

Electronic Supplementary Information

Poly(3,4-ethylenedioxythiophene):sulfonated acetone-formaldehyde: preparation, characterization and performance as hole injection material

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1. Experimental sections

1.1 Materials

3,4-ethylenedioxythiophene (EDOT) was purchased from Bayer AG and preserved at 0°C. PEDOT:PSS (Baytron PVPAl 4083) used for comparison was supplied by Hersbit Chemical Material Co. Ltd. The mass concentration of PEDOT:PSS was 1.0% and the weight ratio of PEDOT/PSS was 1:6. All other chemicals were analytical grade, including acetone, formaldehyde (CH₂O), Na₂SO₃, NaOH and ammonium persulphate (APS).

1.2 Synthesis and Characterization of SAF

Synthesis of SAF SAF can be readily synthesized using one-pot method as following procedures. Formaldehyde (6.0 mL, 37%) and acetone (3.0 mL) were mixed in aqueous solution (about 25 mL) with pH of 10 which was adjusted by NaOH (20%). The mixture was kept at 50°C for one hour, and then 2.5 g of Na₂SO₃ was added after dissolving in 5 mL of water. The polymerization was stopped after the reaction solutions became brownness about 5 hours of reflux at 85 °C. The residual reactants were removed by vacuum rotary evaporation, and then the pH of aqueous product was adjusted to 2-3 by addition of HCl (20%). Subsequently, the acidic product was dialyzed by a dialysis membrane (Special products laboratory, USA, MWCO of 1,000 Da) to remove inorganic salts and excessive starting materials and then freeze-dried under vacuum for 24 hours. The brown solid product showed excellent water solubility (solubility: higher than 400 g/L).

Characterization of SAF The ¹H-NMR spectrum of SAF was recorded by DRX-400 spectrometer (Bruker Co., Ettlingen, Germany) with 200 mg dried sample dissolved in 0.5 mL of deuterium oxide (D₂O) at room temperature. The FTIR spectrum of SAF was performed using the KBr pellets in the 4000-400 cm⁻¹ region by Auto system XL/I-series/Spectrum 2000 spectrometry (Thermo Nicolet Co., Madison, WI, USA). The molecular weight distribution of SAF

was determined by Waters 1515 Isocratic HPLP pump/Waters 2487GPC (Waters Co, Milford, MA, USA) which the calibration standard was PSS and the eluent was 0.10 mol/L NaNO₃ solution at the flow rate of 0.50 mL/min. The element contents of C, H and S were rationed by Vario EL cube (Elementar, Germany) with about 5.0 mg packed in aluminized paper. The particle sizes distribution was monitored on a Zeta PALS instrument (Brookhaven, USA) by dynamic light scattering at the concentration of 0.5 g/L. The AFM image was recorded by Park XE-100 instrument in tapping mode to observe the nanoparticle of SAF. The sample was spread out on a mica plate with the concentration of 0.5 g/L and dried in air at room temperature.

1.3 Preparation and Characterization of PEDOT:SAF

Preparation of PEDOT:SAF The PEDOT:SAF aqueous dispersion was prepared as follows. 1.0 g of dried SAF solid sample was dissolved in 30 mL of deionized water, then 0.5 g of the EDOT monomer was added (mass ratio of EDOT:SAF was controlled as 1:2). After stirring slowly for 10 min, the pH of the solution was adjusted to 2 by adding HCl (20%). Then, 0.96 g of APS used as oxidant was dissolved in water (2 mL) and added in drops. The reaction was kept under high stirring speed and at room temperature after the EDOT monomers being completely reacted (about 48 h). The product was purified by using a dialysis membrane (MWCO of 1,000 Da) to remove inorganic salts and then concentrated to the mass fraction of more than 1.0 wt% by rotary evaporation. The mass fraction was quantified by UV absorption at the wavelength of 800nm. Finally, the blue-green aqueous solution was obtained and named as PEDOT:SAF.

Characterization of PEDOT:SAF The FTIR spectra of EDOT monomer and the sample were using the same method as above. The UV-vis absorption spectra of PEDOT:SAF and PEDOT:PSS (Baytron PVPAl 4083) were measured using a Shimadzu UV-3600 spectrophotometer (Japan). The transmittance spectra of PEDOT:PSS and PEDOT:SAF films were tested using a Shimadzu UV-2600

spectrophotometer (Japan). The films were prepared by dropping the sample on glass and air drying at room temperature. The thicknesses of these films were tested by a step profiler (Dektak150, Veeco, USA). The conductivity and sheet resistance of PEDOT:PSS and PEDOT:SAF films were measured with a KDY-1 four point probes resistivity/resistance measurement system. The films were prepared using the same method as above while their thicknesses were much bigger with several microns. Cyclic voltammetry (CV) test was conducted with a film on glassy carbon electrode against Ag/AgCl (3M KCl solution) reference electrode at scanning rate 100 mV/s. The films were deposited at the surface of the polished glassy carbon electrode immersed in 0.1 M tetra-n-butylammoniumhexa fluorophosphate (nBu₄NPF₆) dichloromethane (DCM) solution used as a supporting electrolyte. The UPS and XPS measurements were conducted on a Thermo Scientific ESCALAB 250Xi with a He (I) UV source (21.22 eV) in ultrahigh vacuum. For testing UPS and XPS, the samples were spin-coated onto ITO glass and kept in an oven at 110 °C for 15 min before the measurement, and all of the experimental processes were conducted in ultrahigh vacuum environment. Wide-angle X-ray diffraction (XRD) was performed on a PANalytical X'pert PRO MPD diffractometer with film thickness around 10 μm using Cu K α radiation at 40 kV. The films were prepared by dropping the sample solutions on a glass substrate and drying naturally at room temperature. Dynamic light scattering (DLS) experiments were performed on a Zeta PALS instrument (Brookhaver, America). Atomic force microscopy (AFM) images were observed by a Park XE-100 in tapping mode with the samples were spin-coated on the ITO conductive substrate. The surface wettability was measured using a static contact angle instrument (Powereach JC2000C1, Shanghai, China).

1.4 Fabrication and Characterization of PHOLED

The configurations of the PHOLEDs were ITO/ HIL (x nm)/ TAPC (30nm)/ mCP(8nm)/ mCP:FIrpic (10wt%,25nm) /TmPyPb (35nm)/ LiF(1nm)/

Al(100nm). ITO-coated glass substrates were cleaned via a series of ultrasonication in detergent, acetone, DI water, isopropyl alcohol and followed by UV ozone plasma treatment. PEDOT:SAF layer was spin-coated onto the pre-patterned ITO glass substrate and annealed using a hot plate at 120 °C for 15 min to remove residual solvents. PEDOT:PSS (Baytron PVPAl 4083) based device was also fabricated as comparison with the same method. Then, the samples were transferred to a thermal evaporator chamber. Under a background pressure of 5×10^{-4} Pa, organic layers and cathode materials were deposited on the substrates without breaking vacuum. 1,1-bis[(di-4-tolylamino)phenyl]cyclohexane (TAPC) was served as the hole transport layer, bis[(4,6-difluorophenyl)-pyridinato-N,C²](picolate)iridium(III) (FIrpic) was the blue lighting phosphor, 1,3-Bis(carbazolyl-9-yl)benzene (mCP) was the host, 1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene (TmPyPb) was the hole-blocking and electron-injecting material, LiF was served as the electron-injecting layer.

A shadow mask was used to define the cathode and make 9 mm² device on each substrate. All steps except for processing of HILs were performed in the glove box. The thickness of the organic films was measured using an α -SE spectroscopic ellipsometry. The current density-voltage (J-V) characteristics were measured using a Keithley 2400 sourcemeter. The photovoltaic devices were characterized using a calibrated AM1.5G solarsimulator (Enlitech, SS-F5, 117-781-007), under light intensity of 100 mW/cm². The device lifetime was measured by using a lifetime tester (Polaronix M6000 PMX). All device performances were measured in ambient condition after encapsulation of the fabricated device.

2. Supplemental Figures and Tables

Figure S1 Molecular weight distribution of SAF.

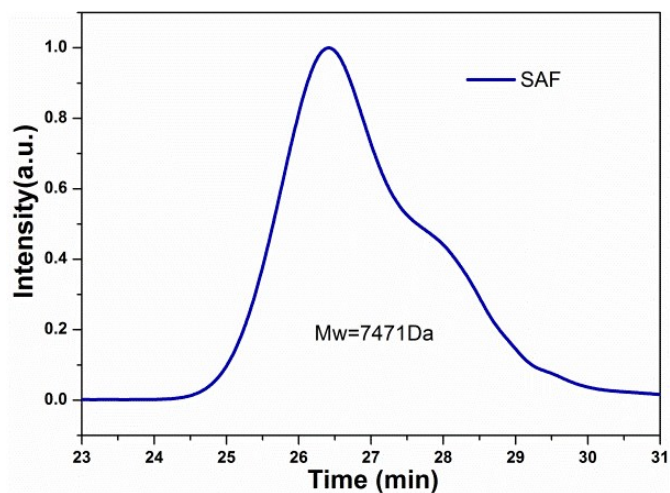


Figure S2 $^1\text{H-NMR}$ and FTIR spectra of SAF, (a) $^1\text{H-NMR}$, 200mg dissolved in 0.5mL D_2O , (b) FTIR.

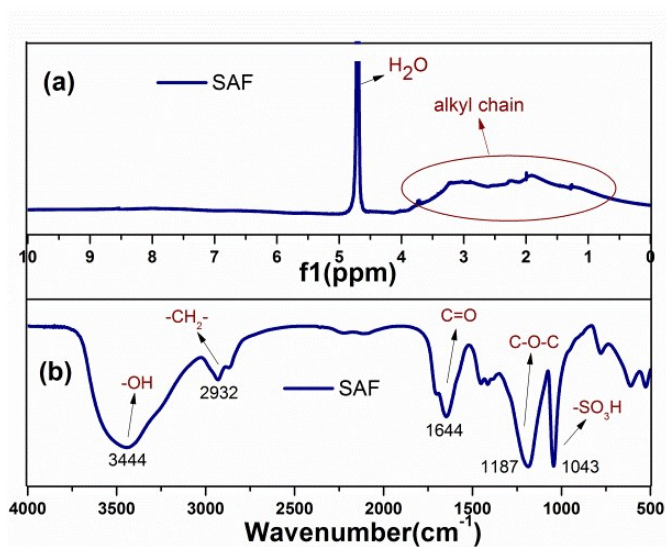


Figure S3 FTIR spectra of PEDOT:SAF, SAF and EDOT monomer.

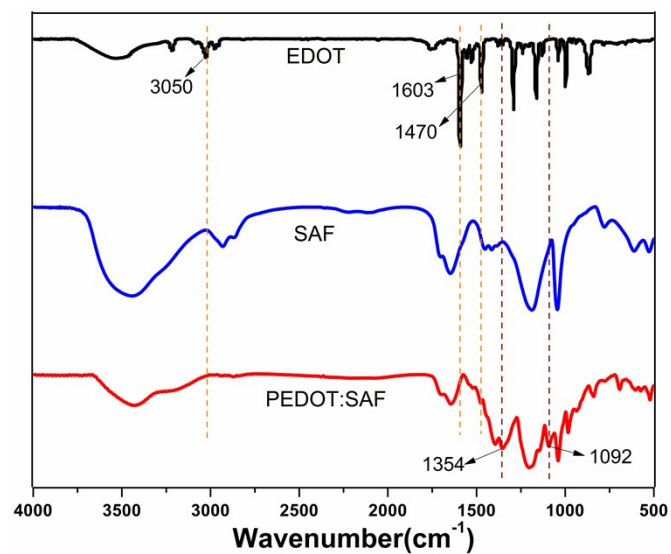


Figure S4 Acidity (pH value) of PEDOT:SAF and PEDOT:PSS aqueous dispersions with the same concentration of 1.0 wt%. Insert picture: their colors displayed on pH paper.

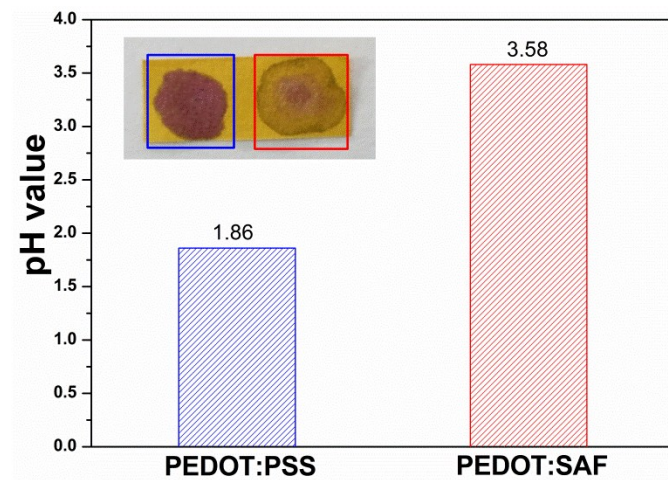


Figure S5 Particle sizes distribution of SAF in water. Inset: AFM image of SAF spread out on mica sheet. $[c] = 0.5\text{g/L}$, the size is $5\mu\text{m}\times 5\mu\text{m}$.

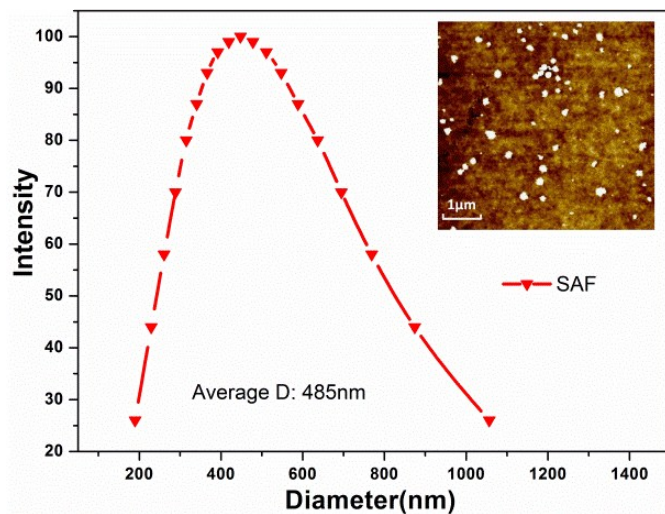


Figure S6 Particle size distribution of PEDOT:PSS and PEDOT:SAF dispersions tested again at five months later. (a) PEDOT:PSS, (b) PEDOT:SAF.

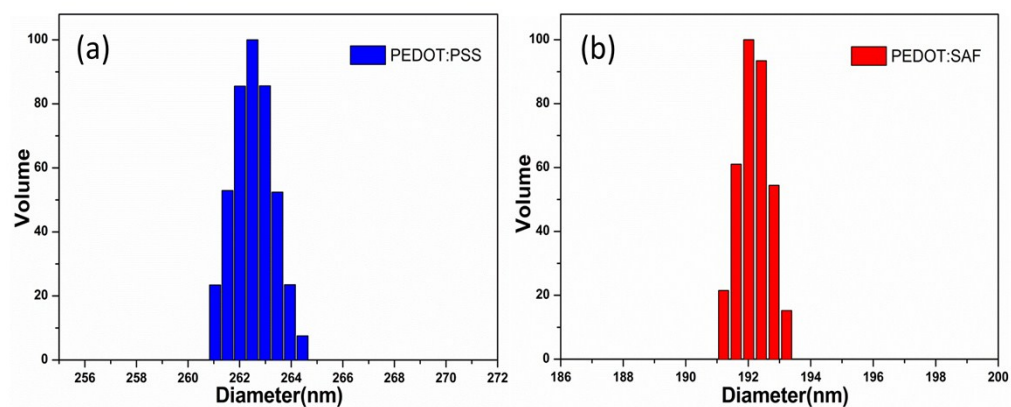


Figure S7 AFM images of PEDOT:PSS and PEDOT:SAF spread out on mica sheet. [c] = 0.5g/L, the size is 1 μm \times 1 μm . (a) PEDOT:PSS, (b) PEDOT:SAF.

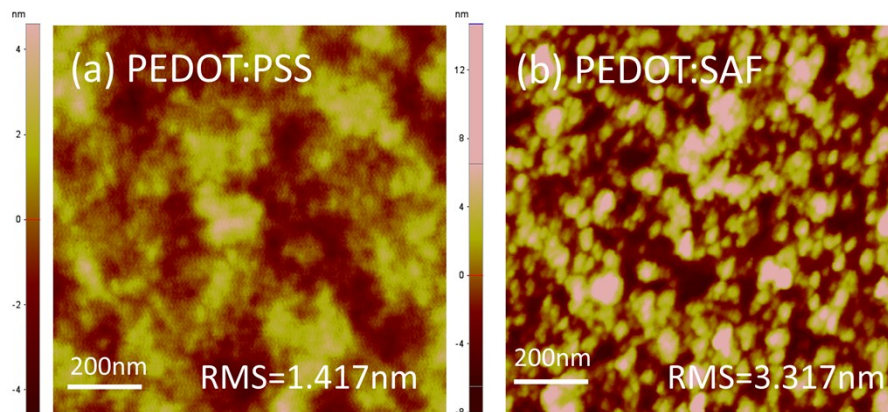


Figure S8 Device lifetime of blue PHOLEDs with PEDOT:PSS and PEDOT:SAF as HILs, respectively.

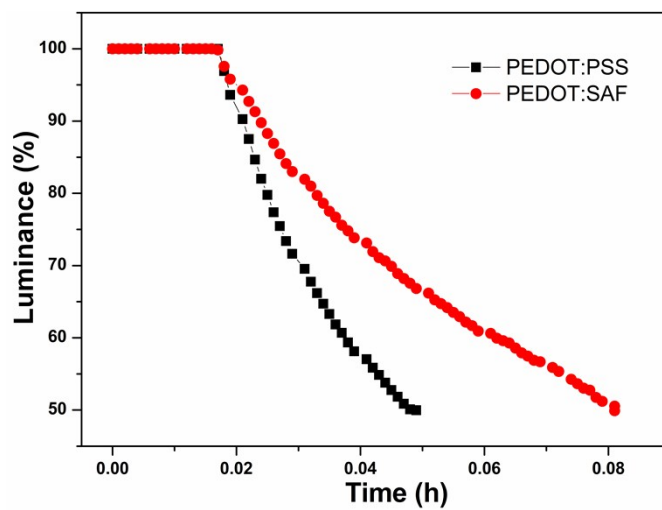


Table S1 The molecule weight, sulfonic acid groups content and element contents of SAF.

Samples	Mw (Da)	-SO ₃ content (mmol/g)	Element contents (%)		
			C	H	S
SAF	7471	3.10	32.98	4.561	9.911

The sulfonic acid group content of PSS is 5.43 mmol/g.

Table S2. The sheet resistances with specific thickness and the doping ratios of PEDOT:PSS and PEDOT:SAF.

Samples	Composition	Film thickness	Sheet resistance
	(w:w)	(nm)	(Ω/\square)
PEDOT:PSS	1:6	6083	134742
PEDOT:SA	1:2	1751	125963

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