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Efficient polymer solar cells based on synergy effect of a novel non-conjugated small-molecule electrolyte and polar solvent

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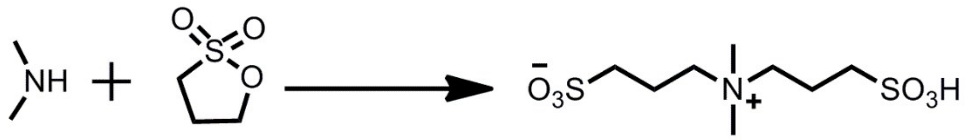
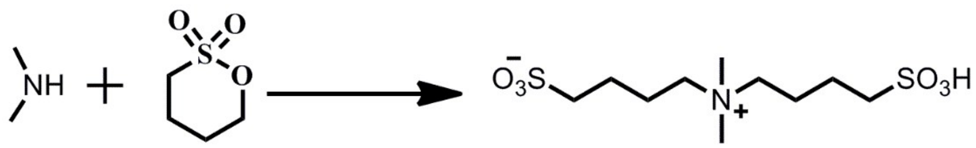
1. Materials



Synthesis of 3-(dimethyl(3-sulfopropyl)ammonio)propane-1-sulfonate (DSAPS)

1, 3-Propanesultone (0.06 mmol, 7.32 g) was added to a solution of dimethylamine (2.0 M solution in tetrahydrofuran, 10 ml) in acetonitrile. The mixed solution was stirred at 70℃ for 2 days under nitrogen. The solution was filtered to give a crude white solid. The crude solid was recrystallized from methanol/ acetonitrile to obtain white crystals (3.5 g, yield: 60%).^{1}H NMR (400 MHz, D_2O), δ (ppm): 3.51-3.47 (m, 4H), 3.13 (s, 6H), 3.00, 2.98, 2.97 (t, 4H), 2.26-2.18 (m, 4H). ^{13}C NMR (400 MHz, D_2O), δ (ppm): 62.57, 50.65, 50.61, 50.57, 47.33, 18.22. MS-ESI-(m/z): calcd. for $C_8H_{19}NO_6S_2$, 289.07; found 287.97.



Synthesis of 4-(dimethyl(4-sulfobutyl)ammonio)butane-1-sulfonate (DSABS)

1,4-butanesultone (0.06 mol, 8.16 g) was added to a solution of dimethylamine (2.0 M solution in tetrahydrofuran, 10 ml) in acetonitrile. The mixed solution was stirred at 70℃ for 2 days under nitrogen. The solution was filtered to give a crude white solid. The crude solid was recrystallized from methanol/ acetonitrile to obtain white crystals (4.2 g, yield: 66%). ^{1}H NMR (400 MHz, D_2O), δ (ppm): 3.28,3.26,3.24(t, 4H), 2.99 (s, 6H), 2.91,2.89,2.87 (t, 4H), 1.89-1.81 (m, 4H), 1.75-1.68 (m, 4H). ^{13}C NMR (400 MHz, D_2O), δ (ppm): 63.54, 50.48, 50.44, 49.97, 21.07, 20.83. MS-ESI-(m/z): calcd. for $C_{10}H_{23}NO_6S_2$, 317.10; found 315.99.

2. Optimized thickness of the DSAPS interlayers.

Table S1. The PTB7:$PC_{71}BM$-based device performance with DSAPS (1.5 mg/mL) interlayer.

the spin speed [rpm]	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE best [%]
1000	0.76	16.04	67.8	8.25
2000	0.76	16.48	68.3	8.55
3000	0.76	17.36	69.6	9.22
4000	0.76	18.42	69.9	9.79
5000	0.76	17.74	69.0	9.29

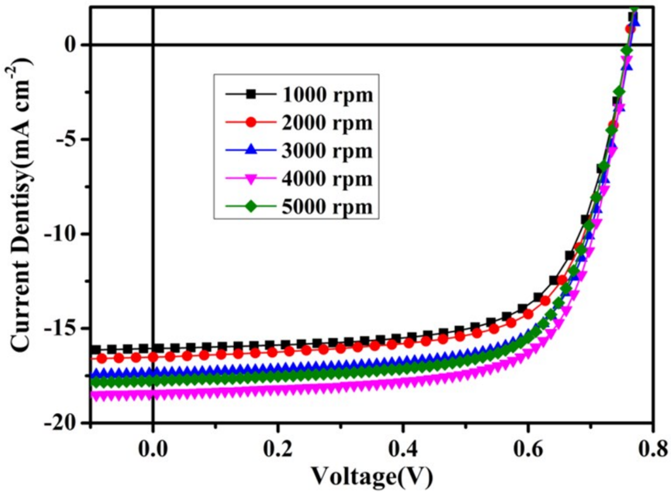


Fig. S1 Current density-voltage (*J-V*) characteristics of the PTB7:$PC_{71}BM$-based devices with DSAPS interlayer.

3. EQE spectra of the conventional PTB7:$PC_{71}BM$ PSCs

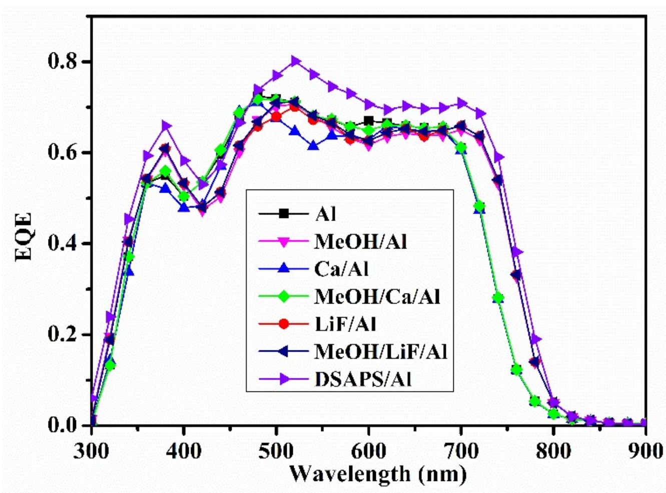


Fig. S2 EQE spectra of the PTB7:$PC_{71}BM$ devices with different treatments.

Table S2. J_{sc}, calculated $J_{sc}{}^{a}$, series resistance (R_s) and shunt resistance (R_{sh}) of the best PTB7:$PC_{71}BM$-based PSCs with or without interlayer and methanol treatment.

Interlayer	J_{sc} [mA cm^{-2}]	$J_{sc}{}^{a}$ [mA cm^{-2}]	R_s [Ω cm^2]	R_{sh} [kΩ cm^2]
None	15.45	15.05	14.59	0.39
MeOH/Al	16.02	15.57	5.53	1.14
Ca/Al	14.94	14.56	7.03	1.28
MeOH/Ca/Al	15.51	15.10	5.72	1.16
LiF/Al	15.83	15.65	8.14	1.25
MeOH/LiF/Al	15.90	15.76	4.39	1.59
DSAPS/Al	18.42	17.74	1.41	0.33

The calculated J_{sc} obtained by integrating the EQE spectra show a ~5% mismatch compared with the J_{sc} value obtained from the *J-V* curves. The mismatch could be explained as follow. First, the illuminating light for *J-V* measurements comprises the full spectrum of simulated sunlight, while the measurements for the EQE test use only single-wavelength light from 300 to 900 nm in intervals of 20 nm. Thus, the light for EQE measurements does not span the full spectrum of simulated sunlight. Second, the EQE is calculated according to the formula EQE= electrons (s)/photons (s). A small deviation (size of the light spot or flatness of the sample) will lead to a reduced EQE. Finally, the EQE measurements were implemented in air without encapsulation, which also affects the value.

4. UPS measurement of ZnO with or without DSAPS interlayer

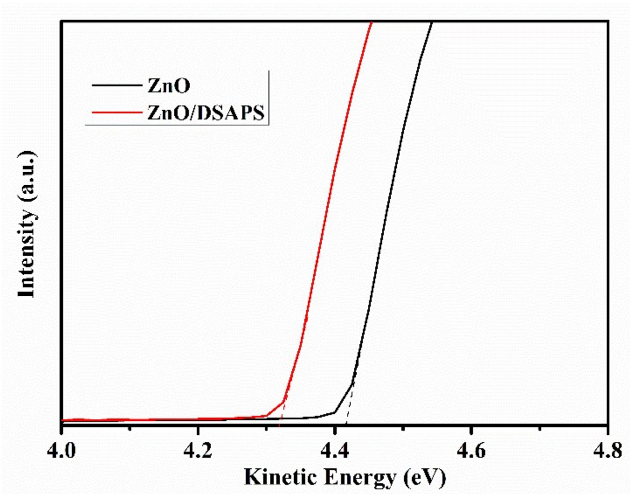


Fig. S3 UPS secondary cutoff of ZnO with or without DSAPS interlayer on top

5. EQE spectra of the inverted PTB7:$PC_{71}BM$ PSCs

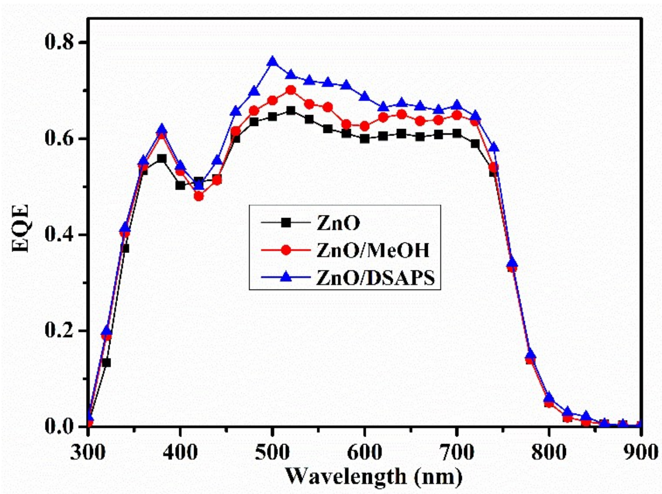


Fig. S4 EQE spectra of the inverted PTB7:$PC_{71}BM$ devices with different treatments.

Table S3. J_{sc}, calculated $J_{sc}{}^{a}$, series resistance (R_s) and shunt resistance (R_{sh}) of the best inverted PTB7:$PC_{71}BM$-based PSCs with different treatment.

Interlayer	J_{sc} [mA cm^{-2}]	$J_{sc}{}^{a}$ [mA cm^{-2}]	R_s [Ω cm^2]	R_{sh} [kΩ cm^2]
ZnO	15.02	14.90	4.84	0.61

ZnO/MeOH	15.80	15.62	4.80	1.07
ZnO/DSAPS	17.01	16.55	4.35	1.52

6. Photovoltaic performance of PTB7:$PC_{71}BM$-based PSCs with DSAPS or DSABS interlayer.

Table S4. Photovoltaic performance of PTB7:$PC_{71}BM$-based PSCs with DSAPS or DSABS interlayer

Interlayer	V_{oc} [V]	J_{sc}[mA cm^{-2}]	FF [%]	PCE best[%]
DSAPS/Al	0.76	18.42	69.9	9.79
DSABS/Al	0.76	18.26	69.7	9.69

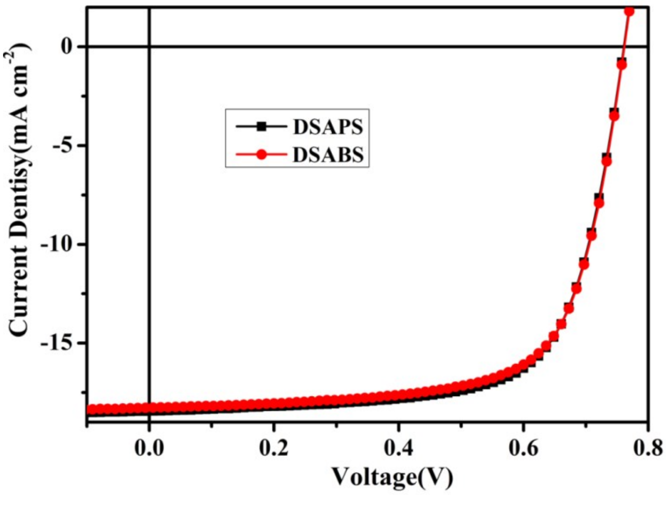


Fig. S5 Current density-voltage (*J-V*) characteristics of the PTB7:$PC_{71}BM$-based devices with DSAPS or DSABS interlayer.

7. UV-vis spectra

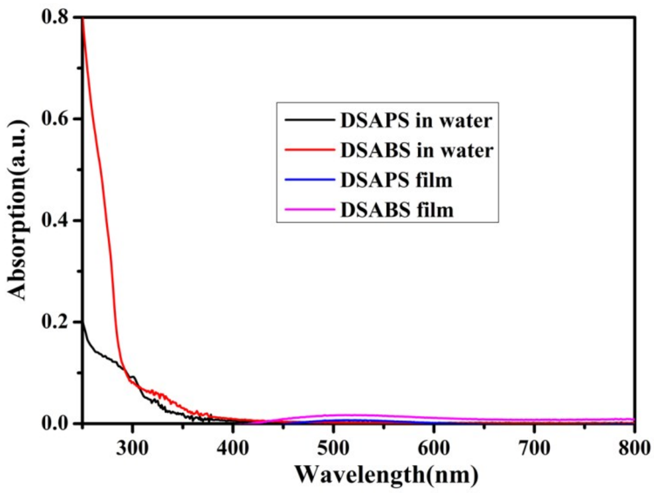


Fig. S6 Absorption (a.u.) of DSAPS and DSABS in water and films in glass.

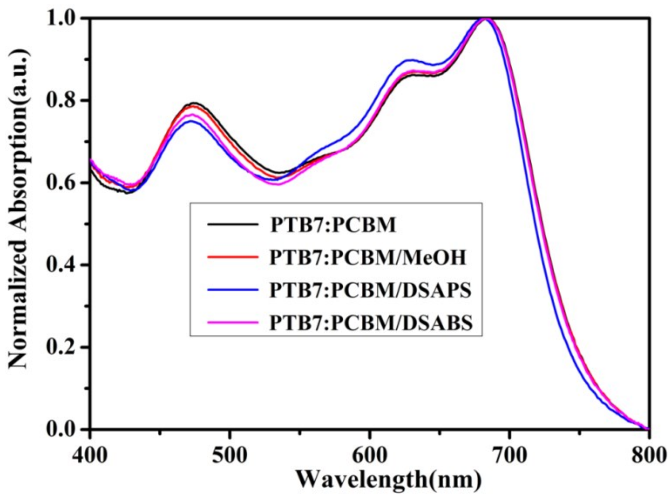


Fig. S7 Normalized absorption(a.u.) of PTB7:$PC_{71}BM$ films with various treatment.

8. The surface morphology and the roughness of AFM images

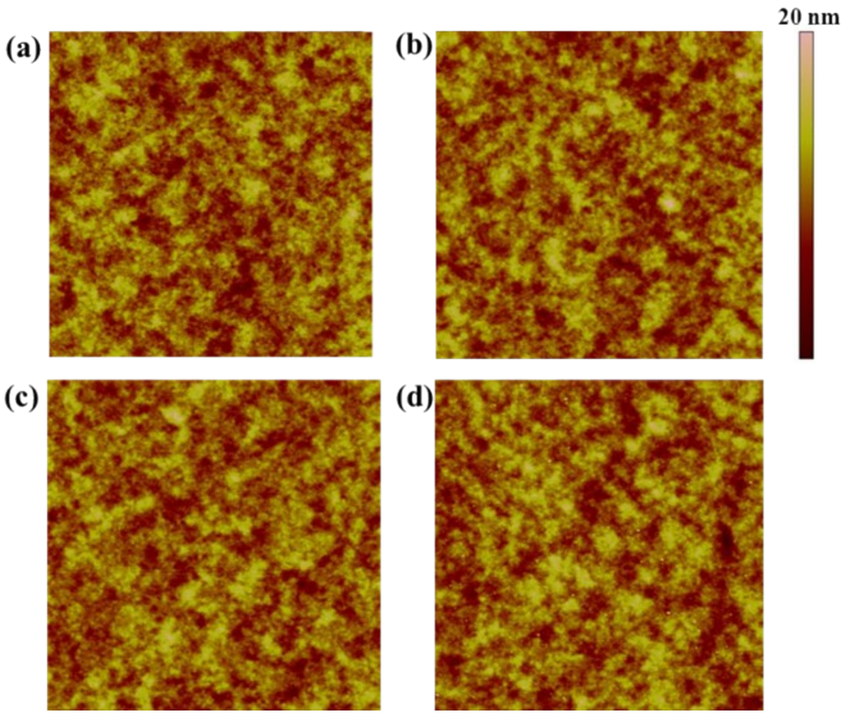


Fig. S8 AFM (5⨯5 μm) images of PTB7:$PC_{71}BM$ films without treatment (a), with methanol treatment (b), with DSAPS interlayer (c), with DSABS interlayer (d).

9. Space charge limited current mobility measurements.

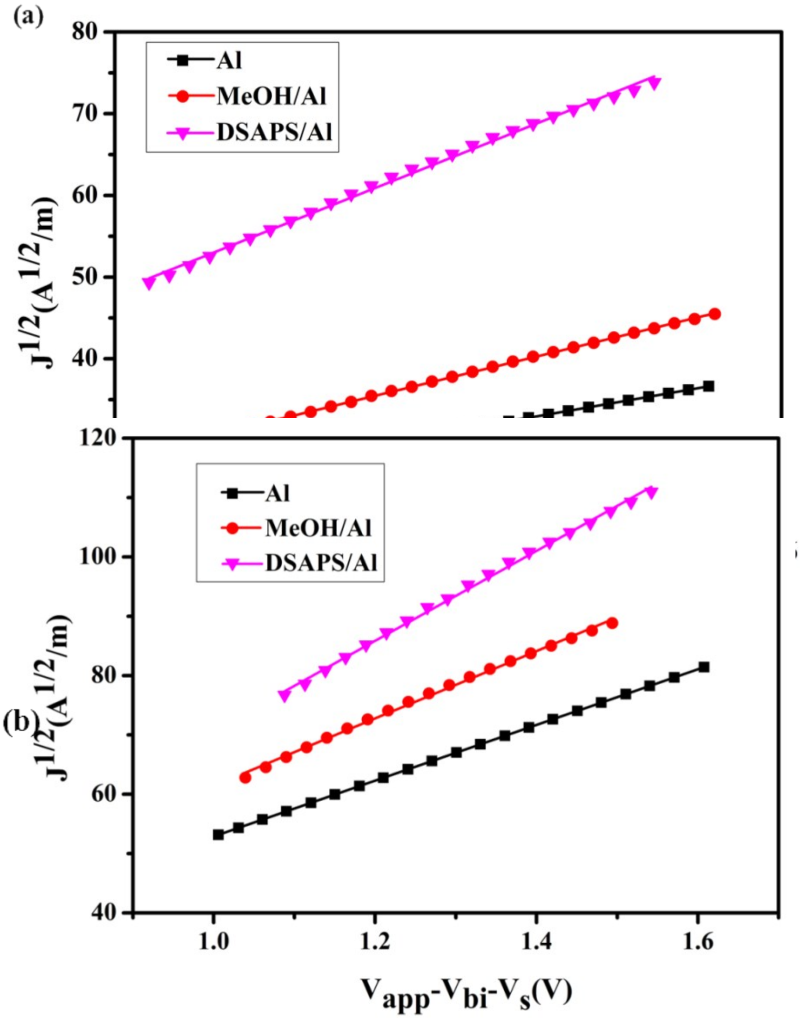


Fig. S9 $J^{1/2}$-V characteristics of hole-only (a) devices and electron-only devices (b).

10. PTB7:PC$_{71}$BM-based PSCs with DSAPS interlayer with different active area

Table S5. Photovoltaic parameters of PTB7:PC$_{71}$BM-based PSCs with DSAPS interlayer with different active area under the illumination of AM 1.5G, 100 mW cm^{-2}.

Active area[mm^2]	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE best (average)^a [%]
4	0.76	18.42	69.9	9.79 (9.68)
12.57	0.76	17.71	69.8	9.41 (9.33)

^{a} The average values of 20 devices

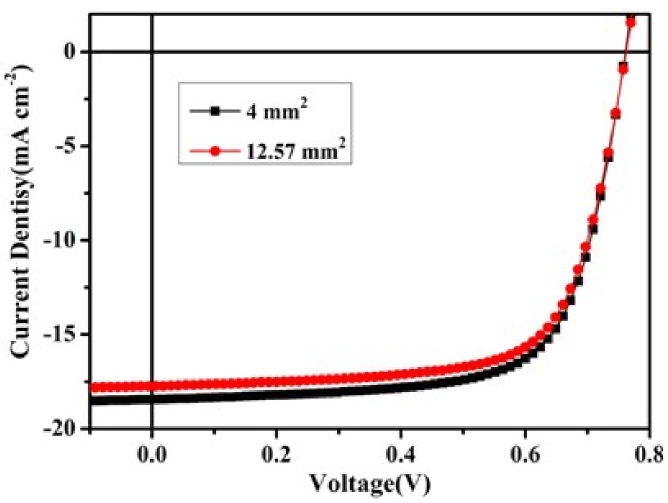


Fig. S10 *J-V* curves of PTB7:$PC_{71}BM$-based PSCs with DSAPS interlayer with different active area.

11. The stability of devices with DSAPS interlayer

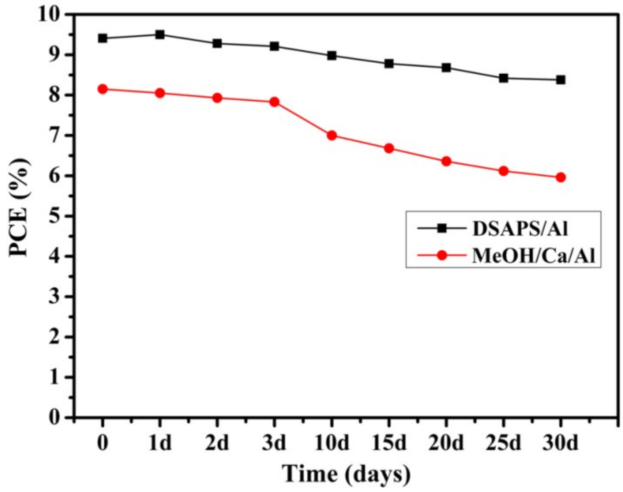


Fig. S11 The curves of PCEs versus time of devices with DSAPS interlayer

12. Some comparisons of the PTB7:$PC_{71}BM$-based PSCs performance with different interlayer modification

Table S6. Some comparisons of the PTB7:$PC_{71}BM$-based PSCs performance with different interlayer modification

Interlayer	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]best	The literature
PFN	0.754	17.46	69.99	9.21	14a
FTBTF-N	0.74	17.23	72.11	9.22	15b
MSAPBS	0.76±0.01	19.25±0.15	68.08±1.0	10.02	17
ZnO/PFN-OX	0.75±0.01	16.63±0.19	74.4±0.8	9.28±0.15	27
DSAPS	0.76	18.42	69.9	9.79	this work