

## Synthesis, crystal structure and spectroscopic properties of an unsymmetrical compound with carbazole and benzothiadiazole units

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**Abstract**—An unsymmetrical organic compound with carbazole (Cz) as donor and benzothiadiazole (BTD) as acceptor (D- $\pi$ -A- $\pi^*$ -D\*) was designed and synthesized via simple Heck reaction. The unique crystal structure of Cz–BTD–Cz\* shows a ladder-like packing mode. A two molecule pair stacks parallelly with each other in each packing unit. In each cell, one Cz moiety is connected with BTD by vinylene bond in same plane. However, the other Cz group is connected to BTD by a one-end vinyl bond in almost perpendicular position to the coplanar part of the molecule. The shortest intermolecular plane distance is  $3.48 \pm 0.1$  Å. The photophysical properties of Cz–BTD–Cz\* in solution and in bulky crystalline powder state were studied. In bulk crystalline powder state, it has a red-shifted emission band peaked at 609 nm relative to that in solution, and the FWHM was reduced to only 58 nm. Electrochemical properties were also investigated.

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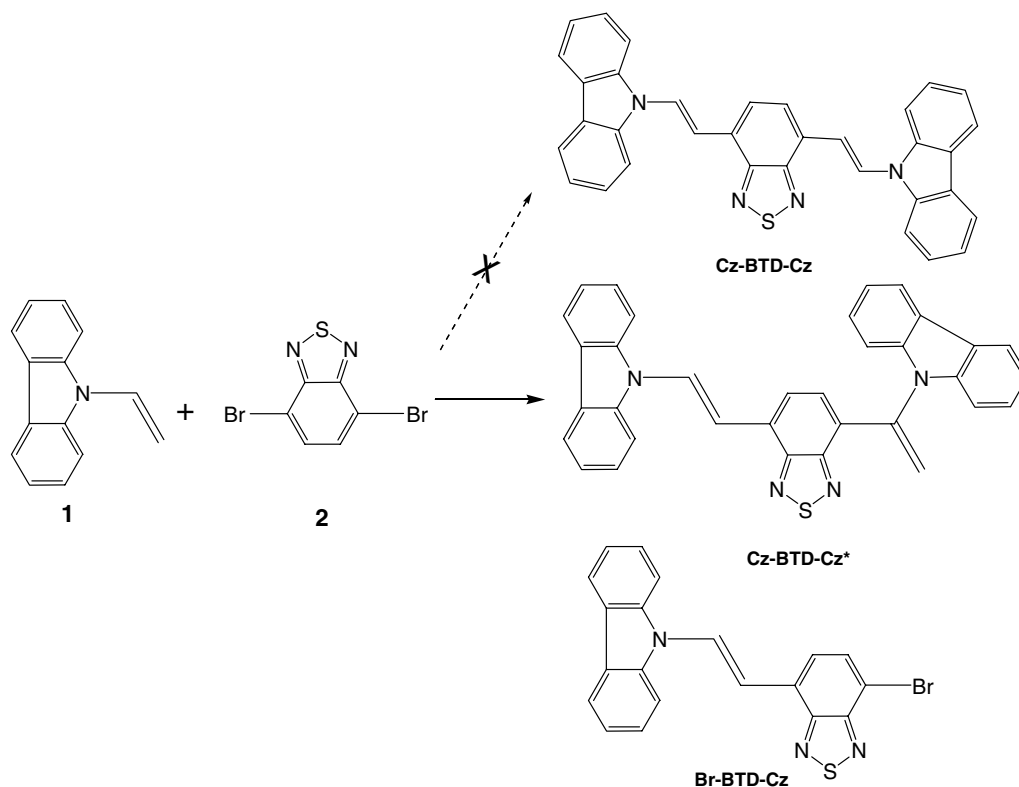
Intramolecular charge transfer state can be used to design low energy-gap optical or electronic functional organic materials.<sup>1</sup> Both triphenylamine<sup>2</sup> and carbazole<sup>3</sup> are ideal electron donors with high carrier mobility, high thermal and photochemical stability, and these properties are commonly used as hole-transporting materials or light emitting materials for balanced charge injection and transport in LED devices. On the other hand, benzothiadiazole<sup>4</sup> is an excellent electron accepting chromophore, which has often been used for constructing materials for red light emission,<sup>5</sup> photovoltaic cell<sup>6</sup> and nonlinear optical materials<sup>7</sup>, etc.<sup>8</sup> Here, we report the design and synthesis of a new bipolar and unsymmetrical compound consisting of carbazole (Cz) and benzothiadiazole (BTD).<sup>9</sup> In each side of the molecule, vinyl bond was adopted as bridge of Cz and BTD to

increase the coplanarity and rigidity of the molecule, and so as to facilitate the intramolecular charge transfer. The bipolar molecule with push–pull structure is beneficial for balanced injection of holes and electrons, and hence to increase the performance of the LED device. Unsymmetrical structures are of great interest both in synthesis and property investigation. Most of the reported bipolar compounds synthesized via Heck reaction are symmetrical in structure, while unsymmetrical compounds with low energy gap are less frequent. Here we report the study on the synthesis,<sup>13</sup> crystal structure and photophysical properties of a structurally unsymmetrical compound (Cz–BTD–Cz\*, see [Scheme 1](#)).

The synthesis of Cz–BTD–Cz\* was carried out via palladium catalyzed coupling reaction of 9-vinyl carbazole (compound **1**) and 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (compound **2**) with DMF as solvent and *n*-Bu<sub>4</sub>NBr as phase transfer catalyst at 100 °C ([Scheme 1](#)). The main product is a red-black mixture possibly resulting from self-condensation of dibromo-benzothiadiazole. Both single-carbazole substituted (with bromo group,

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Scheme 1. Synthetic route for Cz-BTD-Cz\* and Br-BTD-Cz.

named Br-BTD-Cz) and double substituted products (Cz-BTD-Cz\*) were separated. The yields for both compounds are relatively low after purification. We found that prolonged reaction time and/or elevated temperature results in decomposition of vinyl carbazole and a more complicated reaction mixture.

Both Br-BTD-Cz and Cz-BTD-Cz\* were characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, EI and HRMS. The formation of Cz-BTD-Cz\* could be easily monitored with  $^1\text{H}$  NMR by the appearance of one singlet peak at 6.10 ppm and one doublet at 6.83 ppm corresponding to two terminal vinylene protons, respectively. As compared, *N*-vinyl carbazole has two doublet peaks along 5.1–5.5 ppm. There are no terminal vinyl protons observed in Br-BTD-Cz, and two vinyl protons neighboring carbazole and benzothiadiazole were found at around 7.38–7.46 ppm. In addition, HRMS data clearly show a mother peak of the target molecule.

X-ray diffraction crystal analysis further supports a structure of unsymmetrical Cz-BTD-Cz\*, but not a symmetric Cz-BTD-Cz. Herein, we suppose that during the reaction of the first step the terminal carbon atom in vinyl Cz units should be connected directly with dibromo-benzothiadiazole via normal Heck reaction to afford Br-BTD-Cz. After this, oxidative addition would take place between Pd catalyst and C-Br bond in Br-BTD-Cz and a  $\pi$  complex between vinyl carbazole and Pd catalyst will be formed subsequently. Generally,  $\sigma$ -complex will be formed via a linkage of the terminal carbon of vinyl units and Pd intermediate. While for Cz-BTD-Cz\*, the  $\sigma$ -complex should be produced via

the 7-position of benzothiadiazole and the  $\beta$ -carbon of vinyl units. As a result, after reductive elimination of Pd complex, the unsymmetrical compound could be obtained (Supplementary data). The detailed mechanism of why the unfavorable condition for the formation of symmetric compounds exist is still not clear. Corresponding research is currently ongoing in our laboratories.

As shown in Figure 1, the molecule of Br-BTD-Cz exhibits a coplanar conformation from its crystal structure, and it tends to form perpendicular molecular pairs packing in the crystal cell.

Cz-BTD-Cz\* single crystal shows a different packing mode (see Fig. 2). The molecule is composed of two parts. In each molecule, one Cz is connected with BTD by vinylene bond to form a coplanar part. However, another Cz is connected to BTD by a one-end vinyl bond in an almost perpendicular position to the coplanar part (for simplicity, the carbazole deviated from molecular plane was named  $\beta$ -Cz, the other named  $\alpha$ -Cz as indicated). In each cell unit, a molecular pair has parallel packing. Dihedral angle defined by  $\beta$ -Cz and the molecular planar part is  $108.3^\circ$ . Packing mode of Cz-BTD-Cz\* demonstrates a ladder-like structure. The interplanar distance of the two  $\beta$ -Cz is  $10.48 \pm 0.1 \text{ \AA}$ . The interplanar distance between  $\alpha$ -Cz and benzothiadiazole from neighbor molecules is  $3.48 \pm 0.1 \text{ \AA}$ . It is within the distance of  $\pi$ - $\pi$  stacking interaction. Therefore, it is interesting to note that several interactions must coexist in its crystal state. First, there is intramolecular charge transfer between carba-

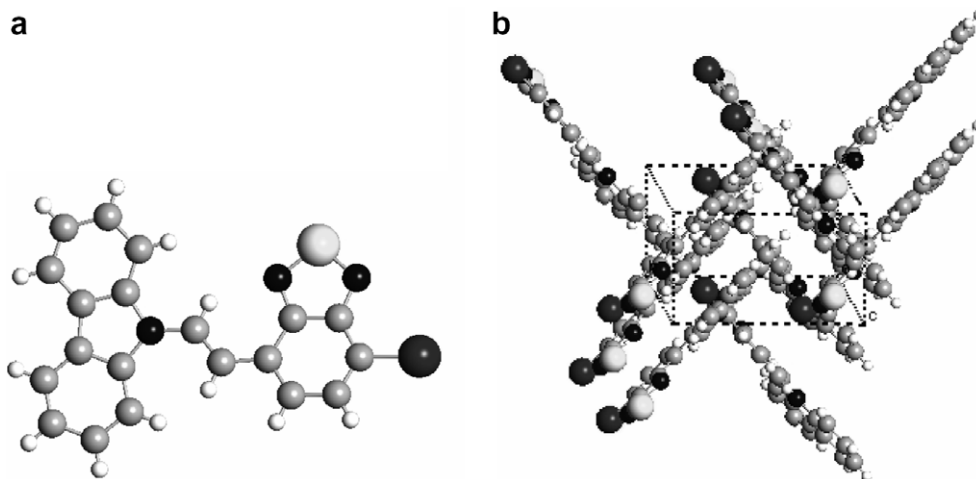


Figure 1. Single crystal structure and packing modes of Br-BTD-Cz.

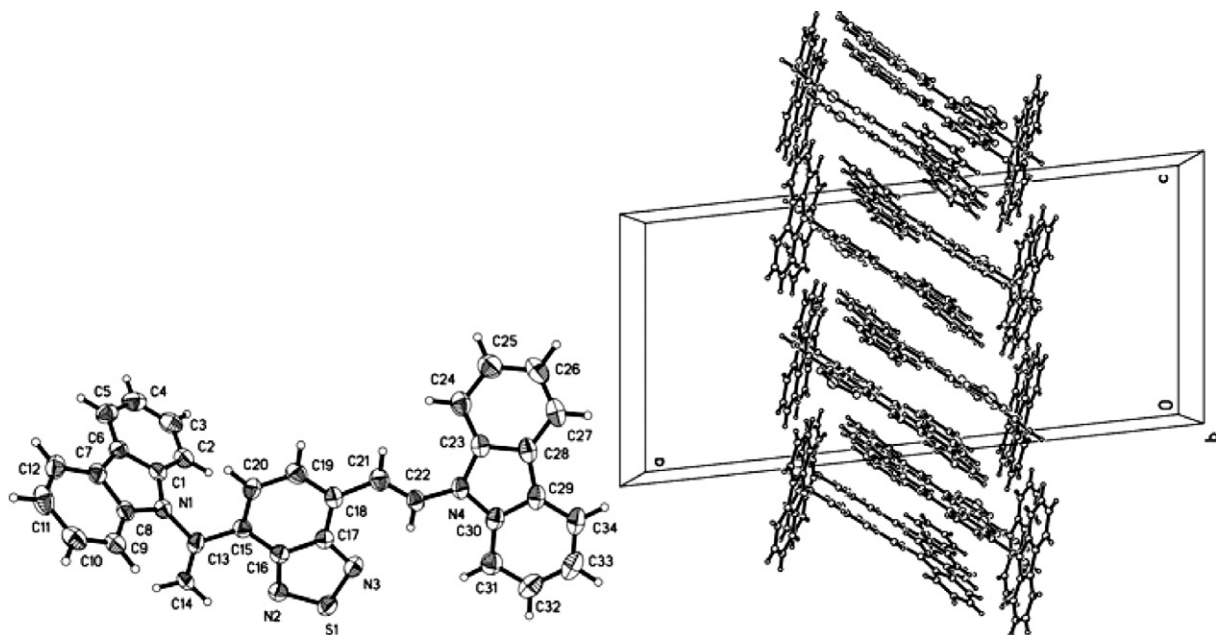
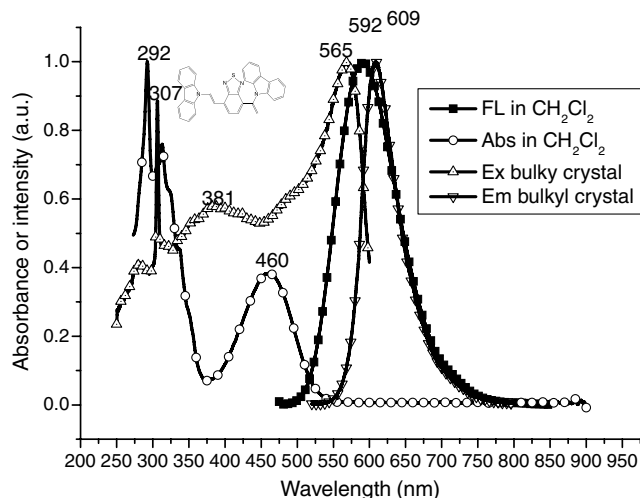


Figure 2. Single crystal and packing modes of Cz-BTD-Cz\*.

zole and benzothiadiazole in one molecule. Second,  $\pi$ - $\pi$  stacking interaction and weak charge transfer interaction are present between the planar parts of the neighbor molecules. This unique structure will lead to its special optical or electronic properties.

Cz-BTD-Cz\* shows three absorption peaks in  $\text{CH}_2\text{Cl}_2$ . Two peaks below 370 nm could be assigned to  $\pi$ - $\pi^*$  transition of carbazole and BTD. Another peak at 457 nm (the lowest energy level to get singlet excited state) may come from the charge transfer band from carbazole to thiodiazole moieties.<sup>12</sup> Only one emission band peaked at about 592 nm with a full width at half maximum (FWHM) of 98 nm was observed in  $\text{CH}_2\text{Cl}_2$ . It must result from the intramolecular charge transfer state. The Stokes shift in solution is as large as 129 nm suggesting a significant conformation transition between its excited state and the ground state. Both excitation

and emission spectra measured from the bulky crystalline powder exhibit a bathochromic shift relative to that in  $\text{CH}_2\text{Cl}_2$  (Fig. 3). It is interesting that in bulky crystal state the FWHM of its emission spectrum was reduced to 58 nm. This value is quite small and different from reported results, such as imidazole and PPV oligomer compounds.<sup>10,11</sup> Another interesting result is the absorption peak measured from solid state which was as large as 105 nm red shifted compared with that in solution, and the Stokes shift in solid state was decreased to only 44 nm. Special luminescence from the solid state is strongly subjected to packing effects including molecular conformation and electronic interaction between the molecules.<sup>11</sup> So according to Cz-BTD-Cz\* crystal structure, the special unsymmetrical conformation, intramolecular charge transfer and intermolecular  $\pi$ - $\pi$  interactions result in different spectroscopic properties in the bulk crystal powder state. A possible

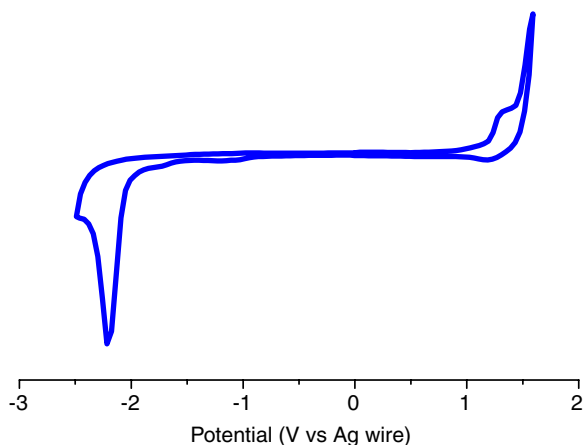


**Figure 3.** Absorption (or excitation) and emission spectra of Cz-BTD-Cz\* in  $\text{CH}_2\text{Cl}_2$  and bulky crystal powder state.

reason for the narrowing spectrum may be the reabsorption in solid state attributed from the extended absorption band which was observed in excitation spectrum (Fig. 3).

Electrochemical properties of Cz-BTD-Cz\* were characterized by cyclic voltammetry (CV) method. The oxidation and reduction potential were determined to be 1.18 and  $-1.98$  V, respectively. Corresponding HOMO and LUMO were estimated to be 5.57 and 2.92 eV with an energy gap of 2.65 eV (see Fig. 4).

In conclusion, a new unsymmetrical compound with carbazole as donor and benzothiadiazole as acceptor was synthesized via palladium catalyst Heck reaction and characterized by NMR, HRMS and X-ray crystallography. The crystal structure of Cz-BTD-Cz\* discloses a ladder arrangement. FWHM of its emission spectrum in bulky crystal powder is only 58 nm relative to 98 nm in  $\text{CH}_2\text{Cl}_2$ . Stokes shift decreased to only 44 nm indicated a rigid and small conformation transition from ground state to excited state in solid state. Coexistence of special unsymmetrical structure, intramolecular charge transfer, intermolecular  $\pi$ - $\pi$  stacking



**Figure 4.** CV of Cz-BTD-Cz\*.

interactions and intermolecular weak charge transfer may be responsible for its special spectroscopic properties. Based on all mentioned above, it is expected Cz-BTD-Cz\* will be very useful in organic functional materials, such as light emitting diode, FET, and so on. Moreover, for its narrowing emission in solid state one may find applications in organic-crystalline based optical pumped lasers.

### Acknowledgements

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### Supplementary data

Crystallographic data (excluding structure factors) for the structures of Br-BTD-Cz and Cz-BTD-Cz in this Letter have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 627088 and 627089. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 0 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

The possible reaction mechanism (Scheme 1S) and spectroscopy of Br-BTD-Cz in  $\text{CH}_2\text{Cl}_2$  are also given as supporting information (Fig. 1S).  $^1\text{H}$  NMR of both Br-BTD-Cz and Cz-BTD-Cz\* are also presented.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.04.063.

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13. *Preparation of (Cz-BTD-Cz\*) and (Br-BTD-Cz):* To a three-necked flask connected with condenser and balloon were added compound **1** (0.5 g, 2.59 mmol), compound **2** (1.67 g, 5.69 mmol), Pd(OAc)<sub>2</sub> (58 mg, 0.259 mmol), *n*-Bu<sub>4</sub>NBr (334 mg), NaOAc (2.3 g, 25.9 mmol). Then 40 mL of freshly distilled and degassed DMF was injected by syringe. The solution was heated to 100 °C and kept overnight. After being cooled to room temperature, the solution was poured into 100 mL of water. The solid was filtered, dissolved in CH<sub>2</sub>Cl<sub>2</sub>, and dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure. Then the mixture was subjected to column separation (SiO<sub>2</sub>, light petroleum ether: CH<sub>2</sub>Cl<sub>2</sub> = 2:1, v/v). Single crystal suitable for X-ray crystallography determination was cultivated in a mixed solvent of hexane/CH<sub>2</sub>Cl<sub>2</sub>. Fresh red rhombus crystal was obtained after three days. Cz-BTD-Cz\*, orange-red solid. Yield, 25%. mp 230 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 6.1 (s, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 7.3–7.43 (multi, 9H), 7.47 (s, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.84 (d, *J* = 8.3 Hz, 2H), 8.08 (d, *J* = 7.2 Hz, 2H), 8.17 (d, *J* = 7.6 Hz, 2H), 9.02 (d, *J* = 14 Hz, 2H); <sup>13</sup>C NMR: 110.42, 111.16, 119.43, 119.89, 120.36, 121.14, 121.43, 123.47, 124.68, 125.50, 125.83, 125.86, 126.03, 126.56, 128.31, 129.21, 130.68, 138.24, 139.33, 141.03, 153.45, 153.64. EI-MS: 518 (M<sup>+</sup>, 100%). HRMS: C<sub>34</sub>H<sub>22</sub>N<sub>4</sub>S, calcd mass 518.1565; found, 518.1564 (M<sup>+</sup>, 100%).
- The crystal data for Cz-BTD-Cz\*: C<sub>34</sub>H<sub>22</sub>N<sub>4</sub>S, Monoclinic, C2/c, cell parameters are *a* = 33.348(4) Å, *b* = 9.7846(12) Å, *c* = 15.5742(19) Å, α = 90°, β = 96.212(2)°, γ = 90°, *V* = 5051.9(11) Å<sup>3</sup>, *z* = 8, *Mr* = 518.62, *D<sub>c</sub>* = 1.364(6) g/cm<sup>3</sup>, *F*(000) = 2160, μ = 0.161 mm<sup>-1</sup>.
- Br-BTD-Cz, Yield, 8%. M.p. 137 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): 7.29–7.33 (m, 3H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.89 (d, *J* = 6.5 Hz, 2H), 8.09 (d, *J* = 7.7 Hz, 2H), 9.01 (d, *J* = 14.5 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 300 MHz): 112.49, 113.76, 121.77, 122.29, 126.01, 127.82, 127.93, 128.42, 130.61, 130.78, 133.78, 140.599, 153.56, 155.30. EI-MS: 406 (M<sup>+</sup>, 100%). HRMS: C<sub>20</sub>H<sub>12</sub>N<sub>3</sub>SBr<sup>79</sup>, calcd mass 404.9935; found, 404.9939. C<sub>20</sub>H<sub>12</sub>N<sub>3</sub>SBr<sup>81</sup>, calcd mass 406.9915; found, 406.9920. The crystal data for Br-BTD-Cz: C<sub>20</sub>H<sub>12</sub>BrN<sub>3</sub>S, Monoclinic, P2(1), cell parameters are *a* = 5.2594(10) Å, *b* = 9.1524(17) Å, *c* = 17.052(3) Å, α = 90°, β = 92.694(3)°, γ = 90°, *V* = 819.9(3) Å<sup>3</sup>, *z* = 4, *Mr* = 406.30, *D<sub>c</sub>* = 1.6458(6) g/cm<sup>3</sup>, *F*(000) = 408.0, μ = 2.641 mm<sup>-1</sup>.