Synthesis, Properties, and Photovoltaic Characteristics of Donor-Acceptor Copolymers Based on Tetrafluoro-Substituted Benzodioxocyclohexene-Annelated Thiophene

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We recently reported that a donor–acceptor (D–A) type copolymer based on our developed tetrafluoro-substituted benzodioxocyclohexene-annelated thiophene (C₀(F₄)) as an acceptor unit and dithienosilole (DTS) as a donor unit shows low photovoltaic characteristics due to the strong electron-accepting nature of C₀(F₄). Here we show that the incorporation of 3-alkylthiophene spacer unit into DTS-C₀(F₄) framework is an effective approach to tune frontier molecular orbital energy levels. Organic solar cells based on blend films of newly synthesized D–A copolymers and [6,6]-phenyl-C₇₁-butyric acid methyl ester showed improved photovoltaic responses with a power conversion efficiency of up to 4.83%. This result indicates that the C₀(F₄) unit can be an effective acceptor unit for D–A copolymers.

Keywords: Organic electronics, Solar cells, Organic semiconductors, Polymeric materials, Donor-acceptor copolymer

1. Introduction

Donor–acceptor (D–A) copolymers are under active development for application in electron-donating semiconductors for organic solar cells (OSCs) [1-5]. This is because the interaction between donor and acceptor units introduced to the \(\pi\)-conjugated framework can broaden the absorption wavelength range via intramolecular charge-transfer absorption. In addition, the increase in the open-circuit voltage \((V_{oc})\) is expected because it has been suggested that the \(V_{oc}\) is related to the energy-level difference between the highest occupied molecular orbital (HOMO) of donor and lowest unoccupied molecular orbital (LUMO) of acceptor [6]. Therefore, the development of new acceptor units is still essential to obtain high photovoltaic characteristics. However, the repertoire of effectively functioning acceptor units remains limited [7-15].

We recently developed fluorine-substituted benzodioxocyclohexene-annelated thiophene units (C₀(F₂) and C₀(F₄)) as new acceptor units (Fig. 1) [16,17]. A D-A copolymer using C₀(F₄) and dithienosilole (DTS) [18-20] as donor units exhibited low photovoltaic characteristics under the combination with [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) as an acceptor [16]. The poor performance is attributed to inefficient charge separation from the photoexcited state because the DTS-C₀(F₄) had the low LUMO energy of \(-4.07\) eV, induced by the high electron-accepting ability of C₀(F₄). In contrast, OSCs based on DTS-C₀(F₂) and PC₇₁BM exhibited good power conversion efficiency (PCE) of \(7.30\%\) [16]. Furthermore, the donor polymer of DTS-T₆-C₀(F₂), incorporating a 3-hexylthiophene (T₆) spacer to improve the hole transport properties, showed the high PCE of \(9.12\%\) [17]. From these results, we expected that the incorporation of thiophene spacer to DTS-C₀(F₄) may increase the energy levels suitable for a donor material. Furthermore, C₀(F₄) has stronger electron-accepting properties than C₀(F₂); therefore, the resulting copolymers absorb longer wavelengths based on intramolecular charge-transfer absorption.
than DTS-T6-C0(F2). Thus, we report the development of new D-A copolymers incorporating various alkyl-substituted thiophenes DTS-T6-C0(F4), DTS-T10-C0(F4), and DTS-TEH-C0(F4) (Fig. 1).

Fig. 1. Chemical structures of donor copolymers used in this study.

2. Experimental

Microwave irradiation was performed by a Biotage Initiator Ver. 2.5. The microwave power output was set at 400 W. The reaction temperature was kept at 180 °C, and internal temperature during the reaction was monitored by IR sensor. Analytical gel-permeation chromatography (GPC) was performed on a Hitachi High-Technologies Corporation L-2420/L-2130 equipped with a Shodex K-803L at 40 °C using chloroform as eluent. UV-vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer. Photoelectron spectroscopy in air (PESA) was carried out using a Riken Keiki Co. Ltd. AC-3 with a light intensity of 10 mW. Organic photovoltaic devices were prepared with a structure of indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/active layer/Ca/Al. ITO-coated glass substrates were first cleaned by ultrasonication in toluene, acetone, H2O, and 2-propanol for 15 min, respectively, followed by O2 plasma treatment for 20 min. The ITO-coated glass substrates were then activated by ozone treatment for 1.5 h. PEDOT:PSS was spin-coated on the ITO surface at 3000 rpm for 1 min and dried at 135 °C for 10 min. Under this condition, the thickness of PEDOT:PSS is ca. 30 nm. The active layers were then prepared by spin-coating on the ITO/PEDOT:PSS electrode at 800 rpm for 2 min in a glove box. Ca and Al electrodes were evaporated on the top of active layer through a shadow mask to define the active area of the devices (0.09 cm²) under a vacuum of 10⁻⁵ Pa to thicknesses of 30 and 70 nm, respectively, determined by a quartz crystal monitor. After sealing the device from the air, the photovoltaic characteristics were measured under simulated AM 1.5G solar irradiation (100 mW cm⁻²) (SAN-EI ELECTRIC, XES-301S). The J–V characteristics of photovoltaic devices were measured by using a KEITHLEY 2400 source meter. The external quantum efficiency (EQE) spectra were measured by using Soma Optics Ltd. S-9240. The surface morphology of organic films was observed by atomic force microscopy (Shimadzu, SPM9600).

The synthetic route of copolymers is shown in Scheme 1.

Synthesis of DTS-T6-C0(F4): DTS-Sn (234 mg, 0.310 mmol), 2a (232 mg, 0.310 mmol), Pd2(dba)3·CHCl3 (13 mg, 0.0124 mmol), and P(o-tolyl)3 (18 mg, 0.059 mmol) were placed in a microtube and dissolved with toluene (2 mL). The mixture was then reacted in a microwave reactor at 180 °C for 40 min, and then cooled to room temperature. The copolymer solution was precipitated into methanol at room temperature. The resulting purple-black solid was filtered into a Soxhlet thimble, and extracted with methanol, hexane, and CHCl3 until the wash from each extraction became colorless. When there was no solid remaining in the thimble, the CHCl3 fraction was concentrated. The copolymer solution was then poured into methanol at room temperature. The obtained precipitate was filtered and dried under vacuum to yield DTS-T6-C0(F4) (72 mg, 72%) as a black solid. 1H NMR (400 MHz, CDCl3, δ): 7.76 (br, 2H), 7.50 (br, 2H), 7.23-7.29 (br, 2H), 2.84 (br, 4H), 1.75 (br, 4H), 0.85-1.58 (br, 52H).

DTS-T10-C0(F4) was synthesized from DTS-Sn and 2b with a yield of 65% by following the procedure used for the preparation of DTS-T6-C0(F4). 1H NMR (400 MHz, CDCl3, δ): 7.76 (br, 2H), 7.31 (br, 2H), 7.23-7.29 (br, 2H), 2.85 (br, 4H), 1.74 (br, 4H), 0.80-1.56 (br, 68H).

DTS-TEH-C0(F4) was synthesized from DTS-Sn and 2c with a yield of 57% by following the procedure used for the preparation of DTS-T6-C0(F4). 1H NMR (400 MHz, CDCl3, δ): 7.75 (br, 2H), 7.31 (br, 2H), 7.23-7.29 (br, 2H), 2.81 (br, 4H), 1.77 (br, 4H), 0.80-1.58 (br, 62H).

3. Results and discussion

3.1. Synthesis

The synthetic route of copolymers is shown in
After the Stille coupling of C0(F4)-Br \[16\] with various stannylthiophenes 1, the bromination of the thiophene α-position by N-bromosuccinimide (NBS) yielded compounds 2a–2c. The target copolymers were obtained through a Stille coupling reaction with DTS-Sn. After eliminating low-molecular-weight components by Soxhlet extraction with methanol and hexane, the copolymer was obtained through chloroform extraction. The number average molecular weights (Mn) and molecular-weight dispersity (Dm) of DTS-T6-C0(F4), DTS-T10-C0(F4), and DTS-TEH-C0(F4) were estimated as 27.5 kg/mol and 1.39, 16.5 kg/mol and 1.38, and 17.8 kg/mol and 1.58, respectively, using GPC measurements. The observed moderate Mn is due to the precipitation of these copolymers under the reaction conditions. Because the Mn of DTS-T6-C0(F4) was the longest, steric factors of the alkyl group are also considered to affect its reactivity during polymerization.

### 3.2. Properties

Figure 2 shows the UV-Vis absorption spectra of the synthesized copolymers, obtained from both CHCl3 solutions and films prepared on glass substrates. All the physical data of the copolymers are summarized in Table 1. Each copolymer shows broad absorption in the visible range of 500–800 nm. The absorption maximum of DTS-T6-C0(F4), which has the longest molecular chain length, in the spectrum obtained in solution is shifted the most towards the longer-wavelength side of the three polymers. Compared to the solution spectra, those of the films are shifted to the longer-wavelength side, suggesting the occurrence of intermolecular interactions. The onset of DTS-T6-C0(F4) (795 nm) is higher than that of DTS-T6-C0(F2) (778 nm), indicating a greater contribution from the D-A properties of DTS-T6-C0(F4) \[17\]. In addition, both absorption onsets are lower than that of DTS-C0(F4) (816 nm) \[16\], which is attributed to the presence of introduced thiophene spacers. The HOMO–LUMO energy gaps (Egap) for DTS-T6-C0(F4), DTS-T10-C0(F4), and DTS-TEH-C0(F4) are 1.56, 1.56, and 1.59 eV, respectively, as estimated from the onset in the film spectra of the molecules. The HOMO energy level (E_HOMO), obtained from the onset value of PESA measurements of the films, was estimated as –5.37 eV for all the copolymers (Fig. 3), verifying that the HOMO level was deeper than that in DTS-T6-C0(F2) (–5.29 eV) \[17\]. From these values, the LUMO energy levels (E_LUMO) of DTS-T6-C0(F4), DTS-T10-C0(F4), and DTS-TEH-C0(F4) were determined as –3.81, –3.81, and –3.78 eV, respectively. Based on these results, the synthesized copolymers had energy levels reflecting the donor properties of the thiophene spacers and the strong acceptor properties of the C0(F4) unit, as expected.
Table 1. Properties of copolymers.

| copolymers       | $\lambda_{onset}$ | $E_{\text{gap}}$ | $E_{\text{HOMO}}$ | $E_{\text{LUMO}}$ |
|------------------|-------------------|------------------|------------------|------------------|
|                  | /nm               | /eV              | /eV              | /eV              |
| DTS-$T_6$-C$_0$(F$_4$) | 795               | 1.56             | -5.37            | -3.81            |
| DTS-$T_{10}$-C$_0$(F$_4$) | 794               | 1.56             | -5.37            | -3.81            |
| DTS-$T_{EH}$-C$_0$(F$_4$) | 782               | 1.59             | -5.37            | -3.78            |
| DTS-C$_0$(F$_4$) | e 816             | 1.51             | -5.59            | -4.08            |
| DTS-$T_6$-C$_0$(F$_2$) | f 778             | 1.59             | -5.29            | -3.70            |

a In films. b $1240/\lambda_{onset}$. c from PESA. d $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{gap}}$. e Ref. 16. f Ref. 17.

3.3. OSC Evaluation

In order to investigate the photovoltaic characteristics of these copolymers, a bulk-heterojunction organic thin-film solar cell with a glass/ITO/PEDOT:PSS/active layer/Ca/Al structure using PC$_{71}$BM as the acceptor was evaluated. The active layer was optimized with the weight ratio of 1:2 for the donor copolymer to PC$_{71}$BM in a 45-mg/mL o-dichlorobenzene solution, which was spin-coated at 800 rpm for 2 min. As an exception, DTS-$T_{EH}$-C$_0$(F$_4$) was optimized at a concentration of 22.5 mg/mL. Thermal annealing or adding additives such as 1,8-diiodooctane did not improve the PCE. Figure 4(a) depicts the current density–voltage ($J$-$V$) characteristic curves measured under optimal conditions during irradiation with simulated sunlight. Table 2 summarizes the parameters deduced from these $J$-$V$ curves. All the copolymers exhibit improved photovoltaic characteristics compared to DTS-C$_0$(F$_4$), demonstrating the efficacy of the thiophene spacer. Regarding the $V_{oc}$, DTS-$T_6$-C$_0$(F$_4$) exhibits a higher value than DTS-$T_6$-C$_0$(F$_2$). This is consistent with the tendency toward a deeper HOMO level when using C$_0$(F$_4$). Meanwhile, the short-circuit current density ($J_{sc}$) and the fill factor (FF) are lower than those in DTS-$T_6$-C$_0$(F$_2$):PC$_{71}$BM. In measuring the EQE, a response occurs for wavelengths reaching 800 nm, consistent with the absorption characteristics of the film absorption spectra.

Table 2. Photovoltaic characteristics of donor copolymers:PC$_{71}$BM-based devices.

| copolymers       | $V_{oc}$ | $J_{sc}$ | FF   | PCE   |
|------------------|----------|----------|------|-------|
|                  | /V       | /mA/cm$^2$ | %   | %     |
| DTS-$T_6$-C$_0$(F$_4$) | 0.79    | 13.07    | 47  | 4.83  |
| DTS-$T_{10}$-C$_0$(F$_4$) | 0.73   | 10.11    | 52  | 3.80  |
| DTS-$T_{EH}$-C$_0$(F$_4$) | 0.80  | 3.92     | 55  | 1.73  |
| DTS-C$_0$(F$_4$) | b 0.81  | 4.32     | 28  | 0.99  |
| DTS-$T_6$-C$_0$(F$_2$) | f 0.77 | 17.72    | 67  | 9.12  |

a 22.5 mg/mL. b Ref. 16. c Ref. 17.

X-ray diffraction (XRD) measurements were performed to investigate the crystallinity of blend films. Even for the best-performance DTS-$T_6$-C$_0$(F$_4$):PC$_{71}$BM film, no obvious diffraction signals could be observed, indicating the amorphous behaviour. The similar amorphous character was observed for the DTS-$T_6$-C$_0$(F$_2$):PC$_{71}$BM and DTS-C$_0$(F$_4$):PC$_{71}$BM blend films [16,17]. These results indicate that variation in the chemical structure of the acceptor and spacer units in copolymers with DTS has little influence on the crystallinity.

To determine the causes of these low $J_{sc}$ and FF values, we evaluated the morphologies of the blended films using atomic force microscopy (AFM). As shown in Fig. 5, each of the films shows a coarse, rough surface morphologies. The structure of DTS-$T_{EH}$-C$_0$(F$_4$):PC$_{71}$BM shows completely isolated grains. From these results, the decreases in $J_{sc}$ and FF are attributed to film structures that inhibit charge separation.
Since surface energy (SFE) is known to affect the formation of various film morphologies in bulk heterojunction OSCs [21-23], we measured the SFE of DTS-T\textsubscript{o}-C\textsubscript{o}(F\textsubscript{4}), DTS-T\textsubscript{10}-C\textsubscript{o}(F\textsubscript{4}), DTS-T\textsubscript{eh}-C\textsubscript{o}(F\textsubscript{4}), and DTS-T\textsubscript{o}-C\textsubscript{o}(F\textsubscript{2}). As summarized in Table 3, the SFEs as well as the contributions of London dispersion (\(\gamma_d\)) and polar (\(\gamma_p\)) components of the C\textsubscript{o}(F\textsubscript{4})-based copolymers were in a narrow range. This result indicates that similar surface natures of the copolymer films rationalize the formation of similar rough morphologies. The SFE of DTS-T\textsubscript{o}-C\textsubscript{o}(F\textsubscript{4}) is close to that of DTS-T\textsubscript{o}-C\textsubscript{o}(F\textsubscript{2}). However, the DTS-T\textsubscript{o}-C\textsubscript{o}(F\textsubscript{2}):PC\textsubscript{71}BM blend film showed a relatively smooth surface with average roughness (\(R_s\)) of 0.82 nm, as compared to that of DTS-T\textsubscript{o}-C\textsubscript{o}(F\textsubscript{2}):PC\textsubscript{71}BM film [17]. We have considered that an increase the number of fluorine atom has led to the appearance of unique intermolecular interactions.

Table 3. SFEs of donor copolymers.

| copolymers     | \(\gamma_d\) (mJ/cm\(^2\)) | \(\gamma_p\) (mJ/cm\(^2\)) | SFE (mJ/cm\(^2\)) |
|----------------|-----------------------------|-----------------------------|-------------------|
| DTS-T\textsubscript{o}-C\textsubscript{o}(F\textsubscript{4}) | 21.7                        | 1.5                         | 23.3              |
| DTS-T\textsubscript{10}-C\textsubscript{o}(F\textsubscript{4}) | 22.8                        | 1.9                         | 24.7              |
| DTS-T\textsubscript{eh}-C\textsubscript{o}(F\textsubscript{4}) | 18.4                        | 3.8                         | 22.3              |
| DTS-T\textsubscript{o}-C\textsubscript{o}(F\textsubscript{2}) | 16.2                        | 6.6                         | 22.7              |

4. Conclusion

As described above, this study developed novel D-A copolymers with C\textsubscript{o}(F\textsubscript{4}) as an acceptor unit. By combining a DTS unit, a thiophene spacer, and a C\textsubscript{o}(F\textsubscript{4}) unit, it was possible to regulate the material properties to simultaneously achieve appropriate energy levels and favorable light absorption characteristics for a donor material. In OSCs, the photovoltaic characteristics were improved by introducing the thiophene spacer. However, morphological control of the blended films using these D-A copolymers remains a room for further improvement. These results indicate the potential of developing a solar cell material exploiting the strong acceptor properties of C\textsubscript{o}(F\textsubscript{4}) by optimizing the structure of the side-chain alkyl groups and the \(\pi\) electron system of the donor unit and spacer.

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