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A Universal Halogen-free Solvent System for Highly Efficient Polymer Solar Cells

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The power conversion efficiencies (PCEs) of state-of-the-art polymer solar cells (PSCs) have been promoted to over 9%. However, halogenated solvents like chlorobenzene (CB), *o*-dichlorobenzene (DCB), 1,8-diiodooctane (DIO) or their mixtures are still predominately used in the fabrications of these high performance PSCs. With the rapid progress in PCEs, to remove the halogenated solvents from the fabrication processes of PSCs becomes an urgent task for the practical utilization of PSC technology. In this contribution, a halogen-free solvent system consisting of *o*-xylene (XY) and N-methylpyrrolidone (NMP) was successfully applied in fabrications of the PSCs based on a variety of highly efficient polymers including PBDT-TS1 and other eight types of photovoltaic polymers. Notably, utilizing XY/2% NMP mixture as processing solvent, PBDT-TS1/PC₇₁BM-based PSC realized a PCE of 9.47%, which is the highest value in halogen-free solvent processed PSCs till now. The photovoltaic properties and nanoscale morphology clearly indicated that the halogen-free solvent system featuring XY/NMP mixture can replace the role of the widely utilized halogenated solvents in fabricating environmental-friendly PSCs with high efficiency.

Introduction

Polymer solar cells (PSCs) have attracted considerable interests due to their potentials in making flexible, light weight, large area device by roll-to-roll printing process.¹⁻⁵ The bulk heterojunction (BHJ) structure is predominately used in PSCs, in which the photovoltaic active layers commonly consist of the interpenetrating networks of a solution processable conjugated polymer as electron donor and a fullerene derivative as electron acceptor. As well known, the backbones of conjugated polymers are rigid and commonly insoluble due to the strong inter-molecular π - π interaction, so that flexible side chains like alkyls have been introduced as the substituent onto the backbones and also organic solvents with strong solvation effect on the organic semiconductors have been used in device fabrication processes.^{5,6} Halogenated solvents, like chloroform (CF), chlorobenzene (CB), *o*-dichlorobenzene (DCB) and so on, play critical roles in the fabrications of PSCs due to their strong solvency to conjugated polymers and fullerene derivatives.

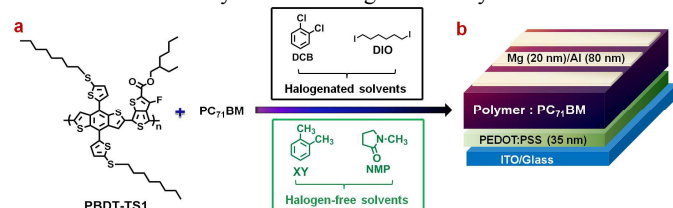
In the past decade, thousands of materials including conjugated polymers and fullerene derivatives and many processing methods for making the active layers of PSCs have been developed and applied for pursuing high photovoltaic performance, and thus the power conversion efficiencies (PCEs) of PSCs with BHJ structure have been improved to over 9%.⁷⁻¹⁹ However, halogenated solvents are still predominately used in the fabrications of PSCs. As known, the harmless treatments of halogenated solvents are very difficult. For example, if the solvent vapor is released directly into the atmosphere, it will cause the depletion of the ozone layer; if the vapor is burned, the result halogen acid will cause acid rain.^{20,21} Therefore, with the rapid progress in PCEs, to remove the

halogenated solvents from the fabrication processes of PSCs becomes an urgent task for the PSC field, that is, the halogenated solvent issue is a huge obstacle to environmental-friendly industrialization of PSCs now.

Fortunately, this problem has drawn attention from the scientists in the PSCs field, and a few interesting results reveal that the PSCs with relatively good efficiencies could be fabricated by using the non-halogenated single solvent or binary solvent with a trace amount of halogenated solvent additives.²²⁻³⁰ For example, Jen *et al.* used *o*-xylene, 1,2,4-trimethylbenzene and 1,2-dimethylnaphthalene as the processing solvent to realize a high PCE of 7.26% in the photovoltaic system of PIDTT-DFBT:PC₇₁BM blend;²⁵ Li *et al.* used toluene and N-methyl pyrrolidone for making the device of P3HT:ICBA blend to produce a desirable PCE of 6.6%;²⁶ Tsai and co-workers applied the chlorine-free solvents in the efficient PSCs based on the low band-gap polymer PBDTTT-C-T:PC₇₁BM blend by blade coating, which delivered a desirable PCE up to the 6.11%.²⁹ Lin *et al.* fabricated "quasi-bilayer" inverted PSCs using halogen-free solvents based on PBDTTT-C-T and PTB7 with PCE up to 6.55% and 7.15%, respectively.³⁰ However, the halogen-free solvents in previous works are merely applied in a few polymers and most of the results obtained from non-halogenated solvent processing are not as high as that from halogenated solvent processing. Considering that halogen-free solvents are still not utilized in the state-of-the-art photovoltaic polymers, it still will be of great importance to the field if we can find a universal green solvent system to reproduce the highly efficient PSCs based on the current photovoltaic materials.

The processing additive plays a critical role in optimizing the morphology of active layer.³¹⁻³³ Since the solubility of fullerene in *o*-

xylene (XY) is unsatisfactory (see Table S1), the morphology of blend film cast from XY happens big size islands. Halogenated additive solvent such as 1,6-diiodohexane (DIH), 1,8-diiodooctane (DIO), 1-chloro-naphthalene (CN) can selective solubility of PCBM and improve the morphology by extended drying time in active layer due to its high boiling point. In order to realize the goal of fabricating PSCs with halogen-free solvent as the processing solvent. *N*-methylpyrrolidone (NMP) meet the requirements for processing additives, a) differential solubility of the fullerene component,³¹ b) higher boiling point (NMP, 202 °C) than the host solvent (XY, 144.5 °C); c) suitable solvent properties match well with the host solvent (see Table S1).²⁶ Consequently, the halogen-free solvent NMP was selected as the processing additive to optimization the morphology of blend film. A halogen-free binary solvent system based on XY and NMP can be used as the processing solvent for making highly efficient PSCs. The initial test of device performance revealed that the PSC processed by the non-halogenated solvent are comparable with that obtained in the PSC processed with halogenated binary solvent, i.e., DCB/DIO. Then, we tried to find out the optimal composition of the solvent mixture of XY and NMP and then investigated the morphological evolution of the PBDT-TS1:PC₇₁BM blend from halogenated solvent processing to halogen-free solvent processing. After that, the halogen-free solvent system with the optimal composition was successfully applied in fabrications of the PSCs based on a variety of highly efficient polymers including PBDTTT-EFT,³⁴ PBDTTT-C-T,³⁵ PBDTBDD-T,³⁶ PTB7,³⁷ PBDT-DPP,³⁸ PDTG-IID,³⁹ PBDT-TPD⁴⁰ and the classical polymer P3HT.⁴¹ Our study clearly indicated that the halogen-free solvent system featuring XY/NMP mixture can replace the role of the widely utilized solvent like DCB/DIO or CB/DIO mixture in fabricating environmental-friendly PSCs with high efficiency.



Scheme 1 (a) The chemical structures of PBDT-TS1, the halogenated and halogen-free solvents involved in this work; (b) Device structure of a typical bulk heterojunction PSC.

Results and discussion

As shown in Scheme 1, the device structure of the PSCs based on PBDT-TS1:PC₇₁BM is ITO/PEDOT:PSS (35 nm)/active layer/Mg (20 nm)/Al (80 nm), which is the same as that in our recent work.¹⁰ At first, the control device was fabricated by using the optimal conditions, i.e. the donor/acceptor (D/A) ratio in the active layer is 1:1.5 (wt/wt), and the mixture of DCB and 3% DIO (v/v) was used as the processing solvent, and the methanol treatment was used to improve the quality of the films. As shown in Fig. 1a and listed in Table 1, the best *PCE* of the control device is 9.32%, with a short circuit current density (J_{sc}) of 17.55 mA/cm², an open-circuit voltage (V_{oc}) of 0.79 V and a fill factor (*FF*) of 67.23%. The photovoltaic parameters of the control device are very similar as those in our recent work.¹⁰ For the device prepared by using pure XY, the device shows a *PCE* of 2.96%, which is much lower than those of the devices processed by pure DCB and DCB/3% DIO, respectively. However, when a trace amount of NMP was used as the solvent

additive, the J_{sc} and *FF* can be improved significantly. As shown in Fig. S1 and Table S2, when 1%, 2% and 4% (vol) NMP were mixed with XY for making the solutions of PBDT-TS1 and PC₇₁BM, respectively, higher J_{sc} and *FF* can be realized, and when 2% NMP was used as the additive, a high *PCE* of 9.47% can be achieved, which is even better than that of the device fabricated by DCB/3% DIO. Methanol treatment is also effective in the XY/NMP case (see Fig. S2 and Table S3) As demonstrated in Fig. 1b, the external quantum efficiency (*EQE*) spectra of the devices processed by DCB, DCB/3% DIO, XY and XY/2% NMP show similar trend as the *J-V* measurements, i.e. the *EQE* of the device processed by XY/2% NMP is much higher than that of the device processed by pure XY and quite similar as that of the device processed by DCB/3% DIO. Moreover, the variations of the photovoltaic parameters of the devices prepared by DCB/3% DIO and by XY/2% NMP were provided in Table 1, and the results clearly demonstrate that these two types of processing solvents are very similar in fabricating highly efficient and reproducible PSCs based on the PBDT-TS1:PC₇₁BM photovoltaic system.

Table 1. The photovoltaic parameters of PBDT-TS1: PC₇₁BM-based PSCs with various solvents under AM 1.5G, 100 mW/cm² illumination.

Solvent	Solvent Additive	V_{oc} (V)	J_{sc} (mA/cm ²)	<i>FF</i> (%)	<i>PCE</i> ^a (^b) (%)	<i>RMS</i> (nm)
DCB	w/o	0.81	15.39	57.37	6.94(7.15)	1.14
DCB	3% DIO	0.79	17.55	67.23	9.15(9.32)	1.02
XY	w/o	0.80	8.55	43.25	2.79(2.96)	20.4
XY	2% NMP	0.79	17.46	68.63	9.11(9.47)	1.21
XY	3% Me-naph	0.80	17.10	64.33	8.67(8.80)	1.18

^a The average *PCE* were obtained from 10 devices. ^b The maximum values of the *PCE*s are provided in the parentheses.

Meanwhile, 1-methylnaphthalene (Me-naph) developed by Jen *et al.* was also selected as halogen-free processing additive to fine-tune the morphology of PBDT-TS1: PC₇₁BM-based PSCs. Similarly, the PSC was optimized by tuning the different volume of Me-naph (see Fig S1 and Table S2), a high *PCE* up to 8.80% was achieved in device employing 2% Me-naph with a V_{oc} of 0.80 V, a J_{sc} of 17.10 mA/cm², and a *FF* of 64.33%, which is inferior compared with PSCs fabricated with NMP as the processing additive under the identical conditions.

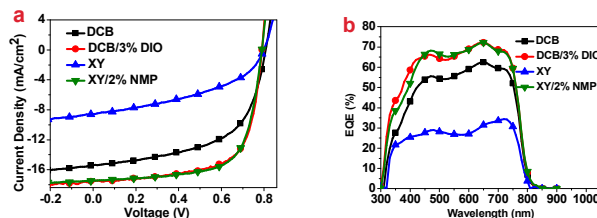


Fig. 1 *J-V* (a) and *EQE* (b) curves based on PBDT-TS1: PC₇₁BM processed from DCB, DCB/3% DIO, XY and XY/2% NMP.

In order to investigate the influence of the processing solvents on the morphological properties of the PBDT-TS1:PC₇₁BM films, the surface and bulk morphologies of the four blend films processed with DCB, DCB/3% DIO, XY and XY/2% NMP are characterized by atomic force microscopy (AFM) and transmission electron microscope (TEM), respectively, and the corresponding AFM and

TEM images are shown in Fig. 2a-2l. The blend films processed with DCB and DCB/3% DIO show very similar morphological properties and little difference in surface and bulk morphology can be observed from the phase and TEM images (see Fig. 2a, 2b, 2e, 2f, 2i and 2j), i.e. the phase separation in these two films are very similar and their root mean square roughness (RMS) values are 1.14 nm and 1.02 nm (see Table 1), respectively. The blend films processed with XY and XY/2% NMP show distinct differences in morphologies. On the basis of the topographies from the AFM measurements (see Fig. 2c and 2d), the addition of 2% NMP into XY is very helpful for getting a smooth surface, i.e. the RMS value of the two blend films are 20.4 nm and 1.21 nm (see Table 1), respectively. The blend film processed with pure XY shows huge ball-like aggregations, ca. a few hundred nanometers in diameter, which can be observed in Fig. 2c, 2g and 2k. Since the ball-like aggregations form dark zones in the TEM image (see Fig. 2k), they should consist of PC₇₁BM.⁶ As known, in order to minimize the recombination of excitons and free carriers, the blend film should have a nanoscale phase separation. The severe phase separation in the blend processed with XY will cause strong recombination, so the corresponding device showed very low photovoltaic performance. Interestingly, after the addition of 2% NMP into XY, the severe phase separation in the blend film can be completely avoided. For instance, the RMS value of the XY/NMP casted blend film reduces to 1.21 nm (see Fig. 2d), which is very similar as that of DCB/DIO casted film in Fig. 2b; Fig. 2h and 2l show very similar phase separation as in Fig. 2f and 2j. Although processing with DCB outperforms processing with XY in surface and bulk morphology, adding small amount of NMP in XY could significantly meliorate the poor phase separation and film quality. These results imply that XY/NMP might perform as well as DCB/DIO in processing polymer:PCBM blend and generate similar morphological features.

Table 2. The top surfaces of blend films with different processing additive were characterized by X-ray photoelectron spectroscopy (XPS).

Solvents	C _{1s} (%)	S _{2p} (%)	F _{1s} (%)	C/S Ratio
XY	67.15	7.47	0.38	8.99
DCB/3%DIO	86.67	8.49	1.30	10.21
XY/3% Me-naph	87.08	8.25	1.24	10.56
XY/2% NMP	87.69	7.8	1.19	11.24

As reported before,²⁵ the Hansen solubility parameters (HSPs) were useful to understand the impact of these binary solvents on morphology (see Fig. S3 and Table S4). According to the Fig. S3, the HSPs of the DCB are located near to that of PC₇₁BM, however, DIO is located far away from that of PC₇₁BM, in view of the PBDD-TS1 and PC₇₁BM shows excellent solubility in DCB (see Table S1), a small amount of DIO adding into DCB will not change the fullerene solubility significantly and the morphology of the PSCs fabricated with DCB/DIO have a lot in common compared to PSCs fabricated with DCB. Although XY is also located far away from that of PC₇₁BM, indicating their poor fullerene solubility, the solubility of fullerenes can be significantly improved by adding a small amount of NMP into XY due to the excellent solubility (110 mg/ml) of PC₇₁BM in NMP solvents (see Table S1). On the other hand, during the process of film formation, the binary solvent parameters would be varying due to differential evaporation rates of the components in the solvent mixture. Therefore, the δ_p and δ_h of the binary solvent will be increased after adding NMP, resulting in a decreased relative energy difference (RED) and better miscibility with PC₇₁BM during the film formation.

Furthermore, the surface compositions of PBDD-TS1: PC₇₁BM-based blend films cast from pure XY, XY/Me-naph and XY/NMP

were examined by X-ray photoelectron spectroscopy (XPS).⁴²⁻⁴³ The C/S ratios are 8.99, 10.56, and 11.24 for the blend films of devices fabricated with pure XY, XY/Me-naph and XY/NMP, respectively (see Table 2). As reported, higher C/S ratio will be observed when more PC₇₁BM is enriched on the top surface, which is subtly beneficial to the performance of PSCs.^{44,45} Therefore, the excellent performance achieved by XY/NMP processing might be partially correlated to the relatively high C/S ratio in top surface. Fig. S4 displays the morphology (AFM and TEM) of films cast from XY/Me-naph and XY/NMP. We found that the BHJ films with NMP as processing additive exhibited much finer D/A phase separation than the film with Me-naph. As a consequence, NMP can replace the role of Me-naph as non-halogen solvent additive in fabricating highly efficient PSCs.

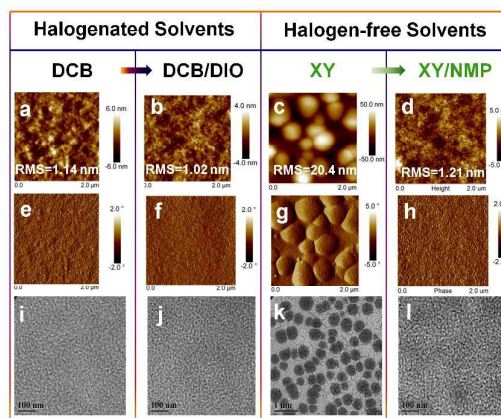
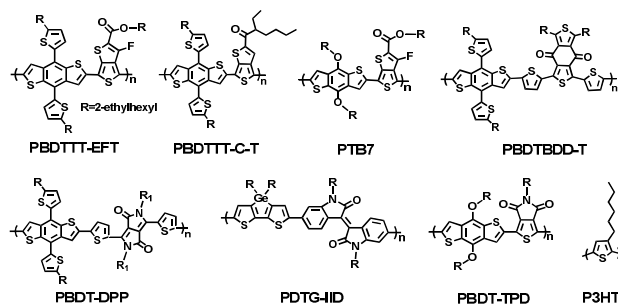


Fig. 2. AFM topography (a, b, c, d), phase (e, f, g, h) and TEM (i, j, k, l) images of the films cast from: DCB, DCB/3% DIO, XY and XY/2% NMP, respectively.



Scheme 2. Molecular structures of the halogen-free solvent processed photovoltaic polymers.

Furthermore, in order to verify the above findings and also to develop a method with wide applicability, the solvent system of XY/2% NMP were used in fabrications of the PSCs based on other conjugated polymers. In this regard, eight photovoltaic polymers with varied but representative backbone structures (see Scheme 2), including PBDDTTT-EFT,³⁴ PBDDTTT-C-T,³⁵ PBDDTDD-T,³⁶ PTB7,³⁷ PBDDT-DPP,³⁸ PDTG-IID,³⁹ PBDDT-TPD⁴⁰ and the classical polymer P3HT.⁴¹ On the basis of the corresponding reported works, the device fabrication processes of the PSCs based on these eight polymers have been fully optimized and the solvent mixture of DCB/3% DIO needs to be used to realize optimal photovoltaic performance in devices. Herein, we only changed the processing solvent from DCB/3% DIO to XY/2% NMP without making any further optimization for the device fabrications. From Fig. S5a to S5h, the four types of devices in each figure, i.e. the device processed respectively by DCB, DCB/3% DIO, XY and XY/2% NMP were fabricated in parallel.

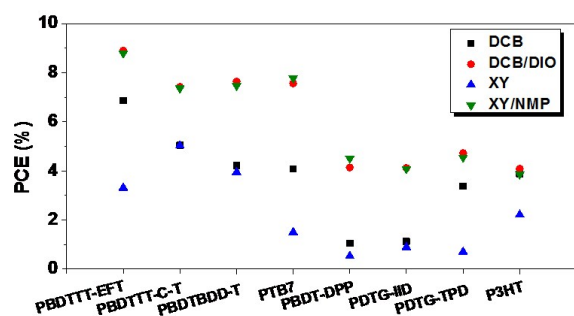


Fig. 3 The PCE of PSCs based on various polymer:PC₇₁BM blends utilizing different solvent as the processing solvent and the symbols (black, red, blue, green) represented the utilized processing solvents (DCB, DCB/3% DIO, XY, XY/2% NMP), respectively.

As shown in Fig. 3, Table 3 and Fig. S5, the comparisons among the *J-V* curves and the parameters can give us two parts of information. First, XY and DCB show much different behaviors in affecting the photovoltaic properties of the PSCs. For instance, when PBDTTT-C-T, PBDTBDD-T or PDTG-IID was used as the donor materials in PSCs, photovoltaic properties of the device processed by DCB are similar as the analogue device processed with XY; however, for PBDTTT-EFT, PTB7 or PBDT-TPD, the device processed with XY shows much lower photovoltaic performance than the corresponding device processed with DCB. Second, for each of the eight polymers, the devices processed by XY/2% NMP and DCB/3% DIO show very similar photovoltaic performances. Owing to the broad spectral coverage, ordered packing and high hole mobility¹⁰, conventional PSC utilizing PBDT-TS1 as donor polymer exhibited a high PCE over 9%, which outperformed other polymers under the similar condition (Table 3). Clearly, the molecular structures play important roles in affecting polymer solubility and crystallinity, and thereby affecting device efficiency for halogenated and halogen-free solvents processed PSCs.

Table 3. Photovoltaic parameters of various polymer:PCBM blends processed by halogenated and halogen-free solvent systems.

Materials	Processing solvent	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE ^a (b) (%)
PBDTTT-EFT	DCB	0.80	14.62	58.71	6.78 (6.87)
	DCB/3% DIO	0.78	16.69	68.39	8.82 (8.90)
	XY	0.79	11.12	37.71	3.03 (3.31)
	XY /2% NMP	0.78	16.33	69.06	8.70 (8.80)
PBDTTT-C-T	DCB	0.80	12.30	51.30	4.91 (5.05)
	DCB/3% DIO	0.78	15.25	62.49	7.30 (7.43)
	XY	0.79	12.08	52.67	4.53 (5.03)
	XY/2% NMP	0.78	15.00	63.03	7.24 (7.37)
PBDTBDD-T	DCB	0.88	8.26	58.04	4.04 (4.22)
	DCB/3% DIO	0.87	12.98	67.67	7.51 (7.64)
	XY	0.87	7.68	59.18	3.81 (3.95)
	XY/2% NMP	0.86	12.78	68.08	7.39 (7.48)
PTB7 ^c	CB	0.74	11.30	48.97	3.92

PBDT-DPP	DCB	0.71	16.52	64.55	7.43 (7.57)
	DCB/3% DIO	0.71	16.52	64.55	7.43 (7.57)
	XY	0.73	5.71	35.88	1.32 (1.50)
PBDT-DPP	XY/2% NMP	0.73	16.40	64.67	7.71 (7.74)
	DCB	0.72	2.36	61.72	0.96 (1.05)
	DCB/3% DIO	0.71	9.39	62.06	4.02 (4.14)
PBDT-DPP	XY	0.73	1.67	43.88	0.36 (0.53)
	XY/2% NMP	0.71	10.44	60.91	4.11 (4.51)
	DCB	0.83	4.02	33.91	1.02 (1.13)
PDTG-IID	DCB/3% DIO	0.83	11.82	42.03	3.96 (4.12)
	XY	0.83	3.49	30.82	0.72 (0.89)
	XY/2% NMP	0.82	11.36	43.91	3.87 (4.09)
PBDT-TPD	DCB	1.00	6.14	54.99	3.12 (3.38)
	DCB/3% DIO	0.98	8.15	59.23	4.58 (4.73)
	XY	0.99	2.00	35.44	0.59 (0.70)
PBDT-TPD	XY/2% NMP	0.97	8.06	58.19	4.41 (4.55)
	DCB	0.63	9.21	66.85	3.78 (3.88)
	DCB/3% DIO	0.63	9.42	69.00	3.94 (4.09)
P3HT ^d	XY	0.62	8.63	41.37	2.11 (2.21)
	XY/2% NMP	0.61	10.47	60.56	3.69 (3.87)

^a The average values of PCEs are obtained from 10 devices.

^b The maximum values of the PCEs are provided in the parentheses.

^c The control devices were fabricated with CB and CB/3% DIO as the halogenated processing solvent.

^d The devices were also processed with thermal annealing, see Table S6.

The morphological properties of the PSCs based on these eight polymer/PCBM blends were characterized and analyzed as described for the PBDT-TS1: PC₇₁BM blends, and the detailed results are provided in Fig. S6-S13. The comparisons among these AFM and TEM images reveal that when pure XY is used as the processing solvent, PC₇₁BM tends to form large size aggregations and also the blend film show higher RMS value; the blend films processed by XY/2% NMP always show very similar surface and bulk morphological features in comparison with their counterparts processed with DCB/3% DIO. Overall, the findings from the morphological data of the blends based on these eight polymer/PCBM blends are coincident with the results obtained from the PBDT-TS1: PCBM blends. Additionally, the morphology and PCE of PBDT-TS1: PC₇₁BM-based devices cast from DCB/3% DIO and XY/2% NMP were no obvious change in eight days (Figure S14). From the above results, it can be concluded that the halogen-free solvent system (XY/NMP) could exhibit a quite similar morphology and device stability to the widely used halogenated solvent.

Experimental

Materials

The donor polymers i.e. PBDT-TS1,¹⁰ PBDTTT-EFT,³⁴ PBDTTT-C-T,³⁵ PBDTBDD-T,³⁶ and PDTG-IID,³⁹ were synthesized in our laboratory according to our previous works. P3HT, PBDT-DPP, PBDT-TPD, PTB7 and PC₇₁BM were purchased from Solarmer Material Inc. All of the solvents are commercially available products and used without any further purification.

Device fabrication details

Solar cells fabricated with an architecture of ITO/PEDOT: PSS (35 nm) /polymer: PC₇₁BM/Mg (20 nm)/Al (100 nm). The ITO-coated glass substrates were first treated with UV/ozone for 20 min. PEDOT: PSS (Clevious P VP AI 4083 H. C. Stark, Germany) layer was deposited onto pre-cleaned ITO-coated glass substrates and dried at 160 °C for 15 min in ambient atmosphere. The PBDT-TS1: PC₇₁BM (1:1.5) composite was dissolved in DCB or XY stirring at 75 °C for 8 h, respectively. The concentration of PBDT-TS1 and PC₇₁BM in DCB or XY solution is 10 and 15 mg/ml, respectively. The active layer thickness is 100 nm. Solvent additive such as DIO, NMP was added into the blend solution to optimizing the morphology before spin casting the active layer. Prior to Mg/Al deposition, methanol treatment of the BHJ films were carried out according to the recent report.⁴⁴ PSCs based on other polymer: PCBM blends were fabricated according to the literatures, see details in supplementary information (Table S5). Finally, the device fabrication was completed by thermal evaporation of a 20 nm thick Mg and a 80 nm thick Al layer as cathode under vacuum at a base pressure of 2×10⁻⁴ Pa.

Device characterizations

The active layer film thickness data was obtained via the surface profilometer (Bruker Dektak XT). The photoactive area of 4.15 mm² was achieved using a shadow mask. The J-V test were measured using a Class AAA solar simulator (SAN-EI) affording a value of 100 mW/cm². The spectral mismatch factor was calibrated to be unity by a National Institute of Metrology (NIM) certificated silicon reference cell with KG3 filter.⁴⁶ The EQE data was obtained using an IPCE measurement system (QE-R3011, Enli Technology Co. Ltd., Taiwan).

Morphology characterizations

The surface topography and phase images of thin film were obtained using the AFM (Multimode 8) in tapping mode. The TEM images were measured by transmission electron microscope (JEOL 2200FS) operating at 200 kV accelerating voltage.

Conclusions

In conclusion, we successfully developed a halogen-free solvent system which consists of XY as the host solvent and 2% NMP as the solvent additive for making highly efficient PSCs. For PBDT-TS1 based devices, the high efficiency of 9.47% has been achieved based on this halogen-free solvent system, which is also slightly higher than that of the devices processed with widely used halogenated solvent mixture (DCB/3% DIO, 9.32%) under the identical experimental conditions. Moreover, the halogen-free mixture solvent (XY/2 %NMP) can be widely applied in various high-efficient active layers including PBDTTT-EFT: PC₇₁BM, PBDTTT-C-T: PC₇₁BM, PTB7:PC₇₁BM, PBDTBDD-T: PC₇₁BM, PBDT-DPP: PC₇₁BM, PBDT-TPD: PC₇₁BM, PDTG-IID: PC₇₁BM and P3HT: PC₇₁BM, and comparable performance were also achieved. More importantly, the halogen-free mixture solvent fulfills the environmental, health and safety (EHS) legislation which is beneficial for fabricating large-area devices in green

printing industry. Therefore, as a kind of environmental-friendly processing solvent system, this halogen-free solvent system has an absolutely potential in replacing conventional halogenated mixture solvents in fabricating highly efficient PSCs.

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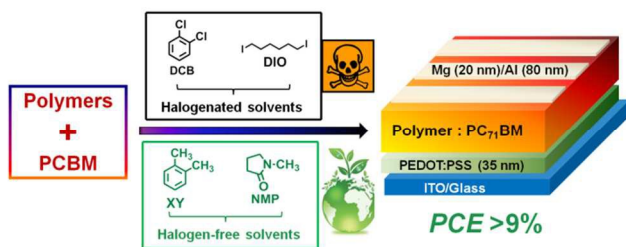
‡ Long Ye and Wenchao Zhao contributed equally in this work

† Electronic Supplementary Information (ESI) available: Additional device fabrication details of polymer/PCBM blends, and the morphological properties of the PSCs based on these eight polymer/PCBM blends See DOI: 10.1039/b000000x/

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Table of Content



A high power conversion efficiency over 9.4% was realized in polymer solar cells by halogen-free solvent processing.