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Benzo[*c*]thiophene–C_{60} Diadduct: An Electron Acceptor for p–n Junction Organic Solar Cells Harvesting Visible to Near-IR Light

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Abstract: We synthesized a new 56-π-electron fullerene derivative through a Diels–Alder cycloaddition of benzo[*c*]thiophene that featured a relatively low temperature, closer to stoichiometric use of the diene, and easy product purification. The 56-π-electron benzo[*c*]thiophene diadduct (**BTCDA**) has a LUMO energy level of 0.09 to 0.18 eV higher than that of 58-π-electron fullerenes, and therefore, the **BTCDA**-based organic photovoltaic device exhibited a higher open-circuit voltage and power-conversion efficiency (PCE). When used with a binary-donor system, including visible-light-harvesting tetrabenzoporphyrin (**BP**) and near-IR-harvesting titanyl phthalocyanine (**TiOPc**), the device had a PCE that was 1.5–3 times higher (2.8%) than that for devices with **BP** or **TiOPc** alone because the binary-donor device can utilize light between $\lambda = 350$ and 950 nm.

Keywords: cycloaddition · electrochemistry · fullerenes · organic photovoltaics · phthalocyanines

Introduction

Fullerene derivatives have found widespread application in organic solar cells as excellent electron acceptors owing to their spherical shapes for three-dimensional charge transport and satisfactory phase separation.[1] Two recent topics in the area are the harvesting of near-IR (NIR) light by enhancing the light absorbance of electron donors[2,3] and the increase of the open-circuit voltage (V_{OC}) of the organic photovoltaic (OPV) devices through control of the energy level of the electron donors and acceptors.[4,5] In this context, 56-π-electron fullerene derivatives have attracted considerable interest.[6,7] A Diels–Alder diadduct of fullerene, an indene–C_{60} diadduct, is one such 56-π-electron compound that has been widely examined for OPV devices.[7a,b] Such devices tend to show higher V_{OC} and power conversion efficiency (PCE) than those using the standard material, [6,6]-phenyl-C_{61}-butyric acid methyl ester (**PCBM**).[1a,8] Despite its popularity, the indene diadduct suffers from some synthetic problems: the use of a large excess of a diene reagent, high reaction temperature, and difficulty of purification because of the similar physical properties of the multiadducts and regio- and stereoisomers that concomitantly form.

We report herein the synthesis and device performance of a benzo[*c*]thiophene–C_{60} diadduct (**BTCDA**) synthesized in 54% yield and purified easily by column chromatography. The introduction of a sulfur atom into the **BTCDA** molecule was expected to afford S–S noncovalent intermolecular bonding interactions, which can improve the charge-transporting properties of the electronic devices. A p–n junction OPV device using a binary-donor layer (tetrabenzoporphyrin (**BP**; absorbing up to 700 nm) and titanyl phthalocyanine (**TiOPc**; up to 950 nm)) had a PCE of 2.8%, which was about 1.5–3 times larger than that obtained by the use of **BP** or **TiOPc** alone, and 20% higher than the performance (2.4%) of the similar binary-donor device using 1,4-bis(dimethylphenylsilylmethyl)[60]fullerene (**SIMEF**) as an acceptor.[3b] The V_{OC} value increased by 0.09 V, which corresponded very well to the higher LUMO value for **BTCDA** than that for **SIMEF**. The short-circuit current density (J_{SC}) and fill factor (FF) also contributed to the increase in PCE. A comparison of device performances when using benzo[*c*]thiophene–C_{60} monoadduct **BTCMA**, diadduct **BTCDA**, and triadduct **BTCTA** as acceptors for devices with **BP** indicated that V_{OC} increased predictably from 0.46 to 0.66 to 0.79 V in accordance with the increase in the LUMO level from −3.79 to −3.65 to −3.52 eV, respectively.

Results and Discussion

Synthesis and Structural Characterization

Benzo[*c*]thiophene **4** was prepared from α,α-dibromo-*o*-xylene (**1**) in three steps.[9] The Diels–Alder reaction between benzo[*c*]thiophene (4 equiv) and C_{60} (1 equiv) in *o*-dichlorobenzene (ODCB) proceeded smoothly at 60°C to afford a mixture of **BTCMA**, **BTCDA**, and **BTCTA**, as shown in Scheme 1. After silica-gel column chromatography

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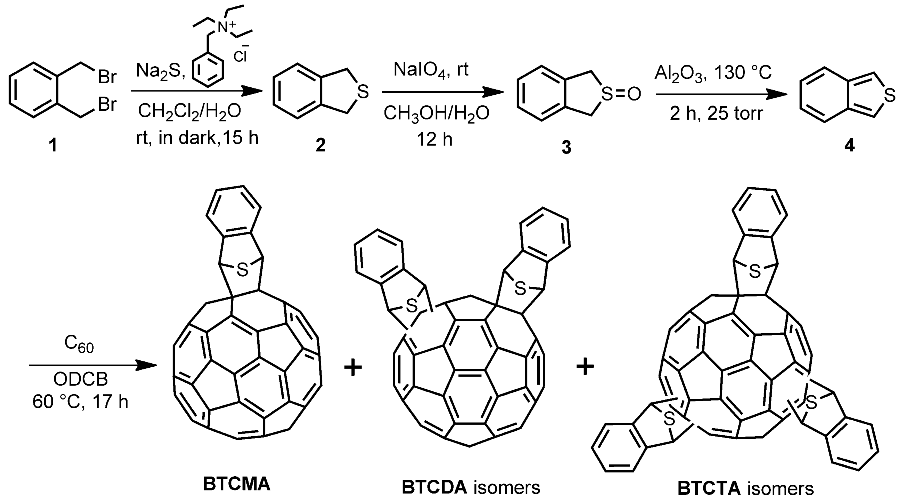

Scheme 1. Synthesis of benzo[*c*]thiophene–C_{60} monoadduct **BTCMA**, diadduct **BTCDA**, and triadduct **BTCTA**.

(eluent: CS_2/*n*-hexane = 1:1), **BTCMA**, **BTCDA**, and **BTCTA** were separated in 3.5, 54, and 27 % yields, respectively, without the use of preparative HPLC or repeated silica-gel column chromatography, which is necessary for the synthesis of the indene C_{60} adducts. The reaction took place at a lower reaction temperature and with reduced amounts of benzo[*c*]thiophene at the expense of a longer reaction time.

As expected, the reaction produced several isomers for **BTCDA** and **BTCTA**, as confirmed by ^{1}H NMR spectra (Figure 1). **BTCDA** and **BTCTA** were more soluble in toluene, chloroform, chlorobenzene, and THF than **BTCMA**, which is insoluble in common organic solvents except for ODCB and CS_2 and hence can be readily removed from the product mixture. The solubility of **BTCDA** was more than 1 wt % in toluene and chlorobenzene.

Abstract in Japanese:

[60]フラーレンにベンゾ[*c*]チオフェンを２つ付加させた二重付加体 **BTCDA** を合成した．**BTCDA** は，最近，有機薄膜太陽電池の電子受容体としてよく用いられるインデン-**C60**-ビスアダクト (**ICBA**) と比較して，合成において用いる試薬の当量が少なくて済む，反応温度が低い，生成物をシリカゲルカラムクロマトグラフィーで精製可能であるという特長をもつ．また，**BTCDA** は汎用の電子受容体 **PCBM**, **SIMEF** と比較して高い LUMO 準位をもつ．**BTCDA** を n 型材料として用いて **p-n** ヘテロ接合素子を作製して太陽電池の評価を行ったところ，p 型材料としてテトラベンゾポルフィリン (**BP**) を用いた素子より，チタニルフタロシアニン (**TiOPc**) を用いた素子のほうが高い変換効率を与えた．また，**TiOPc** を中間層に用いた二成分系ドナー素子 **BP/TiOPc/BTCDA** において，350 nm から 950 nm の近赤外領域までを利用して 2.8%の変換効率を与えた．この値は **SIMEF** を用いた同等のデバイス効率より 40%高く，高い LUMO レベルから予想されるように，0.1 V 高い Voc を与えた．

Optical and Electrochemical Properties

The UV/Vis absorption spectra of benzo[*c*]thiophene–C_{60} adducts are shown in Figure 2. **BTCMA** exhibited a characteristic sharp absorption peak at 431 nm,[10] and both **BTCDA** and **BTCTA** showed higher absorbance in the region of 400–500 nm than **BTCMA.** **BTCMA** and **BTCDA** absorb much stronger at about 700 nm than **BTCTA**.

The cyclic voltammogram for **BTCMA** showed three reversible reduction waves, whereas those for **BTCDA** and **BTCTA** showed two reversible reduction waves in a negative potential range from −0.5 to −3.0 eV versus ferrocene (Fc/Fc$^+$; Figure 3). Notably, the first half-wave reduction potential was much more negative from **BTCMA** to **BTCDA** to **BTCTA** because of the reduced π-conjugation length on the fullerene unit. From the first half-wave reduction potentials, we estimated LUMO levels of −3.79 eV for **BTCMA**, −3.65 eV for **BTCDA**, and

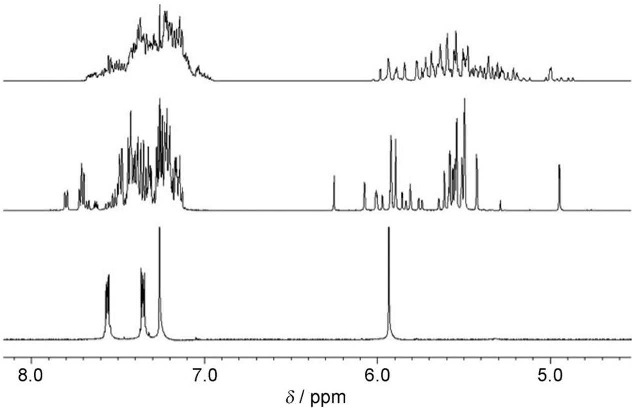

Figure 1. ^{1}H NMR spectra of benzo[*c*]thiophene–C_{60} adduct **BTCMA** in $CDCl_3/CS_2$ (1:1) (bottom), **BTCDA** (middle), and **BTCTA** (top) in $CDCl_3$.

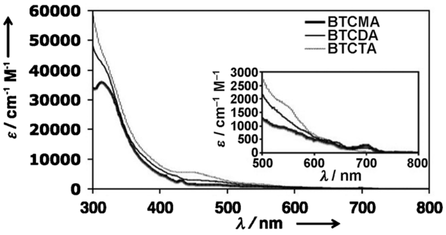

Figure 2. UV/Vis absorption spectra of benzo[*c*]thiophene–C_{60} adducts in dichloromethane at room temperature. Inset shows the absorption spectra in the region of 500–800 nm.

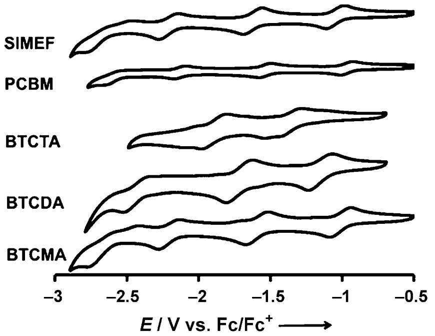

Figure 3. Reductive cyclic voltammograms of benzo[c]thiophene–C_{60} adducts compared with those for **PCBM** and **SIMEF**. Measurements were performed on a solution in THF containing $[Bu_4N][ClO_4]$ (0.1 M) as a supporting electrolyte at 25 °C with a scan rate of 0.1 $V\,s^{-1}$.

−3.52 eV for **BTCTA**. In contrast to **PCBM** and **SIMEF**, the LUMO level increased by 0.18 and 0.09 eV, respectively, for **BTCDA**, as shown in Table 1.

Table 1. Electrochemical properties of adducts relative to **PCBM** and **SIMEF**.

Compound	$E_{1/2}^{\text{red1}}$ [V]	$E_{1/2}^{\text{red2}}$ [V]	LUMO[a] [eV]
BTCMA	−1.01	−1.59	−3.79
BTCDA	−1.15	−1.72	−3.65
BTCTA	−1.28	−1.90	−3.52
SIMEF	−1.06	−1.63	−3.74
PCBM	−0.97	−1.54	−3.83

[a] Values from the vacuum level were estimated by using the following equation: LUMO level $= -(E_{1/2}^{\text{red1}}+4.80)$.[5a,11]

Table 2. Photovoltaic properties of **BP**-based p–n junction photovoltaic devices with different acceptors under AM 1.5 illumination at 100 $mW\,cm^{-2}$.

Active layer	V_{OC} [V]	J_{SC} [$mA\,cm^{-2}$]	FF	PCE [%]
BP/BTCMA	0.46	3.2	0.39	0.6
BP/BTCDA	0.66	3.3	0.47	1.0
BP/BTCTA	0.79	2.8	0.30	0.7
TiOPc/BTCDA	0.76	5.6	0.42	1.8
BP/TiOPc/BTCDA	0.70	8.2	0.48	2.8
BP/TiOPc/SIMEF[a]	0.61	7.7	0.50	2.4
BP/TiOPc/PCBM[a]	0.54	9.4	0.45	2.3

[a] OPV devices with **PCBM** or **SIMEF** as the acceptor were characterized in our previous work.[3b]

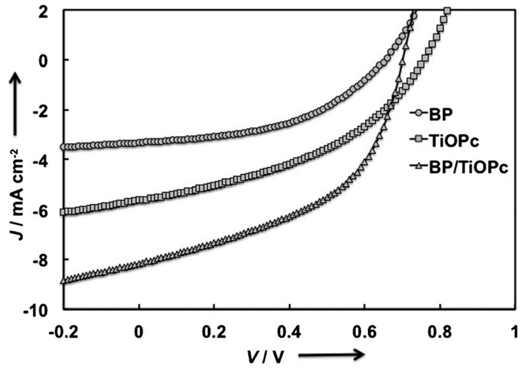

Figure 4. Current density–voltage (J–V) curves of OPV devices with **BP/BTCDA**, **TiOPc/BTCDA**, and **BP/TiOPc/BTCDA** as the active layers under AM 1.5 illumination at 100 $mW\,cm^{-2}$.

Photovoltaic Device Performance

First, to evaluate the fundamental OPV performance of **BTCDA** and congeners, we fabricated p–n OPV devices with **BP**[5c,12] as an electron donor and the new fullerene derivative as an electron acceptor (device configuration: indium tin oxide (ITO)/poly(3,4-ethylenedioxylenethiophene)–polystyrene sulfonic acid (PEDOT:PSS)/**BP**/fullerene/2,9-bis(naphthalen-2-yl)-4,7-diphenyl-1,10-phenanthroline (NBphen; 7 nm)/Al; see Figure 5b below); the results are summarized in the top three rows of Table 2. The device with **BTCDA** as the acceptor exhibited a PCE of 1.0% ($V_{OC}=0.66$ V; $J_{SC}=3.3$ $mA\,cm^{-2}$; FF = 0.47); this was much higher than that for the devices with **BTCMA** and **BTCTA** as the acceptor materials (Figure 4 and Table 2). Having a LUMO level of 0.14 eV lower than that of **BTCDA**, and hence, a lower offset of frontier molecular orbitals ($E^{D}_{HOMO}-E^{A}_{LUMO}$), BTCMA had a V_{OC} value as low as 0.46 V. **BTCTA** has a higher V_{OC} because of its higher LUMO level; it has lower J_{SC} and FF performance, probably because of the disordered molecular alignment in the active layer with the three randomly oriented organic addends.[7e,13]

To utilize NIR light, which accounts for over 40% of total solar energy, we chose **TiOPc** as a p-type layer for device structure optimization.[3,14] **TiOPc** is an interesting nonplanar dye with crystal-polymorph-dependent optoelectronic properties. The phase II form of **TiOPc** shows a particularly extensive and broad visible-to-NIR absorption and good p-type semiconductivity. There are several methods to induce the phase transition from I to II, including solvent vapor exposure,[15] thermal annealing,[16] organic molecular beam deposition,[17] supersonic molecular beam epitaxy,[18] and substrate induction.[19] We recently found that treatment of the **TiOPc** thin film of the device with toluene and chlorobenzene was a very efficient way to transform phase I into phase II in thin films.[3b] The HOMO of **BTCDA** in its film state was estimated to be −5.8 eV by using a photoemission yield spectroscopy (PYS)[20,21] measurement. Together with the reported HOMO and LUMO levels of **BP** and **TiOPc**,[3b,5a] the energy levels of the active layers when using **BP/TiOPc/BTCDA** can be drawn as shown in Figure 5a.

In an attempt to harvest both visible and NIR light, p–n heterojunction OPV devices with **TiOPc/BTCDA** as the active layer were fabricated and compared with the visible-light-absorbing **BP/BTCDA** device and the NIR-absorbing **TiOPc/BTCDA** device. As shown by the external quantum efficiency (EQE) curve in Figure 6, the **TiOPc/BTCDA** device (squares) uses short- and long-wavelength light extending to 900 nm, which is complementary to the **BP/BTCDA** device (circles), which uses light up to 700 nm. The overall efficiency of the **TiOPc/BTCDA** device therefore

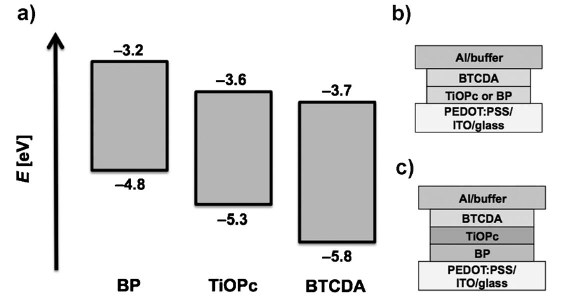

Figure 5. OPV device configurations. a) Energy diagram of **BP**, **TiOPc**, and **BTCDA**. b) The p–n heterojunction OPV device structure with **BP** or **TiOPc** as the single p-type layer. c) OPV device structure with a **TiOPc** interlayer between the **BP** and **BTCDA** layers.

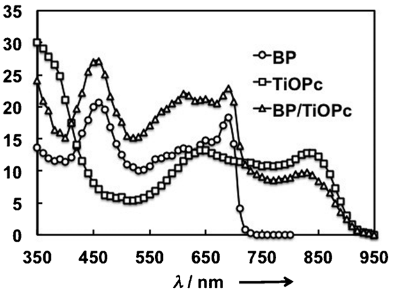

Figure 6. EQE curves of OPV devices with **BP/BTCDA**, **TiOPc/BTCDA**, and **BP/TiOPc/BTCDA** as the active layers under AM 1.5 illumination at 100 mW cm^{-2}.

has an increased PCE of 1.8% (V_{OC} = 0.76 V, J_{SC} = 5.6 mA cm–^{2}, FF = 0.42; see Figure 4 and Table 2).

To our great satisfaction, the performance of the binary-donor device **BP/TiOPc/BTCDA** was the sum of the **BP**- and **TiOPc**-based devices, utilizing the whole range of light between 350 and 950 nm, as shown by the EQE curve in Figure 6. As a consequence, this device showed a PCE value of 2.8% (V_{OC} = 0.70 V; J_{SC} = 8.2 mA cm^{-2}; FF = 0.48; see Figure 4 and Table 2), which was much higher than that of devices with a single-donor layer (shown in the top four rows of Table 2). The **BP/TiOPc/BTCDA** device had a higher PCE than the same binary-donor device with **SIMEF** or **PCBM** mainly because of the higher V_{OC} value, which in turn originated from the higher LUMO level of **BTCDA** than those of the **SIMEF** and **PCBM** acceptors.

Conclusion

New benzo[*c*]thiophene–C_{60} adducts were synthesized through [4+2] Diels–Alder cycloaddition reactions. By using a combination of **BP** and **TiOPc** as p-type layers and **BTCDA** as an n-type layer, the p–n junction OPV performed much better (PCE = 2.8%) than devices with a donor alone (PCE = 1.0 to 1.8%). A large V_{OC} value and broad absorption covering near-UV to NIR light contributed to the improved efficiency.

Experimental Section

General

All reactions with air- or moisture-sensitive compounds were carried out by using standard Schlenk techniques or a glovebox under argon or nitrogen atmospheres. Flash silica-gel column chromatography was performed on silica gel 60N (Kanto Chemical, spherical and neutral, 140–325 mesh). NMR spectra were measured with a JEOL ECA-500 (500 MHz) spectrometer. Spectra are reported in parts per million from internal tetramethylsilane (δ = 0.00 ppm) for ^{1}H NMR spectroscopy, from residual solvent (e.g., δ = 77.00 ppm for chloroform) for ^{13}C NMR spectroscopy. Cyclic voltammetry (CV) was performed by using a HOKUTO DENKO HZ-5000 voltammetric analyzer. All measurements were carried out in a one-compartment cell under argon, equipped with a glassy-carbon working electrode, a platinum wire counter electrode, and an Ag/Ag^{+} reference electrode. Measurements were performed in a solution of THF containing tetrabutylammonium perchlorate (0.1 M) as a supporting electrolyte at 25 °C with a scan rate of 0.1 V s^{-1}. All potentials were corrected against Fc/Fc^{+}. UV/Vis absorption was measured on a Jasco V-570 spectrometer. PYS was measured by using a PCR-101 instrument (Sumitomo Heavy Industries Advanced Machinery).

Materials

Unless otherwise noted, all materials were purchased from Tokyo Kasei, Aldrich, and other commercial suppliers, and used after appropriate purification before use. Anhydrous dichlorobenzene was purchased from WAKO Pure Chemical and purified by a solvent purification system (GlassContour)[22] equipped with columns of activated alumina and supported copper catalyst (Q-5) prior to use.

*Synthesis of Benzo[c]thiophene **4***

1,3-Dihydrobenzothiophene (**2**) was prepared according to a literature method:[9c,d] A mixture of α,α′-dibromo-*o*-xylene (**1**; 3.0 g, 11.4 mmol), sodium sulfide (7.5 g, 31.2 mmol), and benzyltriethylammonium chloride (36 mg, 0.158 mmol) in CH_2Cl_2/H_2O (1:1, 10 mL) was stirred in the dark at room temperature for 15 h. The organic layer was separated, washed several times with water, dried with sodium sulfate, concentrated, and distilled at 80 °C under 0.8 torr pressure to give **2** as a colorless oil (960 mg, 62%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.27 (s, 4H; CH_2S), 7.20–7.24 ppm (m, 4H; Ar–H). ^{1}H NMR data corresponded well with that reported in the literature.[9b,c]

1,3-Dihydrobenzo[*c*]thiophene-2-oxide (**3**) was prepared according to a literature method:[9a,b] Compound **2** (817 mg, 6.00 mmol) was added dropwise to a 50% aqueous stirred solution (30 mL) of sodium periodate (1.28 g, 6.00 mmol) in methanol. After being stirred for 12 h at room temperature, the reaction mixture was filtered to remove inorganic salts, concentrated, and separated by silica-gel column chromatography with ethyl acetate to afford **3** as a white solid (890 mg, 97%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.15 (d, J = 16 Hz, 2H; -CHSO), 4.30 (d, J = 16.1 Hz, 2H; -CHSO), 7.32–7.37 ppm (m, 4H; Ar–H). ^{1}H NMR data corresponded well with that reported in the literature.[9b]

Benzo[*c*]thiophene **4** was prepared according to a literature method:[9a,b] A mixture of **3** (800 mg, 5.26 mmol) and grade I neutral alumina (2.0 g) was heated for 2 h under 25 torr pressure at 130 °C in a sublimer to give **4** as a white solid (607 mg, 86%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.04 (dd, J = 2.9, 6.9 Hz, 2H; 5-,6-H), 7.60 (dd, J = 2.9, 6.9 Hz, 2H; 4-,7-H), 7.65 ppm (s, 2H; 1-,3-H). ^{1}H NMR data corresponded well with that reported in the literature.9b

Synthesis of Benzo[c]thiophene–C_{60} Adducts

The synthetic route is shown in Scheme 1. Benzo[*c*]thiophene (537 mg, 4.00 mmol) and C_{60} (721 mg, 1.00 mmol) were dissolved in ODCB (50 mL) and heated to 60 °C for 17 h. The reaction solution was diluted with methanol (300 mL) to give a brown precipitate. After filtration, the solid was purified by silica-gel column chromatography (eluent: CS_2/hexane = 1:1) to afford **BTCMA** (30 mg, 3.5%), **BTCDA** (530 mg, 54%), and **BTCTA** (300 mg, 27%).

BTCMA: ^{1}H NMR (500 MHz, $CDCl_3/CS_2=1:1$): $\delta=5.94$ (s, 2H), 7.35–7.37 (m, 2H), 7.55–7.57 ppm (m, 2H); ^{13}C NMR (125 MHz, CS_2): $\delta=$ 66.7, 77.7, 122.1, 127.0, 137.5, 138.8, 139.2, 139.7, 141.2, 141.7, 141.9, 142.3, 142.3, 144.0, 144.3, 144.7, 145.0, 145.1, 145.3, 145.7, 145.8, 146.0, 146.1, 146.9, 153.3, 155.0; elemental analysis calcd (%) for $C_{68}H_6S$: C 95.54, H 0.71, S 3.75; found: C 95.62, H 0.89.

BTCDA: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=4.95$–6.25 (m, 4H), 7.12–7.79 ppm (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2=1:4$): $\delta=66.7$, 66.8, 67.0, 67.3, 67.4, 67.5, 67.6, 67.9, 68.0, 68.5, 75.9, 76.4, 76.5, 76.6, 76.7, 76.8, 77.0, 121.7, 121.8, 121.9, 122.0, 122.1, 122.2, 122.3, 126.5, 126.6, 126.7, 126.8, 126.9, 127.0, 127.1, 132.4, 133.5, 133.8, 135.3, 135.8, 135.9, 136.2, 136.5, 136.8, 136.9, 137.6, 137.8, 138.1, 138.2, 138.8, 139.1, 139.3, 139.6, 140.0, 140.5, 140.7, 141.2, 142.0, 142.5, 143.2, 143.6, 143.9, 144.2, 144.3, 144.4, 144.7, 145.0, 145.3, 145.4, 145.5, 145.7, 145.8, 145.9, 146.0, 146.1, 146.5, 147.1, 147.5, 147.6, 147.8, 148.0, 148.1, 148.8, 149.9, 150.3, 150.6, 150.7, 151.6, 151.8, 151.9, 152.1, 152.3, 152.4, 152.6, 152.9, 153.1, 153.3, 153.5, 153.6, 153.7, 153.8, 153.9, 154.3, 154.4, 154.5, 154.6, 155.3, 155.7, 155.8, 155.9, 156.1, 156.4, 157.2, 157.8, 157.9, 158.1, 158.2, 159.0, 159.1, 159.2, 159.5 ppm; elemental analysis calcd (%) for $C_{76}H_{12}S_2$: C 92.29, H 1.22; found: C 92.52, H 1.48.

BTCTA: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=4.95$–6.01 (m, 6H), 6.98–7.67 ppm (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2=1:4$): $\delta=65.8$, 65.9, 66.3, 66.5, 66.7, 66.8, 66.9, 67.0, 67.1, 67.5, 67.7, 67.9, 68.1, 68.3, 75.2, 75.5, 75.6, 75.8, 76.0, 76.1, 121.6, 121.7, 121.8, 121.9, 122.0, 122.1, 122.2, 122.3, 126.4, 126.5, 126.6, 126.7, 126.8, 126.9, 135.0, 136.3, 137.4, 137.5, 137.7, 138.8, 139.0, 140.0, 140.4, 140.5, 140.6, 140.7, 140.8, 140.9, 141.0, 141.1, 141.2, 141.3, 141.9, 142.0, 142.1, 142.2, 142.5, 143.5, 143.9, 144.3, 144.4, 145.1, 145.2, 145.3, 145.4, 145.5, 145.6, 145.7, 145.8, 145.9, 146.0, 146.1, 146.2, 146.3, 146.5, 148.1, 148.3, 148.6, 148.9, 151.0, 151.3, 151.9, 153.0, 154.1, 154.2, 154.4, 154.5, 154.7, 154.8, 154.9, 155.1, 155.2, 155.3, 155.5, 155.7, 156.1, 156.2, 156.3, 156.4, 156.5, 156.6, 156.8, 157.0, 157.8, 157.9, 158.1, 158.2, 158.4, 158.5, 159.8, 159.9, 160.0, 160.1, 160.9, 161.1, 161.3, 161.7, 161.9, 162.0, 162.2 ppm; elemental analysis calcd (%) for $C_{84}H_{18}S_3$: C 89.82, H 1.62; found: C 90.05, H 1.89.

Device Fabrication and Characterization

The p–n heterojunction OPV devices with **BP** as the p layer and benzo[*c*]thiophene–C_{60} adducts as the n layer were fabricated by means of the following procedure. A 145 nm thick, patterned indium tin oxide (ITO) glass with a sheet resistance of 8 Ω/square was used as a substrate. A conducting PEDOT:PSS (Clevios AI4083) layer was formed on the glass/ITO substrate to obtain a thin film that was 30 nm thick. A solution of 1,4:8,11:15,18:22,25-tetraethano-29H,31H-tetrabenzo-[*b,g,L,q*]porphyrin (CP) in a chloroform/chlorobenzene mixture (1:2, w/w) as a **BP** precursor was coated on the glass/ITO/PEDOT:PSS film to form a CP thin film, which was thermally converted at 180 °C for 20 min to obtain a **BP** layer that was 25 nm thick. We fabricated each electron-accepting benzo[*c*]thiophene–C_{60} adduct, **BTCMA** (0.5 wt% in ODCB), **BTCDA** (0.5 wt% in toluene), and **BTCTA** (1.0 wt% in toluene), in solution by spin-coating with thickness of about 30 nm. NBphen (7 nm) was deposited in vacuum (3×10^{-4} Pa) on top of active layers as an exciton blocking layer, followed by the deposition of an aluminum electrode (80 nm) in vacuum and thermal annealing at 80 °C.

The p–n heterojunction OPV devices with **TiOPc** as the p layer and benzo[*c*]thiophene–C_{60} adducts as the n layer were fabricated by means of the following procedure: The ITO and PEDOT:PSS layers were fabricated as described for the previous procedure. Then a **TiOPc** layer that was 20 nm thick was formed by vacuum deposition at a rate of about 1 Å s^{-1}. Phase I-to-II transition of **TiOPc** accelerated by exposure to chlorobenzene extended the wavelength to the NIR region. This made it possible to create electron-acceptor exposure of the deposited **TiOPc** film by spin-coating in solution. Consequently, the phase transition of **TiOPc** concurrently occurred during the fabrication of the acceptor layer. We fabricated the device with **BTCDA** (0.5 wt% in chlorobenzene) by spin-coating to give a thickness of about 25 nm. Finally, the NBphen layer and aluminum electrode were deposited as described for the previous procedure.

The two-donor (**BP/TiOPc**)-based heterojunction OPV devices were fabricated by use of solvent-processed BP and vacuum-deposed **TiOPc**. The ITO, PEDOT:PSS, **BP**, and **TiOPc** layers were fabricated as described above. We fabricated the device with diadduct **BTCDA** (0.5 wt% in chlorobenzene) by spin-coating to give a thickness of about 25 nm. NBphen (7 nm) was deposited in vacuum (3×10^{-4} Pa) on top of active layers as an exciton blocking layer, followed by the deposition of an aluminum electrode (Al, 80 nm) in vacuum, and thermal annealing at 80 °C.

The thickness of spin-coated layers was determined by using a Dektak 6M stylus profiler. All devices were encapsulated in a glove box under a nitrogen atmosphere. The photocurrent of the fabricated OPV devices was investigated with a sweeping voltage by using a Keithley 2400 source measurement unit controlled by a computer under simulated solar light using an AM1.5G light source with 100 mW cm^{-2} intensity. The incident light intensity was calibrated to one sun (100 mW cm^{-2}) with a standard Si photodiode (BS-520, Bunkoukeiki, Japan). The current density versus voltage (*J–V*) characteristics were measured for an area of 0.04 cm^2. EQE was measured under constant power generated by monochromatized photons using a xenon or halogen lamp.

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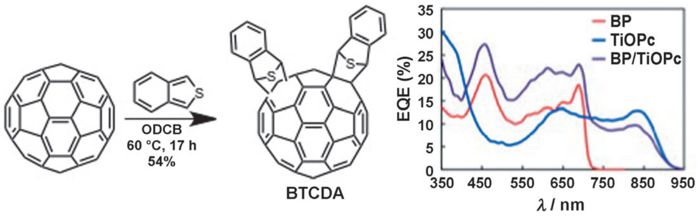

Two donors are better than one: A p–n junction photovoltaic device with benzo[*c*]thiophene–C_{60} diadduct (**BTCDA**) exhibited an improved power conversion efficiency of 2.8 % and was capable of harvesting visible to near-IR light through the insertion of titanyl phthalocyanine (**TiOPc**) between the tetrabenzoporphyrin (**BP**) and **BTCDA** layers (see scheme; ODCB = *o*-dichlorobenzene).

Organic Photovoltaics

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Benzo[*c*]thiophene–C_{60} Diadduct: An Electron Acceptor for p–n Junction Organic Solar Cells Harvesting Visible to Near-IR Light