Electronic Supplementary Information

Template molecular weight-dependent PEDOT surface energy: Impact on the photovoltaic performance of bulk-heterojunctions

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Experimental Section

Materials

PSSs with Mws of 70, 200, 500 and 1000 KDa were purchased form Alfa Aesar, Sigma-Aldrich, Alfa Aesar and Adamas, respectively. EDOT monomer was purchased from Sigma-Aldrich. Ammonium persulfate (APS), $FeCl_3$, ethanediamine reducing agent and organic solvents including acetone, isopropanol, chloroform and methanol were purchased from Sinopharm Chemical and used without further purification. PBDB-T, PM6, D18-Cl, Y6, BTP-ec9 and PDINN were purchased from Solarmer Material Inc.

Synthesis of PEDOT:PSSs

A typical protocol for the synthesis of PEDOT:PSS aqueous dispersion is as follows: PSS powder was added into 30 mL of deionized water, then EDOT monomer was added with slow stirring speed for 60 min and pH was adjusted to 1, followed by dropping binary oxidants of APS and $FeCl_3$ with high speed stirring (800 rpm), the mole ratio of APS to $FeCl_3$ to EDOT is 1.5:0.01:1. The above mixture was stirred at room temperature for 52 h, and dialyzed using a membrane with a 1000 cutoff for 5 d. Then the PEDOT aqueous dispersion was concentrated to the mass concentration of equal to 1.3% by rotary evaporation.

By varying the PSS M_w, four PEDOT:PSS products were synthesized.

Preparation of dedoped PEDOT:PSSs

A typical dedoping protocol is shown as follows: PEDOT:PSS aqueous dispersion (100 uL, 1.3 wt%) was added into 4 mL of deionized water. Then NaOH solution (500 uL, 12 M) was added, followed by ethanediamine (100 uL) under vivid stirring. Subsequently, the mixture was stirred at room temperature for 30 min. Finally, a blue aqueous dispersion was obtained.

Measurements and characterizations

UV-vis-NIR absorption and transmittance spectra were recorded on a UV-3100 UV-VIS spectrophotometer. Dynamic light scattering (DLS) measurements were performed using a Malvern Nano-ZS90 particle size/Zeta potential analyzer. XPS and UPS tests were conducted on a Thermo Scientific ESCALAB 250Xi instrument. AFM

measurements were performed using Park XE-100 instrument by tapping mode. Conductive devices with configuration of ITO/PEDOT:PSS sample/Al were fabricated with the following steps. Firstly, PEDOT:PSS aqueous dispersion was spin-coated onto clean ITO substrate and annealed at 150 °C for 15 min. Then, the samples were transferred into the N_2-filled glovebox. Finally, aluminum (100 nm) was thermally evaporated at about 5×10^{-4} Pa. *I–V* curves were detected in a glovebox by a Keithley 2420 source measurement unit under dark. CV studies were carried out on a CHI660D electrochemical workstation using three-electrode system (a polymer-coated ITO glass working electrode, an Ag/AgCl reference electrode, a Pt wire counter electrode) in dichloromethane solution of 0.1 M tetrabutylammonium hexafluorophosphate. Contact angle studies were carried out on a JC2000C1 static contact angle instrument. An AFM method has been employed for determining microscopic γ_s of PEDOT:PSSs based on the nanofriction investigations, which was described by Zubar et. al in detail [1]. Briefly, the friction force (angle of the cantilever twist) was recorded by an AFM (XE-100, Park Systems, Korea) when scanning in contact with the surface of samples. The scanning speed was 2 μm/s and the normal load was 5 nN. The force constant of AFM probe (DNP-S10, Brucker, Germany) is 0.12 N/m. The curvature radius of AFM probe is about 7 nm. The specific surface energy is proportional to the obtained angle of cantilever twist as follows:

$$\Delta TA \propto F_{fr} \propto \gamma_s$$

where ΔTA represents the angle of the cantilever twist, F_{fr} represents the friction between AFM tip and sample surface, and γ_s represents the specific surface energy.

OSCs fabrication and characterization

OSCs were fabricated as a layer stack of ITO/HTL/BHJ/PDINN/Ag. Firstly, the ITO glass substrates were sequentially sonicated in detergent solution, deionized water, acetone, and isopropanol. Then, the substrates were further dried with nitrogen flow and subjected to an oxygen plasma treatment step for 8 min. Next, PEDOT:PSS P-70 (or P-200, P-500 and P-1000) aqueous dispersion was spin-coated onto the substrate and then annealed at 150 °C for 15 min. The film thicknesses of P-70, P-200, P-500 and P-1000 are 37, 45, 45 and 48 nm, respectively. PBDB-T:Y6 (ratio 1:1.2, 16 mg mL^{-1} in

chloroform, 0.5 vol % 1-chloronaphthalene additive), PM6:Y6 (ratio 1:1.2, 16 mg mL^{-1} in chloroform, 0.5 vol % 1-chloronaphthalene additive), D18:Y6 (ratio 1:1.55, 13 mg mL^{-1} in chloroform), or PM6:BTP-ec9 (ratio 1:1.2, 16.5 mg mL^{-1} in chloroform, 0.5 vol % 1,8-diiodooctane additive) was then spin-coated at 3000 rpm for 30 s. PBDB-T:Y6, PM6:Y6 or PM6:BTP-ec9 film was annealed at 85 °C for 5 min. As for D18:Y6, the film was treated with 0.3 mL chloroform in a culture dish with a diameter of 7 cm for 1 min. The film thicknesses of active layers are 110 nm. Subsequently, PDINN (1 mg mL^{-1} in methanol) was spin-coated at 3000 rpm for 30 s and the film thickness is 8 nm. Finally, Ag was thermally evaporated at about 5×10^{-4} Pa. The device area is 0.045 cm^2. *J–V* characteristics were detected in a glovebox by a Keithley 2420 source measurement unit under 100 mW cm^{-2} (AM 1.5 G) irradiation. Light-intensity dependence measurements were recorded using the same instrument. Hole-only devices were fabricated with a device configuration of ITO/HTL/active layer/MoO_3/Ag. sEQE and EL measurements were performed following the method reported by Sun et al.[2] Surface morphologies of BHJ layers on various HTLs were detected by an Agilent 5400 AFM instrument.

Supplementary Figures and Tables

Table S1. Physico-chemical properties of PEDOT:template conducting complexes reported in literature.

Template	Molecular weight Template (KDa)	Physical-chemical properties PEDOT conducting complex				Reference
		σ (S cm^{-1})	WF (eV)	H_2O resistance	pH	
PSTFSI	350 20	1±0.05 0.7±0.05	5.3 5.3	—	—	*Macromolecule* 2017, 50, 1959.
PSTFSIx-PS18Gr6y	44 96 112 127 144	＜1.36	—	—	—	*Macromol. Rapid Commun.* 2020, 41, 2000134.

	135 208					
poly(ViEtImY)	Unknown	0.064	—	θ_{H2O} 91.2°	—	*J. Polym. Sci., Part A: Polym. Chem*. 2008, 46, 3150.
P(SS-NMA）	Unknown	1.5	—	90% RH Stability	—	*Polymer* 2011, 52, 5065.
P(SS-Co-TFPMA)	Unknown	16.8	5.28	—	—	*ACS Appl. Mater. Interfaces* 2020, 12, 17799.
SPAA	35.5	0.0002	—	—	—	*Polymer* 2010, 51, 1231.
LS (SL)	～10-100	0.027	5.09	θ_{H2O} (120s) ～40°	—	*ACS Sustainable Chem. Eng.* 2019, 7, 961.
	5.5	0.05	—	—	3.6	*J. Mater. Chem. A* 2015, 3,21537.
Nafion (PFSA) (PFI)	Unknown	2.0 ±0.3	—	—	—	*ACS Appl. Mater. Interfaces* 2020, 12, 29807−29817
		0.062	5.4-5.7	θ_{H2O} 90.7°	2.64	*Nat. Energy,* 2022, 7, 352.
		0.594	5.21	θ_{H2O} 107°	—	*Synthetic Metals*. 2012, 162, 941 - 947.
SAF	7.471	3.12	5.1	waterproof	6	*J. Power Sources* 2017, 4, 29-38.
GSL	24.9	0.0264	5.16	—	—	*ACS Appl. Mater. Interfaces* 2016, 8, 12377.
	24.9	0.164	4.92	—	3.40	*J. Mater.*

						Chem. C 2016, 4, 5297.
CS	~10^3	0.576	—	—	—	*J. Mater. Chem. C.* 2015, 3, 8881.
MNSF	~2-3	< 0.0001	5.29	—	2.82	*Adv. Energy Mater.* 2017, 7, 1601499
PTEB	3.7 5.1	4.0 2.8	—	—	—	*J. Polym. Sci., Part A: Polym. Chem..* 2007,46, 2536.
SNC	Unknown	189	—	—		*Chem. Eng. J.* 2021, 418, 129533.
SPI	Unknown	0.004	—	—	—	*Synth. Met.* 2021, 162, 941–947.
BSPF	Unknown	0.048	5.08	—	3.00	*Macromol. Mater. Eng.* 2016, 301, 133.
PDAS	Unknown	0.14	5.38	—	7	*ACS Sustainable Chem. Eng.* 2019, 7, 8206.

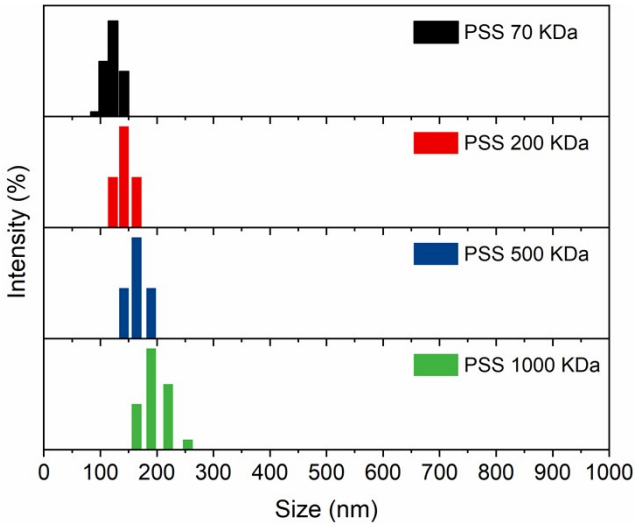

Figure S1. DLS spectra of neat PSS aqueous dispersions

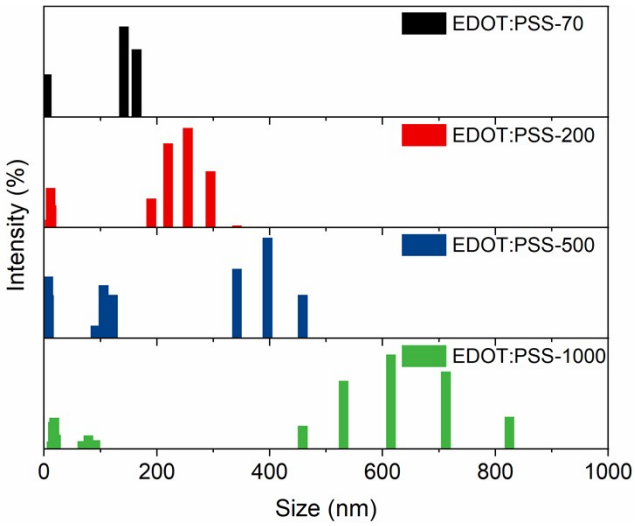

Figure S2. DLS spectra of EDOT:PSS aqueous dispersions

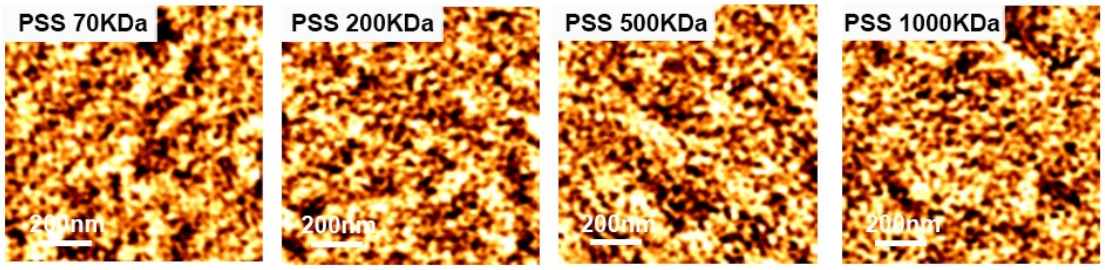

Figure S3. AFM phase images of neat PSS films.

PSS 70KDa	PSS 200KDa	PSS 500KDa	PSS 1000KDa
γ_s=69.74mN/m	γ_s=69.56mN/m	γ_s=67.27mN/m	γ_s=66.67mN/m
Water 20.99°	Water 21.22°	Water 24.77°	Water 25.70°
DIM 33.94°	DIM 34.72°	DIM 41.51°	DIM 43.13°

Figure S4. Contact angles and γ values of neat PSS films.

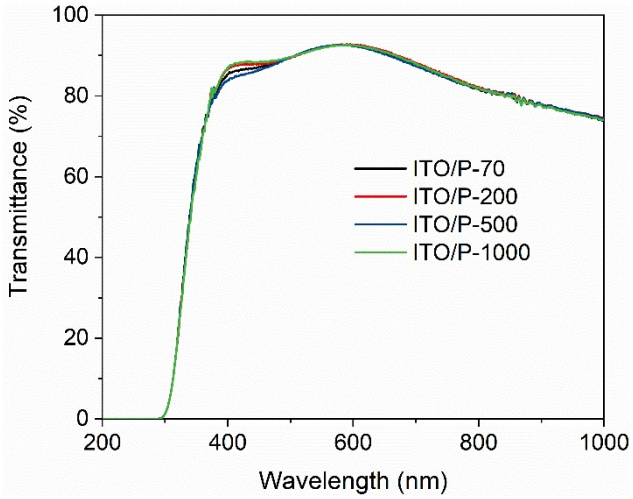

Figure S5. Transmittance spectra of PEDOT:PSS films (~40 nm) spin-coated on ITO glass substrates.

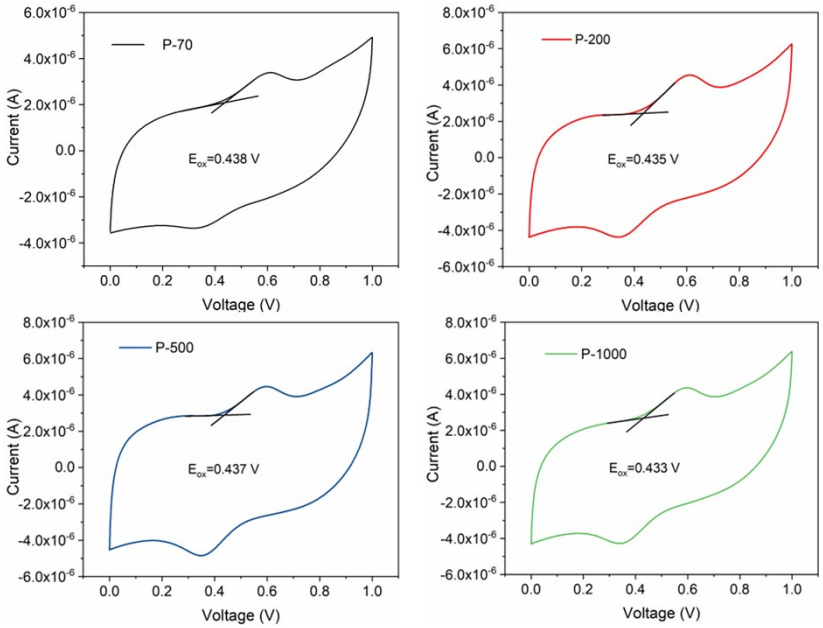

Figure S6. CV curves of PEDOT:PSS films.

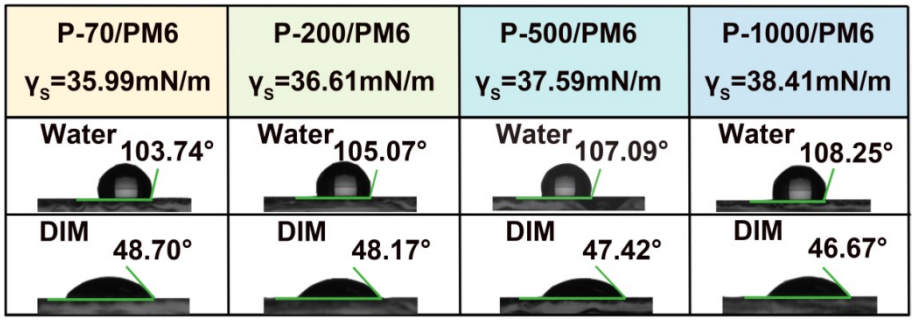

Figure S7. Contact angles and γ_s values of PM6 films coated on various PEDOT:PSSs.

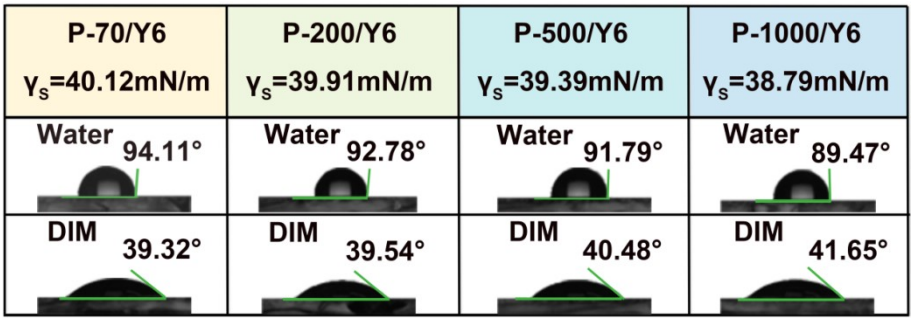

Figure S8. Contact angles and γ_s values of Y6 films coated on various PEDOT:PSSs.

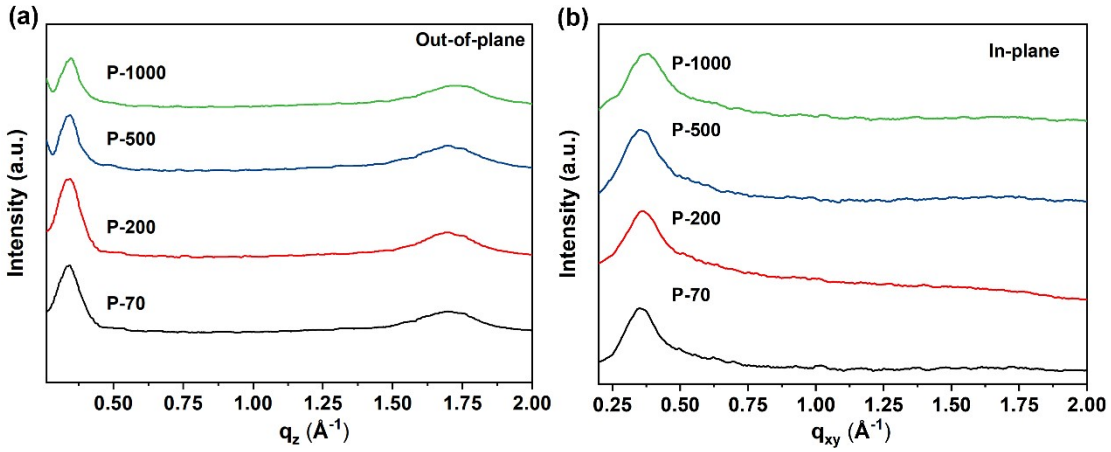

Figure S9. GIWAXS intensity profiles of the PM6:Y6 blends deposited on various PEDOT:PSS AIMs along the out-of-plane (a) and in-plane (b) directions.

Table S2 Detailed GIWAXS peak information of the PM6:Y6 blends deposited on various PEDOT:PSS AIMs.

BHJ	AIM	Out-of-plane		In-plane	
		q (Å^{-1})	CCL (nm)	q (Å^{-1})	CCL (nm)
PM6:Y6	P-70	1.696 0.338	2.15 5.96	0.292	5.95
	P-200	1.693 0.338	2.11 5.98	0.291	5.71
	P-500	1.705 0.357	2.10 5.62	0.293	5.68
	P-1000	1.722 0.358	2.04 5.51	0.297	4.99

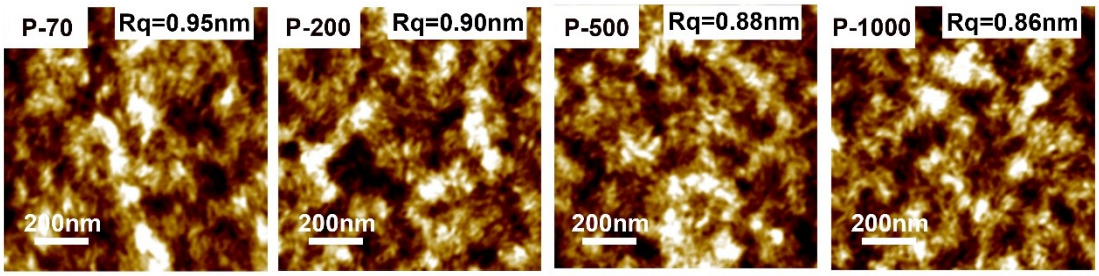

Figure S10. AFM height images of the PM6:Y6 blends deposited on different PEDOT:PSS AIMs.

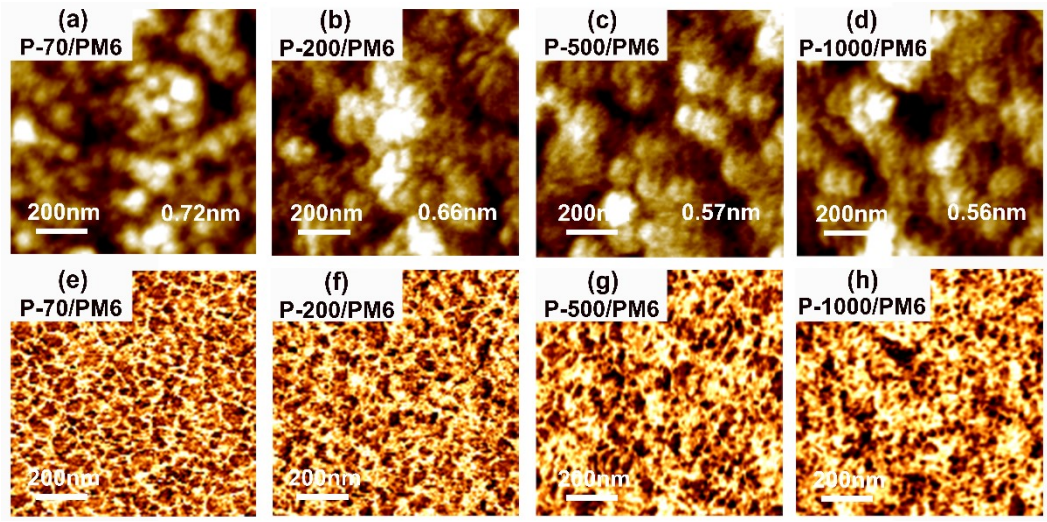

Figure S11. AFM height (a-d) and phase (e-h) images of PM6 films coated on various PEDOT:PSS AIMs.

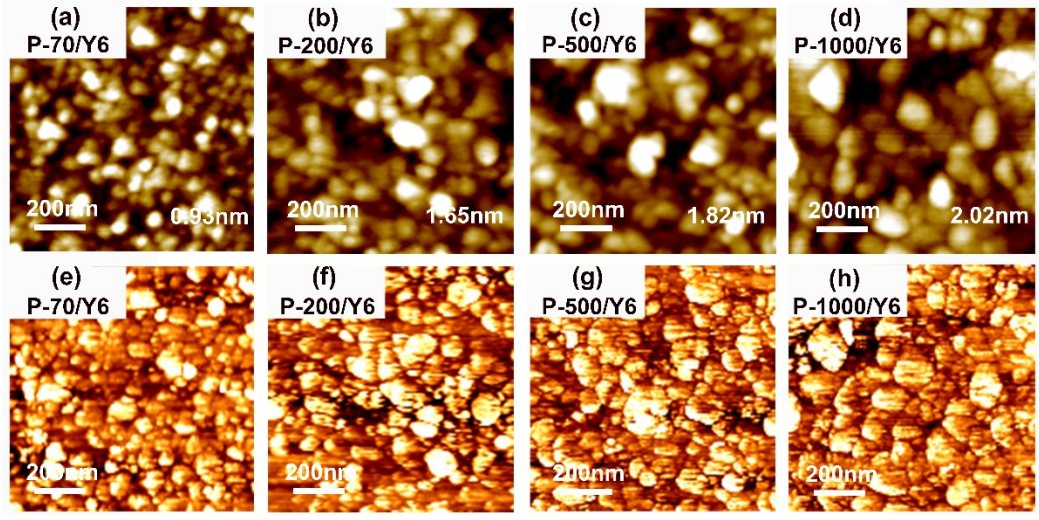

Figure S12. AFM height (a-d) and phase (e-h) images of Y6 films coated on various PEDOT:PSS AIMs.

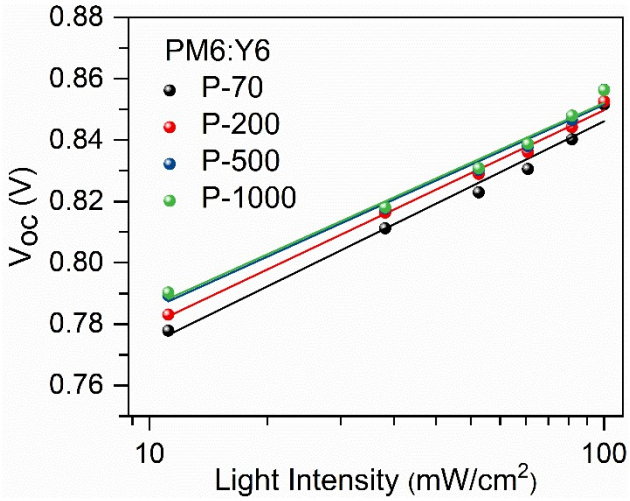

Figure S13. V_{oc} versus light intensity curves of OSCs.

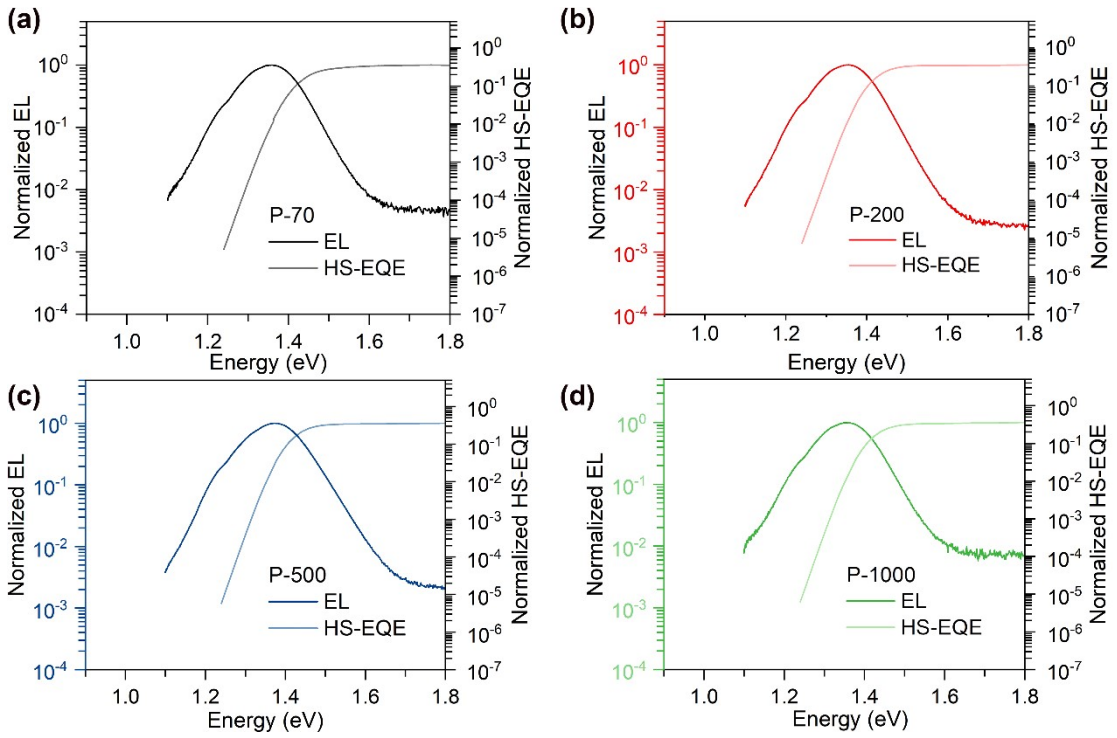

Figure S14. Semi-logarithmic plots of the EL and sensitive EQE as a function of energy for OSCs based on PM6:Y6 blends.

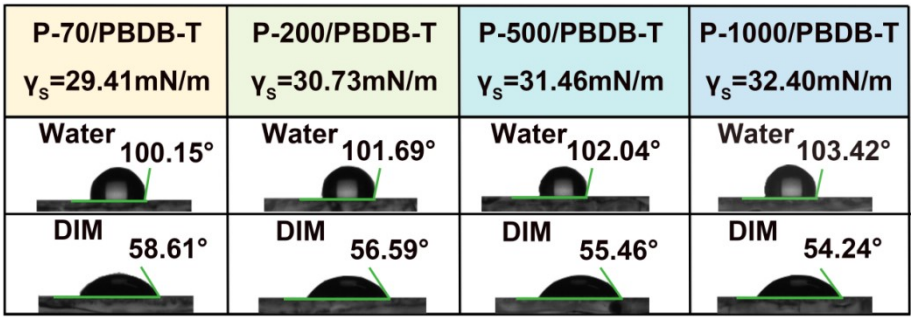

Figure S15. Contact angles and γ_s values of PBDB-T films coated on various PEDOT:PSSs.

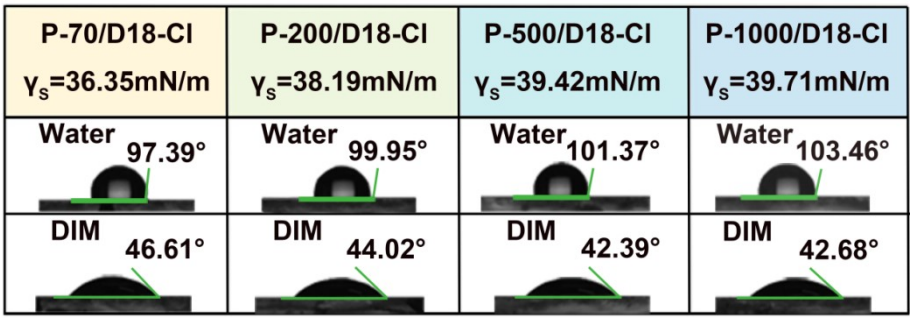

Figure S16. Contact angles and γ_s values of D18-Cl films coated on various PEDOT:PSSs.

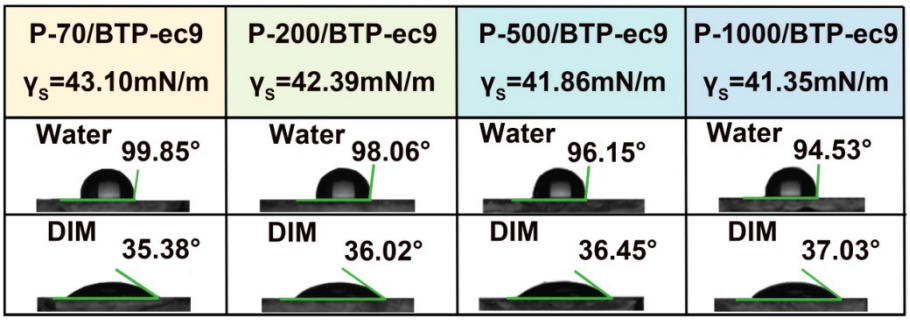

Figure S17. Contact angles and γ_s values of BTP-ec9 films coated on various PEDOT:PSSs.

[1] Zubar, T.I., Fedosyuk, V.M., Trukhanov, S.V., Tishkevich, D.I., Michels, D., Lyakhov, D. and Trukhanov, A.V. Method of surface energy investigation by lateral AFM: application to control growth mechanism of nanostructured NiFe films. Scientific Reports, 2020, 10(1), 1-10.

[2] Li, C., Zhou, J., Song, J., Xu, J., Zhang, H., Zhang, X., Guo, J., Zhu, L., Wei, D., Han, G., Min, J., Zhang, Y., Xie, Z., Yi, Y., Yan, H., Guo, F., Liu, F. and Sun, Y. Non-fullerene

acceptors with branched side chains and improved molecular packing to exceed 18% efficiency in organic solar cells. Nature Energy, 2021, 6(6), 605-613.