



# Solution-processed pH-neutral conjugated polyelectrolytes with one-atom variation (O, S, Se) as a novel hole-collecting layer in organic photovoltaics

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## ABSTRACT

We present pH-neutral hole transporting layers processed from a solution at room temperature for organic photovoltaics (OPVs). Three new conductive conjugated polyelectrolytes (CPEs), identified as PFF, PFT and PFSe, containing aromatic five-membered heterocyclic compounds (furan, thiophene, and selenophene, respectively), are designed and synthesized using the Stille-coupling reaction. These polymers dissolve in water/alcohol as they are comprised of a conjugated backbone with hydrophilic side chains of sodium butane sulfonates. The CPEs with heterocyclic rings having stronger dipole moments decrease the work function of ITO electrodes and the surface potential between the active layer and hole-transporting layer (HTL) effectively. The device with PFSe as a HTL exhibits the best performance (7.2%), with  $J_{SC}$  of  $14.4 \text{ mAcm}^{-2}$ ,  $V_{OC}$  of  $0.677 \text{ V}$  and FF of 69.0%. The device also exhibits improvements in air stability under room temperature due to its neutral nature. Also, 70% of its initial power conversion efficiency (PCE) is maintained upon exposure to ambient air for  $\sim 480 \text{ h}$ , whereas the initial PCE with PEDOT:PSS decreases by more than 50%. Our results indicate that it is possible to improve the performance of OPVs using pH-neutral CPEs as efficient HTLs. We determine the way of molecular design is used to decrease the energy barrier using a heteroatom with a large dipole moment.

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## 1. Introduction

Recently, polymer solar cells (PSCs) have received substantial attention as promising alternatives to inorganic photovoltaic devices in academic research and industrial applications because they are lightweight, flexible, require inexpensive manufacturing and have the possibility of large-scale production via solution processing [1–3]. Molecular design is essential for the development of high performance optoelectronic materials in applications of PSCs. Extensive research has been devoted to achieving the optimal configuration of the chemical and structural parameters, such as conjugated backbones, side chains and substituents [4–8]. After extensive structural optimization, compounds of the PTB family, such as poly({4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl}{3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl}) (PTB7), exhibited excellent photovoltaic performance. A power conversion efficiency (PCE) of approximately 7.4% has been achieved using PTB7/[6,6]-phenyl C71 butyric acid methyl ester (PC<sub>71</sub>BM) conventional solar cell devices

[9]. Furthermore, inverted PSCs have led to PCEs higher than 8.2% [10]. In addition to designing new active materials to enhance the PCE and device stability, morphology optimization and interface engineering of bulk heterojunction (BHJ) solar cells are also fundamentally important [11–14].

To improve the charge selectivity at the electrodes and to minimize the energy barrier for charge extraction, a hole-transporting layer (HTL) with electron-blocking properties is inserted between the anode and the BHJ active layer. Moreover, an electron-transporting layer (ETL) with hole-blocking properties is inserted between the cathode and BHJ active layer [15–17]. The polymer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is the most widely employed as a HTL material for PSCs, because of its solution processability, appropriate work function, sufficient conductivity, and high optical transparency in the visible-NIR region. However, PEDOT:PSS is highly acidic, and the strong anisotropy in electrical conduction in spin-coated PEDOT:PSS layers, originating from their lamellar structures, often limits charge collection in solar cells. In solar cells, the active layer has the chemical interaction at the interface between the active layer and the PEDOT:PSS. Specifically, it determines the chemical instability between the active layer and electrodes in the long-term [18–20]. To overcome

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these deficiencies, conjugated polyelectrolytes (CPEs) are used as an interfacial material for organic photovoltaics. CPEs have received increasing attention because of their ability to improve PCE through solution processing. CPEs comprise  $\pi$ -conjugated backbones (hydrophobic) with ionic functional groups (hydrophilic) and are developed as multifunctional materials [21]. In the past, CPE layers have been utilized as ETLs to improve electron extraction toward the cathode. The advantages of using CPEs as ETLs in BHJ solar cells include reduction of series resistance, increase of internal built-in voltage, and modification of the electron extraction properties of a single device. These advantages facilitate the energy-level-matching at the interface that is essential for these devices to achieve high performance [22–24]. Kim et al. reported that one reason for the improvement is that directly depositing CPE on top of the ITO substrate can tune the electrode's work-function (WF) due to the formation of an aligned interfacial dipole assembly at the metal/organic semiconductor interface. This modifies the energy-level alignment and decreases the charge extraction barrier [25]. In contrast, the function of CPEs in affecting the hole injection/extraction has been rarely addressed.

Although such CPEs show great potential for WF tunability in organic electronic applications, their uses have been limited to lowering the WFs of metals. Thus, some research has been devoted to the development of CPEs by varying their polymeric structures, including their conjugated backbone, ionic functionalities, and the functional group in alkyl side chains [15]. These efforts do not suggest an effective way to modulate dipole strength, which is the determining factor for modifying the WFs of CPE-covered metal electrodes. Lee et al. proposed a doping process to create new dipoles in the functional group of the alkyl side chains and to modulate the WFs of adjacent metal electrodes according to their doping concentrations [26]. However, not all repeating units are oxidized during the oxidation process. This demonstrates the low reproducibility of this method due to the lack of control of the doping concentration using the same oxidants.

Five-membered heterocyclic compounds, such as pyrrole, furan, thiophene and selenophene, have different physical properties because of the different heteroatoms present in each one. Compared with benzenoid compounds, non-benzenoid aromatic compounds have large resonance energy and large dipole moments. The delocalization of the heteroatom lone pairs into  $\pi$ -systems can be inferred from the dipole moments of the aromatic heterocycles, for which the heteroatom is at the negative end of the dipole in the saturated compounds [27,28]. Heteroatoms are incorporated into hybridization, and based on using hybridization and shape molecules can be categorized relative to the strength of their molecular dipole moments.

In this study, we report unique water/alcohol-soluble CPEs: poly[9,9-bis(4'-sulfonatobutyl)fluorene-alt-heterocyclic ring] (PFF, PFT and PFSe). These are utilized instead of acidic PEDOT:PSS as a HTL. We study the effects of the electronic properties at the interface between the anode and the active layer. The interfacial contact changes the device performance of BHJ solar cells based on PTB7 as the electron donor and PC<sub>71</sub>BM as the acceptor. We control the work function and the surface potential between anode/HTL and the active layer using different heteroatoms. We demonstrate that high-efficiency organic BHJ solar cells with PCEs of up to 7.2% are successfully achieved when the PEDOT:PSS HTL is replaced by a PFSe with simultaneous improvement in the short-circuit current ( $J_{sc}$ ) and the fill factor, as well as 19% higher air stability than PEDOT:PSS during 480 h of exposure to ambient air at room temperature.

## 2. Experimental

### 2.1. Materials

All starting materials were purchased from Sigma Aldrich and Alfa Aesar and used without further purification. Sodium 4-(2,7-dibromo-9-(4-sulfonatobutyl)-9H-fluoren-9-yl)butyl sulfite (M1) was synthesized following procedures modified from the literature. In both poly{[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl}{3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]} (PTB7) and 1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]-C<sub>71</sub>BM (PC<sub>71</sub>BM), 1-material products were acquired and used. Commercial poly[9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-diptylfluorene)] (PFN) was utilized as the ETL for comparison.

### 2.2. General polymerizations

Monomer M1 (1.28 g, 2.0 mmol) and M2 (or M3 or M4) (2.0 mmol) were dissolved in 54 mL of DMF. The resulting solution was deoxygenated using nitrogen for 15 min. Then tris(dibenzylideneacetone)dipalladium(0) ( $Pd_2dba_3$ ) (91.6 mg, 0.1 mmol, 5 mol%) and tri-(*o*-tolyl)phosphine (0.12 g, 0.4 mmol, 20 mol%) were added to the stirred solution under the protection of N<sub>2</sub>. The reaction mixture was then heated up to 100 °C and stirred for 48 h. The viscous solution was then poured into 300 mL of acetone. The precipitate was collected via vacuum filtration and washed using acetone (300 mL × 2). The polymer precipitate was then dissolved in water and purified via dialysis using 12 kD molecular-weight-cut off (MWCO) regenerated cellulose membranes. After dialysis, the water was removed via the low temperature drying method. The water-soluble PFF, PFT, and PFSe were obtained as yellow or orange solids.

#### 2.2.1. Poly[9,9-bis(4'-sulfonatobutyl)fluorene-alt-furan] (PFF)

Yellow solid, 0.60 g (yield=55%). <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O, d):  $\delta$  7.78 (m, 2H), 7.58 (m, 2H), 7.32 (m, 2H), 3.53 (t, 2H), 3.45 (t, 2H), 2.83 (m, 2H), 2.50 (m, 2H), 1.64 (m, 6H), 1.56 (m, 2H), 1.38 (m, 2H).

#### 2.2.2. Poly[9,9-bis(4'-sulfonatobutyl)fluorene-alt-thiophene] (PFT)

Yellow solid, 0.65 g (yield=58%). <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O, d):  $\delta$  7.78 (m, 2H), 7.66 (m, 2H), 7.14 (m, 2H), 3.51 (t, 2H), 3.45 (t, 2H), 2.83 (m, 4H), 2.52 (m, 4H), 1.62 (m, 6H), 1.36 (m, 2H).

#### 2.2.3. Poly[9,9-bis(4'-sulfonatobutyl)fluorene-alt-selenophene] (PFSe)

Yellow solid, 0.31 g (yield=25%). <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O, d):  $\delta$  7.62 (m, 4H), 7.46 (m, 2H), 3.52 (t, 2H), 3.44 (t, 2H), 2.82 (m, 2H), 2.50 (m, 4H), 1.99 (m, 4H), 1.37 (m, 4H), 0.54 (m, 2H).

### 2.3. Measurements

The <sup>1</sup>H NMR (400 MHz) spectra were recorded using a Brüker AMX400 spectrometer in D<sub>2</sub>O, and the chemical shifts were recorded in units of ppm, with TMS as the internal standard. All of the GPC analyses were carried out using Buffer pH 9+30% MeOH as the eluent and PEG/PEO as the calibration. The TGA measurements were performed using a TG 209 F3 thermogravimetric analyzer. The work function values and ultraviolet photoelectron spectroscopy (UPS) spectra of the PFT, PFtT, and PFbT thin films on ITO electrodes were obtained using a KP 6500 Digital Kelvin probe (McAllister Technical Services, Co.) and a UPS analysis chamber ( $2 \times 10^{-8}$  Torr) equipped with an AXIS Ultra DLD (KRATOS, Inc.) hemispherical electron energy analyzer with a He I ( $h\nu=21.2$  eV) source. The samples were stored under high vacuum overnight before the UPS measurements, and a sample bias of –8.86 V was

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