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Supplementary Information for

Non-conjugated water/alcohol soluble polymers with different oxidation states of sulfide as cathode interlayers for high-performance polymer solar cells

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Experimental Section

General Details. All reagents, unless otherwise specified, were obtained from Alfa Aesar or Sigma-Aldrich and used without further purification. Some of the solvents used were further purified before use (THF from sodium/benzopheone, acetonitrile from CaH_2, toluene was washed with H_2SO_4 and then treated with $CaCl_2$). ^1H and ^{13}C NMR spectra were measured using a Bruker AV-600. Chemical shifts were expressed in parts per million (ppm), and splitting patterns are designated as s (singlet), d (doublet) and m (multiplet). Molecular weights of the polymers were determined by a Waters GPC 2410 in THF using a calibration curve with polystyrene standards. UV-vis spectra were recorded on a HP 8453 spectrophotometer. Thermogravimetric analyses (TGA) were conducted on a NETZSCH TG 209 under a heating rate of 10 °C/min and a N_2 flow rate of 20 mL/min. Cyclic voltammetry data were measured on a CHI600D

electrochemical workstation by using Bu_4NPF_6 (0.1 M) in acetonitrile as electrolyte and platinum and Ag/Ag^+ (0.1 M of $AgNO_3$ in acetonitrile) as the working and reference electrode, respectively. Elemental analyses were performed on a Vario EL elemental analysis instrument (Elementar Co.). The work functions of Al cathode with various treatments were measured on Scanning Kelvin Probe Microscopy (SKP5050 kp tech).

Solar cell fabrication and characterization. The active layer materials of electron donor PTB7 and electron acceptor $PC_{71}BM$ were purchased from 1-material and Aldrich, respectively. PEDOT:PSS (Baytron PVP Al 4083) was obtained from H.C. Starck Clevios. All materials were used as received. The device structure was ITO/PEDOT:PSS/PTB7:$PC_{71}BM$/CIL/Al. Firstly, PEDOT:PSS was spin-coated on top of a cleaned ITO and annealed in air at 140 ˚C for 10 min. Subsequently, the active layer with a normal thickness of ~100 nm was formed by spin-coating a 25 mg mL^{-1} solution of PTB7:$PC_{71}BM$ (1:1.5, w/w) in the solvent mixture of chlorobenzene/1,8-diiodoctane (97:3, v/v) at 1000 r.p.m. for 2 minutes. The interfacial polymers were dissolved in methanol and their solutions were spin-coated on top of the active layer. The dissolving of PF6NPS, PF6NPSO, and PF6NPSO2 need a small amount of acetic acid. The thicknesses of CILs were controlled by adjusting the solution concentration and spin speed. Typically, a 0.5 mg mL^{-1} solution was used for fabricating the devices depicted in Table 2, while the devices depicted in Table 3 apply the solutions of NWSPs with concentration from 0.2 mg mL^{-1} to 2 mg mL^{-1}. Finally, a 100 nm Al layer was evaporated under 2×10^{-7} mbar. The device area is defined through a shadow mask,

which is 2 × 8 mm^2. All device fabrication processes are carried out in a N_2-filled glovebox (Braun GmbH). For comparison, the control devices applying MeOH/Al, and bare Al cathode are also fabricated under the same conditions. The *J-V* characteristics of the devices were recorded by a Keithley 2400 under AM1.5G illumination and in the dark. The EQE spectra of the devices were measured by a Hypermonolight System (Bunkoh-Keiki SM-250).

Electron-only device fabrication and characterization. The electron-only devices were fabricated with device structures of ITO/Al/PTB7:$PC_{71}BM$ (100nm)/CIL/Al. The fabrication procedure of every single layer was the same as that of corresponding solar cell. The mobilities were determined by fitting the dark *J-V* current to the model of a single-carrier SCLC model, described as $J= (9/8)\varepsilon_0\varepsilon_r\mu((V^2)/(d^3))$, where J is the current, μ is the zero-field mobility, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, d is the thickness of the PTB7:$PC_{71}BM$/CIL double layers, and V is the effective voltage. The effective voltage can be obtained by subtracting the built-in voltage (V_{bi}) and the voltage drop (V_s) from the substrate's series resistance from the applied voltage (V_{appl}), $V= V_{appl}-V_{bi}-V_s$.

Synthesis.

Di(4-bromophenyl)sulfide (1)*:* Diphenylsulfide (4.68 mL, 40 mmol) was dissolved in a mixed solution of H_2O and CH_2Cl_2 (1:1, 180 mL) under argon. Then 30% aqueous hydrogen peroxide (1.72 mL, 72 mmol) and bromine (10 mL, 195 mmol) were added, and the reaction solution was continuously stirred for 8 h at ambient temperature. The resulting mixture was extracted with CH_2Cl_2 with surplus bromine removed by

saturated $Na_2S_2O_3$ solution. After removing the CH_2Cl_2 solvent, the residue was further purified by silica gel column chromatography (petroleum ether) to afford **1** (11.5 g, 84%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.46−7.41 (m, 4H), 7.21−7.17 (m, 4H). ^{13}C NMR (300 MHz, $CDCl_3$, δ, ppm): 134.61, 132.71, 132.57, 121.63.

4,4'-Dibromo diphenyl sulfoxide (2) and 4,4'-dibromo diphenyl sulfone (3): Di(4-bromophenyl)sulfide (**1**) (6.88 g, 20 mmol) was dissolved in 60 mL acetic acid under argon atmosphere. Then 10 mL 30% aqueous hydrogen peroxide were added, and the reaction solution was continuously stirred for about 6 h at 80 ˚C. The completion of the reaction was verified by spot TLC. The resulting mixture was extracted with CH_2Cl_2 with surplus acetic acid removed by Na_2CO_3. After removing the CH_2Cl_2 solvent, the residue was further purified by silica gel column chromatography (petroleum ether/dichloromethane, 1:1) to afford **2** (2.41 g, 34%) and **3** (4.51 g, 61%) as a white solid. **2**: ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.68−7.63 (m, 4H), 7.53−7.48 (m, 4H). ^{13}C NMR (300 MHz, $CDCl_3$, δ, ppm): 144.51, 132.86, 126.31, 126.09. **3**: ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.80−7.76 (m, 4H), 7.67−7.63 (m, 4H). ^{13}C NMR (300 MHz, $CDCl_3$, δ, ppm): 140.36, 132.90, 129.31, 128.96.

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis(6-(N,N-diethylamino)hexyl)-fluorene (4): 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis(6-(N,N-diethylamino)hexyl)-fluorene (4) was prepared according to the published procedures. [1-3]

General Procedure for Preparation Precursor Polymers: Polymerization reactions

were carried out by palladium(0)-catalyzed Suzuki cross-coupling reactions. Diboronic ester monomer (1 mmol) and dibromo monomer (1 mmol) were mixed with $Pd(PPh_3)_4$ (10 mg) in a mixture of 20% aqueous tetraethylammonium hydroxide (2 mL), toluene (10 mL) and THF (8 mL) under argon atmosphere. After degassing, the reaction mixture was vigorously stirred at 90 ˚C for 24 h. After cooling to room temperature, the mixture was poured into methanol. The precipitated material was recovered by filtration through a funnel. The resulting solid material was washed for 24 h using acetone to remove oligomers and catalyst residues. The resulting polymers were soluble in THF, $CHCl_3$, and toluene.

PF6NPS: **4** (1 mmol, 729 mg) and di(4-bromophenyl)sulfide (**1**) (1 mmol, 344 mg) were used in this polymerization to give PF6NPS (565 mg, 82%). GPC (THF, polystyrene standard) analysis showed a *Mn* = 17000 g/mol and *PDI* = 1.9. ^{1}H NMR(300 MHz, $CDCl_3$, δ, ppm): 7.75-7.80 (m, 2H), 7.62-7.65 (m, 4H), 7.57-7.60 (m, 2H), 7.48-7.56 (m, 6H), 2.38-2.43 (m, 8H), 2.22-2.28 (m, 4H), 2.01-2.10 (m, 4H), 1.21-1.30 (m, 4H), 1.01-1.13 (m, 8H), 0.88-0.96 (m, 12H), 0.67-0.76 (m, 4H). Anal. calcd for: C, 81.92; H, 9.36; N, 4.07; S, 4.65, found: C 81.76; H 9.05; N 4.08; S, 4.69.

PF6NPSO: **4** (1 mmol, 729 mg) and 4,4'-dibromo diphenyl sulfoxide (**2**) (1 mmol, 360 mg) were used in this polymerization to give PF6NPSO (536 mg, 84%). GPC (THF, polystyrene standard) analysis showed a *Mn* = 14600 g/mol and *PDI* = 1.9. ^{1}H NMR(300 MHz, $CDCl_3$, δ, ppm): 7.76-7.82 (m, 10H), 7.52-7.58 (m, 4H), 7.57-7.60 (m, 2H), 2.38-2.45 (m, 8H), 2.21-2.26 (m, 4H), 1.98-2.05 (m, 4H), 1.23-1.31 (m, 4H), 1.01-1.13 (m, 8H), 0.85-0.96 (m, 12H), 0.62-0.72 (m, 4H). Anal. calcd for: C, 80.06; H, 9.15;

N, 3.97; O, 2.27; S, 4.55, found: C 76.37; H 8.59; N 4.19; S, 4.23.

PF6NPSO2: **4** (1 mmol, 729 mg) and 4,4'-dibromo diphenyl sulfone (**3**) (1 mmol, 376 mg) were used in this polymerization to give PF6NPSO2 (578 mg, 85%). GPC (THF, polystyrene standard) analysis showed a *Mn* = 16700 g/mol and *PDI* = 2.1. ^{1}H NMR(300 MHz, $CDCl_3$, δ, ppm): 8.03-8.09 (m, 4H), 7.72-7.80 (m, 6H), 7.49-7.58 (m, 4H), 2.32-2.43 (m, 8H), 2.18-2.26 (m, 4H), 1.95-2.03 (m, 4H), 1.18-1.26 (m, 4H), 0.98-1.11 (m, 8H), 0.81-0.95 (m, 12H), 0.60-0.71 (m, 4H). Anal. calcd for: C, 78.29; H, 8.95; N, 3.88; O, 4.44; S, 4.45; S, 4.55, found: C 76.77; H 8.52; N 3.81; S, 4.41.

General Procedure of Quaternization: A 100 mL flask with a magnetic stirring bar was charged the precursor polymer (150 mg) dissolved in 30 mL of THF. To this was added excess bromoethane and 10 mL of MeOH. Once some precipitates appeared, some MeOH was added to dissolve them. The solution was stirred at 40 ˚C for 3 days. THF and extra bromoethane were evaporated. Polymer was precipitated in about 100 mL of ethyl acetate, collected by centrifugation, washed with chloroform and THF, and dried overnight in a vacuum at 80 ˚C.[4]

PF6NPSBr: PF6NPS was used as precursor polymer in the reaction to give PF6NPSBr (105 mg, 70%). ^{1}H NMR(300 MHz, DMSO-*d6*, δ, ppm): 7.93-8.01 (m, 2H), 7.80-7.91 (m, 6H), 7.68-7.76 (m, 2H), 7.45-7.56 (m, 4H), 3.08-3.21 (m, 8H), 2.75-3.04 (m, 10H), 2.05-2.20 (m, 4H), 1.32-1.45 (m, 4H), 1.01-1.15 (m, 24H), 0.55-0.68 (m, 4H). Anal. calcd for: C, 81.98; H, 9.98; N, 3.75; S, 4.29, found: C 73.95; H 8.04; N 3.72; S, 3.78.

PF6NPSOBr: PF6NPSO was used as precursor polymer in the reaction to give PF6NPSOBr (111 mg, 74%). ^{1}H NMR(300 MHz, DMSO-*d6*, δ, ppm): 7.93-8.04 (m,

6H), 7.83-7.92 (m, 6H), 7.70-7.76 (m, 2H), 3.04-3.15 (m, 12H), 2.80-2.98 (m, 8H), 2.08-2.20 (m, 4H), 1.28-1.36 (m, 4H), 0.98-1.15 (m, 22H), 0.58-0.65 (m, 4H). Anal. calcd for: C, 80.26; H, 9.77; N, 3.67; O, 2.10; S, 4.20, found: C 68.48; H 8.09; N 3.57; S, 3.15.

PF6NPSO2Br: PF6NPSO2 was used as precursor polymer in the reaction to give PF6NPSO2Br (102 mg, 68%). ^{1}H NMR(300 MHz, DMSO-*d6*, δ, ppm): 8.01-8.14 (m, 4H), 7.72-7.84 (m, 4H), 7.57-7.68 (m, 6H), 3.18-3.26 (m, 8H), 2.78-3.03 (m, 8H), 2.14-2.28 (m, 6H), 1.21-1.30 (m, 4H), 0.98-1.16 (m, 24H), 0.57-0.68 (m, 4H). Anal. calcd for: C, 78.61; H, 9.57; N, 3.60; O, 4.11; S, 4.11; S, 4.20, found: C 65.56; H 7.86; N 4.46; S, 3.18.

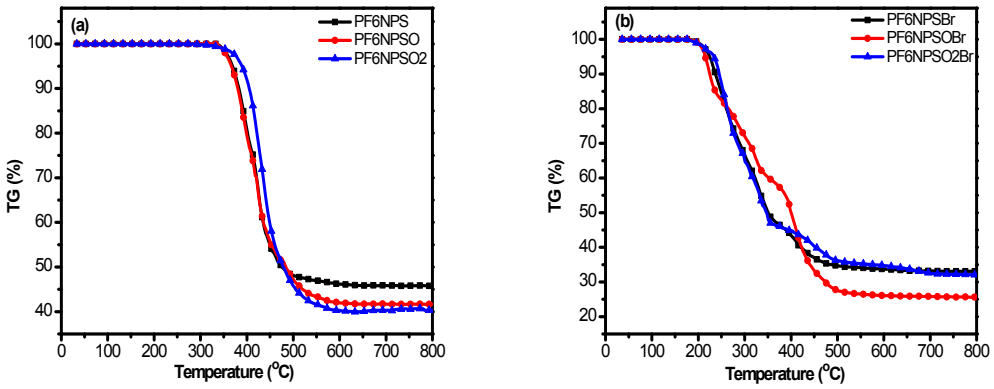

Fig. S1 TGA plots of (a) PF6NPS, PF6NPSO and PF6NPSO2; (b) PF6NPSBr, PF6NPSOBr and PF6NPSO2Br.

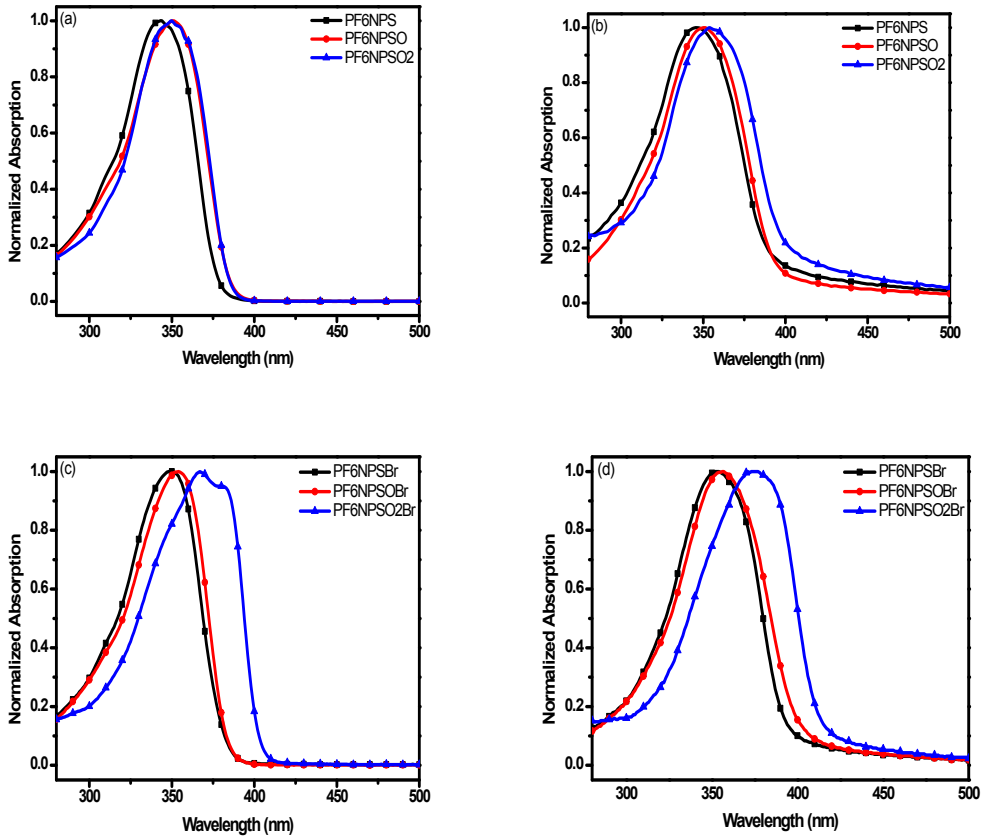

Fig. S2 UV-vis absorption spectra of the polymers. ((a) in chloroform solution for PF6NPS, PF6NPSO, and PF6NPSO2; (b) in solid-state films for PF6NPS, PF6NPSO, and PF6NPSO2; (c) in methanol solution for PF6PSBr, PF6NPSOBr, and PF6NPSO2Br and (d) in solid-state films for PF6PSBr, PF6NPSOBr, and PF6NPSO2Br. The solid films are spin-coating form the corresponding 5 mg mL^{-1} solution.)

Table S1 The work function (WF) data of Al electrode with different treatments using Kelvin probe microscopy

Electrode	Al	MeOH rinsed Al	Al/PF6NPS	Al/PF6NPSO	Al/PF6NPSO2	Al/PF6NPSBr	Al/PF6NPSOBr	Al/PF6NPSO2Br
WF (eV)	4.28	4.26	3.95	3.96	3.99	3.96	3.99	4.03

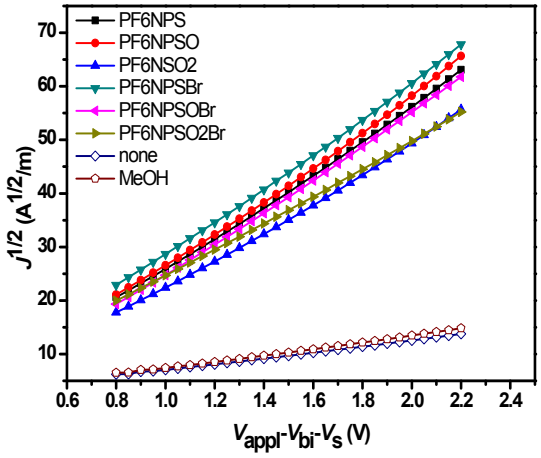

Fig. S4 The $J^{1/2}$-V curves of the electron-only devices.

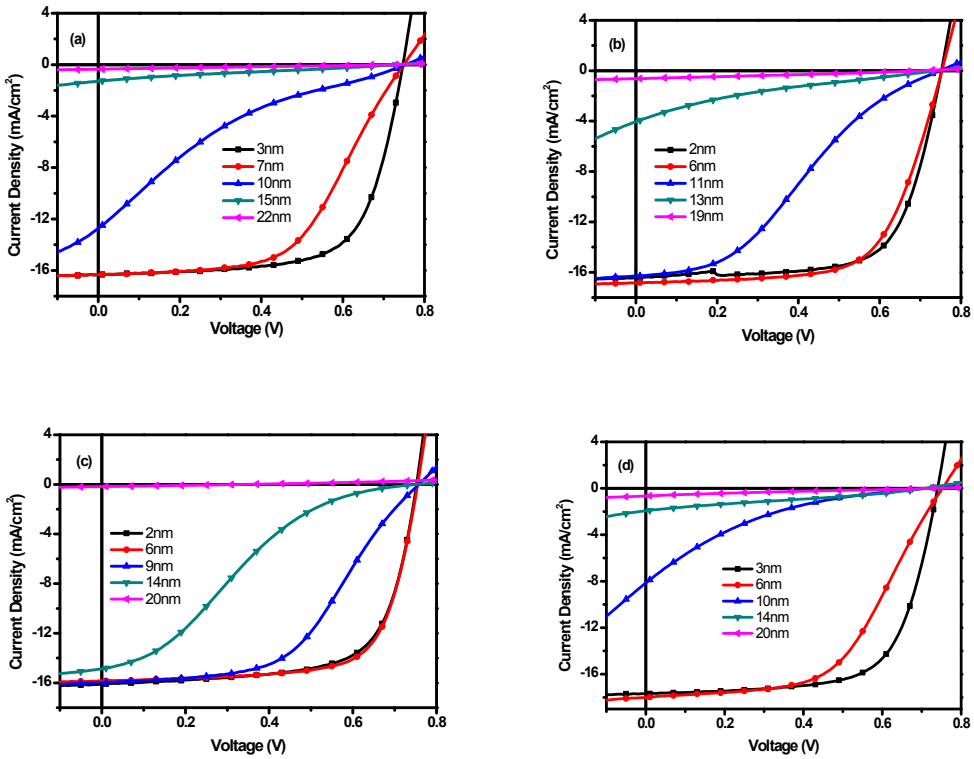

Fig. S5 *J-V* characteristics of the PSCs with varying interlayers thickness under AM 1.5G irradiation (100 mW cm^{-2}), (a) with PF6NPS interlayer, (b) with PF6NPSO interlayer, (c) with PF6NPSOBr interlayer, and (d) with PF6NPSO2 interlayer.

Table S2 Photovoltaic properties of the PSCs with the polymers interlayers of different thickness under AM 1.5G irradiation (100 mW cm^{-2}), a Series resistance (*Rs*) is obtain from the *J-V* curves.

Interlayer	Thickness (nm)	PCE (%)	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	R_s (Ω cm^2)[a]
PF6NPS	3	8.3	16.3	0.75	0.68	5.3
	7	6.7	16.3	0.75	0.55	22.2
	10	1.5	12.7	0.75	0.16	78.5
	15	0.2	1.3	0.73	0.23	503.1
	22	0.06	0.3	0.72	0.25	1264.6
PF6NPSO	2	8.5	16.4	0.75	0.69	5.9
	6	8.3	16.8	0.75	0.66	8.2
	11	3.9	16.3	0.75	0.32	75.4
	13	0.5	4.1	0.74	0.17	254.9
	19	0.1	0.6	0.70	0.28	705.2
PF6NPSOBr	2	8.3	16.1	0.75	0.68	4.5
	6	8.5	15.8	0.75	0.71	5.0
	9	6.2	16.0	0.76	0.50	30.3
	14	2.4	14.8	0.75	0.22	318.9
	20	0.02	0.1	0.34	0.26	1680.0
PF6NPSO2	3	8.8	17.6	0.74	0.67	5.3
	6	7.3	18.0	0.75	0.54	19.9
	10	0.7	8.1	0.72	0.13	384.0
	14	0.4	1.9	0.71	0.27	200.8
	20	0.1	0.6	0.73	0.21	923.1

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