

Supporting information

Development of Julolidine-based Interfacial Modifier for Efficient Inverted Polymer Solar Cells

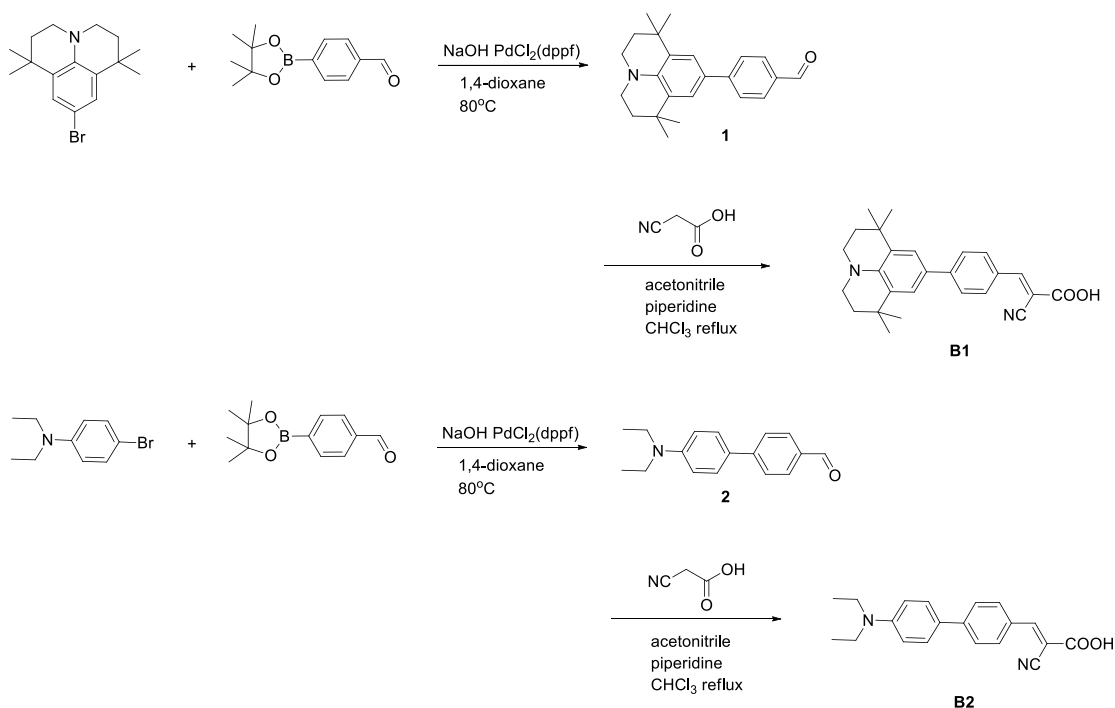
Eun Young Choi,^{a,b} So Youn Nam,^a Chang Eun Song,^a Ki-jeong Kong,^a Changjin Lee,^{a,c} In Hwan Jung^{*a,c} and Sung Cheol Yoon^{*a,b,c}

^a Advanced Materials Division, Korea Research Institute of Chemical Technology (KRICT), Daejeon 305-600, Republic of Korea. E-mail: ihjung@kRICT.re.kr; Tel: +82-42-860-7266 & E-mail: yoonsch@kRICT.re.kr; Tel: +82-42-860-7203.

^b Nanomaterials Science and Engineering, University of Science and Technology (UST), Daejeon 305-350, Republic of Korea,

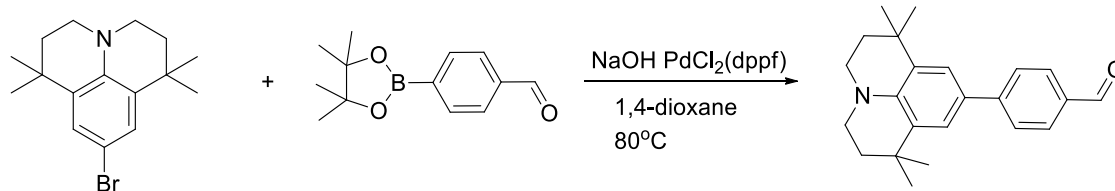
^c Chemical Convergence Materials, UST, Daejeon 305-350, Republic of Korea

1) Synthesis



Scheme S1. Synthetic routes for **B1** and **B2**

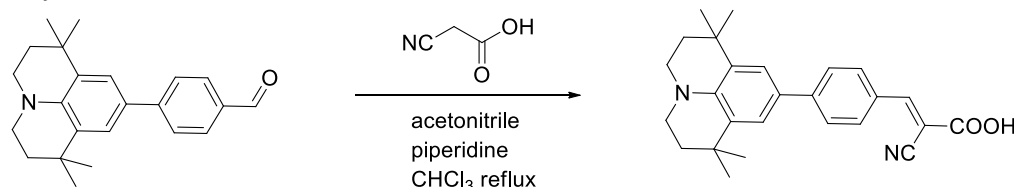
4-(1,1,7,7-tetramethyl-1,2,3,5,6,7-hexahydropyrido[3,2,1-ij]quinolin-9-yl)benzaldehyde (1)



A mixture of 9-bromo-1,1,7,7-tetramethyl-1,2,3,5,6,7-hexahydropyrido[3,2,1-ij]quinoline (2 g, 8.62 mmol), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (2.66 g, 8.62 mmol), NaOH (0.69 g, 17.24 mmol), and PdCl₂(dppf) (0.42 g, 0.52 mmol) was added to dry 1,4-dioxane (80 ml). The reaction mixture was stirred at 80°C under argon for 16h. The mixture was extracted with ethyl acetate. The organic phase was washed with saturated aqueous brine and then dried over anhydrous magnesium sulfate. The solution was concentrated under reduced pressure and purified by column chromatography on silica gel using dichloromethane/hexane (v/v, 1/1). Compound 1 was obtained as a yellow solid (820 mg, 29 %). ¹H NMR (400MHz, CDCl₃) : 9.99 (s, 1H), 7.88 (d, J = 8.4 Hz, 2H), 7.69 (d, J =

8.4 Hz, 2H), 7.36 (s, 2H), 3.24 (t, J = 6.0 Hz, 4H), 1.80 (t, J = 6.0 Hz, 4H), 1.35 (s, 12H)

(E)-2-cyano-3-(4-(1,1,7,7-tetramethyl-1,2,3,5,6,7-hexahydropyrido[3,2,1-ij]quinolin-9-yl)-phenyl)acrylic acid (B1)



A mixture of compound **1** (0.2 g, 0.60 mmol) and cyanoacetic acid (0.15 g, 1.80 mmol) was added to dry chloroform (5 ml), acetonitrile (5 ml) and piperidine (0.12 ml, 1.20 mmol). The solution was refluxed overnight. After cooling the solution was extracted dichloromethane 2 times. Then, the organic layer was washed with saturated aqueous brine and then dried over anhydrous magnesium sulfate. The solution was concentrated by a rotary evaporation and the crude product washed with hexane many times. Compound **B1** was obtained as a dark red solid (178 mg, 74 %). ¹H NMR (400MHz, CD₃CN) : 8.25 (s, 1H), 8.02 (d, J = 8.4 Hz, 2H), 7.78 (d, J = 8.8 Hz, 2H), 7.45 (s, 2H), 3.26 (t, J = 6.0 Hz, 4H), 1.79 (t, J = 6.0 Hz, 4H), 1.33 (s, 12H). MS (MALDI-TOF) *m/z* 400.44 (M⁺), calcd 400.51.

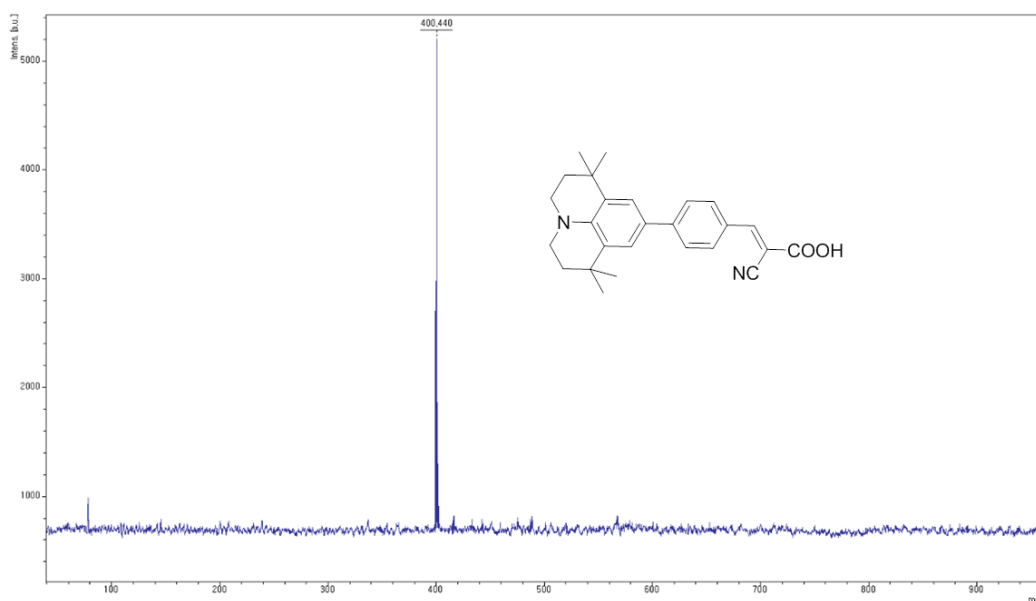
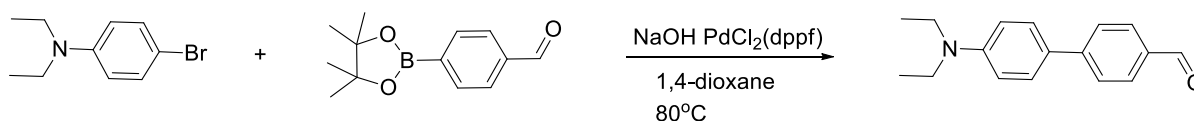


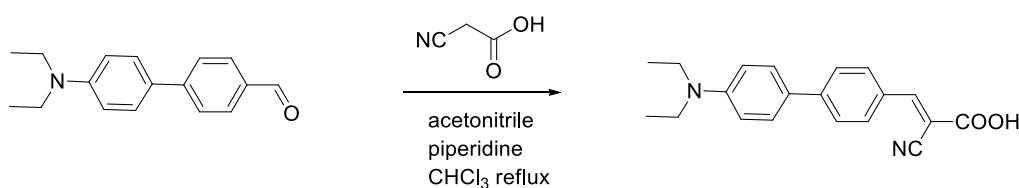
Figure S1. Matrix Assisted Laser Desorption Ionization Mass Spectrometer (MALDI-MS) of **B1**.

4'-(diethylamino)-[1,1'-biphenyl]-4-carbaldehyde (2)



A mixture of 4-bromo-N,N-diethylaniline (1.96 g, 8.60 mmol), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (2 g, 8.60 mmol), NaOH (0.69 g, 17.20 mmol) and PdCl₂(dppf) (0.42 g, 0.52 mmol) was added to dry 1,4-dioxane (80 ml). The reaction mixture was stirred at 80°C under argon for 16h. The mixture was extracted with ethyl acetate. The organic phase was washed with saturated aqueous brine and then dried over anhydrous magnesium sulfate. The solution was concentrated under reduced pressure and purified by column chromatography on silica gel using dichloromethane/hexane (v/v, 1/1). Compound 2 was obtained as a yellow solid (590 mg, 27 %). ¹H NMR (400MHz, CDCl₃) : 9.99 (s, 1H), 7.89 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 9.0 Hz, 2H), 6.76 (d, J = 9.0 Hz, 2H), 3.42 (q, J = 7.2 Hz, 4H), 1.21 (t, J = 7.2 Hz, 6H)

(E)-2-cyano-3-(4'-(diethylamino)-[1,1'-biphenyl]-4-yl)acrylic acid (B2)



A mixture of compound 2 (0.2 g, 0.79 mmol) and cyanoacetic acid (0.20 g, 2.37 mmol) was added to dry chloroform (5 ml), acetonitrile (5 ml) and piperidine (0.16 ml, 1.58 mmol). The solution was refluxed overnight. After cooling the solution was extracted dichloromethane 2 times. Then, the organic layer was washed with saturated aqueous brine and then dried over anhydrous magnesium sulfate. The solution was concentrated by a rotary evaporation, and purified by column chromatography on silica gel using dichloromethane/methanol (v/v, 9/1). Compound B2 was obtained as a yellow solid (230 mg,

90 %). $^1\text{H NMR}$ (400MHz, DMSO- d_6) : 7.89 (d & s, $J = 8.8$ Hz, 3H), 7.70 (d, $J = 8.4$ Hz, 2H), 7.59 (d, $J = 8.8$ Hz, 2H), 6.74 (d, $J = 8.8$ Hz, 2H), 3.42 (q, 4H), 1.12 (t, $J = 7.2$ Hz, 6H). MS (MALDI-TOF) m/z 321.47 (M^+), calcd 320.38.

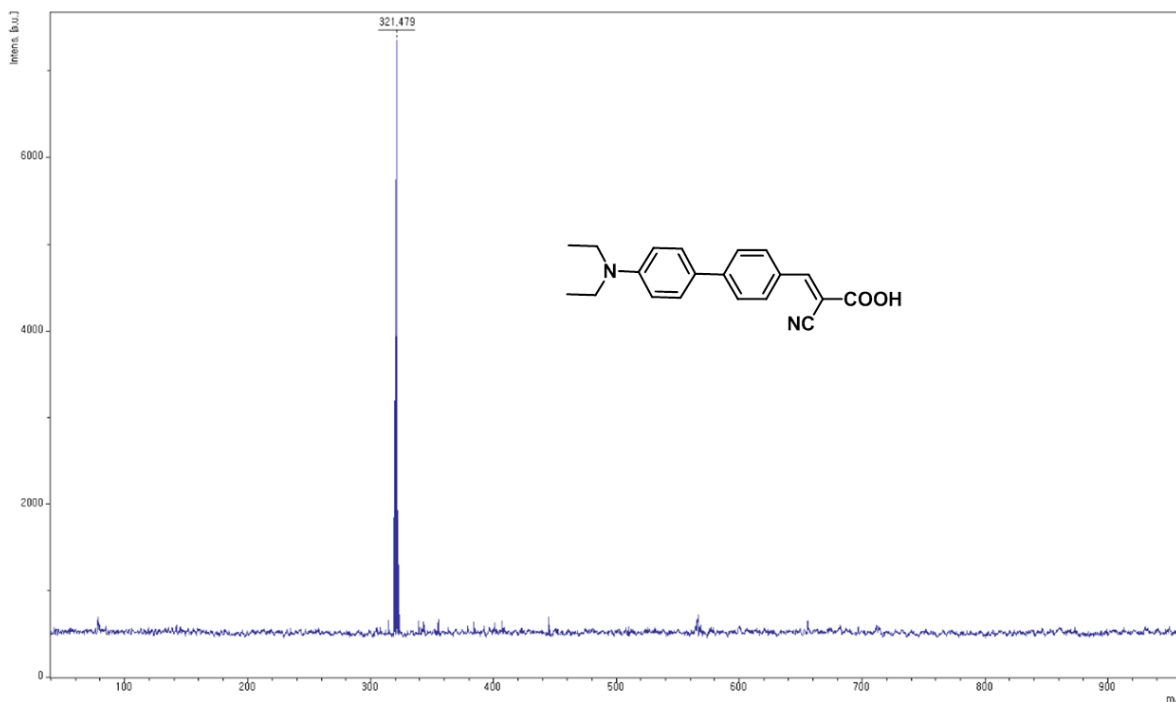


Figure S2. MALDI-MS of **B2**.

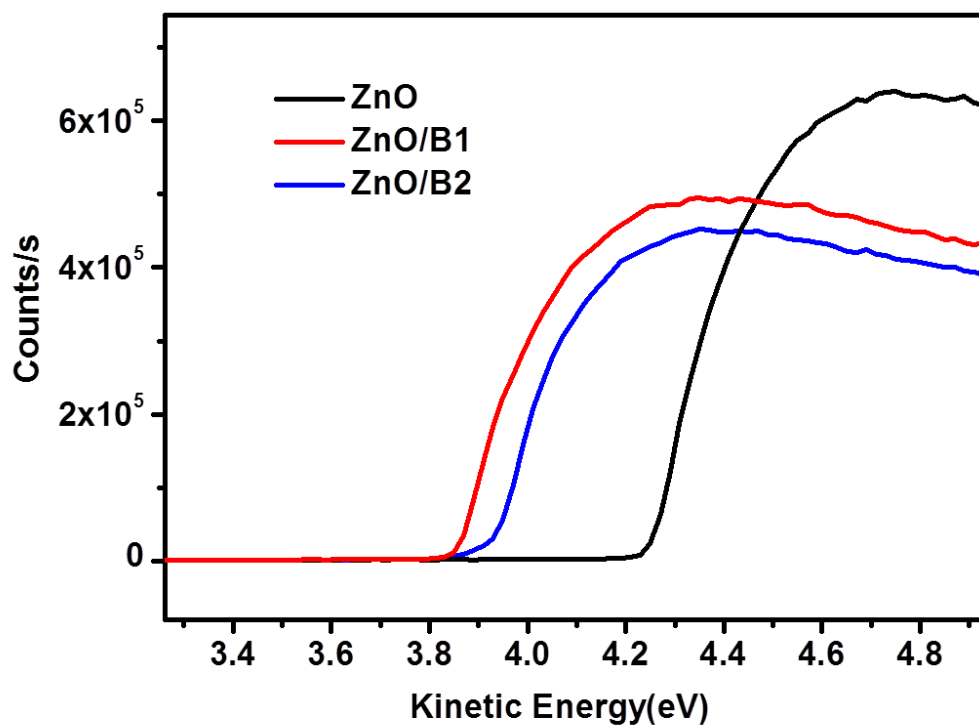


Figure S3. UPS spectra of the ZnO layer with or without IMs in the high binding energy cutoff region.

2) X-ray photoelectron spectroscopy (XPS) study

To provide the surface characteristics of IM coated ZnO film, we conducted XPS analysis for ZnO, ZnO/**B1** and ZnO/**B2**. First of all, Zn 2p 3/2 spectra were shown in Figure S4. As shown Figure S4, 2P 3/2 spectra of bare ZnO film appeared at 1021.6 eV which value is identical with reported previously.¹ The peaks for the ZnO/**B1** and ZnO/**B2** were shifted to the low binding energy of 1021.0 eV and 1021.3 eV, respectively. ZnO/**B1** film showed 0.3 eV lower binding energy than ZnO/**B2** film. These results suggest that ZnO surface make stronger interaction with B1 than B2.²

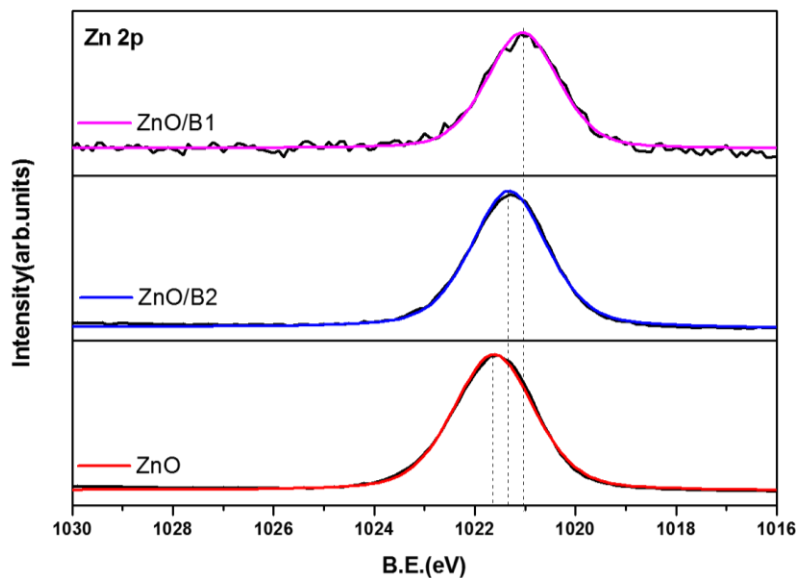


Figure S4. The XPS spectra of Zn 2p of ZnO, ZnO/**B1** and ZnO/**B2**

XPS spectra of O 1s were shown in Figure S5. The peak of ZnO at 530.13 eV due to the O bulk state in ZnO matrix was shifted to 529.80 eV in ZnO/**B1** and 529.84 eV in ZnO/**B2**, respectively.³ The shift to the lower binding energy was caused by hydrogen bonding interaction between the ZnO and IMs. The peak of ZnO at 531.42 eV corresponds to oxygen vacant value in ZnO matrix.⁴ It was also shifted to 531.07 eV in ZnO/**B1** and to 531.16 eV in ZnO/**B2**.

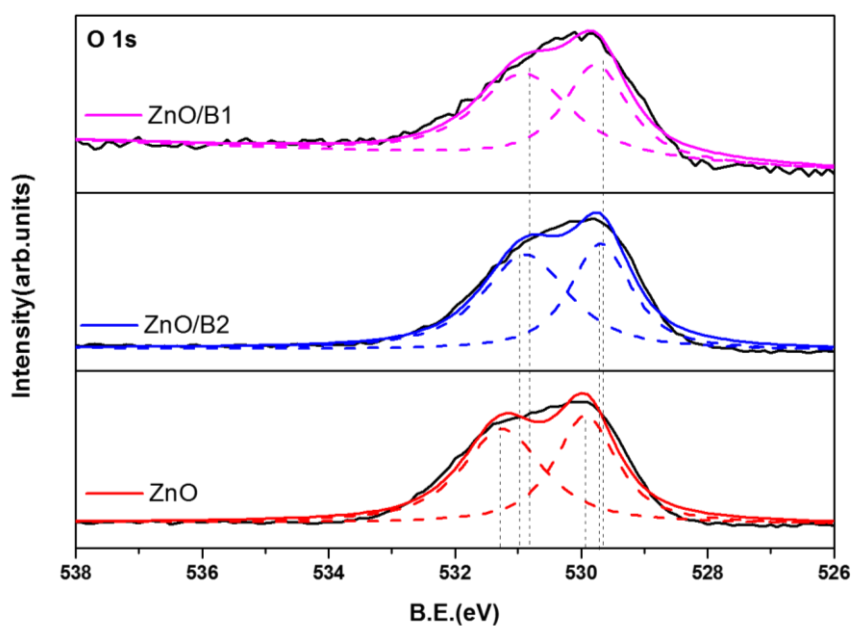


Figure S5. The XPS spectra of O 1s of ZnO, ZnO/B1 and ZnO/B2

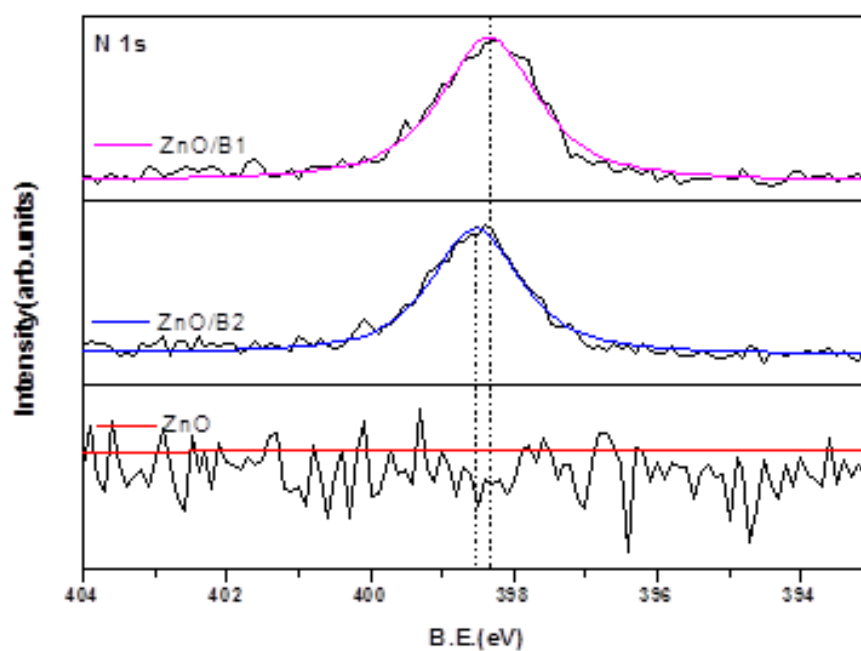


Figure S6. The XPS spectra of N 1s of ZnO, ZnO/B1 and ZnO/B2

The spectra of N 1s were shown in Figure S6. The spectra of N 1s gave direct information about the existence of IM molecules on the ZnO surface because ZnO surface didn't show any nitrogen atoms.

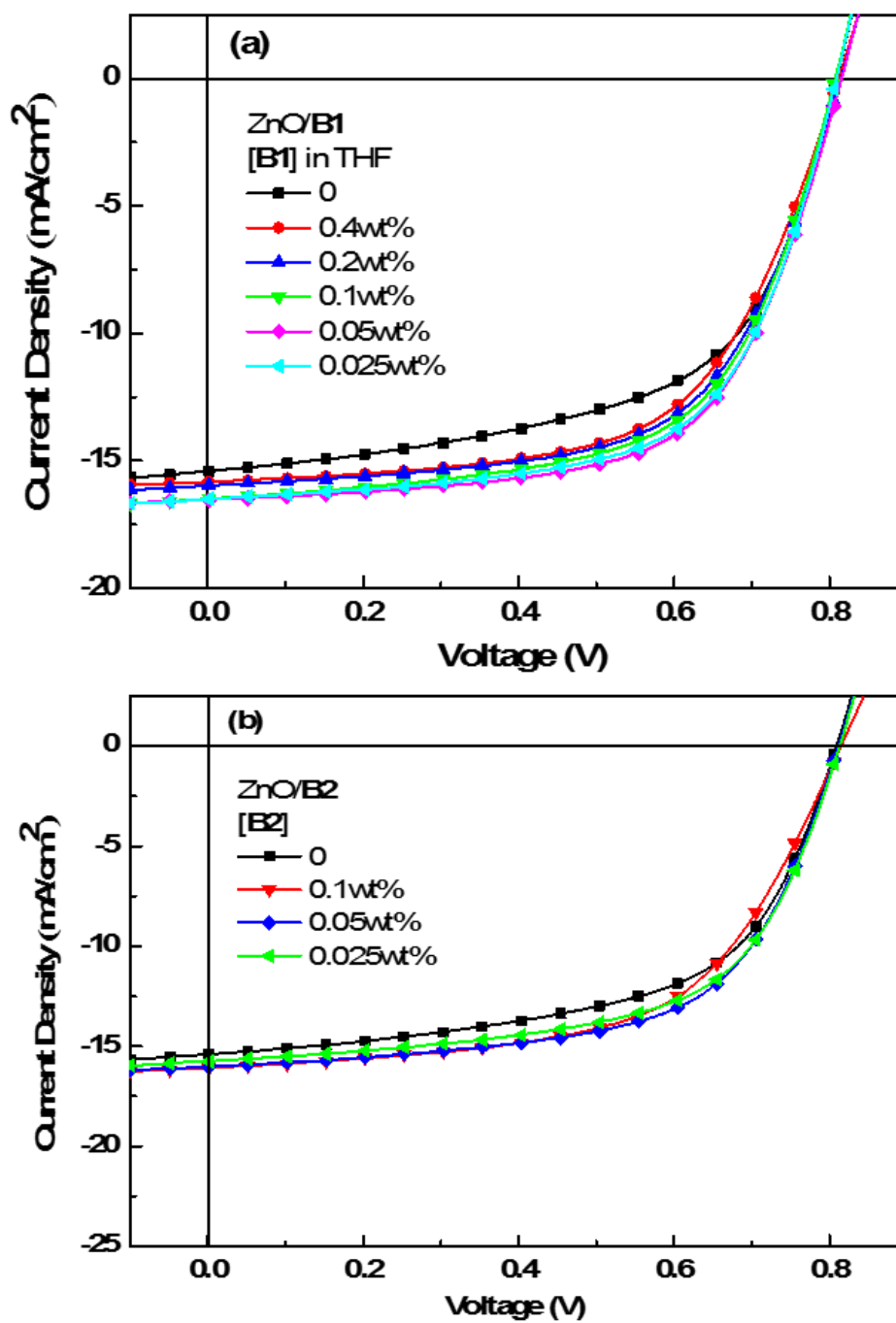


Figure S7. *J-V* characteristics of photovoltaic devices by the concentration of (a) **B1** and (b)

Table S1. The photovoltaic performance of ZnO/**B1** and ZnO/**B2** devices by various conditions in THF

condition	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
ZnO only	0.811 ±0.005	15.30 ±0.15	57.8 ±0.003	7.18 ±0.088
ZnO + B1 0.2 w/v	0.816 ±0.001	16.13 ±0.175	60.8 ±0.003	7.97 ±0.11
ZnO + B1 0.1 w/v	0.807 ±0.004	16.34 ±0.151	62.0 ±0.01	8.16 ±0.10
ZnO + B1 0.05 w/v	0.816 ±0.001	16.55 ±0.150	62.0 ±0.005	8.35 ±0.06
ZnO + B1 0.025 w/v	0.808 ±0.004	16.31 ±0.094	62.7 ±0.004	8.26 ±0.032
ZnO + B2 0.1 w/v	0.812 ±0.004	14.57 ±1.38	59.4 ±0.01	7.533 ±0.040
ZnO + B2 0.05 w/v	0.808 ±0.003	15.78 ±0.256	61.1 ±0.002	7.8 ±0.160
ZnO + B2 0.025 w/v	0.815 ±0.002	15.61 ±0.138	60.3 ±0.010	7.675 ±0.11

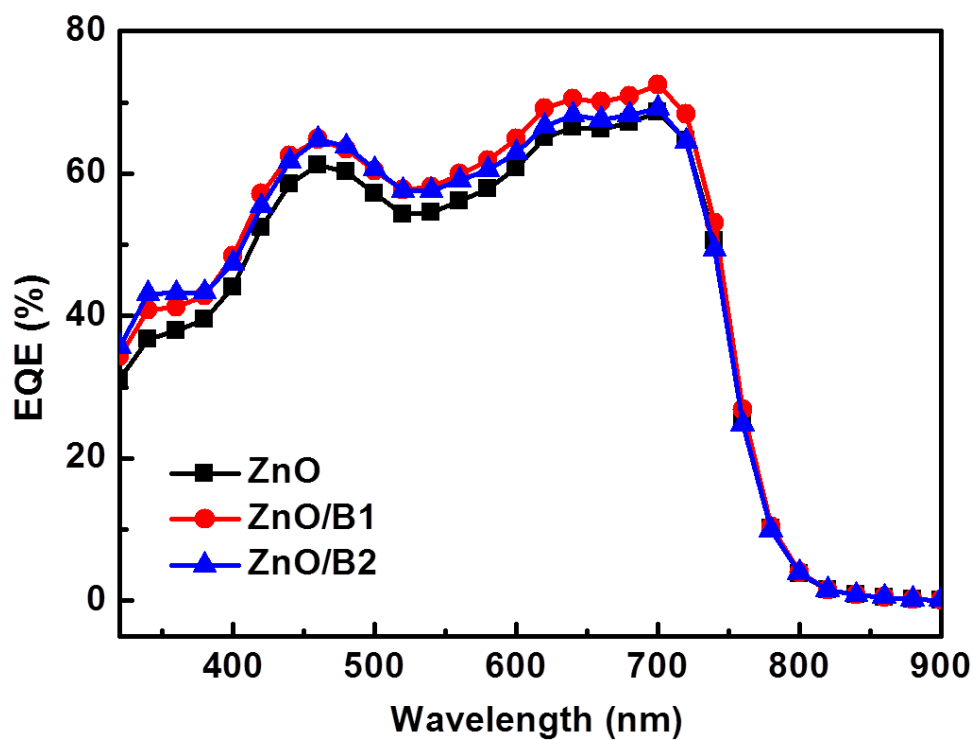
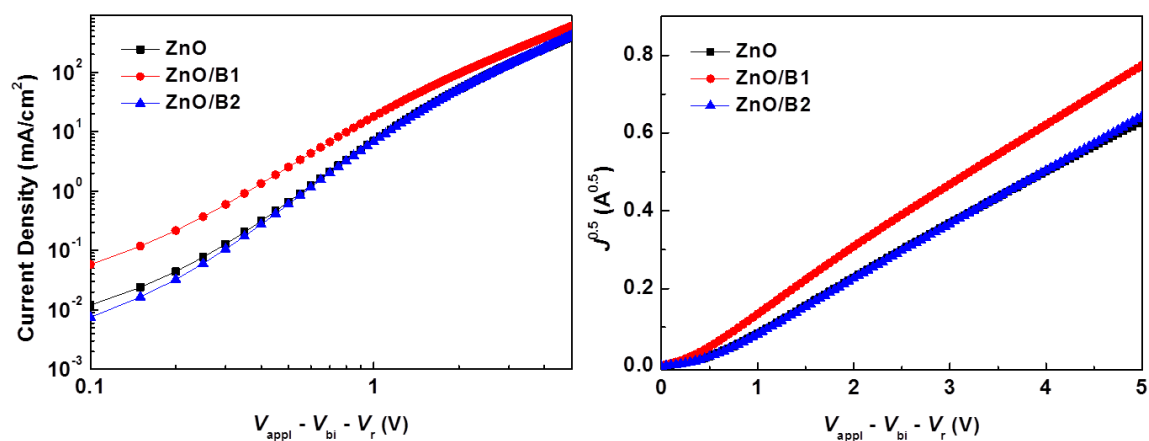


Figure S8. EQE of BHJ photovoltaic devices with an active layer composed of PTB7-Th:PC₇₁BM devices treated with or without IMs, under simulated AM 1.5 G solar irradiation.



ETL	μ_e [cm^2/Vs]
ZnO	1.0×10^{-4}
ZnO/B1	1.5×10^{-4}
ZnO/B2	1.1×10^{-4}

The electron-only devices: ITO/ETL/PTB7-Th:PC₇₁BM/LiF/Al

Figure S9. J - V characteristics of the electron-only devices of PTB7-Th/PC71BM blend films with or without IMs. The mobilities are calculated by fitting the J - V curves in the SCLC regime.

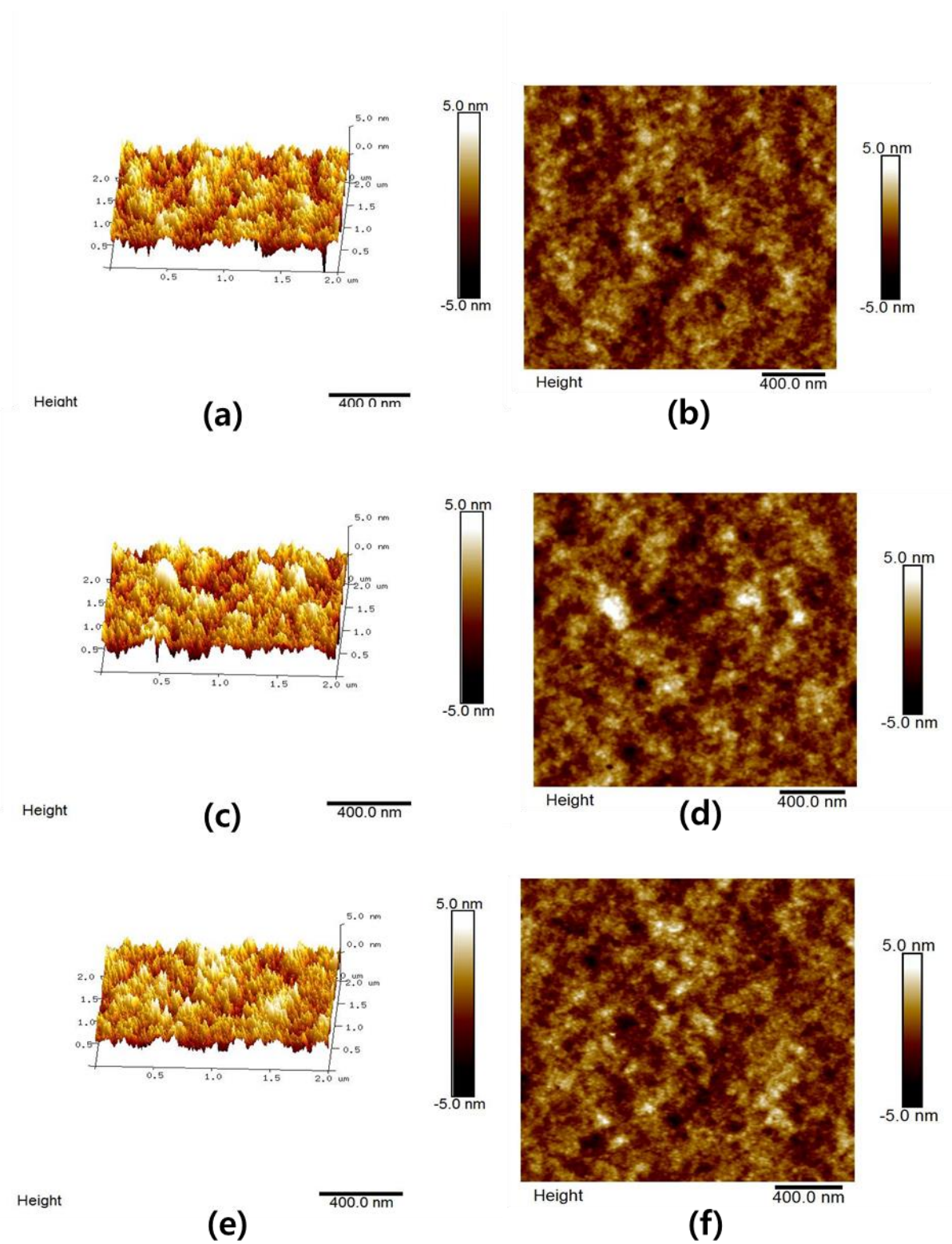


Figure S10. (a, c, e) AFM tapping 3D images ($2\mu\text{m} \times 2\mu\text{m}$) and (b, c, f) height images ($2\mu\text{m} \times 2\mu\text{m}$) of PCE-10:PC₇₁BM active layer: (a, b) ZnO/B1/active layer, (c, d) ZnO/B2/active layer and (e, f) ZnO/active layer

Reference

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