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Research paper

Efficient spirobifluorene-core electron-donor material for application in solution-processed organic solar cells

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ABSTRACT

Efficient spirobifluorene-based organic small molecule (RTh-Sp-CF_3) was synthesized in a simple manner via Suzuki coupling reaction containing an alkyl bithiophene as donor and 3,5-bis (trifluoromethyl) benzene as acceptor unit. The spirobifluorene-based small molecule was utilized as an electron-donor materials with well-known electron-acceptor material, phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) in the solution-processed small molecule organic solar cells (SMOSCs). The incorporation of 3,5-bis (trifluoromethyl) benzene unit as electron-acceptor has significantly tuned the energy levels of small molecule and obtained the HOMO and LUMO energy levels of -5.35 eV and -3.92 eV, respectively. SMOSCs fabricated with RTh-Sp-CF_3 accomplished an overall power conversion efficiency (PCE) of $\sim$2.12% with short circuit current (J_{SC}) of $\sim$8.42 mA/cm^2 and the open-circuit voltage (V_{OC}) of $\sim$0.66 V. The reasonable J_{SC} and V_{OC} of devices might be attributed to the presence of strong electron-withdrawing fluorine units in RTh-Sp-CF_3, which resulted from the improved absorption and electrochemical properties.

1. Introduction

Organic solar cells especially, bulk-heterojunction organic solar cells have owned considerable interest, both academically and industrially due to their versatile merits of low cost, large-scale fabrication, flexibility and diversity of electron-donors [1–4]. Apart from other organic solar cells, the small molecule organic solar cells (SMOSCs) have been growing as an alternative to polymer counterparts in solution-processed bulk-heterojunction (BHJ) owing to their simple molecular structures, easy synthesis and purification techniques [5–7]. Recently, SMOSCs have encountered as highly promising materials for solar cell application, after reaching the highest power conversion efficiencies (PCEs) over 9% [8,9]. For the further improvement in PCEs, it is necessary to design and synthesize new effective small organic molecules for SMOSCs. In this regards, the incorporation of the electron-donor (D) and electron-acceptor (A) units in organic small molecule plays a crucial role for the exciton-formation and its diffusion toward D-A interface which affects charge-transport properties [10–13]. In general, the fabrication of OSCs is carried out by utilizing fullerene derivatives especially, [6,6]-phenyl-C_{61} butyric acid methyl ester ($PC_{61}BM$) or [6,6]-phenyl-C_{71} butyric acid methyl ester ($PC_{71}BM$) as an electron-acceptor materials because of their good electron accepting and electron-transporting ability. PCBM molecules are easily blended with electron-donor materials and produce the excellent film morphologies for excellent charge dissociation and transport. In spites of these good properties, it is difficult to tune the optical or absorption properties and energy level of PCBM molecules by simple chemical modification. Recently, Zhan and Yao described the utilization of non-fullerene organic acceptors in place of PCBM derivatives for the development of high efficiency OSCs [14]. Even though, non-fullerene derivatives show excellent optoelectronic properties, but they do not blend properly with donor molecules and create aggregates of up to hundreds of nanometer over photoactive film which is larger in size to the exciton-diffusion length. As a result, the excitons might be quenched before they reach at the donor-acceptor (D-A) interface and fails to dissociate the excitons [15,16]. On the other hand, $PC_{61}BM$ or $PC_{71}BM$ is easily blended with donor materials, and forms nanoscale aggregates which are similar in size to the exciton-diffusion length [17]. However, the performances of SMOSCs depend on various fabrication parameters such as thickness of films, the composition ratio of donor/acceptor, and annealing time as well as annealing temperature of devices [18–20].

Oligothiophenes have recently been employed as organic electron-donors (D) unit owing to well-defined and planar structure, good solubility, and high electron-density for the designing

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and constructing the optical and organic electronic materials [21]. On the other hand, the trifluoromethyl group (—CF_3) shows a significant structural motif for organic molecules with a wide range of interesting applications in medicinal and agricultural chemistry [22–24]. The fluorinated organic materials have shown the high hydrophobicity and electro negativity which are responsible for the strong polarization behavior and high bond energy (ca. 480 kJ mol^{-1}) of the carbon–fluorine bond [25,26]. The fluorinated organic compounds contain a strong tendency to have hydrogen bonds F···H—C interactions with much lower energy that might play an important role in the solid state organization. Moreover, the conversion of C—H bonds to C—F bonds might have several potential advantages as, the C—F bond is a very effective promoter for radiation-less decay which could reduce the rate of radiationless deactivation and enhance the photoluminescence efficiency [27]. In addition, the morphology of film with CF_3-based material and $PC_{61}BM$ blend is fibrous because the presence of fluorine atom in CF_3 strengthens the intermolecular interactions between two active materials. Thus, the fluorine-termination of organic molecules could induce the morphology of blend film and increase the $\pi-\pi$ interactions between both organic molecules [28]. Recently, the organic small molecules containing trifluoromethylbenzene as the end-group presented high PCE (~6.0%) in BHJ fabricated solar cell devices [29]. It is realized that the subtle changes in the end-groups like fluorinated organic unit in small molecules could significantly influence the photovoltaic parameters of SMOSCs [30].

However, the spiro-based organic molecules with inherent nonlinear and rigid structures have attracted great attentions as the organic functional materials owing to their physical properties, high glass transition temperatures, good solubility and amorphous nature which make them very promising for optoelectronic materials [31,32]. The spirobifluorene-based derivatives have expressed an excellent thermal and chemical stabilities with high quantum efficiencies as well as non-dispersive ambipolar carrier transporting properties [33,34]. Most of the spirobifluorene-based small molecules are synthesized from the central spirobifluorene, but it requires expensive tools and chemicals [35–37]. The introduction of D and A groups in two biphenyl branches of the spirobifluorene core affords a class of spiro compounds with an asymmetric 2,7-substitution pattern, resulting a good candidate for the construction of highly transparent nonlinear organic materials due to the spiro-conjugation effects between the two fluorene units [38,39]. These substitutions induce stability and electron transport or ambipolar transport in organic materials by lowering the energy levels (both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). In this work, a new and effective spirobifluorene-based D-D-A type organic small molecule, RTh-Sp-CF_3 with alkyl bithiophene donor and 3,5-bis (trifluoromethyl) benzene as acceptor, has been synthesized and utilized for SMOSCs. The terminal alkyl group in bithiophene units of the small molecule have considerably improved its solubility in common organic solvents and 3,5-bis (trifluoromethyl) benzene as acceptor unit improves the generation of charge carriers.

2. Experimental

2.1. Materials and equipments

All the chemicals and reagents were purchased from the commercial sources 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 small molecule

The synthetic route of spirobifluorene-based organic small molecule, RTh-Sp-CF_3 is shown in Scheme 1. The monomeric precursors **2**, **3**, of the *n*-hexyl bithiophene boronic acid pinacole ester, **4** and other related intermediates were synthesized as previously reported procedures [40–42]. The intermediate product, **6** (RTh-Sp-Br) was obtained by the successive Suzuki cross-coupling reactions between 2,7-dibromo-9,9′-spirobifluorene, **5** and *n*-hexyl bithiophene boronic-acid pinacole ester, **4** using $Pd(PPh_3)_4$ (2.5 mol%) as catalyst and potassium carbonate as a base in anhydrous toluene solvent and then it finally coupled again by Suzuki coupling with the 3,5-bis(trifluoromethyl)phenyl boronic acid to give the final product, **7** named as RTh-Sp-CF_3. The synthesized small molecule was purified by flash column chromatography and repeated recrystallization in the mixed solvent of dichloromethane/methanol (2:1, v/v) as pale yellow solid (Yield: 69.5%).

2.2.1. 1-(5-(thiophen-2-yl)thiophen-2-yl)hexan-1-one (2)

In a solution of 2,2′-bithiophene 1 (3.17 g, 19.1 mmol) in anhydrous benzene (20 mL), add hexanoyl chloride (4.07 mL, 20.0 mmol) was added at room temperature. The $TiCl_4$ (2.25 mL, 20.5 mmol) was added slowly to the reaction mixture at 0 °C and then stirred for 15 min at 0 °C. After completion of the reaction, ice water was added to quench the reaction and the resulting mixture was diluted with CH_2Cl_2 (50 mL), washed successively with water (200 mL) and saturated aqueous solution of $NaHCO_3$ (100 mL), then dried over $MgSO_4$ and evaporated under reduced pressure evaporator to afford 5.00 g (85%) of yellow solid expected as the desired ketone intermediate which was used for next step without purification.

Under inert atmosphere, a suspension of $LiAlH_4$ (4.6 g, 121 mmol) and $AlCl_3$ (4.03 g, 30.3 mmol) in anhydrous Et_2O (100 mL) was added to the toluene (40 mL) solution of ketone intermediate at 0 °C. Then the reaction was stirred for 1 h at the room temperature. After completion, the reaction mixture was cooled to 0 °C. Afterward, ethyl acetate (20 mL) and HCl (6 M) solution (50 mL) were added to the reaction mixture. The resulting mixture was then extracted with diethyl ether (300 mL), washed with brine solution and water (50 mL), dried over $MgSO_4$ and evaporated in the vacuum oven. The obtained yellow residue was purified by flash column chromatography on silica gel (hexane) to give a colourless oil (6.00 g, 93%). ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.17 (dd, 1H), 7.13 (dd, 1H), 6.95 (dd, 1H), 6.97 (d, 1H), 6.66 (d, 1H), 2.74 (t, 2H), 1.67 (m, 2H), 1.37 (m, 14H), 0.92 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 146.5, 145.3, 138.1, 134.7, 127.4, 125.5, 124.4, 123.9, 123.7, 123.2, 32.1, 31.6, 30.3, 29.7, 29.5, 29.1, 22.7, 14.1.

2.2.2. 5-Bromo-5′-decyl-2,2′-bithiophene (3)

In solution of compound 2 (2.00 g, 6.53 mmol) in dimethylformamide (30 mL), N-bromo succinimide (NBS) (1.22 g, 6.86 mmol) was added slowly and the obtained reaction mixture was stirred for 30 min in dark. The reaction mixture was diluted with hexane (50 mL), and washed with saturated aqueous solution of NH_4Cl (50 mL), dried over $MgSO_4$ and evaporated under reduced pressure. The obtained residue was purified by flash column chromatography on silica gel (hexane) to give a white solid (2.36 g, 94%). mp 35–38 °C; ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 6.96 (d, 1H), 6.91 (d, 1H), 6.87 (d, 1H), 6.69 (d, 1H), 2.75 (t, 2H), 1.65 (m, 2H), 1.37 (m, 14H), 0.93 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 145.3, 139.7, 133.6, 130.1, 130.7, 124.5, 123.5, 123.3, 110.5, 32.3, 31.5, 30.6, 29.7, 29.5, 29.1, 22.7, 14.2.