High efficient polymer solar cell processed by environment-friendly solvent system

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Abstract: In this paper, we fabricate the solution-processed solar cell to investigate the effect of the boiling point of the solvent additive on the performance of the polymer solar cell. We select the non-halogen solvent trimethylbenzene (TMB) as the host solvent and 2,2-(1,2-ethanediyldioxo) diethyl mercaptan (EOS) as the solvent additive to process the solar cell based on the FBT-Th4(1,4): PC71BM. The best power conversion efficiency is over 10%, which is the best result among the solar cells based on FBT-Th4(1,4): PC71BM. It should be noted that EOS can fast remove completely during the film-forming period. In order to investigate the underlying reason that the performance is improved, the TEM and AFM measurement are carried on. At last, we research the air stability and thermal stability of the solar cell processed with the new solvent additive.

1. INTRODUCTION

Organic photovoltaic cell devices based on PBDB-TSF:IT-4F show a record efficiency of 13.1%, which is processed from chlorobenzene and 0.5% DIO volume fraction[1]. The halogenated solvent with the ability of well dissolving PBDB-T and IT-4F makes the donor and acceptor exhibit good miscibility in the halogenated solvent, forming a good interconnection network. In fact, hydrocarbon compounds are more suitable for the large-scale processing of organic photovoltaic cells, and are easily obtained from nature. Halogenated solvents is not economical because of extra exhaust gas recycling cost, so scientists in the field of organic solar cells have been paying attention to these problems that hinder environment-friendly commercial production. Xylene and toluene molecular do not contain halogenated element. The field-effect hole mobility of FBT-Th4(1,4) is as high as 1.92 cm²V⁻¹s⁻¹[2], which is the highest hole mobility of fluorinated BT-based conjugated polymers and has the potential for large-scale high-speed printing mass production. The high hole mobility of FBT-Th4(1,4) ensures good photovoltaic performance even in thicker active layer films. In the first report about this material, the device processed with DIO as a solvent additive showed the short current of 15.1 mA/cm², the open-voltage of 0.75 V, the FF of 57.7%, and the PCE of 6.53% with the active layer thickness of 440 nm. The solar cell shows the best photovoltaic performance with 230 nm active layer, the short-circuit current is 16.2% mA/cm², the FF is 62.1%, and the obtained PCE is 7.64%. By selecting the mixed solvent CB and DCB, meanwhile using light-conductive interface material [3], the polymer solar cell based on FBT-Th4(1,4): PC71BM device exhibits the power conversion efficiency (PCE) of more than 10% at the active layer thickness between 300 nm and 400 nm. The polymer FBT-Th4(1,4) show excellent performance, however these results are obtained in halogen solvents which is harmful to environment. Although there were reports that trimethylbenzene...
(TMB) and phenyl-naphthalene system were used to fabricate the solar cell, but the boiling point of phenyl-naphthalene as the solvent additive is too high. This paper confronts these contradictions to explore low boiling point solvent additives suitable for trimethylbenzene.

2. RESULT AND DISCUSSION
Firstly, we dissolve FBT-Th4(1,4) with TMB at the concentration of $1 \times 10^{-5}$ M, and perform temperature-dependent UV-visible absorption. The solution temperature vary from room temperature. As can be seen from Figure 1, TMB has good solubility in FBT-Th4(1,4) at 80°C.

![Figure 1](image1.png)

**Figure 1.** The UV-absorption spectrum of FBT-Th4(1,4) dissolved in 1, 2,4-trimethylbenzene ($1 \times 10^{-5}$ M) from 35°C to 85°C.

![Figure 2](image2.png)

(a) Structural formula of FBT-Th (1,4) (b) Optical image of gel solution at room temperature.

**Table 1.** Photovoltaic performance of FBT-Th4(1,4): PC71BM active layer with EOS as solvent additive

| Solvent Additive | Volume fraction (%) | Thickness (nm) | $V_{oc}$ (V) | $J_{sc}$ (mA/cm²) | FF (%) | PCE (%) |
|------------------|---------------------|----------------|-------------|-------------------|--------|---------|
| No additive      | 0                   | 200            | 0.67        | 7.71              | 56.3   | 2.91    |
| DIO              | 3                   | 300            | 0.75        | 18.15             | 60.68  | 8.26    |
| EOS              | 0.3                 | 100            | 0.79        | 13.00             | 67.58  | 6.94    |
|                 | 0.6                 | 90             | 0.79        | 12.06             | 70.72  | 6.74    |
|                 | 0.6                 | 100            | 0.79        | 14.63             | 71.72  | 8.29    |
|                 | 0.6                 | 230            | 0.79        | 15.62             | 71.71  | 8.85    |
Here, we introduce a new solvent additive, that is 2,2-(1,2-ethanediylidioxo) diethyl mercaptan (EOS), which has a relatively low boiling point of 225°C, and a small amount of EOS is added into the FBT-Th4(1,4): PC71BM solution dissolved in TMB. We fabricate the inverted solar cell, the performance of the solar cell is shown in Table 1.

It can be found that trace amount of solvent additive EOS can significantly improve the efficiency of photovoltaic cells. A volume fraction of 0.3% can greatly improve the performance of photovoltaic cells, $J_{sc}$ increased from 7.71 mA/cm$^2$ to 13.00 mA/cm$^2$, the open circuit voltage increased from 0.67 V to 0.79 V, FF also increased from 56.30% to 67.58%. The PCE of the photovoltaic cells prepared with 0.3% solvent additives is 6.94%, significantly higher than the performance of the battery devices processed without solvent additive. When the volume fraction of the solvent additive increased to 0.6%, $J_{sc}$ increased to 14.63 mA/cm$^2$, FF exceed 70%, making the PCE 8.29%. When the volume fraction reaches 1%, the open circuit voltage drops to 0.75 V, the photovoltaic efficiency drops to 8.29%, and $J_{sc}$ decreases from 14.63 mA/cm$^2$ to 12.55 mA/cm$^2$, which means that the morphology is destroyed by excess solvent additive.

The key of the successful commercialization for the organic photovoltaic cell technology lies in that it can apply roll-to-roll technology to achieve large-scale printing.$^{[5-8]}$ One of the biggest challenges in printing organic photovoltaic cells is how to obtain the best active layer thickness for high-speed printing. For lots of high-performance material systems, the optimal thickness is at 80 nm-120 nm$^{[9]}$, however, pinhole defects often appear in so thin film when printing speed is high. Unfortunately, due to the limited charge-carrier diffusion length, organic photovoltaic cell with thick film(over 150 nm) often suffer from severe bimolecular recombination and space charge effect, resulting in reduced fill factor and power conversion efficiency. So we are interested in making the thick film solar cell with the EOS as the solvent additive.

![Figure 3](image)

Figure 3 (a) the J-V characteristic curves of organic photovoltaic cells with the different active layer thicknesses with 0.6% volume fraction of EOS solvent additive (b) EQE curves of photovoltaic cells with the active layer thickness of 320 nm with 0.6% EOS

| Additive Volume (vol%) | $J_{sc}$ (mA/cm$^2$) | Voc (V) | FF | PCE (%) |
|------------------------|----------------------|--------|----|---------|
| 0.0                    | 7.71                 | 0.67   | 56.30 | 1.94 |
| 0.3                    | 13.00                | 0.79   | 67.58 | 6.94 |
| 0.6                    | 14.63                | 0.79   | 70.00 | 8.29 |
| 1.0                    | 12.55                | 0.75   | 67.38 | 8.29 |

Here, the solvent EOS is 2,2-(1,2-ethanediylidioxo) diethyl mercaptan (EOS), which has a boiling point of 225°C.
The best photovoltaic performance is obtained when the active layer is about 320 nm, the solar cell exhibits the PCE of 10.08%, the $J_{sc}$ of 18.23 mA/cm$^2$, the FF of 70.02%. The fill factor is the highest in thick film photovoltaic cells. The photovoltaic cell based on a 230 nm thick film showed a $J_{sc}$ of 15.62 mA/cm$^2$, the open-circuit voltage of 0.79 V, the FF of 71.71%, which achieved the PCE of 8.85%. We further increased the thickness to 260 nm, the device still has a high FF of 70.06%, and the obtained PCE is 8.94%. From 100 nm to 320 nm, the photovoltaic cell still shows a high FF of more than 70%, which is attributed to the high mobility of FBT-Th4(1,4).

At 450 nm, the power conversion efficiency is 9.99%, the open circuit voltage is 0.77 V, and the fill factor is 67.30%. Compared with the thinner film, the fill factor decreases, however, the short-circuit current $J_{sc}$ still increased to 19.29 mA/cm$^2$. It is worth noting that for the polymer FBT-Th4(1,4), with strong temperature-dependent aggregation, the key to obtain the optimal photovoltaic performance is to precisely control the best morphology. In fact, consistent with previous reports, the optimal spin-coating speed should be less than 600 rpm.$^{[4]}$ During the spin-coating process, the EOS solvent additive with a low boiling point of 225°C can be quickly removed from the film. The curve of the photovoltaic device is shown in Figure 3.

In order to study the relationship between morphology and photovoltaic performance, the morphology of the film treated with EOS or without EOS is studied by TEM(Transmission electron microscope). The TEM image is shown in the figure 4. The TEM image of the blend film made of FBT-Th4(1,4) with molecular weight of 30 KDa, as shown in Figure 4b, we can clearly see the dark spherical phase of 300-400 nm in diameter surrounded by polymer fibers, and when the molecular weight increased to 70 KDa, as shown in Figure 4a, the morphology of the active layer film processed without the solvent additive changed significantly. These spherical phase domains disappear, the boundary between the two phases is not easy to distinguish, indicating that cross-linked interpenetrating network has been formed for the high molecular polymer. Figure 4c show the TEM image of the blend film of the low molecular weight polymer and PC$_{71}$BM processed by the DIO.$^{[10]}$ Compared with figure 3b, the large PC$_{71}$BM aggregations disappear, It demonstrates that the DIO can effectively reduce the phase separation. Figure 4d show the TEM image of the blend film of the high molecular weight polymer and PC$_{71}$BM processed by EOS, fibrous polymers can also be seen.
Figure 5 (a) the AFM image of the blended film of 70KDa molecular weight polymer and PC71BM processed with 0.3% volume fraction, (b) 0.6% volume fraction of EOS as solution additive.

Table 2. Photovoltaic performance of the solar cell annealed for different time

| Thickness (nm) | Annealing (hours) | $V_{oc}$ (V) | $J_{sc}$ (mA/cm²) | FF (%) | PCE (%) |
|----------------|-------------------|-------------|----------------|--------|---------|
| 430            | 0                 | 0.78        | 19.05           | 66.5   | 9.88    |
|                | 1                 | 0.78        | 18.36           | 58.4   | 8.4     |
|                | 2                 | 0.75        | 18.29           | 55.18  | 7.57    |
|                | 3                 | 0.68        | 18.45           | 51.06  | 6.41    |

Atomic force microscope (AFM) is used to study the surface information of the blended film processed by EOS solvent additives. Figure 5a is the image of the blended film treated with 0.3% EOS volume fraction. Figures 5b are the images of the blended films processed with 0.6% EOS volume fraction. When the content of the additive increases to 1%, the roughness of the film increases significantly.

From the above performance of the photovoltaic cell, we can know the solvent combination using xylene as the main solvent and EOS as the solvent additive successfully make the PCE exceeding 10%, and the open circuit voltage can be above 0.8V. However, the evaluation of the industrial production of the solar cell involve the PCE sustain over 10% for 10 years. So next, we will investigate the thermal stability and air stability of the solar cell based on FBT-Th4(1,4): PC71BM.

We adopt the inverted device structure, with ZnO as the electron transport layer and MoO3 as the hole transport layer, ITO/ZnO/FBT-Th4(1,4): PC71BM/MoO3/Al. The thickness of the active layer is 430 nm, the active layer area is 0.058 cm². The solar cell device is annealed at 85 °C in the glove box. As seen from the table 2, the short circuit current has not vary too much, however, the significant reduction of the fill factor occurred. After annealing for 3 hours, the fill factor decreased from 66.5% to 51.06%. The open circuit voltage of the device also changed significantly, from 0.78 V to 0.68 V.

In order to study the influence of thickness on device stability, the two thicknesses of 90 nm and 430 nm active layer, using EOS as a solvent additive, as shown in table 3, the short-circuit current of the inverted device is 12.12 mA/cm², the fill factor is 70.59%, the open circuit voltage is 0.79 V, the photovoltaic efficiency is 6.76%. When being placed under a certain humidity for 5 days, the photovoltaic efficiency of the obtained cell device was 6.46%, the open circuit voltage was 0.79 V, the short-circuit current decreased slightly, showing 12.03 mA/cm², and the fill factor decreased to 67.99%. For the active layer with the thickness of 430 nm, At the beginning, the photovoltaic performance was 9.99%, the fill factor was 67.3%, the short-circuit current $J_{sc}$ was 19.29 mA/cm², and the open circuit voltage was 0.77 V. After being placed in the air for 5 days, the photovoltaic conversion efficiency dropped to 9.26%, mainly due to the reduction of short-circuit current, and the fill factor was almost unchanged.
Table 3 the effect of aging time on device performance

| Thickness (nm) | Aging Day | $V_{oc}$ (V) | $J_{sc}$ (mA/cm²) | FF (%) | PCE (%) |
|---------------|-----------|--------------|-------------------|--------|---------|
| 90            | 0         | 0.79         | 12.12             | 70.59  | 6.76    |
| 5             | 0         | 0.79         | 12.03             | 67.99  | 6.46    |
| 430           | 0         | 0.77         | 19.29             | 67.3   | 9.99    |
| 5             | 0         | 0.77         | 18.21             | 66.03  | 9.26    |

3. EXPERIMENTAL PART

Device preparation: The series resistance of the ITO glass substrate is 15 ohms per square. The ITO substrate is successively cleaned in acetone, in deionized water twice and isopropanol twice for fifteen minutes per step. For the conventional device, after 2 minutes of oxygen plasma cleaning (Plasma), PEDOT:PSS (Clevios P AI4083) with the thickness of 40 nm was spin-coated on the ITO substrate as a hole transport layer, and then annealed in air at 140 °C for 10 minutes and transferred into the N₂ glove box. For the inverted devices, using 20 nm doped zinc oxide as the electron transport layer, the prepared zinc oxide solution should be allowed to cool to room temperature, and then filtered using 0.25 μm PTFE membrane before it can be used. The ZnO is coated on ITO by sol-gel method, and then transfer the film into the glove box.

Preparing the active layer solution (polymer:receptor mass ratio 1:1.5) in TMB, with different volume of solvent additives. The polymer concentration in the solution is 10.5 mg/ml for low molecular weight 50 KDa, 13 mg/ml high molecular weight for 70 KDa or 110 KDa. The spin coating rate is lower than 580 rpm for 20 s. In order to completely dissolve the polymer, the active layer solution should be stirred on a heating platform at 100°C for at least 1 h. Prior to spin coating, the polymer solution and ITO substrate were preheated on a 100°C heating plate. The active layer was spin-coated on the pre-heated substrate in a N₂ glove box from a hot polymer solution at 600 rpm. For the conventional device, PFN was dissolved in methanol and spin-coated on the surface of the active layer to form a 5 nm thin interface layer.[11] For the inverted devices, at a vacuum of 3×10⁻⁴ Pa, a thin layer (10nm) of MoO₃ was deposited as the anode interface layer, followed by 60 nm Al as the top electrode. The power conversion efficiency of organic photovoltaic cells is measured under one sun, AM 1.5G (Air weight 1.5G) spectrum solar simulation (Japan, SAN-EI, XES-40S1) (100 mWcm⁻²). Using Keithley 2400 current and voltage output source to record J-V characteristics. Organic photovoltaic cells have the device area of 5.8 mm². The EQE of the best ell is measured by Enli Technology. All batteries are first encapsulated with epoxy resin in the glove box.

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