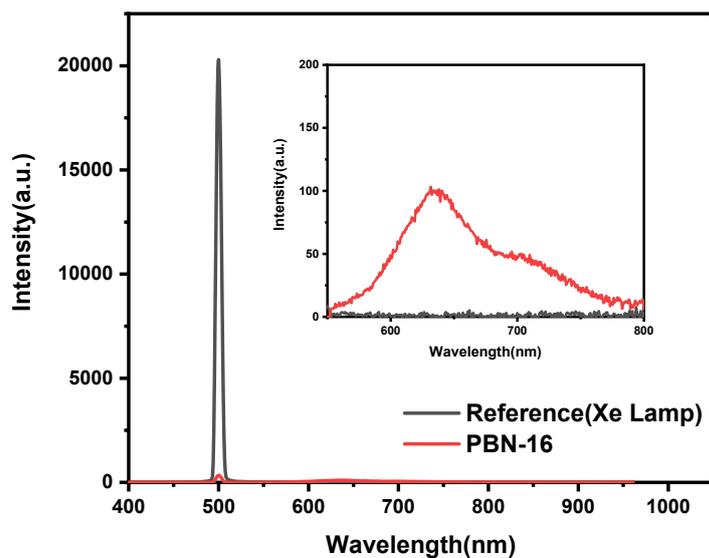
According to the maximum absorption wavelength and maximum fluorescence wavelength of PBN-16, the Stokes-shifts of PBN-16 are calculated to be 20 nm in solution and 21 nm in film.

## 7. Temperature-dependent UV-vis absorption spectra



**Fig. S6** Temperature-dependent UV-vis absorption spectra of PBN-16 in THF solution.

## 8. Fluorescence quantum efficiency in the thin film



**Fig. S7** Excitation light profiles and fluorescence spectrum obtained by 500 nm excitation of reference (Xe Lamp) and PBN-16. The inset is an expanded fluorescence spectrum of PBN-16.

**Table S1** Fluorescence quantum efficiency of PBN-16.

	Number of photons absorbed	Number of photons emitted	Fluorescence quantum efficiency
PBN-16	71762860	7987655	0.111

## 9. OSCs devices

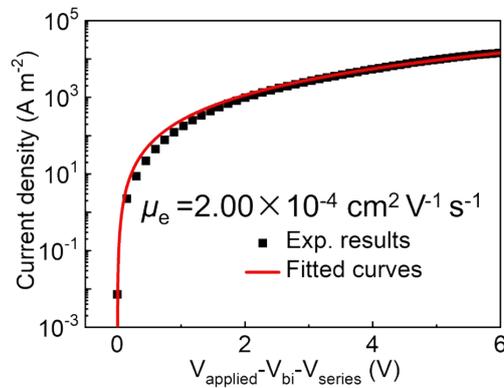
**Material:** The polymer donor CD3 were synthesized in our laboratory according previously reported methods.<sup>3</sup>

**Device fabrication:** ITO glass substrates were cleaned by sequential ultrasonication in detergent, deionized water, acetone, and isopropyl alcohol, followed by drying at 120 °C for 30 min and treating with UV-ozone for 30 min. ZnO precursor was prepared by dissolving 1 g zinc acetate dihydrate and 280  $\mu$ L ethanolamine in 10 ml 2-methoxyethanol under stirring for 12 h for the hydrolysis reaction, 5% wt triethanolamine are added before used. Then the ZnO was spin-coated on the ITO glass substrates at 3500 rpm for 60 s to give a thickness of 40 nm, and baked at 140 °C for 30 min. The ZnO substrates were transferred to a nitrogen-filled glove box. CD3 and PBN-16 with a weight ratio of 1.5:1 were dissolved together in tetrahydrofuran with a total concentration of 7.5 mg mL<sup>-1</sup>, and the solution was stirred at 55 °C for 3 h and then stirred at room temperature for 12 h to ensure the complete dissolution. The active layer solutions were spin-coated on the ZnO substrates at spin-rates of 1600 rpm. CD3:PBN-16 were annealed at 100 °C. At a pressure of  $1.5 \times 10^{-4}$  Pa, MoO<sub>3</sub> (0.5 nm) and Al (100 nm) were sequentially deposited on the top of the active layer to complete the devices. The active area of the devices was 8 mm<sup>2</sup>. A XES-40S2-CE class solar simulator (Japan, SAN-EI Electric Co., Ltd.) was used to provide the AM 1.5G simulated solar light illumination. The light intensity was calibrated to be 100 mW cm<sup>-2</sup> using a certified standard monocrystalline silicon (Si) solar cell (SRC-2020, Enli Technology Co., Ltd.). The lux levels of the LED lamp were measured using a high-precision fibre-optics spectrometer (Maya2000 Pro, Ocean Optics) and the intensity calibration was carried out following the previous reports.<sup>2</sup> The  $J-V$  plots of the device were measured in a glove box filled with nitrogen (oxygen and water contents are smaller than 0.1 ppm) on a Keithley 2400 source meter. A solar cell spectral response measurement system QE-R3011 (Enli Technology Co., Ltd.) was used to characterize the EQE spectrum under the short-circuit condition. The chopping frequency is 165 Hz.

**Hole- and electron-only devices fabrication and mobility measurements:** The hole and electron mobilities were measured by SCLC method. The hole-only device structure is ITO/PEDOT:PSS (40 nm)/active layer/MoO<sub>3</sub> (10 nm)/Al (100 nm) and the electron-only device structure is ITO/PEIE (10 nm)/active layer/Ca (20 nm) /Al (100 nm), respectively.  $J$ - $V$  plots in the range of 0–10 V were measured using a Keithley 2400 source meter, and the mobility was obtained by fitting the  $J$ - $V$  plot near quadratic region according to the modified Mott-Gurney equation:

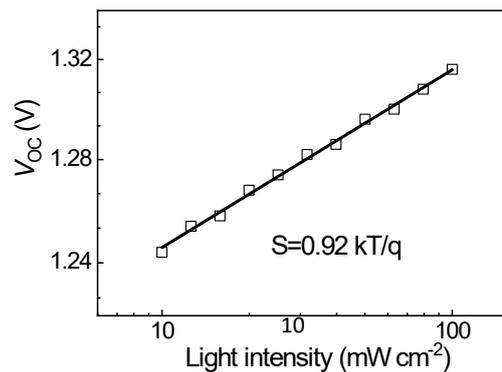
$$J = \frac{9}{8} \epsilon_r \epsilon_0 \mu \frac{V^2}{L^3} \exp\left(0.89\beta \frac{\sqrt{V}}{\sqrt{L}}\right) \quad (1)$$

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 (10–20  $\Omega$ ) were measured using blank device of ITO/PEDOT:PSS/MoO<sub>3</sub>/Al or ITO/PEIE/Ca/Al.



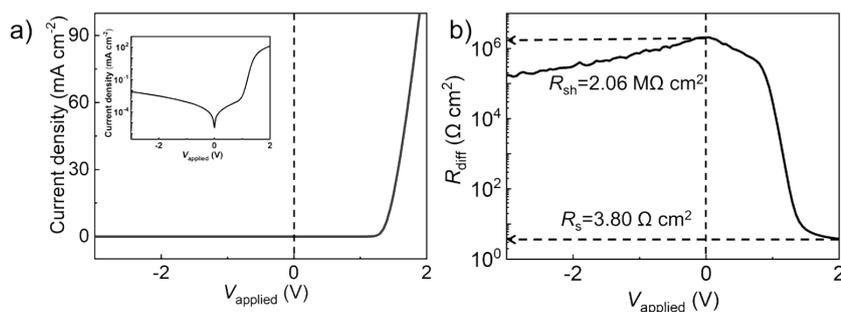
**Fig. S8** Space-charge-limited  $J$ - $V$  plots for the electron-only devices of PBN-16 film.

## 10. OSCs device performance



**Fig. S9** Light intensity dependence of  $V_{OC}$  (solid lines are fitted result) of the photovoltaic devices based on CD3:PBN-16 blend film.

The slope obtained from the fitting of  $V_{OC}$  versus light intensity is  $0.92 \text{ kT/q}$ . The slope is smaller than  $kT/q$ , which suggests that the surface trap recombination may exist in the photovoltaic device.<sup>4,5</sup>



**Fig. S10** a)  $J$ - $V$ -characteristics and b) differential resistance  $R_{diff}$  of the CD3:PBN-16 device in dark.

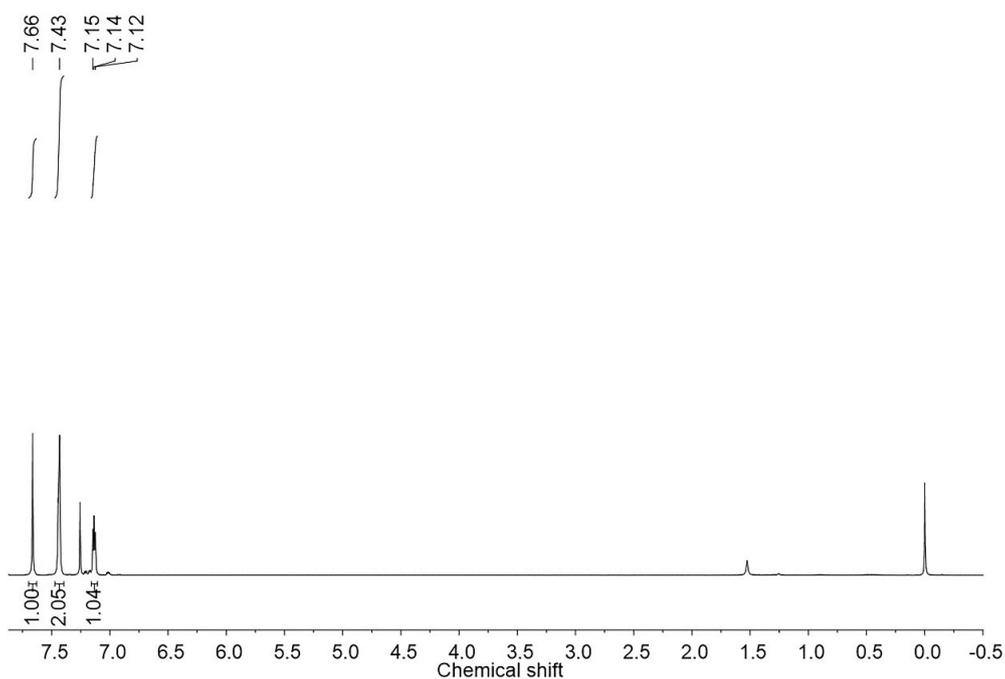
The values of series resistance  $R_{series}$  and shunt resistance  $R_{shunt}$  were calculated by the differential resistance  $R_{diff}$  against the applied bias. The  $R_{series}$  and  $R_{shunt}$  were estimated to be  $3.80 \text{ } \Omega \text{ cm}^2$  and  $2.06 \text{ M}\Omega \text{ cm}^2$ , respectively. The low  $R_{shunt}$  may contribute to the low  $J_{SC}$ .

## 11. OLEDs device fabrication and measurement

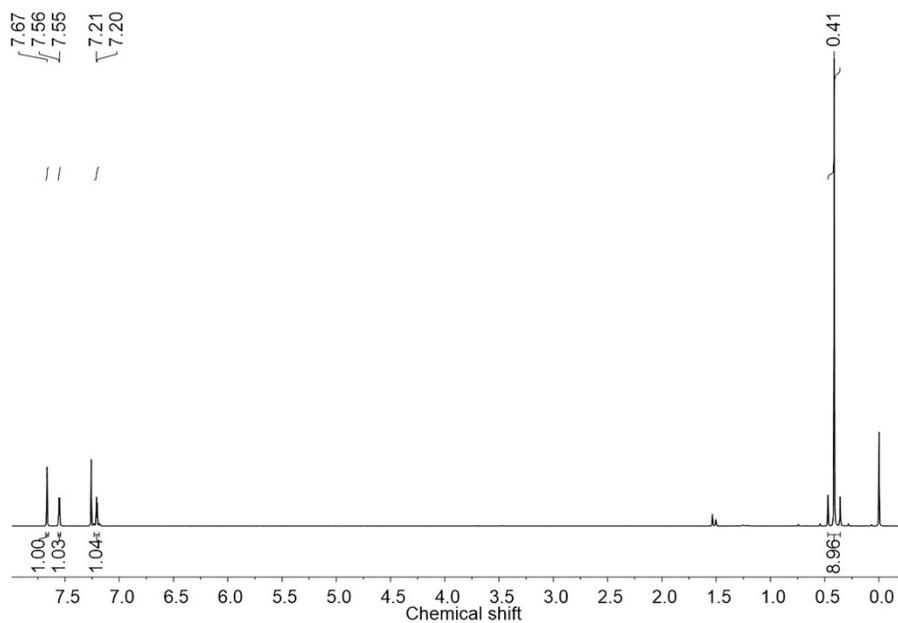
Solution-processed OLEDs were fabricated with device configuration of ITO/PEDOT:PSS&PFI(40 nm)/mCP-CN:PBN-16/SPPO13(50 nm)/LiF(1 nm)/Al(100 nm). The glass substrates coated with ITO ( $15 \text{ } \Omega$  per square) were washed with acetone, isopropanol and deionized water successively, and were dried under  $120 \text{ } ^\circ\text{C}$  for 45 min. Then the substrates were treated by ultraviolet ozone for 45 min. Subsequently PFI was blended into PEDOT:PSS with a volume ratio of 2:3, and utilized as the hole injection layer. The PFI was used to increase the work function of PEDOT:PSS to facilitate hole injection. The hole injection layer was spin-coated onto the substrate in air at a speed of 5000 rpm for 40 s, annealed at  $120 \text{ } ^\circ\text{C}$  for 1 h. After transferring the substrates into glovebox filled with  $\text{N}_2$ , the chlorobenzene solution of mCP-CN and PBN-16 with a concentration of  $10 \text{ mg mL}^{-1}$  was spin-coated on the hole injection layer at a speed of 1800 rpm for 60 s to form the emissive layer. After

transferred into a vacuum chamber, other layers including 50 nm SPP013, 1 nm LiF and 100 nm Al were successively vacuumed, under a low base pressure ( $< 4 \times 10^{-4}$  Pa). EL spectra were measured by a PR650 spectra colorimeter. The  $V$ - $J$ - $B$  characteristics of the OLEDs were measured under ambient atmosphere using Keithley 2400/2000 source meter equipped with a calibrated silicon photodiode. EQE of the devices were calculated based on the  $J$ - $B$  characteristics and the corresponding EL spectra assuming a Lambertian emission distribution.

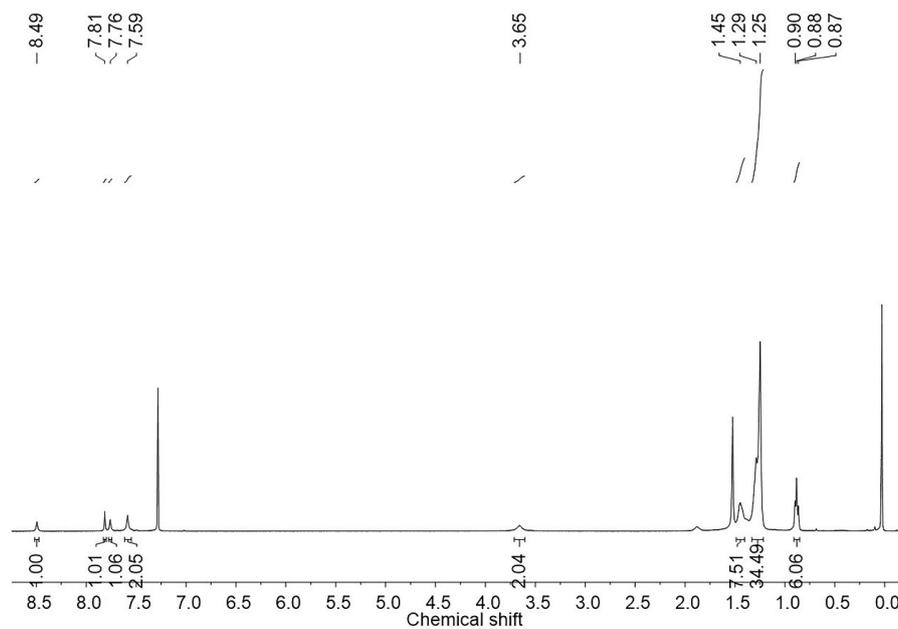
## 12. $^1\text{H}$ NMR



**Fig. S11**  $^1\text{H}$  NMR spectrum of **2** in  $\text{CDCl}_3$ .



**Fig. S12**  $^1\text{H}$  NMR spectrum of **3** in  $\text{CDCl}_3$ .



**Fig. S13**  $^1\text{H}$  NMR spectrum of **PBN-16** in  $\text{CDCl}_3$ .

### 13. Reference

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