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## ARTICLE

## Synthesis, Optical and Electrochemical Properties of Polycyclic Aromatic Compounds with *S,S*-Dioxide Benzothiophene Fused Seven Rings

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A series of novel linearly-fused polycyclic aromatic compounds, *N*-(2-decyltetradecyl)carbazole bis[2,3-*b*;6,7-*b*]benzo[*d*] thiophene-*S,S*-dioxide (**CzBTO**) and 9,9-dioctylfluorene bis[2,3-*b*;6,7-*b*]benzo[*d*]thiophene-*S,S*-dioxide (**FBTO**), incorporating with *S,S*-dioxide benzothiophene unit were efficiently synthesized and detailedly characterized. The key step of preparing **CzBTO** and **FBTO** was related to the triflic acid induced intramolecular electrophilic cyclizing reaction where the corresponding methyl sulfoxides in activated aromatic building blocks may enable the regioselective ring cyclization. From the photoluminescence (PL) spectra, the **CzBTO** and **FBTO** showed very deep blue emission with the emission peaks at 426 and 407 nm, respectively. Through the photoluminescence quantum yield (PLQY) characterization, the **FBTO** gave a high PLQY value of 77% in tetrahydrofuran solution. The DFT and electrochemical studies showed that the **CzBTO** and **FBTO** had large band gaps and very low highest occupied molecular orbital (HOMO) energy levels, which indicated that these two compounds existed the high stability both thermally and optically. From the electrochemical measurement, the HOMO and lowest unoccupied molecular orbital (LUMO) energy levels were -6.04, -6.20 and -2.74, -2.80 eV, with the band gaps of 3.3 and 3.4 eV for **CzBTO** and **FBTO**, respectively.

### Introduction

Recently, organic/polymer light-emitting diodes (O/PLEDs) have attracted considerable attention both in academic institutions and in commercial companies, due to their greatly potential applications in the large-scale and flexible displays.<sup>[1,2]</sup> Specifically, the solution-processing technique is one of the attractive methodologies to fabricate cost-effective flexible O/PLEDs. In order to facilitate the solution-processing technique, conjugated polymers and solution-processable small molecules are usually utilized. In contrast to conjugated polymers, small molecules play a more important role in the O/PLEDs ascribing to their versatile merits in well-defined structures, superior chemical purity and repeatable production.<sup>[3,4]</sup> Therefore, with respect to these merits, large polycyclic aromatic compounds (PACs) which contain hetero atoms, such as sulphur<sup>[5-7]</sup>, oxygen<sup>[6,8]</sup>, selenium<sup>[9]</sup>, nitrogen<sup>[10]</sup>, phosphor<sup>[11]</sup> as well as acenes<sup>[12-16]</sup>, have been studied widely attributing to the large  $\pi$ -conjugated length, highly thermal stability, high fluorescence quantum yield, appropriate charge mobility and feasible structure modification.

For the purpose of obtaining these O/PLEDs materials, the fluorene and carbazole based moieties are ones of the most used candidates. For instance, Monkman et al synthesized a polyspirobifluorene derivative and found that the highest occupied molecular orbital (HOMO) was strongly extend into the side fluorene groups of the spirobifluorene units, which may lead to the development of new materials with optimized charge carrier transporting properties and high luminescence efficiency.<sup>[17]</sup> Yang et

al synthesized the butterfly-shaped tetra-substituted carbazole derivatives as host materials in green phosphorescent OLED devices with a maximum current efficiency of 41.0 cd/A.<sup>[18]</sup> Leclerc et al reported the synthesis of 2,7-carbazole based polymers for blue, green and red (RGB) PLEDs with high fluorescence quantum yields.<sup>[19]</sup> Importantly, *S,S*-dioxide dibenzothiophene (FSO) based derivatives are another kind of novel units to construct high-performance light-emitting molecules or polymers due to their advantageous properties in highly thermal and optical stabilities, and high electron mobility<sup>[20-21]</sup>. In the recent years, Yang and Bryce groups have been studying the application of FSO in O/PLEDs for a long time, respectively. Yang et al introduced FSO isomer into the poly[9,9-bis(4-(2-ethylhexyloxy)phenyl)fluorene-2,7-diyl] main chains which shown a maximum luminous efficiency (LE) of 6.0 cd A<sup>-1</sup> with CIE coordinates of (0.16, 0.19).<sup>[22]</sup> Also, they incorporated a new FSO derivative into the polymer backbones and prepared the green copolymers with a maximal LE of 9.0 cd A<sup>-1</sup> and a CIE coordinates of (0.27, 0.56).<sup>[23]</sup> They further achieved white PLEDs with a superior trade-off between device efficiency, CRI, and colour stability through blending the RGB light-emitting copolymers containing FSO units.<sup>[24]</sup> Moreover, they synthesized hyperbranched polymers containing alkylated FSO unit as host materials with a highly triplet energy level for green phosphorescent PLEDs, where it achieved a maximum LE of 50.5 cd A<sup>-1</sup> as well as a maximum external quantum efficiency (EQE) of 15.3%.<sup>[25]</sup> Besides, resulting from the deep lowest unoccupied molecular orbital (LUMO) energy levels of FSO based polymers, Yang et al also synthesized the alcohol-soluble PFOs containing FSO segments as efficient cathode

interfacial layer in PLEDs and polymer solar cells (PSCs), in which these polymers presented the excellent ability of decreasing the work function of metal electrodes that was very significant for the electron injection from cathode to emitting layer in PLEDs or electron extraction from the active layer to cathode in PSCs.<sup>[26]</sup> At the same time, Bryce et al introduced FSO unit into the fluorene based oligomers, which increased the electron affinity and achieved highly fluorescent co-oligomers with bright blue emission both in solution and in film.<sup>[27]</sup> They also reported a series of ambipolar small molecules containing FSO segment, which can tune the fluorescent emission from deep blue to green.<sup>[28]</sup> Furthermore, they synthesized the alkylated FSO unit and introduced it into the PFO backbones which exhibited a highly pure deep-blue emission with a highly triplet energy level.<sup>[29]</sup>

Although the fluorene, carbazole and FSO based small molecules or polymers exhibit good performance in O/PLEDs, they also suffer from some defects which lead to the limited application of these units in O/PLEDs, for example, the low fluorescence quantum efficiency for carbazole based materials, the low thermal and optical stability for fluorene based materials, and very low solubility for FSO. If we can combine the each advantages and avoid the defects of the fluorene, carbazole and FSO, the freshly prepared molecules can potentially show versatile optoelectronic properties. Therefore, there is an efficient strategy to achieve this concept, which is related to synthesize the large PACs with multiple rings containing the specific hetero atoms. Until now, many studies have been focused on the preparation of this kind of PACs. Suranna et al synthesized the bis-substituted FSO materials with a maximum luminance of 11422 cd m<sup>-2</sup> as well as a maximum LE of 3.25 cd A<sup>-1</sup>.<sup>[30]</sup> Liu et al have synthesized a series of asymmetrically fluorene-based PACs as host materials with the LE approaching to 12 cd A<sup>-1</sup>.<sup>[31]</sup> Müllen et al reported the synthesis of several PACs bearing pyrrole and thiophene rings, which had been defined as the good candidates for organic field electronic transistors (OFETs).<sup>[32]</sup> Patrick et al synthesized a new family of acenedithiophenes through oxidative photocyclization, which shown the high crystalline with a preferred specific orientation.<sup>[33]</sup> Yu et al illustrated the synthesis of a new family of dibenzoannelated tetrathienoacenes as typical p-type organic semiconductors with a maximum mobility of 0.15 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>.<sup>[34]</sup> Takimiya et al elongated the conjugation length of thienoacenes which exhibited the excellent performance in OFET devices with the enhanced mobility up to 0.94 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>.<sup>[7]</sup> Kafafi et al fabricated and characterized a series of OLEDs based on two new dioxolane-substituted pentacene derivatives which gave the maximum EQE of 3.3%.<sup>[35]</sup>

Herein, through combining the fluorene or carbazole with FSO, we designed and synthesized two symmetrically fused PACs incorporating with *S,S*-dioxide benzothiophene unit: N-(2-decyltetradecyl)carbazole bis[2,3-b;6,7-b]benzo[d]thiophene-*S,S*-dioxide (CzBTO) and 9,9-dioctylfluorene bis[2,3-b;6,7-b]benzo[d]thiophene-*S,S*-dioxide (FBTO). Their thermal, optical, electrochemical properties and theoretical computation were characterized in detail.

## Experimental Section

All commercially available reagents were distilled according to standard procedure prior to use. 2,7-dibromo-N-(2-decyltetradecyl)carbazole (1), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-N-(2-decyltetradecyl)carbazole (2), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (4) and 1-bromo-2-(methylsulfinyl)benzene were synthesized according to the previously reported procedures<sup>[36,38]</sup>.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DRX 600 spectrometer (operating at 600 MHz for <sup>1</sup>H NMR, and 150 MHz for <sup>13</sup>C NMR) in deuterated chloroform solution with tetramethylsilane as a reference. Cyclic voltammetry (CV) measurement was carried out at a scan rate of 50 mV/s at room temperature under argon using a CHI660A electrochemical workstation with tetra(n-butyl)ammonium hexafluorophosphate (n-Bu<sub>4</sub>NPF<sub>6</sub>, 0.1 M) in acetonitrile and dichloromethane as the electrolyte. Thermo gravimetric analyses (TGA) were performed on a Netzsch TG 209 at a heating rate of 20 °C min<sup>-1</sup>. The differential scanning calorimetry (DSC) was measured on a Netzsch DSC 204 under nitrogen flow at a heating rate of 10 °C min<sup>-1</sup>. UV-vis absorption spectra were recorded with a HP 8453 spectrophotometer. Photoluminescence (PL) spectra were recorded with a spectrofluorometer (Spex Fluorolog-3). PL quantum yields were measured using an IS080 LabSphere integrating sphere with excitation by a 325 nm HeCd laser (Melles Griot). The theoretical computation was carried out using Gaussian 09 at the B3LYP/6-31G(d) level.

### 2,7-bis(2-methylsulfinylphenyl)-N-(2-decyltetradecyl)carbazole

(3) : A mixture of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-N-(2-decyltetradecyl)carbazole (20 g, 26.5 mmol), 1-bromo-2-(methylsulfinyl)benzene (14.5 g, 66 mmol) and tetrabutyl ammonium bromide (190 mg) was added to in a three-necked flask and dissolved by freshly distilled tetrahydrofuran (300 mL) under argon. Then K<sub>2</sub>CO<sub>3</sub> solution (2 M, 130 mL) was added. Pd(PPh<sub>3</sub>)<sub>4</sub> (2.6 g) and was added in one portion to the reaction mixture, which was heated to reflux for 24 h. The mixture was cooled to room temperature, concentrated and extracted with dichloromethane. The organic layers were dried, evaporated in vacuum, and the residue was purified with column chromatography on silica gel with petroleum ether/ethyl acetate (2:1) as the eluent to give 3 as yellow oil (14.1 g, 68%). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>, δ) 8.19 (t, 4H), 7.67 (t, 2H), 7.60 (t, 2H), 7.45 (t, 4H), 7.27 (d, 2H), 4.20 (d, 2H), 2.33 (s, 6H), 2.13 (s, 1H), 1.16 (m, 40H), 0.85 (t, 6H). <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>, δ) 144.11, 141.45, 140.19, 135.82, 130.65, 129.03, 128.68, 123.55, 122.25, 120.99, 120.41, 109.85, 60.38, 48.14, 41.44, 38.01, 32.09, 31.92, 30.01, 29.65, 29.35, 26.92, 26.82, 26.66, 26.49, 22.69, 21.03, 14.20, 14.12. MS (APCI): m/z (%): 780.6 [M+1]<sup>+</sup>.

### N-(2-decyltetradecyl)carbazolebis[2,3-b;6,7-b]benzo[d]thiophene

(CzBT) : Compound 3 (5 g, 6.4 mmol) was added to trifluoromethanesulfonic acid (9 mL). The solution was stirred at room temperature for 24 h and then poured slowly into ice water. The yellow precipitate was collected by suction filtration and dried under vacuum. The structure of this compound, which was insoluble in a polar organic solvents, was assumed to be the sulfonium salt. Demethylation of the solid was achieved by refluxing in pyridine (150 mL) for 12 h. When the reaction was cooled to room temperature, a large volume of dichloromethane (DCM) was added to extract the product. N-(2-decyltetradecyl)carbazole bis[2,3-b;6,7-b]benzo[d]thiophene was thus obtained as yellow powder after silica chromatography with petroleum as the eluent (2.6 g, 56% yield). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>, δ) 8.54 (t, 2H), 8.21 (d, 2H), 7.98 (t, 2H), 7.87 (m, 2H), 7.47 (m, 4H), 4.22 (d, 2H), 2.27 (s, 1H), 1.19 (m, 40H), 0.88 (t, 6H). <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>, δ) 140.77, 140.72, 135.82, 134.53, 130.31, 126.63, 124.12, 123.13, 123.01, 121.40, 113.76, 100.48, 58.63, 37.45, 32.14, 32.08, 30.11, 29.82, 29.50, 26.78, 22.84, 18.59, 14.27. MS (APCI): m/z (%): 716.4 [M+1]<sup>+</sup>. Elemental analysis calcd (%) for C<sub>48</sub>H<sub>61</sub>NS<sub>2</sub>: C 80.50, H 8.59, N 1.96, S 8.96; found: C 80.30, H 8.41, N 2.24, S 9.26.

**N-(2-decyltetradecyl)carbazolebis[2,3-b;6,7-b]benzo[d]thiophene-S,S-dioxide (CzBTO)** : A mixture of CzBT (1.5 g, 2.1 mmol) and 3-chloroperbenzoic acid (m-CPBA, 7.2 g, 42 mmol) was dissolved in dichloromethane (DCM, 200 mL) and stirred at room temperature for 10 h. Then the mixture was poured into 10% oxyhydrogen sodium solution to remove the residual m-CPBA. The organic layers were washed by water (150 mL×3), dried and evaporated in vacuum. And the residue was purified with column chromatography on silica gel with dichloromethane/tetrahydrofuran(10:1) as the eluent to give CzBTO as white powder(0.9 g, 77%). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>, δ) 8.56 (s, 2H), 7.71 (d, 2H), 7.55 (d, 2H), 7.35 (t, 2H), 7.22 (t, 2H), 7.20 (s, 2H), 4.10 (d, 2H), 1.78 (s, 1H), 1.13 (m, 40H), 0.83 (t, 6H). <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>, δ) 144.27, 138.59, 133.95, 131.54, 130.57, 130.34, 130.05, 123.05, 122.01, 121.86, 114.42, 102.69, 58.46, 47.92, 38.07, 32.06, 31.81, 29.99, 29.76, 29.69, 29.47, 29.43, 26.60, 22.81, 18.60, 14.20. MS (APCI): m/z (%): 780.3 [M+1]<sup>+</sup>. Elemental analysis calcd (%) for C<sub>48</sub>H<sub>61</sub>NS<sub>2</sub>O<sub>4</sub>: C 73.90, H 7.88, N 1.80, S 8.22; found: C 73.73, H 7.57, N 2.04, S 8.46.

**2,7-bis(2-methylsulfinylphenyl)-9,9-dioctylfluorene (5)** : K<sub>2</sub>CO<sub>3</sub> solution (2 M, 30 mL) was added to a mixture of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (3.86 g, 6 mmol) and 2-bromo(methylsulfinyl)benzene (2.9 g, 13.2 mmol) in freshly distilled tetrahydrofuran (60 mL) under argon. Pd(PPh<sub>3</sub>)<sub>4</sub> (350 mg) and tetrabutyl ammonium bromide (190 mg) was added in one portion to the reaction mixture, which was heated to reflux for 24 h. The mixture was cooled to room temperature and extracted with dichloromethane. The organic layers were dried, evaporated in vacuum, and the residue was purified with column chromatography on silica gel with petroleum ether/ethyl acetate (3:1) as the eluent to give 5 as yellow oil (3.6 g, 90%). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>, δ) 8.15 (d, 2H), 7.82 (d, 2H), 7.60 (m, 4H), 7.44 (m, 6H), 2.34 (s, 6H), 2.04 (t, 4H), 1.15 (m, 20H), 0.82 (t, 6H), 0.65 (s, 4H). <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>, δ) 151.57, 143.90, 140.53, 139.67, 137.04, 130.66, 130.34, 128.70, 128.06, 123.71, 123.50, 120.44, 55.54, 41.16, 40.24, 31.72, 29.95, 29.40, 29.16, 24.02, 22.55, 14.01. MS (APCI): m/z (%): 667.5 [M+1]<sup>+</sup>.

**9,9-dioctylfluorenebis[2,3-b;6,7-b]benzo[d]thiophene (FBT)** : Compound 5(0.8 g, 1.2 mmol) was added to trifluoromethanesulfonic acid (4.2 mL). The solution was stirred at room temperature for 24 h and then poured slowly into ice water. The yellow precipitate was collected by suction filtration and dried under vacuum. The structure of this compound, which was insoluble in a polar organic solvents, was assumed to be the sulfonium salt. Demethylation of the solid was achieved by refluxing in pyridine (100 mL) for 12 h. When the reaction was cooled to room temperature, a large volume of dichloromethane (DCM) was added to extract the product. 9,9-dioctylfluorene bis[2,3-b;6,7-b]benzo[d]thiophene was thus obtained as white crystals after silica

chromatography with petroleum as the eluent (0.46 g, 64% yield). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>, δ) 8.23 (d, 2H), 8.21 (s, 2H), 8.10 (s, 2H), 7.87 (d, 2H), 7.47 (m, 4H), 2.17 (t, 4H), 1.04 (m, 20H), 0.74 (t, 6H), 0.68 (s, 4H). <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>, δ) 148.56, 140.43, 140.02, 138.77, 135.75, 135.38, 126.62, 124.46, 123.08, 121.65, 115.80, 113.99, 54.69, 41.73, 31.88, 30.20, 29.34, 23.98, 22.66, 14.13. MS (APCI): m/z (%): 603.6 [M+1]<sup>+</sup>. Elemental analysis calcd (%) for C<sub>41</sub>H<sub>46</sub>S<sub>2</sub>: C 81.67, H 7.69, S 10.64; found: C 82.10, H 8.03, S 10.86.

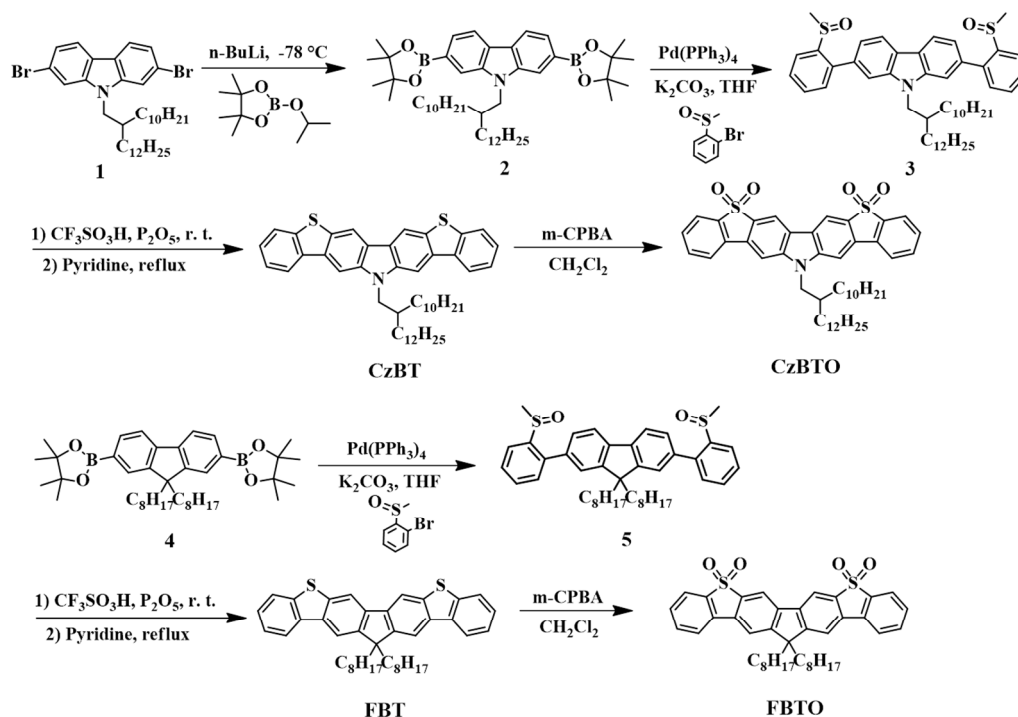
**9,9-dioctylfluorenebis[2,3-b;6,7-b]benzo[d]thiophene-S,S-dioxide (FBTO)** : A mixture of FBT (100 mg, 0.17 mmol) and m-CPBA (570 mg, 3.3 mmol) was dissolved in dichloromethane (DCM, 10 mL) and stirred at room temperature for 10 h. Then the mixture was poured into 10% oxyhydrogen sodium solution to remove the residual m-CPBA. The organic layers were washed by water (150ml×3), dried and evaporated in vacuum. And the residue was purified with column chromatography on silica gel with dichloromethane/ethyl acetate (5:1) as the eluent to give FBTO as white lamellar crystals (100 mg, 90%). <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>, δ) 8.19 (s, 2H), 7.87 (t, 4H), 7.71 (m, 4H), 7.56 (t, 2H), 2.13 (t, 4H), 1.06 (m, 20H), 0.77 (t, 6H), 0.58 (s, 4H). <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>, δ) 157.55, 141.74, 138.55, 137.80, 134.03, 132.18, 131.82, 130.60, 122.50, 121.85, 115.98, 114.50, 56.63, 40.55, 31.80, 29.95, 29.22, 29.20, 23.88, 22.61, 14.12. MS (APCI): m/z (%): 667.2 [M+1]<sup>+</sup>. Elemental analysis calcd (%) for C<sub>41</sub>H<sub>46</sub>S<sub>2</sub>O<sub>4</sub>: C 73.84, H 6.95, S 9.62; found: C 74.33, H 7.54, S 9.58.

## Results and discussion

### Synthesis

The detailed synthetic procedures of FBTO and CzBTO are illustrated in Scheme 1. The precursor of CzBT for preparing CzBTO was synthesized according to the published methods by Klaus Müllen.<sup>[32]</sup> Also, the preparation of FBT was facilitated based on the procedures as the same as the synthesis of CzBT. The key step of this reaction is the intramolecular electrophilic coupling reaction from the corresponding aromatic methyl sulfoxides (3 or 5) by the assistance of triflic acid as the catalyst. In this step, it may enable the regioselective ring cyclization since the transition state of the ring-cyclization reaction was assumed to be the sulfonium salt.<sup>[39,40]</sup> Then, demethylation reaction was carried out by dissolving the sulfonium salt in pyridine. Finally, through the feasible oxidation of CzBT and FBT by m-CPBA in dichloromethane, we can obtain the target products with high yields of 77 % for CzBTO, and 90 % for FBTO, respectively. FBTO can be readily dissolved in common organic solvents, such as toluene, chloroform, tetrahydrofuran (THF) and chlorobenzene; but, CzBTO displays the worse solubility in these solvents, which is possibly ascribing to the higher planarity of CzBTO than FBTO.

## ARTICLE

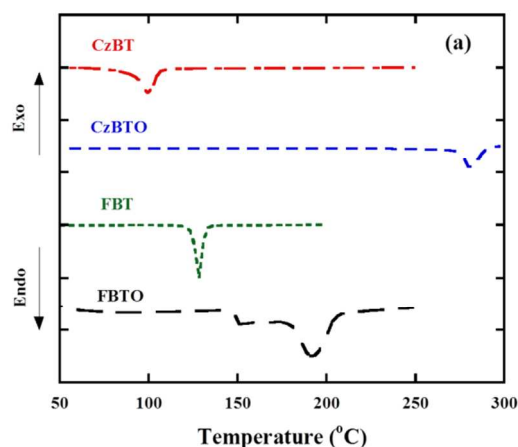


Scheme 1. Synthetic routes of the compounds

## Thermal properties

The thermal properties of CzBT, FBT, CzBTO and FBTO are evaluated by differential scanning calorimetry (DSC) and thermogravimetric analyses (TGA). The corresponding characteristics are shown in Fig. 1, and the related data are summarized in Table 1. It is realized that CzBT and FBT without oxidation on the sulphur, have lower melting point than CzBTO and FBTO, resulting from that the *S,S*-dioxide group in CzBTO and FBTO can improve the rigidity of the rings and enhance the chemical bond energy. The same phenomenon appears in TG analysis in Fig.1(b), in which the CzBTO and FBTO give the much higher decomposition temperatures. Compared with CzBTO, FBTO has a glass transition temperature ( $T_g$ ) of 150 °C, which may be due to a less rigid structure in FBTO. Moreover, it is believed that CzBT and FBT do not exist the  $T_g$  resulting from their lower melting points. From Fig. 1 (a), we can see that the melting points of CzBT, FBT, CzBTO and FBTO are 100, 128, 280 and 191 °C, respectively. Furthermore, TGA measurements illustrate that CzBTO and FBTO show much more thermal stability with the decomposition temperatures ( $T_d$ ) at 5 % weight loss of 406 °C for CzBTO and

416 °C for FBTO, than those of 362 °C for CzBT and 350 °C for FBT, respectively. The outstanding thermal stability of rigid rings in CzBTO and FBTO is essentially positive for the long-time working devices in organic electronics.



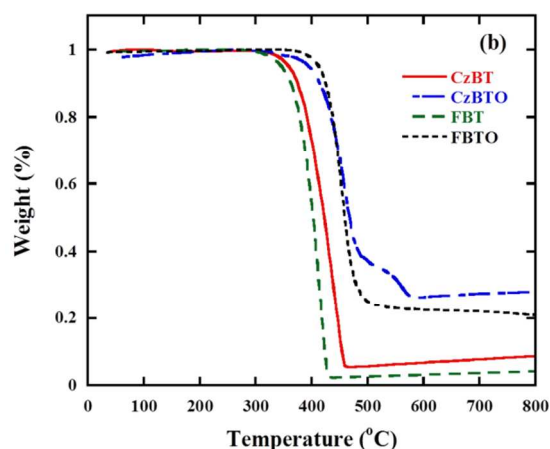


Fig. 1 Differential scanning calorimetry (a) and thermo gravimetric analyses (b) curves of CzBT, CzBTO, FBT and FBTO

Table 1 Thermal properties of the CzBT, CzBTO, FBT and FBTO

| Compounds | $T_g$ (°C) | $T_m$ (°C) | $T_d$ (°C) |
|-----------|------------|------------|------------|
| CzBT      | -          | 100        | 362        |
| CzBTO     | -          | 280        | 406        |
| FBT       | -          | 128        | 350        |
| FBTO      | 150        | 191        | 416        |

### Theoretical computation

In order to understand the frontier molecular orbitals and spectral properties, the density functional theory (DFT) were carried out to analyse these four compounds by using Gaussian 09 at the B3LYP/6-31G(d) level as shown in Fig.2. For FBT and FBTO, the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) are spread out over the entire backbone without distinct localization, indicating that the oxidation has little effect on the spread of the electron density in fluorene based backbones. However, the HOMO state is localized much more intensively on carbazole unit for CzBT than that for CzBTO, which is possibly due to the high electron-donating property of carbazole unit. But, it can be clearly observed that the LUMOs have little change both in CzBT and CZBTO. The HOMO ( $E_{\text{HOMOs}}$ ) and LUMO ( $E_{\text{LUMOs}}$ ) energy levels from CzBT, CzBTO, FBT to FBTO were calculated by DFT studies to be -5.14, -6.17, -5.48, -6.19 eV, and -1.72, -2.24, -1.54, -2.35 eV, respectively. Compared with the CzBT and FBT, the CzBTO and FBTO show much deeper HOMO and LUMO energy levels resulting from the existence of the highly electron-withdrawing sulfonyl group.

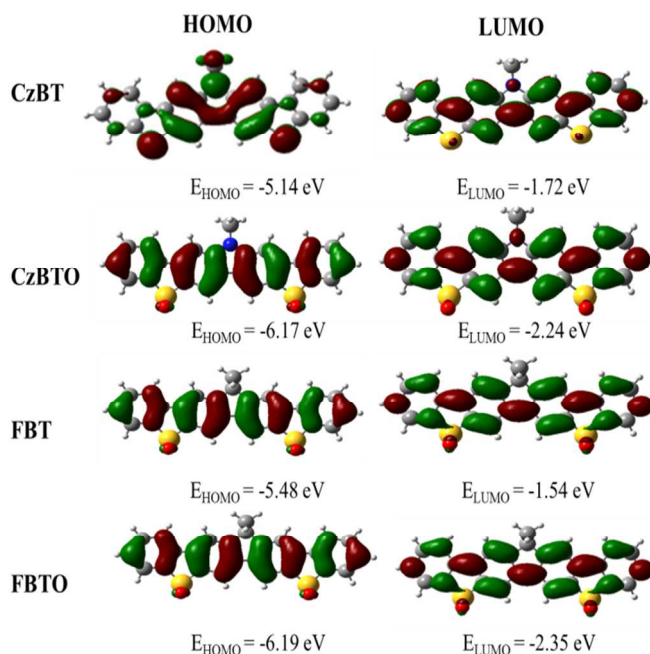
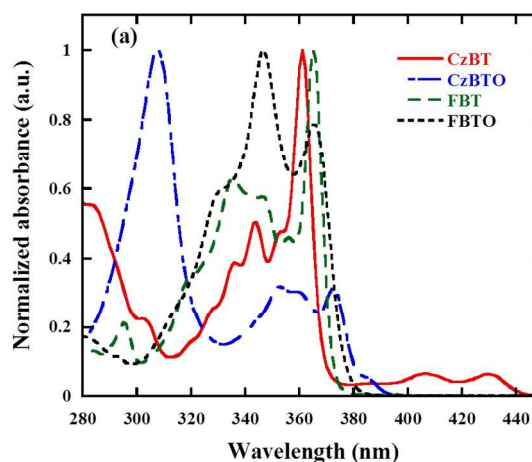


Fig. 2 HOMOs and LUMOs for the CzBT, CzBTO, FBT and FBTO by DFT calculations at the B3LYP/6-31G(d) level.

### Optical properties

UV-vis absorption and photoluminescence spectra (PL) of the CzBT, CzBTO, FBT and FBTO both in solution and in film are shown in Fig.3 and Fig.4, respectively. For the UV-vis spectra of CzBT and CzBTO in dichloromethane in Fig.3(a), the absorption spectra at 344 nm and 361 nm for CzBT as well as 308 nm, 353 nm and 373 nm for CzBTO can be realized to the  $\beta$  band of  $\pi$ - $\pi^*$  transitions of the benzothienocarbazole backbones. Besides, the absorption spectra at longer wavelength from 400 to 450 nm for CzBT and 350 to 400 nm for CzBTO can be illustrated as the  $\alpha$  and/or  $p$  band of the  $\pi$ - $\pi^*$  transitions.<sup>[41]</sup> For the UV-vis absorption of these four compounds in films, they show the regularity as the same as that in solution. Moreover, we can only observe the  $\beta$  band of  $\pi$ - $\pi^*$  transitions in FBT and FBTO, not found the absorption in the longer wavelength.



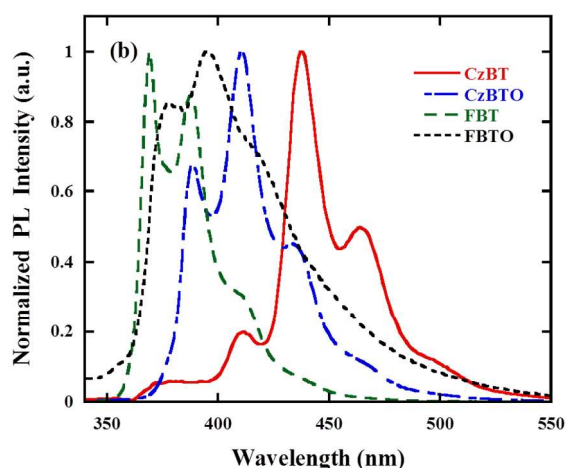


Fig. 3 Ultraviolet-visible(a) and Photoluminescence(b) spectra of fused rings in dichloromethane

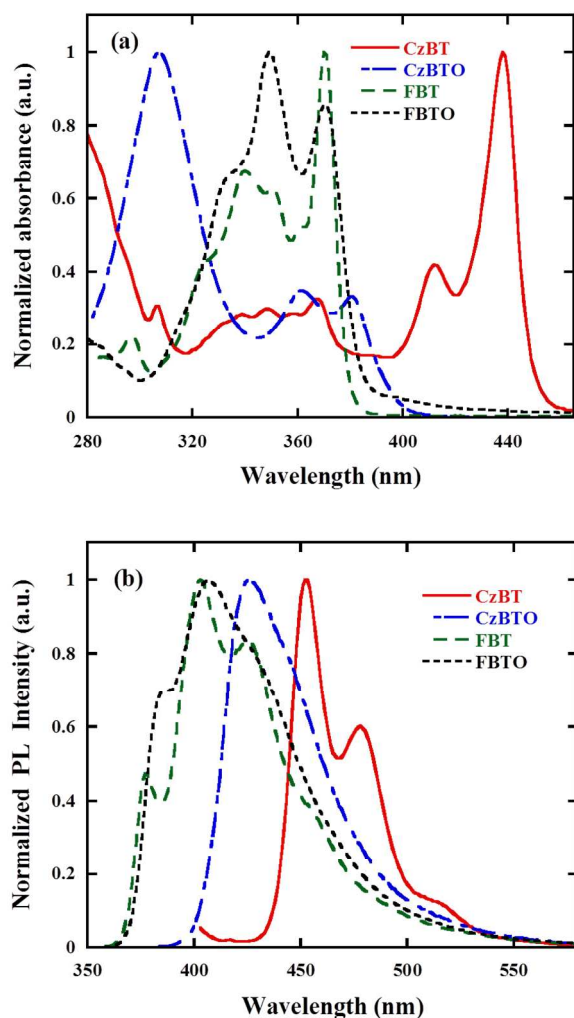


Fig.4 Ultraviolet-visible(a) and Photoluminescence(b) spectra of the CzBT, CzBTO, FBT and FBTO in films

Table 2. Photophysical properties of the CzBT, CzBTO, FBT and FBTO

| Compounds | $\lambda_{\text{abs, DCM}}$<br>(nm) | $\lambda_{\text{abs, film}}$<br>(nm) | $\lambda_{\text{PL, DCM}}$<br>(nm) | $\lambda_{\text{PL, film}}$<br>(nm) | PLQY<br>(%) |
|-----------|-------------------------------------|--------------------------------------|------------------------------------|-------------------------------------|-------------|
| FBT       | 335                                 | 340                                  | 369                                | 377                                 | 17          |
|           | 365                                 | 370                                  | 388                                | 403                                 |             |
|           |                                     |                                      |                                    | 426                                 |             |
| FBTO      | 347                                 | 349                                  | 377                                | 385                                 | 77          |
|           | 365                                 | 370                                  | 395                                | 407                                 |             |
| CzBT      | 344                                 | 368                                  | 412                                | 452                                 | 4           |
|           | 361                                 | 412                                  | 438                                | 478                                 |             |
|           |                                     | 438                                  | 464                                |                                     |             |
| CzBTO     | 308                                 | 307                                  | 388                                | 426                                 | 15          |
|           | 353                                 | 360                                  | 410                                |                                     |             |
|           | 373                                 | 380                                  | 434                                |                                     |             |

In the PL spectra, FBTO is slightly red-shifted in solution compared to the FBT, however, there is little difference both in solution and in film for FBT and FBTO. It is possibly because the fluorene is a weak electron-donating unit which can't support sufficient electron density and leads to the very shared electron cloud in the entire molecular backbones. This phenomenon can be also illustrated by theoretical computation in Fig.2. It can be seen that FBT and FBTO have almost the same distribution of electron cloud in HOMOs and LUMOs. But, there exists much more blue-shift in CzBTO than CzBT. This is ascribing to that the carbazole is a stronger electron-donating unit than fluorene, and through the oxidation the bis(sulfonyl) groups in CzBTO can withdraw the electron cloud to the side benzene rings and decrease the electron density in carbazole core. Based on the observation from the theoretical computation, we also see that the CzBTO shows much more shared electron cloud in HOMO than CzBT, which is in agreement with the results of blue shift in PL spectra.

In order to investigate the PL properties of these four compounds penetratingly, we characterized the PL spectra in different polar solvents from toluene, trichloromethane, DMF to methanol. In Fig.3, it can be illustrated that the solvents do not affect the spectra for CzBT and FBT. But, the PL spectra are broadened obviously for CzBTO and FBTO; especially, the CzBTO shows a large solvatochromism from 409 nm in toluene to 427 nm in methanol. This phenomena is possibly inferred that the strong electron-withdrawing sulfury groups existed in FBTO and CzBTO enable the strongly intermolecular interaction between the polar solvents and FBTO or CzBTO.<sup>[42, 43]</sup> Through characterizing the photoluminescence quantum yield (PLQY) of CzBT, CzBTO, FBT and FBTO, it is illustrated that the oxidized compounds of CzBTO and FBTO can largely improve the PLQY by five times than that of CzBT and FBT in THF solution under the concentration of  $10^{-5}$  mol  $L^{-1}$ . From the PLQY data, FBTO has the PLQY of 77 %, and CzBTO gives the PLQY of 15 %. Here, the FBTO shows the highest PLQY which could be concluded that the intramolecular CT transition from the electron-donating fluorene group to the electron-withdrawing unit may be an important factor in suppressing fluorescence quenching in the solution state.<sup>[44,45]</sup>

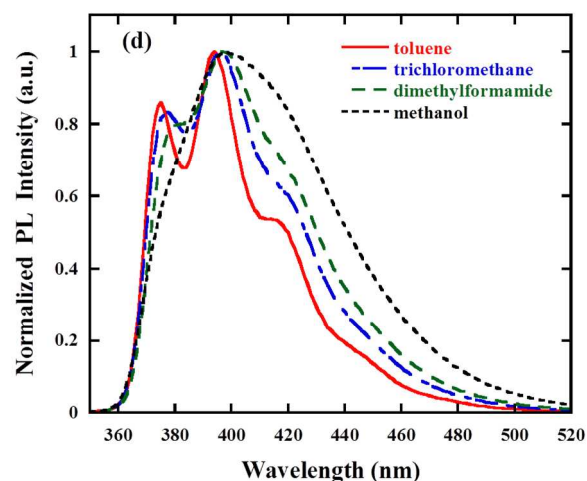
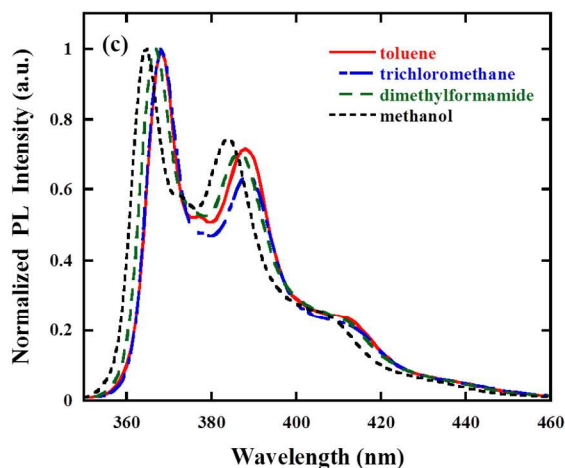
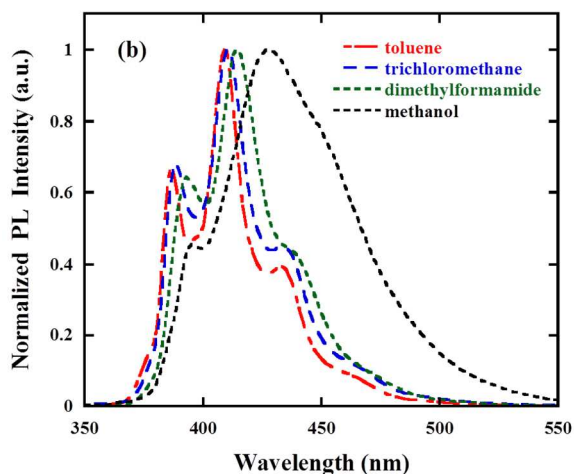
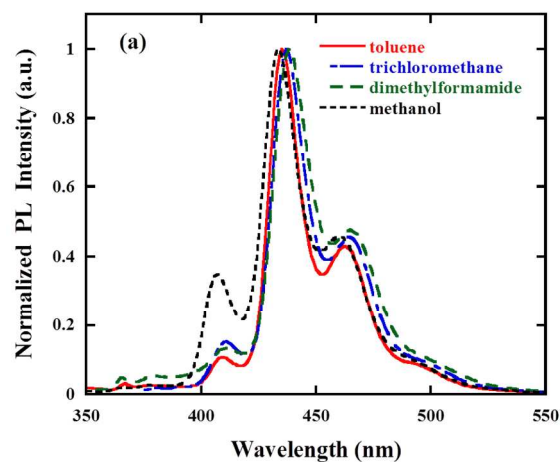


Fig.5 Photoluminescence spectra of the CzBT(a), CzBTO(b), FBT(c) and FBTO(d) in solvents with different polarity

### Electrochemical properties

The electrochemical properties of these four small molecules were examined by cyclic voltammetry (CV) under inert atmosphere with the graphite, platinum wire and Ag/AgCl as the working electrode, counter electrode and reference electrode, respectively. All measurements were carried out in tetrabutyl ammonium hexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ ) solution ( $0.1\text{M}$  in acetonitrile and dichloromethane) with concentration of  $10^{-5}\text{ mol L}^{-1}$  for the CzBT, CzBTO, FBT and FBTO each, at a scan rate of  $50\text{ mV s}^{-1}$ . The corresponding CV curves are shown in Fig.6, and the detailed data are summarized in Table 3 and Fig.7. The  $E_{\text{HOMO}}$ s and  $E_{\text{LUMO}}$ s are calculated according to the empirical formula of  $E_{\text{HOMO}} = -e(E_{\text{ox}} + 4.8 - E_{1/2, (\text{Fc}/\text{Fc}^+)})$  and  $E_{\text{LUMO}} = -e(E_{\text{red}} + 4.8 - E_{1/2, (\text{Fc}/\text{Fc}^+)})$ , where  $E_{\text{ox}}$  and  $E_{\text{red}}$  are the onset of the oxidation and reduction potential relative to Ag/AgCl, respectively. It can be well illustrated that FBTO and CzBTO have lower HOMO energy levels by  $0.6\text{ eV}$  than the FBT and CzBT, indicating that the existence of sulfonyl can largely decrease the HOMO energy levels. Similarly, they have the same regularity in LUMO energy levels. The HOMOs and LUMOs of CzBT, CzBTO, FBT and FBTO, are  $-5.65$ ,  $-6.20$ ,  $-5.41$ ,  $-6.04\text{ eV}$  and  $-2.21$ ,  $-2.80$ ,  $-2.38$ ,  $-2.37\text{ eV}$ , respectively. It shows that FBTO and CzBTO have deeper HOMOs; and FBTO and FBT have almost the similar band gaps ( $E_{\text{g}}$ ) while CzBTO has larger  $E_{\text{g}}$  than CzBT. These are coincident with the results from the UV, PL spectra and theoretical calculation.



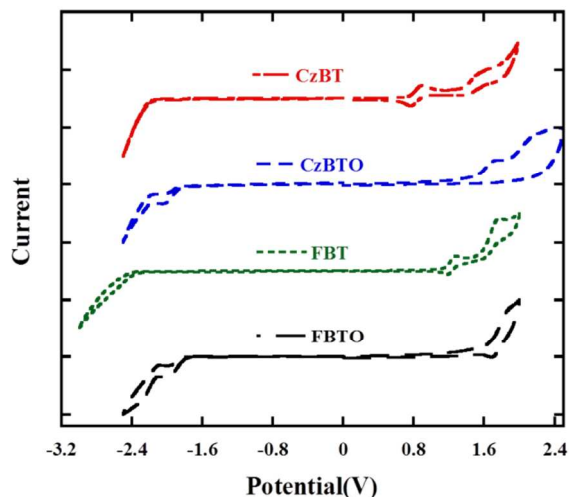


Fig.6 Cyclic voltammograms curves of the CzBT, CzBTO, FBT and FBTO in acetonitrile and dichloromethane electrolyte solution with  $n\text{-Bu}_4\text{NPF}_6$  (0.1 M).

Table 3 Electrochemical properties of the CzBT, CzBTO, FBT and FBTO.

| Compounds | $E_{\text{ox}}$ (V) | $E_{\text{red}}$ (V) | $E_{\text{HOMO}}$ (eV) | $E_{\text{LUMO}}$ (eV) | $E_{\text{g}}^{\text{cv}}$ (eV) | $E_{\text{g}}^{\text{opt}}$ (eV) |
|-----------|---------------------|----------------------|------------------------|------------------------|---------------------------------|----------------------------------|
| CzBT      | 0.82                | -2.21                | -5.41                  | -2.38                  | 3.03                            | 2.81                             |
| CzBTO     | 1.45                | -1.85                | -6.04                  | -2.74                  | 3.30                            | 3.16                             |
| FBT       | 1.06                | -2.38                | -5.65                  | -2.21                  | 3.44                            | 3.27                             |
| FBTO      | 1.61                | -1.79                | -6.20                  | -2.80                  | 3.40                            | 3.23                             |

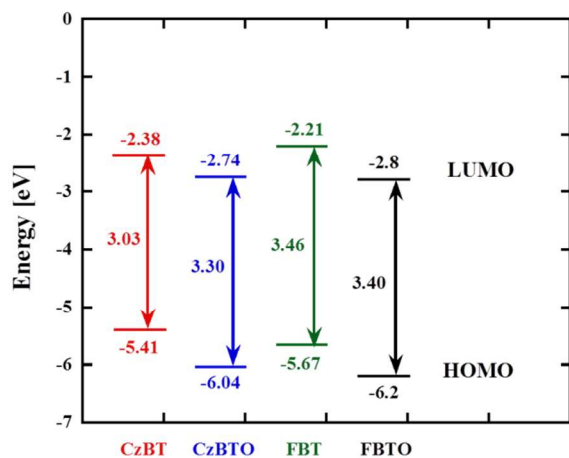


Fig.7 Energy levels diagram for the CzBT, CzBTO, FBT and FBTO

## Conclusions

In summary, we have reported the synthesis and properties of two symmetrically linear PACs with *S,S*-dioxide benzothiophene fused seven rings, FBTO and CzBTO. These two compounds show high melting points and decomposition temperatures which mean that they have the very highly

thermal stability. By the DFT, photophysical and electrochemical studies, they suggest that FBTO and CzBTO have much deeper HOMO energy levels than most of the cyclized aromatic compounds. Also, the PL spectra of FBTO and CzBTO become broad and red-shifted when increase the polarity of the solvents, which is due to the formation of strongly intermolecular interaction between the solvents and the FBTO or CzBTO. Through the characterization of PLQY, FBTO shows the highest PLQY of 77 %. This high PLQY value indicates that FBTO will be a versatile candidate for constructing high-efficiency light-emitting materials. Furthermore, the CzBT, CzBTO, FBT and FBTO may be the good constructing units in organic photovoltaic cells (OPVs) and OFETs due to their largely planar structures.

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## Notes and references

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