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Novel liquid crystalline oligomer with thiazolothiazole-acceptor for efficient BHJ small molecule organic solar cells

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ABSTRACT

A Novel and efficient π-conjugated, liquid crystalline semiconducting oligomer comprised of thiazolothiazole (acceptor) and two different donor units as – terminal alkyl-bithiophene (D_1) and triphenyl amine (D_2) was strategically designed and synthesized in four steps synthetic route via-Suzuki cross-coupling reactions. The presence of terminal alkyl unit might induce good solubility as well as liquid-crystal (LC) property of oligomer. Differential scanning calorimetry reveals the presence of different LC phases of oligomer which affects the morphology of devices during solution-processed fabrication process by acquiring self-assembly behaviour. As photoactive materials, π-conjugated oligomer based organic solar cell showed significantly high photocurrent density of ~12.05 mA/cm^2 with reasonably good power conversion efficiency of ~2.43%. The high performance might due to the good absorption with improvement in the thin film morphology and good intermolecular interaction behaviour of the oligomer blending with fullerene ($PC_{60}BM$) acceptor.

1. Introduction

Organic photovoltaic devices especially, small molecules organic solar cells (SMOSCs), received a great deal of interest as an alternative and cheap source of renewable energy [1–3]. Small organic molecules display numerous advantages such as low band gap, ease and reproducibility of synthesis, ease of purification process and high solubility in common organic solvents [4–6]. Among SMOSCs, solution processed π-conjugated semiconducting oligomer of donor–acceptor–donor (D–A–D) type have shown high power conversion efficiency (PCE) (≥6%) owing to their strong absorption property, good solution processability and uniform thin-layer morphology [7–9]. A–D–A type linear organic molecule, DR_3TBDT demonstrated the PCE of ~7.38% in SMOSCs [10]. Various SMOSCs device parameters like D/A ratios, thermal annealing temperature, film thickness and solvent additive influence the overall performance of devices during the fabrication process [11–13]. The efficiency of SMOSCs is also determined by the designing of small organic molecules, molecular structures, high absorption edge and good solubility in common organic solvents [14,15].

D–A–D type small molecules can have intramolecular charge transfer (ICT) absorption bands that increase absorption in the red part of the solar spectrum [16,17]. SMOSCs based on D–A–D system present the higher PCE as compared to other types of small organic molecules [18,19]. D-π-A molecules containing triphenylamine (TPA) unit based SMOSCs are fabricated by various researchers because of its high mobility, good solubility and 3D type propeller structure [20–25]. In continuation, Li et al. synthesized TPA containing D–A type small molecules with different acceptor units in linear or star-shaped manner and manifested reasonable PCE up to ~1.33% for SMOSCs [26].

Thiazolothiazole unit shows high electron accepting tendency due to the presence of imine backbone in fused ring system [27]. In general, the fused thiazolothiazole rings show resonance which substantially stabilize the oligomer, increase the rigidity and co-planarity of the oligomeric backbone [28]. Thiazolothiazole as acceptor moiety has much importance for the designing of D–A–D or A–D–A type oligomers because they show good photoactive properties for solution processed SMOSCs [29,30].

In the present paper, a novel thiazolothiazole-based liquid crystalline oligomer, 4-(5-(5-(5-(5-(5-hexylthiophen-2-yl) thiophen-2-yl) thiophene-2-yl) thiazolo[5,4-d]thiazol-2-yl) thiophene-2-yl)-N,N-diphenyl-benzenamine (TPTzR) has been synthesized, characterized and applied as a photoactive oligomer in the solution processed BHJ SMOSCs. This study reveals that the solubility of synthesized oligomer is substantially improved due to the presence of terminal alkyl chain and absorption enhancement via extending conjugation length due to the presence of TPA unit. Furthermore, TPA unit enhances the absorption spectra; reduces HOMO energy level as well as the optical band gap of oligomer.

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2. Experimental

2.1. Materials and equipments

All the chemicals and reagents were purchased from commercial sources (Sigma–Aldrich, Alfa-aesar, TCI) and used as received without further purification. Flash column chromatography was performed on a column packed with silica gel (300–400 mesh). Thin layer chromatography (TLC) was performed on Merck TLC-plates of aluminium coated with silica gel 60 F254. Ultra violet–visible (UV–vis) absorption and photoluminescence spectra (PL) were recorded by V-670 (JASCO) spectrophotometer and FP-6500 (JASCO) fluorometer, respectively. Fourier transform-infrared (FTIR) spectroscopy was performed by FT/IR-4100 (JASCO) spectrometer. The cyclic voltammetry (CV) measurements were done using WPG 100 Potentiostat/Galvanostat (WonATech) at a scan rate of 50 mV/s with a three-electrode cell consisting of a glassy carbon working electrode, a saturated calomel reference electrode (SCE) and a platinum wire as counter electrode. Herein, TPTzR was dissolved in chloroform solvent and thin film was deposited on the glassy carbon working electrode by drop casting and dried at 60 °C for 4 h under nitrogen. CV measurement was performed in 0.1 M solution of tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in acetonitrile as the supporting electrolyte. Thermo-gravimetric analysis (TGA) was carried out with a TA instruments Q-50 thermogravimetry analyzer at a scan rate of 10 °C/min under inert atmosphere. The differential scanning calorimetry (DSC) was characterized by TA instrument DSC-2910 at heating rate of 10 °C/min under nitrogen atmosphere. NMR spectra were obtained in $CDCl_3$ solvent (^1H at 600 MHz and ^{13}C at 100 MHz) using JEOL FT-NMR spectrophotometer. For NMR analysis, $CDCl_3$ is used as the solvent and chemical shift values (δ values) were considered in parts per million (ppm) with tetramethylsilane (TMS) as internal reference.

2.2. Synthesis

Compound 2,5-bis(thiophen-2-yl)thiazolo[5,4-d]thiazole (**1**) was synthesized by a ring-closing reaction of 2-thiophenecarboxaldehyde and dithiooxamide followed by bromination with N-bromosuccinimide gives 2,5-bis(5-bromothiophen-2-yl)thiazolo[5,4-d]thiazole (**2**) [31]. The detailed structural characterizations of the synthesized oligomer are provided in the supporting information (*ESI*[1]).

2.2.1. Synthesis of 2,5-bis(thiophen-2-yl) thiazolo[5,4-d]thiazole, (1)

A solution of thiophene-2-carboxaldehyde (2.46 g, 22 mmol) and dithiooxamide (0.120 g, 10 mmol) in N,N-dimethylformamide (30 mL) was heated to reflux for 6 h under inert atmosphere. The colour of the reaction changed to dark brown after 1 h which was monitored by TLC. The reaction then cooled to room temperature and then, poured into water (100 mL) and extracted with dichloromethane (DCM). The organic layer was collected and washed with water and brine solution then dried over anhydrous $MgSO_4$. After the removal of solvent by the reduced pressure, the residue was purified by flash column chromatography on silica gel with hexane: DCM (2:1, v:v) as eluent followed by recrystallization from chloroform:methanol (5:1, v:v) to get the target product, **2** (1.02 g, 33% yield) as a brown solid. ^1H NMR (600 MHz, $CDCl_3$, ppm) δ: 7.52 (d, 2H), 7.44 (d, 2 H), 7.06 (m, 2H). FT-IR (KBr, cm^{-1}): 3089, 3069, 2947, 2927, 1558, 1540, 1520, 1507, 1458, 1411, 1338, 1265, 1244, 1222, 1187, 1173, 1060, 1040, 1010, 971, 826, 815, 800, 710, 640, 617, 591, 566, 540.

2.2.2. Synthesis of 2,5-bis(5-bromo-thiophen-2-yl)thiazolo[5,4-d] thiazole, (2)

2,5-Bis (thiophen-2-yl)thiazolo [5,4-d] thiazole, **1** (0.62 g, 2 mmol) was dissolved in anhydrous dimethyl formamide (20 mL). NBS (0.82 g, 4.5 mmol) was added drop-wise to the solution and the reaction mixture was heated at 80 °C for 2 h and then cooled to room temperature. The precipitate was collected and dissolved in dichloromethane (DCM). After the removal of solvent by the reduced pressure, the residue was purified by flash column chromatography on silica gel with hexane:DCM (5:1, v:v) followed by recrystallization from hexane to get the target product, **2** (0.81 g, 85% yield) as yellow crystals. ^1H NMR (600 MHz, $CDCl_3$, ppm) δ: 7.08 (d, 2H), 7.31 (d, 2H) FT-IR (KBr, cm^{-1}): 3097, 3056, 2942, 2927, 2853, 1738, 1584, 1466, 1407, 1327, 1238, 1208, 989, 968, 835, 786, 607.

2.2.3. Synthesis of 4-(5-(5-(5-bromothiophen-2-yl) thiazolo [5,4-d]thiazol-2-yl) thiophen-2-yl)-N,N-diphenyl-benzenamine, (4)

A mixture of 2,5-bis(5-bromothiophen-2-yl)thiazolo[5,4-d]thiazole, **2** (0.37 g, 1.2 mmol), 4-(diphenylamino) phenylboronic acid, **3** (0.375 g, 1.3 mmol) and $Pd(PPh_3)_4$ (15 mg, 5 mol%) were refluxed in nitrogen-degassed toluene (~10 mL) and an aqueous K_2CO_3 solution (2 M) (4 mL) for 24 h under argon atmosphere. The reaction mixture was cool to room temperature and deionized (DI) water was added to quench the reaction and diluted with hexane. The organic layer was separated by extracting with dichloromethane (20 mL), washed with DI water, brine solution and dried over $MgSO_4$. After drying the solvent by rotary evaporator, the compound was dried in vacuo for several hours. The crude product was purified by flash column chromatography using hexane:DCM (2:1, v:v) followed by recrystallization from DCM:methanol (4:1, v:v) to get the target product, **4** (0.54 g, 72% yield) as red crystals. ^1H NMR (600 MHz, $CDCl_3$, ppm) δ: 6.71–6.74 (d, 2H), 6.99–7.15 (m, 6H), 7.44–7.52 (m, 8H), 7.69–7.74 (d, 2H). FTIR (KBr pellets, cm^{-1}): 3439, 3028, 2962, 2855, 1731, 1653, 1587, 1485, 1404, 1323, 1256, 1228, 1099, 1022, 976, 948, 836, 792, 691.

2.2.4. Synthesis of 4-(5-(5-(5-(5-(5-hexylthiophen-2-yl) thiophen-2-yl) thiophen-2-yl) thiazolo [5,4-d]thiazol-2-yl) thiophen-2-yl)-N,N-diphenylbenzenamine, (6)

A suspension of n-hexyl bithiophene pinacole boronic ester, 5 (0.18 gm, 0.50 mmol) in ethanol (5 mL) and aqueous solution (2 M) of K_2CO_3 (5 mL) were added to a solution of intermediate bromide, 4 (0.28 g, 0.45 mmol) and Pd (PPh_3)$_4$ (10 mg, 0.01 mmol) as catalyst in anhydrous toluene (~10 mL) solvent. Reaction mixture was degassed and vacuum several times then, heated to reflux for 24 h in inert atmosphere. After completion of the reaction (as monitored by TLC), it was cooled to room temperature and diluted with the hexane (20 mL). The boronic acid pinacole ester was used in access to ensure the completion of the coupling reaction. The organic layer was extracted with CH_2Cl_2 (20 mL × 3) and washed with DI water, brine and dried over $MgSO_4$ and then concentrated in vacuo. The crude product was purified by flash column chromatography using hexane:DCM (5:1, v:v) followed by recrystallization from DCM:methanol (2:1, v:v) to get the target product, 6 (0.25 g, 68% yield) as shine red crystals. ^1H NMR (600 MHz, $CDCl_3$, ppm) δ: 0.86–0.89 (t, 3H), 1.21–1.30 (m, 6H), 1.81 (t, 2H), 3.48 (t, 2H), 6.97–7.02 (d, 2H), 7.06–7.15 (m, 8H), 7.44–7.52 (m, 10H), 7.69–7.75 (d, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ: 161.32, 161.18, 153.59, 145.93, 145.79, 144.86, 132.85, 132.21, 128.17, 128.03, 126.49, 126.08, 125.38, 123.97, 123.69, 123.55, 122.71, 122.43, 122.29,

[1] Electronic supplementary information (ESI) available.