



Development of intrinsically fullerene-compatible polymers: Strategy for developing high performance organic solar cells using a non-halogenated solvent



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ABSTRACT

Because large amounts of solvents are needed for large-scale fabrication of organic solar cells, it is important to develop solar cell processes using environmentally friendly solvents. In the research, we introduce a new approach to control the morphology of polymer:PC₇₁BM blend films by an additive-free and non-halogenated solvent system. Incorporation of a fullerene-compatible *o*-dichlorobenzene group as the side chain of polythienothiophene-co-benzodithiophene derivatives importantly enhances the compatibility of the polymer with PC₇₁BM and improves the nano-scale morphology of the blend film processed from *o*-xylene. We studied the effect of introducing the *o*-dichlorobenzene group onto the polymer on the morphology, charge mobility, and solar cell performances as comparing the cases of the polymer before modification. The developed polymer:PC₇₁BM-based solar cells prepared using *o*-xylene show a remarkably improved performance with a PCE of 6.07%.

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1. Introduction

Organic photovoltaic (OPV) technology has developed remarkably since the use of polymer bulk heterojunctions (BHJs) as active layers. The power conversion efficiencies (PCEs) of polymer BHJ OPVs have risen above 10% owing to the development of high performance photo-active [1] and interfacial materials [2], and the optimization of device-processing methods [3]. However, to achieve a fully mature technology from the current level of research and development into cost-effective products for commercialization, many research challenges need to be overcome [4], such as ensuring the long-term stability of the OPV devices and developing the solution-processing techniques and module architectures for large-scale device fabrication. It is necessary to replace the toxic halogenated organic solvents that are currently used to prepare the BHJ active layers to non-halogenated solvents that are environmentally friendly. Moreover, it is important to prepare the BHJ active films without using solvent additives such as halogenated 1,8-diiodooctane and 1-chloronaphthalene [5].

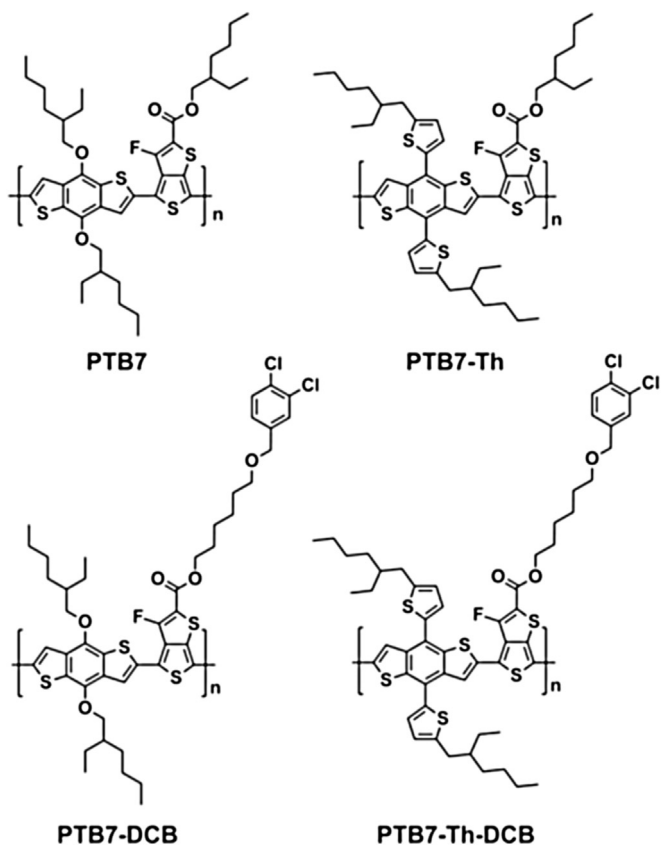
The morphology of the BHJ active layer is strongly dependent on

the processing solvent, and most polymer BHJ films prepared by using a non-halogenated solvent have an inappropriate morphology with large phase separations between the electron-donating conjugated polymer and the electron-accepting fullerene derivative. Several attempts to find fabrication methods that use solvents such as toluene, *o*-xylene, and 1,2,3-trimethylbenzene and provide the BHJ films with appropriate morphologies have achieved solar cell devices with PCEs above 6% [6]. However, the developed methods are appropriate only for a few polymers and thus their ranges of applications are limited.

One main reason for the poor morphology of the BHJ films is a low miscibility of the pull–push low bandgap polymers with phenyl-C₆₁ (or C₇₁)-butyric acid methyl esters (PCBMs). The pull–push conjugated polymers usually show good π - π interactions between the polymer chains due to their rigid backbones, however, which sometimes result in unfavorable properties of the polymers such as low solubilities in non-halogenated solvents and low miscibilities with PCBMs [6a,b,i]. Therefore, it is important to develop new electron-donating polymers that show high solubilities and are miscible with fullerene derivatives regardless of the processing solvent and solvent additive. In our previous report, we demonstrated that the incorporation of the *o*-dichlorobenzyl group, which is fullerene-compatible due to a similar Hansen solubility

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Scheme 1. Chemical structures of conjugated polymers.

parameter to those of fullerene derivatives, at the end of the conjugated polymer's side chain produces increased miscibility between the polymer and PCBM [7]. Inspired by this result, conjugated polymer donors based on polythienothiophene-co-benzodithiophene were prepared herein by introducing the fullerene-compatible *o*-dichlorobenzene-terminated side chains onto pull–push type conjugated polymers (Scheme 1). This approach is expected to make the polymers more miscible with PCBMs in non-halogenated solvents, which can induce proper phase separations in the polymer:PCBM blend films after spin-coating. We investigated the effects of the side chain modification on the morphology and photovoltaic properties of the BHJ films processed by the representative non-halogen solvent, *o*-xylene. When compared with the polymer analogues without the side chain modification, it was found that the synthesized polymers exhibit similar optical and electrochemical characteristics. However, the polymer films blended with PC₇₁BM by using *o*-xylene without an additive exhibit a much improved morphology with significantly reduced phase separations. As a result, the solar cell devices introducing the resulting BHJ active layers were found to

yield remarkably enhanced performances with the PCEs up to 6.07%.

2. Results and discussion

In our study, we use polythienothiophene-co-benzodithiophene as the basic polymer backbone because it is a good low bandgap polymer for the BHJ solar cells. Therefore, PTB7-DCB and PTB7-Th-DCB polymers bearing an *o*-dichlorobenzyl group at the ends of their alkyl side chains were synthesized via Stille coupling reactions in a toluene/DMF cosolvent with Pd(PPh₃)₄ as the catalyst. The detailed synthesis and purification procedures are described in Scheme S2. The number average molecular weights (M_n) and polydispersities (PDIs) of the resulting polymers were measured with gel permeation chromatography (GPC) by using chlorobenzene as the eluent. As listed in Table 1, all polymers have similar molecular weights in the range of 42–51 kg/mol and PDI values of 2.09–2.64 regardless of the side chain modification, which suggests that the effects of their molecular weight on the morphology of their polymer:PCBM blend films and thus on their photovoltaic properties are not significant.

The optical properties of the synthesized polymers were explored with UV–Vis absorption spectroscopy, as shown in Fig. 1a and b. The absorption spectra of PTB7-DCB and PTB7-Th-DCB in an *o*-xylene solution are very similar to those of the corresponding polymers without the *o*-dichlorobenzyl group over the whole wavelength range, with absorption maximum peaks at 676 nm and 705 nm for PTB7-DCB and PTB7-Th-DCB, respectively. However, the spectra of the PTB7-DCB and PTB7-Th-DCB films contain slight red-shifts in their absorption onsets compared with those of the PTB7 and PTB7-Th films, although the overall shapes of the absorption spectra are similar between the polymers with and without the *o*-dichlorobenzyl group. The optical bandgaps (E_g) of the polymers were estimated from the absorption onsets in the film spectra to be 1.61, 1.60, 1.56, and 1.55 eV for PTB7, PTB7-DCB, PTB7-Th, and PTB7-Th-DCB, respectively.

The electrochemical properties of the polymers were investigated with cyclic voltammetry and their individual cyclic voltammograms and calculated energy levels are shown in Fig. 1c and Table 1. The highest occupied molecular orbital (HOMO) energy levels of PTB7-Th (−5.31 eV) and PTB7-Th-DCB (−5.27 eV) are deeper than those of PTB7 (−5.22 eV) and PTB7-DCB (−5.19 eV), which is probably due to the weaker electron-donating ability of the thienyl side chain [8]. Notably, when the *o*-dichlorobenzyl group is incorporated into the polymer, PTB7 and PTB7-Th consistently show slightly increased HOMO energy levels, which is probably due to the molecular conformational change of the polymer chain.

The influence of the *o*-dichlorobenzyl group on the miscibility between the polymer and PC₇₁BM was studied by photoluminescence (PL) measurements. Fig. S1a and b show the PL spectra of the PC₇₁BM films including various amounts of PTB7 or PTB7-DCB, which were recorded with excitations at 380 nm [7], and Fig. S1c exhibits a comparison of the normalized PL intensity

Table 1
Characteristics of polymers.

Polymer	M_n (kg/mol)	PDI	$\lambda_{\max}^{\text{solution}}$ (nm)	$\lambda_{\max}^{\text{film}}$ (nm)	E_g^a (eV)	HOMO (eV)	LUMO ^b (eV)
PTB7	45	2.09	680	680	1.61	−5.22	−3.61
PTB7-DCB	44	2.64	676	686	1.60	−5.19	−3.59
PTB7-Th	51	2.38	703	704	1.56	−5.31	−3.75
PTB7-Th-DCB	42	2.16	705	713	1.55	−5.27	−3.72

^a Determined from the onset of UV–Vis absorption spectra.

^b E_g + HOMO.

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