## Vinylene-Bridged Difluorobenzo[c][1,2,5]-thiadiazole (FBTzE): A New Electron-Deficient Building Block for High-Performance Semiconducting Polymers in Organic Electronics

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Vinylene-Bridged Difluorobenzo[c][1,2,5]-thiadiazole (FBTzE): A New Electron-Deficient Building Block for High-Performance Semiconducting Polymers in Organic Electronics

Yuya Asanuma, Hiroki Mori, Ryosuke Takahashi and Yasushi Nishihara

A new class of an acceptor unit, vinylene-bridged 5,6-difluorobenzo[1,2,5]-thiadiazole (FBTzE), has been developed. Palladium-catalyzed Migita-Kosugi-Stille coupling reactions of 1 with 2, yielding 3 and its sequential dehydrogenative coupling with 4, readily afforded FBTzE-containing monomers 5a-5c that have lower lowest unoccupied molecular orbital (LUMO) energy level and smaller energy gap than those of 5,6-difluorobenzo[1,2,5]thiadiazole (DFBT). Subsequently, three types of FBTzE-containing copolymers 3T, 4T, and 2TTT were synthesized by Migita-Kosugi-Stille coupling of monomers 5a-5c with distannylated thiophene, bithiophene, and thiennothiophene, respectively and their physicochemical properties and solar cell performances were evaluated. As a result of cyclic voltamogram, the synthesized FBTzE-based polymers have deeper highest occupied molecular orbital (HOMO) and LUMO energy levels, and stronger intermolecular interactions than those of DFBT-based polymer PFBT4T-DT. Although 3T/PC_{70}BM blended film formed favorable face-on orientation with short d_{h} of 3.57 Å, its solar cell showed poor PCE of 2.7% owing to the construction of large phase separation structure with a domain size over 100 nm. In a sharp contrast, 2TTT/PC_{70}BM formed unsuitable edge-on orientation with short d_{h} of 3.49 Å, but its film formed optimal nanoscale phase separation, leading to a good performance with PCE of up to 5.2%.

Introduction

Donor-Acceptor (D-A) type semiconducting polymers have been widely utilized for the development of high-performance p-type and n-type semiconductors in organic field-effect transistors (OFETs) and organic photovoltaic cells (OPVs). Main advantages of D-A polymers are electron delocalization and the construction of quinoidal structures through a mesomeric effect, leading to broad absorption with a small bandgap. Among the developed strong acceptors including diketopyrrolopyrrole (DPP), isindigo (IID), naphthalenediimide (NDI), naphthobisthiadiazole (NTZ), and a double B → N bridged bipyridyl (BNBP), 5,6-difluorobenzo[c][1,2,5]thiadiazole (DFBT, Figure 1) is the well-known strong acceptor unit for both high-performance OFETs and OPVs, because of the following reasons. First, not only the electron-deficient 1,2,5-thiadiazole ring and o-benzoquinoidal structure of a DFBT core, but also two fluorine atoms can offer the low-lying LUMO and HOMO energy level and narrow bandgap. Therefore, DFBT-containing polymers have high air-stability and high light-harvesting ability. Second, since a DFBT core can facilitate the intra- and intermolecular non-covalent interactions such as N· · · H, F· · · S, and F· · · H between neighboring aromatic π-spacer or polymer backbones, DFBT-based copolymers have high coplanarity with dihedral angles of nearly 0° and can promote the π-orbital overlap between polymer backbones, which can provide a strong aggregation. Indeed, it is reported that simple DFBT-quaterthiophene copolymers (PFBT4T-R, Figure 1a) exhibited strong temperature-dependent aggregation. Moreover, this strong aggregation behavior can facilitate the high crystalline thin films, resulting in a high field-effect hole mobility of nearly 2 cm^{2} V^{-1} s^{-1}. In addition, since DFBT copolymers also formed the long-range ordered structure even
in the blended films with soluble fullerene, space-charge limited current (SCLC) hole mobility reached $10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$, and thus the fabricated OPV exhibited excellent PCE of nearly 12%. However, to the best of our knowledge, despite these excellent features, a new type of DFBT-containing acceptor units have not been developed. Therefore, the development of a new class of acceptor unit bearing a DFBT unit is highly important to develop high-performance p-type and n-type OFETs and OPVs.

**Experimental**

**General**

All the reactions were carried out under an Ar atmosphere using standard Schlenk techniques. Glassware was dried in an oven (130 °C) and heated under reduced pressure prior to use. Dehydrated tetrahydrofuran (THF), dimethylsulfoxide (DMSO), and toluene were purchased from Kanto Chemicals Co., Ltd. For thin layer chromatography (TLC) analyses throughout this work, Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm) were used. Silica gel column chromatography was carried out using silica gel 60 N (spherical, neutral, 40-100 μm) from Kanto Chemicals Co., Ltd. The $^1$H, $^{13}$C($^1$H), $^{39}$F($^1$H) NMR spectra were recorded on a Varian 400-MR (400 MHz) and Varian INOVA-600 (600 MHz) spectrometer. Infrared spectra were recorded on a Shimadzu IRPrestige-21 spectrophotometer. Elemental analyses were carried out with a Perkin-Elmer 2400 CHN elemental analyzer at Okayama University. Polymerizations were performed with a Biotage initiator microwave reactor. Molecular weights of polymers were determined by gel-permeation chromatography (GPC) with a TOSOH HLC-8321GPC/HT and TSKgel GMH prevail columns, and Shimadzu RID-10 refractive index detector. Chloroform was used as the mobile phase at room temperature with a flow rate 14 mL min$^{-1}$. 4-Bromo-5,6-difluoro-4(4,7-bis(5-bromo-4-(2-(difluorobenzo[1,2,5]thiadiazol-4-yl)]ethene (DFBT) for high-performance semiconducting polymers. Here, each FBTzE and bis(4-methylthiienyl)FBTzE has four possible conformations. From DFT calculations, conformers 1 and 5 is the most thermodynamically stable structure (Figure S2). Thus, we hereafter describe chemical structures of FBTzE-based copolymers with these conformations.

![Figure 1](image)

**Figure 1**  Chemical structures of DFBT, FBTzE, and its copolymers.

in terms of the new high-performance p-type and n-type semiconductors based on a DFBT unit, we newly designed and synthesized vinylene-bridged DFBT unit (FBTzE, Figure 1b). The presence of two DFBT units in the FBTzE core might enhance the electron affinity, which can lower HOMO and LUMO energy levels. In fact, the DFT calculation revealed that model compound of FBTzE-quaterthiophene copolymer has lower HOMO and LUMO energy levels than those of a DFBT counterpart (Figure S1). This feature is highly advantageous for high-performance OPVs and n-type semiconductors. In addition, more rigid and π-extended structure of the FBTzE core owing to various intramolecular non-covalent interaction can enhance the effective π-orbital overlaps, compared to those of DFBT-based polymers, which may lead to the construction of high crystalline thin-film with longer-range ordered structure. Herein, we report the synthesis of three bis(4-alkylthienyl)FBTzE monomers and the three copolymers containing thiophene, bithiophene, and thienothiophene as the spacers (Figure 1b). In addition, their physicochemical properties, thin-film structure analyses, and solar cell characteristics were investigated to evaluate the potential of
(Pd(dbta)3)2HCl, 110 mg, 0.11 mmol) and tri(o-toly)phosphine (P(o-toly)3, 130 mg, 0.43 mmol). The reaction mixture was heated to a gentle reflux for 12 h. The resulting mixture was cooled to room temperature and added 1 M potassium fluoride (KF) aqueous solution (100 mL). The crude mixture was extracted with chloroform (100 mL × 5) and washed with brine and dried over MgSO4. After the removal of the solvent under reduced pressure, obtained solid was washed with hexane and purified by passing through pad of Florisil with chloroform as the eluent to afford 3 (772 mg, 2.1 mmol), quantitatively, as a yellow solid. Mp 255–256 ºC. FT-IR (KBr, cm−1): 3107 (w), 2974 (w), 1528 (m), 1466 (s), 1350 (m), 1308 (s), 1182 (s), 974 (s), 937 (m), 872 (m), 843 (s), 438 (m).1H NMR (600 MHz, CDCl3, δ): δ7.71 (t, J = 8.4 Hz, 2H), 8.88 (s, 2H).13C{1H} NMR (151 MHz, CDCl3, δ): δ105.50, 116.74, 125.46, 149.86, 151.03, 152.46. Anal. Calcd for C56H46Br2F2N4S4: C, 45.65; H, 1.09; N, 15.21%. Found: C, 45.70; H, 0.88; N, 15.20%.

**Typical Procedure for the Synthesis of (E)-1,2-bis-(7-(5-bromo-4-(2-decyltetradecyl)thiophen-2-yl)-5,6-difluorobenzoc][1,2,5]-thiadiazol-4-yl)-5,6-difluorobenzoc][1,2,5]-thiadiazol-4-yl)ethene (5a).** In a 50 mL Schlenk tube, 2-bromo-3-(2-hexyldecyl)thiophene (4a, 1.79 g, 4.66 mmol) was added to a mixture of compound 3 (423 mg, 1.15 mmol), palladium(II) trifluoroacetate (Pd(tfa)2, 70 mg, 0.23 mmol), and silver(I) carbonate (Ag2CO3, 2.54 g, 9.2 mmol) in DMSO (25 mL). The reaction mixture was stirred at 140 ºC for 24 h. After cooling to room temperature, the mixture was extracted with dichloromethane (50 mL × 3), washed with 1 M HCl aqueous solution and brine, and then dried over MgSO4. After the removal of the solvent under reduced pressure, obtained solid was purified by silica gel chromatography with hexane and hexane-dichloromethane (1:1) as the eluents (Rf = 0.21). Mp 73−75 ºC. FT-IR (KBr, cm−1): 3436 (w), 2967 (s), 2932 (m), 2871 (w), 1651 (m), 1597 (w), 1543 (m), 1456 (s), 1439 (m), 1381 (s), 1354 (m), 1344 (m), 1324 (m), 1273 (m), 1228 (m), 1176 (m), 1146 (m), 1095 (m), 1053 (s), 982 (m), 851 (m), 721 (m), 536 (m).1H NMR (600 MHz, CDCl3, δ): δ0.87 (t, J = 6.8 Hz, 12H), 1.20–1.40 (m, 64H), 1.67 (m, 2H), 2.42 (d, J = 7.2 Hz, 4H), 7.70 (s, 2H), 8.10 (s, 2H).13C{1H} NMR (150 MHz, CDCl3, δ): δ13.40, 22.84, 26.69, 29.57, 29.86, 30.93, 32.26, 33.12, 36.81, 39.08, 38.67, 112.15, 113.83, 116.06, 123.40, 131.24, 132.44, 141.75, 148.55, 148.99, 150.05, 152.45.19F{1H} NMR (376 MHz, CDCl3, δ): δ−130.62 (d, J = 14.7 Hz), −128.54 (d, J = 14.7 Hz). Anal. Calcd for C56H46Br2F2N4S4: C, 56.93; H, 6.19; N, 4.92%. Found: C, 56.98; H, 6.15; N, 4.87%.

**Typical Procedure for the Synthesis of Polymers (PFBTzE4T-OD, 3T).** Monomers 5b (62.6 mg, 0.05 mmol), 2,5-bis(trimethylstannyl)thiophene (6, 20.5 mg, 0.05 mmol), tetrakis(triphenylphosphine) palladium(0) (Pd[PPh3]4, 1.2 mg, 2 µmol), copper iodide(I) (CuI, 1.0 mg, 5 µmol) and toluene (2.5 mL) were added to a reaction vessel, which was sealed and heated to a gentle reflux for 12 h. The resulting mixture was heated at 140 ºC for 2 h in a microwave reactor. After being cooled to room temperature, the reaction mixture was poured into 100 mL of methanol containing 5 mL of concentrated hydrochloric acid and stirred for 3 h. The precipitate was then subjected to sequential Soxhlet extraction with methanol, hexane, and chloroform to remove low molecular-weight fractions. The residue was extracted with chlorobenzene, and concentrated solution was poured into 50 mL of methanol. The formed precipitates were collected by filtration and dried in vacuo to afford 3T (44.7 mg, 76%) as a metallic purple solid. GPC (SEC-D, 140 ºC): Mn = 46.9 kDa, Mw = 31.6 kDa, PDI = 1.98. Anal. Calcd for C50H40Br2F2N4S4: C, 66.86; H, 7.52; N, 4.61%.

**PFBTzE4T-OD, 3T.** Monomers 5c (68.2 mg, 0.05 mmol), 5,5′-bis(trimethylstannyl)-2,2′-bithiophene (7, 24.6 mg, 0.05 mmol), tetrakis(triphenylphosphine)palladium(0) (Pd[PPh3]4, 1.2 mg, 2 µmol), and toluene (2.5 mL) were subjected to the polymerization procedure, and the reaction mixture was heated at 140 ºC for 30 min in a microwave reactor. Sequential Soxhlet extraction with the same solvents used for 3T was employed to obtain 4T (40.6 mg, 59%) as a metallic purple solid. GPC (PDMS, 140 ºC): Mn = 138.3 kDa, Mw = 139.8 kDa, PDI = 2.39. Anal. Calcd for C52H40Br2F2N4S4: C, 68.38; H, 7.95; N, 4.09%. Found: C, 68.37; H, 8.01; N, 3.94%.

**PFBTzE2TTT-OD, 3TT.** Monomers 5e (68.2 mg, 0.05 mmol), 2,5-bis(trimethylstannyl)thieno[3,2-b]thiophene (8, 23.3 mg, 0.05 mmol), tetrakis(triphenylphosphine)palladium(0) (1.2 mg, 2 µmol), and toluene (2.5 mL) were subjected to the polymerization procedure, and the reaction mixture was heated at 140 ºC for 30 min in a microwave reactor. Sequential Soxhlet extraction with the same solvents used for 3T was employed to obtain 2TTT (39.9 mg, 59%) as a metallic purple solid. GPC (PDMS, 140 ºC): Mn = 76.4 kDa, Mw = 166.7 kDa, PDI = 2.18. Anal. Calcd for C76H80Br2F2N4S4: C, 67.91; H, 7.95; N, 4.17%. Found: C, 67.65; H, 7.95; N, 3.92%.
Instrumentation and Theoretical Calculation

UV-vis absorption spectra were measured using a Shimadzu UV-2450 UV-vis spectrometer. Cyclic voltammograms (CVs) were recorded on an Electrochemical Analyzer CHI-660B in acetonitrile containing tetraethylammonium hexafluorophosphate (TBAP, 0.1 M) as supporting electrolyte at a scan rate of 100 mV/s. A Pt electrode (surface area: A = 0.071 cm\(^2\), BAS), an Ag/Ag\(^{+}\) (Ag wire in 0.01 M AgNO\(_3\)/0.1 M TBAPF\(_6\)/CH\(_2\)Cl\(_2\) or CH\(_3\)CN), and a Pt wire electrode were used as working, reference, and counter electrodes, respectively. Samples of the polymer films were prepared by drop-casting on a working electrode from their chloroform solutions. All the potentials were calibrated with the standard ferrocene/ferrocinium redox couple (Fc/Fc\(^{+}\): \(E^{1/2}\) = +0.52 V for CH\(_2\)Cl\(_2\) or CH\(_3\)CN measured under identical conditions). Dynamic force-mode atomic force microscopy was carried out using an SPA 400-DFM (SII Nano Technologies). Grazing incidence wide-angle X-ray diffraction (GIWAXS) analyses were carried out at SPring-8 on beamline BL46XU. The samples were irradiated at a fixed angle on the active area of the solar cell with a xenon lamp (Bunkokeiki OTENTO-SAN III type G2) as the light source, under AM 1.5 G simulated solar irradiation at 100 mWcm\(^{-2}\) at room temperature under a solar simulator.

Fabrication of Inverted Bulk-heterojunction Solar Cells

The inverted bulk-heterojunction solar cells were fabricated as follows. ZnO precursor solution was prepared by hydrolysis of Zn(OAc)\(_2\). The ITO substrates (ITO, Geomatec Co. Ltd., thickness = 150 nm, sheet resistance < 12 Ω sq\(^{-1}\), transmittance (\(λ = 550\) nm) ≥ 85%) were successively washed using ultrasonication in a neutral detergent, deionized water, acetone, and isopropanol at room temperature, and in hot isopropanol, for 10 min, respectively. Then ITO substrates were treated with UV-ozone for 20 min. Pre-cleaned ITO substrates were spin-coated with 0.4 M ZnO precursor solution at 4000 rpm for 30 sec, and then immediately baked at 200 °C for 30 min in air. After gradual cooling to room temperature, the substrates were rinsed with acetone and isopropanol at room temperature, then in hot isopropanol for 5 min. The substrates were dried and immediately transferred into a nitrogen-filled glove box. The active layers with PC\(_{61}\)BM were deposited by spin-coating (at 600 rpm for 60 sec for 3T, and at 600 rpm for 30 sec for 4T and 2TTT) from a solution containing a polymer sample (10.0 mg/mL for 3T, 3.3 mg/mL for 4T, and 6.0 mg/mL for 2TTT) and a respective amount of PC\(_{61}\)BM in anhydrous chlorobenzene (CB). The solution was kept at 100–140 °C (100 °C for 3T, and 140 °C for 4T and 2TTT) for 30 min, and the hot solution was spin-coated on the substrate (at room temperature for 3T, and preheated at 140 °C for 4T and 2TTT before spin-coating). p/n Ratio is weight ratios of polymers and PC\(_{61}\)BM. 1,8-Diodooctane (DIO, 1 vol%) or diphenyl ether (DPE, 2.5 vol% for 3T and 4 vol% for 2TTT) were used as the solvent additives. The active layer thickness of 3T, 4T, and 2TTT was 100-130 nm, respectively. The uniform 4T/PC\(_{61}\)BM blended film could not be obtained, due to too strong aggregation tendency of 4T. MoO\(_3\) (6 nm) as an anode interlayer and an Ag (50 nm) layer were deposited under high vacuum (~6 × 10\(^{-5}\) Pa) through a shadow mask. The active area of all devices was 0.16 cm\(^2\). The thickness of the active layer was measured with an AlphaStep\(^{®}\) IQ surface profiler (KLA Tencor).

The characteristics of the solar cell devices were measured through a 4 × 4 mm photo-mask, with a Keithley 2401 semiconductor analyzer, using a Xe lamp (Bunkokeiki OTENTO-SAN III type G2) as the light source, under AM 1.5 G simulated solar irradiation at 100 mWcm\(^{-2}\) at room temperature under a solar simulator.

Scheme 1 Synthesis of FBTzE 3, monomers 5a-5c, and Copolymers.
nitrogen atmosphere. The light intensity was determined by a calibrated standard silicon solar cell (Bunkokeiki, BS-S208K). External quantum efficiency (EQE) was measured using a Bunkokeiki SM-250 Hyper Monolight System.

**Fabrication and Characterization of Hole-only Devices**

Hole-only devices were fabricated as follows. ITO substrates were washed and treated with UV-ozone in the same manner as described above. Then, ITO substrates were spin-coated with poly(3,4-ethylene-dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Clevios P VP Al 4083) through a 0.45 µm PVDF syringe filter at 5000 rpm for 30 sec, and dried at 120 °C for 10 min in air. After being dried, the substrates were immediately transferred into a nitrogen-filled glove box. Thin films of an active layer were deposited by the same procedure as described above (high concentration solution was used, 13.3 mg/mL for 3T and 8.0 mg/mL for 2TTT). The active layer thickness of 3T and 2TTT was 240 and 220 nm, respectively. After the thin films were dried, MoO$_3$ (6 nm) and Al (80 nm) layers with an active cathode area of 0.16 cm$^2$ were deposited under high vacuum (~6 × 10$^{-5}$ Pa) through a shadow mask.

Current density-voltage ($J$-$V$) characteristics of the fabricated devices were measured using a Keithley 2401 Source Meter in the dark. Voltage sweeps were performed in the range of 0-8 V, and hole mobilities were estimated from the $J$-$V$ curve of the Mott-Gurney space charge limited current (SCLC) law:

$$J = \frac{9}{8} \epsilon_0 \epsilon_r \mu \left(\frac{V^2}{L^3}\right)$$

where $\epsilon_0$ is the permittivity of free space, $\epsilon_r$ is the dielectric constant of the polymer, $\mu$ is the hole mobility, $L$ is the thickness of the active layer, and $V$ is the voltage drop across the device ($V = V_{appl} - V_b$). $\epsilon_r$ is assumed to be 3, which is a typical value for semiconducting polymers.

**Results and Discussion**

**Synthesis of FBTzE Derivatives and FBTzE-Based Copolymers**

Scheme 1 shows synthetic routes of FBTzE, monomers 5a-5c, and three copolymers. Migita-Kosugi-Stille coupling of 4-bromo-5,6-difluorobenzo\[c\][1,2,5]thiadiazole (1) and trans-1,2-bis(tributylstannyl)ethylene (2) afforded FBTzE in 99% yield. Then, FBTzE-containing monomers 5a-5c were synthesized by dehydrogenative coupling of 3 with 2-bromo-3-(2-alkyl)thiophenes 4a-4c. After optimization of the palladium catalyst, oxidant, and additive, we could obtain compound 5a in 52% isolated yield (Table S1). Accordingly, with the same reaction conditions in hand, monomers 5b and 5c with different side chains were also synthesized. When 5a was used for copolymerization with distannylated bithiophene 7, soluble polymers were not obtained due to its insufficient solubility. Therefore, Migita-Kosugi-Stille coupling reactions of 5b with distannylated thiophene 6, and of 5c with distannylated bithiophene 7 and thiophene 8 yielded three copolymers PFBBzEAr in 76% (Ar = 3T), 59% (Ar = 4T), and 59% (Ar = 2TTT), respectively. In the case of 3T, the addition of Cu and longer time were needed to obtain high-molecular-weight copolymers.

![Figure 2](image-url) The optimized molecular structures and calculated dihedral angles of model compounds by DFT using M06-2X/6-31G** level.
From high-temperature gel-permeation chromatography (GPC) analyses, all three polymers have high molecular weight over 40 kDa. Among them, the number-average molecular weight ($M_n$) of 4T and 2TTT polymers ($M_n = 133.8$ and 76.4 kDa) are significantly higher than that of 3T ($M_n = 46.9$ kDa). This result might be attributed to the high aggregation in the solution. In fact, GPC curves of 4T and 2TTT showed obvious dual peaks at high and low retention time region, and $M_n$ of the polymer obtained from a low-concentration solution of 4T and 2TTT become a lower value than that from high-concentration solution (Figure S5, Table S2). Therefore, polymers 4T and 2TTT have stronger intermolecular interaction, likely due to their higher symmetry of polymer backbones.\textsuperscript{55}

Computational Study of FBTzE and Its Derivatives

In order to evaluate the non-covalent intermolecular interaction, the optimized structures of several model compounds were calculated by density functional theory (DFT) using M06-2X/6-31G** level.\textsuperscript{35} Figure 2 shows the optimized structure and dihedral angle of non-substituted and fluorinated trans-stilbenes, vinylene-bridged benzothiadizoles, and FBTzE derivatives. trans-Stilbene (I) has a large dihedral angle of $18.2^\circ$ between benzene rings and a vinylene moiety owing to a steric repulsion of each hydrogen atom (Figure 2a). On the other hand, by introducing fluoride atoms or a fused thiadiazole ring instead of two hydrogen atoms, the dihedral angles of fluorinated trans-stilbene (II) and vinylene-bridged benzothiadiazole (III) were drastically decreased to $0.67^\circ$ and $0.05^\circ$, respectively (Figure 2b,c). This suggests that N···H or F···H interaction can increase the coplanarity of a FBTzE framework. Especially, N···H can provide the higher coplanarity than that of F···H, likely due to the existence of stronger hydrogen bond. Furthermore, FBTzE 3 with both thiadiazole ring has a completely coplanar structure with a dihedral angle of $0^\circ$ (Figure 2d). In thiophene-containing compounds, bisthienyl-trans-stilbene (IV) also has a large dihedral angle of $27.2^\circ$ between benzene and adjacent thiophene rings (Figure 2e). On the other hand, model compounds V and VI have largely decreased dihedral angles of $18.8^\circ$ and $13.9^\circ$, respectively, but they do not have completely planar structures (Figure 2f,g). In contrast, the dihedral angle of bisthienyl FBTzE (VII) is less than $1^\circ$, indicating that both N···H and F···S interactions are required to afford the completely planar structure (Figure 2h). These N···H and F···S interactions between benzothiadiazole derivatives and neighboring thiophene ring is well-known and evaluated by single-crystal structure analysis.\textsuperscript{42,56,57} These calculation results are consistent with previously reported polymers.

![Figure 3](image-url)
results. From these results, highly coplanar structure of FBTzE and its derivative can be expected to give the densely packing structure in the solid state.

Physicochemical Properties of FBTzE Derivatives

UV-vis absorption spectra and cyclic voltammograms of 3 and monomers 5b and 5c are shown in Figure 3a,b, and the results are summarized in Table 1, comparing the physicochemical properties of the standard DFBT and DFBT monomer (DFBT2T-DT-Br, Figure 1a) (Figures S6a,b). The UV-vis absorption spectrum of 3 showed the absorption maximum at 385 nm, which is 78 nm red-shifted absorption than that of DFBT. In addition, the optical energy gap ($E_g$) of 3 (2.81 eV) is significantly smaller than that of DFBT (3.71 eV), indicating the effective π-extension of FBTzE core. In monomers 5b and 5c, the 32 nm red-shifted absorption (483 nm) and about 0.2 eV smaller $E_g$ were observed, compared to those of DFBT2T-DT-Br. Furthermore, the absorption coefficients of 5b and 5c are ca. 3.5 times higher (~55,000 M$^{-1}$ cm$^{-1}$) than that of DFBT2T-DT-Br. This results indicates that FBTzE derivatives 5b and 5c have stronger absorption, which is beneficial for solar cells.

The electrochemical properties of 3 and monomers 5b and 5c were investigated (Figure 3c). FBTzE 3 exhibited clear one oxidation and reduction waves. The estimated HOMO and LUMO energy level are ~−6.20 and ~−3.26 eV, respectively, both of which are lower than that of DFBT (HOMO = −6.03 eV and LUMO = −2.98 eV). This indicates that 3 has larger electron affinity due to the existence of two DFBT in its core. On the other hand, 5b and 5c have significantly higher HOMO energy levels around −5.7 eV, and their LUMO energy level are slightly lower than that of 3. From DFT calculations, the coefficient of LUMO in 5b and 5c strongly localized on the central FBTzE core, but HOMO coefficient delocalized on the entire the molecules (Figure S3). Therefore, the difference of LUMO energy level between 3 and monomers 5b and 5c is rather small. Such tendency is in a good agreement with DFT calculations (Figure S1).

Physicochemical Properties of FBTzE-based Copolymers, 3T, 4T, and 2TTT

UV–vis absorption spectra of PFBTzEAr polymers are depicted in Figures 4a and 4b, and the extracted parameters are summarized in Table 1. Figure S6c also showed absorption spectra of DFBT-based polymer PFBT4T-DT for the comparison. 4T has the almost similar $E_g$ (1.55 eV) to that of the representative reported polymer PFBT4T-DT (1.58 eV) in the solid state (Figure 4b and S6c). One possible reason for such similar $E_g$ may be a similar effective π-conjugation length. In fact, DFT calculations of their model compounds revealed that the difference of $E_g$ between 4T and PFBT4T-DT decreased with an increase of repeating units (Figure S1). Interestingly, both 4T and PFBT4T-DT showed strong temperature-dependent aggregation, but quite different behaviors were observed.
(Figure S6c and S7b). Upon heating at ca. 80 °C in solution, 4T exhibited slight blue-shifted spectra and the decrease of an intensity, while PFBT4T-DT showed significantly hypochromic shifted absorption spectrum and one broad absorption at longer wavelength region, indicating that 4T formed partial aggregate in the high temperature solution, whereas PFBT4T-DT showed completely disaggregated behavior. These results suggest that 4T has stronger intermolecular interaction than that of PFBT4T-DT due to its extended n-electron system. Cyclic voltammograms of polymers revealed that 4T have lower HOMO and LUMO energy levels (~5.33 and ~3.69 eV) than those of PFBT4T-DT (~5.25 and ~3.62 eV) (Figures 4c,d and S6d, Table 1). This may be attributed to a larger electron affinity of the FBTzE core, which are consistent with DFT calculations. Such low-lying HOMO and LUMO energy levels of FBTzE-based polymer are beneficial for the development of high-performance p-type polymers and n-type semiconductors in OPVs. All the three polymers 3T, 4T, and 2TTT exhibited similar absorption spectra with almost same $E_g$ (Figure 4a,b and Table 1). The intensity in absorption spectra of 4T and 2TTT was significantly decreased (Figure S7 and Table S3). This indicates that polymers 4T and 2TTT have partial aggregation in the high-temperature solution, and thus have a strong intermolecular interaction. In thin film, the absorption spectrum of 2TTT is identical to that of its room-temperature solution, indicating that 2TTT formed the highly ordered packing structure in room-temperature solution. On the other hand, the absorption spectrum of 4T-based film showed slightly blue-shifted compare to room-temperature solution. One possible reason for such difference may be attributed to the different packing motif in the solid state. Such tendency is also observed in high molecular-weight PFBT4T-DT,33 but actual reason has not been described. Polymer 3T has a similar absorption before and after heating. In addition, the spectrum of 3T in solution at room temperature is almost identical to that in its thin film. This suggests that 3T seems to form large aggregate even in the high-temperature solution, which is inconsistent with the result of GPC trace. Polymer 3T has a higher solubility and lower viscosity in high concentration solution than that of the other polymers 4T and 2TTT. In addition, 3T showed ~10-20 nm blue-shifted spectra than that of 4T and 2TTT. From these results, we concluded that 3T did not form large aggregate in the room-temperature solution and has weaker intermolecular interactions. One possible reason for such difference among three polymers is their symmetry of the polymer backbones. From DFT calculations of a dimer structure, 3T formed a twisted backbone due to the steric hindrance between two alkyl side chains onto terthiophene unit, whereas 4T and 2TTT have a relatively coplanar structure owing to their higher regioregularity (Figure S4). Such coplanar structure can enhance the effective $\pi-\pi$ overlap,59,60 or arising from the terthiophene unit having the reduced electron-donating ability.61

Photovoltaic Properties of Polymer/PC$_{61}$BM-Based Solar Cells

To evaluate the potential of FBTzE for high-performance electronics, typical inverted solar cells with device structure of ITO/ZnO/(polymer:PC$_{61}$BM)/MoO$_3$ (6 nm)/Ag (50 nm) were fabricated and characterized. Typical current density ($J$)-Voltage ($V$) characteristics of the fabricated solar cells under AM 1.5 G simulated solar irradiation at 100 mW cm$^2$ are depicted in Figure 5a, and the extracted solar cell parameters are summarized in Table 2 and Table S4. The solar cell based on 4T did not show photovoltaic response due to the current leakage, because uniform thin-film was not fabricated due to its strong aggregation behavior. The best p/n ratio of 3T and 2TTT-based devices were found to be 1:1 and 1:2. The best solar cell performances were obtained, when the substrate temperature is room temperature for 3T and 140 °C for 2TTT, respectively.

**Table 2 Solar Cell Performances of Polymer/PC$_{61}$BM-based Devices**

<table>
<thead>
<tr>
<th>device</th>
<th>$J_s$/mA cm$^{-2}$</th>
<th>$V_{oc}$/V</th>
<th>FF</th>
<th>PCE (PCE$_{avg}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3T</td>
<td>7.00</td>
<td>0.88</td>
<td>0.43</td>
<td>2.66 (2.60)</td>
</tr>
<tr>
<td>2TTT</td>
<td>11.47</td>
<td>0.80</td>
<td>0.57</td>
<td>5.23 (5.09)</td>
</tr>
</tbody>
</table>

$^*$Average values are shown in parentheses. $^*$For 3T, the polymer/PC$_{61}$BM blend ratio is 1:1 (w/w), solvent = chlorobenzene (CB) + 2.5 vol% diphenyl ether (DPE); For 2TTT, the polymer/PC$_{61}$BM blend ratio is 1:2 (w/w), solvent = CB + 4 vol% DPE.

**Figure 5** (a) J-V curves and (b) EQE spectra of 3T and 2TTT/PC$_{61}$BM-based solar cells.
Both 3T- and 2TTT-based devices without optimization exhibited poor solar cell performances with PCE of 0.87% (for 3T) and 3.09% (for 2TTT), due to their low short-circuit current density ($J_{sc}$) and fill factor (FF). When 2.5% and 4% of diphenyl ether (DPE) were used as the solvent additive in 3T and 2TTT-based solar cells, respectively, the best OPV performances were observed. Since 3T has a deeper HOMO energy level, its solar cell exhibited higher open-circuit voltage ($V_{oc}$) (0.88 V) than that of 2TTT-based solar cell (0.80 V). However, 2TTT-based cell showed significantly higher $J_{sc}$ (11.47 mA cm$^{-2}$) and FF (0.57) than those of 3T-based cell ($J_{sc} = 7.00$ mA cm$^{-2}$, FF = 0.43), and thus higher PCE of 5.23%. From EQE spectra, 2TTT-based solar cell has a higher photocurrent conversion with maximum EQE of 48% in all regions, compared to the 3T-based device (Figure 5b), leading to a high $J_{sc}$. In order to understand the difference of solar cell performances between 3T and 2TTT, the hole-only devices with the device configuration of ITO/(PEDOT:PSS)/(polymer:PC$_{61}$BM)/MoO$_3$ (6 nm)/Al (80 nm) were fabricated and characterized to estimate their SCLC hole mobility (Figure S8). However, despite higher FF, SCLC hole mobility of the 2TTT-based hole-only device ($\mu_h = 5.40 \times 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$) is lower than that of 3T-based device ($\mu_h = 7.66 \times 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$). We speculated that low mobility balance of 3T-based device may lead to low FF, because such mobility balance strongly affects FF of solar cells.42

**Figure 6** 2D GIWAXS images of (a,b) polymer and (c,d) polymer/PC$_{61}$BM blended films on ITO/ZnO substrate; (a) 3T, (b) 3T/PC$_{61}$BM (p/n = 1:1, CB+2.5 vol% DPE), (c) 2TTT, and (d) 2TTT/PC$_{61}$BM (p/n = 1:2, CB+4 vol% DPE). 1D cross-sectional profiles of (e,f) pure polymer films and (h,g) polymer/PC$_{61}$BM blended films on ITO/ZnO substrate; (e,g) out-of-plane and (f,h) in-plane.

**Figure 7** Topological (left) and error-signal (right) images of polymer/PC$_{61}$BM blended films on ITO/ZnO substrate; (a) 3T/PC$_{61}$BM (p/n = 1:1, CB+2.5 vol% DPE), and (b) 2TTT/PC$_{61}$BM (p/n = 1:2, CB+4 vol% DPE). Scale bar is 500 nm.
with short π-stacking distance ($d_{sc}$) of 3.57 Å. In addition, 3T/PC$_{61}$BM blended film also formed predominantly face-on orientation with almost same lamellar distance ($d_{lm}$) of 21.1 Å and short $d_{sc}$ of 3.57 Å (Figure 6g,h). Although 3T has favorable molecular orientation in both pure polymer and blended film with PC$_{61}$BM, it formed large-scale phase separation with the domain size of 300-500 nm (Figure 7a). Such unfavorable phase separation structure must prevent the effective photocurrent generation, leading to a poor $J_{sc}$. In contrast, 2TTT exhibited strong lamellar diffraction (100) at 0.298 Å$^{-1}$ in $q_z$ axis and π-stacking diffraction (010) at 1.805 Å$^{-1}$ in $q_y$ axis, which are completely opposite direction compared to 3T film (Figure 6b,e,f). This indicates that 2TTT formed unsuitable edge-on orientation with a short $d_{sc}$ of 3.49 Å. Moreover, 2TTT/PC$_{61}$BM blended film also exhibited almost same diffraction patterns with almost same lamellar distance ($d_{lm}$) of 21.5 Å and short $d_{sc}$ of 3.49 Å (Figure 6d,g,h). Such unfavorable orientation may limit the efficient carrier transport, leading to low hole mobility. However, 2TTT/PC$_{61}$BM blended film formed well-separated phase separation with a smaller domain size (Figure 7b). Therefore, 2TTT-based cell showed higher $J_{sc}$ than that of 3T-based cell, resulting in a higher PCE.

Conclusions

In summary, we have successfully synthesized FBTzE as a new class of an acceptor unit via Migita-Kosugi-Stille coupling and dehydrogenative coupling. In addition, three FBTzE-based copolymers, 3T, 4T, and 2TTT were also synthesized. FBTzE-containing compounds showed lower LUMO energy levels and smaller $E_g$ than those of a standard DFBT core, due to its larger electron affinity and π-extended core. In addition, FBTzE-based copolymers have lower-lying HOMO and LUMO energy levels, stronger interaction than those of the parent DFBT-based polymer PHBT4T-DT, which are beneficial for high-performance electronics. Among the three polymers, 2TTT-based solar cell exhibited good solar cell performance with PCE of 5.23%, although 2TTT formed unfavorable edge-on orientation with a short $d_{sc}$ of 3.49 Å. Thus, the FBTzE core is a potential building block for high-performance D-A semiconducting polymers. Currently, we are investigating to improve the molecular orientation by optimizing solubilizing side chains and donor units.

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References

Vinylene-Bridged Difluorobenzo[c][1,2,5]-thiadiazole (FBTzE): A New Electron-Deficient Building Block for High-Performance Semiconducting Polymers in Organic Electronics

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A new class of an acceptor unit, vinylene-bridged 5,6-difluorobenzothiadiazole FBTzE, and three FBTzE-containing copolymers has been synthesized and characterized.