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Halogen-Free Processed High Performance Organic Solar Cells

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The processing of polymer solar cells with non-halogenated solvents is highly desirable in order to achieve an environmentally friendly, sustainable large-scale fabrication of organic photovoltaics. This work demonstrates device processing free of halogenated solvents yielding high-performance polymer:fullerene bulk-heterojunction solar cells comprising a conjugated polymer poly{[4,8-bis-(2-ethyl-hexyl-thiophene-5-yl)-benzo[1,2-b:4,5-b0]dithiophene-2,6-diyl]-alt-[2-(20-ethyl-hexanoyl)-thieno[3,4-b]thiophen-4,6-diyl]} (PBDTTT-CT) and a fullerene derivative [6,6]-phenyl-C70-butyric acid methyl ester (PC₇₀BM). As compared to chlorobenzene/ortho-dichlorobenzene cast devices the overall solar cells performance could be improved from 6.71% up to 7.15% by using xylene-based solvent systems.

1. Introduction

Recently the power conversion efficiency (PCE) of polymer based bulk heterojunction (BHJ) organic solar cells have overcome the 10% barrier for tandem devices,¹ and a number of reports claim solution processed single bulk heterojunctions with efficiencies ranging between 8-10% PCE.²⁻⁸ Unfortunately, all these record devices have in common that no further efforts were made to exclude chlorinated solvents. However, in order to transfer the lab-based devices on a large-scale roll-to-roll production⁹ these processing solvents and other conditions need to be seriously reconsidered.^{10,11} To date, most of the common solvents used for making high-performance OPVs are based on halogenated chlorobenzene (CB), 1,2-(ortho)-dichlorobenzene (o-DCB) and chloroform (CF).¹²⁻¹⁶ Unfortunately, these solvents have strong negative impact on human health and the environment due to their toxicity. Moreover, it is expensive and energy-consuming to produce them and it is complicated to design the processing equipment to work with them. Even though a lot of efforts have been devoted to find eco-friendly replacements for chlorinated solvents only limited success has been achieved so far.¹⁷⁻²⁸ Most successful applications of non-chlorinated solvent systems were proven for the standard material system P3HT:PC₆₀BM as, for example, compatible efficiencies of 3.5% were achieved with tetralene¹⁸ applying low temperature drying process, which enhanced nucleation of P3HT crystallites and improved P3HT/PCBM dispersion to avoid the problem if excessive aggregation associated with tetralene. Other approach of improving P3HT:PC₆₀BM blend morphology is blending the acetophenone and mesitylene, which allowed to reach the efficiency of 3.4%.¹⁹ Unfortunately, this could not be easily transferred to other material combinations.^{19,29-31} Recent studies on BHJ based devices that were processed from chlorine-free solvents such as toluene, isomers of xylene, and trimethylbenzenes showed that they are very attractive candidates due to their comparable properties to the halogenated analogs and additionally from cost and sustainability points.^{18,25} Unfortunately, non-chlorinated solvents were often neglected due to, generally, low solubility of existing high performing polymer-fullerene combinations.^{20,21,25,27} This often results in severe phase segregation of large fullerene-rich grains in the cast films, limiting the corresponding device performance.¹² Thus, it remains a very critical issue to either enhance the fullerene

solubility in these solvents, or find other more suitable solvent systems.

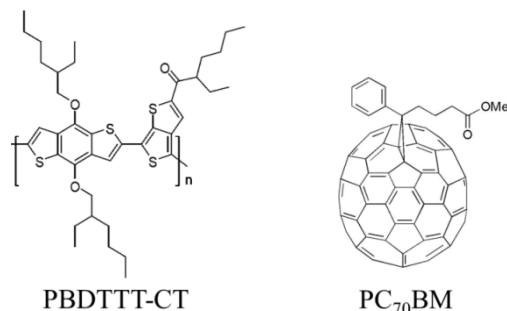
One of the high performing low band-gap donor-acceptor polymers with an unusually high solubility in o-xylene and m-xylene is poly[4,8-bis-substituted-benzo[1,2-b:4,5-b0]dithiophene-2,6-diyl-alt-4-substituted-thieno[3,4-b]thiophene-2,6-diyl] (PBDTTT).³² Previously, devices based on PBDTTT³³⁻⁴¹ derivatives demonstrated high performance (~ 8% efficiency) in chlorinated solvents. Ye *et al.*⁴¹ demonstrated that addition of an appropriate amount of diiodooctane (DIO) in DCB solution leads to an improvement of the overall performance up to 7.53% of PBDTTT-CT-based solar cells. An addition of small amount of DIO resulted in optimized performance and formation of favourable morphology and was also reported for other material systems.^{42,43} Adhikari *et al.*³³ could reach 8% efficiency for PBDTTT-CT-based solar cells by using a chlorinated solvent in combination with an UV-ozone treatment of the electron transport layer.

In this work, we demonstrate the successful replacement of a chlorinated solvent system based on a 1:1 mixture of chlorobenzene and ortho-dichlorobenzene by the chlorine-free solvent xylene, resulting in a halogen-free processing – except for the small amount of diiodooctane additive. In fact we were able to improve the overall power conversion efficiency from 6.71% for the chlorinated solvents to 7.15% for the chlorine-free solvent m-xylene.

2. Experimental

2.1 Materials. Scheme 1 demonstrate the Poly{[4,8-bis-(2-ethyl-hexyl-thiophene-5-yl)-benzo[1,2-b:4,5-b0]dithiophene-2,6-diyl]-alt-[2-(20-ethyl-hexanoyl)-thieno[3,4-b]thiophen-4,6-diyl]} (PBDTTT-CT) which was purchased from Solarmer Material Inc. and used as received. Phenyl-C70-butyric acid methyl ester (PC₇₀BM) was purchased from Solenne and used as received. HIL1.3 was employed as holes transporting layer and used as received from Heraeus Precious Metals. The molecular energy levels of PBDTTT-CT are located at -5.11 eV (HOMO) and -3.25 eV (LUMO).

2.2 Device fabrication and characterization. Solar cell device preparation involved etching part of the ITO-layer on glass for



Scheme 1. Molecular structures of the polymer PBDTTT-CT and PC₇₀BM.

selectively contacting the back electrode, followed by cleaning in ultrasonic bath using acetone and isopropanol. HIL1.3 was spin-cast from aqueous solution on top of ITO and served as the hole transporting layer. It was annealed on a hot plate for 15 minutes at 180°C in order to drive the water out of the film. The photo-active layer was prepared from PBDTTT-CT:PC₇₀BM in 1:1 ortho-dichlorobenzene:chlorobenzene (DCB:CB), *m*-xylene and *o*-xylene solutions with polymer:fullerene blending ratios of 1:1.5 at 1wt.-% each. For the additive containing solutions from DCB:CB, *m*-xylene and *o*-xylene, 5% DIO was added into the host solution. Solutions were stirred overnight at 45°C in a N₂ glovebox and then spin-cast on top of the HIL1.3. For the top electrodes, 50 nm of magnesium and 100 nm of aluminium were deposited sequentially by thermal evaporation through a shadow mask, resulting in solar cells with an active area of 0.42 cm². All samples were encapsulated under glass prior to characterization.

Current–voltage (IV) measurements of the solar cell devices were performed under a class A AM1.5 solar simulator and were recorded with a Keithley 2400 Source-Measure-Unit. External quantum efficiencies (EQE) were recorded under monochromatic light with an additional halogen bias light, providing an excitation intensity of about one sun. Absorption spectra were obtained from transmission and reflection spectra recorded on a Varian Cary 5000. Photoluminescence spectra were recorded using a fiber spectrometer and optical excitation by laser light at 445 nm. Topography scans were made with a Dimension 3100 Nanoscope atomic force microscope (AFM) in tapping mode.

3. Results and discussion

At first we investigated the optical properties of the pristine PBDTTT-CT and PBDTTT-CT:PCBM in thin films spin coated from DCB:CB, *m*-xylene and *o*-xylene, respectively. As summarized in Figure 1a the pristine PBDTTT-CT films showed strong absorption in the range from 550 nm to 750 nm. Films of pristine polymer spin coated from *m*-xylene and *o*-xylene did not differ from each other, however, as compared to DCB:CB they exhibited a slight red shift of the absorption peak at 645 nm and an increase of the absorption peak at 710 nm, indicating some increased order by stacking.^{44,45} Upon blending with PC₇₀BM, films spin coated from *o*-xylene revealed similar red shift of absorption compared with DCB:CB. However, for *o*-xylene-based blend films the relative proportion of two peaks at 655nm and 645 nm and 710 nm was changed indicating that the polymer order was disturbed upon blending with the fullerene derivative. The films spin coated from *m*-xylene upon blending with PCBM demonstrated stronger absorption in the range between 450 nm and 550 nm with decrease of the absorption strength above 700 nm. This indicates that the order of the polymer was more affected upon blending with PC₇₀BM.

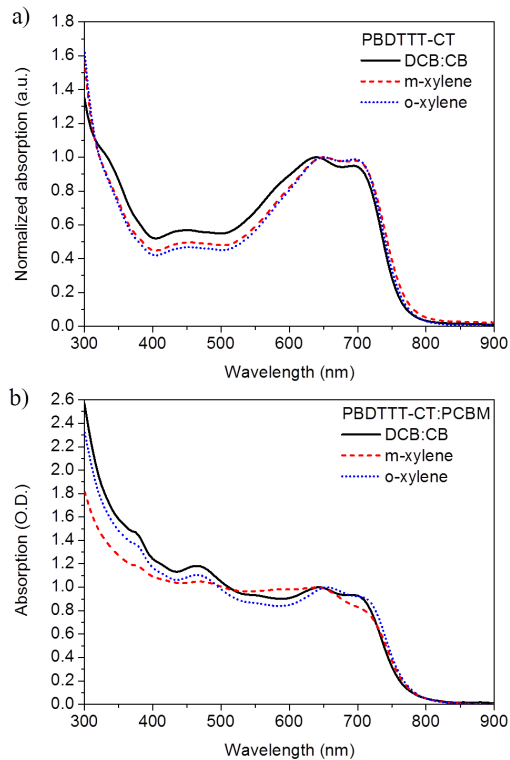


Figure 1. Optical absorption of a) pristine PBDTTT-CT (normalized to the absorption value at 645 nm) and b) PBDTTT-CT:PC₇₀BM blend films.

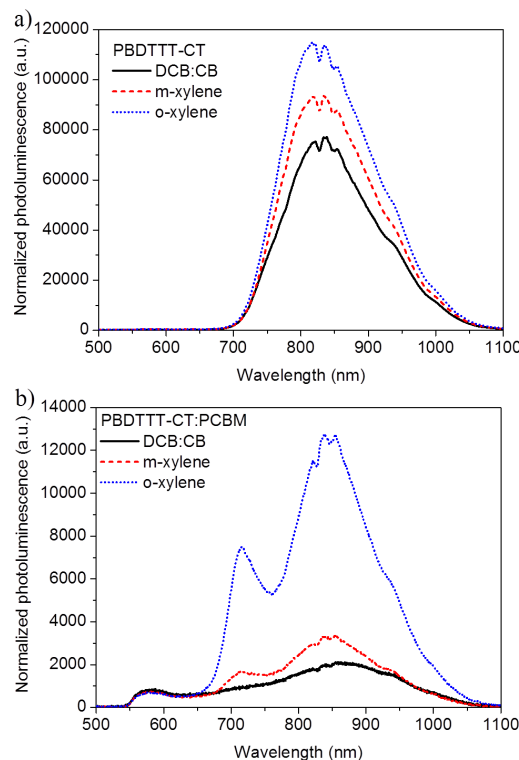


Figure 2. Photoluminescence normalized to absorption at 445 nm of a) pristine PBDTTT-CT and b) PBDTTT-CT:PC₇₀BM blend films.

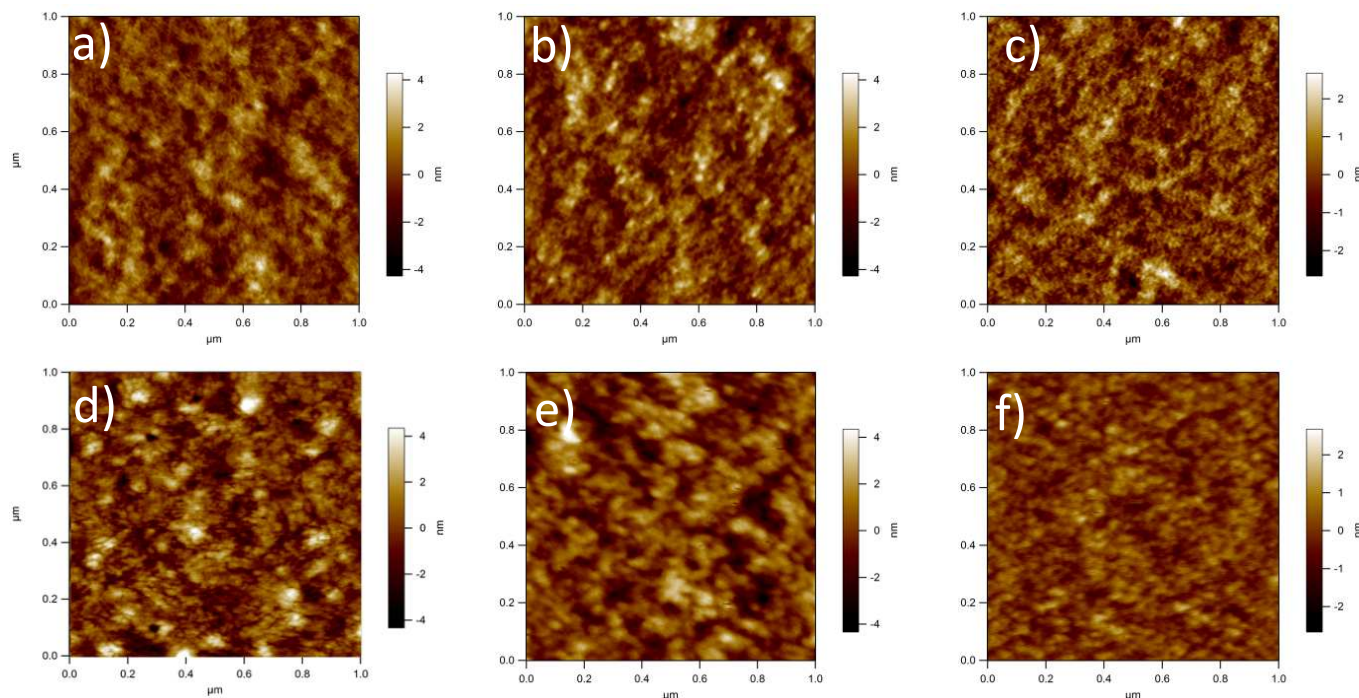


Figure 3. Atomic force microscopy images for pristine PBDTTT-CT films spin coated from a) DCB:CB, b) m-xylene and c) o-xylene, as well as PBDTTT-CT:PC₇₀BM (d,e,f) cast from same solvents, respectively.

Two peaks which are visible for pristine polymer in m-xylene are almost absent in after blending with PCBM, which can indicate stronger intermolecular interaction comparing with o-xylene.

Interestingly, the photoluminescence of the pristine PBDTTT-CT films (Figure 2a) did not reveal any spectral shifts but only some variation in the signal intensity. However, the PBDTTT-CT:PC₇₀BM films (Figure 2b) demonstrated strong variation in photoluminescence for all solvents. Whereas the peak at 560 nm can be attributed to the remaining laser signal, the significant difference at 850 nm indicates strong variation of phase separation for different solvents. This is in addition pronounced for the o-xylene cast blend films, as a significant photoluminescence of the PC₇₀BM was observed peaking at 715 nm. Thus, the o-xylene cast films exhibit a much higher degree of phase separation indicating presence of polymer and fullerene aggregates, which may provide the reason for the decrease of the solar cell performance. Whereas, for films comprised from DCB:CB the peak at 710 nm is not visible anymore, which indicates intimate intermixing between PBDTTT-CT and PCBM. However, this can also disturb the solar cell performance as a minimum degree of phase separation is necessary in providing percolation pathways for charge transport to the electrodes.

To further investigate morphological changes of the pristine PBDTTT-CT and blends with PC₇₀BM upon application of different solvents, atomic force microscopy (AFM) in tapping mode was used

in order to obtain topography images (Figure 3). The pristine polymer spin coated from DCB:CB revealed formation of polymer fibers which became less pronounced for o-xylene and almost not visible for m-xylene (Figure 3 a-c). AFM images of blend films (Figure 3 d-f) demonstrated different levels of phase separation, which is in agreement with the photoluminescence results. The PBDTTT-CT:PCBM blend film cast from DCB:CB displayed some level of phase separation with different grain sizes. Interestingly, the m-xylene cast blend films exhibited some aggregation close to the top surface. The difference in phase separation observed for m-xylene may potentially yield to improved charge percolation in photovoltaic devices.

Figure 4 a) shows the *JV*-characteristics of PBDTTT-CT:PCBM BHJ solar cells processed using the various solvents. We found that photovoltaic cells based on PBDTTT-CT:PC₇₀BM processed with non-halogenated solvents generally exhibited comparable or even – in the case of m-xylene – improved photovoltaic parameters as compared to the chlorinated solvent blend. The data obtained from Figure 4 are summarized in Table 1, considering EQE-corrected photocurrents, displayed in Figure 4 b). The statistics was collected from more than 600 devices for each optimization parameter. It should be noticed, that addition of DIO in xylenes solutions resulted in increase of overall solar cells performance for ~15% which is in the same range as for DCB:CB blend.

Table 1. Photovoltaic performance of the BHJ solar cells composed of PBDTTT-CT:PC₇₀BM fabricated from various solvents.

Solvent	J _{SC} (mA/cm ²)	J _{SC, EQE cor} (mA/cm ²)	V _{OC} (mV)	FF (%)	PCE avg (%)	PCE best (%)	PCE best, EQE cor (%)	R _S (Ω)	R _P (Ω)
DCB:CB	11.81±0.01	11.98	760±1	62.74±1	5.45	5.63	5.71	6.2	793
DCB:CB+DIO	14.05±0.02	13.9	748±2	64.55±1	6.52	6.78	6.71	7.9	1248
m-xylene+DIO	14.39±0.02	14.45	771±2	64.45±1	6.9	7.1	7.15	9.2	1759
o-xylene+DIO	14.75±0.03	14.57	744±2	57.37±1	5.98	6.09	6.22	8.9	1051

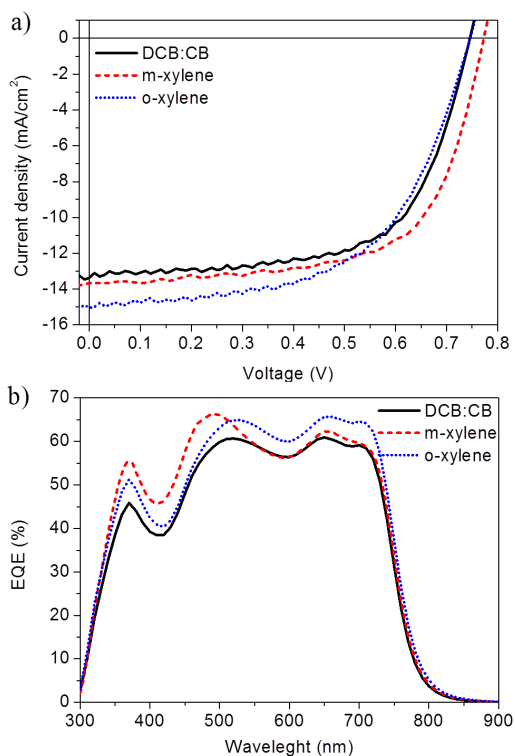


Figure 4. a) *JV*-characteristics and corresponding b) EQE spectra of the PBDTTT-CT:PC₇₀BM spin coated from different solvents as shown in the graphs.

The *JV*-curves clearly show a notable improvement for the photovoltaic performance fabricated with *m*-xylene and a comparable one for *o*-xylene to chlorinated solvent mixture. The best cells spin coated from *m*-xylene demonstrated 7.15% power conversion efficiency, while cells prepared from DCB:CB solution yielded only 6.71%. The strongest improvement for the *m*-xylene devices was found in increase of the open circuit voltage from about 748 mV to 771 mV and of the short circuit current from 13.9 mA/cm² to 14.45 mA/cm² in case of *m*-xylene which were recalculated from EQE-data. The differences in the EQE spectra can be assigned to differences observed in absorption spectra found for various solvents. The *o*-xylene devices showed generally higher EQE as compared to DCB:CB with slight red shift. The *m*-xylene devices demonstrated the highest EQE peaking at 360 nm, generally assigned to PCBM, and a higher EQE signal up to 500 nm.

The typically observed higher performance of PBDTTT-CT:PC₇₀BM solar cells from the non-chlorinated solvent *m*-xylene make this polymer a promising candidate for large area device fabrication by roll-to-roll processing techniques.

Conclusions

In summary, we demonstrated well performing organic solar cells based on PBDTTT-CT:PC₇₀BM fabricated from *o*-xylene and *m*-xylene solutions. As these are non-halogenated solvents, they are much more suitable for commercialization and roll-to-roll fabrication. The highest efficiency of 7.15% was demonstrated using *m*-xylene-based solutions, making this material combination a promising candidate for an environmentally friendly processing approach.

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Notes and References

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