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D-π-A-π-D type thiazolo[5,4-*d*]thiazole-core organic chromophore and graphene modified PEDOT:PSS buffer layer for efficient bulk heterojunction organic solar cells

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ABSTRACT

A new thiazolo[5,4-*d*]thiazole-core organic chromophore with furan spacer (TP-FTzF-TP) was synthesized and PEDOT:PSS buffer layer was modified by graphene (Gr) for the efficient solution-processed bulk-heterojunction (BHJ) small molecule organic solar cells (SMOSCs). The introduction of furan as spacer in the thiazolo[5,4-*d*]thiazole-core based organic chromophore tuned the absorption and the electrochemical properties. The synthesized TP-FTzF-TP chromophore exhibited good optical parameters and a suitable HOMO/LUMO values of −5.33 eV/−3.15 eV. The synthesized organic chromophore with triphenylamine as a strong electron-donor and furan spacer promoted the charge transfer and charge extraction in fabricated SMOSCs. The modification of PEDOT:PSS by Gr considerably increased the roughness of thin film. The power conversion efficiency (PCE) of ~3.63% was achieved by fabricated SMOSC device with ITO/Gr-PEDOT:PSS/TP-FTzF-TP:$PC_{60}BM$ (1:2, w/w)/Au architecture. It was found that the Gr-PEDOT:PSS as a buffer layer significantly enhanced PCE by two time factor as compared to the SMOSC device (PCE = ~2.13%) with pristine PEDOT:PSS layer.

1. Introduction

An emerging thin film photovoltaic especially, organic solar cell (OSCs), has received a great attention as renewable energy sources due to its light-weight, cost-effective synthesis, easy-processability, and better compatibility (Yang et al., 2016; Bin et al., 2016; Hu et al., 2015). Peculiarly, small organic molecules due to their versatile properties, well-defined structure, facile synthesis, definite molecular weight, and ease of purification are used as active materials for the applications in SMOSCs (Lin et al., 2012; Hains et al., 2010). In general, SMOSCs are comprised of small molecules/fullerene bulk heterojunction (BHJ) composite in which small molecules work as photoactive layer sandwiched between the anode and cathode (Yao et al., 2015; Yaacobi-Gross et al., 2015). In bulk-heterojunction (BHJ) solar cells, organic small molecules with donor-acceptor (D/A) components show an interpenetrating network that plays a crucial role for the fabrication of the devices (Lee et al., 2011; Sun et al., 2012; Huo et al., 2011). The performance of SMOSCs usually depends on the structural modifications, optical and redox properties, charge-carrier mobility, thermal stability, and the thin film morphology of the devices in solid states (Dimitrov et al., 2014; Burkhard et al., 2012). The electron acceptor molecule especially fullerene derivatives like $PC_{60}BM$ has majorly contributed for the charge-collection and charge transport at the D-A interface (Zhang et al., 2011; Yang et al., 2013).

Last few years, thiazolo[5,4-*d*]thiazole-core based organic molecules because of their rigid fused ring system and planar backbone with an extended π-conjugated electronic structure are widely explored for several optoelectronic applications such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), organic photovoltaics (OPVs) and sensors (Bevk et al., 2013; Reginato et al., 2016). Thiazolo[5,4-*d*]thiazole derivatives exhibit excellent oxidative stability and electron-deficient behavior due to the presence of the nitrogen atoms in the heterocyclic ring (Ie et al., 2015; Wang et al., 2014; Cheng et al., 2013). Additionally, thiazolo[5,4-*d*]thiazole derivatives also display a strong π–π stacking tendency and a better overlapping of the orbitals in the solid state which results to high charge-carrier mobility (Chen et al., 2014; Woodward et al., 2017). On the other hand, triphenylamine (TPA) moiety is found promising due to its strong

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electron-donating and hole-transporting capability, and ease in the chemical modification of small organic molecules (He et al., 2011; Liang and Chen, 2013; Kakiage et al., 2015). The nonplanar structure of TPA unit could improve the optical and electronic properties of the organic materials which might result in better hole-transporting ability (Ning et al., 2010; Che et al., 2014; Tang et al., 2010; Lin et al., 2014). Recently, the incorporation of π-spacer like furan spacer is known to enhance the optical and morphological properties of the molecules (Nazim et al., 2015; Qu and Tian, 2012; Qu et al., 2012). Furan unit is more efficient for molecular packing and the stability of organic dyes owing to its less resonance energy (16 kcal mol^{-1}) which is lower than thiophene (29 kcal mol^{-1}) and benzene (36 kcal mol^{-1}) (Sonar et al., 2015; Yiu et al., 2012; Chen et al., 2013). The organic polymers with furan spacer displays excellent performance for the optoelectronic applications and the development of OFETs (Sonar et al., 2014; Sonar et al., 2016).

Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) is commonly used as a buffer layer for organic electronic devices due to its high transparency, good electrical conductivity, easy solution casting, and a high thermal stability (Yoo et al., 2014; Chou et al., 2015). However, the hygroscopic nature of PEDOT-PSS hinders the homogenous deposition of active layer. The morphology and hygroscopic behavior of PEDOT:PSS thin film could be improved by mixing of carbon nanomaterials like graphene, carbon nanotubes, etc. in PEDOT:PSS (Liu et al., 2016). It is assumed that the hydrophobic nature of Gr surface and its low surface free energy can prevent the complete and uniform wetting of the PEDOT:PSS layer on ITO substrate (Wang et al., 2009). Additionally, the introduction of Gr in PEDOT:PSS buffer layer can improve the charge mobility and uniformity of film morphology, as reported earlier (Kim et al., 2012).

In this work, a new thiazolo[5,4-*d*]thiazole-core organic chromophore, 2,5-bis(5-(5-(5-hexylthiophen-2-yl)thiophen-2-yl)furan-2-yl) thiazolo[5,4-*d*]thiazole (TP-FTzF-TP) has been synthesized by Suzuki cross coupling reaction with Pd (0) catalyst and the surface of PEDOT:PSS buffer layer has modified by Gr. The synthesized TP-FTzF-TP chromophore applied as electron-donor material and Gr-PEDOT:PSS as buffer layer are used for the fabrication of SMOSCs. This study reveals that TPA units with the furan spacer in thiazolo[5,4-*d*]thiazole-core organic chromophore tunes the energy level as well as the optical band gap. TP-FTzF-TP chromophore also exhibits excellent solubility and a strong light absorption due to the presence of TPA units via extended conjugation length and hence, the performance of solar cell devices. Furthermore, the incorporation of Gr in PEDOT-PSS has shown a great impact in enhancing the performance of SMOSCs.

2. Experimental

2.1. Materials and equipments

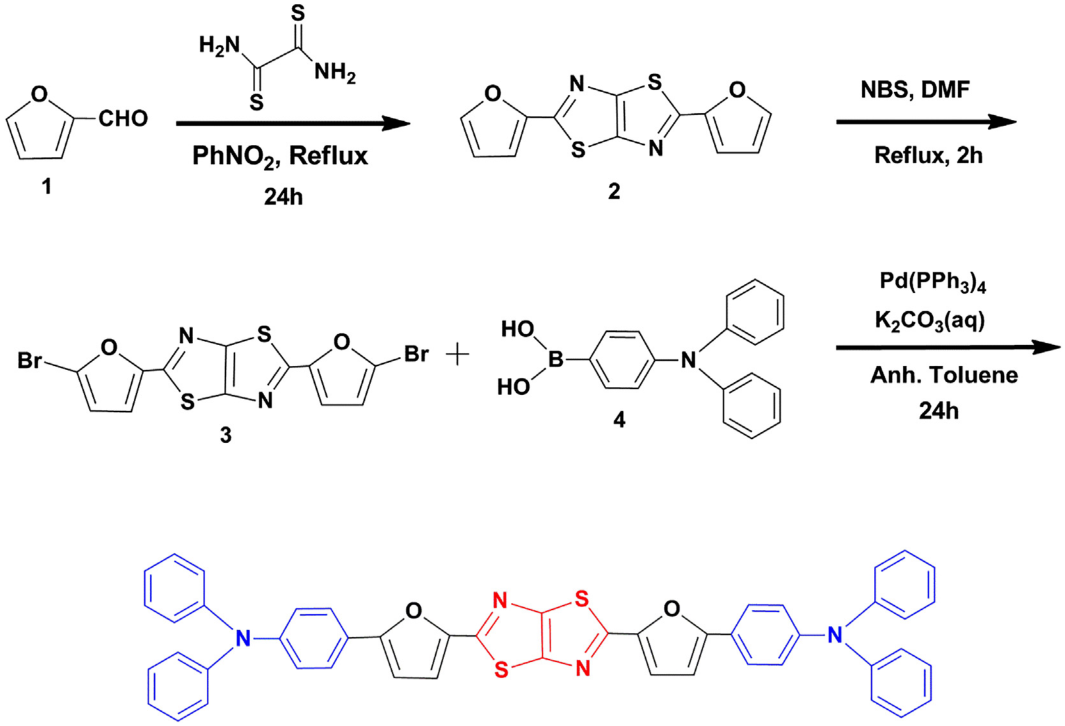
Unless otherwise noted, all the reagents and chemicals were purchased from the commercial sources (Sigma Aldrich, TCI Chemicals, Alfa Aeser) and used without further purification. The flash column chromatography was performed on a column packed with silica gel (300–400 mesh). The thin layer chromatography (TLC) plates of aluminum silica gel 60 F254 (Merck) were used to monitor the reaction progress.

2.2. Synthesis of chromophore

The synthetic route of organic chromophore, TP-FTzF-TP, is shown in Scheme 1. The precursors of thiazolo[5,4-*d*]thiazole-based material were synthesized by the procedures reported earlier (Jung et al., 2010; Hu et al., 2013). Compound, 5-di(furan-2-yl)thiazolo[5,4-*d*]thiazole (2) was synthesized by reaction of furfural (1) and rubeanic acid which gives precursor 2,5-bis(5-bromofuran-2-yl)thiazolo[5,4-*d*]thiazole (3) on bromination with N-bromosuccinimide. The final product was obtained by palladium catalyzed suzuki cross-coupling reactions between 3 and 4 under inert atmosphere.

2.3. Synthesis of 2,5-di(furan-2-yl)thiazolo[5,4-d]thiazole, 2

Furfural, 1 (960 mg, 10 mmol) and rubeanic acid (480 mg, 4 mmol) were dissolved in nitrobenzene (20 ml) and degassed for 15 min. Then, the reaction was heated at 130 °C for 24 h under nitrogen atmosphere



Scheme 1. Synthesis of thiazolothiazole-based organic chromophore, TP-FTzF-TP.