



Fluorine-functionalization of an isoindoline-1,3-dione-based conjugated polymer for organic solar cells



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ARTICLE INFO

Keywords:

4,7-dibromo-2-(2-butyloctyl)-5,6-difluoroisoindoline-1,3-dione
Backbone fluorination
Electron donor-and-acceptor copolymers
Bulkheterojunction
Organic solar cell

ABSTRACT

We report the first synthesis of a difluorinated 4,7-dibromo-2-(2-butyloctyl)-5,6-difluoroisoindoline-1,3-dione (dibromoffIDD) unit flanked with 3-octylthieno[3,2-b]thiophene π -bridges to form the novel acceptor unit dibromoffIDD, which was then polymerized with a donor unit based on benzo[1,2-b:4,5-b']dithiophene (BDT) to yield the polymer PBDT-TTffIDD for applications in organic solar cells (OSCs). To determine the effects in this system of fluorination on photovoltaic performance, we designed two electron donor-and-acceptor copolymers, difluorinated PBDT-TTffIDD and unfluorinated PBDT-TTIDD, and studied their properties systematically. The maximum power-conversion efficiencies of OSCs based on PBDT-TTffIDD:PC₇₁BM and PBDT-TTIDD:PC₇₁BM were found to be 4.1% and 3.8% respectively.

1. Introduction

The fluorination of electron donor-and-acceptor (D-A) conjugated copolymers is a promising approach to increasing their efficiency in organic solar cells (OSCs) [1]. Fluorine (F) has a higher Pauling electronegativity (4.0) than hydrogen (2.2) [2]. As a result, when F atoms are incorporated into a D-A conjugated polymer, their strong electron-withdrawing properties lower the energy levels of both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) [3]. The effect on the HOMO energy level is stronger than that on the LUMO level, so the optical bandgap of the resulting copolymer increases [3–5]. The decrease in the HOMO level of the polymer leads to an increase in its open-circuit voltage (V_{OC}) because V_{OC} is closely related to the energy difference between the HOMO energy level of the electron donor and the LUMO energy level of the electron acceptor [4,6]. However, the visible-spectrum absorbance of the fluorinated polymer is blue-shifted due to the increase in the bandgap; this change reduces the current density (J_{SC}). Fluorine substituents on the polymer backbone interact non-covalently with adjacent atoms (H...F, S...F, and F...F) and also with those on other polymer chains, which can induce strong π - π interactions and as a result increase both the crystallinity of the film and its charge carrier mobility (μ). Furthermore, by selecting the appropriate additives and solvents for film preparation, the fill factor (FF) can be increased [7].

Fluorination of various D-A conjugated copolymers has been found

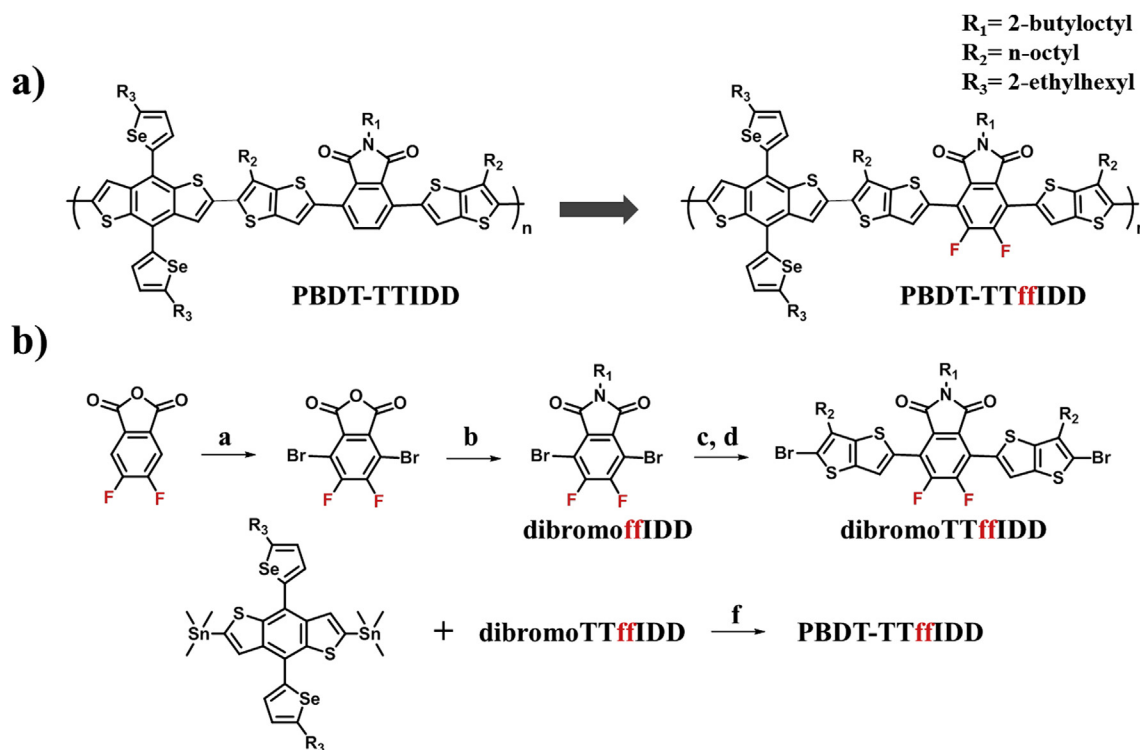
to enable the fabrication of highly efficient OSCs [1,6,8,9]. The fluorinations of acceptor units (e.g., benzothiadiazole, benzotriazole, isoindigo, thienothiophene, quinoxaline), donor units, and the side groups on D-A backbones (e.g., benzo[1,2-b:4,5-b']dithiophene (BDT), benzene, thiophene) have been reported. However, the efficiency of OSCs utilizing BDT-based copolymers decreases drastically upon the direct F-substitution of the BDT units [3]. To the best of our knowledge, the fluorination of the backbones of the acceptor units of conjugated copolymers is more effective than fluorination of their side-group units [10].

Herein, we synthesized the monomer 4,7-dibromo-2-(2-butyloctyl)isoindoline-1,3-dione (dibromoffIDD) as an acceptor unit, then polymerized it with the donor unit benzo[1,2-b:4,5-b']dithiophene (BDT) and the π -bridge 3-octylthieno[3,2-b]thiophene (TT); in the resulting polymer PBDT-TTIDD, the BDT unit is a versatile core for the addition of various side groups [11]. Alkylselenophenyl can be introduced as an effective side group on the BDT-based donor unit because of its high polarizability; the resulting polymers exhibit higher μ values than their S-based polymer counterparts [12]. The TT π -bridge flanking the IDD units provides a backbone-conjugation extension for D-A copolymers and so improves their photovoltaic properties [13]. To quantify the effects of F atoms on the IDD-based D-A conjugated copolymer, we synthesized difluorinated dibromoffIDD as a new acceptor unit, and systematically compared the molecular structures of the PBDT-TTIDD and PBDT-TTffIDD films. OSCs based on PBDT-TTffIDD:PC₇₁BM were

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Scheme 1. a) Chemical structures of PBDT-TTIDD and PBDT-TTffIDD. b) Synthetic route to PBDT-TTffIDD polymer. a) oleum for 4 h and then dibromoisocyanuric acid, 24 h; b) $R_1\text{NH}_2$, HOAC, 12 h; c) trimethyl(6-octylthieno[3,2-b]thiophen-2-yl)stannane, $\text{Pd}_2(\text{dba})_3$, $\text{P}(\text{o-tolyl})_3$, toluene, DMF, 12 h; d) NBS, THF, HOAC, 12 h; e) $\text{Pd}_2(\text{dba})_3$, $\text{P}(\text{o-tolyl})_3$, toluene, DMF, 2 days. HOAC: acetic acid, DMF: N,N-dimethylformamide, NBS: N-bromosuccinimide, dba: dibenzylideneacetone.

found to exhibit higher PCEs than OSCs based on PBDT-TTIDD:PC₇₁BM; this difference clearly shows the benefits of fluorination of the polymer backbone.

2. Results and discussion

The polymers PBDT-TTIDD and PBDT-TTffIDD were prepared by performing Pd-catalyzed Stille couplings (Scheme 1). The number-average molecular weights \overline{Mn} and polydispersity indexes ($\text{PDI} = \overline{Mw}/\overline{Mn}$) of the polymers were obtained with high-temperature size-exclusion chromatography in 1,2,4-trichlorobenzene eluent at 160 °C. PBDT-TTffIDD has a higher \overline{Mn} , 63.0 kDa, than PBDT-TTIDD, 44.9 kDa (Table 1); this difference might arise because the solubility of difluorinated derivatives is higher than that of non-fluorinated derivatives, i.e., the dibromoTTffIDD monomer is more polar than the dibromoTTIDD monomer, so more BDT-TTffIDD than BDT-TTIDD is dissolved in the reaction solvents (toluene, DMF) during polymerization, and as a result the degree of polymerization is higher for PBDT-TTffIDD [14].

The UV-Vis absorption spectra of the synthesized polymers contain

Table 1

Polymerization results, optical properties, and related energy levels of the synthesized conjugated polymers.

Polymer	Yield [%]	\overline{Mn}^{a} [kDa]/PDI	E_g^{b} (optical)	HOMO ^c	LUMO ^d	HOMO ^e (calculated)	LUMO ^e (calculated)
			[eV]	[eV]	[eV]	[eV]	[eV]
PBDT-TTIDD	76.1	44.9/2.7	2.02	-5.35	-3.47	-4.94	-2.34
PBDT-TTffIDD	69.6	63.0/3.0	2.04	-5.54	-3.55	-5.00	-2.43

^a Number average molecular weight (\overline{Mn}). Determined by GPC in 1,2,4-trichlorobenzene at 160 °C.

^b $E_g = 1240/\lambda_{\text{onset}}$.

^c $\text{HOMO} = -(4.80 + E_{\text{onset, ox}})$.

^d $\text{LUMO} = -(4.80 + E_{\text{onset, re}})$.

^e HOMO and LUMO energy levels simulated by DFT calculation.

two absorption bands (Fig. 1). The high-energy band at 300–400 nm was assigned to localized $\pi\text{-}\pi^*$ transitions and the low-energy band at 500–600 nm was attributed to the intramolecular charge transfer (ICT) interactions of the D-A copolymers [15,16]. The absorption spectrum of PBDT-TTffIDD in the film state (Fig. 1b) is red-shifted significantly toward the near-infrared with respect to that of the solution state (Fig. 1a), which is possibly due to the non-covalent interactions induced by the fluorination of the D-A copolymer (Fig. S4) [17]. The hypsochromic shift of the absorption bands of PBDT-TTffIDD with respect to the absorption spectrum of PBDT-TTIDD might be one of the reasons for the reduction in the HOMO energy level of the solid film (Fig. 1b) and the peak of photo absorption in solution corresponds to the π -conjugation length, which is supposed to be shorter for PBDT-TTffIDD than PBDT-TTIDD. This shift widens the optical bandgap of the fluorinated D-A copolymer compared to that of the unfluorinated form. The HOMO and LUMO energy levels of the D-A copolymers were determined by using cyclic voltammetry (CV) (Fig. S2); due to the ability of F to withdraw electrons from the polymers, both levels are lower in PBDT-TTffIDD than in PBDT-TTIDD (Table 1).

Density functional theory (DFT) calculations were performed by

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