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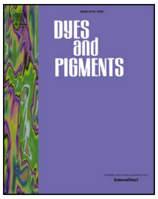

Bis(dithienyldiketopyrrolopyrrole) compounds with a diethynylbithienyl linkage for organic solar cells

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ABSTRACT

We present the synthesis of a bis(dithienyldiketopyrrolopyrrole) organic semiconductor **BT(DTDPPA)$_2$** comprising a 2,2'-(bithienyl-5,5′-diyl)diethynyl linkage and its doubly end-benzofuranated derivative **BT(BFu-DTDPPA)$_2$**. **BT(BFu-DTDPPA)$_2$** shows a redshifted absorption maximum at 645 nm in solution and tends to form *J*-aggregates as film yielding a well-defined shoulder with strong absorption at 705 nm. Thermal annealing produces no obvious effect on the absorption of **BT(BFu-DTDPPA)$_2$** below a temperature of 120 °C while significant *H*- to *J*-aggregation transition occurs to **BT(DTDPPA)$_2$**. The cyclovoltammetry experiments revealed that benzofuranation leads to a lower oxidation onset at ca. 0.78 V vs. Ag/AgCl. Both **BT(DTDPPA)$_2$** and **BT(BFu-DTDPPA)$_2$** exhibit a hole mobility of up to $10^{-3}\,cm^2\,V^{-1}\,s^{-1}$. However, blending with $PC_{61}BM$ causes a more severe deterioration of the hole mobility for **BT(DTDPPA)$_2$** as 2.71×10^{-5} vs $2.63 \times 10^{-4}\,cm^2\,V^{-1}\,s^{-1}$ for **BT(BFu-DTDPPA)$_2$**. The photovoltaic devices (ITO/PEDOT:PSS/**BT(BFu-DTDPPA)$_2$**:$PC_{61}BM$/Al) that consisted of the thermally annealed active layer provided a PCE of 4.6% ($V_{oc} \approx 0.80\,V$, $J_{sc} \approx 9.0\,mA\,cm^{-2}$ and $FF \approx 63\%$) involving no high-boiling-point solvent additive or solvent vapor annealing, in contrast with 1.45% for **BT(DTDPPA)$_2$**. The inferior performance of the latter is attributed to the unfavorable phase separation in the active layer.

1. Introduction

Aryl acetylenes have been of considerable interest for organic electronics, which offer several benefits [1]: i) The weak electron withdrawing nature due to the *sp*-hybridized carbon atoms may provide a deeper HOMO level; and ii) The cylinder-like *p*-electron density is more adaptable to conformational and steric constraints. Hence, aryl acetylenes may present a platform to construct high-mobility and air-stable organic semiconductors [2]. Moreover, green synthesis can be anticipated without involving toxic stannyl intermediates or even risky lithiation reagents [3,4].

In this context, a number of aryl acetylenic compounds have been investigated as electron donors for organic solar cells (OSCs) [5–10]. Through optimizing the morphology of the active layer, power conversion efficiencies (PCEs) of 7–12% have been obtained in single-junction/tandem solar cells utilizing thermal annealing, high-boiling-point solvent additive, or solvent vapor annealing (SVA). Recently we have reported a PCE of 7.1% by increasing the crystallinity of a solution-processed bis(dithienyldiketopyrrolopyrrole) −porphyrin conjugate with an acetylenic linkage in the inverted ternary solar cells, where no solvent additive or SVA was involved [10a]. It is worth noting that dithienyldiketopyrrolopyrrole (DT-DPP) remains an attractive electron-accepting building block for electron donors in OSCs because of its intrinsic characteristics, such as high planarity, synthetic availability and strong absorption in the visible region [11–13].

In this contribution, we present simple bis(dithienyldiketopyrrolopyrrole) compounds **BT(DTDPPA)$_2$** and **BT(BFu-DTDPPA)$_2$** with a diethynylbithienyl linkage for organic solar cells (Fig. 1). The double end-benzofuranation leads to the red-shift of the absorption both in solution and as film and provides a hole mobility value of $10^{-3}\,cm^2\,V^{-1}\,s^{-1}$ upon thermal annealing. Consequently we obtained an improved PCE of 4.6% with $V_{oc} = 0.81\,V$, $J_{sc} = 9.05\,mA\,cm^{-2}$ and $FF = 62.7\%$ without utilizing solvent additive or solvent vapor annealing.

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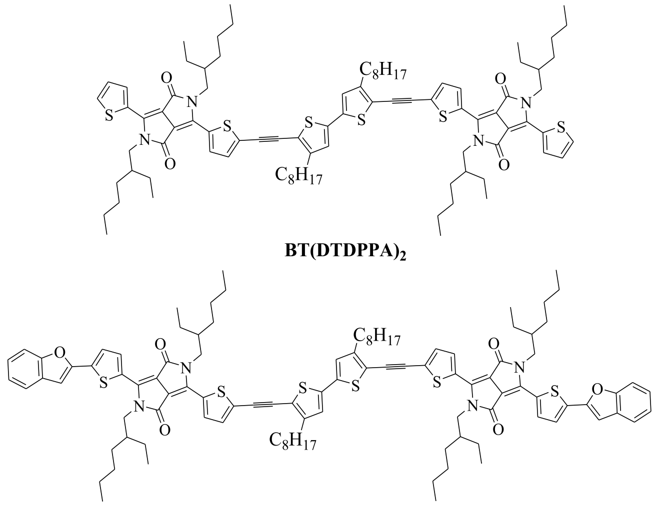

BT(DTDPPA)$_2$

BT(BFu-DTDPPA)$_2$

Fig. 1. Chemical structure of **BT(DTDPPA)$_2$** and **BT(BFu-DTDPPA)$_2$**.

2. Results and discussion

2.1. Synthesis

BT(DTDPPA)$_2$ and **BT(BFu-DTDPPA)$_2$** are facilely synthesized through Sonogashira reaction of 3-(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(thiophen-2-yl)-pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione **(1)** [14] and its benzofuranated derivative (**2**) [15] with 5,5′-bis(ethyn-2-yl)-4,4′-diotcyl-2,2′-bithiophene (**3**) [16], respectively (Fig. 2). No toxic stannyl intermediates or risky lithiation reactions are involved in the synthetic processes [3b].

The identity and purity of the new compounds are evidenced by TLC, ^{1}H NMR, mass spectroscopy and elemental analysis (See Fig. S1-3).

2.2. Optical and electrochemical properties

The solution and thin-film optical absorption spectra of **BT(DTDPPA)$_2$** and **BT(BFu-DTDPPA)$_2$** are presented in Fig. 3 and the data are summarized in Table 1.

In dilute solution, **BT(BFu-DTDPPA)$_2$**, which is functionalized with benzofuranyl endgroups, exhibits a red-shifted absorption peak at ca. 645 nm by 50 nm against **BT(DTDPPA)$_2$**. In solid states, **BT(BFu-DTDPPA)$_2$** shows an absorption maximum at ca. 625 nm with a well-formed shoulder at ca. 709 nm, while **BT(DTDPPA)$_2$** possesses a major absorption peak at 600 nm with a shoulder at ca. 642 nm. The optical bandgap of **BT(DTDPPA)$_2$** and **BT(BFu-DTDPPA)$_2$** were estimated to be 1.71 and 1.59 eV, respectively, based on the absorption onset of the as-cast films.

We show that thermal annealing **BT(BFu-DTDPPA)$_2$** at the temperature ranging from 50 to 120 °C appears to have no obvious effect on the optical absorption spectra, in contrast with **BT(DTDPPA)$_2$**. The latter seemed to undergo *H*- to *J*-aggregation transition with increasing temperature since an emerging peak at 678 nm becomes dominant, relative to the original shoulder at 642 nm, which is also accompanied by splitting of the absorption maximum at 600 nm into separated peaks at ca. 575 and 623 nm, respectively.

The electrochemical properties of the new compounds are characterized by cyclic voltammetry performed in CH_2Cl_2 in the presence of n-Bu_4NPF_6 (0.1 M) as supporting electrolyte. As shown in Fig. 4, **BT(DTDPPA)$_2$** and **BT(BFu-DTDPPA)$_2$** displayed a quasi-reversible oxidation with the onset at 0.78 and 0.88 V vs Ag/AgCl, respectively. Based on the electrochemical data, the HOMO level was estimated as −5.30 eV for **BT(DTDPPA)$_2$** and −5.20 eV for **BT(BFu-DTDPPA)$_2$** with reference to the energy level of ferrocene. Therefore, the LUMO levels for **BT(DTDPPA)$_2$** and **BT(BFu-DTDPPA)$_2$** were similar as ca. −3.6 eV, roughly derived from the corresponding HOMO level and absorption onset of their thin films.

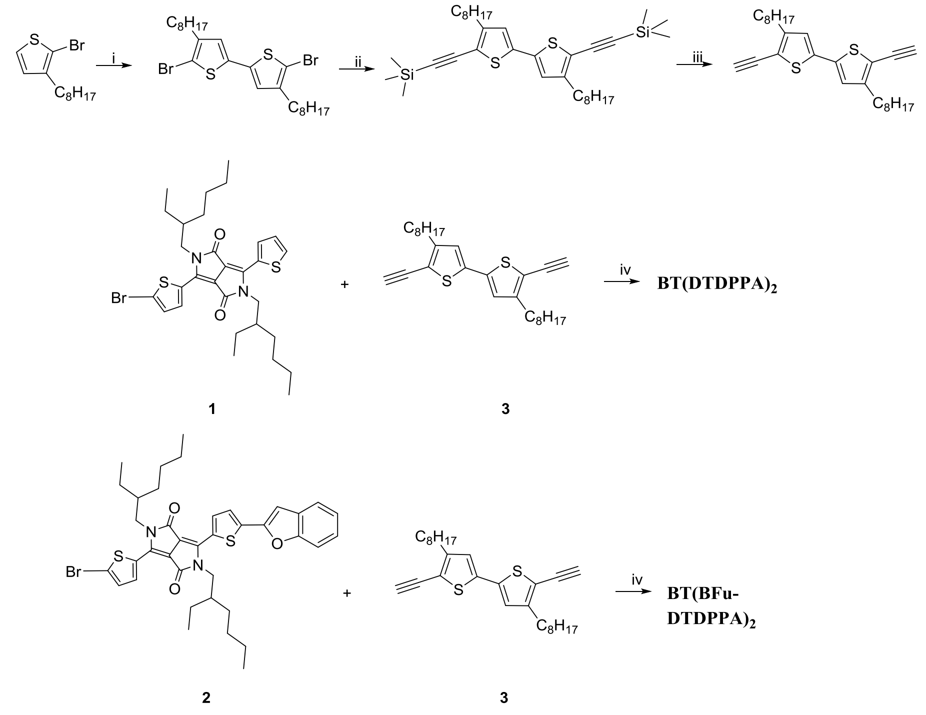

Fig. 2. Synthetic routes to **BT(DTDPPA)$_2$** and **BT(BFu-DTDPPA)$_2$**: i) $AgNO_3$, KF, $Pd(PPh_3)_4$, DMSO, 60 °C, overnight; ii) trimethylsilylacetylene, CuI, diisopropylamine, THF, Pd$(PPh_3)_2Cl_2$, 60 °C, overnight; iii) K_2CO_3, CH_3OH/THF, room temperature, 4 h; iv) CuI, $Pd(PPh_3)_4$, triethylamine, toluene, 80 °C.