

## Supporting Information

### Stable Radical based Conjugated Electrolytes as Thickness-Insensitive Cathode Interlayer for Organic Solar Cells with Thickness-Insensitive Fill Factors

Jie Fang,<sup>‡a</sup> Ziwei Zhang,<sup>‡a, c</sup> Zhou Zhang,<sup>‡b</sup> Yingzi Han,<sup>d</sup> Dongdong Xia,<sup>a</sup> Chaowei Zhao,<sup>\*a</sup> Yuefeng Zhang,<sup>a</sup> Lingling Wang,<sup>a</sup> Chengyi Xiao,<sup>b</sup> Shengyong You,<sup>a</sup> Yonggang Wu,<sup>c</sup> and Weiwei Li<sup>\*b</sup>

---

<sup>a</sup> Institute of Applied Chemistry, Jiangxi Academy of Sciences, Nanchang 330096, P. R. China. E-mail: zhaochaowei@jxas.ac.cn.

<sup>b</sup> Beijing Advanced Innovation Centre for Soft Matter Science and Engineering & State Key Laboratory of Organic–Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, P. R. China. E-mail: liweiwei@iccas.ac.cn.

<sup>c</sup> College of Chemistry and Environmental Science, Hebei University, Baoding 071002, P. R. China.

<sup>d</sup> State Key Laboratory for Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, P. R. China.

<sup>‡</sup> These authors contributed equally to this work.

## **Contents**

- 1. Materials and measurements**
- 2. Synthesis of materials**
- 3. Physical properties**
- 4. Photostability**
- 5. Fitting of SCLC**
- 6. GIWAXS**
- 7. AFM**
- 8. Device performance**
- 9. References**

## 1. Materials and measurements

Commercial chemicals (from J&K Chemical, Sunatech Inc, Energy Chemical, Solarmer Materials Inc, sigma-Aldrich and Innochem) were used as received. The active layer materials and cathode interface layer materials PNDIT-F3N-Br were purchased from Solarmer Materials Inc. Thin-layer chromatography (TLC) plates were visualized by exposure to ultraviolet light and/or staining with the solvent of phosphomolybdic acid. Flash chromatography was carried out using silica gel (200-300 mesh) manufactured by Qingdao Haiyang Chemical Group Co. (China)

$^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra of intermedia products and monomers were recorded at 400 MHz and 100 MHz on a Bruker AVANCE spectrometer. The spectra were recorded in  $\text{CDCl}_3$  as solvent at room temperature,  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts are reported in ppm relative to the residual solvent peak. The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale ( $\text{CDCl}_3$ :  $\delta_{\text{H}} = 7.26$  ppm,  $\delta_{\text{C}} = 77.00$  ppm; Data for  $^1\text{H}$  and  $^{13}\text{C}$  NMR are reported as follows: chemical shift ( $\delta$  ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets), integration, coupling constant (Hz) and assignment. High resolution mass spectra (HRMS) were recorded on a Bruker Apex II mass instrument with Electron Spray Ionization (ESI) resource.

UV-visible absorption spectrum of film and solution were recorded on a HITACHI U-2910 spectrometer with a slit width of 2.0 nm and a scan speed of 10 nm/s. Infrared (IR) spectrums were obtained in the 400-4000  $\text{cm}^{-1}$  range using a Nicolet 330 Spectrometer. Ultraviolet photo-electron spectroscopy (UPS) were performed on the Omicron Nanotechnology Model ESCA+S, consisting of a helium discharge lamp (He I line, 21.22 eV) as the UV excitation source and a hemispherical SPHERA energy analyzer. All samples were biased by -3 V to compensate for the instrument work function difference repelling the low-kinetic energy electrons, shifting the energy scale of experimental graphs by 3 eV. Electron paramagnetic resonance (EPR) spectrum was recorded using Bruker EMXplus with the magnetic field at 319.4 mT to 339.4 mT. The Molecular weight was determined with gel permeation chromatography (GPC) at 25 °C on a Agilent PL-GPC50 system using 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) as the eluent. Thermogravimetric analysis (TGA) and

differential scanning calorimeter (DSC) was conducted on Mettler Toledo TGA/DSC 3+ system. Cyclic voltammetry was performed under an inert atmosphere at a scan rate of  $0.1 \text{ V s}^{-1}$  and 1 M tetrabutylammonium hexafluorophosphate in acetonitrile as the electrolyte, a glassy-carbon working electrode coated with samples, a platinum-wire auxiliary electrode, and an Ag/AgCl as a reference electrode.

**Solar cells.** The ITO glass substrates were cleaned in detergent solution, deionized water, ethanol and isopropyl alcohol under ultra-sonication for 10 minutes each followed by drying in an oven at  $80 \text{ }^{\circ}\text{C}$ . Before spin coating, they were activated in UV- $\text{O}_3$  cleaner generator for 20 min. The PEDOT:PSS (Clevios P VP AI 4083) were spin-coated at 6000 rpm/min for 50 s to form the PEDOT:PSS film with thickness of about 20 nm and then annealed at  $150 \text{ }^{\circ}\text{C}$  for 30 min in air. Next, the ITO glasses were transferred into the  $\text{N}_2$ -filled glove box. The photoactive layer was deposited by spin-coating different solution containing the donor and acceptor. For the PM6:L8-BO (1:1.2, w/w, 15 mg/mL in chloroform with 12 mg/mL additive of 1,3-dibromo-5-chlorobenzene (DBCl)), which were spun at 3200 rpm for 50 s and then annealing at  $80 \text{ }^{\circ}\text{C}$  for 5 min. For the PM6:BTP-4Cl (1:1.2, w/w, 22 mg/mL in chlorobenzene with 0.4 vol% additive of DIO), which were spun at 3000 rpm for 50 s and then were annealed at  $80 \text{ }^{\circ}\text{C}$  for 10 min. For PM6:IT-4F (1:1.2, w/w, 22 mg/mL in chlorobenzene with 0.4 vol% additive of DIO), which were spun at 3000 rpm for 50 s and then annealing at  $100 \text{ }^{\circ}\text{C}$  for 10 min. Notably, all photoactive layer solution was magnetically stirred at room temperature overnight. After that, different cathode interface materials were spin-coating on the active layers using the 2,2,2-trifluoroethanol (TFE) solutions. The CIL thickness was tuned by elevating the solution concentration. Particularly, for PDIN-TEMPO and PDIN-Br, different concentrations, 1 mg/mL, 2 mg/mL, 3 mg/mL, 4 mg/mL, 6 mg/mL, 8 mg/mL and 12 mg/mL, correspond to CILs of 5 nm, 10 nm, 20 nm, 40 nm, 60 nm, 80 nm and 100 nm, respectively. For TEMPO-Br, concentrations of 1 mg/mL, 2 mg/mL and 4 mg/mL correspond to CILs of 5 nm, 10 nm and 20 nm, respectively. Finally, Ag (80 nm) was deposited by vacuum evaporation at ca.  $5 \times 10^{-5} \text{ Pa}$  as the cathode electrode. The inverted OSCs were fabricated by casting PDIN-TEMPO onto ITO with

annealing at 80 °C for 5 min, and then the photoactive layer. After thermal annealing at 100 °C for 10 min, MoO<sub>3</sub> (10 nm) and Ag (80 nm) were evacuated in turn.

The thicknesses of all films were estimated by the surface profiler manufactured by Bruker (model DEKTAK-XT). Particularly, for the thickness of CIL layers, ~90 nm PM6:L8-BO active layers were firstly prepared and annealed at 100 °C for 10 min, and then CIL layers with different concentrations were spin-coated on top. The thicknesses of CILs were finally determined by conducting measurements on Dektak by subtracting the active layer thickness.

The effective area of the cells was defined by a mask to be 0.04 cm<sup>2</sup>. The *J-V* characteristics were measured by a Keithley 2400 source meter unit under AM1.5G spectrum from a solar simulator (Enlitech model SS-F5-3A). Solar simulator illumination intensity was determined at 100 mW/cm<sup>2</sup> using a mono-crystal silicon reference cell with KG5 filter. Short circuit currents under AM1.5G conditions were estimated from the spectral response and convolution with the solar spectrum. The external quantum efficiency (EQE) was measured by a Solar Cell Spectral Response Measurement System QE-R3011 (Enli Technology Co., Ltd.).

**SCLC.** The electron mobility of PDIN-TEMPO, PDIN-Br and TEMPO-N were measured by space charge limited current (SCLC) measurement with the device configuration of ITO/ZnO/active layer/CILs/Ag. All film samples were prepared with the same measurement of the solar cell devices by spin-coating solutions in an N<sub>2</sub>-filled glove box. The electron mobilities were calculated with the Mott-Gurney equation in the SCLC region (slope = 2 in log*J* vs log*V* plots):

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{L^3} \quad (\text{eq. 1})$$

Where  $\varepsilon_0$  is the permittivity of the vacuum,  $\varepsilon_r$  is the dielectric constant of the CIL materials, and  $L$  is the thickness of the CILs.

**Stability test.** For degradation experiments, the unencapsulated cells were loaded into a sealed chamber inside the glovebox and stored at room temperature. This chamber was continuously purged with nitrogen with the humidity lower than 0.01

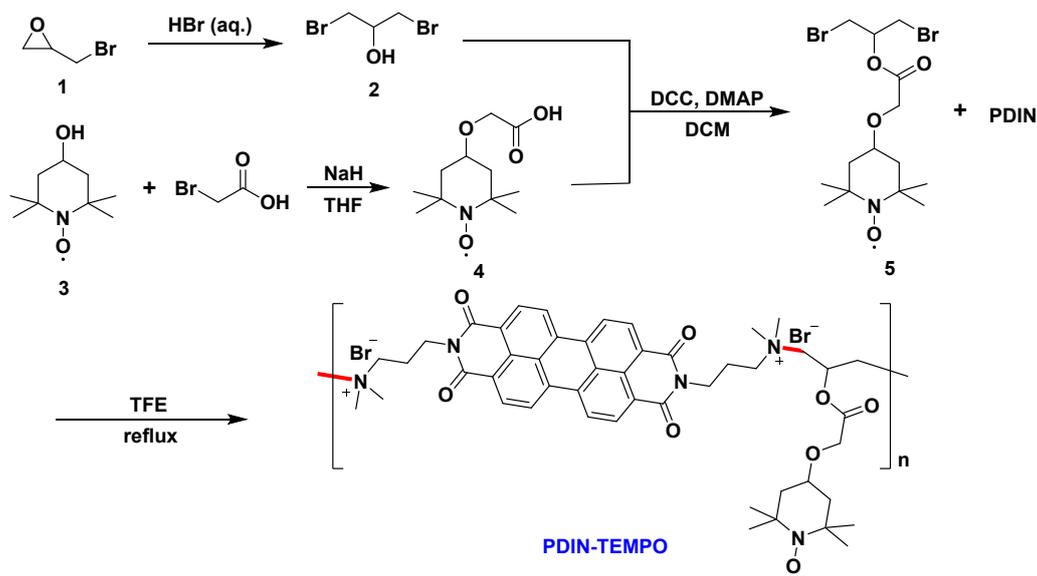
ppm and then put under LED illumination. The LED illumination intensity was equal to one sun.

**GIWAXS** measurements were conducted on a Xenocs-SAXS/WAXS system with X-ray wavelength of 1.5418 Å. The film samples were irradiated at a fixed angle of 0.2°. All film samples were prepared by spin-coating CIL solutions on Si substrates. The film thickness of these polymers were ca 60 nm for all GIWAXS measurements. The rest trace amount of solvent was removed under high vacuum before measurement.

**AFM.** The morphology of CIL films was test by spin-coating CIL solutions on active layers. AFM images were recorded using a Digital Instruments Nanoscope IIIa multimode atomic force microscope in tapping mode under ambient conditions.

## 2. Synthesis of materials

### The synthesis of PDIN-TEMPO



**Fig. S1** The synthetic routes of the monomer DiBr-TEMPO and the polymer PDIN-TEMPO.

#### 1,3-dibromopropan-2-ol, 2

To a solution of 1-bromo-2,3-epoxypropane **1** (4 g, 29 mmol) was added 40% HBr aq. (5.87 g, 29 mmol) dropwise at 0°C. The mixture was stirred at 0°C for 8 h, then the reaction was quenched with water, and extracted with EA (three times). The organic layers were combined, washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated get the product 1,3-dibromopropan-2-ol **2** in 85% yield as the colorless oil without further purification. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) = 4.08 - 4.01 (m, 1H), 3.58 (d, *J* = 5.32 Hz, 4H), 3.28 (br 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) = 69.9, 35.4.

#### TEMPO-COOH, 4

A flame dried 250 mL two-necked flask was equipped with a magnetic stir bar and a reflux condenser, NaH (1.2 g, 60%, 30 mmol) was then suspended in dry THF (20 mL)

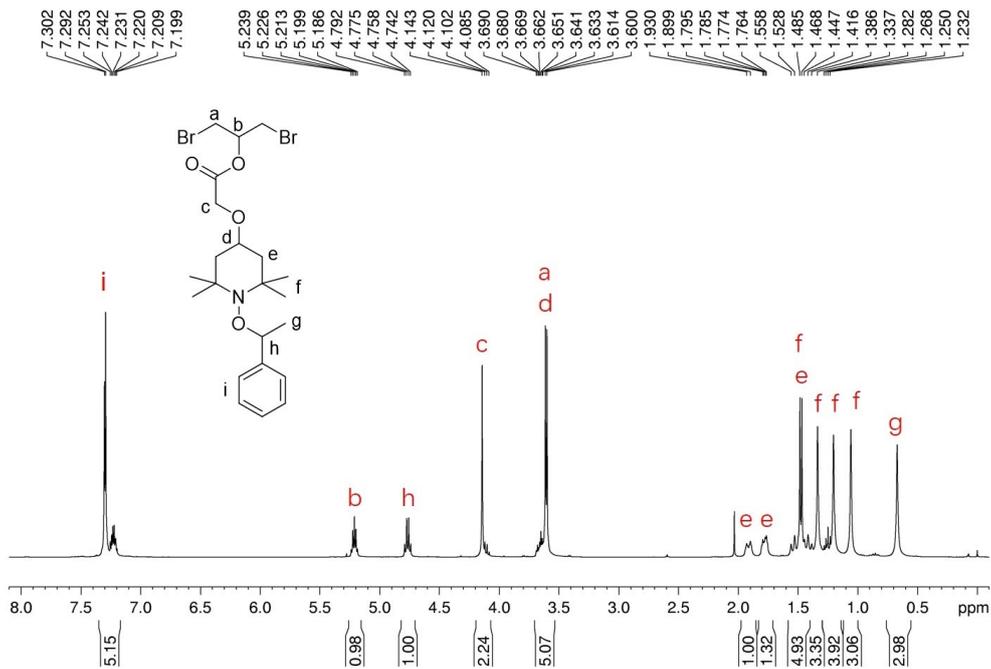
at 0°C under argon. 4-OH-TEMPO **3** (4-hydroxy-2,2,6,6-tetramethyl-piperidinoxy, 10 mmol) dissolved in dry THF (30 mL) was then added slowly. After 30 min, bromoacetic acid (10 mmol) dissolved in dry THF (30 mL) was added dropwise. The mixture was heated to reflux and the progress of the reaction was monitored by TLC. Upon completion of the reaction, the mixture was cooled down to room temperature, and diluted with water, extracted with EA (100 ml × 2). The aqueous layer was acidified with HCl (2 M) until pH 2 was reached, extracted with EA (150 mL × 3). The organic layers were combined and washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated get the product TEMPO-COOH **4** in 71% yield as the orange oil without further purification.

### **DiBr-TEMPO, 5**

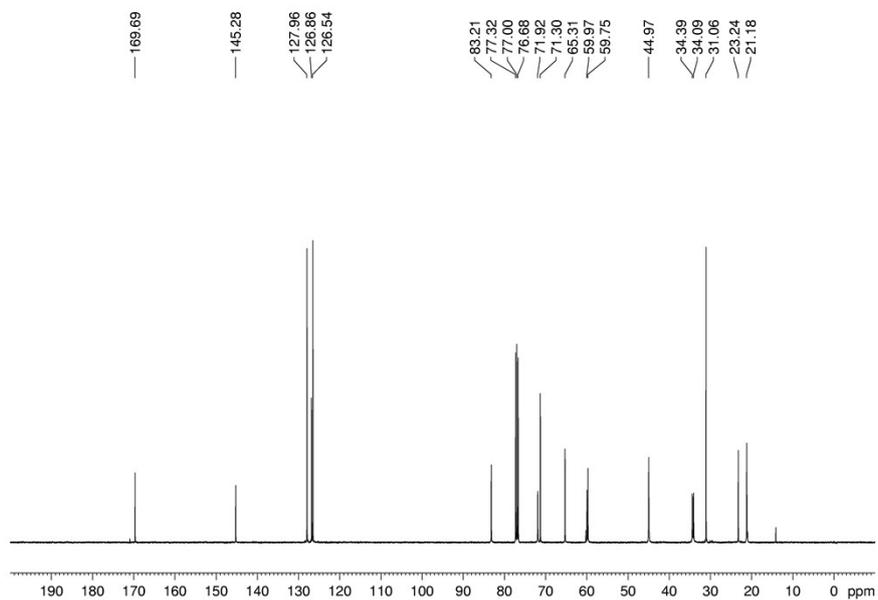
The DCC (N,N'-dicyclohexylcarbodiimide, 8 mmol) was added to a solution of 1,3-dibromopropan-2-ol **2** (6 mmol), DMAP (4-dimethylaminopyridine, 0.5 mmol) and TEMPO-COOH **4** (5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) at 0°C. After addition, the resulting mixture was allowed to warm up to room temperature and stirred for another 8 h. The by-product was removed by passage of the solution through Celite and washed with CH<sub>2</sub>Cl<sub>2</sub>, the filtrate was washed with 1M HCl, brine successively and concentrated. The crude product was purified by column chromatography on silica gel (PE:EA = 15:1) to afford the desired product (DiBr-TEMPO) as orange solid in 85% yield. **HR-MS** (ESI, Dichloromethane) for C<sub>14</sub>H<sub>25</sub>Br<sub>2</sub>NO<sub>4</sub><sup>+</sup> [M+H]<sup>+</sup> calcd. 429.0145, found 429.0142. Anal. Calcd for C<sub>14</sub>H<sub>24</sub>Br<sub>2</sub>NO<sub>4</sub>: C, 39.09; H, 5.62; N, 3.26. Found: C, 39.09; H, 5.40; N, 3.09.

To further confirm the structure of the DiBr-TEMPO, a derivatization reaction was conducted with aldehyde giving the derivative **6** (Fig S2),<sup>[1]</sup> which can be fully characterized by NMR and MS.

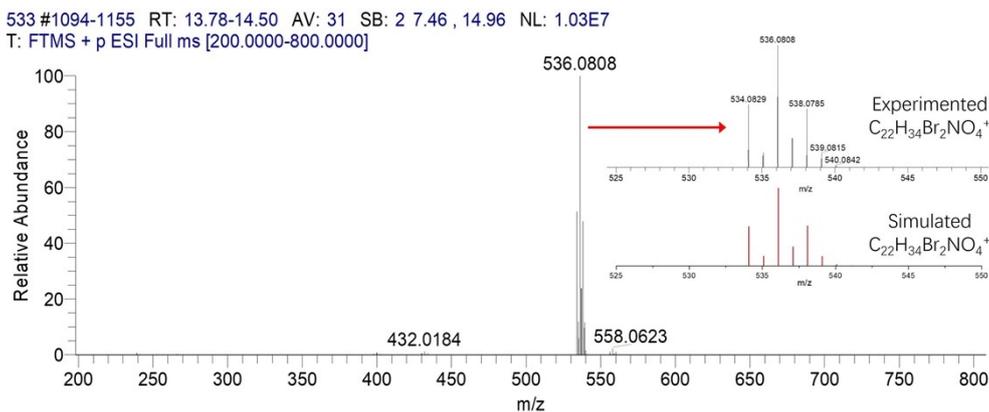




**Fig. S3** The  $^1\text{H}$  NMR spectra of derivative 6.



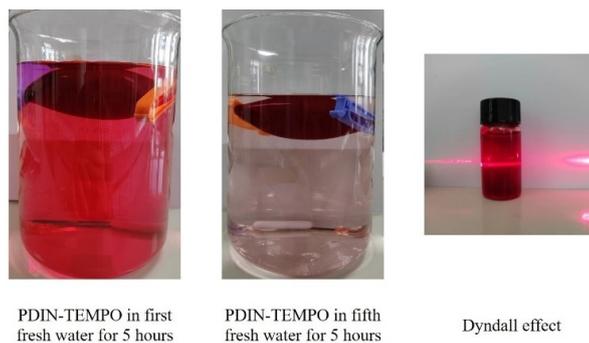
**Fig. S4** The  $^{13}\text{C}$  NMR spectra of derivative 6.



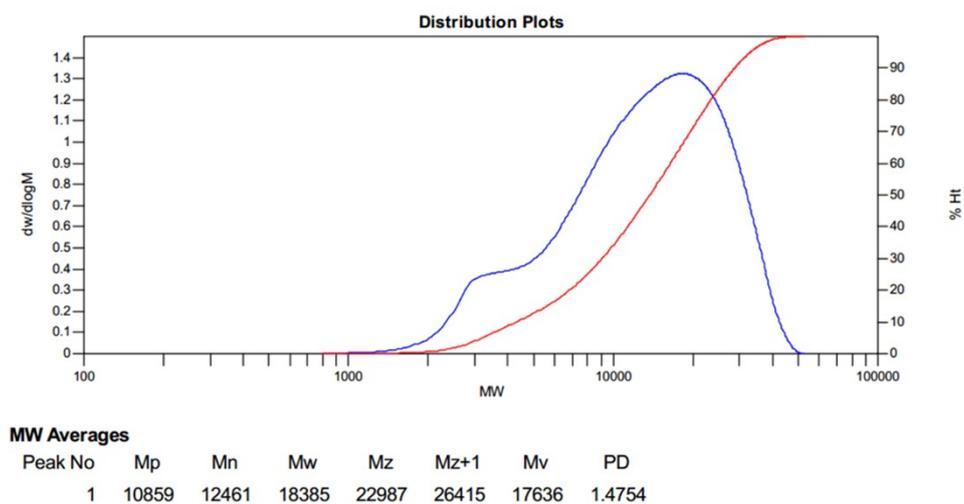
**Fig. S5** The ESI-MS spectra of derivative **6**. Inset shows the experimented and simulated pattern of protonated  $C_{22}H_{34}Br_2NO_4^+$  species.

### Synthesis of PDIN-TEMPO

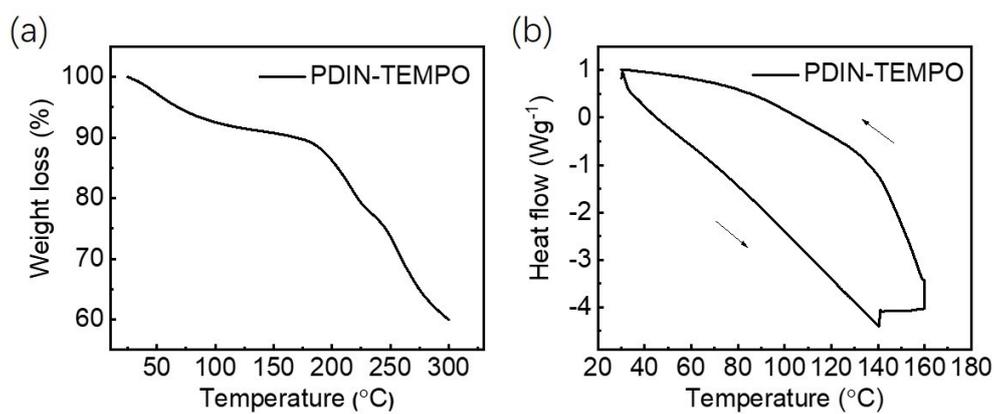
In a general procedure, the appropriate amounts of **DiBr-TEMPO 5** (1.2 mmol), PDIN (1 mmol) and TFE (1.5 mL) were added to a 10 mL vial equipped with a magnetic stir bar. The vial was purged with nitrogen and placed in an 80°C oil bath for 72 h. The reaction mixture was precipitated into THF, filtered, and washed with THF, then the resulting solids were purified by Soxhlet extraction with chloroform (24 h) and dried in vacuo. The crude product was dissolved in TFE (30 mL), then poured into a dialysis membrane (MWCO 3.5 kDa). The content of the dialysis bag was dialyzed against pure water in a 4 L beaker for 48 hours, during which time the water in the beaker was renewed for five times. Finally, the solvent of solution in the dialysis bag was evaporated under reduced pressure. The product was obtained as a black solid (40 % yield) and further characterized by IR and GPC (5 mg/mL in HFIP,  $M_n = 12.46$  kDa). **IR** (KBr pellet) [ $cm^{-1}$ ]: 3431(m), 3027(w), 2953(w), 2870(w), 1695(s), 1649(s), 1594(s), 1575(m), 1475(m), 1440(s), 1402(m), 1382(s), 1344(s), 1249(m), 1158(w), 1128(w), 1063(w), 968(w), 857(w), 809(m), 743(m). Molecular weight by GPC using 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) as the eluent:  $M_n = 12.46$  kg/mol,  $M_w = 18.39$  kg/mol and  $D = 1.48$ .



**Fig. S6** The dialysis process of PDIN-TEMPO and the dyndall effect.

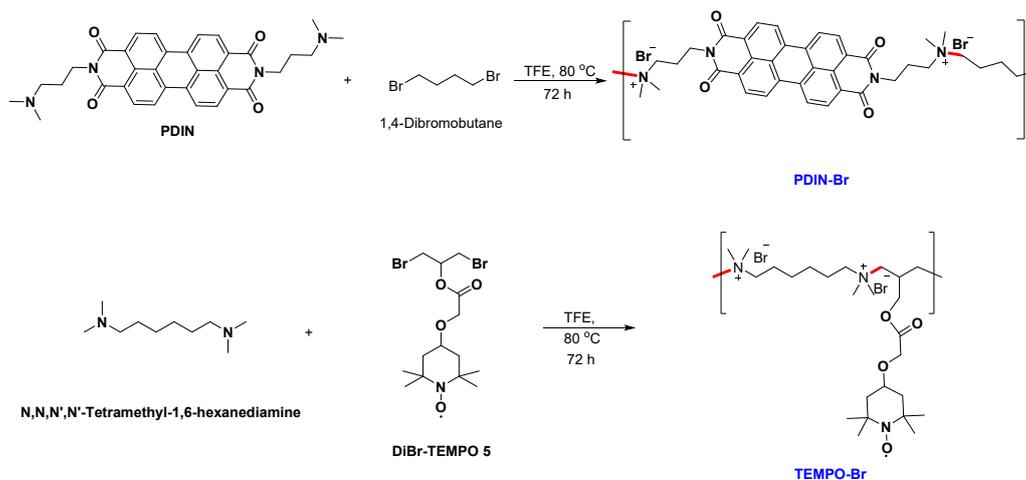


**Fig. S7** GPC of PDIN-TEMPO.



**Fig. S8** TGA and DSC of PDIN-TEMPO.

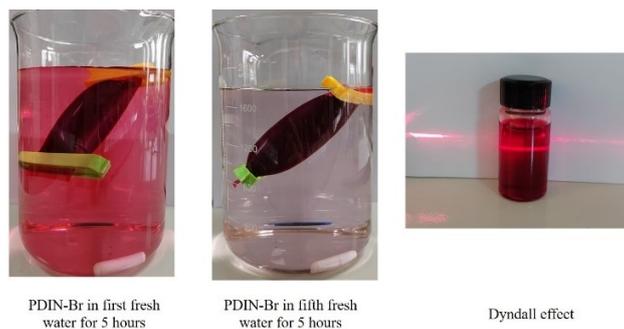
## The synthesis of PDIN-Br and TEMPO-Br



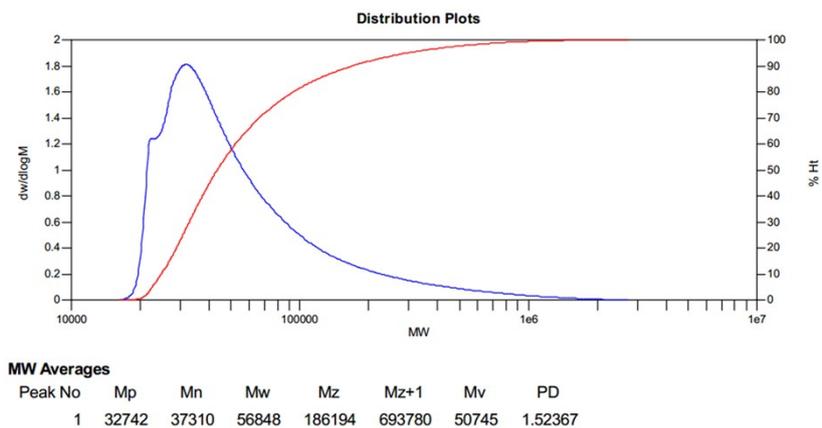
**Fig. S9** The synthesis of PDIN-Br and TEMPO-Br.

### PDIN-Br

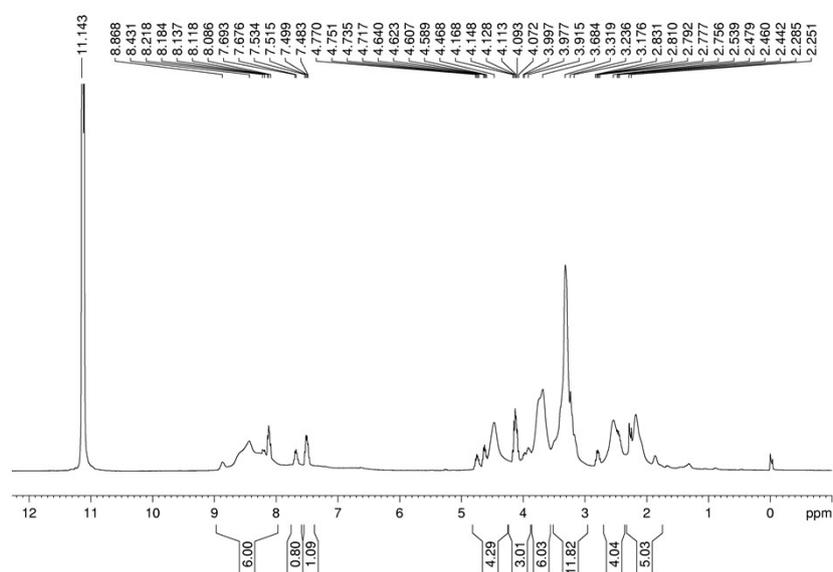
In a general procedure, the appropriate amounts of 1,4-dibromobutane (1.2 mmol), PDIN (1 mmol) and TFE (1.5 mL) were added to a 10 mL vial equipped with a magnetic stir bar. The vial was purged with nitrogen and placed in an 80°C oil bath for 72 h. The reaction mixture was precipitated into THF, filtered, and washed with THF, then the resulting solids were purified by Soxhlet extraction with chloroform (24 h) and dried in vacuo. The crude product was dissolved in TFE (30 mL), then poured into a dialysis membrane (MWCO 3.5 kDa). The content of the dialysis bag was dialyzed against pure water in a 4 L beaker for 48 hours, during which time the water in the beaker was renewed for five times. Finally, the solvent of the solution in dialysis bag was evaporated under reduced pressure. The product was obtained as a black solid (40 % yield) and further characterized by IR and GPC (5 mg/mL in HFIP,  $M_n = 37.31$  kDa). **IR** (KBr pellet) [( $\text{cm}^{-1}$ ): 3421(s), 3031(w), 2957(w), 2884(w), 1757(w), 1691(s), 1647(s), 1592(s), 1575(s), 1561(m), 1479(m), 1441(s), 1402(m), 1344(s), 1279(m), 1248(m), 1153(m), 1129(w), 1063(w), 988(w), 914(w), 857(m), 809(s), 744(s), 726(w). Molecular weight by GPC using 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) as the eluent:  $M_n = 37.31$  kg/mol,  $M_w = 56.85$  kg/mol and  $D = 1.52$ .



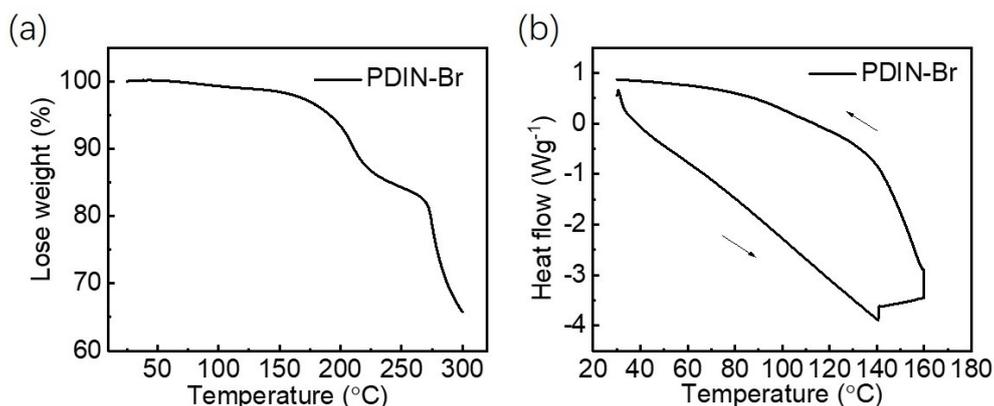
**Fig. S10** The dialysis process of PDIN-Br and the dyndall effect.



**Fig. S11** GPC of PDIN-Br.



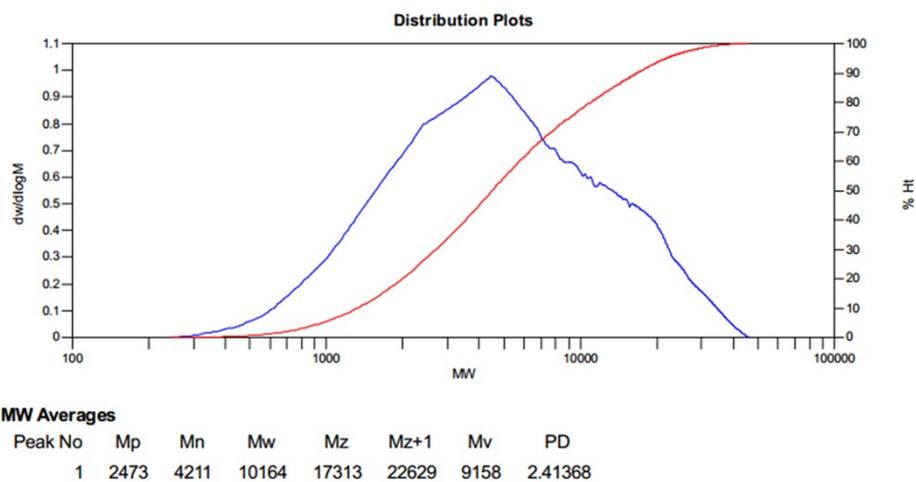
**Fig. S12**  $^1\text{H}$  NMR of PDIN-Br ( $\text{CF}_3\text{COOD-dl}$ ).



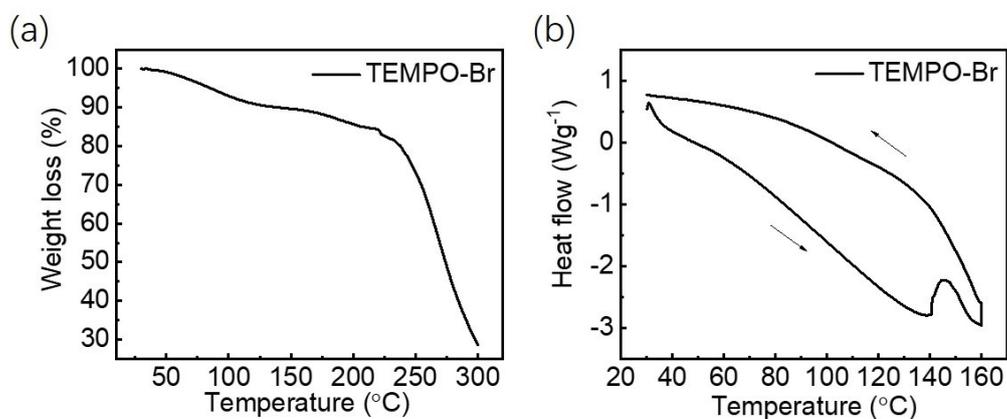
**Fig. S13** TGA and DSC of PDIN-Br.

### TEMPO-Br

In a general procedure, the appropriate amounts of TEMPO-diBr 5 (1.2 mmol), N,N,N',N'-tetramethyl-1,6-hexanediamine (1 mmol) and TFE (1.5 mL) were added to a 10 mL vial equipped with a magnetic stir bar. The vial was purged with nitrogen and placed in an 80°C oil bath for 72 h. The reaction mixture was precipitated into THF, filtered, and washed with THF, then the resulting solids were purified by Soxhlet extraction with THF (24 h) and dried in vacuo, give the product as a yellow solid (moisture absorption is strong, 70 % yield), HFIP GPC ( $M_n = 4.21$  kDa). **IR** (KBr pellet) [(cm<sup>-1</sup>): 3435(s), 3022(w), 2949(w), 2870(w), 1636(s), 1470(s), 1388(m), 1291(w), 1234(w), 1134(w), 1098(m), 1055(m), 993(w), 943(w), 910(s), 859(w), 733(m). Molecular weight by GPC using 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) as the eluent:  $M_n = 4.21$  kg/mol,  $M_w = 10.16$  kg/mol and  $D = 2.41$ .

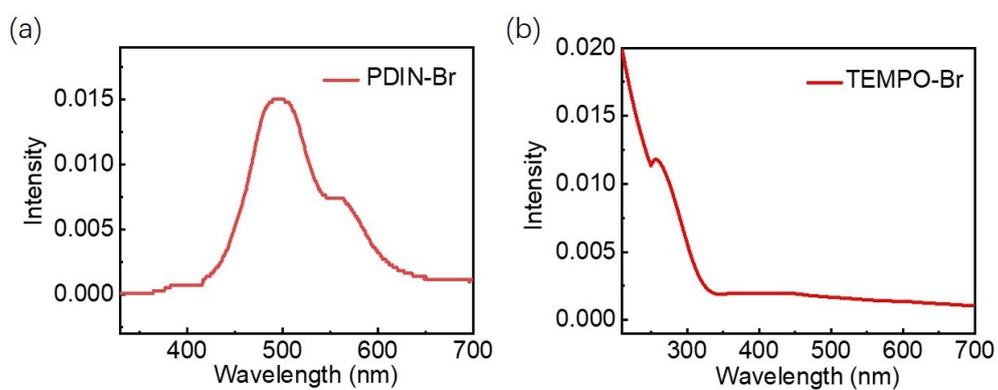


**Fig. S14** GPC of TEMPO-Br.

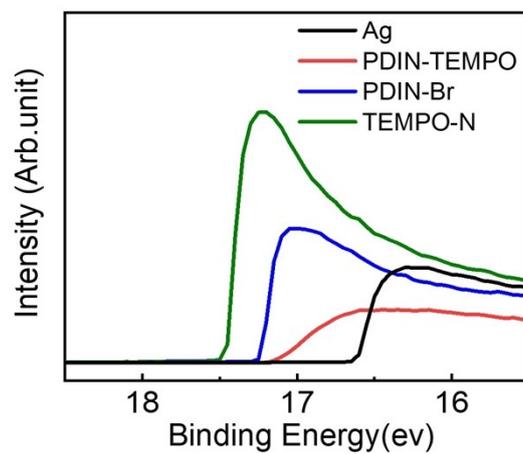


**Fig. S15** TGA and DSC of TEMPO-Br.

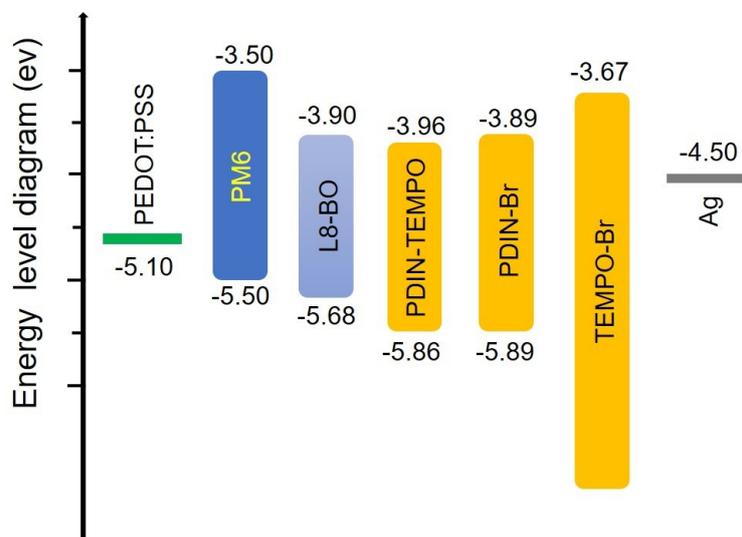
### 3. Physical properties



**Fig. S16** The UV-vis spectra of PDIN-Br and TEMPO-Br in thin film, respectively.

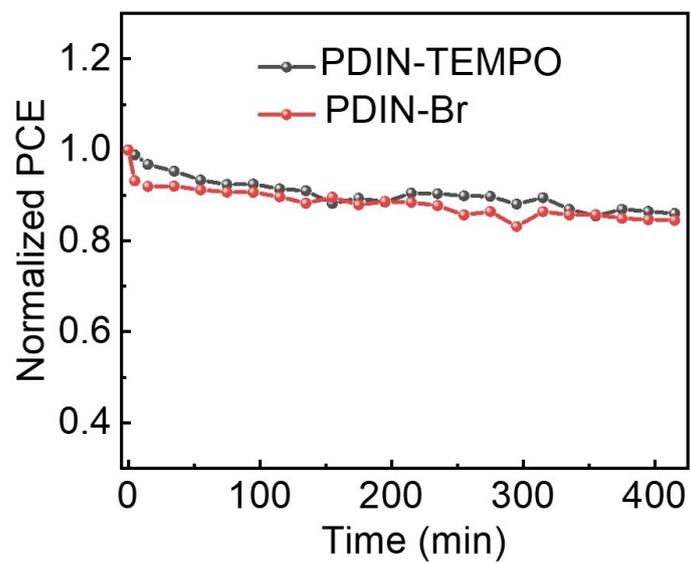


**Fig. S17** UPS spectra of different materials on bare Ag.



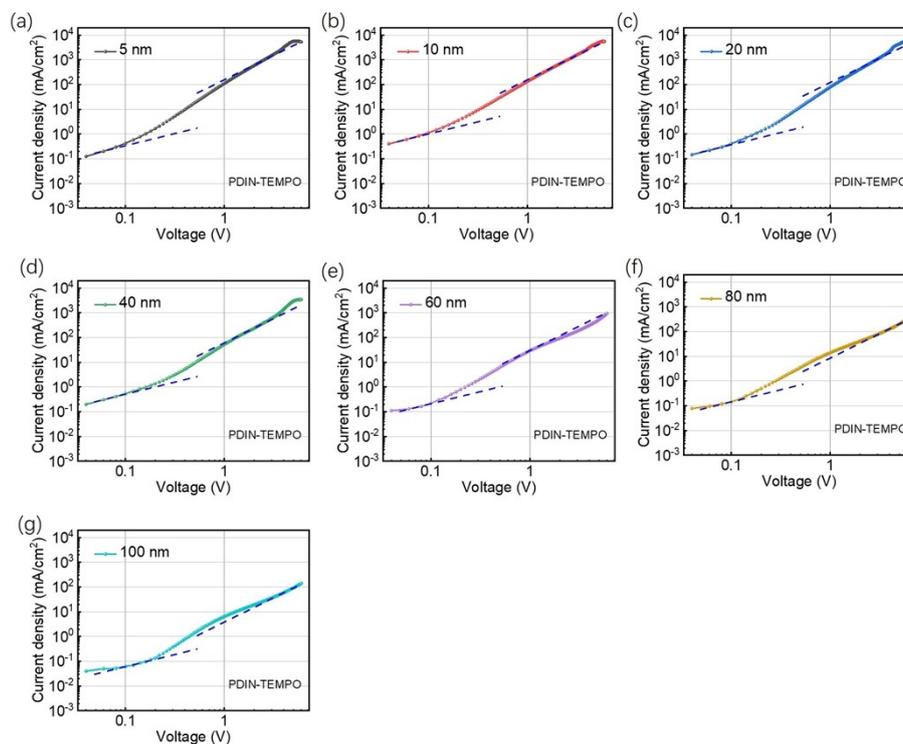
**Fig. S18** The energy level diagram of the materials in this work.

#### 4. Photostability

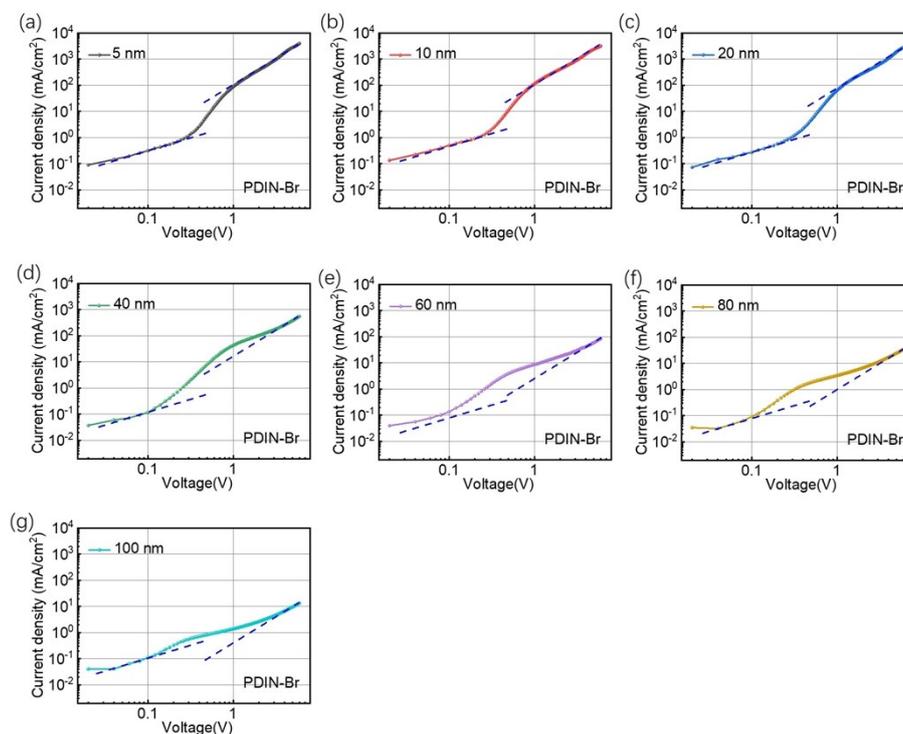


**Fig. S19** The photostability of PDIN-TEMPO and PDIN-Br based OSCs. The measurement was conducted using the AM1.5G illumination (100 mW/cm<sup>2</sup>).

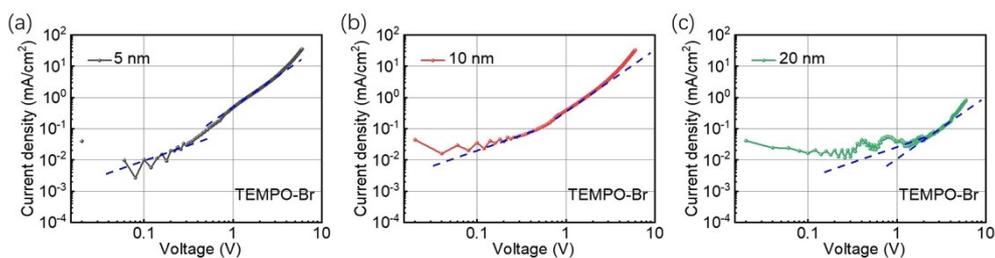
## 5. Fitting of SCLC



**Fig. S20** The fitting data of SCLC using PDIN-TEMPO with different thicknesses.

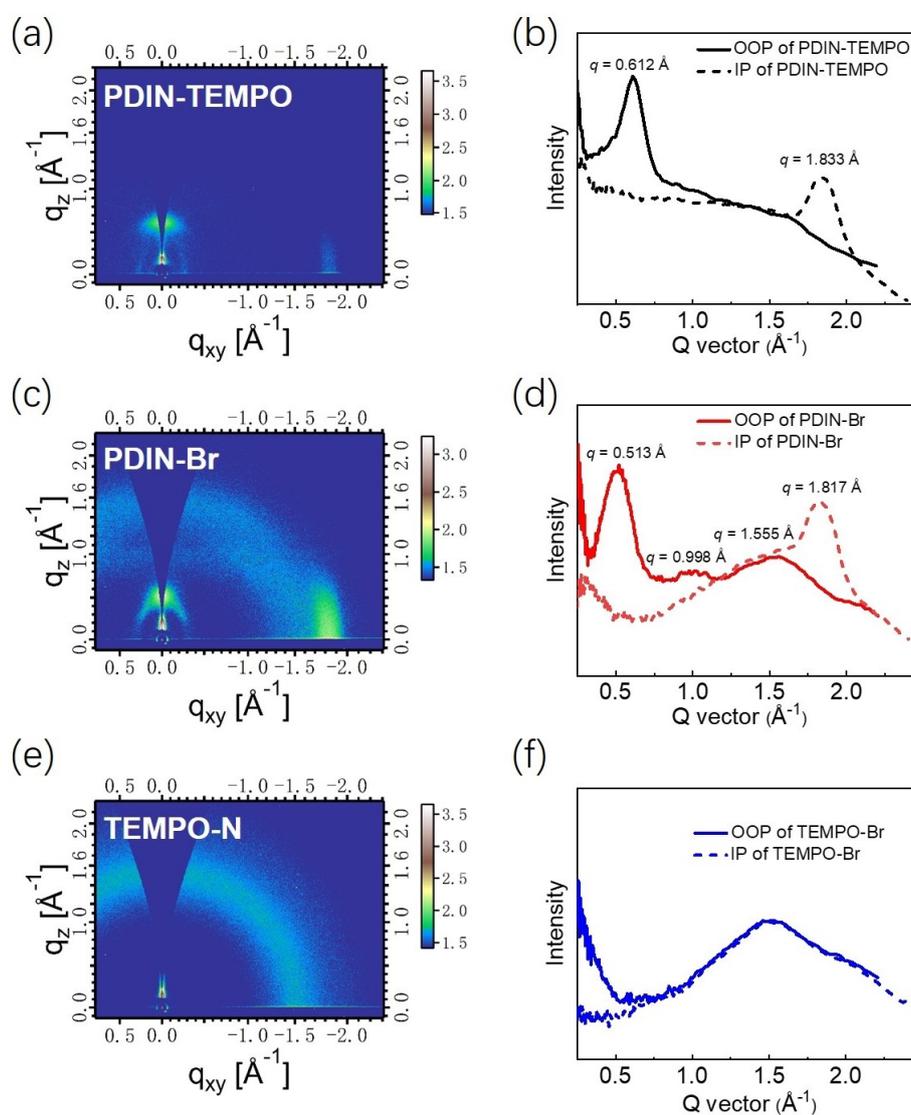


**Fig. S21** The fitting data of SCLC using PDIN-Br with different thicknesses.



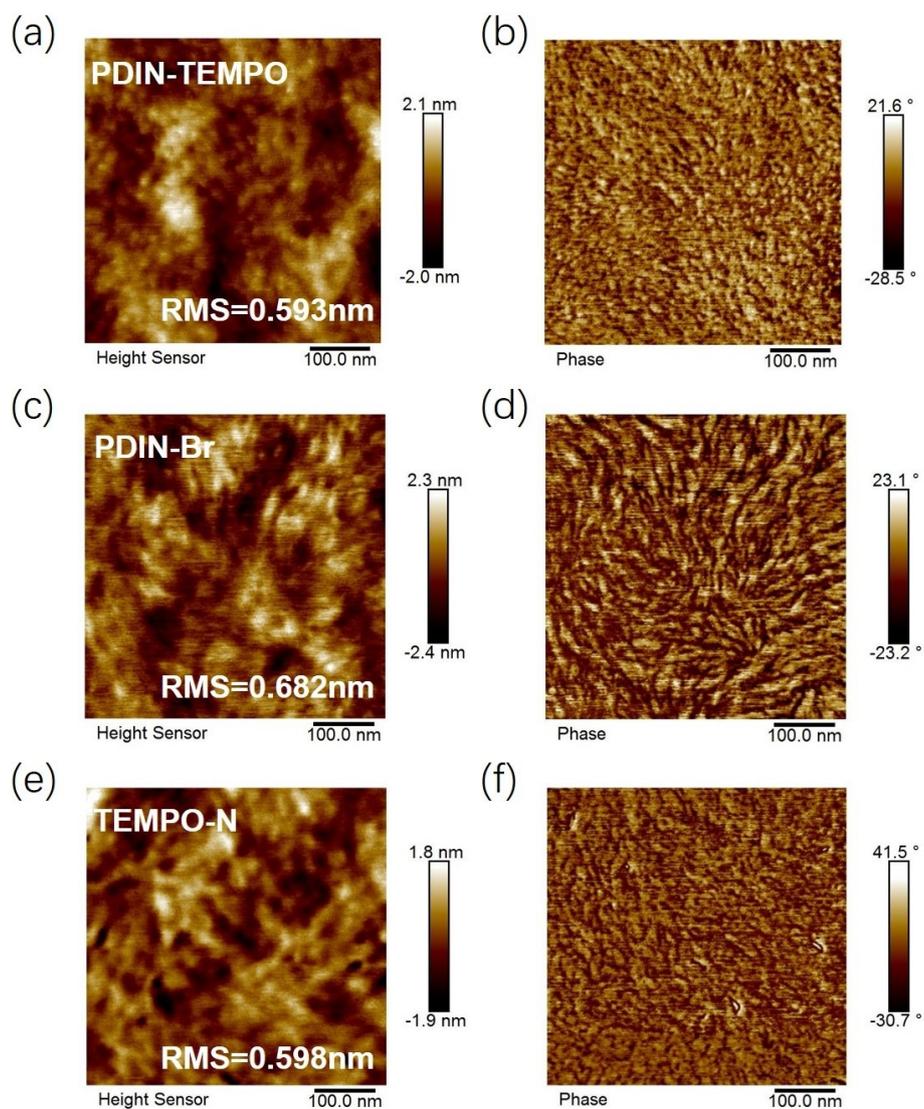
**Fig. S22** The fitting data of SCLC using TEMPO-Br with different thicknesses.

## 6. GIWAXS



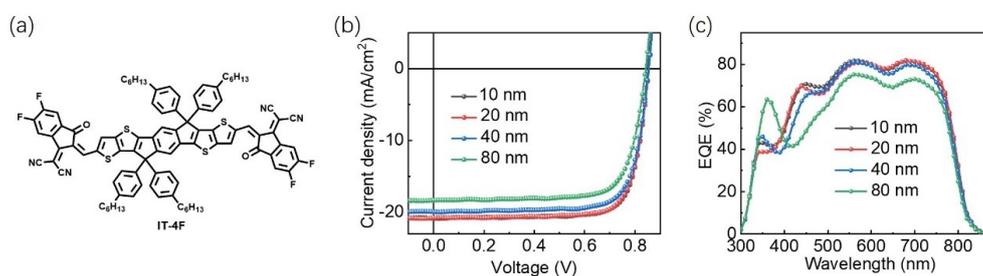
**Fig. S23** GIWAXS profiles (a, c, e) of PDIN-TEMPO, PDIN-Br, TEMPO thin films and corresponding in-plane and out-of-plane plots (b, d, f).

## 7. AFM

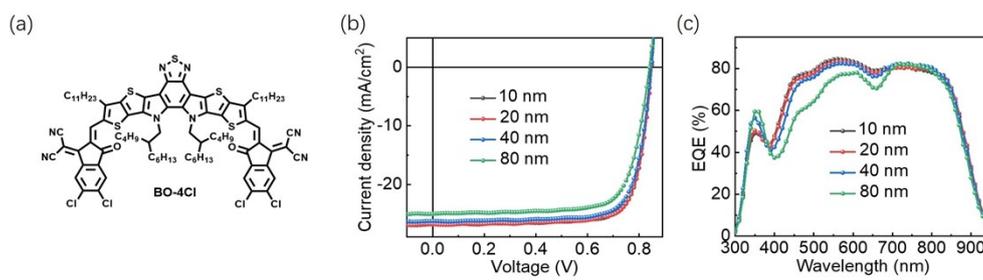


**Fig. S24** AFM height (a, c, e) and phase (b, d, f) images of CIL films on the photoactive layer.

## 8. Device performance



**Fig. S25** The *J-V* curves and EQEs of PM6:IT-4F based OSCs using PDIN-TEMPO with different thicknesses.



**Fig. S26** The *J-V* curves and EQEs of PM6:BO-4Cl based OSCs using PDIN-TEMPO as CIL with different thicknesses.

**Table S1.** Summary of the CIL thickness dependent OSC performance in the literatures.

| Entry | PCE <sub>best</sub><br>(%) | PCE with thick<br>CIL (%) | CIL thickness<br>(nm) | PCE/PCE <sub>best</sub> | Ref.         |
|-------|----------------------------|---------------------------|-----------------------|-------------------------|--------------|
| 1     | 16.86                      | 13.65                     | 35                    | 0.81                    | [2]          |
| 2     | 17.6                       | 14.47                     | 53                    | 0.82                    | [3]          |
| 3     | 11.23                      | 9.02                      | 40                    | 0.80                    | [4]          |
| 4     | 10.49                      | 9.37                      | 50                    | 0.93                    | [5]          |
| 5     | 9.45                       | 8.3                       | 52                    | 0.88                    | [6]          |
| 6     | 16.57                      | 15.33                     | 30                    | 0.93                    | [7]          |
| 7     | 10.11                      | 8.04                      | 102                   | 0.80                    | [8]          |
| 8     | 17.98                      | 16.9                      | 33                    | 0.94                    | [9]          |
| 9     | 17.05                      | 15.14                     | 40                    | 0.89                    | [10]         |
| 10    | 10.5                       | 9.3                       | 35                    | 0.89                    | [11]         |
| 11    | 15.56                      | 13.55                     | 50                    | 0.87                    | [12]         |
| 12    | 10.72                      | 10.03                     | 48                    | 0.94                    | [13]         |
| 13    | 10.48                      | 7.62                      | 47                    | 0.73                    | [14]         |
| 14    | 10.48                      | 9.56                      | 60                    | 0.91                    | [15]         |
| 15    | 16.61                      | 15.5                      | 37                    | 0.93                    | [16]         |
| 16    | 17.02                      | 13.55                     | 37                    | 0.80                    | [17]         |
| 17    | 16.71                      | 15.88                     | 25                    | 0.95                    | [18]         |
| 18    | 18.48                      | 18.09                     | 5                     | 0.98                    | This<br>work |
| 19    |                            | 18.48                     | 10                    | 1.00                    |              |
| 20    |                            | 18.02                     | 20                    | 0.98                    |              |
| 21    |                            | 17.94                     | 40                    | 0.97                    |              |
| 22    |                            | 17.69                     | 60                    | 0.96                    |              |
| 23    |                            | 17.27                     | 80                    | 0.93                    |              |
| 24    |                            | 15.86                     | 100                   | 0.86                    |              |

**Table S2.** Summary of the parameters of PM6:IT-4F based device using PDIN-TEMPO as CIL with varied thicknesses.

| CIL Thickness<br>[nm] | $V_{oc}$<br>[V]        | $J_{sc}$<br>[mA/cm <sup>2</sup> ] | FF<br>[%]             | PCE<br>[%]            |
|-----------------------|------------------------|-----------------------------------|-----------------------|-----------------------|
| 10                    | 0.851<br>(0.847±0.002) | 20.86<br>(20.60±0.17)             | 77.81<br>(78.40±0.41) | 13.81<br>(13.68±0.06) |
| 20                    | 0.855<br>(0.849±0.003) | 20.76<br>(20.74±0.13)             | 77.58<br>(76.82±0.66) | 13.76<br>(13.53±0.18) |
| 40                    | 0.855<br>(0.850±0.003) | 19.93<br>(19.80±0.15)             | 76.34<br>(75.89±0.38) | 13.00<br>(12.78±0.18) |
| 80                    | 0.843<br>(0.844±0.002) | 18.33<br>(18.31±0.10)             | 75.48<br>(74.56±0.67) | 11.66<br>(11.51±0.16) |

**Table S3.** Summary of the parameters of PM6:BO-4Cl based device using PDIN-TEMPO as CIL with varied thicknesses.

| CIL Thickness<br>[nm] | $V_{oc}$<br>[V]        | $J_{sc}$<br>[mA/cm <sup>2</sup> ] | FF<br>[%]             | PCE<br>[%]            |
|-----------------------|------------------------|-----------------------------------|-----------------------|-----------------------|
| 10                    | 0.845<br>(0.845±0.003) | 26.82<br>(26.80±0.15)             | 77.95<br>(77.36±0.45) | 17.67<br>(17.52±0.10) |
| 20                    | 0.849<br>(0.845±0.003) | 26.82<br>(26.74±0.08)             | 78.03<br>(76.83±0.64) | 17.76<br>(17.36±0.22) |
| 40                    | 0.845<br>(0.843±0.004) | 26.58<br>(26.45±0.16)             | 76.43<br>(75.72±1.62) | 17.17<br>(16.88±0.40) |
| 80                    | 0.840<br>(0.840±0.001) | 25.05<br>(24.84±0.13)             | 74.80<br>(75.16±0.34) | 15.74<br>(15.68±0.05) |

## 9. References

- [1] Zhang Y., Park A. M., McMillan S. R., Harmon N. J., Flatté M. E., Fuchs G. D., Ober C. K., *Chem. Mater.*, **2018**, 30(14), 4799-4807.
- [2] Zhao Y., Liu X., Jing X., Liu S., Liu H., Liu Y., Yu L., Dai S., Sun M., *Chem. Eng. J.*, **2022**, 441(
- [3] Zi M., Chen X., Tan S., Weng C., Zhao B., *Chem. Eng. J.*, **2022**, 443(
- [4] Song C., Liu X., Li X., Wang Y. C., Wan L., Sun X., Zhang W., Fang J., *ACS Appl. Mater. Interfaces*, **2018**, 10(17), 14986-14992.
- [5] Jia J., Fan B., Xiao M., Jia T., Jin Y., Li Y., Huang F., Cao Y., *Macromolecules*, **2018**, 51(6), 2195-2202.
- [6] Xu R., Zhang K., Liu X., Jin Y., Jiang X. F., Xu Q. H., Huang F., Cao Y., *ACS Appl. Mater. Interfaces*, **2018**, 10(2), 1939-1947.
- [7] Yu Y., Tao W., Wang L., Tao Y.-D., Peng Z., Zheng X., Xiang C., Zhao B., Li C.-Z., Tan S., *J. Mater. Chem. A*, **2021**, 9(40), 22926-22933.
- [8] Wu Z., Sun C., Dong S., Jiang X. F., Wu S., Wu H., Yip H. L., Huang F., Cao Y., *J. Am. Chem. Soc.*, **2016**, 138(6), 2004-2013.
- [9] Liu M., Jiang Y., Liu D., Wang J., Ren Z., Russell T. P., Liu Y., *ACS Energy Lett.*, **2021**, 6(9), 3228-3235.
- [10] Liu M., Li M., Jiang Y., Ma Z., Liu D., Ren Z., Russell T. P., Liu Y., *ACS Appl. Mater. Interfaces*, **2021**, 13(35), 41810-41817.
- [11] Sharma A., Singh S., Song X., Rosas Villalva D., Troughton J., Corzo D., Toppare L., Gunbas G., Schroeder B. C., Baran D., *Chem. Mater.*, **2021**, 33(22), 8602-8611.
- [12] Liu Z., Tang H., Feng H., Tan C. H., Liang Y., Hu Z., Zhang K., Huang F., Cao Y., *Macromol. Rapid Commun.*, **2022**, e2200190.
- [13] Wang L., Chen Y., Tao W., Wang K., Peng Z., Zheng X., Xiang C., Zhang J., Huang M., Zhao B., *Macromol. Rapid Commun.*, **2022**, e2200119.
- [14] Liu Y., Sheri M., Cole M. D., Emrick T., Russell T. P., *Angew. Chem. Int. Ed.*, **2018**, 57(31), 9675-9678.
- [15] Liu Y., Sheri M., Cole M. D., Yu D. M., Emrick T., Russell T. P., *Angew. Chem. Int. Ed.*, **2019**, 58(17), 5677-5681.
- [16] Liu M., Fan P., Hu Q., Russell T. P., Liu Y., *Angew. Chem. Int. Ed.*, **2020**, 59(41), 18131-18135.
- [17] Yao J., Qiu B., Zhang Z. G., Xue L., Wang R., Zhang C., Chen S., Zhou Q., Sun C., Yang C., Xiao M., Meng L., Li Y., *Nat. Commun.*, **2020**, 11(1), 2726.
- [18] Cai C., Yao J., Chen L., Yuan Z., Zhang Z. G., Hu Y., Zhao X., Zhang Y., Chen Y., Li Y., *Angew. Chem. Int. Ed.*, **2021**, 60(35), 19053-19057.