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Experimental and theoretical study of three new benzothiazole-fused carbazole derivatives

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ABSTRACT

Three new D– π –A type compounds, each containing one benzothiazole ring as an electron acceptor and one N-ethylcarbazole group as electron donor, were synthesized and characterized by elemental analysis, NMR, MS and thermogravimetric analysis. The absorption and emission spectra of three compounds were experimentally determined in several solvents and were simultaneously computed using density functional theory (DFT) and time-dependent density functional theory (TDDFT). The calculated reorganization energy for hole and electron indicates that three compounds are in favor of hole transport than electron transport. The calculated absorption aperts are well coincident with the measured data. The calculated lowest-lying absorption spectra can be mainly described as originating from an excited state with intramolecular charge transfer (ICT) character. The results show that three compounds exhibited excellent thermal stability and high fluorescence quantum yields, indicating their potential applications as excellent optoelectronic material in optical field.

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1. Introduction

Carbazole is an important heterocyclic compound with a nitrogen atom as an electron donor. It has high thermal stability and excellent photophysical property [1,2]. Because its ring is easily functionalized and covalently linked to other molecules, a large number of derivatives have been generated through chemical modification [3–8]. Owing to their great potential applications in many fields, carbazole and its derivatives have been extensively investigated during the past years [9–14].

The photophysical properties of carbazole can be improved readily through derivatives. Thus, the development of new materials with high-performance constitutes a very active area of research [15–24].

Up to now, the π -conjugated carbazole derivatives of the general type D- π -D, D- π -A, D- π -A- π -D and A- π -D- π -A, where D and A denote electron donating and accepting groups have been studied widely by many research groups. A number of the literatures have

** Corresponding author at: School of Chemistry and Chemical Engineering, Shanxi University, Taiyuan 030006, PR China. Tel.: +86 351 7018094; fax: +86 351 7011688. *E-mail addresses*: hepingshi@sxu.edu.cn (H.-p. Shi), fangli@sxu.edu.cn (L. Fang). highlighted the design and investigations of carbazole derivatives containing $D-\pi-A$ structure.

Carbazole derivatives with D $-\pi$ -A structures have, in general, a large electron delocalization length and the ability of experiencing intramolecular charge transfer (ICT) from the electron donating groups to electron accepting groups. In addition, the investigation of carbazole derivatives with D $-\pi$ -A structure has been greatly increased by the recent progresses in developing novel and efficient active materials because of a series of new applications.

Recently, series novel carbazole derivatives with $D-\pi$ -A structures have 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 carbazole group as the electron donor (D). They have large electron delocalization lengths and are able to be experienced intramolecular charge transfer (ICT) from the electron donor to the electron acceptors of the molecule. Their photophysical properties have also been investigated in detail [25–28].

The carbazole derivatives with $D-\pi-A$ structure have great potential applications. Therefore, the molecular design and synthesis of novel carbazole derivatives with $D-\pi-A$ structure need to be further developed by the structural modification, in order to improve the properties and establish the relation between structures and properties.

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For this reason, we report the synthesis, structures and spectral properties of three novel $D-\pi$ -A type carbazole derivatives containing an electron donating carbazole and an electron withdrawing benzothiazole in this paper. We also attempt to elucidate the structure-property correlation of these molecules using experimental and theoretical methods. Our results show that these carbazole derivatives exhibited excellent thermal stability and eminent photophysical properties as well as could served as useful photoluminescence materials with blue-light emission. The results will increase the knowledge to design and synthesize novel carbazole derivatives with excellent photophysical properties.

2. Experimental

2.1. Reagents

9-H-carbazole and 1-bromo-4-iodobenzene were purchased from Alfa Aesar and used without further purifications, 2-aminothiophenol, 2-methylbenzothiazole and 2-ptolylbenzothiazole were purchased from Aacros, and other reagents were purchased from Beijing Chemical plants, DMF, DMSO, Et₂O, THF, toluene, CCl₄, etc. were purified according to standard methods used before. All reactions were carried out under an inert atmosphere of nitrogen.

2.2. Apparatus

Melting points were determined on an X-5 melting point detector and uncorrected. All NMR spectra were measured on a Bruker DLX 300 MHz spectromenter with CDCl₃ or DMSO as solvent. Thermogravimetric analyses were performed with a TA TGA 2050 thermogravimetric analyzer under nitrogen atmosphere with a heating rate of 20°C/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 singlequadrupole mass spectrometer detector (Waters). UV-vis spectra were obtained on a shimadzu UV-2450 spectrophotometers. Fluorescence spectra were obtained on a F-4500 fluorothotometer. Fluorecence quantum yields were determined using the a standard actinometry method. Quinine sulfate was used in the actinometer with a known fluorescence quantum yield of 0.55 in 0.1 mol/L sulphuric acid, 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.

2.3. Procedures

The synthesis of these compounds were described in Section 2.4. All spectral experiments were carried out at room temperature. The concentration of compounds is 1.0×10^{-5} mol/L in spectral experiments. All emission spectra were corrected. Excitation and emission slits width were both set at 2.5 nm.

2.4. Synthesis and characterization of the compounds

The synthetic route of three compounds is shown in Scheme 1.

2.4.1. Synthesis of 9-(4-(benzothiazol-2-yl)phenyl)-9H-carbazole (3)

2.4.1.1. Synthesis of 9-(4-bromo-phenyl)-9H-carbazole (1). 9-(4-bromo-phenyl)-9H-carbazole (1) was synthesized following a literature method [29]. A mixture of 1.67g 9-H-carbazole

(10 mmol), 2.82 g 1-bromo-4-iodobenzene (10 mmol), 0.53 g 18crown-6 (2.0 mmol), 6.07 g K₂CO₃ (44 mmol) and 1.47 g Cu (23 mmol) were dissolved in 60 ml DMF in a 100 ml flask under nitrogen atmosphere. The mixture was refluxed for 24 h under nitrogen atmosphere. After cooling to room temperature, the mixture was poured into ice-water and extracted with CH₂Cl₂ (3 × 50 ml). The combined organic layer was dried with anhydrous Na₂SO₄ and evaporated to dryness. The compound was obtained as a white solid by crystallized from ethanol (2.45 g, yield: 76%). m.p. 142–144 °C [30]. ¹H NMR (CDCl₃, 300 MHz): δ_{ppm} 8.17–8.20 (d, 2H), 7.76–7.87 (d, 2H), 7.49–7.60 (d, 2H), 7.43–7.48 (t, 2H), 7.41–7.43 (d, 2H), 7.34–7.39 (t, 2H). MS (M⁺): 321.0351. Anal. Calcd. for C₁₈H₁₂NBr: C, 67.10%; H, 3.75%; N, 4.35%. Found C, 66.93%; H, 3.71%; N, 4.31%.

2.4.1.2. Synthesis of 4-(9H-carbazol-9-yl)benzaldehyde (2). To a solution of 0.90 g 9-(4-bromo-phenyl)-9H-carbazole(1)(2.8 mmol) in 30 ml anhydrous Et₂O was added 1.34 ml of 2.5 M n-BuLi in hexane (3.4 mmol) at -78 °C under nitrogen atmosphere. After the reaction mixture was warmed to 0° C, 0.26 ml DMF(3.4 mmol) was added at -78 °C. The resulting mixture was allowed to warm to room temperature and stirred at room temperature overnight. Then the mixture was poured into ice water and 5% HCl (aq.) (5 ml) was added and the two layers were separated. The aqueous layer was extracted with $Et_2O(3 \times 20 \text{ ml})$ and the combined organic layer was washed with brine (15 ml), dried with MgSO₄ and evaporated under reduced pressure, a yellow power was obtained by crystallized from ethanol (0.39g, yield:51%). m.p. 148–150 °C [31]. ¹H NMR (300 MHz, CDCl₃) δ_{ppm} 10.12–10.20 (s, 1H), 8.12-8.16 (m, 4H), 7.78-7.86 (d, 2H), 7.49-7.63 (d, 2H), 7.32-7.44(t, 2H), 7.19-7.30(t, 2H), MS(M⁺) 271.0997. Anal. Calc. for C₁₉H₁₃ON: C, 84.13%; H, 4.80%; N, 5.17%. Found: C, 84.40%; H, 4.77%; N, 5.12%.

2.4.1.3. Synthesis of 9-(4-(benzothiazol-2-yl)phenyl)-9H-carbazole (**3**). A mixture of the corresponding 0.41 g 4-(9H-carbazol-9-yl)benzaldehyde (**2**) (1.50 mmol), 0.20 ml 2-aminothiophenol (1.87 mmol), and 30 ml DMSO was heated in an oil bath to 120 °C, held at that temperature for 12 h, then poured into water and extracted with CH₂Cl₂ (3 × 10 ml). The combined organic layer was dried with anhydrous Na₂SO₄ and evaporated to dryness. The crude compound was stirred for 15 min in 30 ml of boiling ethanol, then the solution was cooled, and the pure product was isolated by filtration. (0.48 g, yield: 86%). m.p. 190–193 °C. ¹H NMR (300 MHz, CDCl₃) δ_{ppm} 8.11–8.17 (m, 2H), 7.82–7.97 (m, 4H), 7.72–7.75 (d, 2H), 7.50–7.59 (d, 2H), 7.41–7.46 (d, 2H), 7.25–7.34 (m, 4H). MS(M⁺) 376.1382. Anal. Calc. for C₂₅H₁₆N₂S; C, 79.78%; H, 4.26%; N, 7.45%. Found: C, 80.02%; H, 4.12%; N, 7.27%.

2.4.2. Synthesis of

9-(4-(2-(benzothiazol-2-yl)vinyl)phenyl)-9H-carbazole (4) 2.4.2.1. Synthesis of 1-(4-(9H-carbazol-9-yl)phenyl)-2-

(*benzothiazol-2-yl*)*ethanol.* Under nitrogen, to a solution of 0.16 ml (1.2 mmol) of 2-methylbenzothiazole in 10 ml of anhydrous THF at -78 °C was added dropwise, 0.56 ml (1.4 mmol) of 2.5 M *n*-BuLi in hexane. The mixture was stirred at -78 °C for 30 min, then 0.27 g (1.0 mmol) of 4-(9H-carbazol-9-yl)benzaldehyde in 5 ml of anhydrous THF was added dropwise. The reaction was stirred at -78 °C for 1 h, then allowed to warm to ambient temperature and stirred overnight. Next, 0.20 ml of acetic acid was added, and the mixture was diluted with 50 ml of CH₂Cl₂. The solution was dried over MgSO₄, filtered, and concentrated in vacuo. A yellow power was obtained by recyrstallized from ethanol. (0.38 g, yield: 75%). m.p. 176.5–178 °C. ¹H NMR (300 MHz, CDCl₃) δ_{ppm} 7.88–7.94 (d, 2H), 7.70–7.72 (d, 1H), 7.52–7.59 (d, 1H), 7.50–7.51 (d, 2H),





e: (i) NBS, CCl₄, reflux, 4h (ii) PPh₃, CHCl₃, reflux, 24h (iii) n-BuLi, THF, -78°C

Scheme 1. The synthetic route of three compounds.

7.40–7.43 (m, 2H), 7.27–7.30 (m, 6H), 7.26 (m, 2H), 5.44–5.46 (m, 1H), 3.55–3.57 (m, 2H), 2.84–2.85 (s, 1H). MS(M⁺) 420.1356. Anal. Calc. for $C_{27}H_{20}N_2OS$: C, 77.12%; H, 4.79%; N, 6.66%. Found: C, 77.20%; H, 4.84%; N, 6.72%.

2.4.2.2. Synthesis of 9-(4-(2-(benzothiazol-2-yl)vinyl)phenyl)-9H-carbazole (**4**). To a mixture of 0.38 g (0.90 mmol) of 1-(4-(9H-carbazol-9-yl)phenyl)-2-(benzothiazol-2-yl)ethanol and 0.02 g (0.09 mmol) of p-toluenesulfonic acid monohydrate was added 20 ml of toluene. The reaction was heated at reflux for 3 h, then cooled to ambient temperature and concentrated in vacuo. The crude product was recyrstallized from ethanol to give a brown yellow power. (0.18 g, yield: 51%). m.p. 195.3–196.8 °C. ¹H NMR (300 MHz, CDCl₃) δ_{ppm} 8.15–8.17 (d, 2H), 8.03–8.04 (d, 1H), 7.89–7.90 (d, 1H), 7.82–7.83 (d, 2H), 7.63–7.66 (m, 2H), 7.48–7.51 (m, 4H), 7.41–7.47 (m, 4H), 7.30–7.32 (t, 2H) MS(M⁺) 402.1197. Anal. Calc. for C₂₇H₁₈N₂S: C, 80.57%; H, 4.51%; N, 6.96%. Found: C, 80.49%; H, 4.53%; N, 6.88%.

2.4.3. Synthesis of

9-(4-(4-(benzothiazol-2-yl)styryl)phenyl)-9H-carbazole (5)

2.4.3.1. Synthesis of 2-(4-(bromomethyl)phenyl)benzothiazole [27]. 2.71 g 2-p-Tolylbenzothiazole (12 mmol) and 2.14 g N-bromosuccinimide (NBS) (12 mmol) were dissolved in 50 ml of CCl₄. The solution was heated under reflux for 4 h. The precipitated succinimide was filtered, and the solvent was evaporated from the solution. The remaining gray oil was recrystallized from ethanol. The obtained white crystalline powder was dried in vacuum (3.43 g, 94%). m.p. 132–133 °C [27]. ¹H NMR (300 MHz, CDCl₃): δ_{ppm} 8.08–8.13 (d, 3H), 7.92–7.99 (d, 1H), 7.53–7.76 (m, 3H), 7.42–7.50 (t, 1H), 4.55–4.62 (s, 2H). MS(M⁺): 302.9717 Anal. Calc. for C₁₄H₁₀BrNS: C, 55.45%; H, 3.30%; N, 4.62%. Found: C, 55.38%; H, 3.40%; N, 4.57%.

2.4.3.2. Synthesis of 4-(2-benzothiazolyl)- benzyl triphenyl phosphonium bromide. Under nitrogen atmosphere, a mixture of compound 3.04 g 2-(4-(bromomethyl)phenyl)benzothiazole (10 mmol), 2.62 g triphenyl phosphine (10 mmol) and 50 ml of freshly distilled CHCl₃ was heated to refluxed for 24 h. On cooling, the solvent was removed under reduced pressure gave the white solid which was recrystallized from Et₂O (4.98 g, yield: 88%). m.p. 295–297 °C. ¹H NMR (300 MHz, CDCl₃): δ_{ppm} 7.98–8.08 (d, 3H), 7.72–7.84 (d, 1H), 7.48–7.70 (m, 15H) 7.43–7.45 (m, 3H), 7.26–7.33 (t, 1H), 5.72–5.77 (s, 2H) MS(M⁺): 566.0217 Anal. Calc. for C₃₂H₂₅BrNSP: C, 67.84%; H, 4.42%; N, 2.47%. Found: C, 67.79%; H, 4.40%; N, 2.53%.

2.4.3.3. Synthesis of 9-(4-(4-(benzothiazol-2-yl)styryl)phenyl)-9Hcarbazole (5). Under nitrogen atmosphere, a stirred slurry of 1.00 g 4-(2-benzothiazolyl)-benzyl triphenyl phosphonium bromide (1.77 mmol) in 30 ml anhydrous THF was cooled to $-78 \degree C$, 0.70 ml of 2.5 M n-BuLi in hexane (1.77 mmol) was added and the mixture was warmed to room temperature over 2 h. Then a solution of 0.48 g 4-(9H-carbazol-9-yl)benzaldehyde (2)(1.77 mmol) in 10 ml THF was added dropwise with vigorous stirring at -78 °C. The reaction was warmed to room temperature and stirred for 12 h. Then the THF was evaporated at reduced pressure and the residue was separated by column chromatography (petroleum ether/methylene chloride 1:3) to give a yellow power.(0.20 g, yield: 24%). m.p. 263–265 °C. ¹H NMR (300 MHz, CDCl₃): δ_{ppm} 8.11–8.13 (m, 1H), 7.94-7.82 (m, 1H), 7.69-7.71 (m, 2H), 7.60-7.62 (m, 4H), 7.51-7.53 (d, 2H), 7.42-7.45 (d, 2H), 7.38-7.40 (m, 2H), 7.26-7.36 (d, 2H), 7.21-7.24 (m, 4H), 7.15-7.18 (m, 2H). MS(M⁺): 478.1528. Anal. Calc. for C₃₃H₂₂N₂S: C, 82.85%; H, 4.60%; N, 5.86%. Found: C, 82.91%; H, 4.58%; N, 5.77%.

The thermal stability of three compounds was measured using thermogravimetric analysis (TGA). The result reveals that three



Fig. 1. The molecular structures as calculation models.

compounds exhibits excellent thermal stability up to 250 $^\circ\text{C}$, 280 $^\circ\text{C}$ and 350 $^\circ\text{C}$, respectively.

3. Calculation method and models

The ground-state geometries as well as their ionic structures of three carbazole derivatives were optimized at B3LYP level with 6-31G(d, p) basis set [32,33]. The vibration frequencies and the frontier molecular orbital characteristics were analyzed on the optimized structures at the same level. The ionization potential (IP), electron affinity (EA), reorganization energy, and HOMO-LUMO gap of them were calculated by DFT method based on the optimized geometry of the neutral and ionic molecules. The excited-state geometries of three derivatives were optimized at the configuration interaction with single excitation (CIS) level with 6-31G(d, p) basis set [34]. The absorption spectra and the emission spectra of three derivatives were carried out using time-dependent density functional theory (TD-DFT) 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) [35,36]. All calculations were carried out with the Gaussian03 program package [37]. All the calculations were performed using the advanced computing facilities of supercomputing center of computer network information center of Chinese Academy of Sciences. The molecular structures as calculation models are shown in Fig. 1.

4. Results and discussion

In this paper, we described methods for the preparation of carbazole derivatives. First, 4-(9H-carbazol-9-yl)benzaldehyde (**2**) was synthesized as the key intermediate for the whole procedure via a two step reaction as shown in Scheme 1. This compound (**2**) served as the central core. Second, 9-(4-(benzothiazol-2-yl)phenyl)-9H-carbazole (**3**) was prepared in high yield by stirring 2-aminothiophenol and 4-(9H-carbazol-9-yl)benzaldehyde (**2**) in DMSO at 120 °C.

Then 9-(4-(2-(benzothiazol-2-yl)vinyl)phenyl)-9H-carbazole (**4**) was synthesized from the reaction between 2-methylbenzothiazole and 4-(9H-carbazol-9-yl)benzaldehyde (**2**) via lithiation with *n*-butyllithium. Finally, 9-(4-(4-(benzothiazol-2-yl)

4.1. Structures of the compounds

The optimized geometrical parameters for the three compounds in the ground state are compiled in Table S1. Table S1 is placed in supporting information. and the optimized geometries of these compounds in the ground state are shown in Fig. 2. According to the data listed in Table S1, we can see three compounds possess similar molecular structures. Each compound contains two planar moiety in its molecular structure, one planar moiety is carbazole ring and the other is the rest of the molecular. The dihedral angles C4–N7–C14–C15 and C4–N7–C14–C19 of the two planar moiety are –52.24° and 127.74°, 52.11° and –127.71° as well as 53.08° and –126.69° in compound (**3**), compound (**4**) and compound (**5**), respectively. It is concluded that three compounds show the distorted geometrical structures.

4.2. Frontier molecular orbitals of three compounds in the ground state

The frontier molecular orbitals are the most important indication in determining the spectral properties and the ability of electron or hole transport of molecules [38]. In general, extended conjugation decreases the gap between the HOMO and LUMO, thus causing bathochromic shift in UV-vis absorbtion.

The contour plots of HOMO and LUMO of the three compounds were exhibited in Fig. 3. It can be seen from Fig. 3 that the election density of HOMO is mainly localized on the carbazole ring of each compound and it is π -bonding orbitals. And the election density of LUMO is mainly localized on the benzothiazole ring of each compound and it is π -bonding orbitals.

The energies of the HOMO and LUMO as well as the HOMO–LUMO energy gap of three compounds are given in Table 1. As shown in Table 1, with the increase of conjugation, the energy of highest occupied molecular orbital (HOMO) is increased, while the energy of lowest unoccupied molecular orbital (LUMO) is reduced. The energy gap of three compounds was reduced with the increase of conjugation. The electronic transition from the ground state to the excited state is mainly about an electron flowing from the carbazole ring of each compound to the benzothiazole ring of each compound, which belongs to π - π * transition.

4.3. Charge injection and transport properties of three compounds in their ground states

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 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 three compounds, we calculated their ionization potentials, electronic affinities. The calculated results are listed in Table 2. As shown in Table 2, the compound (**5**) has lower IP value, it is easier to transport hole than other compounds and the compound (**5**) has higher EA value, it is easier to transport electron than other compounds. These results are consistent with the indication from the energies analysis of their HOMOs and LUMOS.







Fig. 2. The optimized geometries of three compounds 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) [39].

Table 1

HOMO and LUMO energy, and HOMO–LUMO energy gap of three compounds obtained from DFT/B3LYP/6-31G(d, p) calculation (eV).

Compounds	НОМО	LUMO	$\Delta E_{\text{HOMO-LUMO}}$
Compound 3	-5.415	-1.769	3.646
Compound 4 Compound 5	-5.361 -5.279	-2.095 -2.095	3.266 3.184

Table 2

Ionization potentials, electron affinities and reorganization energy of three compounds obtained from DFT/B3LYP/6-31G(d, p) calculation (eV).

Compounds	IP_{v}	IPa	λ_{Hol}	EAv	EAa	λ_{Ele}
Compound 3	6.698	6.635	0.128	0.403	0.596	0.415
Compound 4	6.567	6.483	0.171	0.780	0.980	0.411
Compound 5	6.371	6.279	0.186	0.928	1.098	0.347

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

where *h* is Planck's constant and k_B is Boltzmann's constants, *T* is the temperature, *t* is the electronic transfer integral between the donor and acceptor molecules, and $\lambda_{hole/electron}$ is the reorganization energy for hole or electron transfer between both 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 [40].



Fig. 3. The contour plots of HOMOs and LUMOs of three compounds in the ground state.

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

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

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

where $E_0(M^+)$ and $E_0(M)$ represent the energies of the neutral molecule at the cation geometry and at the optimal ground-state geometry, respectively. $E_1(M)$ and $E_1(M^+)$ 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

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

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

where $E_0(M^-)$ and $E_0(M)$ represent the energies of the neutral molecule at the anion geometry and at the optimal ground-state geometry, respectively. $E_1(M)$ and $E_1(M^-)$ 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. Where λ_{hole} exhibits lower value than corresponding $\lambda_{electron}$. It indicates that three compounds are in favor of hole transport than electron transport, thus these compounds are potential hole transport materials.

4.4. UV-vis spectra of three compounds

The UV–vis absorption spectra of three compounds have been studied in various solvents of different polarity and the spectral data have been collected in Table 3. The spectra are shown in Fig. 4. As indicated in the absorption spectra, three compounds exhibit two absorption bands at 266–303 and 300–400 nm due to π – π * electronic transitions, which are almost the same in the different polar solvents meaning the independence of UV absorption to the solvent polarity. The low-energy broad band at 300–400 nm assigned to an intramolecular charge transfer (CT) band from the carbazole ring of each compound to the benzothiazole ring of each compound in all solvents.

In order to gain a detailed insight into the nature of the UV–vis absorption of three compounds observed experimentally, we computed singlet–singlet electronic transition in gas phase and in different polar solvents based on the optimized geometries of the ground state of three compounds, using time-dependent DFT

10000



Hex CH₂Cl₂ Fluorence Intensity(a.u.) 8000 CHCl3 Acetone 6000 CH₃CN CH₃OH DMSO 4000 2000 0 450 350 400 500 550 600 Wavelength(nm) compound (3) 1800 Hex 1600 CH₂Cl₂ Fluorence Intensity(a.u.) CHCl₃ 1400 Acetone CH₃CN 1200 CH₃OH 1000 DMSO 800 600 400 200 0 400 450 600 650 500 550 Wavelength(nm) compound (4) 10000 Hex CH₂Cl₂ CHCI3 Fluorence Intensity(a.u.) 8000 Acetone CH₃CN сн₃он 6000 DMSO 4000 2000 0 400 450 500 550 600 650 Wavelength(nm) compound (5)

Fig. 5. Emission spectra of three compounds in different polar solvents.

Fig. 4. The UV-vis spectra of three compounds in different polar solvents.

method at the B3LYP/6-31G (d, p) level. The computed data of vertical electronic transitions of $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_3$ are collected in Table S2. Table S2 is placed in supporting information. On the basis of the calculated vertical excited energy and their corresponding oscillator strengths, the continuous absorption spectra were simulated with the help of SWIZARD software with the width at half-height of 2500 cm⁻¹. The simulated absorption spectra of three compounds are shown in Fig. S1. Fig. S1 is placed in supporting

information. As seen in Fig. S1 and Table S2, the electronic transitions are of $\pi\pi^*$ type. The calculated $S_0 \rightarrow S_1$ excitation energy, oscillator strength of three compounds in different polar solvents are 25,480–25,661 cm⁻¹, 0.5277–0.5586 and 23,167–23,396 cm⁻¹, 0.7812–0.8460 as well as 22,795–23,016 cm⁻¹, 1.2464–1.3942, respectively. All the electronic transitions herein are strongly allowed. The calculated $S_0 \rightarrow S_1$ vertical excitation energy data of three compounds are lower than the experimental value in different polar solvents. This is due to that the solvent effect is taken into account, but the role of the solvent effect has not been well

Table 3
UV-vis spectra data and fluorescence spectra of three compounds in several solvents

Compounds	Solvents	UV wavelengths (λnm)	FL wavelengths (λnm)	Stokes shift (cm ⁻¹)
Compound 3	Hexane	343	394	3774
	Dichloromethane	343	436	6219
	Chloroform	343	427	5736
	Acetone	342	445	6766
	Acetonitrile	341	463	7728
	Methanol	341	470	8049
	DMSO	345	453	6911
Compound 4	Hexane	339	422	5802
	Dichloromethane	342	466	7781
	Chloroform	341	459	7540
	Acetone	341	481	8536
	Acetonitrile	341	493	9042
	Methanol	340	498	9332
	DMSO	343	500	8788
Compound 5	Hexane	357	438	5180
-	Dichloromethane	364	468	6106
	Chloroform	363	460	5809
	Acetone	362	474	6527
	Acetonitrile	361	497	7581
	Methanol	361	499	7661
	DMSO	371	498	6874

reflected. However, the change trends of the absorption spectra in different solvents could be well reflected. Therefore, we can know that this calculation method is imperfect in the calculation of the solvent effect on the absorption spectra, and it needs further improvement.

4.5. Fluorescence spectra of three compounds

The steady-state fluorescence spectra of three compounds were measured in different polar solvents and were shown in Fig. 5. Their spectral data were collected in Table 3. The emission spectra of three compounds consist of one broad band except in *n*-hexane, where some structure could be observed. This band can be assigned to the $S_1 \rightarrow S_0$ electronic transition. The spectra of three compounds show a large stokes shift in polar solvents, accompanied by losing of the fine structure and an increase in the fluorescence half-width.

As can be seen in Fig. 5 and Table 3, with the solvent changes from *n*-hexane to acetonitrile (ACN), the maximum emission wavelengths of three compounds were redshifted from 393 to 461 nm, 427 to 496 nm and 436 to 497 nm, respectively. The stocks shifts for three compounds are larger in polar solvents than in non-polar solvents showing a energetic stabilization of the excited state in polar solvents.

In order to gain insight into the nature of the fluorescence emission observed for three compounds, the geometries of the first excited singlet state (S_1) were optimized for three compounds. The optimized geometrical parameters for three compounds in the first excited state are also compiled in Table S1. According to the data listed in Table S1, we can see these compounds possess similar molecular structures in the first excited state and in the ground state, respectively. The dihedral angles C4–N7–C14–C15 and C4–N7–C14–C19 are –48.41° and 131.36°, 50.90° and –129.23° as well as 54.82° and –125.19° in compound (**3**), compound (**4**) and compound (**5**), respectively.

The optimized geometries of three compounds in the first excited state (S_1) were used as input to calculate singlet–singlet electronic transition using time-dependent DFT method at the B3LYP/6-31G(d, p) level in gas phase and in different polar solvents, respectively, yielding the vertical electronic transitions energy of $S_1 \rightarrow S_0$. The computed data are collected in Table S3. Table S3 is placed in supporting information. 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 three compounds are shown in Fig. S2. Fig. S2 is placed in supporting information. 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, oscillator strength of three compounds in different polar solvents are 23,166-23,318 cm⁻¹, 0.8633-0.9095 and 20,798-20,985 cm⁻¹, 1.1756-1.2396 as well as 20,523-20,732 cm⁻¹, 1.6607-1.7945, respectively. All these electronic transitions are strongly allowed. The simulated maximum emission wavelengths of three compounds are 432, 481 and 487 nm in different polar solvents. The simulated emission spectra are in relatively good agreement with the experimental fluorescence spectra of three compounds. But the maximum FL wavelength of compounds 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 have not been well reflected. However, the change trends of the emission spectra in different solvents could be 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. Simulation emission spectra show three compounds in different polar solvents can emit blue light and it might be potential luminescent materials with blue light emission.

4.6. molecular photophysical properties

The fluorescence quantum yields of three compounds were measured in several organic solvents at room temperature by a relative method using quinine bisulfate in 0.1 M sulphuric acid as a standard. The fluorescence quantum yield was calculated from Eq. (6) [41].

$$\phi_s = \phi_r \frac{F_s}{F_r} \frac{A_r}{A_s} \left(\frac{n_r}{n_s}\right)^2 \tag{6}$$

In the above equation, Φ is the fluorescence quantum yield, *F* is the integration of the emission intensities, *n* is the index of refraction of the solution, 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 quantum yields (Φ) and the fluorescence lifetimes (τ , ns) of three compounds in different polar solvents.

Solvents	Fluorescence quantum yields (Φ)			Fluorescence lifetime (τ , ns)		
	Compound 3	Compound 4	Compound 5	Compound 3	Compound 4	Compound 5
Hexane	0.34	0.14	0.19	3.66	2.43	1.49
Dichloromethane	0.54	0.22	0.46	3.98	2.68	1.65
Chloroform	0.56	0.17	0.44	4.11	2.76	1.67
Acetone	0.42	0.22	0.43	4.15	2.69	1.75
Acetonitrile	0.37	0.12	0.38	4.15	2.74	1.73
Methanol	0.19	0.08	0.36	2.12	1.70	1.29
DMSO	0.32	0.17	0.32	4.13	2.73	1.80

The fluorescence decay behaviors of three compounds were also studied in several solvents. The decay profile of compound (3) was shown in Fig. S3 as representative. Fig. S3 is placed in supporting information. The fluorescence lifetimes (τ, ns) were collected in Table 4. For three compounds, the fluorescence decay curves were mono-exponential model.

5. Conclusions

In this paper, three new $D-\pi-A$ type compounds, namely 9-(4-(benzothiazol-2-yl)phenyl)-9H-carbazole 9-(4-(3) (2-(benzothiazol-2-yl)vinyl)phenyl)-9H-carbazole (4)and 9-(4-(4-(benzothiazol-2-yl)styryl) phenvl)-9H-carbazole (5) were synthesized and characterized by elemental analysis. NMR. MS and thermogravimetric analysis. The calculated absorption and emission wavelengths are well coincident with the measured data. The calculated reorganization energy for hole and electron indicates that three compounds are in favor of hole transport than electron transport. The calculated lowest-lying absorption spectra can be mainly attributed to intramolecular charge transfer (ICT). And the calculated fluorescence spectra can be mainly described as originating from an excited state with intramolecular charge transfer (ICT) character. The results show that three compounds exhibited excellent thermal stability and high fluorescence quantum yields, indicating their potential application as excellent optoelectronic material in optical field. Such studies are currently under way in our laboratory, and the results will be released soon.

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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.2011.07.017.

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