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Electronic Supplementary Information

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1. General Information

Materials

The pre-prepared K-Na alloy was used to dry tetrahydrofuran at its boiling temperature for several days, then tetrahydrofuran was distilled before use. In all the above process, dry argon was used to make an inert atmosphere. Zinc dust was purchased from a company (Sinopharm Chemical Reagent Co., Ltd; SCRCL), which was activated by 1.5 M HCl aqueous.

(4-Methoxyphenyl)(phenyl)methanone, 3-chloro-*N*,*N*-dimethylpropan-1-amine-hydrochloride and bis(4-methoxyphenyl)methanone were purchased from Energy Chemical. *n*-Butyllithium, diphenylmethane, tetrabutylammonium perchlorate and 1,2-oxathiolane-2,2-dioxide were purchased comercially from different companies of Aladdin, Sigma-Aldrich, and Alfa Aesar, respectively, while 1-Material for PTB7, American Dye Source, Inc. For PC₇₁BM, Acros for 1,8-diiodooctane (DIO), and Baytron Company for PSS:PEDOT. *p*-Toluenesulfonic acid monohydrate, boron tribromide and all others were obtained commercially from SCRCL. The ITO glasses with the characteristics of $\leq 15 \Omega$ /square, 1.2 mm thick, and the transmittance > 90%, were bought from a company with the name of Nippon Sheet Glass Company, Ltd. The glasses, before use, should be completely cleaned by utilizing different slovents in the order of deionized H₂O (40 min), alcohol (40 min), acetone (40 min) and 2-propyl alcohol (40 min), then the glassess were further treated by being exposed to UV-ozone (20 min). The nanoparticles of TPE-1 and TPE-2 were prepared by suspending TPE-1 in water (0.50 mM) and TPE-2 in methanol (0.50 mM) by ultrasonic, respectively.

The configuration of device was ITO glass/PSS:PEDOT/PC₇₁BM:PTB7/in the presence or absence of the interficial layer/aluminum layer. The solution of PSS:PEDOT in H₂O was filtered carefully by utilizing a special filter (0.45 μ m), then the filtrate was spin-coated (4000 rpm, 1 min) onto the ITO glass, which was pre-treated according to the procedure described above. The resultant films on the glass substrate were further annealed (10 min) at the temperature of about 140 °C. After this, through the process of spin-casting (2000 rpm, 2 min), PC₇₁BM:PTB7, as the active layer with the thickness of ~110 nm, was fabricated onto the above obtained glass substrate, in which, the weight ratio of PC₇₁BM and PTB7 was fixed at 1.5:1, and the concentration of PTB7 is strictuly fixed to be 10 mg/mL by using the mixture solvent of 1,8-diiodoctane and chlorobenzene (3:97 in volume). After this, the obtained glasses with thin films were dried in vacuum (0.5 h). The interlayer materials were dissolved in methanol in the presence of acetic acid (4:1 vol%) and their solutions (1 mg/mL) were spin-coated onto the active layer and put in vacuum for 30 min. The electrode of aluminum could be conveniently obtained in a chamber with high vacuum (~3 ×10⁻⁹ bar) by the evaporating process, and the thickness was controlled to be 100 nm, and the active area was controlled to be about 0.1257 cm² by utilizing a special mask.

Characterization and Measurement

A Varian Mercury (300 MHz), Bruker spectrometer (ARX 400), a Shimadzu UV-2550, and a PerkinElmer-2 spectrometer, were utilized for the measurement of ¹H NMR and ¹³C NMR, UV-Visible, and FT-IR spectra. A Hitachi F-4600, a Hamamatsu C11347 Quantaurus-QY and Hamamatsu C11367-1 Quantaurus-Tau, were utilized for the measurement of photoluminescence spectra, fluorescence lifetimes and quantum yields. A ZEISS-SIGMA and a JEM-2010-FEF (200 KV) were utilized for the measurement of SEM and TEM. GIXRD patterns were performed on RigakuSmartLab 9KW with an X-ray source of Cu K α 1 (λ = 1.5406 Å) at 45 KV and 200 mA (scan range: 1.5-30°) A Nanoscope atomic force microscope (Icon) and a OCA20, were utilized for the measurement of AFM iamges, SKPM and contact angles. A CHI voltammetric analyzer was utilized for the measurement of cyclic voltammetry in DMSO (anhydrous) solution (the scanning rate: 100 mV s¹), by using a platinum column, Ag/AgCl, and Pt wire (embraced in glass) as the counter, reference, and working electrodes respectively, and tetrabutylammonium perchlorate (100 mM) was added in this process, which acted as the essential supporting electrolyte. In all the above process, dry argon was used to make an inert atmosphere. The software with the name of Gaussian 09, was utilized for the calculation of molecular orbitals and energy levels. A Newport-Oriel® Sol3A, with the maximum power of 450W, was utilized for the measurement of space charge limited current without the simulated solar light and *J-V* curves of the devices with a simulated solar light of Newport-Oriel® Sol3A (450W, AM 1.5 G, 100 mW cm⁻²) in Ar atmosphere. A Keithley 2440 was utilized for the measurement of different device parameters. Bought from the company of PV measurements Inc., a Silicon photodiode detector, which has been calibrated by NREL, was utilized for the measurement of the intensity of light as reference. A IQE 200TM (Newport-Oriel®) which has been calibrated by standard solar cell of silicon/germanium, was utilized for the measurement of EQE spectra. A Dektak 150 was utilized for the measurement of films thickness.

2. Charts, figures and tables



Chart S1. Molecular structures of the reported CILs compounds with high efficiencies.



Figure S1. UV-vis spectra in different states. (a) TPE-1; (b) TPE-2.

Table S1. Opto-electronic properties of TPE-1 and TPE-2.

	solution ^a	na	noaggreg	gate ^b			film				
Compound	λ_{abs}	λ_{abs}	λ_{PL}	Δλ	•	λ_{abs}	λ_{PL}	Δλ	HOMO ^c	LUMO ^c	$E_g^{\ c}$
	[nm]	[nm]	[nm]	[nm]		[nm]	[nm]	[nm]	[eV]	[eV]	[eV]
TPE-1	310	329	443	114		317	483	166	-5.20	-2.80	2.40
TPE-2	316	315	427	112		348	433	85	-5.38	-2.77	2.61

^{a)}In methanol; ^{b)} TPE-1: in water; TPE-2: in methanol; ^{c)} The HOMO /LUMO levels and electrochemical band gaps are calculated based on the CV results, by using E_{HOMO} =-(E_{on}^{ox} - $E_{(Fc/Fc}^+)$ +4.8), E_{LUMO} =-(E_{on}^{red} - $E_{(Fc/Fc}^+)$ +4.8), E_g^{CV} = E_{on}^{ox} - E_{on}^{red} .



Figure S2. Cyclic voltammograms. The balck curve for blank solvent DMSO, while the red one for TPE-1 and the blue one for TPE-2.

Spin speed	$V_{ m oc}$	$J_{ m sc}$	FF	PCE best
[rpm]	[V]	$[mA cm^{-2}]$	[%]	[%]
2000	0.76	15.46	66.98	7.93
3000	0.76	15.85	66.44	8.06
4000	0.76	16.02	68.08	8.27
5000	0.76	15.91	67.12	8.15

Table S2. The PC71BM:PTB7-based device performance with TPE-1 (1 mg/mL) interlayer at different spin speed.



Figure S3. *J-V* characteristics of the devices based on $PC_{71}BM$:PTB7 with TPE-1 interlayer at different spin speed.

Table S3. The PC71BM:PTB7-based device performance with TPE-2 (1 mg/mL) interlayer.

Spin speed	$V_{ m oc}$	$J_{\rm sc}$	FF	PCE best
[rpm]	[V]	$[mA cm^{-2}]$	[%]	[%]
2000	0.77	15.86	66.25	8.09
3000	0.76	16.13	67.08	8.22
4000	0.76	16.86	69.70	8.94
5000	0.76	16.21	67.52	8.35



Figure S4. J-V characteristics of the devices based on PC₇₁BM:PTB7 with TPE-2 interlayer.



Figure S5. The SPD of active blend films with different treatments.



Figure S6. After different treatments, EQE spectra of the devices based on PC₇₁BM:PTB7.

Table S4. Carrier mobility of PC71BM:PTB7 based PSCs incorporated with/without CILs.					
CIL	Hole mobility	Electron mobility			
	$(\text{cm}^2 \text{V}^{-1}/\text{s})$	$(cm^2 V^{-1}/s)$			
None	1.01×10^{-4}	8.36×10 ⁻⁴			
MeOH	2.69×10^{-4}	9.31×10 ⁻⁴			
PFN	3.26×10^{-4}	1.12×10^{-3}			
TPE-1	3.83×10^{-4}	1.41×10^{-3}			
TPE-2	4.39×10^{-4}	1.63×10^{-3}			



Figure S7. The graphical electron distribution of TPE-1 and TPE-2 derived from DFT calculations. The inset figure depicts HOMO /LUMO energy levels of TPE-1 and HOMO-1 /HOMO /LUMO energy levels of TPE-2.



Figure S8. (a) AFM (5×5 μ m) images of PC₇₁BM:PTB7 films without treatment, (b) with TPE-1 interlayer, (c) with TPE-2 interlayer.



Figure S9. After various treatments to the films of PC₇₁BM:PTB7, normalized UV-Visible spectra.



Figure S10. a) PL spectrum of TPE-1 (100 μ M) in the solution of methanol and water. b) AIE titration curves of TPE-2 (10 μ M) in ether/DMSO mixtures with different ether fractions (f_e). The inset photos demonstrate their pictures of emission in aggregation (left) and solution (right); the excited wavelength is 365 nanometer.



Figure S11. FL spectra in different states. (a) TPE-1; (b) TPE-2. The inset photos depict their emission images of solution, nanoparticle and thin film.



Figure S12. Images of TPE-1 and TPE-2 films on a quartz substrate by fluorescence microscopy in the bright filed (left) and under UV illumination (right). The scale bars: $10 \,\mu$ m.

3. Synthetic experiments



Scheme S1. The synthetic route of TPE-1 and TPE-2.

Synthesis of compound 3

Into a Schlenk tube with a volume of 200 mL, we dissolved diphenylmethane (3.36 g, 20 mmol) in 80 mL of tetrahydrofuran (completely dry). After replacing the atmosphere of Schlenk tube by N_2 and cooling the mixture to 0 %, 9.1 mL of *n*-butyllithium in n-C₆H₁₄

was added. The solution changed to red and kept stirring at 0 °C for 0.5 h. Then we dissolved (4-Methoxyphenyl)(phenyl)methanone in 20 mL of tetrahydrofuran, which was added into the Schlenk tube. After its temperature raising slowly to room temperature (RT), the mixture continued to stire another six hours. As monitored by TLC plate, after the reaction was completed, we terminated the reaction by adding saturated solution of NH₄Cl in H₂O. We extracted the solution with CH₂Cl₂ and collected the organic layer. After washed with saturated solution of NaCl in H₂O and dried over MgSO₄ (anhydrous), the organic solvent was removed by rotary evaporation to yield intermediate products. Into a round-bottom flask with the volume of 250 mL, we dissolved the obtained intermediate products in 80 mL of toluene and then heated to 100 °C, then added *p*-toluenesulfonic acid (570 mg, 3.0 mmol) and refluxed overnight. After its temperature cooling to RT, we added 50 mL of the solution of NaHCO₃ in water (10% weight) and collected the toluene layer. The toluene layer was dried over MgSO₄ (anhydrous) and the solvent was removed. The crude product was purfied by silica gel column chromatography with petroleum ether eluent. A white solid was obtained (5.93 g, 90.1%). ¹H NMR conducted in the solvent of CDCl₃ (300 MHz): δ 7.09-7.03 (m, 15 H), 6.94 (d, 2H, J = 8 Hz), 6.64 (d, 2H, J = 8 Hz), 3.74 (s, 3H).

Synthesis of compound 4

Into a Schlenk tube with the volume of 100 mL, after replacing the atmosphere of tube by N₂, we added 10 mL of CH₂Cl₂ (completely dry), which had been dried and stilled over CaH₂, to dissolve compound **3**. Then we cooled the mixture to -78 °C and added a CH₂Cl₂ solution of boron tribromide (1.7 mL, 3.6 mmol) dropwise. Keeping stirred for 60 minutes, and after its temperature raising to RT, we let it stirred for another 12 hour. Afterwards, we added cold water to the solution dropwise to quench the reaction and subside the product. We got the product by filtration and washed the product with de-ionized H₂O. After dried by vacuum drying oven, we got a white solid. ¹H NMR conducted in the solvent of CDCl₃ (300 MHz): δ 7.10-7.04 (m, 14H), 6.90 (d, 2H, *J*= 8 Hz), 6.57 (d, 2H, *J*= 8 Hz), 4.60 (s, 1H). ¹³C NMR conducted in the solvent of THF-*d*₈ (100 MHz,): δ 157.1, 145.0, 141.7, 140.2, 135.2, 133.1, 132.0, 128.1, 126.7, 115.1. IR (KBr) υ (cm⁻¹): 3274, 3054, 3023, 1605, 1510, 1492, 1443, 1265, 1171, 1102, 1030, 829.

Synthesis of compound 5

Into a 200 mL Schlenk tube, after replacing the atmosphere of tube by N₂, we added 15 mL of actone to dissolve compound **4** (696.8 mg, 2.0 mmol) and NaOH (240 mg, 6 mmol).Then after the mixture refluxed for 30 minutes, we added the hydrochloride salt of 3-chloro-*N*,*N*-dimethylpropan-1-amine (470 mg, 3,0 mmol) to the solution quickly under the protection of N₂. After refluxed for 36 hrs and cooled to RT, we removed the salt by filtration and washed the filtrate with 50 mL H₂O in 3 times. We extracted the solution with CH₂Cl₂ and collected the organic layers. After dried over MgSO₄ (anhydrous) and filtered, the solvent was evaporated. We purified the crude product by a silica gel column with the utilization of acetone/N(C₂H₅) (10/1 in volume) as eluent. A white solid was obtained (480 mg, 55.1%). ¹H NMR conducted in the solvent of CDCl₃ (300 MHz): δ 7.12-6.98 (m, 15 H), 6.91 (d, 2H, *J*= 8.7 Hz), 6.51 (d, 2H, *J*= 8.7 Hz), 3.93 (t, 2H, *J*= 6.3 Hz), 2.42 (t, 2H, *J*= 7.2 Hz), 2.24 (s, 6 H), 1.95-1.89 (m, 2 H). ¹³C NMR conducted in the solvent of CDCl₃ (75 MHz): δ 157.7, 144.2, 140.7, 140.2, 136.2, 132.7, 131.5, 127.8, 126.5, 113.8, 66.1, 56.6, 45.6, 27.6. IR (KBr) ν (cm⁻¹): 3054, 3025, 3054, 2946, 2862, 2816, 2766, 1603, 1506, 1465, 1443, 1285, 1244, 1177, 1055, 1034, 826.

Synthesis of TPE-1

Into a 50 mL round bottom flask, we dissolved compound **5** in 3 mL of CH₃COOC₂H₅. Then, we added 1,3-propanesulfonate (305 mg, 2.5 mmol) in 10 mL of CH₃COOC₂H₅ to the solution. Stirred for 5 days at RT, we got the target product by filtration and washed the filter with 15 mL of acetone in 3 times. We recrystallized the product by methanol and obtained a white powder (443 mg, 79.8%). ¹H NMR conducted in the solvent of CD₃OD (300 MHz): δ 7.08-6.99 (m, 15 H), 6.92 (d, 2H, *J*= 8.4 Hz), 6.70 (d, 2H, *J*= 8.4 Hz), 4.03 (t, 2H, *J*= 5.7 Hz), 3.58-3.50 (m, 4H), 3.13 (s, 6H), 2.87 (t, 2H, *J*= 6.3 Hz), 2.28-2.21 (m, 4H). IR (KBr) v (cm⁻¹): 3415, 3047, 2926, 2878, 1602, 1486,

1442, 1181, 1042, 824. HRMS (ESI, m/z): calculated result of $[M + Na]^+$ for $C_{34}H_{37}O_4NaS$, 578.2336; found, 578.2341.

Synthesis of compound 7

Compound **7** was synthetized under the same conditions as the preparation of **3** (white powder, 1.68 g, 53.4%). ¹H NMR conducted in the solvent of CDCl₃ (300 MHz): δ 7.10-7.06 (m, 6H), 7.03-7.00 (m, 4H), 6.93 (d, 4H, *J*= 8.1 Hz), 6.63 (d, 4H, *J*= 8.1 Hz), 3.74 (s, 6H).

Synthesis of compound 8

Compound **8** was synthetized under the same conditions as the preparation of **4** (white powder, 1.07 g, 98.2%). ¹H NMR conducted in the solvent of DMSO- d_6 (300 MHz): δ 9.32 (s, 2H), 7.12-7.09 (m, 6H), 6.93-6.91 (m, 4H), 6.73 (d, 4H, J= 8.1 Hz), 6.48 (d, 4H, J= 8.1 Hz,).

Synthesis of compound 9

Compound **9** was synthetized under the same conditions as the preparation of **5** (white powder, 1.01 g, 63.1%). ¹H NMR conducted in the solvent of CDCl₃ (300 MHz): δ 7.10-7.06 (m, 6H), 7.03-7.00 (m, 4H), 6.91 (d, 4H, *J*= 9.0 Hz), 6.62 (d, 4H, *J*= 9.0 Hz), 3.93 (t, 4H, *J*= 6.3 Hz), 2.42 (t, 4H, *J*= 7.8 Hz), 2.24 (s, 12H), 1.93-1.88 (m, 4H). ¹³C NMR conducted in the solvent of CDCl₃ (75 MHz): δ 157.5, 144.4, 140.2, 139.2, 136.4, 132.6, 131.4, 127.7, 126.1, 113.7, 66.0, 56.5, 45.5, 27.5. IR (KBr) ν (cm⁻¹): 3053, 2946, 2862, 2816, 2765, 1604, 1507, 1465, 1389, 1285, 1244, 1176, 1056, 955, 834.

Synthesis of **TPE-2**

TPE-2 was synthetized in the same conditions as the preparation of **TPE-1** (white powder, 400 mg, 51.3%). ¹H NMR conducted in the solvent of CD₃OD (300 MHz): δ 7.10-7.07 (m, 6H), 6,99-6.97 (m, 4H), 6.91 (d, 4H, *J*= 8.4Hz), 6.70 (d, 4H, *J*= 8.4 Hz), 4.04 (t, 4H, *J*= 5.7 Hz), 3.55 (m, 8H), 3.13 (s, 12H), 2.87 (t, 4H, *J*= 6.3 Hz), 2.28-2.20 (m, 8H). IR (KBr) v (cm⁻¹): 3423, 3038, 2928, 2880, 1603, 1503, 1288, 1248, 1205, 1182, 1062, 1037, 853. HRMS (ESI, m/z): calculated result of [M + H]⁺ for C₄₂H₅₅O₈S₂, 779.3395; found, 779.3400.



Figure S13. FT-IR spectra of TPE-1 and TPE-2 and their neutral precursor compound 5 and compound 9.