



Synthesis, photophysical and electrochemical properties of a carbazole dimer-based derivative with benzothiazole units

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ABSTRACT

A novel A- π -D- π -D- π -A type compound, containing two benzothiazole rings as electron acceptors and two N-ethylcarbazole groups as electron donors, (E)-1,2-bis(3-(benzothiazol-2-yl)-9-ethylcarbazol-6-yl)ethene (BBECE), was synthesized and characterized by elemental analysis, NMR, MS and thermogravimetric analysis. Electrochemical property of compound BBECE was studied by cyclic voltammetry analysis. The absorption and emission spectra of BBECE was experimentally determined in several solvents and simultaneously computed using density functional theory (DFT) and time-dependent density functional theory (TDDFT). The calculated absorption and emission wavelengths are coincident with the measured data. The lowest-lying absorption spectra can be mainly attributed to intramolecular charge transfer (ICT), and the fluorescence spectra can be mainly described as originating from an excited state with intramolecular charge transfer (ICT) character. The molecular orbitals (HOMO and LUMO), the ionization potential (IP), the electron affinity (EA) and reorganization energy of compound BBECE were also investigated using density functional theory (DFT). The results show that compound BBECE exhibited excellent thermal stability and electrochemical stability as well as high fluorescence quantum yield, indicating its potential applications as an excellent optoelectronic material in optical fields.

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1. Introduction

Organic light-emitting diodes (OLEDs) have attracted a great deal of attention due to their potential use in low-cost, full color flat panel displays [1,2]. Tang and Van Slyke demonstrated that the use of hole transporting layers (HTLs) for hole injection from the anodes into the light-emitting layer provides the significant improvement of the OLED device performance [3]. Since then, many aspects related to OLEDs research, ranging from new materials design and synthesis to OLEDs fabrication technique, have been carried out [4,5].

In order to improve the efficiency and stability of OLEDs, great efforts have been made to develop high-performance materials with desirable properties [6–8]. There are many kinds of the high-performance materials; carbazole derivatives are one type of

them. Carbazole derivatives have high thermal stability and excellent photophysical property, they are effective hole-transporting materials and have great potential applications in many fields. Thus, the design and synthesis of new carbazole derivatives with high-performance constitutes a very active area of research [9–18].

Recently, a series of novel carbazole derivatives with D- π -A structures has been synthesized as efficient emitting materials in organic devices. Many of these derivatives possess one or more benzothiazole rings as the electron acceptors (A) and one or more carbazole rings as the electron donor (D). They have large electron delocalization lengths and are able to be experienced intramolecular charge transfer (ICT) from the electron donors to the electron acceptors of the molecule. Their photophysical properties have also been investigated in detail [19–22].

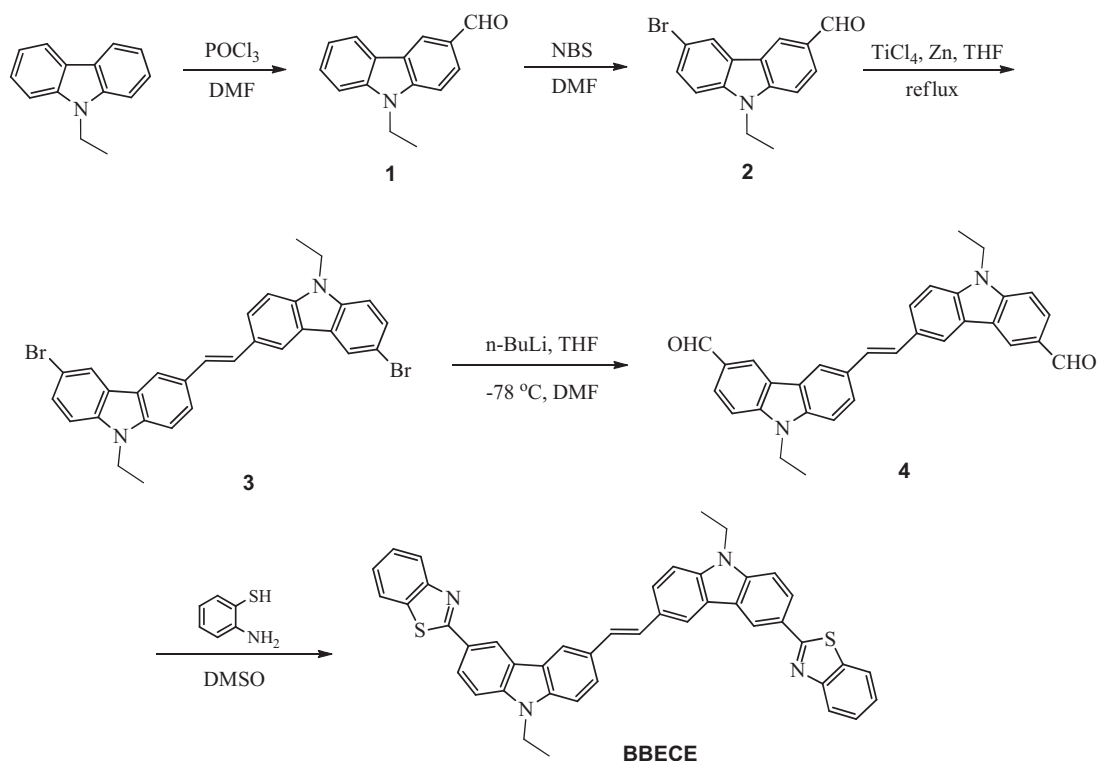
In view of this type of carbazole derivatives have great potential applications, the molecular design and synthesis of novel carbazole derivatives with D- π -A structure need to be further developed by the structural modification in order to improve the properties and establish the relation between structures and properties.

In this paper, a novel carbazole derivative, (E)-1,2-bis(3-(benzothiazol-2-yl)-9-ethylcarbazol-6-yl)ethene (BBECE), is synthesized using a carbazole dimer as the rigid core with two benzothiazole groups linked to the core through the 3,3' positions.

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Scheme 1. The synthetic route of compound BBECE.

The intermediate, namely (E)-1,2-bis(3-bromo-9-ethylcarbazol-6-yl)ethene (**3**), is obtained by incorporating two carbazole moieties with McMurry coupling reaction. The novel carbazole derivative, a new A- π -D- π -D- π -A type molecule, combines the excellent properties of carbazole and benzothiazole, containing a large π -conjugated coplanar system and two electron-donor carbazole units (D) as well as two electron-acceptor benzothiazole units (A). The synthetic details are illustrated in Scheme 1. The structure of the compound BBECE was characterized by elemental analysis, ^1H NMR, ^{13}C NMR and MS. Its optical properties were studied by UV-vis and FL spectra, electrochemical properties were studied by cyclic voltammetry analysis and thermal property was studied by thermogravimetric analysis. With the aim of gaining a deeper insight into electronic structure, charge injection and transport properties as well as the electronic absorption and emission spectra, theoretical calculation of BBECE have been carried out. The results will increase the knowledge to design and synthesize novel carbazole derivatives with excellent photophysical properties.

2. Experimental

2.1. Reagents

Carbazole and 2-aminothiophenol were purchased from Alfa Aesar and used without further purification, and other reagents were purchased from Beijing Chemical Plants. DMF, DMSO, THF, etc. were freshly distilled according to standard methods used before. All reactions were carried out under a nitrogen atmosphere by using Schlenk techniques.

2.2. Apparatus

Melting points were determined on an X-5 melting point detector and uncorrected. All NMR spectra were measured on a Bruker Avance 600 MHz NMR spectrometer with CDCl_3 or DMSO-d_6 as

solvents. Thermogravimetric analyses were performed with a TGA 2050 thermogravimetric analyzer under nitrogen atmosphere with a heating rate of $20^\circ\text{C}/\text{min}$ from room temperature to 600°C . Elemental analyses were performed with an Elementar Analysensysteme (GmbH). Mass spectra were recorded with the LC-MS system consisted of a Waters 1525 pump and a Micromass ZQ4000 single quadrupole mass spectrometer detector. Cyclic voltammetry experiments were performed with a CHI-600C electrochemical analyzer, the measurements were carried out with a conventional three-electrode configuration consisting of a glassy carbon working electrode, a platinum-disk auxiliary electrode and a Ag/AgCl reference electrode, and the scan speed is 50 mV/s . UV-vis spectra were obtained on a Shimadzu UV-2450 spectrophotometer. Fluorescence spectra were obtained on an F-4500 fluorophotometer. Excitation and emission slit widths were both set at 2.5 nm . Fluorescence quantum yields were determined using a standard actinometry method. Quinine sulfate was used in the actinometer with a known fluorescence quantum yield of 0.55 in 0.1 M ; the sample was excited at 350 nm . The fluorescence decay curves were recorded with Time-Correlated Single Photon Counting (TCSPC) technique using a commercially available Edinburgh Instruments. All measurements were performed at room temperature (20°C).

2.3. Synthesis of BBECE

2.3.1. 9-Ethylcarbazole-3-carbaldehyde (**1**)

9-Ethylcarbazole-3-carbaldehyde (**1**) was synthesized according to literature procedures [23]. M.p.: $89.7\text{--}90.5^\circ\text{C}$. ^1H NMR (600 MHz, CDCl_3) δ (ppm): 10.09 (s, 1H), 8.61 (d, $J = 1.5\text{ Hz}$, 1H), 8.16 (d, $J = 7.8\text{ Hz}$, 1H), 8.01 (dd, $J = 8.5, 1.6\text{ Hz}$, 1H), 7.54 (ddd, $J = 8.3, 7.2, 1.2\text{ Hz}$, 1H), 7.47 (t, $J = 7.9\text{ Hz}$, 2H), 7.35–7.31 (m, 1H), 4.41 (q, $J = 7.3\text{ Hz}$, 2H), 1.47 (t, $J = 7.3\text{ Hz}$, 3H).

2.3.2. 6-Bromo-9-ethylcarbazole-3-carbaldehyde (**2**)

9-Ethylcarbazole-3-carbaldehyde (**1**) (10 g, 44.8 mmol) was dissolved in DMF (150 mL) and the solution was cooled in an ice

bath. A solution of NBS (8.77 g, 49.3 mmol) in DMF (50 mL) was added dropwise. The reaction mixture was allowed to stir for 12 h at room temperature. Then, the mixture poured into ice water, and the white precipitate was collected by filtration to afford 6-bromo-9-ethylcarbazole-3-carbaldehyde (**2**). Yield: 82%. M.p.: 131.4–132.2 °C. ¹H NMR (600 MHz, CDCl₃) δ (ppm): 10.09 (s, 1H), 8.53 (d, *J* = 1.2 Hz, 1H), 8.25 (d, *J* = 1.9 Hz, 1H), 8.03 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.61 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.33 (d, *J* = 8.6 Hz, 1H), 4.38 (q, *J* = 7.3 Hz, 2H), 1.46 (t, *J* = 7.3 Hz, 3H).

2.3.3. (E)-1,2-bis(3-bromo-9-ethylcarbazol-6-yl)ethene (**3**)

6-Bromo-9-ethylcarbazole-3-carbaldehyde (**2**) (10 g, 33.1 mmol) and Zn powder (8.656 g, 132.4 mmol) were suspended in anhydrous THF (200 mL) under N₂. Titanium(IV) chloride (7.28 mL, 66.2 mmol) was added dropwise to the reaction mixture at –78 °C. Then, the cooling bath was removed, and the mixture was refluxed for 10 h. After cooling to room temperature, ice water (200 mL) was added and the reaction mixture was stirred for a further 0.5 h. The mixture was extracted with CH₂Cl₂ and the combined organic extracts were dried over anhydrous MgSO₄, filtered, and concentrated on vacuum. The residue was purified by flash chromatography on silica gel (CH₂Cl₂/hexane) to afford (E)-1,2-bis(3-bromo-9-ethylcarbazol-6-yl)ethene (**3**). Yield: 75%. M.p.: 251.2–52.5 °C. ¹H NMR (600 MHz, CDCl₃) δ (ppm): 8.24 (d, *J* = 1.9 Hz, 2H), 8.19 (s, 2H), 7.73 (dd, *J* = 8.5, 1.1 Hz, 2H), 7.54 (dd, *J* = 8.6, 1.8 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.32 (s, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 4.34 (q, *J* = 7.2 Hz, 4H), 1.44 (t, *J* = 7.3 Hz, 6H).

2.3.4. (E)-1,2-bis(3-formyl-9-ethylcarbazol-6-yl)ethene (**4**)

3 (1.72 g, 3 mmol) was dissolved in anhydrous THF (40 mL) under N₂ at –78 °C. To this solution, *n*-BuLi (3.3 mmol, 1.6 M solution in hexanes) was injected. The resulting mixture was allowed to stir for 4 h. Then dry DMF (0.31 mL, 4 mmol) was added dropwise and the reaction was stirred at room temperature for 12 h. The mixture was quenched with aqueous NH₄Cl and extracted with CH₂Cl₂. The organic layer was washed with water and dried over anhydrous MgSO₄. After the solvents were removed, the crude product was recrystallized from MeOH to yield (E)-1,2-bis(3-formyl-9-ethylcarbazol-6-yl)ethene (**4**) as a yellow powder. Yield: 70%. ¹H NMR (600 MHz, CDCl₃) δ (ppm): 10.13 (s, 2H), 8.66 (s, 2H), 8.34 (s, 2H), 8.03 (dd, *J* = 8.5, 1.2 Hz, 2H), 7.79 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.51–7.45 (m, 4H), 7.39 (s, 2H), 4.43 (q, *J* = 7.3 Hz, 4H), 1.50 (t, *J* = 7.3 Hz, 6H). MS (*m/z*): 470.2005 (M⁺). Anal. calcd. for C₃₂H₂₃N₂O₂: C, 81.68%; H, 5.57%; N, 5.95%. Found: C, 81.30%; H, 5.37%; N, 5.72%.

2.3.5. (E)-1,2-bis(3-(benzothiazol-2-yl)-9-ethylcarbazol-6-yl)ethene (BBECE)

A mixture of 0.71 g **4** (1.50 mmol), 0.20 ml 2-aminothiophenol (1.71 mmol), and 30 ml DMSO was heated to 170 °C for 12 h. The reaction mixture was cooled to room temperature and poured into water. The organic component was extracted with CH₂Cl₂. The combined organic layers were washed with water and dried over MgSO₄. Evaporation of the solvent gave a residue that was purified column chromatography on silica gel (CH₂Cl₂/hexane) to give BBECE. Yield: 40%. ¹H NMR (600 MHz, DMSO-*d*₆) δ (ppm): 9.00 (s, 2H), 8.72 (s, 2H), 8.23 (d, *J* = 9.8 Hz, 2H), 8.17 (d, *J* = 7.9 Hz, 2H), 8.07 (d, *J* = 7.3 Hz, 2H), 7.81 (d, *J* = 9.1 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.60–7.54 (m, 4H), 7.50–7.42 (m, 4H), 4.55 (q, *J* = 7.2 Hz, 4H), 1.40 (t, *J* = 6.9 Hz, 6H). ¹³C NMR (600 MHz, DMSO-*d*₆) δ (ppm): 176.1, 156.5, 145.4, 144.6, 142.8, 134.9, 131.2, 129.8, 129.0, 126.9, 125.1, 124.7, 124.1, 112.2, 110.8, 47.2, 23.1. MS (*m/z*): 680.2132 (M⁺). Anal. calcd. for C₄₄H₃₂N₄S₂: C, 77.62%; H, 4.74%; N, 8.23%. Found: C, 77.48%; H, 4.52%; N, 8.17%.

The thermal stability of the compound was measured using thermogravimetric analysis (TGA). The result reveals that the compound exhibits excellent thermal stability up to 400 °C.

3. Calculation method and models

The ground-state geometry as well as its ionic structure of the derivative were optimized at B3LYP level with 6-31G(d, p) basis set [24,25]. The vibration frequencies and the frontier molecular orbital characteristics were analyzed on the optimized structure at the same level. The ionization potential (IP), electron affinity (EA) and reorganization energy of compound BBCE were calculated by DFT method based on the optimized geometry of the neutral and ionic molecules. The excited-state geometry of compound BBCE was optimized at the configuration interaction with single excitation (CIS) level with 6-31G(d, p) basis set [26]. The absorption spectra and the emission spectra of BBCE were carried out using time-dependent density functional theory (TDDFT) method based on the optimized ground state structures and the lowest singlet excited state structures, respectively. Solvent effects were also taken into account by using the polarized continuum model (PCM) [27,28]. All calculations were carried out with the Gaussian03 program package [29]. All the calculations were performed using the advanced computing facilities of supercomputing center of computer network information center of Chinese Academy of Sciences.

4. Results and discussion

In this paper, we described methods for the preparation of a carbazole dimer-based derivative with benzothiazole units. First, 9-ethylcarbazole-3-carbaldehyde (**1**) was obtained starting from ethylation of carbazole followed by treating the resulting 9-ethylcarbazole with POCl₃ and DMF via Vilsmeier–Haack reaction in 65% yield. Second, 6-bromo-9-ethylcarbazole-3-carbaldehyde (**2**) was prepared in high yield by 9-ethylcarbazole-3-carbaldehyde (**1**) reacted with NBS. Third, (E)-1,2-bis(3-bromo-9-ethylcarbazol-6-yl)ethene (**3**) was synthesized by McMurry coupling reaction under nitrogen. Then, (E)-1,2-bis(3-formyl-9-ethylcarbazol-6-yl)ethene (**4**) was synthesized via lithiation of **3** with *n*-butyllithium and reacted with DMF. Finally, (E)-1,2-bis(3-(benzothiazol-2-yl)-9-ethylcarbazol-6-yl)ethene (BBECE) was resulted by the condensation of **4** with 2-aminothiophenol in DMSO at 170 °C. All of the new compounds were characterized by elemental analysis, mass spectrometry and ¹H NMR; further details are given in Section 2.

4.1. Molecular structure

The molecular structure of compound BBCE studied in the present work has been shown in Scheme 1. The geometry of BBCE in the ground state was optimized using the DFT/B3LYP/6-31G(d, p) method. The optimized structure is shown in Fig. 1. The values of the parameters are listed in Table 1. As can be seen from the data of Table 1, BBCE has a planar geometrical structure and contains two carbazole rings as electron-donating groups and two benzothiazole rings as electron-accepting groups. Two carbazole rings are conjugated by double bonds as the rigid core and two benzothiazole rings are linked to the core through the 3,3' positions as the terminal. The dihedral angles C4–C1–C2–C3, C5–C4–C1–C2 and C1–C2–C3–C10 of the two carbazole rings planar moiety are 180°, –179.63° and 179.72°, respectively. The dihedral angles C21–C22–C34–N35, C21–C22–C34–S38, C25–C26–C33–N39 and C25–C26–C33–S42 of the carbazole rings planar moiety and benzothiazole rings planar moiety are –0.86°, 179.10°, 0.83° and –179.14°, respectively.

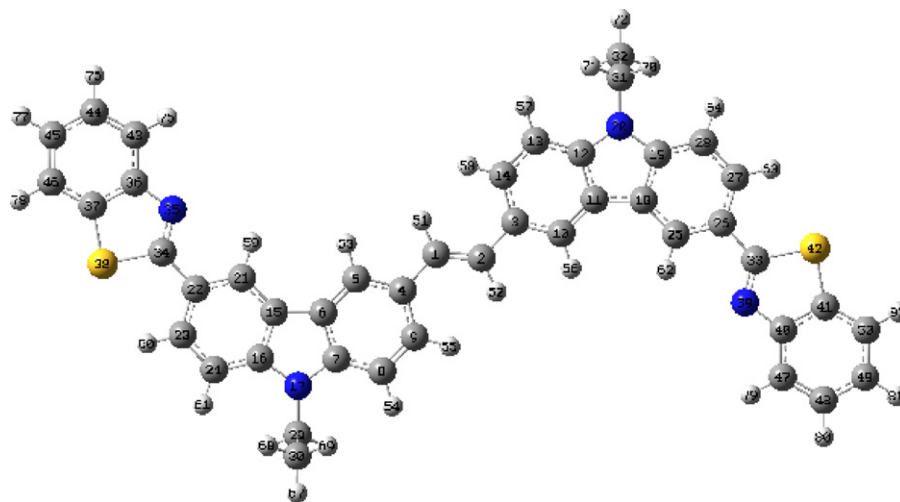


Fig. 1. The optimized geometry of compound BBECE in the ground state.

4.2. Frontier molecular orbitals

The frontier molecular orbitals, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), can provide a reasonable qualitative indication of the excitation properties and the ability of electron or hole transport [30]. In general, extended conjugation decreases the gap between the HOMO and LUMO. The energies of the HOMO and LUMO orbitals of BBECE were investigated at the DFT/B3LYP/6-31G(d, p) level. The calculated HOMO and LUMO energy levels are -4.85 eV and -1.39 eV, respectively. The HOMO–LUMO gap is 3.46 eV; it is similar to the optical energy band gap determined from electrochemical measurement. The isodensity surface plots of HOMO and LUMO were exhibited in Fig. 2. It can be seen from Fig. 2 that the electron density of HOMO is mainly localized on the carbazole dimer rings and it is π -bonding orbitals. And the electron density of LUMO is mainly localized on the benzothiazole rings and it is π^* -bonding orbitals. The electronic transition from the ground state to the excited state is mainly about an electron flowing from the carbazole rings to the benzothiazole rings, which belongs to π – π^* transition.

Table 1
Selected energy, dipole moment, optimized bond length and dihedral angle of compound BBECE in its ground state and excited state at B3LYP/6-31G(d, p) level.

Parameters	The ground state	The excited state
Energy (au)	–2711.49071325	–1462.49126980
Dipole moment, μ (D)	0.0039	0.8251
Bond length (Å)		
C1–C2	1.34938	1.40049
C22–C34	1.46530	1.46980
C26–C33	1.46530	1.46938
C34–N35	1.29970	1.2753
C34–S38	1.79517	1.76998
C33–N39	1.29970	1.27521
C33–S42	1.79517	1.76979
Dihedral angle (°)		
C4–C1–C2–C3	180	–179.41403
C21–C22–C34–N35	–0.86334	0.00908
C23–C22–C34–N35	178.94663	179.88604
C21–C22–C34–S38	179.09909	180
C23–C22–C34–S35	–1.09094	–0.12534
C25–C26–C33–N39	0.82552	180
C25–C26–C33–S42	–179.14208	–179.9329
C27–C26–C33–N39	–178.98540	–179.93818
C27–C26–C33–S42	1.047	0.06891

4.3. Electrochemical properties

The electrochemical properties of the BBECE and its the highest occupied molecular orbital (HOMO) as well as the lowest unoccupied molecular orbital (LUMO) energy levels were investigated by cyclic voltammetry measurements. The measurement was performed with 1×10^{-3} mol/L solution of the samples under argon in a three electrode cell using 0.1 mol/L tetrabutylammonium perchlorate in anhydrous CH_3CN as the supporting electrolyte. The CV curves remained unchanged under multiple successive potential scans, indicating its excellent stability against electrochemical oxidation. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels can be calculated by using the empirical equation $\text{HOMO} = -(E_{\text{ox}} + 4.40)$ eV and $\text{LUMO} = -(E_{\text{red}} + 4.40)$ eV, where E_{ox} and E_{red} stand for the onset potentials for oxidation and reduction, respectively. Therefore, the HOMO and LUMO levels of BBECE were estimated by using the onset potentials for oxidation and reduction (0.91 V and -1.98 V) and were found to be -5.31 eV and -2.42 eV, respectively. The low HOMO energy level of BBECE suggests that the compound has high oxidative stability and potential application for hole injection and transport material in OLEDs.

4.4. Charge injection and transport properties

The charge injection and transport ability are important parameters for OLEDs. In general, ionization potential and electronic affinity are used to evaluate the energy barrier for injection holes and electrons. Normally, the lower IP value of the hole-transport layer (HTL), the easier the entrance of holes from ITO anode to HTL; and the higher EA value of the electron transport layer (ETL), the easier the entrance of electrons from cathode to ETL. In order to further understand charge injection and transport properties of the compound, we calculated the ionization potential and electronic affinity. The calculated results are listed in Table 2. As shown in Table 2, compound BBECE has lower IP value [31,32], it is easier to transport hole. The results are consistent with the indication from the cyclic voltammetry measurement of its HOMO and LUMO.

Table 2
Ionization potential (IP), electron affinity (EA) and reorganization energy of compound BBECE obtained from DFT/B3LYP/6-31G(d, p) calculation (eV).

Compound	IP _v	IP _a	λ_{HOL}	EA _v	EA _a	λ_{ELE}
BBECE	5.87	5.78	0.214	0.536	0.606	0.140

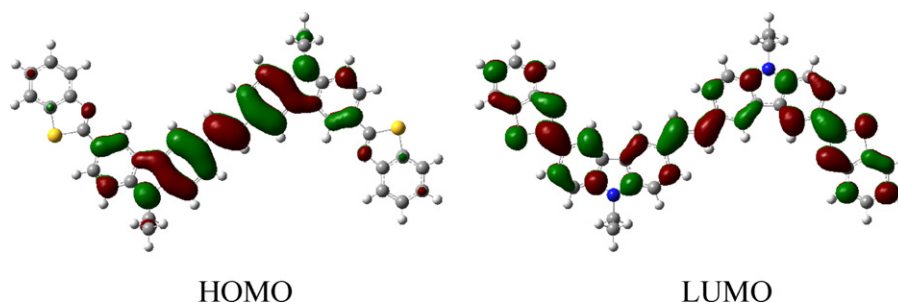


Fig. 2. The contour plots of HOMO and LUMO of compound BBECE in the ground state.

The charge mobility in organic materials is often described by a hopping model. The charge transport rate can be approximated by the Marcus electron-transfer theory with Eq. (1) [33].

$$k_{\text{hole/electron}} = \frac{4\pi^2}{h} \frac{1}{\sqrt{4\pi\lambda_{\text{hole/electron}}k_{\text{B}}T}} t^2 \exp\left(-\frac{\lambda_{\text{hole/electron}}}{4k_{\text{B}}T}\right) \quad (1)$$

where h is Planck's constant and k_{B} is Boltzmann's constants, T is the temperature, $\lambda_{\text{hole/electron}}$ is the reorganization energy for hole or electron transfer between both molecules and t is the electronic transfer integral between the donor and acceptor molecules. Therefore, the transport process is determined by two important molecular parameters: the reorganization energy (λ) which needs to be small for an efficient charge-transport and the intermolecular hole or electron transfer integral (t) which describes the strength of the electronic coupling between adjacent molecules [34].

The reorganization energy for hole transfer, λ_{hole} , is the sum of two contributions, $\lambda_{+1} + \lambda_{+2}$, that are defined as

$$\lambda_{+1} = E_0(\text{M}^+) - E_0(\text{M}) \quad (2)$$

$$\lambda_{+2} = E_1(\text{M}) - E_1(\text{M}^+) \quad (3)$$

where $E_0(\text{M}^+)$ and $E_0(\text{M})$ represent the energies of the neutral molecule at the cation geometry and at the optimal ground-state geometry, respectively; $E_1(\text{M})$ and $E_1(\text{M}^+)$ represent the energy of the charged state at the neutral geometry and optimal cation geometry, respectively.

Similarly, the reorganization energy for electron transfer, $\lambda_{\text{electron}}$, is also the sum of two contributions, $\lambda_{-1} + \lambda_{-2}$, that are defined as

$$\lambda_{-1} = E_0(\text{M}^-) - E_0(\text{M}) \quad (4)$$

$$\lambda_{-2} = E_1(\text{M}) - E_1(\text{M}^-) \quad (5)$$

where $E_0(\text{M}^-)$ and $E_0(\text{M})$ represent the energies of the neutral molecule at the anion geometry and at the optimal ground-state geometry, respectively; $E_1(\text{M})$ and $E_1(\text{M}^-)$ represent the energy of the charged state at the neutral geometry and optimal anion geometry, respectively.

In terms of above calculated model, the calculated reorganization energy for hole and electron are also listed in Table 2. It indicates compound BBECE is potential hole transport material.

4.5. UV-vis spectra and electronic absorption spectra

The UV-vis absorption spectra of compound BBECE have been studied in various solvents of different polarity and the spectral data were collected in Table 3. The absorption spectra (Fig. 3) are almost same in the different solvents meaning the independence of solvent polarity. This indicates that the structural and electronic characteristics of the ground and Franck-Condon (FC) excited states do not differ much with a change in solvent polarity. As shown in the

absorption spectra, the compound exhibits two absorption bands at 300–340 nm and 340–380 nm assigned to π - π^* electronic transitions and a low-energy broad band occurs at around 380–420 nm assigned to the overlapping intramolecular charge transfer (ICT) band from the donor (carbazole group) to the acceptor (benzothiazole group).

In order to gain a detailed insight into the nature of the UV-vis absorption of the compound observed experimentally, we computed singlet-singlet electronic transition in different polar solvents based on the optimized geometry of the ground state of the compound, using time-dependent DFT method at the B3LYP/6-31G(d, p) level. The computed data of vertical electronic transitions of $S_0 \rightarrow S_1$, $S_0 \rightarrow S_5$ and $S_0 \rightarrow S_7$ are collected in Table S1 (in SI). On the basis of the calculated vertical excited energy and their corresponding oscillator strengths, the continuous absorption spectra are simulated with the help of SWIZARD Software with the width at half-height of 2500 cm^{-1} . The simulated absorption spectra of the compound are shown in Fig. S1 (in SI). The calculated $S_0 \rightarrow S_1$ excitation energy and oscillator strength of compound BBECE in different polar solvents are 23,717–23,917 cm^{-1} and 1.3250–1.3787, respectively. All the electronic transitions herein are strongly allowed. The calculated $S_0 \rightarrow S_1$ vertical excitation energy data of compound BBECE are in relatively good agreement with the experimental data.

4.6. Fluorescence spectra and electronic emission spectra

The steady-state fluorescence spectra of the compound were measured in different polar solvents and the spectral data were also collected in Table 3. The emission spectra of compound BBECE (Fig. 4) consist of one broad band. This band can be assigned to the $S_1 \rightarrow S_0$ electronic transition. In contrast to the independence of solvent polarity in absorption spectra, the differences in the corresponding fluorescence spectra are strongly dependent on solvent polarity. As shown in Fig. 4 and Table 3, compound BBECE displayed

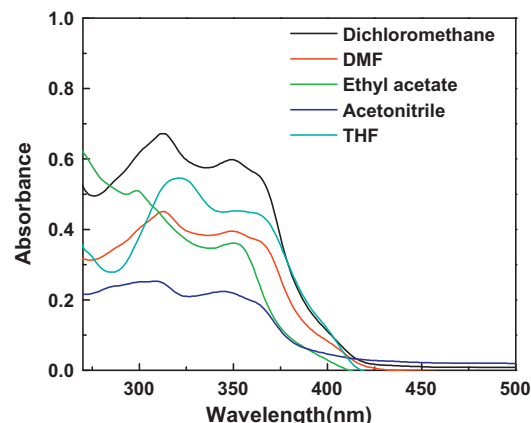


Fig. 3. UV-vis spectra of compound BBECE in different polar solvents.

Table 3
UV–vis spectra and fluorescence spectra data of compound BBECE in several solvents.

Compound	Solvents	UV wavelength, λ (nm)	FL wavelength, λ (nm)	Stokes shift (cm^{-1})
BBECE	Acetonitrile	360	491	7411
	Dichloromethane	362	442	5000
	DMF	362	449	5352
	THF	361	408	3191
	Ethyl acetate	360	412	3506

Table 4
Fluorescence quantum yields (Φ) and fluorescence lifetimes (τ , ns) of compound BBECE in different polar solvents.

Solvents	DMF	THF	Dichloromethane	Acetonitrile	Ethyl acetate
Fluorescence quantum yields, Φ	0.32	0.65	0.50	0.26	0.58
Fluorescence lifetime, τ (ns)	5.03	4.35	4.18	4.16	4.67

significant solvatochromism and a bathochromic shift of 83 nm was observed when the solvent polarizability increased from THF (408 nm) to CH_3CN (491 nm). The Stokes shifts for compound BBECE are larger in polar solvents than in non-polar solvents showing a more polar solvent is able to stabilize such a polarized excited state by the reorientation of the solvent molecules to accommodate the increased dipole, lowering the energy of the system and thereby leading to the bathochromic shift in the fluorescence spectra of BBECE.

In order to gain insight into the nature of the fluorescence emission observed for the compound, the geometry of the first excited singlet state (S_1) were optimized for the compound. The optimized geometrical parameters for the compound in the first excited state are also compiled in Table 1. According to the data listed in Table 1, we can see the compound possess similar molecular structure in the first excited state and in the ground state. The dihedral angles C4–C1–C2–C3, C5–C4–C1–C2 and C1–C2–C3–C10 of the two carbazole rings planar moiety are -179.4° , -179.52° and -179.57° , respectively. The dihedral angles C21–C22–C34–N35, C21–C22–C34–S38, C25–C26–C33–N39 and C25–C26–C33–S42 of the carbazole rings planar moiety and benzothiazole rings planar moiety are 0° , 180° , 180° and -179.90° , respectively.

The optimized geometry of the compound in the first excited state (S_1) was used as input to calculate singlet–singlet electronic transition using time-dependent DFT method at the B3LYP/6-31G(d, p) level in different polar solvents, respectively, yielding the vertical electronic transitions energy of $S_1 \rightarrow S_0$. The computed data are collected in Table S2 (in SI). On the basis of the calculated vertical excited energy and their corresponding oscillator strengths, the continuous emission spectra were simulated with the help of SWIZARD Software with the width at half-height of 2500 cm^{-1} . The simulated emission spectra of the compound are

shown in Fig. S2 (in SI). As can be seen in Fig. S2 and Table S2, the electronic transitions are of the π – π^* type. The calculated $S_1 \rightarrow S_0$ emission energy and oscillator strength of the compound in different polar solvents are $21,664$ – $21,819 \text{ cm}^{-1}$ and 1.6547 – 1.6939 , respectively. The electronic transitions are strongly allowed. The simulated maximum emission wavelengths of the compound are around 460 nm in different polar solvents. The simulated emission spectra are in relatively good agreement with the experimental fluorescence spectra of the compound. But the maximum FL wavelength of compound does not show red-shift in polar solvents. This is due to that the solvent effect is taken into account, but the polarity of the solvents on the emission spectra has not been well reflected. Therefore, we can know that this calculation method is imperfect in the calculation of the solvent effect on the emission spectra, and it needs further improvement. Fluorescence spectra show the compound in different polar solvents can emit blue light and it might be potential luminescent materials with blue light emission.

4.7. Molecular photophysical properties

The fluorescence quantum yields of the compound were measured in several organic solvents at room temperature by a relative method using quinine bisulfate in 0.1 mol/L sulphuric acid as a standard. The fluorescence quantum yield was calculated from Eq. (6) [35].

$$\Phi_s = \Phi_r \frac{F_s A_r \left(\frac{n_r}{n_s}\right)^2}{F_r A_s} \quad (6)$$

where F is the integration of the emission intensities, n is the index of refraction of the solution, Φ is the fluorescence quantum yield and A is the absorbance at the excitation wavelength, the subscripts “r” and “s” denote the reference and unknown samples, respectively. The fluorescence quantum yields (Φ) were collected in Table 4.

The fluorescence decay behaviors of compound BBECE was also studied in several solvents. The fluorescence lifetimes (τ , ns) of compound BBECE were also collected in Table 4. For the compound, the fluorescence decay curves were mono-exponential model.

5. Conclusions

In this paper, a novel A– π –D– π –A type compound, namely (E)-1,2-bis(3-(benzothiazol-2-yl)-9-ethylcarbazol-6-yl)ethene (BBECE) was synthesized and characterized by elemental analysis, NMR, MS and thermogravimetric analysis. The electrochemical measurements indicate BBECE possess excellent stability against electrochemical oxidation. The calculated absorption and emission wavelengths are coincident with the measured data. The calculated reorganization energy for hole and electron indicates compound BBECE is potential hole transport material. The lowest-lying

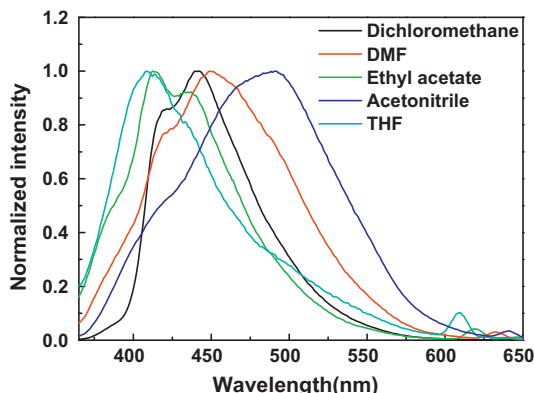


Fig. 4. Fluorescence spectra of compound BBECE in different polar solvents.

absorption spectra can be mainly attributed to intramolecular charge transfer (ICT), and the fluorescence spectra can be mainly described as originating from an excited state with intramolecular charge transfer (ICT) character. The results show that compound BBECE exhibited excellent thermal stability and electrochemical stability as well as high fluorescence quantum yields, indicating its potential applications as an excellent optoelectronic material in optical fields.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2012.02.087.

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