

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Performance evaluation of PTB7:PC₇₁BM based organic solar cells fabricated by spray coating method using chlorine free solvent

Murugesan Vijay Srinivasan¹, Norio Tsuda¹, Paik-Kyun Shin³, and Shizuyasu Ochiai^{2*}

¹Department of Electrical Engineering, Aichi Institute of Technology, Toyota 470-0392, Japan.

²Professor emeritus, Aichi Institute of Technology, Toyota-470-0392, Japan

³Department of Electrical Engineering, Inha University, Incheon 402-751, Korea.

*Corresponding author: ochiai@aitech.ac.jp

Abstract

The PTB7:PC₇₁BM polymer based solar cells have been successfully fabricated by spin and spray coating technique using chlorine-free solvent (xylene), which are desirable to reduce environmental issues. The surface morphology of fabricated film characterized by AFM reveals that the surface morphology of the film is uniform and smooth when xylene is used as compared with chlorobenzene. The highest power conversion efficiency (PCE) (5.07 ± 0.6) was achieved using spray-coating technique than that of spin coating technique (PCE of 4.47 ± 0.6). The enhancement in the performance of the polymer solar cell could be attributed to the improved charge carrier transportation due to additive. The combination of chlorine-free solvent and spray-coating method minimize the waste material and reduce the environmental problem in large-area production of organic solar cells (OSCs).

Key words: Organic solar cells, Chlorine free solvents, PTB7 and PC₇₁BM, Spray coating

1.1 Introduction

Currently, research focused on conversion of solar energy into electrical energy is due to our energy demand per annum (1.6×10^{10} kW). The earth receives 175 peta watts (pW) of energy from the sun, which can provide us 3.8×10^{23} kW per one hour to meet our energy demands. With an average power conversion (cannot start with) efficiency of 10%, solar panels covering only 0.08% of the surface of the earth would provide the world's current consumption rate of energy (10 TW). The silicon solar cells have a much better efficiency and higher life span as compared to other light energy conversion method. However, production cost, recycling and environment pollution is major drawback in silicon solar cell. Therefore, research community extensively focused on developing new materials to achieve a higher energy conversion with low cost production and environmentally compatible using inorganic (silicon) or organic solar cells. Organic photovoltaic has attractive features like low cost, light weight, flexible, large area fabrication, high speed production and solution process compare with inorganic solar cell.¹⁻⁶ The highest efficiency of OSCs reported around 10–11%, which is still inferior to those silicon solar cells. In this most high efficient polymer solar cells are made up with chlorinated solvents. However, chlorine containing solvents are highly toxic and hazardous to environment and this is major problem in the mass production of polymer solar cells even though of the advantage of low-cost and large area solution fabrication.^{24, 27-28} In this present investigation, we fabricated the high performance assessment of PTB7:PC₇₁BM based organic thin film solar cell device using chlorine-free solvent by spin and spray coating technique. The active layers were prepared using PTB7:PC₇₁BM with 1,8-diiodooctane (DIO) in xylene and chlorobenzene. PTB7 and fullerene exhibit poor solubility in commonly used chlorine-free solvents, the addition of DIO in the active layer enhances the solubility.^{7, 15} and optimizing the desired donor-acceptor phase separation with nano-morphology and it results enhance the photovoltaic performance. To

improve the device performance, the solar cell was fabricated with spray coating techniques. The spray coating has an advantage of exhibiting large-area uniformity, preventing of inter layer dissolution and better mixing during spray coating.³⁵ Hence, the chlorine-free solvents with highest power conversion efficiencies by spray coating technique than that of spin coating technique.

The polymer-fullerene bulk heterojunction (BHJ) solar cells are widely used and currently attracting a great deal of attention and gaining the power conversion efficiency over 8–10% for single BHJ^{3–8} and greatly improved PCEs 8–12% for tandem device.^{1–2, 10–14} In this most high efficient polymer solar cells are made up of low band-gap polymers with toxic chlorinated solvents due to their high boiling point and solubility.^{15–23} The higher boiling solvent evaporates slowly during the device fabrication and it exhibits desired donor–acceptor phase separation along with higher solubility of the solvent which results in satisfactory efficiencies.^{24–26} At present, processes of polymer solar cell by chlorine-free solvents are very attractive candidates such as toluene, isomers of xylene, and trimethylbenzenes due to their comparable properties with the halogenated analogs. These solvents have the advantage of cost and sustainability points.^{24, 27–31} Unfortunately, some of the low band-gap polymers and fullerene exhibit poor solubility in commonly used chlorine-free solvents. This often results in no uniform phase segregation due to large fullerene / polymer rich grains in the cast films, reveals limiting the device performance³² This critical issue was solved by adding the more suitable additive with solvent and it enhances the fullerene solubility and exhibit enhanced device performance.^{26, 31, 33} Recently, 6–7% power conversion efficiency has been reported for polymer solar cells by spin and blade coated in a halogen-free solvent.^{24, 27} However, spray-coating techniques are being explored for large-area, uniform thin film and wastage of material is low compare with other method. In addition, it can

facilitate much more dilute solutions than the other method, allowing the use of various organic materials that have poor solubility in solvents.^{13, 34-43} Therefore, development of polymer solar cell using chlorine-free solvents by spray coating is capable of delivering large-area, uniform films with small amounts of material, which is having the compatibility for roll-to-roll fabrication is crucial.

2 Experimental Works

2.1 Materials

PTB7 was purchased from Ossila, England and used as p-type organic donor material. PC₇₁BM was purchased from American Dye Source, Inc and used as n-type organic acceptor material. PEDOT:PSS (Clevios™ PH1000) was purchased from Heraeus, Germany and used as hole transport layer between anode ITO and active layer of PTB7:PC₇₁BM. Xylene, chlorobenzene, acetone, ethanol and all other chemicals were obtained from Sigma-Aldrich are used as received.

Figure 1 shows that the molecular structures of PTB7 and PC₇₁BM.

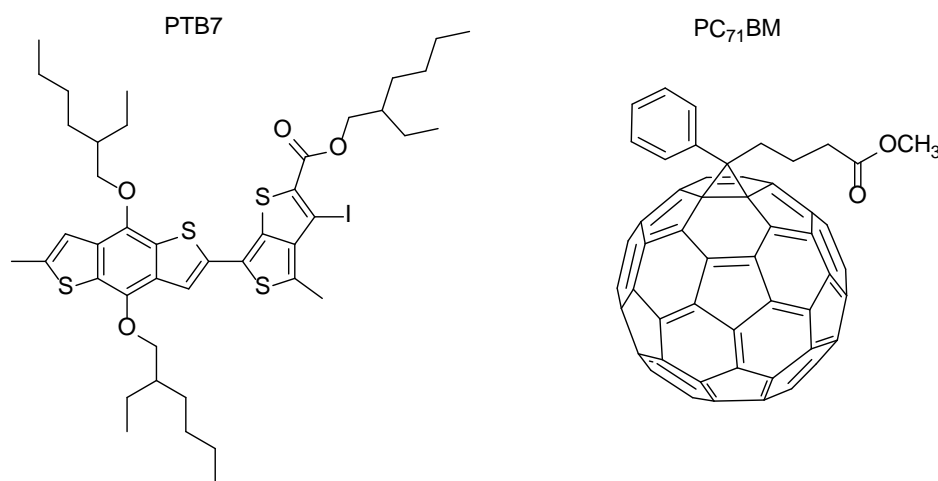


FIGURE 1: Molecular structures of PTB7 and PC₇₁BM.

2.2 Fabrication and characterization of organic thin film solar cell device.

The organic thin film solar cell(OTFSC) device was fabricated using indium doped tin oxide (ITO) conducting glass substrate (Aldrich; 8–12 Ω /sq). ITO substrate was patterned by longitudinal direction in the width of 5 mm by using an ultra-tape on a glass substrate, substrate was immersed in dilute hydrochloric acid (HCl) for 10 min followed by washed with water for another 10 min. The ITO conducting substrates were cleaned ultrasonically in sequential steps by using a neutral detergent, acetone, ethanol and distilled water for 10 min in each step. The cleaned ITO was exposed to UV ozone for 10 min to achieve hydrophilic state of the ITO surface. PEDOT:PSS was cast by spin coating technique at spin speed of 5000 rpm for 30s, followed by heat treated about 150°C in an oven for 10 min. The composite active layers of PTB7:PC₇₁BM with a relative ratio of 1(9.0 mg):1.5(13.5 mg) was prepared using different solvents like xylene and chlorobenzene with and without DIO. The active layer was coated by spray coating technique at 25s with a distance of 15 cm from nozzle-to-substrate. To avoid residues of DIO, the spray-coated active layers of PTB7:PC₇₁BM thin films were dried for 24 h in a physical vapor deposition (PVD) chamber. Three different OTFSC devices were fabricated with (1) PTB7:PC₇₁BM w/o DIO in xylene, (2) PTB7:PC₇₁BM + 3% DIO in XY and (2) PTB7:PC₇₁BM + 3% CB by spray coating method for evaluation photovoltaic performance using chlorine-free solvent presence or absence of DIO. Then, the active layer was coated by a spray coating technique using spray gun of 2 mm in diameter with N₂ pressure 0.05MPa. Finally, Aluminum (Al) metal was deposited using shadow mask with diameter of 5mm width in a high vacuum of 1.3×10^{-6} Pa. The active area of the device was 0.25 cm². The thickness of the PEDOT:PSS, active layer and Al electrode was measured as ~45, ~86 and ~100 nm, respectively. Figure 3 shows the energy band diagram of OTFSC device. For comparison, the solar cell was fabricated using conventional spin-coating techniques. For that, the precursor solution was

prepared in 1:1.5 ratio of PTB7:PC71BM with and without DIO using XY and CB. The active layers were coated with a spin speed of 1000 rpm by conventional spin coating method at 2 min (~84 nm thickness), then cathode Al was deposited on the top of the active layer by physical vacuum chamber using shadow mask.

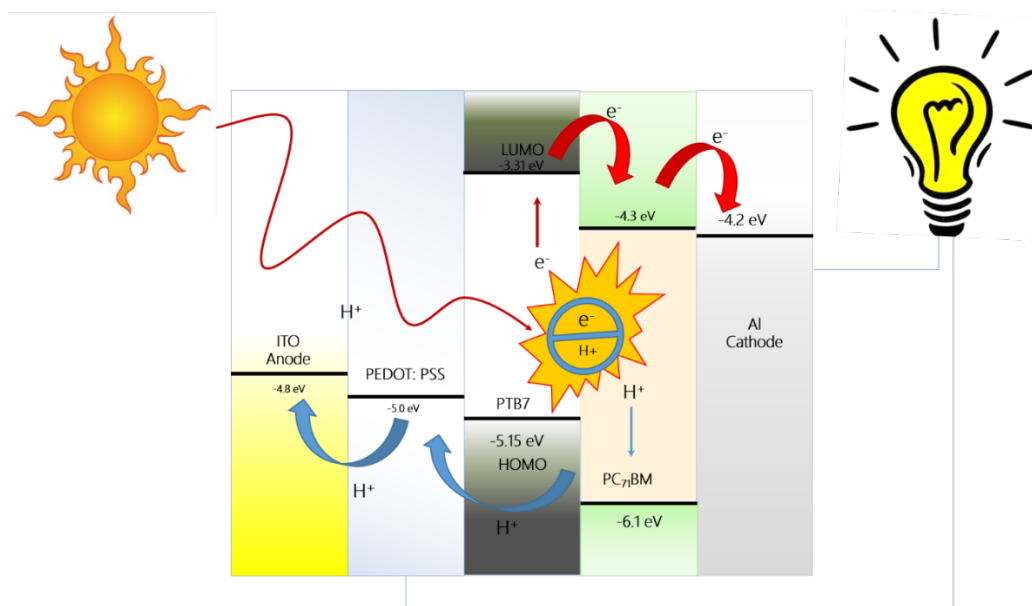


Figure 2. Energy diagram organic thin film solar cell

2.3. Characterization Techniques.

Surface morphology of the organic thin films was investigated using Seiko Instrument SPA400-SPI4000 atomic force microscope (AFM) and all AFM images were taken in dynamic force mode at optimal force. The thickness of the active layer and Aluminum was measured using a Dektak II profilometer. Performance of the OTFSC devices was examined by measuring photocurrent density-voltage (J - V) characteristics was measured standard solar simulator Newport 66902 150W (with an Oriel Cornerstone 130 monochromator and Xe lamp equipped with an Air Mass of 1.5 G (AM 1.5 G) filter was used as the white light source; 100 mW/cm^2). A thick black sheet was used as a shadow mask, which is placed in front of the active device area in

order to avoid the over-estimation of the current density and PCE. The J - V characteristics were measured using an Advantest-R-6441 A.C. source meter unit. All measurements were carried out in air without any encapsulation.

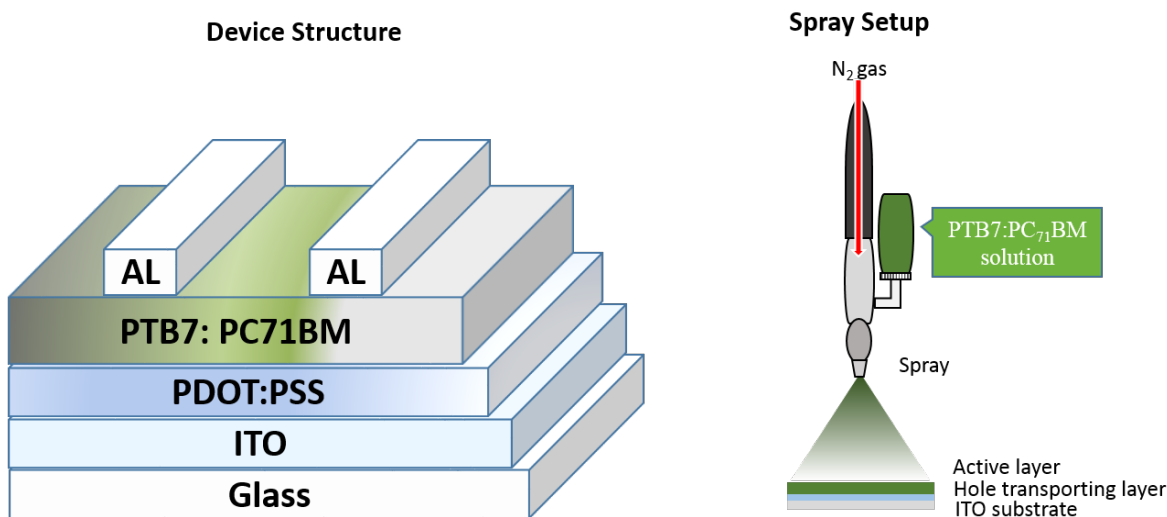


Fig. 3 Schematic representation of OTFSCs and spray coating setup

3 Results and Discussion

3.1 Surface Morphology and Absorption Studies

Surface morphology plays a vital role on the photovoltaic characteristics of OTFSC. The surface morphology of OTFSCs is controlled by altering blend ratio of donor and acceptor. However, the polarity and boiling point of solvent are major factor influencing the device performance.^{14, 25-27,}

⁴⁰ To understand the surface morphology of PTB7:PC₇₁BM on photovoltaic performance, the active layer are fabricated with spin and spray coating method using non-chlorinated/chlorinated solvent with and without additives DIO. The effects of additive on the surface morphology of the resulting thin-films of blended PTB7/PC₇₁BM were examined by atomic force microscopy (AFM), which is shown in the Figure 4. Surface roughness parameters of the PTB7:PC₇₁BM

prepared in XY and CB with different solvent with and without solvent are presented in Table 1; peak-valley (P-V) and root-mean-square of roughness (R_{RMS}).

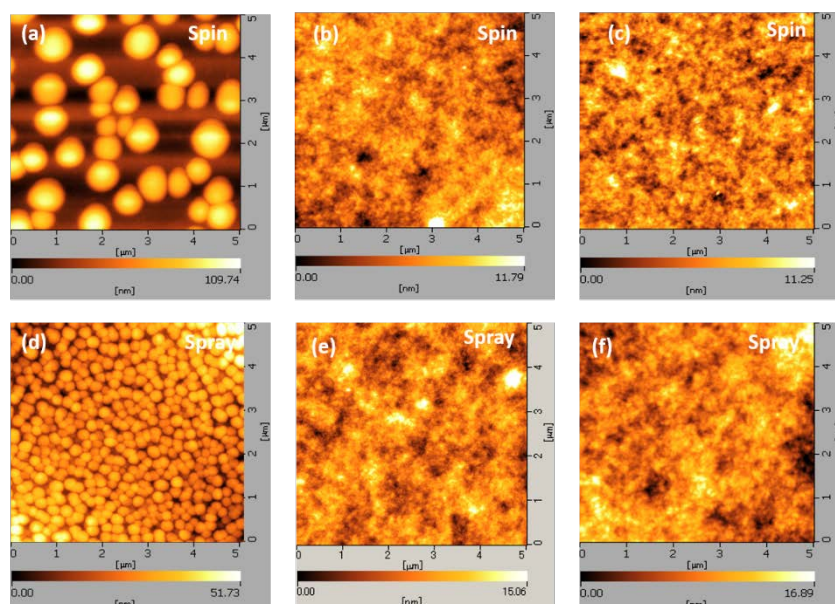


Figure 4. AFM image of PTB7:PC₇₁BM based active layer (a, d) W/o DIO in XY, (b, e) 3% DIO in XY, and (c, f) 3% DIO in CB fabricated by spin and spray coating method.

Figure 4a clearly shows that there are large domains in the PTB7:PC₇₁BM blend film prepared in pristine xylene. It implies that molecules of PTB7 and PC₇₁BM might have insufficient mutual solubility and it could not dissolve the surface aggregates of PC₇₁BM molecule during the thin film formation process. The larger the surface aggregates will diminish exciton migration to the donor/acceptor interface and is not favorable for charge separation, it leads to poor (diminish) the device performance.¹²⁻¹⁵ Whereas the active layer prepared in XY with additive DIO reveals noticeably smaller micro grains (Figure 4b) compare with pristine XY. The addition of DIO to the active layer dissolves the surface aggregates of PC₇₁BM molecules in the PTB7:PC₇₁BM matrix. The PC₇₁BM is well known for electron-deficient in nature and the iodine atom (DIO) is well known to bear a partial negative charge. This reveals strong interaction between the DIO and PC₇₁BM which enhances the solubility of PC₇₁BM. This leads to greater inter-penetrated

blending between the donor and acceptor which could be formed with smaller micro grains of nano-morphology. This might be suggested that better contact between donor and acceptor in the active layer which enhance the charge-carrier-transport between donor and acceptor in the active layer. It also suppresses the recombination charge carrier and improves the device performance,^{12-15, 41} The surface roughness of active layers prepared with 3% DIO in XY and CB show R_{RMS} =1.76 and 1.73 nm, respectively. It is reveals that surface morphology of active layer prepared from non-chlorinated solvent (XY) similar to the chlorinated solvent.

Table 1. Surface characteristic of active layer of PTB7:PC71BM were fabricated from various solvents without and with DIO by spin and spray coating method.

| PTB7: PC ₇₁ BM | Coating Method | P-V (nm) | R_{RMS} (nm) |
|---------------------------|----------------|----------|----------------|
| W/o DIO -XY | Spin | 10 | 2.65 |
| 3% DIO - XY | Spin | 21 | 1.76 |
| 3% DIO -CB | Spin | 19 | 1.73 |
| W/o DIO-XY | Spray | 58 | 8.2 |
| 3% DIO - XY | Spray | 25 | 2.27 |
| 3% DIO - CB | Spray | 19 | 2.67 |

Further to understand the effect of spray coating on surface morphology of active layer prepared with non-chlorinated and chlorinated solvent, we measured the surface morphology of the spray coated film. This result shows that the surface roughness values of active layers fabricated with pristine XY shows higher R_{RMS} =8.1nm than and without DIO (R_{RMS} = 2.3 nm). As discussed earlier, addition of additive dissolve the surface aggregates and subsequently increasing the degree of phase separation reveal smaller micro grain with nano-morphology, which might improve the device performance. The surface roughness values of active layers prepared in XY (R_{RMS} =2.6) very close to chlorinated solvent (R_{RMS} =2.3), it reveals that surface morphology of active layer prepared in XY is similar when compared with chlorinated solvent

(CB). The surface morphology of active layer fabricated with XY by spray coating is compared with spin coating method. The surface roughness of active layers fabricated by spray coating exhibit higher surface roughness $R_{\text{RMS}} = 2.6$ nm than spin coating method ($R_{\text{RMS}} = 1.7$ nm). The higher surface roughness of the film might increase the contact area between the active layer and the contact electrode, as well as increase the charge collection. Furthermore, the increased surface roughness may increase internal reflection in the active layer and improve light collection leading to increase in device efficiency.³⁴

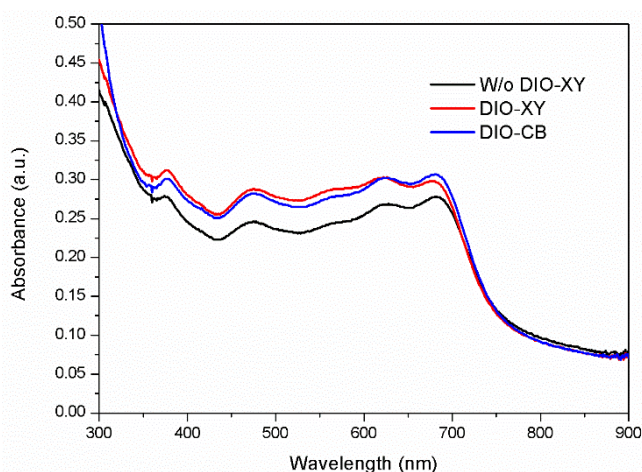


Fig. 5. Absorption spectra of PTB7:PC₇₁BM films prepared in XY with and without DIO.

The absorption spectra of active layers of PTB7:PC₇₁BM prepared in XY with and without CB are depicted in Figure 5 shows that strong absorption between 320 and 700 nm. Two broad absorption peaks, around 624 nm and 682 nm, are attributed to the characteristic π - π^* transition⁵ of the PTB7 polymer whereas the broad absorption coverage in the range from 320 to 500 nm is due to absorption by PC₇₁BM. The Figure 5 indicates that the absorption spectra of the PTB7:PC₇₁BM film with additives shows slightly higher absorption in the region of 300-700 nm than PTB7:PC₇₁BM film prepared in the absence of additives, which might be due to differences in the degrees of dispersion of PC₇₁BM in PTB7. This implies that the

addition of DIO added into XY dissolves the PC71BM molecule reveals greater inter-penetrated blending between the donor and acceptor interface. These results increase the absorption of blend layers and can harvest solar photons more effectively than the film prepared from pristine XY under the same conditions. Comparing the absorption spectra of the films prepared with and without solvent additives, the result indicates that there is no significant peak shift observed for the films prepared with organic additives from that of the film prepared with pristine XY. It implies that the thin films prepared with additives have amorphous phase. The absorption spectra of the films prepared with XY additives shows stronger absorption in the range between 450 nm and 550 nm. This slight red shift can be observed for the absorption peak at 645 nm with the decrease of absorption peak at 710 nm as compared to the films prepared CB with additives, indicating that the order of the polymer was more affected by PC₇₁BM. The absorption spectra slightly increases between 320 nm - 550 nm, indicating that PC₇₁BM has stronger absorption in the range between 320 nm and 550 nm attributed due to enhanced solubility of PCBM with better mixing. These results suggest that the absorption properties of active layer film prepared from XY is almost similar to CB and hence the toxic solvents could be avoided. Further, the effects of the organic solvent on the surface morphology of the PC71BM thin films were studied by *J-V* characteristics measurement.

3.2. Photocurrent density-Voltage (*J-V*) characteristics.

The polymer solar cells are prepared by spray coating method and its photovoltaic performance, which is compared with conventional spin coating method, was processed using non-halogenated solvent. The *J-V* characteristics and photovoltaic performance of the devices are given in Table 1 by spin and spray coating. Figure 5 shows the *J-V* characteristics of PTB7:PC₇₁BM based OTFSC fabricated by spray coating using xylene and chlorobenzene with

and without DIO. From this Table 2, the OTFSC prepared in xylene with 3% DIO exhibits higher PCE =5.07% than without DIO (PCE =2.90%). This implies that the addition of DIO in active layer reveals increase in the J_{sc} =12.07 mA/cm², FF=56 %, R_{sh} =398 Ω cm² and decreases the R_s =5.5 Ω cm², as a result of drastic improvement in the PCE =5.07% than without DIO, PCE=2.90%.

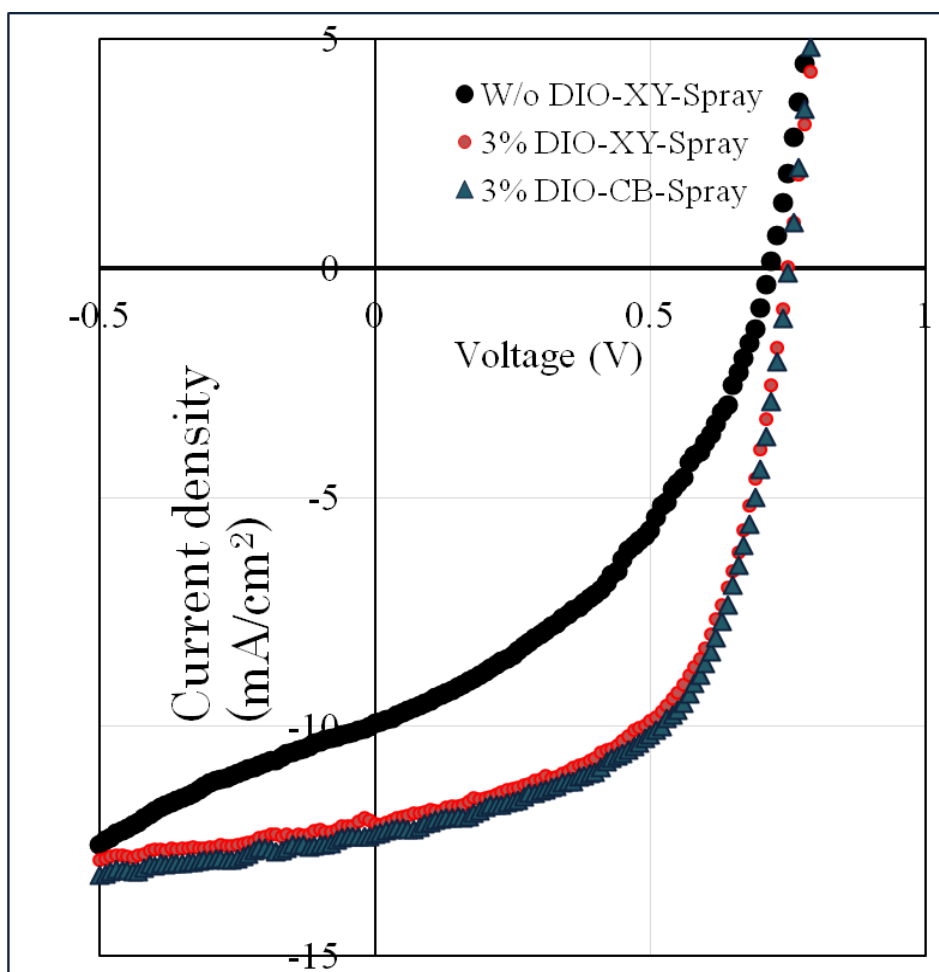


Figure 5. J - V characteristics of PTB7:PC₇₁BM based OSC devices with and without DIO using spray coating method.

The AFM studies reveals that the pristine xylene exhibits larger surface aggregates due to improper mixing between donor and acceptor, which will diminish exciton migration and is not

favorable for charge separation between donor/acceptor interfaces. The larger surface aggregates may contain a high concentration of grain boundaries and as a result form photo-carrier recombination centers. Furthermore, the large grains in the active layer may cause poor contact with cathode electrode and hole transporting layer and possible for recombination holes and electron as a result lower PCE =2.90%. Whereas the processing additives have been found to enhance device performance by dissolving the PC₇₁BM aggregates in the PTB7:PC₇₁BM matrix. Which facilitates integration of the PC₇₁BM molecules into the PTB7 resulting in a greater donor-acceptor interface and it could be formed with smaller micro grains. The results increases the surface interface between donor and acceptor in the active layer, which will enhance the exciton migration between the donor/acceptor interface and favorable for charge separation. Further, the additive DIO has higher boiling point of 169 °C could influence the formation of nanoscale morphology of molecules due to slow evaporation, result in decrease of series resistance and enhance the charge carrier transport properties, as well as increase of shunt resistance due to suppression of charge carrier recombination in the active layer.^{7, 14, 15, 34} This reveals that decreases of series resistance $R_s = 6.1 \Omega$ resulting in enhanced J_{sc} of 12.09 mA/cm², increase of FF=56 % as well as increases the shunt resistance $R_{sh} = 397 \Omega$ observed results improvement for device performance PCE 5.07%. There is an increase in the FF (from 40 % to 56%) due to the reduction of series resistance (R_s) and enhancement of shunt resistance (R_{sh}). The R_s is closely related with active layer morphology, intrinsic resistance and thickness of the active layer. The R_{sh} is related with the pin holes and traps presents in the morphology cause charge carrier recombination and leakage current. This suggests that the addition of additive dissolves the PC₇₁BM in the active layer and more integration, which results in increase of contact area between donor and acceptor, leads to decrease in the series resistance and enhance the charge

carrier transport properties, as well as increase of equivalent parallel resistance due to suppression of charge carrier recombination at the interface result enhancement in the device performance.

Table 2. *J-V* characteristics of PTB7:PC₇₁BM based OTFSC with and without DIO using spin and spray coating method.

| PTB7: PC ₇₁ BM | Coating Method | J_{sc} (mA/cm ²) | V_{oc} (V) | FF (%) | R_s (Ω cm ²) | R_{sh} (Ω cm ²) | PCE η (%) |
|---------------------------|----------------|--------------------------------|--------------|--------|------------------------------------|---------------------------------------|----------------|
| W/o DIO -XY | Spin | 9.33 | 0.62 | 41 | 8.7 | 155 | 2.38 |
| 3% DIO - XY | Spin | 13.70 | 0.71 | 46 | 8.6 | 179 | 4.47 |
| 3% DIO -CB | Spin | 13.49 | 0.72 | 49 | 8.5 | 250 | 4.79 |
| W/o DIO-XY | Spray | 9.93 | 0.71 | 40 | 6.1 | 193 | 2.90 |
| 3% DIO - XY | Spray | 12.09 | 0.74 | 56 | 5.5 | 397 | 5.07 |
| 3% DIO - CB | Spray | 12.37 | 0.75 | 57 | 3.9 | 407 | 5.31 |

The performance of spray coated solar cells device is compared with conventional spin coated device. The *J-V* characteristics of PTB7:PC₇₁BM based OTFSC prepared in xylene with and without additive DIO by spin coating method are shown in Figure 5. The spray-coated solar cells shows higher PCE ($\eta=5.07\%$) than spin coated device, PCE=4.47%. The photovoltaic performance of spray-coated device enhanced PCE due to increase in the surface roughness ($R_{RMS}=2.6$) than spin coated device ($R_{RMS}=1.7$ nm). The higher surface roughness of the film might increase the contact area between the active layer and the contact electrode as well as improve the charge collection. Furthermore, the increased surface roughness may increase internal reflection in the active layer and improve light collection leading to increase in device efficiency. This results shows that spray-coated PTB7:PC₇₁BM + 3% DIO based device exhibit higher $V_{oc}=0.74$ V, FF=56%, and significantly improved PCE=5.07 % than spin-coated device. Further, these device performance of chlorinated solvent compared with non-chlorinated solvent exhibits slightly higher PCE=5.31%, it implies that performance of non-chlorinated closer to chlorinated solvent and it might be considered as an alternate for conventional use of toxic

chlorinated solvent. The performance of non-halogenated device compared with chlorobenzene device exhibited slightly higher PCE=4.79% with additive. This implies that performance of non-chlorinated device closer to chlorinated solvent and it might be attributed due to similar surface morphology of active layer with nano-structure like chlorobenzene. The results show that smoother surface results in better contact between active layer and electrode leads to satisfactory device performance.

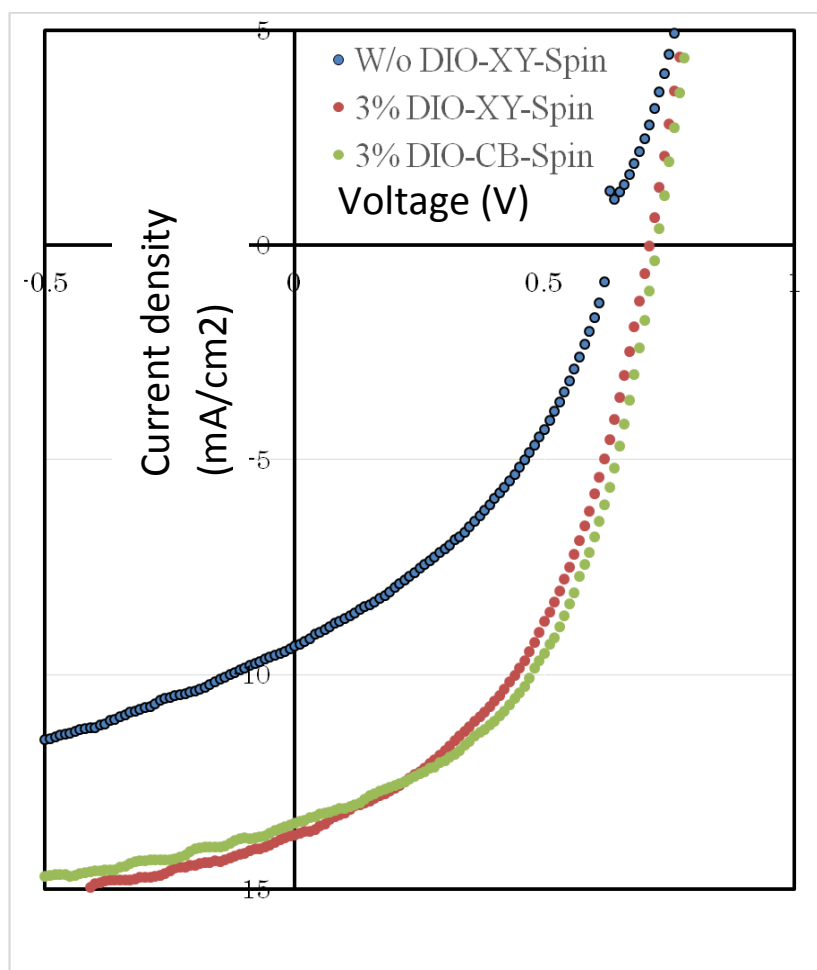


Figure 6. *J-V* characteristics of PTB7:PC₇₁BM based OSC devices with and without DIO using spin coating method.

Conclusion

PTB7:PC₇₁BM+3% DIO polymer solar cell is successfully fabricated with non-halogenated solvent by spin and spray coating method and its conversion efficiency was examined. The effect of solvents on active layer is studied by surface morphology and *J-V* measurement. This photovoltaic performance result shows that solar cell prepared by xylene yielding higher PCE =5.07 % with DIO than without DIO (PCE =2.90%) using spray coated method. The additive dissolve the PC₇₁BM aggregates in the PTB7:PC₇₁BM matrix favoring interblending between donor and acceptor and it could be formed nano-morphology. This surface morphology of the active layer fabricated with xylene forms more uniform surface which enable better contact between donor and acceptor, improving the charge carrier transport results and enhancing the device performance. The device performance of non-chlorinated solvent results is closer to chlorinated solvent, which is considered to be a replacement for conventional use of toxic chlorinated solvent. The spray-coated solar cells compare with conventional spin coating method reveals that spray-coated device shows significantly higher PCE=5.07 % than spin coated device (PCE=4.47%). The spray-coated device exhibit higher performance with more uniform film can be applied for roll-to-roll and it is considered to be an alternative of conventional spin coating. These results indicates that the combination of chlorine-free solvents and spray-coating method minimize the waste material and reduce environmental problem in large-area production of organic solar cell.

Acknowledgements

This research was partly supported by the MEXT Private University Project Grant (No. S1001033), the Japan Science and Technology-Adaptable and Seamless Technology Transfer

Program (R&D No. AS232Z02610B), and Joint Research between Aichi Institute of Technology and NDS.

Notes

²Professor emeritus, Aichi Institute of Technology, Toyota-470-0392, Japan.

E-mail:ochiai@aitech.ac.jp.

³Department of Electrical Engineering, Inha University, Incheon 402-751, Korea.

References

1. Youa, L. Doua, Z. Hongc, G. Li and Y. Yanga, *Prog Polym Sci*, 2013, **38** (12), 1909-2070.
2. O. Adebajo, P. P. Maharjan, P. Adhikary, M. Wang, S. Yangc and Q. Qiao, *Energ. Environ. Sci*, 2013, **6**, 3150-3170.
3. C. Gu, Y. Chen, Z. Zhang, S. Xue, S. Sun, C. Zhong, H. Zhang, Y. Lv, F. Li, F. Huang, Y. Ma, *Adv Energy Mater*, 2014, **4** (8), DOI: 10.1002/aenm.201301771.
4. Z. He, C. Zhong, S. Su, M. Xu, H. Wu and Y. Cao, *Nat Photonics*, 2012, **6**, 591-595.
5. H. Zhou, Y. Zhang, J. Seifert, S. D. Collins, C. Luo, G. C. Bazan, T.-Q. Nguyen and A.J. Heeger, *Adv Mater*, 2013, **25**, 1646-1652.
6. Z. He, C. Zhong, X. Huang, W. Wong, H. Wu, L. Chen, S. Su and Y. Cao, *Adv Mater*, **2011**, **23**, 4636-4643.
7. Y. Liang, Z. Xu, J. Xia, S.-T. Tsai, Y. Wu, G. Li, C. Ray and L. Yu, *Adv Funct mater*, 2010, **22**, E135-E138.
8. R. F. Stephen, *Nature*, 2004, **428**, 911-918.
9. You, L. Dou, K. Yoshimura, T. Kato, K. Ohya, T. Moriarty, K. Emery, C.-C. Chen, J. Gao, G. Li and Y. Yang, *Nat Commun*, 2013, **4**, Article No.1446, 1-10.
10. R. C. Chiechi, R.W.A. Havenith, J. C. Hummelen, L. J. A. Koster and M. A. Loi, *Mater*

- Today*, 2013, **16** (7–8), 281-289.
11. V. Kaltenhauer, T. Rath, M. Edler, A. Reichmann and G. Trimmel, *RSC Adv*, 2013, **3**, 18643-18650.
 12. C. C. Chen, W. H. Chang, K. Yoshimura, K. Ohya, J. You, J. Gao, Z. Hong and Y. Yang, *Adv Mater*, 2014, 26 (32), 5670-5677.
 13. H.-C.Liao, C-C. Ho, C.-Y.Chang, M.-H. Jao, S.B. Darling and W.-F.Su, *Mater Today*, 2013, **16** (9), 326-336.
 14. M. Ito, K. Palanisamy, A. Kumar, V. S. Murugesan, P-K. Shin, N. Tsuda, J. Yamada, S. Ochiai, *Int. J. Photoenergy*. 2014, Article ID 694541, 1-8.
 15. S. J. Lou, J.M. Szarko, T. Xu, L. Yu, T. J. Marks and L.X. Chen, *J Am Chem Soc*, 2011, **133**, 20661-20663.
 16. M. Lenes, M. Morana, C. J. Brabec, P. W. M. Bolam. *AdvFunct Mater*; 2009, **19**, 1106-1111.
 17. R. Xia, D-S. Leem, T. Kirchartz, S. Spencer, C. Murphy, Z. He, H. Wu, S. Su, Y. Cao, J-S. Kim, J. C. deMello, D.D.C. Bradley and J. Nelson, *Adv. Energy Mater*, 2013, **3**, 718-723.
 18. S. Ochiai, P. Kumar, K. Santhakumar and P-K. Shin, *Electron Mater Lett*, 2013, **9** (4), 399-403.
 19. J. K. Lee, W. L. Ma, C. J. Brabec, J. Yuen, J. S. Moon, J. Y. Kim, K. Lee, G. C. Bazan, and A.J. Hegger, *J Am ChemSoc*, 2008, **130**, 3619-3623.
 20. H. Yu, H. Jianhui, Z. Shaoqing, L. Yongye, Y. Guanwen, Y. Yang, Y. Luping, W. Yue, and L. Gang, *Nat Photonics*, 2009, **3**, 649-653.
 21. W. Zhang, B. Zhao, Z. He, X. Zhao, H. Wang, S. Yang, H. Wu and Y. Cao, *Energy Environ Sci*, 2013, **6**, 1956-1964.
 22. Y-W. Su, S.-C. Lan, K-H. Wei, *Mater Today*, 2012, **15** (12), 554-562.
 23. E. Stratakis and E. Kymakis, *Mater Today*, 2013, **16** (4), 133-146.
 24. P.-T. Tsai, C.-Y. Tsai, C.-M. Wang, Y-F. Chang, H.-F. Meng, Z-K. Chen, H.-W. Lin, H.-W. Zan, S.-F. Horng, Y.-C. Lai and P. Yu, *Org Electron*, 2014, **15**, 893-903.
 25. G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery and Y. Yang, *Nat. Mater.* 2005, **4**, 864-868.
 26. L. Ye, Y. Jing, X. Guo, H. Sun, S. Zhang, M. Zhang, L. Huo, and J. Hou, *J PhysChem C*, 2013, **117**, 4920-4930.
 27. C. Duan, W. Cai, B. B. Y. Hsu, C. Zhong, K. Zhang, C. Liu, Z. Hu, F. Huang, G. C. Bazan, A.

- J. Heeger, Y. Cao, *Energy Environ Sci*, 2013, **6**, 3022-3034.
28. O. Synooka, K-R. Eberhardt and H. Hoppe, *RSC Adv*, 2014, **4**, 16681-16685.
29. C.-C. Chueh, K. Yao, H.-L. Yip, C.-Y. Chang, Y.-X. Xu, K.-S. Chen, C.-Z. Li, P. Liu, F. Huang, Y. Chen, W.-C. Chen and A. K.-Y. Jen, *Energy Environ Sci*, 2013, **6**(11), 3241-3248.
30. Y. Zhang, J. Zou, C-C. Cheuh, H-L. Yip, and A. K.-Y. Jen, *Macromolecules*, 2012, **45**, 5427-5435.
31. A. K. K. Kyaw, D. H. Wang, C. Luo, Y. Cao, T.-Q. Nguyen, G. C. Bazan and A. J. Heeger, *Adv Energy Mater*, 2014, **4** (7), DOI: 10.1002/aenm.201301469.
32. H. Hoppe and N. S. Sariciftci, *J Mater Chem*, 2006, **16**, 45.
33. Y. Sun, G. C. Welch, W. L. Leong, C. J. Takacs, G. C. Bazan and A. J. Heeger, *Nat. Mater*, 2011, **11**(1), 44-61.
34. P. Kumar, S. Kannappan, P-K. Shin and S. Ochiai, *J. Korean Phys. Soc.* 2013, **62** (8), 1169-1175.
35. L.-M. Chen, Z. Hong, W.L. Kwan, C-H. Lu, Y-F. Lai, B. Lei, C-P. Liu, Y. Yang, *ACS. Nano*. 2010, **4**(8), 4744-4752.
36. S. Kannappan, K. Palanisamy , J. Tatsugi, P-K. Shin and S. Ochiai, *J Mater Sci*, 2013, **48**, 2308-2317.
37. Y. Zheng , R. Wub, W. Shi , Z. Guan and J. Yu, *Sol Energ Mat Sol C*, 2013, **111**, 200-205.
38. P-K. Shin, P. Kumar, A. Kumar, S. Kannappan and S. Ochiai, *Int. J. Photoenergy*. 2014, Article ID 786468, 1-8.
39. Y. Zheng, S. Li, X. Yu, D. Zheng and J. Yu, *RSC Adv*, 2014, **4**, 16464-16471.
40. M. V. Srinivasan, M. Ito , P. Kumar , K. Abhirami , N. Tsuda, J. Yamada, P-K. Shin, and S. Ochiai, *IndEngChem Res*, 2015, **54** (1), 181-187.
41. P. Kumar, K. Santhakumar, J. Tatsugi, P-K. Shin, and S. Ochiai, *Jpn J ApplPhys*, 2014, **53**, 01AB01-08.
42. C. Kastner, S. Rathgeber, D. A. M. Egbe and H. Hoppe, *J Mater Chem A*, 2013, **1** (12), 3961-3969.
43. S. Engmann, V. Turkovic, P. Denner, H. Hoppe and G. Gobsch, *J PolymSci Part B PolymPhys*, 2012, **50**(19), 1363-1373