Novel ethanol soluble all-furan based copolymer for organic Photovoltaics

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Abstract. A new ethanol soluble all-furan based copolymer (PFF) was firstly designed and synthesized. PFF exhibits strong absorption in the range of 300-700 nm, and presents a highest occupied molecular orbital energy level of $-5.21$ eV. The organic photovoltaics based on PFF: PCBO-12 display a low power conversion efficiency (PCE) of 0.49% when fabricated with ethanol. Interestingly, the PCE would be improved to 0.66% along with simultaneous enhancement of all photovoltaic parameters for devices by applying 1.5% p-anisaldehyde additive. The experiment analysis indicates the low PCE of the optimized device is ascribed to severe phase segregation and the large surface roughness of the active layer, which were verified by the TEM and AFM characterization.

1. Introduction
Solution-processed organic photovoltaics (OPVs) have been paid great attention in academia and industry due to their intrinsic characteristics, such as low-cost, mechanical flexibility, light-weight et al.
Up to now, the state-of-the-art power conversion efficiency (PCE) of OPVs has exceeded 18%, which approaches the threshold of the commercial application [1].

Generally, OPVs are consisted of the electrode, the charge selective layer and the active layer, where the active layer is mainly composed of the mixture of p-type and n-type organic semiconducting materials [2]. Up to date, those high-performance OPVs are fabricated via toxic solvent and additives, i.e., chloroform, chlorobenzene, and chloronaphthalene et al. Normally, these toxic materials could endow greatly harmful effect to the ambient environment and the human being. What’s more, these halogenated materials are not natural, which usually requires huge cost to prepare. Therefore, these imperfect features would greatly hinder the industrilization and application of OPVs in future.

In the above regarding, herein, we design and synthesize a novel all-furan-based copolymer, namely PFF. The target polymer displays a good solubility in ethanol, and it exhibits strong absorption in the range from 300 nm to 700 nm. In addition, PFF displays a suitable highest occupied molecular orbital energy level of $-5.21$ eV. When constructing OPVs based on PFF: PCBO-12, the devices obtain a poor PCE of 0.49% without any post-treatment and additives. However, the PCE of devices could be improved to 0.66% via applying 1.5% p-anisaldehyde additives. This work paves a new avenue to develop ethanol soluble copolymer.
2. Experimental

2.1. Materials and characterization
All solvents and chemicals were purchased from Aladdin and used as received without further purification. The chemical structures of PFF and PCBO-12 are depicted in Figure 1. The synthetic procedure of PFF is outlined in Scheme 1, and PCBO-12 was prepared according to the reported literature [3].

UV-Vis spectra was conducted via Cary 5000 UV-Vis-NIR Spectrophotometer. The electrochemical cyclic voltammetry was performed through a computer controlled CHI600E electrochemical workstation in acetonitrile with 0.1 M of tetrabutylammonium hexafluorophosphate with a scan rate of 50 mV/s. Size exclusion chromatography (SEC) analysis was carried out through Agilent PL-GPC 50 equipment.

![Figure 1. Chemical structures of PFF and PCBO-12](image)

2.2. OPVs fabrication and characterization
The patterned ITO-coated glass (15Ω/sq) were cleaned with deionized water, acetone and isopropanol in sequence. Following, the substrate was dried with nitrogen flow and treated with plasma processing for 5 mins. Then, the ZnO precursor solution was spin-coated upon the substrate. The ZnO film was annealed at 220 °C for 40 mins in air. Next, the substrate was transferred into a glove box with nitrogen, and a solution of PFF and PCBO-12 in ethanol was spin-coated on top of ZnO film with thickness of ca. 94 nm. Finally, the active layer was placed in evaporation chamber and pumped down to vacuum (~5×10⁻⁴ Pa), and thermally evaporated the MoO₃ (8 nm) and Ag (100 nm) in sequence. The active area of device defined by shadow mask was 0.0314 cm².

2.3. The synthesis of PFF
Compound 1 (124 mg, 0.3 mmol) and compound 2 (119 mg, 0.3 mmol) were placed into a 25 mL single-neck flask under N2 protection. Then, Pd2(dbA)3 (11 mg, 0.012 mmol), P(o-tol)3 (12 mg, 0.04 mmol), 10 mL of toluene and 1 mL of N, N-dimethylformamide were rapidly added into the flask. Afterwards, the flask was vacuumed and refilled with N2 for three times. Next, the flask was slowly heated to 100 oC and consecutively stirred for 12 h. Following, 0.1 mL of 2-(tributylstannyl) furan was injected the flask via a syringe and consecutively stirred for another 2 h. Similarly, 0.1 ml of 2-bromofuran was injected he flask via a syringe and consecutively stirred for another 2 h. After the mixture was cooled to room temperature, it was slowly poured into 100 mL hexane and stirred for 2 h. Next, the precipitate was collected and placed into a soxhlet extractor. And the mixture was extracted with petroleum ether, hexane and chloroform for 8h in sequence. The chloroform fraction was precipitated in hexane again. Finally, the mixture was filtrated and dried at 50 oC under vacuum to obtain PFF as dark-blue solid (59 mg, 61% yield).
Scheme 1. The synthetic route of PFF.

3. Result and discussion

Figure 2. a) The UV-Vis spectra of PFF and PCBO-12; b) J-V curves of devices; c) TEM pattern and d) AFM height image of the PFF: PCBO-12 film with 1.5% p-anisaldehyde.

Table 1. Photovoltaic parameters of the optimized devices.

|            | Voc (V) | Jsc (mA/cm²) | FF (%) | PCE (%) |
|------------|---------|--------------|--------|---------|
| as-prepared| 0.516   | 2.97         | 31.8   | 0.49    |
| with additive | 0.597   | 3.26         | 33.9   | 0.66    |

3.1. The optical property

The UV-Vis absorption spectra of PFF and PCBO-12 film is displayed in Figure 2a. As shown in Figure 2a, PFF depicts featureless absorption profile with a broad range from 300 nm to 700 nm. PCBO-12 presents a narrow absorption, which agree well with the reports. It is noted that PFF exhibits a complementary absorption with PCBO-12, benefiting for harvesting the photon and improving the Jsc for the derived devices.

3.2. The photovoltaic property

To evaluate the photovoltaic performance of PFF, OPVs with a configuration of ITO/ZnO/PFF: PCBO-12/MoO3/Ag were fabricated, and the detailed fabrication procedure of devices is shown in the experimental section. The current density-voltage (J-V) curves of the optimized devices are presented in Figure 2b and the corresponding photovoltaic parameters of devices are summarized in Table 1.

As displayed in Figure 2b, the as-prepared devices display a poor PCE of 0.49% along with a Voc of 0.516 V, a Jsc of 2.97 mA/cm², and a FF of 31.8%. However, the PCE of the devices via applying 1.5% p-anisaldehyde is obviously improved to 0.66% accompanied with the simultaneous enhancement
of all the photovoltaic parameters, where the optimized devices deliver Voc of 0.597 V, Jsc of 3.26 mA/cm², and FF of 33.9%.

3.3. The morphology property

The morphology of the optimized active layer was investigated by transmission electron microscope (TEM) and atomic force microscopy (AFM). As shown in Figure 2c, the optimized active layer displays discontinuous phase separation and large domain size exceeding 100 nm, which is detrimental for the exciton dissociation and charge transfer. Moreover, some islands are heterogeneously distributed on the surface of the active layer, which features a large root mean square roughness of 12.8 nm (Figure 2d). The poor morphology of the optimized active layer should be ascribed to the inferior miscibility between PFF and PCBO-12, which could result in the severe charge recombination and the low photovoltaic performance for the derived devices.

4. Conclusion

In summary, we developed a novel ethanol soluble all-furan-based copolymer (PFF). PFF features a broad absorption and a deep HOMO energy level. The OPVs based on PFF: PCBO-12 get a low PCE of 0.49% without any treatment. Furthermore, the devices could deliver a higher PCE of 0.66% when adopting 1.5% p-anisaldehyde additive. Our work provides a new strategy for designing environmentally benign copolymer for OPVs.

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