

Carbazole-based small molecule electron donors: Syntheses, characterization, and material properties



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ABSTRACT

Efficient synthetic methods for carbazole-based small molecule electron donors with donor–acceptor (*D–A*) and *A–D–A* type structures were developed. In order to study the relation between chemical structures and material properties, the prepared compounds were characterized in detail using absorption spectroscopy, differential pulse voltammetry, and computational methods. In addition, symmetrical *A–D–A* type compounds were tested as an active layer component in bulk heterojunction based organic solar cell (OSC) devices with conventional structure. The results show that the two compound types have many similar properties. However, the extended molecular structure of *A–D–A* type compounds offer better film forming properties and higher molar absorption coefficients compared with the *D–A* type materials. Furthermore, the attachment of fluoro substituents in the *A* units has a positive effect on all solar cell device parameters. Moreover, the computational studies revealed that the molecular structures are twisted between the central carbazole *D* unit and π -bridge which may result in inefficient intramolecular charge transfer and, also, relatively limited short-circuit currents in OSC devices.

1. Introduction

In the recent years, solution processed small molecule donors have attracted attention as alternatives to conjugated polymer-based donors in organic solar cells (OSCs). These materials show several advantages compared to their polymeric counterparts, such as well-defined structures without the end group contaminants, simple synthesis and purification, low dispersity, and excellent batch-to-batch reproducibility [1–7].

One of the most efficient structures of small molecule donor materials has turned out to be the *A–D–A* type structure in which *A* refers to an electron acceptor unit and *D* refers to an electron donor unit. Often, these kinds of molecules are also termed *push–pull–push* type donor materials. By changing both the central *D* and terminal *A* units and a possible π -conjugation bridge in between the *A* and *D* units, desired material properties can be tailored and high power conversion efficiencies (PCEs) achieved [8]. For example, one of the best-performing small molecule donors is p-DTS(FBTTh₂)₂ (Fig. 1) [5]. Up to 8.9% PCE has been reported with this molecule by optimizing the OSC device structure [9]. Moreover, it has been demonstrated that some small molecule materials can produce very high PCEs both in bulk

heterojunction (BHJ) based OSCs and in perovskite solar cells [10].

Especially, 2,1,3-benzothiadiazole (BT) unit and its substituted derivatives have been widely utilized as building blocks (*A* units) in both polymer and small molecule electron donor materials [11,12]. Moreover, various *D* units have been studied as a component of OSC donor materials [12,13]. Carbazole (Cz) has been employed as the *D* unit in various semiconducting polymers and dye molecules [14,15]. The main advantage of the poly(2,7-carbazole)-based OSC devices is high open circuit voltages (V_{oc}). Moreover, internal quantum efficiency can be close to 100% [16]. Few years ago, Cz-based small molecule materials showed promising results as donor components in BHJ OSCs [17,18]. Since then, small molecule materials containing Cz as the *D* unit have gained growing interest and shown promising results. At least, three main structures *A–D–A* [19,20], *D–A* [21,22], and *D–A–D* [23–26] have been introduced. However, more experimental studies are needed to discover new state-of-the-art small molecule electron donors and, in particular, to gain systematic information about the relationships between their chemical structures, material properties, and performance in OSC applications.

Recently, we reported a synthetic pathway to BT-based building blocks [27]. Since then, we have further developed the synthetic

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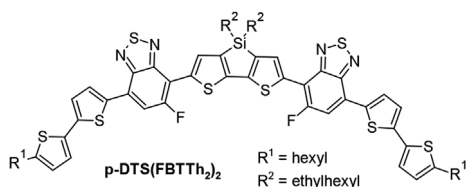


Fig. 1. The chemical structure of p-DTS(FBTTh₂)₂.

strategy and, here, we present the syntheses of two unsymmetrical *D–A* and two symmetrical *A–D–A* type small molecules. In these compounds, Cz acts as a *D* unit and either BT or its fluoro-substituted derivative as an *A* unit. Thiophene and thiazole have been used as a π -bridge between the *D* and *A* units. In order to find out how the changes in molecular structures affect the material properties, the prepared *D–A* and *A–D–A* type small molecule compounds have been characterized by spectroscopic, electrochemical, and computational methods. Moreover, the symmetrical *A–D–A* type compounds have been tested as electron donor materials in BHJ-based OSC devices.

2. Experimental section

Commercial reagents were used as received. 2-(3-Hexylthiophen-2-yl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiazole and compound **3b** were synthesized using the previously published methods [27]. The chemical structures of new compounds were characterized by using NMR and HRMS techniques. Melting points (reported as peak values) of compounds **2**, **3a**, **4a**, **4b**, **5a**, **5b**, **6a**, **6b**, and **7** were measured using Mettler Toledo DSC 1 apparatus. Samples of 1.0–2.9 mg were placed in 40 μ L Al crucibles with pierced lids. The DSC scans were carried out from 5 °C to 300 °C at the heating rate of 20 °C min⁻¹ under a nitrogen flow of 60 mL min⁻¹.

2.1. Syntheses

2.1.1. Synthesis of 4-bromo-5-fluoro-7-(5-hexylthiophen-2-yl)-2,1,3-benzothiadiazole (**2**)

Toluene (6 mL), DMA (6 mL), distilled water (1.5 mL), and 5-hexyl-2-thiopheneboronic acid pinacol ester (1.02 equiv, 140.6 mg, 0.48 mmol) were deoxygenated with argon for 15 min in a reaction tube with a magnetic stirring bar. 4,7-Dibromo-5-fluoro-2,1,3-benzothiadiazole (**1**) (146.9 mg, 0.47 mmol), Cs₂CO₃ (2.5 equiv, 384.1 mg, 1.18 mmol), Pd(OAc)₂ (2.6 mol%, 2.8 mg, 12 μ mol), and Xantphos (2.6 mol%, 6.8 mg, 12 μ mol) were added. The sealed tube was evacuated and backfilled with argon five times. The reaction mixture was stirred and heated in an oil bath (60 °C) for 3 h. The reaction mixture was filtered through a thin pad of silica gel rinsing with toluene and evaporated under reduced pressure. The product was purified by using flash chromatography (SiO₂, toluene 1: 1 *n*-heptane). The isolated product **2** was collected as a yellow solid (186.7 mg) in > 99% yield. Mp 90 °C. ¹H NMR (400 MHz, CDCl₃) δ ppm 0.91 (t, *J* = 6.9 Hz, 3H), 1.32–1.38 (m, 4H), 1.38–1.46 (m, 2H), 1.75 (quin, *J* = 7.5 Hz, 2H), 2.89 (t, *J* = 7.7 Hz, 2H), 6.88 (d, *J* = 3.7 Hz, 1H), 7.62 (d, *J* = 10.0 Hz, 1H), 7.95 (d, *J* = 3.7 Hz, 1H). HRMS (ESI+, TOF) *m/z*: [M+H]⁺ Calcd for C₁₆H₁₇N₂S₂BrF 399.0001; Found 398.9999.

2.1.2. Synthesis of compound **3a**

Toluene (2.5 mL), DMA (2.5 mL), and distilled water (0.5 mL) were deoxygenated with argon for 15 min in a reaction tube with a magnetic stirring bar. Compound **2** (99.9 mg, 0.25 mmol), 2-(3-hexylthiophen-2-yl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiazole (1.04 equiv, 99.2 mg, 0.26 mmol), Cs₂CO₃ (2.5 equiv, 204.9 mg, 0.63 mmol), *t*-Bu₃P·HBF₄ (12 mol%, 8.7 mg, 30 μ mol) and Pd₂(dba)₃ (3 mol%, 6.9 mg, 7.5 μ mol) were added. The sealed tube was evacuated and backfilled with argon five times. The reaction mixture was stirred and heated in an

oil bath (90 °C) for 21 h. The reaction mixture was filtered through a thin pad of silica gel rinsing with toluene and evaporated under reduced pressure. The product was purified by using flash chromatography (SiO₂, toluene). The isolated product **3a** was collected as a red solid (100.4 mg) in 70% yield. Mp 79 °C. ¹H NMR (400 MHz, CDCl₃) δ ppm 0.90–0.94 (m, 6H), 1.33–1.54 (m, 12H), 1.73–1.81 (m, 4H), 2.90 (t, *J* = 7.6 Hz, 2H), 3.05 (t, *J* = 7.9 Hz, 2H), 6.90 (d, *J* = 3.7 Hz, 1H), 7.02 (d, *J* = 5.1 Hz, 1H), 7.35 (d, *J* = 5.1 Hz, 1H), 7.70 (d, *J* = 13.0 Hz, 1H), 8.00 (d, *J* = 3.7 Hz, 1H), 8.90 (s, 1H). HRMS (ESI+, TOF) *m/z*: [M+H]⁺ Calcd for C₂₉H₃₃N₃S₄F 570.1541; Found 570.1534.

2.1.3. Synthesis of compound **4a**

Compound **3a** (80.2 mg, 0.14 mmol) was dissolved in CH₂Cl₂ (10 mL) and NBS (1.1 equiv, 27.8 mg, 0.16 mmol) was added. The reaction mixture was stirred at room temperature for 20 h. The solvent was evaporated and the crude product was subjected to flash chromatography (SiO₂, toluene). The pure compound **4a** was isolated as a red solid (80.0 mg) in 88% yield. Mp 96 °C. ¹H NMR (400 MHz, CDCl₃) δ ppm 0.90–0.95 (m, 6H), 1.32–1.51 (m, 12H), 1.69–1.80 (m, 4H), 2.90 (t, *J* = 7.6 Hz, 2H), 2.95 (t, *J* = 7.8 Hz, 2H), 6.89 (d, *J* = 3.7 Hz, 1H), 6.96 (s, 1H), 7.67 (d, *J* = 13.0 Hz, 1H), 7.98 (d, *J* = 3.7 Hz, 1H), 8.84 (s, 1H). HRMS (ESI+, TOF) *m/z*: [M+H]⁺ Calcd for C₂₉H₃₂N₃S₄BrF 648.0646; Found 648.0643.

2.1.4. Synthesis of compound **4b**

The synthesis was carried out using the same procedure as for compound **4a**. The specific amounts of reagents used were: compound **3b** (71.7 mg, 0.130 mmol), NBS (1.02 equiv, 23.5 mg, 0.132 mmol), and CH₂Cl₂ (4.8 mL). Pure compound **4b** was isolated as a red solid (42.9 mg) in 52% yield. Mp 130 °C. ¹H NMR (400 MHz, CDCl₃) δ ppm 0.90–0.95 (m, 6H), 1.32–1.51 (m, 12H), 1.70–1.80 (m, 4H), 2.90 (t, *J* = 7.7 Hz, 2H), 2.96 (t, *J* = 7.8 Hz, 2H), 6.90 (d, *J* = 3.8 Hz, 1H), 6.97 (s, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.99 (d, *J* = 3.8 Hz, 1H), 8.69 (s, 1H). ¹³C NMR (100.6 MHz, CDCl₃) δ ppm 14.1, 14.1, 22.6, 22.6, 28.8, 29.2, 29.8, 30.2, 30.3, 31.6, 31.6, 114.8, 122.3, 124.8, 125.4, 126.4, 127.2, 128.1, 133.2, 133.5, 134.1, 136.4, 141.7, 142.8, 148.6, 152.3, 152.5, 159.9. HRMS (ESI+, TOF) *m/z*: [M+H]⁺ Calcd for C₂₉H₃₃N₃S₄Br 630.0741; Found 630.0746. A small amount of byproduct **7** was isolated for analyses. Mp 90 °C. ¹H NMR (400 MHz, CDCl₃) δ ppm 0.90–0.94 (m, 6H), 1.32–1.51 (m, 12H), 1.70–1.79 (m, 4H), 2.87 (t, *J* = 7.5 Hz, 2H), 2.96 (t, *J* = 7.8 Hz, 2H), 6.88 (s, 1H), 6.98 (s, 1H), 7.93 (d, *J* = 7.6 Hz, 1H), 8.07 (d, *J* = 7.6 Hz, 1H), 8.74 (s, 1H). ¹³C NMR (100.6 MHz, CDCl₃) δ ppm 14.1, 14.1, 22.6, 22.6, 28.8, 29.2, 29.7, 30.2, 30.2, 31.1, 31.5, 31.6, 109.5, 115.0, 124.2, 125.5, 125.8, 128.3, 129.8, 129.9, 133.3, 133.5, 133.7, 142.3, 143.0, 148.2, 152.0, 153.5, 160.4. HRMS (ESI+, TOF) *m/z*: [M+H]⁺ Calcd for C₂₉H₃₂N₃S₄Br₂ 707.9846; Found 707.9836.

2.1.5. Synthesis of compound **5a**

Toluene (2.25 mL), DMA (2.25 mL), and distilled water (0.5 mL) were deoxygenated with argon for 15 min in a reaction tube with a magnetic stirring bar. Compound **4a** (75.9 mg, 0.117 mmol), 9-ethyl-carbazole-3-boronic acid (1.05 equiv, 29.3 mg, 0.123 mmol), Cs₂CO₃ (2.5 equiv, 96.1 mg, 0.29 mmol), Pd(OAc)₂ (6 mol%, 1.5 mg, 6.7 μ mol), and Xantphos (5 mol%, 3.4 mg, 5.9 μ mol) were added. The sealed tube was evacuated and backfilled with argon five times. The reaction mixture was stirred and heated in an oil bath (100 °C) for 1.5 h. The reaction mixture was filtered through a thin pad of silica gel rinsing with toluene and evaporated under reduced pressure. The product was purified by using flash chromatography (SiO₂, toluene). The solid product was boiled in acetone-methanol mixture (1:2), cooled to room temperature, filtered and washed with acetone-methanol mixture several times. The isolated product **5a** was collected as a deep dark red solid (87.2 mg) in 98% yield. Mp 102 °C. ¹H NMR (400 MHz, CD₂Cl₂) δ ppm 0.91–0.98 (m, 6H), 1.33–1.49 (m, 13H), 1.57 (quin, *J* = 7.1 Hz, 2H), 1.75 (quin, *J* = 7.5 Hz, 2H), 1.84 (quin, *J* = 7.6 Hz, 2H), 2.88 (t,

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