

## Solvent mixtures for improving device efficiency of polymer photovoltaic devices

Fang-Chung Chen, Hsin-Chen Tseng, and Chu-Jung Ko

Citation: [Applied Physics Letters](#) **92**, 103316 (2008); doi: 10.1063/1.2898153

View online: <http://dx.doi.org/10.1063/1.2898153>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/92/10?ver=pdfcov>

Published by the [AIP Publishing](#)

---

### Articles you may be interested in

[Roles of donor and acceptor nanodomains in 6% efficient thermally annealed polymer photovoltaics](#)

Appl. Phys. Lett. **90**, 163511 (2007); 10.1063/1.2730756

[High efficiency polarization-sensitive organic photovoltaic devices](#)

Appl. Phys. Lett. **88**, 253506 (2006); 10.1063/1.2214175

[Morphology-dependent exciton emission and energy transfer in fluorene-polymer-related fluorescent and phosphorescent composite films spin cast from a mixture of two dissimilar organic solvents](#)

J. Appl. Phys. **98**, 103510 (2005); 10.1063/1.2132510

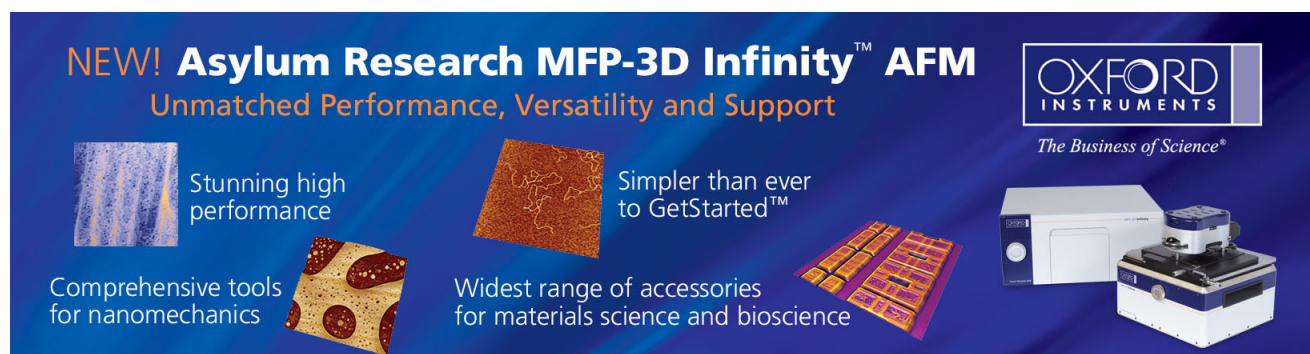
[Improved morphology of polymer-fullerene photovoltaic devices with thermally induced concentration gradients](#)

J. Appl. Phys. **97**, 036103 (2005); 10.1063/1.1845574

[Creation of a gradient polymer-fullerene interface in photovoltaic devices by thermally controlled interdiffusion](#)

Appl. Phys. Lett. **81**, 4607 (2002); 10.1063/1.1522830

---

The advertisement features a dark blue background with white and orange text. At the top left, it reads 'NEW! Asylum Research MFP-3D Infinity™ AFM' in large white letters, followed by 'Unmatched Performance, Versatility and Support' in orange. To the right is the Oxford Instruments logo, which includes the text 'OXFORD INSTRUMENTS' and the tagline 'The Business of Science®'. Below the main text are four images: a textured surface, a circular pattern, a grid of small squares, and the AFM instrument itself. Each image is accompanied by a short text description: 'Stunning high performance', 'Simpler than ever to GetStarted™', 'Comprehensive tools for nanomechanics', and 'Widest range of accessories for materials science and bioscience'.

## Solvent mixtures for improving device efficiency of polymer photovoltaic devices

Fang-Chung Chen,<sup>1,2,a)</sup> Hsin-Chen Tseng,<sup>1,2</sup> and Chu-Jung Ko<sup>3,4</sup>

<sup>1</sup>Department of Photonics, National Chiao Tung University, Hsinchu, Taiwan 300, Republic of China

<sup>2</sup>Display Institute, National Chiao Tung University, Hsinchu, Taiwan 30010, Republic of China

<sup>3</sup>Institute of Electro-optical Engineering, National Chiao Tung University, Hsinchu, Taiwan 30010, Republic of China

<sup>4</sup>National Nano Device Laboratories, Taiwan 30078, Republic of China

(Received 8 January 2008; accepted 22 February 2008; published online 14 March 2008)

In this work, we used solvent mixtures, consisting of 1-chloronaphthalene (Cl-naph), one solvent with a high boiling point, and *o*-dichlorobenzene, to prepare the polymer films for polymer photovoltaic devices. Because of the lower vapor pressure of the solvent mixtures, the polymer films dried slower. With higher Cl-naph concentration in the organic solvent, the polymer chains had longer time to self-organize themselves. As a result, the higher degree of crystalline led to lower device series resistance, thereby increasing the performance of the photovoltaic devices. © 2008 American Institute of Physics. [DOI: 10.1063/1.2898153]

Continuous growth in world energy consumption, declining fossil reserves, and increasing climate change concerns have led to an enormous increase in demands for alternative and economical energy sources. Solar energy is one of the renewable sources, which are clean and naturally replenished. Among the solar energy technologies, organic photovoltaic (OPV) devices have received much attention because they have potential advantages, such as mechanical flexibility, light weight, and low cost.<sup>1</sup> Recently, OPV devices based on polymer blends have been studied extensively.<sup>2</sup> The most common and efficient material system so far for polymer devices is the one consisting of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM). In addition, several groups have developed methods to improve the power conversion efficiency (PCE) of the solar cells using the P3HT/PCBM system.<sup>3-5</sup> For example, Padinger *et al.* used thermal annealing processes to improve the morphology.<sup>5</sup> Ma *et al.* found that the PCE of solar cells can be achieved up to 5.1% after postthermal annealing.<sup>4</sup> On the other hand, several works also discovered that the physical behavior of the organic solvent used to dissolve the polymer blend dramatically affect the device performance.<sup>6-10</sup> For example, Li *et al.* found that the PCE could be improved by reducing the solvent evaporation rate.<sup>7</sup> The so-called “solvent annealing” slows down the solvent evaporation by creating one solvent saturated environment. Therefore, the polymer chains have more time to undergo the self-organization process before complete solification. Apparently, the reduction of evaporation rate is a key step toward obtaining high device PCE.

The other possible method of reducing the solvent evaporation rate is to use a solvent with a high boiling point. For example, Vanlaeke *et al.* compared the devices made from two kinds of solvents with different boiling points and found that the polymer film made from the solvent having a higher boiling point has higher crystallinity, resulting in higher device performance.<sup>10</sup> Few studies, however, focus on solvent mixtures for polymer solar cells.<sup>6</sup> Here, we elabo-

ately choose one solvent with a high boiling point, 1-chloronaphthalene (Cl-naph) (bp=259 °C), as the additive in *o*-dichlorobenzene (DCB), (bp=179 °C) to dissolve the P3HT/PCBM blends. The device efficiency was improved by using the solvent mixture. Because no solvent saturated environment is involved, the fabrication procedure has been simplified.

The solar cells were made on indium tin oxide (ITO)-coated glass substrates. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Baytron® PVP P) was first spin coated onto the ITO substrates. After baking of the PEDOT:PSS film at 120 °C for 1 h, the P3HT/PCBM (1/1 in weight ratio) blends dissolved in the solvent mixtures, which were consisting of different composition of Cl-naph and DCB, were then spin-coated to form 250 (±10) nm-thick active layers. The layers were spontaneously dried in a N<sub>2</sub>-filled glove box. No solvent saturated environment was intentionally created. After spin coating, the color of the active layer gradually turned from light orange to dark purple; we defined the time taken by this process as the drying time (*t<sub>d</sub>*). After the drying process, the polymer films were thermally baked at 110 °C for 15 min. The metals, Ca (50 nm) and Al (100 nm), were thermally deposited on the active layer as the cathode. The current density-voltage (*J-V*) curves were measured using a Keithley 2400 source-measure unit. The photocurrent was obtained under illumination from a Thermal Oriel solar simulator (AM1.5G). The illumination intensity was calibrated using a standard Si photodiode detector equipped with a KG-5 filter (Hamamatsu, Inc).<sup>11</sup> The absorption spectra were measured by Lambda 650 UV-Vis spectrometer (Perkin-Elmer). The atomic force microscopy (AFM) images were taken on DI-Veeco multimode AFM with nanoscope controller. The grazing incident x-ray diffraction (GIXRD) patterns were recorded by a Philip X'pert Pro diffractometer.

Initially, we tried to use neat Cl-naph as the solvent to fabricate the devices. However, because of the strong surface tension, the P3HT/PCBM solution exhibited poor wetting behavior on the surface of PEDOT:PSS. The as-prepared films had poor uniformity and high density of defects. Owing

<sup>a)</sup>Electronic mail: fchen@mail.nctu.edu.tw.

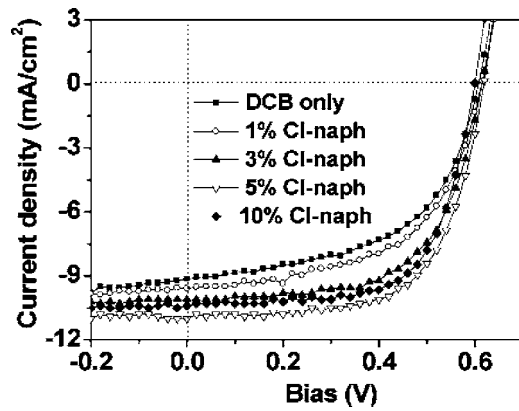


FIG. 1.  $J$ - $V$  curves of the polymer solar cells fabricated from various solvent mixtures. The measurement was performed under illumination at  $100 \text{ mW/cm}^2$  (simulated AM1.5G).

to the strong intermolecular force, an organic solvent with a high boiling point and low vapor pressure usually has higher surface tension. Therefore, although the drying speed becomes slower, the dewetting behavior limits the formation of high-quality films.

On the other hand, when Cl-naph was used as a cosolvent, the device exhibited improved performance. Figure 1 displays the  $J$ - $V$  characteristics under illumination for devices fabricated from various solvents. The cell made from neat DCB exhibited an open circuit voltage ( $V_{oc}$ ) of 0.61 V, a short-circuit current density ( $J_{sc}$ ) of  $9.1 \text{ mA/cm}^2$ , and a fill factor (FF) of 55.2%. The PCE of the device was therefore calculated as 3.1%. However, when the content of Cl-naph was 5.0% (in volume ratio) in the solvent mixture, the  $J_{sc}$ , FF, and PCE reached  $11.1 \text{ mA/cm}^2$ , 64.1%, and 4.3%, respectively. In contrast, when the concentration of Cl-naph was further increased to 10%, both  $J_{sc}$  and  $V_{oc}$  decreased, resulting in a lower PCE. The lower  $V_{oc}$  is probably due to the change in morphology or to the increased number of pinholes and/or microcracks of the polymer film. Table I summarizes the overall device performance with respect to the Cl-naph concentration. The  $t_d$  increased with the concentration of Cl-naph, suggesting that the evaporation rate indeed slowed down after the addition of Cl-naph. Because the vapor pressure of Cl-naph is 0.029 mm-Hg, which is much lower than that of DCB (1.2 mm-Hg), the solvent mixture becomes less volatile. Hence, the drying speed was lower after the addition of Cl-naph.

The use of Cl-naph as a cosolvent has several benefits. First, because the buckminsterfullerene has higher solubility in Cl-naph than that in DCB,<sup>12</sup> Cl-naph may help the dispersion of PCBM in the P3HT polymer matrix, resulting in

TABLE I. The performance of polymer solar cells made from different solvent mixtures under illumination with AM1.5G spectra ( $100 \text{ mW/cm}^2$ ).

Solvent	$V_{oc}$ (V)	$J_{sc}$ ( $\text{mA/cm}^2$ )	FF (%)	PCE (%)	$R_s^a$ ( $\Omega \text{ cm}^2$ )	Drying time (min)
DCB only	0.61	9.1	55.2	3.1	9.46	6
1.0% Cl-naph	0.61	9.6	57.2	3.3	10.16	8
3.0% Cl-naph	0.61	10.1	62.1	3.8	8.81	12
5.0% Cl-naph	0.61	11.0	64.1	4.3	7.98	18
10% Cl-naph	0.59	10.4	66.2	4.1	6.71	36

<sup>a</sup>Extracted from the  $J$ - $V$  curves under illumination (Ref. 15).

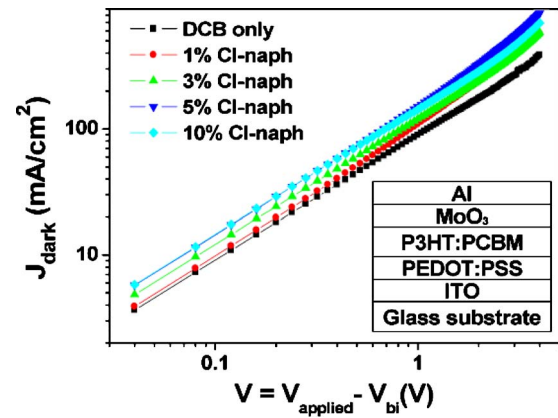


FIG. 2. (Color online) The  $J$ - $V$  characteristics of the hole-only devices measured in the dark. The bias was corrected for the built-in potential ( $V_{bi}$ ), which is 0.1 eV, owing to the difference in the work functions between the two electrodes. The inset shows the device structure of the hole-only devices. The thickness of  $\text{MoO}_3$  was 50 nm.

higher electron donor/acceptor interfacial area. Second, due to the slower evaporation rate, the P3HT polymer chains have longer time to self-organize themselves. As a result, the higher ordering of molecular structure leads to a higher hole mobility.

To measure the hole mobilities directly, we have fabricated hole-only devices using a high-work-function material, molybdenum oxide ( $\text{MoO}_3$ ), as the buffer layer at the cathode to block the injection of electrons.<sup>9</sup> The hole mobilities of the polymer blends were extracted from the  $J$ - $V$  curves of these hole-only devices in the dark, following the conventional model of space-charge limited current.<sup>9</sup> As shown in Fig. 2, the hole mobility for the device using the neat DCB as the solvent was  $4.68 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ . The mobility increased with the increasing concentration of Cl-naph in the solvent mixtures and became  $8.36 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$  when the content of Cl-naph was 5.0%. Apparently, the use of the

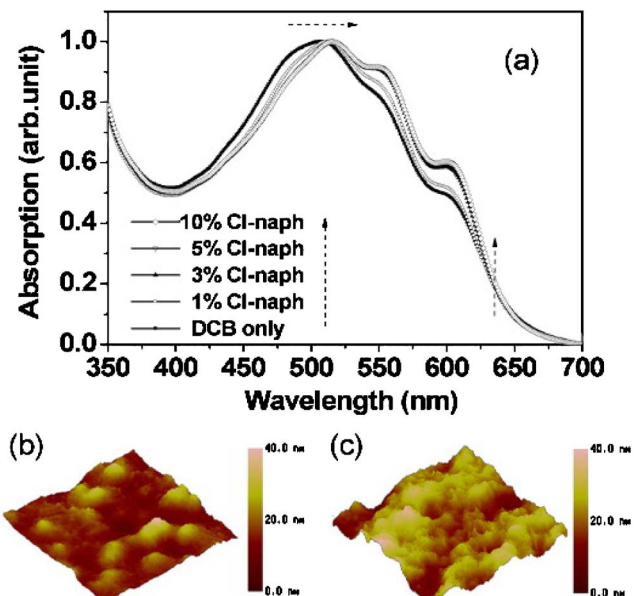


FIG. 3. (Color online) (a) Absorption spectra for P3HT:PCBM films fabricated from various solvent mixtures. (b) The AFM image, showing the surface morphology of the P3HT/PCBM blend films, deposited from neat DCB (rms roughness = 5.10 nm). (c) The AFM image of the polymer blend deposited from a 5% Cl-naph solvent mixture (rms roughness = 7.38 nm).

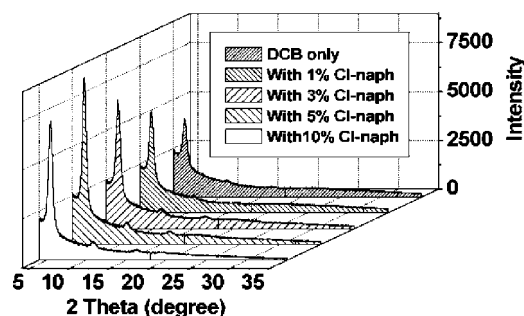


FIG. 4. GIXRD spectra for P3HT/PCBM films deposited from different solvent mixtures.

solvent mixtures indeed improves the hole mobility.

To confirm the increased degree of the polymer chain alignment, the morphology of the polymer films was further examined. First, the adsorption spectra of the P3HT/PCBM films were obtained as Fig. 3(a). For the film spin coated from the neat DCB solution, the absorption peak was at 506 nm and two shoulders were at 545 and 600 nm. After the addition of Cl-naph, the three vibronic absorption peaks became more pronounced, indicating enhanced ordering of P3HT.<sup>13</sup> Further, the redshift of the absorption peaks also implies better crystallinity, because lower density of conformational chain defects would lead to a longer  $\pi$ -conjugation length and, hence, a lower bandlike energy.<sup>14</sup>

Figures 3(b) and 3(c) show the AFM images for various films prepared from different solvents. Apparently, the surface of the film spin coated from the solvent mixture was rougher than that prepared from neat DCB. The previous report by Li *et al.* indicated that the rough surface is probably a signature of polymer organization.<sup>7</sup> In Fig. 3(c), the rough surface made from the solvent mixture also suggests a higher degree of ordering. This order structure reduces the internal series resistance of the device, thus increasing the photocurrent.

Another evidence of self-organization of polymer chains comes from the GIXRD results. The diffraction pattern (Fig. 4) displays two sets of reflections: the three low-angle diffraction peaks indexed ( $h00$ ) ( $h=1-3$ ) and the peak indexed (010), which can be attributed to the reflections of P3HT.<sup>4</sup> The former peaks are associated with the crystallographic

direction along the alkyl side chains ( $a$  axis); the latter is associated with the  $\pi$ -stacking direction of the backbones ( $b$  axis). From the enhanced intensity of the (100) peak, it is proved that the crystallinity was indeed improved after the use of the solvent mixture.

In conclusion, we have used solvent mixtures to reduce the solvent evaporation rate during the preparation of polymer solar cells. With higher Cl-naph concentration in the solvent mixtures, the polymer chains have longer time to self-organize themselves. As a result, the higher degree of crystalline leads to lower device series resistance, thereby increasing the device PCE of the photovoltaic devices.

The authors would like to thank the financial support from National Science Council Grant No. (NSC-96-2628-E-009-022-MY2) and Ministry of Economic Affairs Grant No. (96-EC-17-A-08-S1-015) and Ministry of Education ATU Program.

<sup>1</sup>P. W. M. Blom, V. D. Mihailesti, L. J. A. Koster, and D. E. Markov, *Adv. Mater. (Weinheim, Ger.)* **19**, 1551 (2007).

<sup>2</sup>G. Yu, J. Gao, J. C. Hummelen, F. Wudl, and A. J. Heeger, *Science* **270**, 1789 (1995).

<sup>3</sup>J. Y. Kim, K. Lee, N. E. Coates, D. Moses, T. Q. Nguyen, M. Dante, and A. J. Heeger, *Science* **317**, 222 (2007).

<sup>4</sup>W. L. Ma, C. Y. Yang, X. Gong, K. Lee, and A. J. Heeger, *Adv. Funct. Mater.* **15**, 1617 (2005).

<sup>5</sup>F. Padinger, R. S. Rittberger, and N. S. Sariciftci, *Adv. Funct. Mater.* **13**, 85 (2003).

<sup>6</sup>C. N. Hoth, S. A. Choulis, P. Schilinsky, and C. J. Brabec, *Adv. Mater. (Weinheim, Ger.)* **19**, 3973 (2007).

<sup>7</sup>G. Li, V. Shrotriya, J. S. Huang, Y. Yao, T. Moriarty, K. Emery, and Y. Yang, *Nat. Mater.* **4**, 864 (2005).

<sup>8</sup>V. D. Mihailesti, H. X. Xie, B. de Boer, L. M. Popescu, J. C. Hummelen, P. W. M. Blom, and L. J. A. Koster, *Appl. Phys. Lett.* **89**, 043504 (2006).

<sup>9</sup>V. Shrotriya, Y. Yao, G. Li, and Y. Yang, *Appl. Phys. Lett.* **89**, 063505 (2006).

<sup>10</sup>P. Vanlaeke, G. Vanhoyland, T. Aernouts, D. Cheyns, C. Deibel, J. Manca, P. Heremans, and J. Poortmans, *Thin Solid Films* **511**, 358 (2006).

<sup>11</sup>V. Shrotriya, G. Li, Y. Yao, T. Moriarty, K. Emery, and Y. Yang, *Adv. Funct. Mater.* **16**, 2016 (2006).

<sup>12</sup>R. S. Ruoff, D. S. Tse, R. Malhotra, and D. C. Lorents, *J. Phys. Chem.* **97**, 3379 (1993).

<sup>13</sup>T. A. Chen, X. M. Wu, and R. D. Rieke, *J. Am. Chem. Soc.* **117**, 233 (1995).

<sup>14</sup>O. Inganäs, W. R. Salaneck, J. E. Osterholm, and J. Laakso, *Synth. Met.* **22**, 395 (1988).

<sup>15</sup>A. Moliton and J. M. Nunzi, *Polym. Int.* **55**, 583 (2006).