Supplementary Information

Simple molecular structure and efficient triazine-based interfacial layer for high performance organic electronics

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EXPERIMENTAL SECTION:

Materials and Characterization. All reagents were purchased from Sigma-Aldrich (Korea) and Solarmer (China) and used without further purification. Moisture-sensitive reactions were conducted in a N₂ atmosphere. The other materials were common chemicals and were used as received. THF was predried by passage through an alumina column followed by storage over Na/benzophenone prior to use. ¹H NMR spectra were recorded on a Varian Mercury Plus 300 MHz spectrometer (USA) in CDCl₃ using tetramethylsilane as an internal reference. The chemical shifts were recorded in ppm related to the singlet of CDCl₃ at 7.26 for ¹H NMR spectroscopy. The UV-visible absorption spectra were recorded on a JASCO V-570 spectrophotometer (USA). Thermal analysis was carried out on a Mettler Toledo TGA/SDTA 851e (Switzerland) under N₂ atmosphere at a heating rate of 10 °C/min. The performances of conventional OSCs, IOSCs, and PSCs were measured using a calibrated air mass (AM) 1.5 G solar simulator (Oriel Sol3A Class AAA solar simulator, models 94043A (Newport Stratford, Inc.,USA)) with a light intensity of 100 mW/cm² adjusted using a standard PV reference cell (2 cm × 2 cm monocrystalline silicon solar cell, calibrated at NREL, Golden, CO) and a computercontrolled Keithley 2400 (Keithley Instruments, Inc. USA) source measure unit. The external quantum efficiency (EQE) spectrum was measured using an Oriel IQE-200 (Newport Stratford,Inc.,USA) equipped with a 250-W quartz tungsten halogen lamp as the light source and a monochromator, an optical chopper, a lock-in amplifier, and a calibrated silicon photodetector. While measuring the J-V curves for the OSC devices, a black mask was used and only the effective area of the cell was exposed to light irradiation. Atomic force microscopy (AFM) was used to measure film thickness, roughness, and surface morphologies in tapping mode acquired with a XE-100 (Park System Corp, Korea). Electrochemical impedance

spectroscopy (EIS) was measured with a VersaSTAT-3 (Princeton Applied Research, USA) work station with an ac signal of 25 mV in the frequency range of 1 Hz-1 MHz. Mott-Schottky analysis was performed in dark. The capacitance-voltage measurements were conducted at a frequency of 100 kHz. All photoemission measurements were carried out in a PHI-5000 Versa Probe II (ULVAC-PHI, Inc. Japan) ultrahigh vacuum surface analysis system equipped with a He-discharge lamp (21.22 eV) and a monochromatic Al k α X-ray. All spectra were measured at a pressure of 1 × 10⁻⁶ Pa. Water contact angles were measured using a contact angle 101 measuring system (Plasma systems and materials, Korea).

Conventional OSCs fabrication:

Indium tin oxide (ITO)-coated glass substrates were cleaned by sonication in acetone, detergent, deionized water, and IPA, and then dried in an oven, followed by a plasma treatment. A thin hole-collection layer (ca. 35 nm) of PEDOT:PSS (Clevios P VP AI 4083, filtered at 0.45 μ m) was spin-cast on the pre-cleaned ITO-coated glass substrates and baked at 140 °C for 15 min under ambient conditions. The photoactive layer PTB7:PC₇₁BM (10:15 mg mL⁻¹) was prepared by spin casting in chlorobenzene (CB) solution with the addition of a small amount of 1,8-diiodooctane (DIO) (CB:DIO = 100:3, V/V) at 1000 rpm for 40 s in a dry box, dried in covered glass petri dishes at room temperature for 30 min. The thickness of the PTB7:PC₇₁BM photoactive layer was about 100 nm. PO-TAZ and Ph₃P=O were spin cast atop the photoactive layer from IPA solution at a concentration of 0.5 mg mL⁻¹ at 2500 rpm. The thickness of the PO-TAZ layer was about ~5 nm. For reference device, LiF was thermally deposited for 0.7 nm. The Al electrode was thermally deposited for 100 nm through a mask under vacuum. All steps except

the processing of PEDOT:PSS were performed in a glove box. The photoactive area of the device was 0.09 cm².

IOSCs fabrication:

The IOSCs were fabricated using commercial ITO glass an R_{sheet} value of ~12 Ω sq⁻¹. The ZnO precursor solution was spin-cast on top of the ITO glass substrate. The films were annealed at 150 °C for 10 min in air. The ZnO-coated substrates were transferred to a N₂-filled glove box. A solution containing a mixture of PTB7:PC₇₁BM (8:12 mg) was dissolved in CB (1 mL). PTB7 used in this study was purchased from 1-material (Korea); PC₇₁BM was purchased from Solenne BV (Netherlands). The mixed solutions were stirred at 50 °C for 12 h. DIO was then added at a volume ratio of 3% to the solutions containing PTB7:PC₇₁BM before the spin-coating process. The active layer was then deposited onto the ZnO-coated ITO glass by spin coating at 1,200 rpm for 40 s, after passing the solution through a 0.20-µm PTFE syringe filter. The photoactive layer was approximately 100 nm thick. The PEDOT:PSS (Clevios P VP AI 4083), diluted using IPA with a ratio of PEDOT:PSS:IPA of 1:10, PO-TAZ (0.5 mg mL⁻¹), was deposited onto the active layer by spin coating at 2500 rpm in a glove box. Finally, the top-electrode Ag metal was deposited through a shadow mask by thermal evaporation in a vacuum of approximately 3 × 10⁻⁶ Torr. The device area, defined through the shadow mask, was 0.11 cm².

PSCs fabrication:

Two-step process: The ZnO precursor solution was spin-cast on top of the commercial ITO electrode. The films were annealed at 150 °C for 10 min in air. To deposit the perovskite (CH₃(NH₃)PbI₃) layer, first, a layer of PbI₂ (Aldrich) was spin-coated on top of the ZnO-coated

ITO substrate using a 0.87 M DMF solution. After the PbI₂ layer was dried in air, a CH₃NH₃I/IPA solution (40 mg/mL) was spin-coated on top of the PbI₂ layer at a spin rate of 6,000 rpm to form the perovskite structure. Then, a thin PO-TAZ layer was spin-coated on top of the ZnO layer. A ~200-nm-thick HTM layer was deposited by spin coating the Spiro-OMeTAD solution. A Spiro-OMeTAD solution was prepared by dissolving 80 mg of Spiro-OMeTAD in 1 mL of CB, to which 28.5 μ L of 4-tert-butyl pyridine (t-BP) and 17.5 μ L of lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI) solution (520 mg LI-TSFI in 1 mL of acetonitrile, Sigma-Aldrich (99.8%) (Korea) were added. Finally, a ~150-nm-thick Ag electrode was deposited by thermal evaporation.

OFETs fabrication:

OFETs with bottom contact and top gate structure were fabricated on pre-cleaned glass substrates. Au (20 nm) bottom contact source/drain electrodes were deposited by thermal evaporation after the lithography process. PO-TAZ (5 nm) was spin coated on top of the Au electrode and then annealed at 150 °C to remove residual solvent. NDI polymer solution (poly[N,N'-bis(2-octyldodecyl)-naphthalene-1,4:5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-(2,2'-bithiophene), (P(NDI2OD-T2), Polyera ActivInk N2200) was prepared by dissolving P(NDI2OD-T2) in a mixture of anhydrous 1,2-dichlorobenzene (Sigma-Aldrich, Korea) anhydrous at 1 wt % concentration. Poly[2,5-bis(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione-(*E*)-[2,2-bithiophen]-5-yl)-3-(thiophen-2-yl)acrylonitrile]-co-selenophene-vinylene-selenophene [CNTVT:SVS (9:1)] copolymers were dissolved in anhydrous 1,2,4-trichlorobenzene (Sigma-Aldrich, Korea) with 0.5% concentration and heated at 80 °C overnight. The poly(methyl methacrylate) (PMMA, 400 nm) layer was coated by spin casting at 2000 rpm

for 60 s. The PMMA films were annealed at 80 °C for 20 min. All spin coating and annealing processes were carried out in a N₂-filled dry box. Al (50 nm) gate electrodes were deposited by thermal evaporation through a shadow mask. The electrical characterizations of OFETs were carried out in a N₂-filled glove box (O₂, H₂O < 0.1 ppm). Bottom gate top source/drain contact PC₇₁BM OFETs were fabricated on heavily doped *n*-type silicon substrates with a 300-nm-thick thermally grown SiO₂, which served as the gate dielectric. Then, a 30-nm-thick PC₇₁BM layer was spin coated on the substrates and annealed at 120 °C for 20 min. PO-TAZ (5 nm) was spin coated on top of the PC₇₁BM layer and then annealed at same conditions with semiconductor film. Samples were then loaded into a vacuum thermal evaporation system and a 50-nm-thick Au layer was deposited through a shadow mask. Then, the samples were transferred into a N₂-filled glove box for electrical testing.



Fig. S1 (a) Synthetic pathway of PO-TAZ. (b) TGA thermogram. (c) UV-Visible absorption spectra in CF and thin film state.

Synthesis

2-Chloro-4,6-diphenoxy-1,3,5-triazine (1). 2,4,6-Trichloro-1,3,5-triazine (cyanuric chloride) (2.5 g, 14 mmol) was dissolved in acetone (200 mL) and cooled to 0 °C. In a different flask, phenol (2.6 g, 28 mmol) was reacted with NaOH (1.1 g, 28 mmol) in water (200 mL) to form a clear aqueous solution. Then, the aqueous solution was added dropwise to the cyanuric chloride solution. After stirring at 0 °C for 12 h, the mixture was poured into water (200 mL) to form a white precipitate. The white precipitate was filtered and washed with water and then ethanol. The product was purified by recrystallization with hexane to produce a white solid. Yield: 77%. ¹H NMR (300 MHz, CDCl₃, δ): 7.43 (m, 4H), 7.28 (dd, 2H), 7.14 (m, 4H). ¹³C NMR (300 MHz, CDCl₃, δ): 121.19, 121.39, 126.09, 126.52, 129.48, 129.69, 151.26, 151.52, 172.39, 173.66, 173.72.

2-(2,4-Difluorophenyl)-4,6-diphenoxy-1,3,5-triazine (2). Toluene (24 mL), ethanol (12 mL), and 2 M aqueous Na₂CO₃ (15 mL) were added to a mixture of 2-chloro-4,6-diphenoxy-1,3,5-triazine (1 g, 3 mmol), 2,4-difluorophenylboronic acid (0.53 g, 2 mmol), and tetrakis(triphenylphosphine)palladium (0.134 g, 0.2 mmol). The mixture was refluxed for 12 h under a N₂ atmosphere. After cooling to room temperature, the mixture was extracted with dichloromethane and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using dichloromethane/hexane (4:1) as the eluent to produce a white solid. Yield: 58%. ¹H NMR (300 MHz, CDCl₃, δ): 8.24 (m, 1H), 7.45 (t, 4H), 7.28 (m, 6H), 6.92 (m, 2H). ¹³C NMR (300 MHz, CDCl₃, δ): 105.14, 105.48, 105.81, 111.60, 111.65, 111.88, 111.94, 119.66, 119.72, 119.77, 121.33, 121.38, 121.48, 126.03, 129.10, 129.46, 133.69, 133.72, 133.86, 151.51, 151.66, 161.22, 161.39, 163.85, 164.01, 164.74, 164.90, 167.24, 173.49.

2-(3-(Diphenylphosphoryl)-2,4-difluorophenyl)-4,6-diphenoxy-1,3,5-triazine (PO-TAZ). In a 50-mL three-neck flask, 2-(2,4-difluorophenyl)-4,6-diphenoxy-1,3,5-triazine (1.5 g, 4 mmol) was dissolved in 30 mL of THF and the temperature of the reaction was cooled down to -78 °C. To the reaction mixture, lithium diisopropylamide (2 M, 2.5 mL) was added dropwise, and the temperature of the reaction was maintained at -78 °C for another 1 h. Then, 2 mL of chlorodiphenylphosphine (1.1 g, 5 mmol) was added to the mixture and the solution was stirred overnight. The reaction was quenched with water, extracted with ethyl acetate (EA), and dried over anhydrous Na₂SO₄. After removing the solvent, the residue was diluted with 30 mL of dichloromethane and 20 mL of hydrogen peroxide (30%), and then stirred at room temperature for 3 h. The crude product was extracted with chloroform and purified by column chromatography on silica gel using pure EA as an eluent to afford PO-TAZ as white solid. The overall yield was 72%. ¹H NMR (300 MHz, CDCl₃, δ): 8.24 (m, 1H), 7.74 (m, 4H), 7.59-7.42 (m, 6H), 7.34 (m, 4H), 7.21 (m, 2H), 7.16 (d, 4H), 6.98 (m, 1H). ¹³C NMR (300 MHz, CDCl₃, δ): 111.25, 112.45, 112.95, 113.27, 120.73, 120.79, 120.87, 121.35, 126.05, 128.56, 128.73, 129.46, 131.10, 131.24, 131.88, 132.24, 132.27, 133.36, 137.71, 137.75, 127.87, 151.52, 161.16, 161.27, 164.74, 164.85, 164.96,168.33, 168.43, 172.54, 172.98, 173.06. MS (EI, m/z): [M]+ calcd for C₃₃H₂₂F₂N₃O₃P, 577.52; found, 578.14.



Fig. S2 ¹H NMR of PO-TAZ (top) and magnified image of aromatic region (bottom).



Fig. S3 XPS core level spectra for PO-TAZ on Al.



Fig. S4 Secondary cut-off spectra for PO-TAZ thin layer on ITO substrate.



Fig. S5 UPS spectra of PTB7:PC₇₁BM devices without and with PO-TAZ.



Fig. S6 EQE spectra of PTB7:PC₇₁BM-based conventional OSCs (a) and IOSCs (b) without or with PO-TAZ.



Fig. S7 AFM images of PTB7:PC₇₁BM (a) and PTB7:PC₇₁BM/PO-TAZ (b) thin films.



Fig. S8 Contact angles of PTB7:PC₇₁BM and PTB7:PC₇₁BM/PO-TAZ using water and diiodomethane droplets.



for the Fig. **S9** Schematic energy diagrams devices with device structure (a) ITO/ZnO/PTB7:PC71BM/PEDOT:PSS/Ag. ITO/ZnO/PO-TAZ/ (b) PTB7:PC71BM /PEDOT:PSS/Ag. The vacuum level shift and energy band bending is depicted under open circuit conditions (flat band condition) and under short-circuit conditions.



Fig. S10 Dark *J*–*V* curves of PTB7:PC₇₁BM-based IOSCs without or with PO-TAZ.



Fig. S11 Contact angles of thin films of (a) ZnO and (b) ZnO/PO-TAZ using water droplets.



Fig. S12 (a) *J*–*V* curves of PTB7-Th:PC₇₁BM-based IOSCs without or with PO-TAZ.

(b) EQE spectra of PTB7- Th:PC₇₁BM-based IOSCs without or with PO-TAZ.



Fig. S13 (a, b) Schematic of electron-only device structure for the devices without or with PO-TAZ. (c) electron mobility graphs of the devices without or with PO-TAZ.



Fig. S14 (a) Nyquist plots of the IOSCs without or with PO-TAZ at 0 V with frequency ranging from 1 Hz to 1 MHz. (b) Bode phase plots of the IOSCs without or with PO-TAZ. (c) Mott-Schottky plots of the IOSCs without or with PO-TAZ.



Fig. S15 (a) Dark *J–V* curve of PSCs without or with PO-TAZ. (b) histogram of PSCs (ITO/ZnO/perovskite (CH₃(NH₃)PbI₃)/Spiro-OMeTAD/Ag) efficiencies for 20 samples without PO-TAZ. (c) with PO-TAZ. The Gaussian fits are provided as a guide for better understanding.



Fig. S16 Transfer curves of (a) pristine P(NDI20D-T2), (b) CsF-treated and (c) PO-TAZ-treated devices during 50 cycles scan in bias stress test.



Fig. S17 Transfer curve of (a) pristine $PC_{71}BM$, (b) PO-TAZ-treated devices during 50 cycles scan in bias stress test.

Cathada	Voc	J _{SC}	FF	PCE ^a	Average	R _S	
Cathode	(V)	(mA cm ⁻²)	(%)	(%)	PCE (%)	$\Omega~{ m cm^2}$	
LiF/Al	0.74	14.56	65.91	7.14	7.07	2.59	
Ph ₃ P=O/Al	0.70	15.00	57.71	6.12	6.04	5.13	

Table S1. Summary of the photovoltaic properties of conventional OSC devices with LiF and Ph₃P=O as the interlayer.

^aThe PCE values are obtained from over 10 devices.

Table	S2.	Summary	of c	contact	angles	and	surface	energies	of the	devices	without	and	with	PO-
TAZ.														

Film	θ (H ₂ O) (Degree)	θ (CH ₂ I ₂) (Degree)	γ ^{d a} (mJ m ⁻²)	γ ^{d b} (mJ m ⁻²)	$\gamma_s = (\gamma^{d a} + \gamma^{p b})$ (mJ m ⁻²)
PTB7:PC71BM	119	92.2	11.6	0.2	11.8
PTB7:PC71BM/PO-TAZ	92.1	48	34.2	1.2	35.4

 γ_s : surface energy

 $\gamma^{d\ a}$: Dispersion of surface tension.

 $\gamma^{p \ b} :$ Polar component of surface tension.