# Mixed Solvents for Active-Layer Morphological Modifications of Polymer Bulk Heterojunction Solar Cells

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# 1. Introduction

Recently, many investigations have revealed that the active layer morphology of bulk heterojunction (BHJ) organic solar cells is an important factor in determining photoelectric conversion efficiency [1]. Smaller phase separation results in more donor and acceptor (D/A) junctions, and thus photovoltaic characteristics of devices. This attribute improves the efficiency of exciton separation and overcomes the short diffusion lengths of excitons. However, larger phase separation results in higher carrier mobility and better carrier transport path. The ideal films need to satisfy two conditions, namely, a larger D/A junction and a better carrier transport path. Various modifications for film structures have continued to improve in recent years to achieve the desired thin film structure [2]. These improvements include thermal annealing and solvent treatment. Mixed solvents have the advantage of simple preparation process and low cost.

Mixed solvents include the following: (i) good/good solvent; (ii) good/selective solubility solvent; and (iii) good/poor solvent. The mixed solvent can effectively modify the morphology of the active layer. For example, incorporation of ethanol into chloroform can improve crystalline polythiophene and enhance phase separation between polythiophene and fullerene derivatives [3]. There are significant increases in the red region of absorption of the film when ethanol composition is 8%, which indicates that the degree of crystalline polythiophene increases significantly. Furthermore, the reduction of photoluminescence quenching reveals that polythiophene and fullerene derivatives have large phase separations.

In this study, the mixed solvent of chloroform and ethanol was used to prepare the active layer with the aim of controlling morphology. Different amounts of alcohol were introduced into the chloroform as the co-solvents to prepare the poly(3-hexylthiophene) (P3HT):[6, 6]-phenyl- $C_{61}$ -butyric acid methyl ester (PCBM) blending films, as an active layer. The active layers were studied using Raman spectroscopy and atomic force microscopy (AFM). The correlation between microstructural properties of active layers and photovoltaic performance of polymer BHJ solar cells was also examined.

#### 2. Experimental Methods

A 10 mg ml<sup>-1</sup> solutions of the P3HT:PCBM was used. Mixed solvents were composed of 0.4%, 4%, 6%, 8%, and 10% ethanol. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Baytron AI4083) was spin-coated on indium tin oxide (ITO) at 3000 rpm and baked at 150 °C for 30 min. After heating the solvents at 50 °C for 1 h, the P3HT:PCBM blending films were spin-coated on the top of PEDOT:PSS at 1000 rpm and baked at 130 °C for 2 h. Finally, 10 nm of calcium and 100 nm of aluminum were thermally evaporated on the active layer. Micro-Raman spectroscopy produced by lattice phonons was measured using a JobinYvonLabRam HR spectrometer. AFM (Veeco, DI Dimension 3100) in the noncontact mode was used to measure surface topological images of the P3HT:PCBM blend films. Electrical characteristics of the polymer solar cells were measured using a solar simulator with an AM1.5 filter and Labview-controlled Keithley 2400 SourceMeter.

### 3. Results and Discussion

Regarding the microstructural studies on P3HT:PCBM blending films in Fig. 1, the position of 1444.4 cm<sup>-1</sup> in the Raman spectrum shifts to the low-frequency area when ethanol composition is increased. According to the reference [4], Raman peak red-shifts when P3HT is self-assembled well and when P3HT has a longer effective conjugation length ( $L_{eff}$ ). Raman spectrum results revealed that incorporating ethanol into chloroform results in a significantly longer  $L_{eff}$  of P3HT chains in the crystalline region. Moreover, it results in considerable increases in proportions of the crystalline regions and improves the uniformity of the P3HT crystalline region.



Fig. 1 Raman spectroscopy of P3HT:PCBM with various compositions of ethanol,  $\lambda_{exc}$ =633 nm.

The AFM images in Fig. 2 were used to examine the surface morphologies of P3HT:PCBM blending films with different ethanol compositions. The scanning region measures  $10 \ \mu m \times 10 \ \mu m$ . AFM analysis results suggest a significant phase separation between P3HT and PCBM. In addition, the results also indicate a larger P3HT grain when the ethanol composition is increased.

Finally, we discussed photovoltaic performance. In Table I, the fill factor (FF) value improved from 0.45 to 0.59 when 8 v% ethanol was incorporated into the chloroform. The short-circuit current and open-circuit voltage decrease gradually with ethanol concentrations of 6% and above because the crystalline P3HT proportion is increased. Thus, the P-N junction is reduced and the separation rate of excitons is lowered. The incorporation of ethanol into chloroform effectively adjusts the active layer structures. Therefore, it provides better pathways in reducing the loss of charge carriers during transportation and increases the FF value of polymeric BHJ solar cells.



Fig. 2 AFM 2D images of the P3HT:PCBM blending fims made from various compositions of ethanol: (a) 0%; (b) 4%; (c) 6%; (d) 8%; (e) 10%.

Table I The photovoltaic parameters of P3HT:PCBM-based organic solar cells made from chloroform-ethanol co-solvents with different fraction of ethanol.

Blend ratio	J <sub>SC</sub> (mA/cm <sup>2</sup> )	V <sub>oc</sub> (V)	F.F.	PCE (%)
Ethanol 0 v%	7.99	0.58	0.44	2.01
Ethanol 4 v%	8.05	0.59	0.46	2.16
Ethanol 6 v%	7.97	0.57	0.56	2.51
Ethanol 8 v%	6.61	0.51	0.59	1.98
Ethanol 10 v%	4.18	0.46	0.55	1.06

## 4. Conclusions

The present study investigated the effect of incorporating different ethanol compositions into chloroform on the active layer structure of P3HT:PCBM and photovoltaic properties of BHJ solar cells. Raman spectrum results revealed that incorporating ethanol into chloroform results in a significantly longer  $L_{eff}$  of P3HT chains in the crystalline region. AFM images showed significant phase separation between P3HT and PCBM. The photovoltaic properties improved when mixed solvents were used in the active-layer morphological modifications. The film structure of organic solar cells can be optimized to achieve better electric characteristics.

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