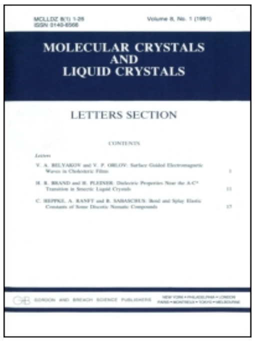

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Synthesis of TPD–thiophene-based small molecule donor for organic photovoltaic cells

Eunhee Lim

Department of Chemistry, Kyonggi University, Gyeonggi, Republic of Korea

ABSTRACT
The donor–acceptor–donor (D–A–D) type small molecule, **TPD2T**, was synthesized by the Stille coupling reaction and consisted of the electron-withdrawing thiene[3,4-c]pyrrole-4,6-dione (TPD) unit as an electron-accepting (A) core and electron-rich bithiophene units as electron-donating (D) groups. The absorption maximum of the **TPD2T** film was observed at 460 nm, and was broader and red-shifted compared to that in solution ($\lambda_{max} = 450$ nm). Organic photovoltaic cells fabricated with the conventional and inverted structures both exhibited similar power conversion efficiencies of 0.14–0.15%. Despite the low short-circuit current values, the **TPD2T** devices showed high open-circuit voltages of over 1.0 V owing to the relatively low-lying HOMO level of **TPD2T** (−5.4 eV).

KEYWORDS
small molecule; organic photovoltaic cells; OPV

1. Introduction

Organic photovoltaic cells (OPVs) have attracted significant interest and a high power conversion efficiency (PCE) of 10.6% has been achieved with OPVs based on blends of polymer donors and fullerene acceptors [1]. However, OPVs based on polymer donors suffer from a number of limitations such as poor synthetic reproducibility, difficult purification procedures, and broad molecular weight distributions [2]. Small molecular donors may act as counterparts for the polymers owing to their well-defined molecular structure and high purity [3]. Various donor–acceptor (D–A) structures have been used to develop low band gap small molecules for use in OPVs. Such molecules can efficiently extend the absorption band via intramolecular charge transfer in the D–A structure to obtain high PCE in OPVs [1].

The representative electron-accepting units are benzothiadiazole (BT) [4] and diketopyrrolopyrrole [5]. Recently, the easily-synthesized TPD unit has also been widely used as an electron-accepting unit. This unit exhibits a symmetric, rigidly fused, planar structure and strong electron-withdrawing properties induced by the imide moiety [6]. The imide moiety in the TPD unit can be easily modified with alkyl chains to improve the solubility of the materials. Moreover, the highest occupied molecular orbital (HOMO) level of the materials could be efficiently lowered by the presence of the electron-withdrawing imide moiety in the TPD units, while maintaining or reducing the band gap [7]. High PCEs of more than 8% have been achieved with devices based on the dithienogermole–TPD-based polymer in the inverted structure [8].

CONTACT Eunhee Lim ✉ ehlim@kyonggi.ac.kr

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Oligothiophenes have been widely studied and used for organic thin-film transistors due to their high hole mobilites [9]. Our group also previously reported a series of oligothiophenes for OPV application, [10] in which the optical and electrochemical properties of the oligothiophenes could be easily controlled by introducing the electron-accepting BT unit as a core into the conjugation system. The BT-containing small molecule, 4,7-bis(5′-hexyl-2,2′-bithiophene-5-yl)benzothiadiazole (**DH5TB**), showed higher OPV performance than all-thiophene-based analogues, α,α'-dihexylquinquethiophene (**DH5T**), owing to its low band gap and good film morphology. The HOMO levels of **DH5TB** and **DH5T** were −5.3 eV and −5.1 eV, respectively [10].

In this study, we synthesized another D–A–D linear-type oligothiophene, 1,3-di(bithophen-5′-yl)-5-(2-ethylhexyl)thieno[3,4]pyrrole-4,6-dione (**TPD2T**), composed of TPD and bithiophene units as electron-withdrawing and electron-donating units, respectively. OPV devices were fabricated in the conventional and inverted structures by using **TPD2T** as a donor material in combination with [6,6]-phenyl-C_{71} butyric acid methyl ester ($PC_{71}BM$) as an acceptor material. The optical, electrochemical, and photovoltaic properties of the small molecule were investigated and compared with the properties of other linear-type oligothiophenes, **DH5TB** and **DH5T**.

2. Experimental

2.1. Materials

Thiophene-3,4-dicarboxylic acid was purchased from Frontier Scientific. 2-(Tributy-lstannyl) thiophene, tris(dibenzyllidenacetone)dipalladium(0) ($Pd_2(dba)_3$), tri-*o*-toly-phosphine (P(*o*-tol)$_3$), 2-ethylhexylamine and *N*-bromosuccinimide (NBS) were purchased from Aldrich. 5-(2-Ethylhexyl)thieno[3,4-c]pyrrole-4,6-dione (**1**), 1,3-dibromo-5-(2-ethylhexyl) thieno[3,4-c]pyrrole-4,6-dione (**2**), 1,3-di(thien-2′-yl)-5-(2-ethylhexyl)thieno[3,4-c]pyrrole-4,6-dione (**3**), and 1,3-di(2′-bromothien-5′-yl)-5-(2-ethylhexyl)thieno[3,4]pyrrole-4,6-dione (**4**) were prepared according to the literature procedures [6].

2.2. Physical measurements

NMR spectra were recorded on a Bruker AVANCE III HD 400 spectrometer. UV-vis spectra were obtained using a Shimadzu UV/vis spectrometer. Elemental analyses were performed with a Flash EA 1112 series from Thermo Electron Corporation. The electrochemical properties of the small molecule were characterized by cyclic voltammetry (CV) with a BAS 100B electrochemical analyzer and calibrated using the ferrocenium/ferrocene redox value of −4.8 eV as the standard.

2.3.1. Synthesis of compound (1)

A solution of thiophene-3,4-dicarboxylic acid (3.00 g, 17.4 mmol) in acetic anhydride (62.8 mL) was stirred at 140°C overnight. After removal of the solvent, the resulting brown solid was dissolved in toluene (160 mL); 2-ethylhexylamine (3.37 g, 26.1 mmol) was then added and the mixture was refluxed for 24 h. After cooling the mixture and removing the solvent, the crude solid was dissolved in thionyl chloride (136 mL) and the mixture was refluxed for 4 h. The white solid product was obtained by column chromatography using dichloromethane:hexane (2:1). Yield: 3.40 g (73.6%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.80 (s, 2H), 3.60 (d, 2H), 1.37 (m, 9H), 0.90 (m, 6H).

2.3.2. Synthesis of compound (2)

Compound **1** (1.40 g, 5.28 mmol) was dissolved in sulfuric acid (7.8 mL) and trifluoroacetic acid (26 mL). While stirring, NBS (2.81 g, 15.8 mmol) was added and the reaction mixture was stirred at room temperature overnight. The mixture was poured into water and extracted with dichloromethane. The organic phases were combined, washed with brine, and dried with magnesium sulfate. The product was obtained by column chromatography using chloroform:hexane (2:1). Yield: 1.70 g (76.2%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.60 (d, 2H), 1.37 (m, 9H), 0.90 (m, 6H).

2.3.3. Synthesis of compound (3)

Compound **2** (0.59 g, 1.4 mmol), 2-(tributylstannyl)thiophene (1.2 g, 3.1 mmol), $Pd_2(dba)_3$ (0.088 g, 0.096 mmol), and P(*o*-tol)$_3$ (0.046 g, 0.15 mmol) were dissolved in toluene (23 mL). The mixture was heated overnight at 90°C. The reaction mixture was extracted with dichloromethane and water. The organic phases were combined, washed with brine, and dried with magnesium sulfate. The yellow solid product was obtained by recrystallization from methanol. Yield: 0.35 g (58.2%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.21 (d, 2H), 7.95 (d, 2H), 7.33 (t, 2H), 3.60 (d, 2H), 1.37 (m, 9H), 0.9 (m, 6H).

2.3.4. Synthesis of compound (4)

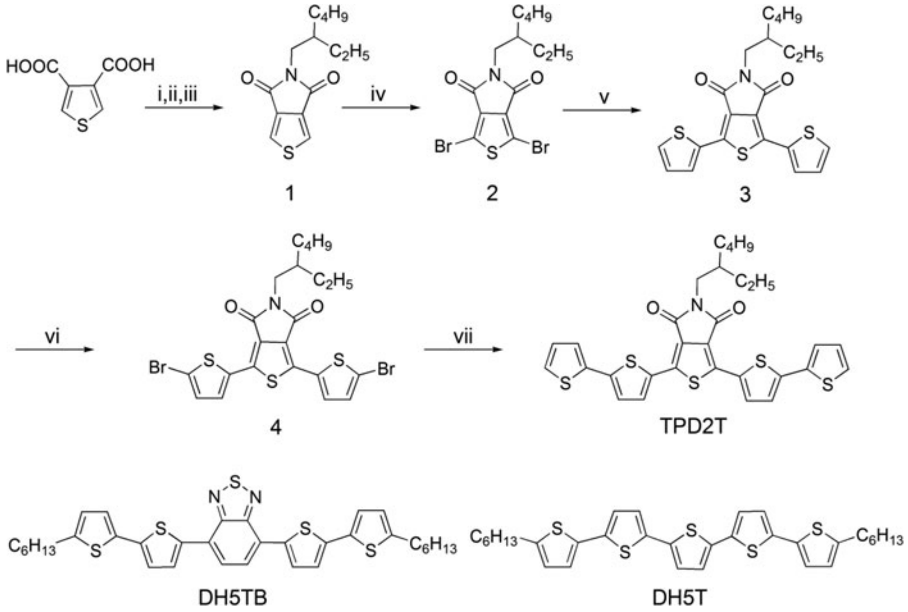
Compound **4** was synthesized in a manner similar to that used for compound **2** by using compound **3** (0.39 g, 0.91 mmol), chloroform (15 mL), acetic acid (15 mL), and NBS (0.36 g, 2.0 mmol). Yield: 0.47 g (88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.67 (d, 2H), 7.09 (d, 2H), 7.33 (t, 2H), 3.6 (d, 2H), 1.37 (m, 9H), 0.9 (m, 6H).

2.3.5. Synthesis of TPD2T

TPD2T was synthesized in a manner similar to that used for compound **3** by using compound **4** (0.30 g, 0.51 mmol), 2-(tributylstannyl)thiophene (0.76 g, 2.0 mmol), $Pd_2(dba)_3$ (0.027 g, 0.0291 mmol), P(*o*-tol)$_3$ (0.017 g, 0.056 mmol), and toluene (10 mL). The orange solid product was obtained by column chromatography using dichloromethane:hexane (1:1). Yield: 0.13 g (43%). Mp: 135°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.97 (d, 2H), 7.30 (d, 4H), 7.20 (d, 4H), 7.00 (t, 2H), 7.50 (t, 8H), 3.60 (d, 2H), 1.37 (m, 9H), 0.90 (m, 6H). Anal. calcd for $C_{30}H_{27}NO_2S_5$: C, 60.7; H, 4.58; N, 2.36; O, 5,39; S, 27.0, Found: C, 59.7; H, 4.86; N, 1.79; S, 27.9.

2.4. Fabrication of OPV devices

The OPVs were fabricated with the configuration ITO/PEDOT:PSS/**TPD2T**:$PC_{71}BM$ (2:1)/LiF/Al. A chloroform solution of small molecule and $PC_{71}BM$ was spin-coated at 3000 rpm and annealed for 10 min. A LiF/Al layer was then deposited on the active layer. The OPVs in inverted structure were also fabricated with the configuration ITO/ZnO/**TPD2T**:$PC_{71}BM$ (2:1)/MoO_3/Ag. A thin layer of sol-gel ZnO layer was spin-coated



Scheme 1. Synthetic schemes and chemical structures of the small molecules: (i) Ac_2O, 140°C, overnight; (ii) n-$C_8H_{16}NH_2$, toluene, reflux, 24 h; (iii) $SOCl_2$, reflux, 12 h; (iv) H_2SO_4, CF_3COOH, NBS, room temperature, overnight; (v) 2-(tributylstannyl)thiophene, $Pd_2(dba)_3$, P(o-tol)$_3$, toluene, 90°C; (vi) AcOH, NBS, chloroform, room temperature, overnight; (vii) 2-(tributylstannyl)thiophene, $Pd_2(dba)_3$, P(o-tol)$_3$, toluene, 90°C.

onto the ITO surface and then cured at 200°C for 60 min. After the active layer was spin-coated, MoO_3 and Ag layers were formed on the active layer through thermal evaporation. The current-density versus voltage (J–V) curves were measured using a Keithley 236 source measure unit in air under AM 1.5 G illumination, 100 mWcm^{-2}. The external quantum efficiency (EQE) was measured using a reflective microscope objective to focus the light output from a 100 W halogen lamp outfitted with a monochromator and an optical chopper.

3. Results and discussion

3.1. Synthesis and physical properties

The D–A–D type small molecule, **TPD2T**, was designed to have an electron-deficient TPD unit as an electron-accepting core (A) and electron-rich bithiophene groups as electron-donating end groups (D). Initially, the ethylhexyl-substituted TPD (**1**) was synthesized in three steps. After bromination by NBS, the thiophene-flanked TPD (**3**) was synthesized by the Stille coupling reaction. Compound **3** was brominated by NBS to obtain TPD–thiophene-based bromide (**4**). Finally, compound **4** was reacted with 2-(tributylstannyl)thiophene using the Stille coupling reaction. The synthesized donor molecules were successfully characterized by ^{1}H NMR and EA. The synthetic routes are shown in Scheme 1.

The UV-vis absorption spectra of the small molecules in chloroform solution and in the film state are shown in Figure 1. The UV-vis absorption spectrum of **TPD2T** in solution features a single peak with an absorption maximum at 450 nm. The peak in the absorption spectrum of the **TPD2T** film ($\lambda_{max} = 460$ nm) was broader and red-shifted compared to that in solution ($\Delta\lambda = 10$ nm) due to increased intermolecular π–π^* stacking interaction between the ordered molecules in the film [11]. In comparison, **DH5TB** showed two absorption bands.

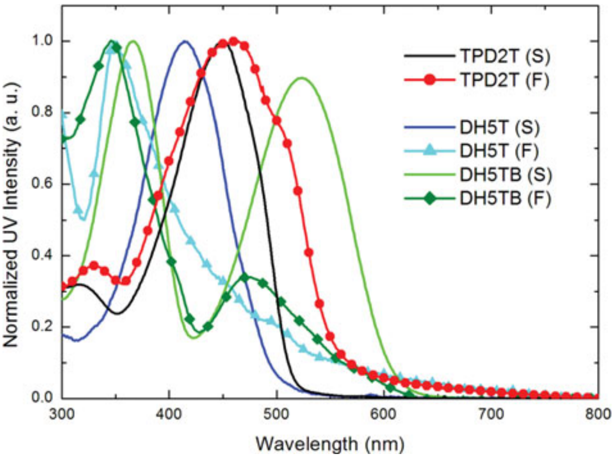


Figure 1. UV-vis absorption spectra of the small molecules in the solution (S) and film (F) states.

One absorption band was observed for **TPD2T**, similar to the spectrum of **DH5T**, indicative of relatively weaker intramolecular charge transfer of TPD compared to BT [5]. In addition, the optical band gap (E_g) of **TPD2T** was determined to be 2.2 eV from the absorption onset wavelength of the **TPD2T** film ($E_g = 1240/\lambda_{\text{onset}}$ (eV)).

The electrochemical properties of the small molecule were characterized by CV analysis (Figure 2). The onset of oxidation was observed at 1.0 V for **TPD2T** in the anodic scan. The HOMO level of **TPD2T** was −5.4 eV, according to the empirical relationship proposed by Leeuw et al. ($I_p(\text{HOMO}) = -(E_{\text{onset}} + 4.39)$ (eV), where E_{onset} is the onset potential of oxidation[12]. Notably, **TPD2T** has a relatively low-lying HOMO level compared to those of the previously reported benzothiadiazole (BT)-thiophene-based small molecule **DH5TB** (−5.3 eV) and alkyl-substituted quinquethiophene **DH5T** (−5.1 eV) [10]. TPD-based molecules commonly have low-lying HOMO levels because TPD has an imide group that efficiently lowers the HOMO level of the materials [7]. Consequently, **TPD2T** may exhibit a higher V_{OC} than **DH5TB** and **DH5T** in OPV application. From the optical E_g and HOMO level, the lowest unoccupied molecular orbital (LUMO) level of **TPD2T** was calculated to be −3.2 eV.

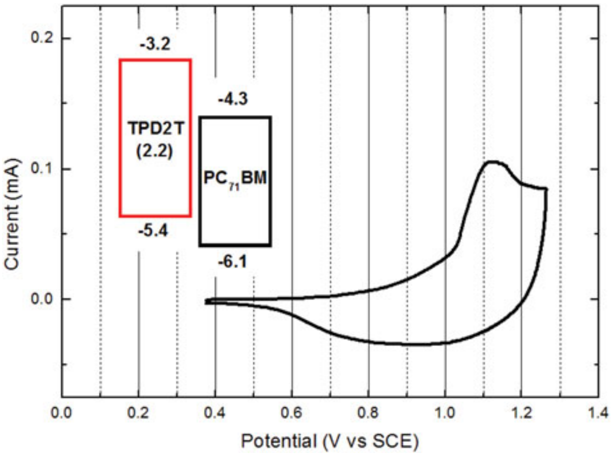


Figure 2. CV curve of **TPD2T** (inset shows HOMO and LUMO levels of **TPD2T** and $PC_{71}BM$).

Table 1. Photovoltaic properties of OPV devices[a].

Small molecules	T_a (°C)[e]	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
TPD2T[b]	80	0.96 (1.03)	0.67 (0.66)	22 (21)	0.14 (0.14)
TPD2T[c]	110	1.04 (0.93)	0.68 (0.64)	22 (23)	0.15 (0.14)
DH5TB[d]	w/o	0.55	4.75	34	0.89
DH5T[d]	w/o	0.51	4.25	37	0.80

[a] The values in parentheses were obtained from devices without annealing.
[b] ITO/PEDOT:PSS/small molecule:PC$_{71}$BM (2:1)/LiF/Al
[c] ITO/ZnO/small molecule:PC$_{71}$BM (2:1)/MoO$_X$/Ag
[d] Data from ref. [10]
[e] T_a: annealing temperature (w/o = without annealing)

3.2. Organic photovoltaic properties

Finally, OPV devices were fabricated with both conventional and inverted structures. The photovoltaic performances were 0.14–0.15% and thermal annealing did not cause any improvement in the device performance. The relatively low device performance of **TPD2T** is due to the low J_{SC} of 0.68 mA cm^{-2} and fill factor (FF) of 22%. In general, the low FF of solution-processed small molecule-based OPVs is attributed to their poor film quality and inferior charge transport to the electrodes [13]. The photovoltaic properties of the blend films are summarized in Table 1. The device fabricated with **TPD2T** showed a high V_{OC} of up to 1.04 V, which is higher than the values for other oligothiophenes having similar linear-type structures (0.55 V for **DH5TB** and 0.51 V for **DH5T**) [10]. The high V_{OC} is derived from the relatively low-lying HOMO level (−5.4 eV). In general, the HOMO levels are strongly dependent on the energy difference between the HOMO of the donor and the lowest unoccupied molecular orbital of the acceptor [14].

Figure 3 shows the EQE curve for the inverted structure device. The curve of the EQE response and the UV absorption of the **TPD2T** film are well matched, indicative of photocurrent generation by **TPD2T**. The maximum EQE response of 7.5% was observed at 460 nm, which is the absorption maximum of the **TPD2T** film. In this study, introduction of the electron-withdrawing TPD unit proved to be a good strategy for improving the V_{OC} of the OPV device due to the low HOMO level induced by the electron-withdrawing imide moiety

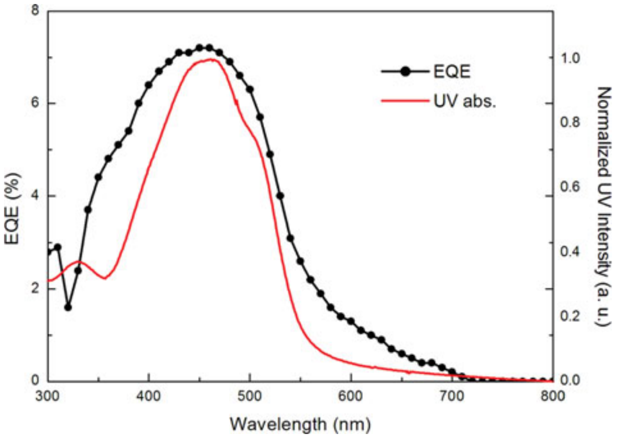


Figure 3. Comparison of EQE curve of the **TPD2T**:PC$_{71}$BM device with the UV-vis absorption spectrum of the **TPD2T** film.

in the TPD unit. Future studies may focus on modification of **TPD2T** by introducing other alkyl groups or changing the electron-rich end groups.

4. Conclusions

The D–A–D type small molecule **TPD2T** composed of electron-withdrawing TPD and electron-donating thiophene units was successfully synthesized. The OPV device based on **TPD2T** and $PC_{71}BM$ exhibited a higher V_{OC} of 1.04 V owing to the low-lying HOMO level than the previously reported linear-type oligothiophenes (**DH5TB** and **DH5T**).

Acknowledgments

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