Supporting Information

Efficient Interface Modification via Multi-Site Coordination for Improved Efficiency and Stability in Organic Solar Cells

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Supporting data



Fig. S1 Absorption spectra of 1-DPAQ and $SnO_2/1$ -DPAQ films and those treated with CF rinsing.



Fig. S2 Water contact angles (WCAs) and diiodomethane contact angles (DCAs) of ITO/SnO₂/PM6 and ITO/SnO₂/BTP-eC9.

Table S1	WCA, DCA and the calculated	l surface free energy (y _s) of PM6 and BTP-eC9.

ETL	WCA (°)	DCA (°)	γ _s (mN/m)
PM6	104.4	52.6	34.61
BTP-eC9	93.5	45.4	37.17



Fig. S3 The conductivity curves of SnO_2 , 1-DPAQ and $SnO_2/1$ -DPAQ based on the device structure: ITO /ETL (100 nm)/Al (100 nm).



Fig. S4 Chemical structures of the active layer materials used in this work.



Fig. S5 Energy level diagram of the materials used in this work.



Fig. S6 (a) Current density-voltage (*J-V*) and (b) external quantum efficiency (EQE) curves of the inverted OSCs using SnO_2 , 1-DPAQ and $SnO_2/1$ -DPAQ as ETLs with a different concentration of 1-DPAQ.



Fig. S7 (a) *J-V* and (b) EQE curves of the PM6:BTP-eC9-based OSCs using SnO_2 , 1-DPAQ and $SnO_2/1$ -DPAQ as ETLs with a different annealing temperature of 1-DPAQ.



Fig. S8 EQE curves of the PM6:PB2F:BTP-eC9-based OSCs with SnO₂/1-DPAQ as ETL.



Fig. S9 Dark-current of the inverted PM6:BTP-eC9-based OSCs using SnO_2 , 1-DPAQ and $SnO_2/1$ -DPAQ as ETLs.



Fig. S10 (a) V_{OC} and (b) J_{SC} versus light intensity for the initial and aged devices (without capsulation) in ambient air for 24 h based on different ETLs.

Table S2 Comparison of slope values for the V_{OC} and J_{SC} versus light intensity plots for the initial and aged devices (without capsulation) in ambient air for 24 h based on different ETLs.

ETL	Initial		Aged	
	Slope (V _{OC})	Slope (J _{SC})	Slope (V _{oc})	Slope (J _{SC})
SnO ₂	1.27 k _в T/q	0.98	1.40 k _B T/q	0.98
1-DPAQ	1.47 k _B T/q	0.97	1.46 <i>k</i> _B T/q	0.97
SnO ₂ /1-DPAQ	1.19 k _B T/q	0.99	1.21 k _B T/q	0.99

Materials

Etched indium tin oxide (ITO) glass (surface resistance is $10 \Omega \cdot sq^{-1}$) was purchased from CSG HOLDING Co., Ltd (China). PM6 and BTP-eC9 were purchased from Solamer.

Chlorobenzene (CB), methanol (MAL) and 1,8-diiodooctane (DIO) were all purchased from Alfa Aesar. PB2F was synthesized by our laboratory.

Synthesis of 1-DPAQ

1-chloroanthraquinone (10.72 g, 44.3 mmol) and 3-dimethylaminopropylamine (155 mL) were stirred in a 500 ml flask. After heated at 100°C for 4 h, the flask cooled to room temperature and condensed by rotary evaporator. Then, the solution was washed by the mixed solution of CH_2Cl_2 and HCl. 25 g NaOH was then added to adjust basicity for aqueous phase, which was then washed by CH_2Cl_2 . The obtained organic phase was dried using anhydrous Na_2SO_4 . The product was purified by chromatography using the mixed eluent of CH_2Cl_2 and MeOH. The quality of the dried product is 13.0 g (95% yield). δ H(600 MHz, CDCl₃) 9.78 (1H, s), 8.30–8.26 (1H, m), 8.24 (1H, dd, J 7.6, 0.6), 7.76 (1H, td, J 7.6, 1.1), 7.70 (1H, td, J 7.6, 1.1), 7.59 (1H, d, J 7.1), 7.54 (1H, t, J 7.9), 7.10 (1H, d, J 8.5), 3.41 (2H, dd, J 12.5, 6.9), 2.45 (2H, t, J 7.0), 2.28 (6H, s), 1.93 (2H, p, J 7.0).



Scheme 1. Synthesis route of 1-DPAQ.

Device Fabrication

The glass substrates sputtered with indium tin oxide ITO were ultrasonic twice with detergent, tap water, deionized water and ethanol before use, and then blown dry with nitrogen. The washed ITO glass substrate was dried and treated with UV-ozone (UVO) for 15 min, and then SnO₂ solution was spin-coated at a speed of 3000 rpm for 30 s, and the obtained layers were treated with or w/o thermal annealing at 150 °C for 10 min. 1-DPAQ of 0.2 mg/mL in methanol solution was coated onto the SnO₂ layer, which was sequentially moved to the N₂-glovebox. The photoactive layer was formed by spinning PM6:BTP-eC9 (1:1.2 w/w, with concentration of 8 mg/ml in CF) blend solution with 0.5 vol% DIO as additive and then annealed at 90 °C for 10 min. Ternary active layer is composed of PM6, PB2F and BTP-eC9 with a weight ratio of

0.8:0.2:1.2 and the film fabrication processes are consistent with those of the binary systems. The obtained active layer thickness was about 100 nm. Finally, MoO_3 (10 nm) and Al (100 nm) was thermally evaporated in a vacuum with base pressure 3×10^{-5} mbar as the top electrode.

Instrumentation and Characterization

Heating stage SH-2 was purchased from Oriental Equipment (Beijing) Co. Ltd. Device characterization of current density-voltage (J-V) performance was tested in a N_2 -filled glove box with a standard sunlight AM 1.5G (100 mV/cm² from SAN-EI LTD, AAA grade) by computer controlled Keithley 2400 Source Meter. EQE curves are measured in atmospheric environment on the QE-R3011 system provided by Enli technology (Taiwan) Co. LTD. The film thickness of the device was measured by spectroscopic ellipsometry (SE 850 DUV). The UV-Vis absorption spectra were measured by Shimadzu UV-2600. XPS data were measured by an ESCA Lab220i-XL electron spectrometer (VG Scientific Ltd., UK) from VG Scientific using 300 W Al Ka radiation operated at a base pressure of 3×10^{-9} mbar. UPS measurement was carried out by the KRATOS Axis Ultra DLD spectrometer with a bias voltage of –9 V under room pressure of 3×10^{-8} Torr and He I (21.22 eV) was applied as the excitation source. Contact angel results were measured by Krüss DSA30 optical contact angle meter. Electrochemical impedance spectroscopy was performed using a two-electrode system under dark with CHI660E electrochemical workstation with the frequency range from 1 MHz to 100 Hz. AFM was measured by Bruker-Fastscan ultrafast DI atomic force microscope. Platinum wire electrode, glass carbon electrode and silver ion electrode were purchased from Aidahengsheng Technology development Co. LTD. We have simulated the J-V characteristic of OSC with an equivalent circuit, and a wellknown equation can be obtained:

$$J = J_{ph} - J_0 \left\{ exp \left[\frac{q(V + AJR_s)}{k_B T} \right] - 1 \right\} - \frac{V + AJR_s}{AR_{sh}} \# (1)$$

Where J_{ph} is the photocurrent, J_0 is the reverse dark current density, q is the electron charge, k_B is the Boltzmann constant, A is the solar cell area, T is the ambient

temperature, R_s is the series resistance and R_{sh} is the shunt resistance. Under the open circuit condition and $J_{ph}=J_{sc}$, the equation can be transformed into:

$$V_{OC} \approx \frac{k_B T}{q} \ln \left(\frac{J_{SC}}{J_0} \right) \#(2)$$

Theory Calculation Details

The binding interactions of the molecules and SnO₂ surfaces were performed using the DFT plane-wave method and the Vienna ab initio simulation package (VASP).¹ The projector-augmented wave (PAW) method was used to describe the ionelectron interactions. ² The generalized gradient approximation (GGA) parametrized by Perdew, Burke, and Ernzerhof (PBE) was applied for the exchange-correlation functional.³ The cutoff energy for the plane wave basis set was 400 eV. The convergence criterion for the self-consistent iteration was set at 10⁻⁵ eV. The Gamma centered Monkhorst-Pack scheme with $4 \times 4 \times 2$ *k*-points were set to be. ⁴ Molecules were simulated in a cubic box that was 20 × 20 × 50 Å long on each side-sufficiently large to ensure negligible interactions between neighboring cells.

Reference

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