Molecular design toward efficient polymer solar cells processed by green solvents

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A novel BDT-based conjugated polymer, PBDTTT-S-TEG, and a series of new fullerene derivatives were designed, synthesized and applied to green solvent processable polymer solar cells. By rationally screening processing solvents, a PCE of 4.50% was firstly achieved with definitely low toxic, no halogenated and safe solvent fabrication, which is almost identical to that processed with *o*-dichlorobenzene.

Introduction

In the past decades, great efforts have been devoted to developing new photovoltaic materials for making highly efficient polymer solar cells (PSCs), and the power conversion efficiencies (PCEs) of PSCs have been promoted to over 10%.[1] With the rapid progress of PCE, PSCs show more potentials in making large area, light-weight and flexible solar cells thought roll-to-roll printing technologies. However, up to now, most of the high performance PSCs based on bulk heterojunction (BHJ) are fabricated by using highly toxic and harmful halogenated solvents, such as chlorobenzene (CB) or *o*-dichlorobenzene (DCB). Clearly, since these kinds of solvents have been well recognized as the contaminants to the environment and human health,[2] the PSCs fabricated by these types of solvents cannot be used in industrial application. Therefore, to develop new photovoltaic materials that can be processed through low- or non-toxic solvents becomes a critical issue for the PSCs field.

As known, conjugated polymers and fullerene derivatives are commonly used as the electron donor and acceptor materials in active layers of the PSCs with BHJ structure, respectively. In order to form bi-continuous nanoscale phase separation in the active layers, which is crucial for facilitating the exciton diffusion, charge separation and transport in PSCs,[3-9] the donor and acceptor materials must be well soluble in the processing solvents for device fabrication. Since chlorinated and/or aromatic solvents, like CB, DCB, toluene and chloroform etc., show strong solvation effects for conjugated polymers and fullerene derivatives, these solvents are broadly employed in device fabrications of PSCs. Moreover, in order to finely tune morphological properties of the donor and acceptor blend films, solvent mixtures are usually adopted in device fabrication of PSCs. In this case, low boiling point (b.p.) solvents that showing good solubilities to both the donor and acceptor materials, like toluene, CB or DCB, can be used as the host solvents, and high b.p. solvents that showing asymmetric solvencies to the solutes with the host solvents, such as 1,8-diiodooctane (DIO) or 1-chloronaphthalene (CN), can be employed as the solvent additives.[10-12] Therefore, to develop PSCs processed by green solvents, not only the host solvents but also the solvent additives must be taken into consideration.

Recently, quite a few research groups showed interests in removing chlorinated and/or aromatic solvents from PSCs fabrication processes. For example, Jen et al. used the solvent mixture of *o*-xylene and 1,2-dimethylnaphthalene (1,2-DMN) to fabricate the PSCs based on PBDT-DTNT and PC$_{71}$BM, and the device show similar PCE as the device processed by DCB and DIO.[13] Li et al. employed toluene and NMP to fabricate the P3HT:ICBA-based device and realized a PCE similar to that of the counterpart prepared from DCB.[14] Hou et al. used the triethylene glycol monoether (TEG) functional group to modify the conjugated polymer based on benzodithiophene (BDT) and thieno[3,4-b]thiophene (TT) and the resulting polymer (PBDTTT-TEG) showed excellent solubility in some types of non-halogenated and non-aromatic solvents; as a result, a PCE of 1.55% was obtained by using NMP as the processing solvent for device fabrication, and after adding 5% volume ratio of DIO as the additive, a PCE of 5.23% can be realized.[15] Although the non-halogenated solvents can be used as the host, there are

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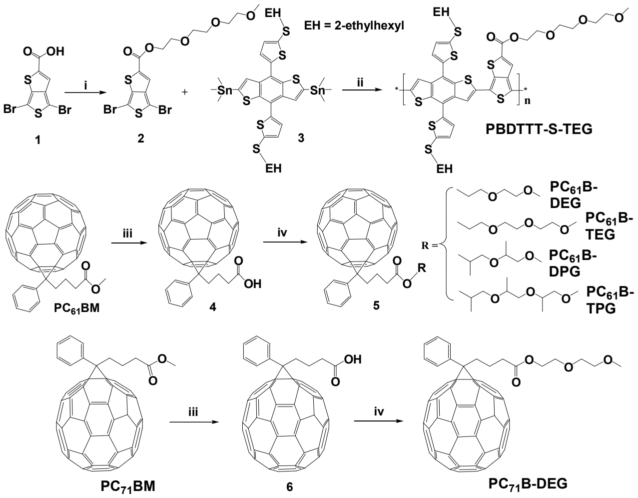

Scheme.1 Molecular structures and synthetic routes of materials applied in this work. i) 4-dimethylaminopyridine (DMAP), *N,N′*-dicyclohexylcarbodiimide (DCC), CH_2Cl_2, room temperature; ii) $Pd(PPh_3)_4$, toluene/*N,N*-dimethylformamide (DMF) (5:1), reflux, 48 h; iii) HCl/CH_3COOH (5:3), toluene, reflux; iv) DMAP, DCC, CH_2Cl_2/CS_2 (1:1), room temperature.

still some drawbacks in these reported works: firstly, harmful solvents like DIO and CN must be used as the additives to control the morphology of the active layer, because PCBM is apt to form large size aggregations in the blend films due to its limited solubility in the non-chlorinated host solvents;[16-18] secondly, at ambient temperature, the saturated vapor pressures of the solvent additives and some types of non-chlorinated solvents like *N*-methyl-2-pyrrolidone (NMP) and its derivatives are very low so that the drying process of the blend films would take a quite long time, which is acceptable for spin-coating process for making small area devices but extremely inconvenient to practical roll-to-roll printing. Therefore, in order to remove harmful solvents from device fabrication process, both the donor and acceptor materials, i.e. conjugated polymers and fullerene derivatives, must be re-designed, and also environmentally friendly solvents with appropriate properties should be applied.

Although many benzene derivatives, especially for commonly used solvents like toluene, xylene, CB and DCB, are detrimental to the environment and human health, this type of solvents possess strong solvencies to conjugated polymers and fullerene derivatives, which is of great importance to solution coating process in PSCs fabrication. Therefore, in order to minimize the difficulty of molecular design of the active layer materials, we tried to look over the properties of the benzene derivative solvents. At this moment, anisole attracted our attention. As known, anisole shows a b.p. of 153.8^{o}C and a moderate saturated vapor pressures, which are between those of CB and DCB. The toxicity of anisole is much lower than the commonly used halogenated aromatic solvents, and it can even be used as the spice for cosmetics and as the additive for food. Moreover, anisole is biodegradable so that it will not cause accumulative damage to the environment. Thus, anisole may be a potential green solvent for fabrication of PSCs.

In this work, by incorporating the superior photovoltaic properties of alkylthio-substituted benzo[1,2-b:4,5-b']dithiophene (BDT-TS)[19] units and the excellent solubility in non-chlorinated solvents of the TEG-substituted thieno[3,4-b]thiophene (TEG-TT) units,[15] a new polymer donor material named as PBDTTT-S-TEG was designed and synthesized (see **Scheme 1**). The number-average molecular weight (M_n) of PBDTTT-S-TEG was 87.3 kDa, which was estimated by gel-permeation chromatography (GPC) with tetrahydrofuran as the eluent. The thermogravimetry analysis (TGA) plot shows the polymer has a good thermal stability with an onset of decomposition temperature at ca. 320^{o}C (see Supporting Information (SI), **Figure S1**). According to differential scanning calorimetry (DSC) measurements, neither endo- nor exothermic processes can be found in the 0-300^{o}C range, at a scanning rate of 10 ^{o}C min^{-1} (**Figure S2**).

Results and discussion

UV-vis absorption spectra of PBDTTT-S-TEG in solution state and as solid films are shown in **Figure 1a**. The comparison between the absorption spectra of the solutions and the films reveals that, from solution to solid film, the two absorption peaks are slightly red-shifted, which is often observed in conjugated polymers and can be ascribed to the enhanced intermolecular interaction in solid state. On the other hand, since the absorption spectrum of the anisole solution is almost identical to that of the DCB solution, anisole may have similar solvency to the polymer as DCB. The absorption spectrum of the film shows an absorption edge (λ_{edge}) at the 783 nm, corresponding to an optical bandgap (E_g^{opt}) of 1.58 eV, which is similar to those of the polymers based on BDT and TT.[20-23] The electrochemical cyclic voltammetry (CV) measurement was employed to determine the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the polymer. As shown in **Figure 1b**, the onset oxidation and reduction potentials (φ_{ox} and φ_{red}) are at 0.92 V and -1.05 V (vs Ag/Ag$^+$), corresponding to a HOMO of -5.24 eV and a LUMO of -3.27 eV, respectively.

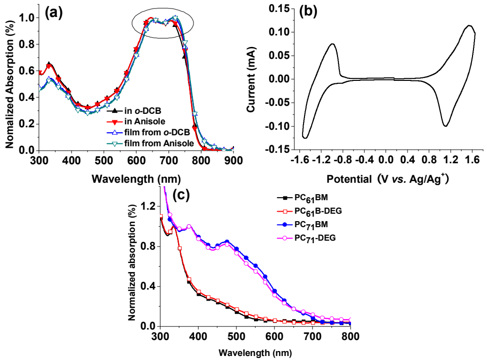

Fig.1 a) Normalized UV/Vis absorption spectra of PBDTTT-S-TEG in solution state (solid) and solid films (open); b) the cyclic voltammograms of the PBDTTT-S-TEG; c) the absorption spectra of PC$_{61}$BM, PC$_{61}$B-DEG, PC$_{71}$BM and PC$_{71}$B-DEG films on the quartz substrates.

Since the polymer with TEG groups show good solubility in anisole, TEG group and the likes were used to replace the methyl group on $PC_{61}BM$ and thus to improve solubility of the acceptor in anisole. Herein, diethylene glycol monomethyl ether (DEG), TEG, dipropylene glycol monomethyl ether (DPG) and tripropylene glycol monomethyl ether (TPG) were used to get four novel $PC_{61}BM$ derivatives as shown in **Scheme 1**. The synthesis methods of the fullerene derivatives are provided (see **SI**) and thermogravimetric analysis (TGA) proves their good thermal stabilities (**Figure S3**). In comparison with $PC_{61}BM$, the newly synthesized fullerenes exhibit much higher solubilities (>40 mg ml^{-1}) in anisole, and it also can be easily dissolved in other types of solvents like chloroform, tetrahydrofuran (THF), NMP, *N,N*-dimethylformamide (DMF) and etc. The optical and electrochemical properties of the four fullerene derivatives were characterized, and $PC_{61}BM$ was also tested in parallel to make clear comparisons. As shown in **Figure S4**, either in solution state or in solid films, the absorption spectra of these four fullerene derivatives are identical to that of $PC_{61}BM$. In CV measurements (**Figure S5**), the φ_{red} values of these four fullerene derivatives are all at ca. -0.57 V, which is similar as that of $PC_{61}BM$ and corresponding to a LUMO of -3.75 eV. These results indicate the substitutions of TEG group and the likes have little influence on absorption spectrum and LUMO level of $PC_{61}BM$.

We fabricated PSCs with a device structure of ITO/PEDOT:PSS/PBDTTT-S-TEG:Fullerene derivative/Ca/Al. Initially, DCB, the commonly used solvent, was used as the processing solvent to make the devices for screening the D/A ratio in the active layers. It was found that the optimal D/A ratios of the devices based on different fullerenes are all 1:1 (*w/w*). **Figure 2a** and **2b** show the current density-voltage (I-V) and external quantum efficiency (EQE) curves of the PSCs under the D/A ratio of 1:1 fabricated with DCB (under the illumination of AM 1.5G, 100 mW cm^{-2}), and the photovoltaic data of the PSCs including the open circuit voltage (V_{oc}), short circuit current (J_{sc}), fill factor (FF) and PCEs, are summarized in **Table 1**. The device based on PBDTTT-S-TEG:$PC_{61}B$-DEG shows V_{oc}= 0.750 V, J_{sc} = 12.42 mA cm^{-2}, FF = 47.78% and PCE = 4.45%, and these parameters are very similar to the values obtained from the device based on PBDTTT-S-TEG:$PC_{61}BM$, i.e. V_{oc} = 0.748 V, J_{sc} = 12.45 mA cm^{-2}, FF = 49.73 and PCE = 4.63%. The PCEs of the devices with $PC_{61}B$-TEG, $PC_{61}B$-DPG and $PC_{61}B$-TPG are 3.77%, 2.06% and 3.17%, respectively.

The EQE of the devices based on the fullerene derivatives are provided in **Figure 2b**. As shown, the three devices based on $PC_{61}B$-DEG, $PC_{61}B$-TEG and $PC_{61}B$-TPG show similar EQE spectra, which are also similar as that of the device based on $PC_{61}BM$. However, the device based on PBDTTT-S-TEG:$PC_{61}B$-DPG exhibits much lower EQE values than the other four types of devices, and as a result, this device shows the lowest Jsc value. Moreover, the hole and electron mobilities (μ_h and μ_e) of the five types of blend films were evaluated by using space-charge-limited-current (SCLC) method. As shown in **Figure S6** and **Table 1**, the μ_h and μ_e of the PBDTTT-S-TEG:$PC_{61}B$-DEG blend film are 1.36×10^{-4} cm^2 V^{-1} s^{-1} and 1.56×10^{-4} cm^2 V^{-1} s^{-1} (a little better in the film processed with anisole, see **Table S1**), respectively, which are similar to those of the blend film containing PBDTTT-S-TEG:$PC_{61}BM$. On the other hand, the μ_h and μ_e of the PBDTTT-S-TEG:$PC_{61}B$-DEG blend film are symmetric and higher than those of the blend films with the other three $PC_{61}BM$ derivatives. Overall, according to the initial photovoltaic testing and mobility results, for the PSCs using PBDTTT-S-TEG as donor material, $PC_{61}B$-DEG should be the best acceptor material among these fullerene derivatives.

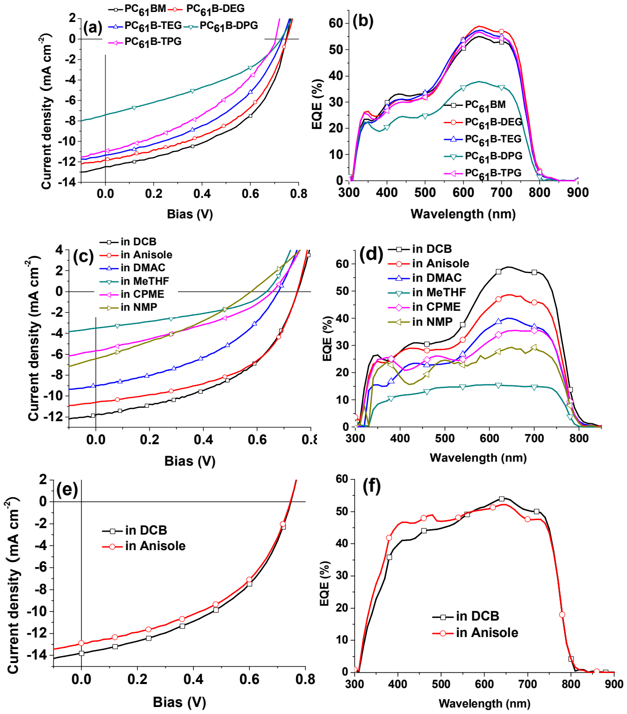

Fig.2 a) *I-V* curves of the PSCs fabricated with DCB based on the blend of PBDTTT-S-TEG as donor and different fullerene derivatives as acceptor (1:1, *w/w*) and b) the corresponding EQE curves; c) *I-V* curves of the PSCs based on PBDTTT-S-TEG:$PC_{61}B$-DEG in various solvents and d) the corresponding EQE curves; e) *I-V* curves of the PSCs based on PBDTTT-S-TEG:$PC_{71}B$-DEG in compared solvents and f) the corresponding EQE curves.

As shown in **Figure 1a**, the polymer shows weak absorption at the short wavelength range, i.e. from 400 nm to 600 nm, and as known, fullerene derivatives based on C[60] often have weak absorption at this range. As a result, the EQE curves in **Figure 2b** exhibit low values at the range from 400 nm to 600 nm. Considering that the application of $PC_{71}BM$ has been proved to be an efficiently way to utilize the sunlight at the short wavelength range,[24] we tried to use $PC_{71}BM$ as the starting material and synthesize a new acceptor named as $PC_{71}B$-DEG (**Scheme 1**). Similarly, the electrochemical property and thermal stability of $PC_{71}B$-DEG were characterized (**Figure S7-9**), and the results show that it has similar properties as those of $PC_{61}B$-DEG, and as expected, $PC_{71}B$-DEG shows much stronger absorption at the visible range than $PC_{61}B$-DEG as shown in **Figure 1c**. Then, $PC_{71}B$-DEG was used as the acceptor in PSCs for further testing. As shown in **Figure 2e** and listed in **Table 3**, when DCB was used as the processing solvent, the device shows V_{oc} = 0.746 V, J_{sc}= 12.91 mA cm^{-2}, FF = 47.26%

Table 1. Photovoltaic performance of the PSCs based on PBDTTT-S-TEG as donor and different fullerene derivatives as acceptor (1:1, *w/w*) with DCB processing under illumination of AM 1.5G, 100 mW cm^{-2}

Acceptor	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)		Mobility (cm^2 V^{-1} s^{-1})	
				best	average	μ_h	μ_e
$PC_{61}BM$	0.748	12.45	49.73	4.63	4.55	2.45 x 10^{-4}	3.00 x 10^{-4}
PC_{61}B-DEG	0.750	12.42	47.78	4.45	4.40	1.36 x 10^{-4}	1.56 x 10^{-4}
PC_{61}B-TEG	0.732	11.94	43.23	3.77	3.70	3.12 x 10^{-5}	0.85 x 10^{-4}
PC_{61}B-DPG	0.726	7.78	36.49	2.06	1.98	4.80 x 10^{-5}	0.72 x 10^{-4}
PC_{61}B-TPG	0.703	11.55	39.01	3.17	3.05	2.50 x 10^{-5}	4.67 x 10^{-5}

Table 2. Comparisons among the manufacturing issues of the solvents studied in this work for PSC processing.

Solvent	B.P. (^{o}C)	PCBM solubility [a)]	Toxicity	Environment issues	GHS [b)] label elements	
					Pictogram	Signal word
DCB	198	100[18]	High	Hazardous (accumulative)		Warning
DMAC	165	<1	medial	Low risk (biodegradable)		Danger
NMP	202	48	low	Low risk (biodegradable)		Danger
MeTHF	78	<1	low	Low risk (degradable)		Danger
CPME	106	<1	low	Low risk (degradable)		Danger
Anisole	154	18	low	Low risk (biodegradable)		Warning

[a] measurement unit of solubility is mg mL^{-1}; [b)]GHS stands for <Globally Harmonized System of Classification and Labeling of Chemicals>.

Table 3. Photovoltaic performance of the PSCs processed with various solvents based on PBDTTT-S-TEG as donor and PC_{61}B-DEG(PC71B-DEG) (1:1, *w/w*) under the illumination of AM 1.5G, 100 mW cm^{-2}

Acceptor	Processing solvents	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)	
					best	average
PC_{61}B-DEG	DCB	0.750	12.42	47.78	4.45	4.40
	Anisole	0.749	10.61	51.46	4.09	4.01
	DMAC	0.680	9.01	42.10	2.57	2.46
	MeTHF	0.634	3.51	37.72	0.84	0.78
	CPME	0.656	5.68	34.11	1.27	1.16
	NMP	0.577	6.42	31.98	1.19	1.08
PC_{71}B-DEG	DCB	0.746	12.91	47.26	4.55	4.48
	Anisole	0.746	12.41	48.57	4.50	4.46

and PCE = 4.55%. In comparison with the data obtained for the device based on PC_{61}B-DEG, the PC_{71}B-DEG device shows similar V_{oc} and FF values but improved EQE at the range from 400 nm to 600 nm (**Figure 2f**) and thus higher J_{sc}. The results clearly demonstrate that the application of PC_{71}B-DEG in device is helpful to utilize the sunlight at short wavelength range.

Since the donor PBDTTT-S-TEG and the acceptor DEG substituted fullerene derivatives can be easily dissolved into many types of non-aromatic or/and non-halogenated high polar solvents, we got the chance to use different solvents to make PSCs. Herein, besides of anisole, the other four types of solvents were selected in device fabrication. For example, as concluded in **Table 2**, dimethylacetamide (DMAC) was selected because it has similar properties but more stable than DMF; 2-methyltetrahydrofuran (MeTHF) and cyclopentyl methyl ether (CPME) was used because they are broadly used as green solvents with low toxicity; NMP was used because it is a biodegradable solvent with low toxicity and flammability.

The I-V curves and photovoltaic parameters of the devices based on PBDTTT-S-TEG:PC_{61}B-DEG (1:1, *w/w*) processed by the varied solvents are shown in **Figure 2c**, **2d** and **Table 3**.The device processed with anisole performs V_{oc} = 0.749 V, J_{sc} = 10.61 mA cm^{-2}, FF = 51.46% and PCE = 4.09%, which is comparable to the devices fabricated with DCB. In DMAC processing, the device still works well and give out V_{oc} = 0.68 V, J_{sc} = 9.01 mA cm^{-2}, FF = 42.10% and PCE = 2.57%. Moreover, the PCE of 1.16%, 1.08% and 0.78% was achieved with CPME, NMP and MeTHF as processing solvents, respectively.

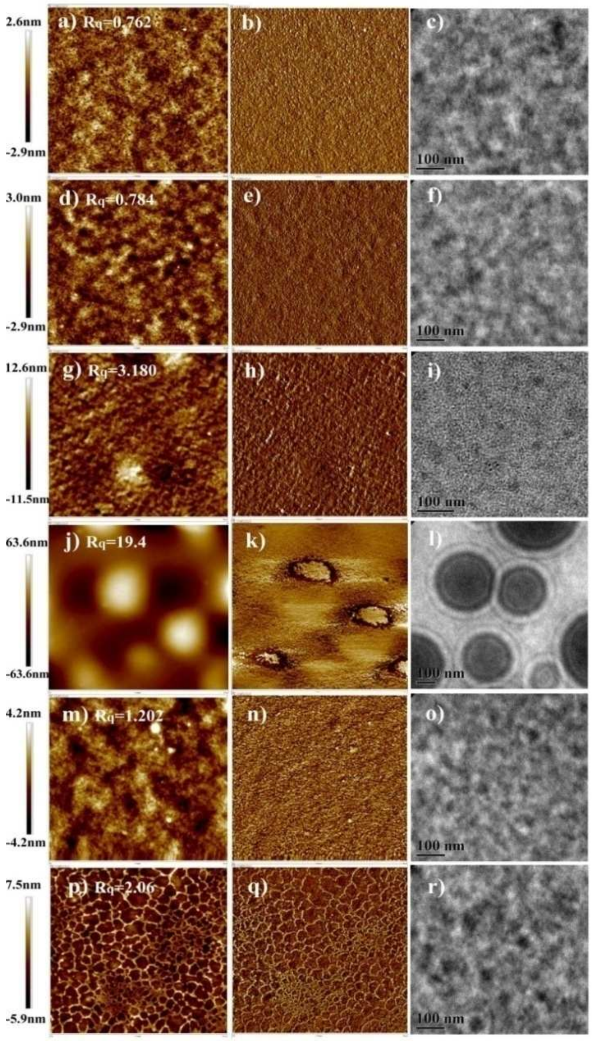

Fig.3 Tapping-mode AFM and TEM images of blend films based on PBDTTT-S-TEG/PC61B-DEG (1:1,*w*/*w*) cast from (a-c) DCB; (d-f) anisole; (g-i) DMAC; (j-l) MeTHF; (m-o) CPME; (p-r) NMP. The sized of the AFM images are 5 µm×5 µm. The scale bars in the TEM images are 100 nm.

To investigate the reasons for the differences in various solvents processing, the atomic force microscopy (AFM) and transmission electron microscopy (TEM) were employed to study the topography and the bulk morphology of the active layers. As shown in **Figure 3**, it is clear that, either on the surface or in the bulk, the micro morphology of the film casted from anisole is almost the same to the one casted from DCB, which shows the surface root-mean-square (RMS) R_q of 0.784 compared to the R_q of 0.762 under DCB processing. Thus, these results lead to the similar PCE. As DMAC and CPME were used as processing solvent, the R_q increased a little to 3.18 and 1.20, respectively, and the phase separation became blurred. In MeTHF processing, big size aggregations can be found and a high R_q of 19.4 was observed, it should be ascribed to the low b.p. of MeTHF and relatively poorer solubility of PCB-DEG in this solvent. In NMP processing, although the phase separation seems to be acceptable in the bulk morphology, the polymer separated out from the solution and formed into the network on the surface, which should be due to the limited solubility of polymer and long drying process of NMP. These results prove that the anisole is indeed an alternative of DCB as the environment friendly processing solvent for PSCs fabrication.

In order to further enhance the device performance, we applied $PC_{71}B$-DEG as the acceptor into device fabrication with anisole processing. As expected, it gives out V_{oc} = 0.746 V, J_{sc} = 12.41 mA cm^{-2}, FF = 48.57% and PCE = 4.50%, and either device performance or film morphology is very similar to the results with DCB processing (**Table 3** and **Figure S10**). Several solvent additives, like DIO, NMP and 1,8-octanedithiol (OT), were employed to the anisole processed PSCs, but no obvious improvement in PCE can be observed (**Figure S11** and **Table S3**).

Conclusions

In conclusion, a novel alkylthio-substituted conjugated polymer, PBDTTT-S-TEG, was synthesized and characterized, which possesses comparatively higher V_{oc} than the commonly used PBDTTT-based polymers and can be dissolved well in many types of solvents. In order to further improve the processability of PSCs in green solvents, four new types of green solvents processable fullerene derivatives substituted with oligo ether diols, $PC_{61}B$-DEG, $PC_{61}B$-TEG, $PC_{61}B$-DPG and $PC_{61}B$-TPG were designed, synthesized and applied as acceptor in PSCs, respectively. The device based on PBDTTT-S-TEG:$PC_{61}B$-DEG gave out the best performance and highest charge carrier mobility. Then, several green solvents were screened as the processing solvents for device fabrication, and anisole was found to be the ideal alternative for green solvent processing rather than DCB. Due to the stronger absorption of C[70] in the range from 400 nm to 600 nm compared with C[60], the DEG substituted C[70] derivative, named as $PC_{71}B$-DEG, was synthesized and applied in device fabrication as well, which can lead a higher J_{sc} and thus increased PCE. As expected, a PCE = 4.50% (V_{oc} = 0.746 V, J_{sc}= 12.41 mA cm^{-2}, FF = 48.57%) was achieved by using anisole as the processing solvent,and this result is almost identical to the device processed with DCB. Overall, with the rapid development of PSCs, the industrial manufacturability of PSCs has become one of the key issues for real applications, which requires all the procedures of manufacturing must be benign and safe for the environment and human health. Herein, we firstly demonstrated the green solvents processable PSCs starting from the perspective of molecular design and realized almost the same PCE by using anisole, a much more green solvent compared to CB, DCB and so on. Therefore, this work will be of great significance to pave the road for the industrialization of PSCs.

Acknowledgements

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Experimental

Materials synthesis:

Experimental details of all materials synthesis and characterization (i.e., measurements and instruments used) are included in Electronic Supplementary Information (ESI).

Device fabrication:

Polymer solar cell devices with the structure of ITO/PEDOT-PSS/PBDTTT-S-TEG:fullerene derivatives/Ca/Al were fabricated under conditions as follows: patterned indium tin oxide (ITO)-coated glass with a sheet resistance of 10-15 ohm/square was cleaned by a surfactant scrub and then underwent a wet-cleaning process inside an ultrasonic bath, beginning with deionized water followed by acetone and isopropanol. After oxygen plasma cleaning for 10 min, a 40 nm thick poly (3, 4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Bayer Baytron 4083) anode buffer layer was spin-cast onto the ITO substrate and then dried by baking in an oven at 150 ^{o}C for 15 min. The active layer, with a thickness in the range of 80-100 nm, was then deposited on top of the PEDOT: PSS layer by spin-coating from a 15 mg ml^{-1} blend solution of PBDTTT-TEG and fullerene derivatives, followed by the common methanol treatment. Finally, 20 nm Ca and 100 nm Al layer were successively deposited in vacuum onto the active layer at a pressure of ca. 3×10^{-4} Pa. The overlapping area between the cathode and anode defined a pixel size of 4 mm^2. Except for the deposition of the PEDOT:PSS layers, all the fabrication processes were carried out inside a controlled atmosphere of nitrogen dry box containing less than 5 ppm oxygen and moisture. The mobility was measured by the space charge limited current (SCLC) method by a hole-only device with a structure of ITO/PEDOT: PSS/Active layer/Au or an electron-only device with a structure of ITO/TIPD/Active layer/Al and estimated through the Mott-Gurney equation.

Notes and references

1 a) J. B. You, L. T. Dou, K. Yoshimura, T. Kato, K. Ohya, T. Moriarty, K. Emery, C. C. Chen, J. Gao, G. Li, Y. Yang, *Nat. Commun.* 2013, **4**, 1446; b) C. C. Chen, W. H. Chang, K. Yoshimura, K. Ohya, J. B.You, J. Gao, Z. R. Hong, Y. Yang, *Adv. Mater.* 2014, **26**, 5760.

2 a) Guidance on the application of the CLP Criteria, version. 4.0, EUROPEAN CHEMICALS AGENCY (ECHA), 2013; b) E. S. Beach, Z. Cui, P. T. Anastas, *Energy Environ. Sci.* 2009, **2**, 1038.

3 G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, *Science.* 1995, **270**, 1789.

4 C. J. Brabec, S. Gowrisanker, J. J. M. Halls, D. Laird, S. J. Jia, S. P. Williams, *Adv. Mater.* 2010, **22**, 3839.

5 M. Jørgensen, K. Norrman, S. A. Gevorgyan, T. Tromholt, B. Andreasen, F. C. Krebs, *Adv. Mater.* 2012, **24**, 580.

6 S. M. Menke, W. A. Luhman, R. J. Holmes, *Nat. Mater.* 2013, **12**, 152.

7 A. E. Jailaubekov, A. P. Willard, J. R. Tritsch, W. L. Chan, N. Sai, R. Gearba, L. G. Kaake, K. J. Williams, K. Leung, P. J. Rossky, X. Y. Zhu, *Nat. Mater.* 2013, **12**, 66.

8 A. J. Heeger, *Adv. Mater.* 2014, **26**, 10.

9 W. W. Li, K. H. Hendriks, A. Furlan, W. S. C. Roelofs, M. M. Wienk, R. A. J. Janssen, *J. Am. Chem. Soc.* 2013, **135**, 18942.

10 P. L. T. Boudreault, A. Najari, M. Leclerc, *Chem. Mater.* 2011, **23**, 456.

11 J. Peet, J. Y. Kim, N. E. Coates, W. L. Ma, D. Moses, A. J. Heeger, G. C. Bazan, *Nat. Mater.* 2007, **6**, 497 .

12 C. V. Hoven, X. D. Dang, R. C. Coffin, J. Peet, T. Q. Nguyen, G. C. Bazan, *Adv. Mater.* 2010, **22**, E63.

13 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. W. Chen, W. C. Chen, A. K. Y. Jen, *Energy Environ. Sci.* 2013, **6**, 3241.

14 X. Guo, M. J. Zhang, C. H. Cui, J. H. Hou, Y. F. Li, *ACS Appl. Mater.Interfaces*, 2014, **6**, 8190.

15 Y. Chen, S. Q. Zhang, Y. Wu, J. H. Hou, *Adv. Mater.* 2014, **26**, 2744.

16 K. R. Graham, P. M. Wieruszewski, R. Stalder, M. J. Hartel, J. G. Mei, F. So, J. R. Reynolds, *Adv. Funct. Mater.* 2012, **22**, 4801.

17 Y. Yao, J. H. Hou, Z. Xu, G. Li, Y. Yang, *Adv. Funct. Mater.* 2008, **18**, 1783.

18 F. Machui, S. Langner, X. D. Zhu, S. Abbott, C. J. Brabec, *Solar Energy Materials & Solar Cells.* 2012, **100**, 138.

19 a) C. H. Cui, W. Y. Wong, Y. F. Li, *Energy Environ. Sci.* 2014, **7**, 2276; b) L. Ye, S. Q. Zhang, W. C. Zhao, H. F. Yao, J. H. Hou, *Chem. Mater.* 2014, **26**, 3603.

20 H. Y. Chen, J. H. Hou, S. Q. Zhang, Y. Liang, G. Yang, Y. Yang, L. Yu, Y. Wu, G. Li, *Nat. Photon.* 2009, **3**, 649.

21 Y. Y. Liang, D. Feng, Y. Wu, S. T. Tsai, G. Li, C. Ray, L. P. Yu, *J. Am. Chem. Soc.* 2009, **131**, 7792.

22 L. J. Huo, S. Q. Zhang, X. Guo, F. Xu, Y. F. Li, J. H. Hou, *Angew. Chem. Int. Ed.* 2011, **50**, 9697.

23 A. C. Stuart, J. R. Tumbleston, H. X. Zhou, W. T. Li, S. B. Liu, H. Ade, W. You, *J. Am. Chem. Soc.* 2013, **135**, 1806.

24 J. C. Hummelen, B. W. Knight, F. LePeq, F. Wudl, J. Yao, C. L. J. Wilkins, *J. Org. Chem.* 1995, **60**, 532.