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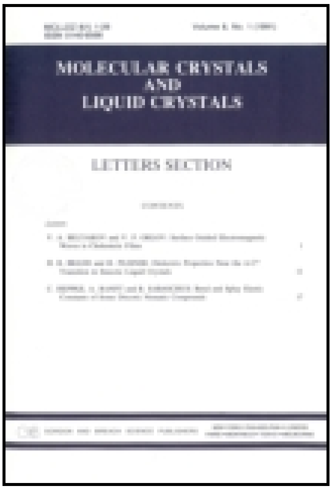
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Syntheses and Photovoltaic Properties of Octyl Cyanoacetate Terminated Small Molecules Based on Benzo[1,2-b:4,5-b′]dithiophene for OPVs

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Syntheses and Photovoltaic Properties of Octyl Cyanoacetate Terminated Small Molecules Based on Benzo[1,2-b:4,5-b']dithiophene for OPVs

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There have been tremendous efforts to synthesize photoactive materials that are consisted of both donor and acceptor components together to increase the power conversion efficiency (PCE) of organic photovoltaic cells (OPVs). In order to improve the performance of the OPVs, in this study, we proposed new A-D-A (Acceptor-Donor-Acceptor) type small molecular donors based on the donor unit of benzo[1,2-b:4.5-b']dithiophene (BDT) with an acceptor unit of alkyl cyanoacetate. We characterized prepared photoactive materials using ^1H NMR spectroscopy, DSC, CV (cyclic voltammetry), and UV/Vis spectroscopy. We also investigated the relationship between PCEs of OPVs and the active materials with variation of substituted methyl groups. The OPVs based on synthesized photoactive materials with different methyl substitutions showed different PCEs. Our results indicate that synthesized small molecular donor materials are promising donor materials for performance OPVs

Keywords Organic photovoltaic cells; small molecular donor; octyl cyanoacetate; benzo[1,2-b:4,5-b′]dithiophene

1. Introduction

Solution processed organic photovoltaics (OPVs) are attracting tremendous interest as sustainable clean energy source due to its low-cost possibility, fabrication of large-area device, flexibility, and light weight[1–4]. Currently, power conversion efficiencies (PCEs) of OPV have obtained nearly 8% by using low-band gap polymer donors in bulk heterojunction (BHJ) architecture[5–9]. However, when it comes to preparation of OPV using polymer materials, polymer for OPVs cannot be easily synthesized, and its poor reproducibility is another main issue. On the contrary, small molecules have various advantages such as

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simple synthesis, easier purification, and exact molecular structure. Recently, there has been increasing research on the use of small molecule materials for OPV to obtain good performance, instead of using polymer materials. Recently, PCE of 8.12% has been achieved for DR3TBDTT (Rhodamine terminated molecule) based organic OPVs with $PC_{71}BM$ as the acceptor[10–12]. The better PCEs were achieved by improving the short-circuit current density (Jsc) without sacrificing the high open-circuit voltage (Voc) and fill factor through the strategy of incorporating the advantages of both conventional small molecules and polymers for OPVs.

In this work, we designed a series of planar small molecules with electron-donating group (donor:D) and electron-withdrawing group (acceptor:A), which is consist of benzodithiophene (BDT) core,[1]. bithienyl bridge, and octyl cyanoacetate terminals. Also, we studied on the photophysical/electrochemical properties and photovoltaic performance with variation of methyl substituent position on the bithienyl bridge.

2. Experiment

Materials

(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl)bis(trimethylstannane) was purchased from Solarmer Materials. Pd_2dba_3, P(*o*-tol)$_3$, Na_2SO_4, dichloromethane, *n*-hexane, toluene, and chloroform were purchased from Aldrich. All chemicals were used without further purification. All reaction were carried out under nitrogen atmosphere, 5′-Bromo-[2,2′-bithiophene]-5-carbaldehyde **(Br-TTA)**, 5′-bromo-3,4-dimethyl-[2,2′-bithiophene]-5-carbaldehyde **(Br-TMTA)**, and 5′-bromo-3′,4′-dimethyl-[2,2′-bithiophene]-5-carbaldehyde **(Br-TTMA)** were synthesized according to the literature[13–15]. Fullerene (C60) was purchased from BuckyUSA. PCBM was synthesized according to the literature[16]. PEDOT-PSS (AI4083) was purchased from Heraeus.

Synthesis of New A-D-A Type Donor Materials

5′,5′′′-(4,8-Bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl)-bis-(([2,2′-bithiophene]-5-carbaldehyde)) ***BDT(TTA)$_2$*****.** A mixture of ***Br-TTA*** (1.5 g, 5.49 mmol) and (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl)bis(trimethylstannane) (BDT) (2.48 g, 2.74 mmol), tri(o-tolyl)phosphine (0.067 g, 0.22 mmol)), and tris(dibenzylideneacetone)dipalladium(0) (0.050 g, 0.055 mmol) in toluene (300 mL) was stirred under reflux at 100°C for 3 hr. The reaction mixture was extracted with dichloromethane, washed with water, dried over Na_2SO_4, and the solvent was removed in vacuo. Recrystallization of the crude product from dichloromethane and *n*-hexane to afford a orange neddle-like solid (yield = 42%). ^1H NMR (300 Mz, $CDCl_3$, δ, ppm) : 9.84 (s, 2H), 7.6 5 (d, 4H, J = 4.2 Hz), 7.31 (d, 2H, J = 3.6 Hz), 7.27 (s, 1H), 7.21 (m, 4H), 6.95 (d, 2H, J = 3.6 Hz), 2.91(d, 4H, J = 6.6 Hz), 1.75–1.71 (m, 2H), 1.50–1.37 (m, 16H), 1.01–0.92 (m, 12H).

5′,5′′′-(4,8-Bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl)bis-(3,4-dimethyl-[2,2′-bithiophene]-5-carbaldehyde) ***BDT(TMTA)$_2$*****.** A mixture of ***Br-TMTA*** (1.5 g, 4.98 mmol) and (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl)bis(trimethylstannane) (BDT) (2.25 g, 2.49 mmol) in toluene (270 mL) was added tri(o-tolyl)phosphine (0.061 g, 0.20 mmol), tris(dibenzylideneacetone)dipalladium (0) (0.046 g, 0.05 mol), and the solution was stirred for 3 hr at 100°C. The reaction mixture was extracted with dichloromethane, washed with water, dried over Na_2SO_4. After removal of solvent, the crude product was purified by silica gel column chromatography. Recrystallization of the crude product from dichloromethane and *n*-hexane to afford a scarlet solid (yield = 46%), ^{1}H NMR (300 Mz, $CDCl_3$, δ, ppm) : 9.89 (s, 2H), 7.35 (d, 2H, J = 3.3 Hz), 6.92 (d, 2H, J = 3.3 Hz), 2.88 (d, 4H, J = 6.6 Hz), 2.40 (s, 12H), 1.72–1.68 (m, 2H), 1.47–1.25 (m, 16H), 0.98–0.91 (m, 12H).

5′,5‴-(4,8-Bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl)bis-(3′,4′-dimethyl(2,2′-bithiophene)-5-carbaldehyde) ***BDT(TTMA)₂.*** A mixture of ***Br-TTMA*** (1.0 g, 3.32 mmol) and (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b*′]dithiophene-2,6-diyl)bis(trimethylstannane) (BDT) (1.5 g, 1.66 mmol), tri(*o*-tolyl)phosphine (0.04 g, 0.13 mmol) and tris(dibenzylideneacetone)dipalladium (0) (0.30 g, 0.03 mmol) in toluene was stirred under reflux at 100°C for 3 hr. Then the reaction mixture was poured into water, extracted with dichloromethane, and washed with water. The organic layer was dried over Na_2SO_4, and the solvent was removed *in vacuo*. The crude product was purified by silica gel column chromatography (yield = 39%).^{1}H NMR (300 Mz, $CDCl_3$, δ, ppm) : 10.02 (s, 2H), 7.67 (s, 2H), 7.32 (d, 2H, *J* = 3.3 Hz), 7.25–7.20 (m, 4H), 6.95 (d, 2H, *J* = 3.9 Hz), 2.91 (d, 4H, *J* = 6.9 Hz), 2.49 (s, 6H), 2.35 (s, 6H), 1.75–1.70 (m, 2H), 1.42–1.01 (m, 16H), 0.99–0.86 (m, 18H).

Dioctyl 3,3′-((4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl)bis(([2,2′-bithiophene]-5′,5-diyl)))(2E,2′E)-bis(2-cyanoacrylate) ***BDT(TTCAO)₂.*** A solution of ***BDT(TTA)₂*** (0.5 g, 0.53 mmol) in chloroform (120 mL) was stirred, and little drops of triethylamine. Then octyl cyanoacetate (1.3 ml, 6.38 mmol) [17] was added, and the solution was stirred for 48 hr at room temperature. The reaction mixture was extracted with dichloromethane, washed with water, dried over Na_2SO_4, and concentrated in vacumm. Recrystallization of the crude product from chloroform and *n*-hexane provided compound **BDT(TTCAO)₂** as claret color powder (yield = 81%). ^{1}H NMR (300 Mz, $CDCl_3$, δ, ppm) : 8.17 (s, 2H), 7.59 (t, 4H), 7.30 (d, 4H, J = 3.3 Hz), 7.24 (d, 2H, J = 3.9 Hz), 7.15 (d, 4H, J = 3.9 Hz), 6.96 (d, 2H, J = 3.3 Hz).

Dioctyl 3,3′-((4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl)bis(3′,4′-dimethyl-[2,2′-bithiophene]-5′,5-diyl))(2E,2′E)-bis(2-cyanoacrylate) ***BDT(TMTCAO)₂.*** A mixture of ***BDT(TMTA)₂*** (0.5 g, 0.49 mmol), little drops of triethylamine, and octyl cyanoacetate (1.24 ml, 5.9 mmol) in chloroform (120 mL) was stirred for 48 hr at room temperature. The reaction solution was extracted with dichloromethane, washed with water, dried over Na_2SO_4. Column chromatography and recrystallization of the crude product from dichloromethane and *n*-hexane to afford a claret color powder (yield = 40%). ^{1}H NMR (300 Mz, $CDCl_3$, δ, ppm) : 8.26 (s, 2H), 7.75 (m, 2H), 7.71 (s, 2H, J = 1.5 Hz), 7.36 (m, 2H), 7.26 (m, 2H), 6.93 (m, 2H), 4.29 (t, 4H), 2.89 (d, 4H, J = 6.6 Hz), 2.41 (s, 12H), 1.77–1.70 (m, 6H), 1.45–1.25 (m, 36H), 0.99–0.83 (m, 18H).

Dioctyl 3,3′-((4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl)bis(3,4-dimethyl-[2,2′-bithiophene]-5′,5-diyl))(2E,2′E)-bis(2-cyanoacrylate) ***BDT(TTMCAO)₂.*** A solution of ***BDT(TTMA)₂*** (0.50 g, 0.49 mmol) in 1,2-dichloroethane (100 mL) was stirred, and little drops of triethylamine. Then octyl cyanoacetate (1.24 ml) was added, and the solution was stirred under reflux for 4 days at 100°C. After removal of solvent, reaction mixture was extracted with dichloromethane, washed with water, dried over Na_2SO_4, and concentrated *in vacuo.* Recrystallization of the crude product from chloroform and *n*-hexane provided compound **BDT(TTMCAO)₂** as metal powder. ^{1}H NMR (300 Mz, $CDCl_3$, δ, ppm) : 8.33 (s, 2H), 7.55 (s, 2H), 7.30 (d, 2H, J = 3.3 Hz), 7.22 (d, 2H, J = 4.2 Hz), 7.16 (d, 2H, J = 3.9 Hz), 6.96 (d, 2H, J = 3.3 Hz), 4.25 (t, 4H), 2.93 (d, 4H, J = 6.6 Hz), 2.34 (s, 12H), 1.76–1.58 (m, 6H), 1.52–1.25 (m, 36H), 1.03–0.87 (m, 18H).

Measurements

^{1}H NMR spectra were recored using Bruker 300 spectrometer. The UV/Vis absorption spectrum of each compound was measured in solution state dissolved in chloroform by SHIMADZU UV-2550. Electrochemical properties of compounds were measured by Cyclic-voltametry (CV, WonATech BAS 100B). The CV was performed in a 0.1 M chloroform solution containing electrolyte of $Bu_4N(PF_6)$. A molded platinum electrode (0.3 mm diameter) was used as a working electrode, a Pt wire was used as a counter electrode, and a Ag/Ag+ was used as the reference electrode. And solution of reference electrode was used with 0.01 M silver nitrate ($AgNO_3$). CV was measured positive state at room temperature. Measured curve was shown for highest occupied molecular orbital (HOMO) energy level. And we predicted lowest unoccupied molecular orbital (LUMO) energy level using optical band-gap. Atomic force microscopy (AFM) images were taken with a Digital Instruments Nanoscope IV operating in tapping mode in air. BHJ film morphology of a mixture of one of donors and PCBM is measured AFM (Digital Instruments). The BHJ film formed on indium tin oxide (ITO) glass. First, poly(3,4-ethylenedioxythiophene)poly(styrenesulfonate) (PEDOT:PSS) (Clevious AI 4083) was spin-coated on ITO glass and annealed at 150°C for 18 min. Finally, a mixture of SM donor and PCBM on coated PEDOT:PSS spin coated by and fired at 90°C for 10 min.

Device Fabrication

The SM photovoltaic devices were formed in sandwiched structure of BHJ between a transparent anode and cathode. Transparent anode used ITO having 10 Ω/sq of sheet resistance. Patterned ITO glasses were prepared for sonication process with detergent in distilled water and boiling process with acetone and isopropanol. After this process, ITO glasses were cured with UV/Ozon during 20 min. On the prepared ITO glasses spin coated by PEDOT:PSS at 40 nm followed thermal treatment at 150°C for 18 min. Active layers were spin coated by mixture of SM donor and PCBM with chloroform followed thermal treatment at 90°C for 10 min. Finally, metal cathode was deposed by thermal evaporation consisted with LiF and Al approximately 0.5 Å and 120 nm thickness.

J-V Measurements

Photocurrent-voltage curve measurements of each device were performed at room temperature. The currentvoltage *I-V* curves of the devices were obtained using a Keithley 2400 Source Measure Unit under AM 1.5 simulated light (ORIEL 300 W Xenon lamp). The intensity of light (100 mA/cm^2) from the illumination source was confirmed by using a standard silicon photodiode (BS520, Bunkoh-Keiki).

3. Result and Discussion

Syntheses of BDT(TTCAO)$_2$, BDT(TMTCAO)$_2$, and BDT(TTMCAO)$_2$

The three diformyl derivatives, BDT(TTA)$_2$, BDT(TMTA)$_2$, and BDT(TTMA)$_2$ were synthesized through most popular Stille coupling reaction of (4,8-bis(5-(2-ethylhexyl) thiophen-2-yl)benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl)bis(trimethylstannane) with bromobithiophenyl aldehyde derivatives in moderate yield. And then, prepared **BDT(TTCAO)$_2$** and **BDT(TMTCAO)$_2$** can be easily prepared from the reaction of BDT(TTA)$_2$, BDT(TMTA)$_2$ with octyl cyanoacetate at room temperature in the yield of 81 and 40%, respectively. However, **BDT(TTMCAO)$_2$**, dimethyl thienyl aldehyde containing molecule, was not synthesized at the room temperature condition. It is possible that reactivity of formyl group with nucleophile was drastically decreased due to electron donating methyl group in *o*-position of thienyl aldehyde. Thus, we elevated the reaction temperature up to 90°C, and then **BDT(TTMCAO)$_2$** can be obtained successfully in moderate yield. The synthetic scheme of three small molecular donors is shown in Fig. 1.

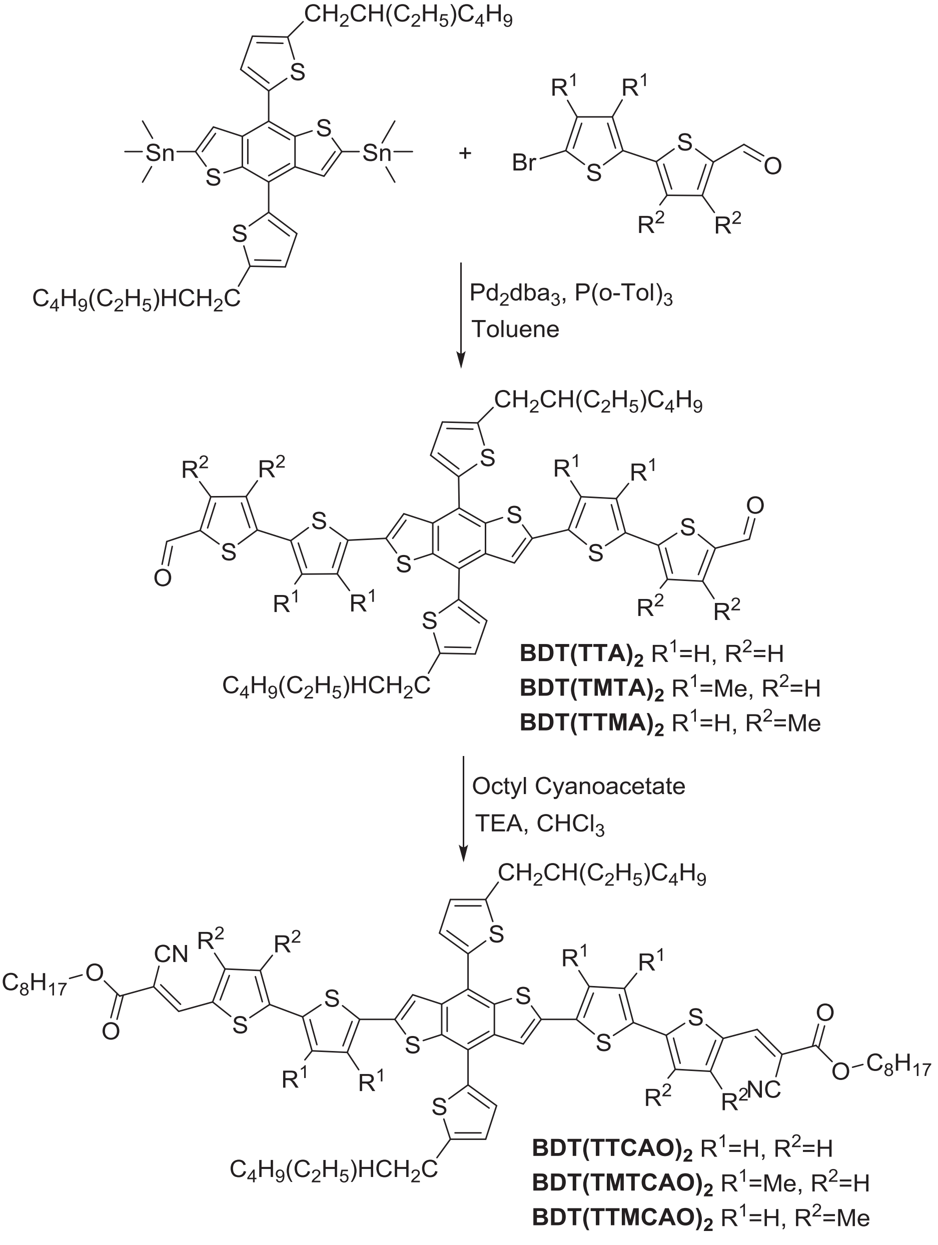

Figure 1. Syntheses of BDT(TTCAO)$_2$, BDT(TMTCAO)$_2$, and BDT(TTMCAO)$_2$.

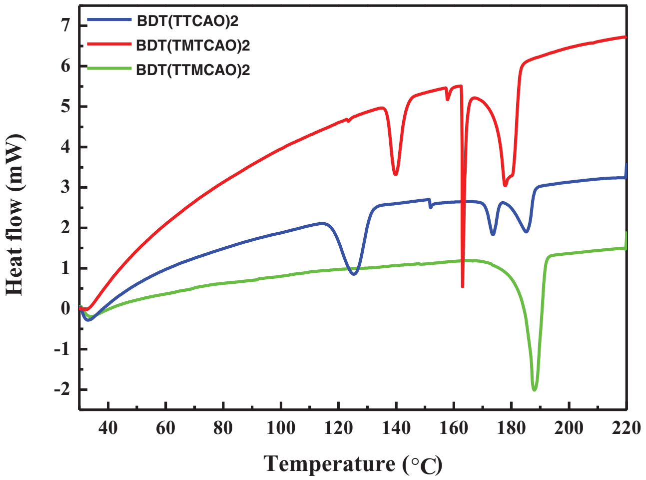

Figure 2. Thermal properties of **BDT(TTCAO)$_2$**, **BDT(TMTCAO)$_2$**, and **BDT(TTMCAO)$_2$**.

Thermal Property

The thermal properties of three small molecular donors were analyzed by differential scanning calorimetry (DSC). We observed exothermic or endothermic peaks in the temperature range of 30–250°C, and especially **BDT(TTCAO)$_2$** and **BDT(TMTCAO)$_2$** showed two endothermic melting peaks resulted from liquid crystal behavior. The **BDT(TTCAO)$_2$** and **BDT(TMTCAO)$_2$** show two distinctive endothermic peaks at 118/180°C and 137/163°C, respectively. On the other hand, **BDT(TTMCAO)$_2$** showed only one endothermic melting peak about 188°C as shown in Fig. 2. From this result, we can confirmed that our small molecular donors have quite different thermal property with variation of substituted methyl group's position. It is expected that how device performance can be changed by this different thermal property of each small molecular donors.

Photophysical and Electrochemical Properties

Figure 3 show the UV/Vis absorption spectra of the **BDT(TTCAO)$_2$**, **BDT(TMTCAO)$_2$**, **and BDT(TTMCAO)$_2$** in chloroform solution and films on a quartz plate. As a result of the optical analysis, UV/Vis spectra of the three materials were displayed in similar absorption characteristic from 350 nm to 600 nm. The solution of **BDT(TTCAO)$_2$**, shows an absorption peak at 513 nm and absorption edge at 591 nm with molar absorption coefficient of 1.35 ×

Table 1. Optical and electrochemical properties of three donor materials

Material	HOMO (eV)	LUMO (eV)	Abs. on set (nm)	Optical band gap (eV)
BT(TTCAO)$_2$	−5.30	−3.41	657	1.89
BDT(TMTCAO)$_2$	−5.25	−3.38	663	1.87
BDT(TTMCAO)$_2$	−5.23	−3.39	674	1.84

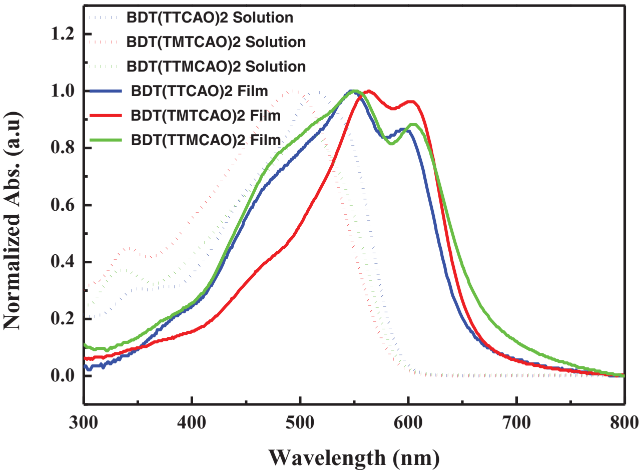

Figure 3. Absorption spectra of **BDT(TTCAO)$_2$**, **BDT(TMTCAO)$_2$**, and **BDT(TTMCAO)$_2$** in $CHCl_3$ solution and as a thin film.

10^5 $M^{-1}cm^{-1}$ The **BDT(TTCAO)$_2$**, film was observed absorption peak at 547 nm with shoulder peak at 596 nm and absorption edge at 657 nm, which is red-shifted by 34∼66 nm in comparison with in solution. The **BDT(TMTCAO)$_2$** has an absorption peak at 453 nm with an absorption coefficient of 5.6×10^4 M^{-1} cm^{-1}. Absorption edge was observed at 663nm, which is slightly red-shifted than **BDT(TTCAO)$_2$**. For **BDT(TTMCAO)$_2$**, absorption peak showed at 509 nm with an absorption coefficient of 8.6×10^4 M^{-1} cm^{-1} in solution. The solution absorption edge showed at 585 nm, film absorption edge of **BDT(TTMCAO)$_2$** is red-shifted by approximately 100 nm. Optical band-gaps were calculated from the edge of the absorption in the film spectra. As shown in Fig. 3, cyclic voltammetry was used to investigate electrochemical properties of three donor materials. The energy levels of

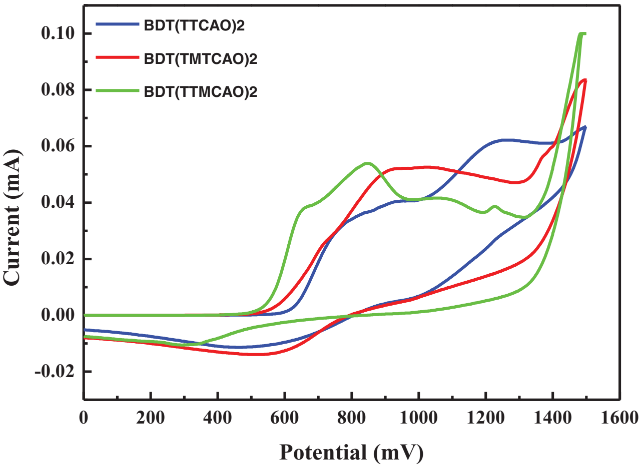

Figure 4. Cyclic voltammograms of **BDT(TTCAO)$_2$**, **BDT(TMTCAO)$_2$**, and **BDT(TTMCAO)$_2$** with scan rate of 50 mV.

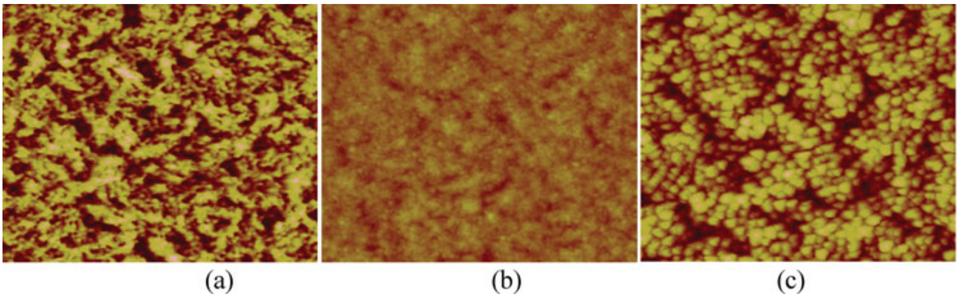

Figure 5. AFM image of active films spin coated on ITO/PEDOT:PSS substrates and foamed various donors. (a) **BDT(TTCAO)$_2$**. (b) **BDT(TMTCAO)$_2$**. And (c) **BDT(TTMCAO)$_2$**. The scan size for all images is 5 μm × 5 μm. The height scale for all images is 20 nm.

the HOMO and LUMO, which are – 5.30 and −3.41 eV for **BDT(TTCAO)$_2$**, −5.25 and −3.38 eV for **BDT(TMTCAO)$_2$**, and −5.23 eV and −3.39 eV for **BDT(TTMCAO)$_2$**, were estimated from the onset oxidation potential and optical band gap (Table 1). As a result, we could obtain that substitution of dimethyl group or free dimethyl group has little effect of energy level control.

Morphology of BHJ Film

Atomic force microscopy (AFM) was used to investigate morphology of active layer surface. As shown in Fig. 5, surface images display three distinct feature types. The *rms* (root mean square) roughness of film is 5.68 nm, 1.22 nm and 4.52 nm for **BDT(TTCAO)$_2$**/PCBM, **BDT(TMTCAO)$_2$**/PCBM and **BDT(TTMCAO)$_2$**/PCBM film, respectively (Table 2). For **BDT(TMTCAO)$_2$**, material have a best morphology by *rms* and Rmax than comparable films produced by two other materials. So we expect that **BDT(TMTCAO)$_2$** shows highest *PCE*s due to the smooth surface and good miscibility. For **BDT(TTCAO)$_2$** and **BDT(TTMCAO)$_2$**, a similar trend for surface roughness is obtained. In the case of **BDT(TMTCAO)$_2$**, roughness of surface is extreme and current flow is not significantly disturbed by connection between grains. On the other hand, blend film of **BDT(TTMCAO)$_2$**, in Fig. 5c shows an approximately increase in the surface roughness due to rising of grain boundary. As a result, **BDT(TTMCAO)$_2$** cannot make an efficient BHJ for OPVs due to too large domain formation about several hundreds nm as shown in Fig. 5c.

Table 2. Surface morphology of BHJ films with a mixture of SM donor and PCBM from AFM image

Material	Rq (nm)	Ra (nm)	rms (nm)	Rmax (nm)
BT(TTCAO)$_2$	6.00	4.71	5.68	51.0
BDT(TMTCAO)$_2$	1.31	1.03	1.22	11.9
BDT(TTMCAO)$_2$	4.91	3.87	4.52	39.4

Photovoltaic Properties

We explored the photovoltaic properties of three donor material based BHJ devices with structure of ITO/PEDOT:PSS/SM donor:PCBM/LiF/Al. Fig. 6 and Table 3 show the *J-V* curves of the OPVs and photovoltaic parameters. The OPV based on **BDT(TTCAO)$_2$**/PCBM displays a *PCE* of 1.31% along with a V_{oc} of 1.08 V, a *J*sc 2.57 mA/cm^2, and a *fill factor* of 47.26%. And OPV using **BDT(TMTCAO)$_2$** shows best performance about 3.66% of PCE with a V_{oc} of 1.08 V, a *J*sc 6.26 mA/cm^2, and a fill factor of 54.0%. As a result, we can conclude that **BDT(TMTCAO)$_2$** having dimethylthienyl beside BDT shows higher OPV performance compare to **BDT(TTCAO)$_2$** and **BDT(TTMCAO)$_2$**.

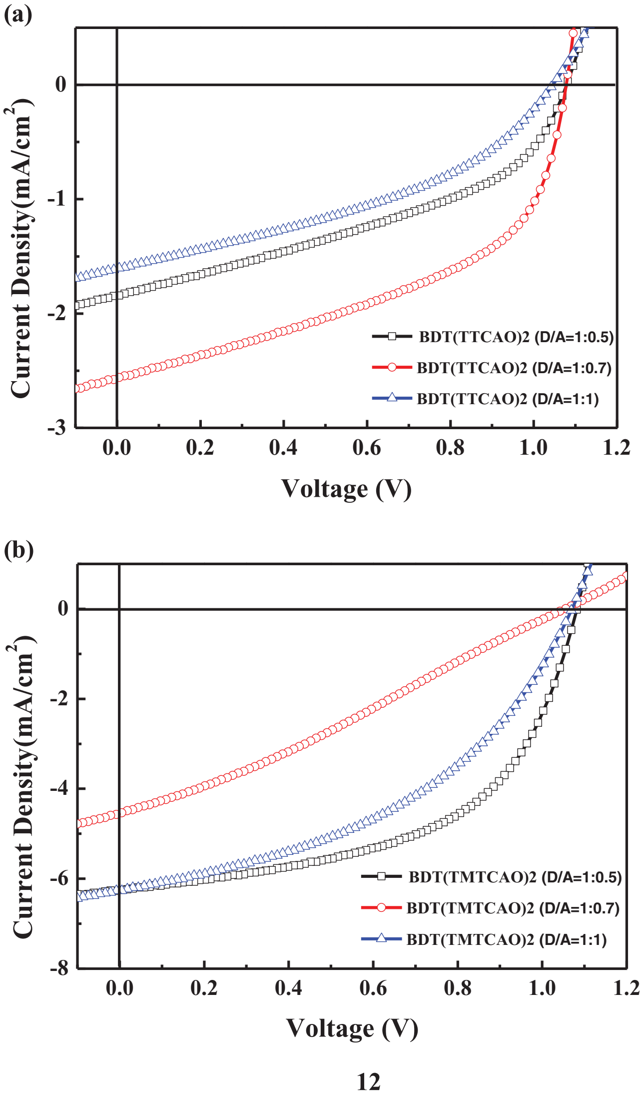

Figure 6. *J-V* characteristics of ITO/PEDOT:PSS/ SM donor : PCBM /LiF/Al. SM donor is (a) **BDT(TTCAO)$_2$** and (b) **BDT(TMTCAO)$_2$**.

Table 3. Photovoltaic parameter of OPVs based on **BDT(TTCAO)$_2$** or **BDT(TMTCAO)$_2$** as donor and PCBM as acceptor

Material	D/A Ratio	Voc (V)	*Jsc* (mA/Cm^2)	Fill Factor (%)	PCE (%)
BDT(TTCAO)$_2$	1:0.5	1.08	1.84	40.2	0.80
	1:0.7	1.08	2.57	47.3	1.31
	1:1	1.05	1.60	38.9	0.66
BDT(TMTCAO)$_2$	1:0.5	1.08	6.26	54.0	3.66
	1:0.7	1.05	4.54	28.4	1.36
	1:1	1.07	6.27	43.3	2.91

It is certain that this result is originated from surface morphology of active layer as mentioned in AFM analysis. Unfortunately, device using **BDT(TTMCAO)$_2$** as donor with PCBM acceptor shows extremely low photocurrent density below 0.1 mA/cm^2 due to large domain formation as shown in Fig. 5c.

Especially, the *Voc* values of all devices show very high almost 1.1 V. As you know, *Voc* of OPVs was determined by the energy gap between HOMO level of donor and LUMO level of acceptor. From CV measurement, we already have confirmed our synthesized SM donors have low HOMO energy level from −5.25 to −5.30 eV, and *Voc* can be improved to 1.08 V. If we can optimize coating condition of active layer using additives and so on, the surface morphology can be improved to more smooth and we can obtain improved *PCE* using our SM donors.

4. Conclusion

We synthesized three new planar small molecules, **BDT(TTCAO)$_2$, BDT(TMTCAO)$_2$**, and **BDT(TTMCAO)$_2$**, which are consist of benzodithiophene (BDT) core, bithienyl bridge, and cyanoacetate terminals. The absorption spectra of **BDT(TTCAO)$_2$** observed in similar wavelength region. 3.66% of PCEs can be obtained using a mixture of **BDT(TMTCAO)$_2$** and PCBM as a photoactive layer at the pristine condition with a Voc of 1.08 V, a Jsc of 6.26 mA/cm^2, and fill factor of 54.0%. The performance of OPVs based on the **BDT(TMTCAO)$_2$** showed a quadruple higher than **BDT(TTCAO)$_2$** without dimethyl substituent due to the better surface morphology. Our results indicate that synthesized A-D-A type small molecules are promising donor materials for OPVs with high Voc value almost 1.1 V.

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