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Dual substitution at 4,9-positions of carbazole in donor-π-acceptor copolymer enhances performance of bulk-heterojunction organic solar cells

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ABSTRACT

Several carbazole-2,7-diyl units with alkoxy substituents at the 4-position in addition to branched (1-alkyl)alkyl substituents at the 9-position were developed and combined with difluorinated dithienylbenzothiadiazole by using a Suzuki coupling reaction to synthesize donor–π–acceptor-type copolymers. X-ray diffraction analyses of these copolymers revealed that the 4,9-disubstituted carbazole unit contributed to form a balanced interdigitated structure, which resulted in smaller π-stacking distances (4.0–3.5 Å) of the polymer backbone, a narrower bandgap (2.0–1.8 eV), and higher hole mobilities (4.2×10^{-4} to 2.9×10^{-3} $cm^2 V^{-1} s^{-1}$) than those of the carbazole copolymer without the 4-substituent (**PCDT2FBT**). A bulk heterojunction organic photovoltaic device with a configuration of ITO/PEDOT:PSS/polymer:$PC_{70}BM$/LiF/Al exhibited a power conversion efficiency of 5.46%, a short-circuit current density of 12.4 mA cm^{-2}, a fill factor of 0.58, and an open-circuit voltage of 0.76 V. The photovoltaic performance was much higher than that of **PCDT2FBT**. These results demonstrate that incorporation of the side chains into the 4,9-positions of carbazole is a novel approach to obtain self-organizing carbazole polymers, enabling improvement in light absorption, hole mobility, and photovoltaic performance.

1. Introduction

Poly(2,7-carbazole-alt-dithienylbenzothiadiazole) (**PCDTBT**) has drawn much attention as an electron-donating polymeric material for bulk heterojunction (BHJ) organic photovoltaic (OPV) cells because of its high photovoltaic performance and outstanding environmental stability [1–3]. **PCDTBT**-based OPVs have been optimized over the past few years, and their power conversion efficiencies (PCEs) now exceed 7% [4–8]. However, **PCDTBT** has a large bandgap (E_g) and its hole mobility (μ_h) is low compared to those of typical semiconducting polymers; these shortcomings have limited further improvements in the PCE of **PCDTBT**-based OPVs. Therefore, numerous researches have focused on designing and synthesizing low-bandgap polymers (LBPs) with high charge-carrier transportability [3,9–13]. According to the donor–π–acceptor strategy (D–π–A), introducing thiadiazole derivatives with a strong electron-accepting capability is a powerful method for constructing LBPs [9,14–16]. Among various thiadiazole derivatives, 5,6-difluoro-2,1,3-benzothiadiazole (**BTF_2**) has been considered as one of the most promising electron-accepting units that lowers the energy level of the highest occupied molecular orbital (E_{HOMO}) and enhances intermolecular interactions between the polymer backbones. In fact, several conjugated polymers composed of the **BTF_2** unit exhibit a narrow E_g and a PCE greater than 7% [17–19]. However, in previous attempts to combine the **BTF_2** unit with the carbazole unit, **PCDT2FBT** (Fig. 1) did not extend photoabsorption bands to the near-infrared region and the PCE of the **PCDT2FBT**-based OPVs was at most 2% [20,21]. One of the reasons for this low PCE could be the poor solubility of **PCDT2FBT**. The preparation of highly soluble D–π–A-type carbazole based copolymers composed of the **BTF_2** unit necessitates the

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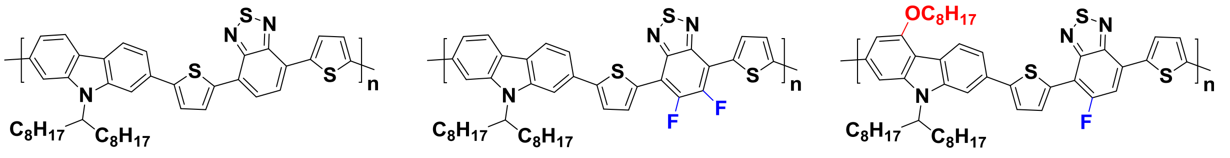


PCDTBT **PCDT2FBT** **PCOC$_8$-TBTF$_1$**

Fig. 1. Chemical structures of π-conjugated alternating copolymers **PCDTBT**, **PCDT2FBT**, and **PCOC$_8$-TBTF$_1$**.

development of a carbazole unit, which can enhance the solubility of the polymers in organic solvents. Thus, besides elongation of the alkyl side chain at the 9-position of carbazole, another alkyl side chain should be introduced elsewhere in a carbazole unit to produce the processable polymers.

In our previous study [22], we combined a newly developed 4-octyloxycarbazole-2,7-diyl unit with a 5-fluorobenzothiadiazole (**BTF$_1$**) unit to synthesize the D–π–A-type copolymer **PCOC$_8$-TBTF$_1$**, which is shown in Fig. 1. Our results revealed that the introduction of the side chain at the 4-position of carbazole, in addition to the already-present 9-substituent, resulted in good solubility of the polymer, which enabled the construction of D–π–A-type copolymers consisting of various thiadiazole derivatives [22]. Furthermore, the absorption bands of **PCOC$_8$-TBTF$_1$** in the film state exhibited a large bathochromic shift, and its π–π stacking distance of 3.57 Å was smaller than that of **PCDTBT** (4.08 Å) [22]. As a result, **PCOC$_8$-TBTF$_1$** exhibited a narrower E_g (1.76 eV) and a higher μ_h (5.5×10^{-3} cm^2 V^{-1} s^{-1}) compared to **PCDTBT** (E_g = 1.90 eV, μ_h = 1.0×10^{-3} cm^2 V^{-1} s^{-1}) [8,22]. Meanwhile, such a close π–π stacking distance comparable to that of a benzo[1,2-*b*:4,5-*b*']dithiophene-based copolymer [23,24] has never been observed for **PCDTBT** having **BTF$_1$** [20]. These results imply that dual substitution at the 4,9-positions enhances self-organization of the polymer. Arrangement of the backbone has already been suggested in the case of a dual-substituted poly(4-alkoxy-9,9-diphenylfluorene) [25].

In this paper, highly soluble 4,9-disubstituted carbazole units were combined with a 5,6-difluorodithienylbenzothiadiazole (**TBTF$_2$**) unit to synthesize several processable D–π–A conjugated copolymers, poly[9-(alkyl)-4-alkoxycarbazole-2,7-diyl-*alt*-(4,7-bis(thiophene-2-yl)-5,6-difluoro-2,1,3-benzothiadiazole)-5,5-diyl] (**P1**, **P2**, and **P3**), shown in Scheme 1 as the **PCOC-TBTF$_2$** series. The fundamental properties and characteristics of these polymers were investigated and compared to those of **PCDT2FBT**. The results demonstrated that the 4,9-disubstitution of carbazole enables the development of a series of processable and well-arranged **PCOC-TBTF$_2$** with a μ_h and PCE greater than those of the established **PCDT2FBT**.

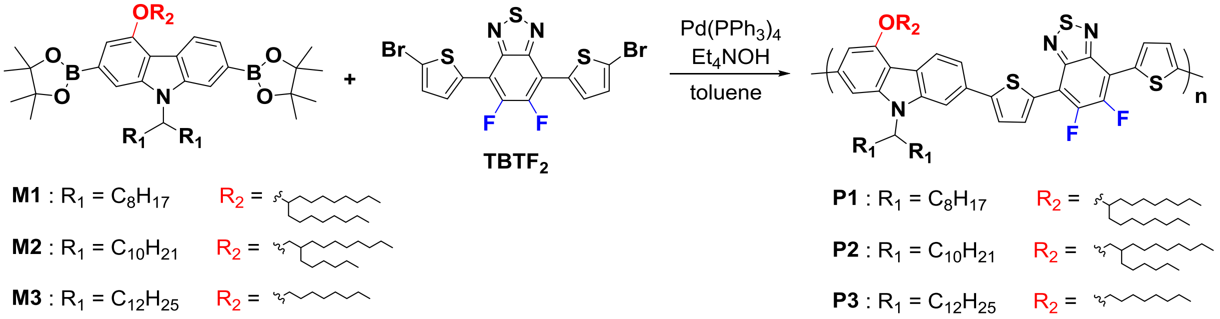
2. Experimental

2.1. Measurements

^{1}H NMR and ^{13}C NMR spectra were collected with a JEOL JNM-ECS 400 at a resonance frequency of 400 MHz for ^{1}H and 100 MHz for ^{13}C; the samples were dissolved in CDCl$_3$. UV–vis spectra of the polymers were collected on a Shimadzu UV-1800 spectrophotometer. The elemental analysis of C, H, and N were performed with a Perkin-Elmer 2400 CHN elemental analyzer. X-ray diffraction (XRD) analyses of drop-cast polymer films prepared at room temperature were carried out using a Rigaku MiniFlex600. The number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (PDI) of the chloroform-soluble fraction of the polymers were determined by gel permeation chromatography (GPC) on an instrument calibrated against polystyrene standards; chloroform was used as the eluent, and the separations were conducted at room temperature. The atomic force microscopy (AFM) measurement of the surface morphology of the samples was conducted on a Nanocute (SII NanoTechnology Inc.) operated in the tapping mode. The thermal properties of the polymers were analyzed by differential scanning calorimetry (DSC) using an EXSTAR 7000 (Seiko) at a heating/cooling rate of 5 °C min^{-1}. The E_{HOMO} of the polymers were estimated by photoelectron yield spectroscopy using an AC-3 spectrometer (Riken Keiki) [26].

2.2. Materials

All chemical reagents were purchased from Kanto Chemical Co., Inc.; Tokyo Chemical Industry Co., Ltd.; Nacalai Tesque Inc.; or Sigma-Aldrich Co., LLC, and were used without further purification unless stated otherwise. Toluene and bromobenzene were purified by distillation according to common methods. 2-Hexy-1-bromodecane, 4,4'-dibromo-2,2'-dinitrobiphenyl, 9-heptadecane *p*-toluenesulfonate, toluene-4-sulfonic acid 1-decylundecyl ester, **TBTF$_2$**, and **M3** were synthesized according to literature methods [22,27,28]. The experimental details of the syntheses of 4,4'-dibromo-2'-methoxy-2-nitrobiphenyl (**1**), 2,7-dibromo-4-



Scheme 1. Synthesis of **P1**, **P2**, and **P3**.