



The synthesis and optical properties of benzothiazole-based derivatives with various π -electron donors as novel bipolar fluorescent compounds

Haiying Wang, Gang Chen, Xiaoping Xu, Hua Chen, Shunjun Ji*

Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Ren'ai Road, Suzhou Industrial Park, Suzhou 215123, People's Republic of China

ARTICLE INFO

Article history:

Received 9 November 2009

Received in revised form

19 January 2010

Accepted 19 January 2010

Available online 28 January 2010

Keywords:

Benzothiazole

Bipolar

Optical

Chemical calculation

Electrochemical

π -Bridge

ABSTRACT

Novel bipolar benzothiazole-based derivatives with various π -electron donors were synthesized and characterized using ^1H and ^{13}C NMR and mass spectrometry; their thermal, optical and electrochemical properties were also investigated. Optoelectronic properties are reported and discussed in terms of the distribution of the highest occupied molecular orbital and the lowest unoccupied molecular orbital and the conjugative pathway between the electron-donating moieties and electron-accepting moieties. The compounds exhibited high fluorescence quantum yield, desirable HOMO levels and high thermal stability. Quantum chemical calculations were used to study optimized ground-state geometry as well as spatial distributions of HOMO and LUMO levels of the compounds.

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1. Introduction

Organic fluorescent compounds have been extensively investigated for various potential applications including biological labels, photovoltaic cells, light-emitting diodes (LEDs), and optical sensors [1–14]. Fluorescent characteristics rely largely on molecular structure and molecular assembly. Low band gap conjugated materials are of interest because of their high tendency for harvesting visible wavelength photons, tunable red-ox and utility in ambipolar transistors [15–24]. In particular, a promising strategy is to develop bipolar molecules bearing both electron-donating moiety (D) and electron-accepting moiety (A) capable of matching for charge carrier injection and acceptance of both holes and electrons [25–29]. An important property to this end is the modulation of the HOMO–LUMO (highest occupied molecular orbital–lowest unoccupied molecular orbital) gap of conjugated molecules, which can be achieved by simple introduction of the appropriate D and A units in the molecule [30–35]. In such systems, interactions of the HOMO of the electron-donating moiety (D) and the LUMO of the electron-accepting moiety (A) cause the reduction of the band gap of these materials [36–40]. Meanwhile, the levels of the HOMO and LUMO as well as the emission color of the D–A molecule can be controlled

to a fine degree [25–29], making such systems increasingly attractive for use in a single-layer OLEDs [41,42]. Kannan et al. also reported that the benzothiazole moiety is an excellent acceptor. It gives rise to a D- π -A type compound that shows an optimized two-photon-absorption (TPA) cross-section compared with the asymmetrical diphenylaminofluorene-based chromophores (designated as AFX) series of TPA compounds [43–45]. By fixing the benzothiazole unit as an optimized acceptor, the change by a series of different donors or π -bridges of the molecular structures may further optimize the TPA of the compounds. Carbazole derivatives have been widely utilized as a functional building block in the fabrication of the organic photoconductors, non-linear optical materials, and photorefractive materials in OLEDs due to their excellent solubility, stability and the excellent hole-transporting capability (the electron-donating properties) [46–49].

Based on these ideas, we recently synthesized a series of new bipolar compounds, where D is a carbazole groups, A is fixed as a benzothiazole unit and the π -bridge is extended to conjugated styryl units. We believed that the skeleton of this π -bridge is maintained basically planar, since planarity is commonly regarded as a positive structural factor in enhancing the molecular fluorescent properties. As expected, the emission color of these compounds can be easily tuned from blue to green by increasing conjugation length. Particularly, all of the compounds exhibited desirable HOMO levels (–5.30 to –5.48 eV) and high thermal stability, which have promising potential for application in OLEDs.

* Corresponding author. Tel./fax: +86 512 65880307.

E-mail address: chemjsj@suda.edu.cn (S. Ji).

2. Experimental

2.1. Chemicals and instruments

All solvents were carefully dried and freshly distilled according to common laboratory techniques. All reactants were commercially available and used without further purification. Melting points were recorded on Electrothermal digital melting point apparatus and were uncorrected. ^1H and ^{13}C NMR spectra were recorded at 295 K on a Varian INOVA 400 MHz or a Varian NMR System 300 MHz spectrometer using CDCl_3 or $\text{DMSO}-d_6$ as solvent and TMS as internal standard. UV–vis spectra were recorded on a Shimadzu UV-2501PC spectrometer. Fluorescence spectra were obtained on a Hitachi FL-2500 spectrofluorometer. HRMS data were measured using TOF-MS(EI+) instrument and microTOF-Q(ESI) instrument. Thermal properties was performed under nitrogen on a thermogravimetric analysis SDT 2960 (heating rate of $10^\circ\text{C min}^{-1}$) and a differential scanning calorimetry (DSC) 2010 instruments (scanning rate of $10^\circ\text{C min}^{-1}$). Cyclic voltammetry was carried on a Chi 1200A electrochemical analyzer with three electrode cell (Platinum was used as working electrode and as counter electrode, and SCE (saturated calomel electrode) as reference electrode) in CHCl_3 solution in the presence of TBAHFP (tetrabutylammonium hexafluorophosphate) (0.10 mol L^{-1}) as supporting electrolyte.

2.2. General procedure for the synthesis of compounds (3)

A mixture of the corresponding aromatic aldehyde (**2**) (1 mmol), 2-aminothiophenol (**1**) (1.25 mmol, 1.25 equiv), and DMSO (30 mL) was heated in an oil bath to a bath temperature of 195°C , held at that temperature for 2 h, and then poured into water. The separated solids were collected, reslurried in 1:4 acetic acid–water (50 mL), filtered, and washed with water and dilute sodium bicarbonate solution. These solids were then reslurried in hot ethanol (50 mL), cooled, and filtered to give the compounds.

2-*p*-Tolylbenzothiazole (**3a**): yield 86%, m.p. $85\text{--}86^\circ\text{C}$ (lit. [50] $85\text{--}86^\circ\text{C}$), yellow powder, $^1\text{H NMR}$ (400 MHz, $\text{DMSO}-d_6$): $\delta = 8.17$ (d, $J = 8.0\text{ Hz}$, 1H), 8.08 (d, $J = 8.0\text{ Hz}$, 1H), 8.04 (d, $J = 8.4\text{ Hz}$, 2H), 7.77–7.79 (m, 2H), 7.55–7.59 (m, 1H), 7.47–7.51 (m, 1H) ppm.

2-(4-Bromophenyl)benzothiazole (**3b**): yield 88%, m.p. $131\text{--}132^\circ\text{C}$ (lit. [51] $131\text{--}132^\circ\text{C}$), yellow powder, $^1\text{H NMR}$ (400 MHz, $\text{DMSO}-d_6$): $\delta = 8.14$ (d, $J = 10.4\text{ Hz}$, 1H), 8.05 (d, $J = 10.8\text{ Hz}$, 1H), 7.99 (d, $J = 10.4\text{ Hz}$, 2H), 7.55 (t, $J = 10.0\text{ Hz}$, 1H), 7.45 (t, $J = 10.0\text{ Hz}$, 1H), 7.39 (d, $J = 10.4\text{ Hz}$, 2H), 2.40 (s, 3H) ppm.

2.3. 2-(4-(Bromomethyl)phenyl)benzothiazole (4)

Compound **3a** (27.1 g, 120 mmol) and *N*-bromosuccinimide (NBS) (21.4 g, 120 mmol) were dissolved in 500 mL of CCl_4 . 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 a vacuum (34.3 g, 94%). m.p. $130\text{--}131^\circ\text{C}$, white powder, $^1\text{H NMR}$ (300 MHz, CDCl_3): $\delta = 8.07\text{--}8.09$ (d, $J = 6.9\text{ Hz}$, 3H), 7.90–7.93 (d, $J = 8.1\text{ Hz}$, 1H), 7.48–7.53 (m, 3H), 7.40 (t, $J = 7.5\text{ Hz}$, 1H), 4.54 (s, 2H) ppm. HRMS M^+ : Calcd for $\text{C}_{14}\text{H}_{10}\text{BrNS}$: 302.9717, Found: 302.9716.

2.4. 9-Alkylcarbazole (7)

To a stirred solution of carbazole **8** (20.0 g, 120 mmol) and tetrabutylammonium bromide (TBAB) (0.8 g) in DMSO (100 mL), 70.0 g 50% KOH (aq) was added. Then the corresponding alkylbromide (140 mmol) was added dropwise. After complete addition,

the reaction mixture was heated under reflux for 16 h. The organic layer was separated, washed with water, dried over MgSO_4 and concentrated. Pure product was obtained after silica gel column chromatography (ethyl acetate/petroleum ether, 1/100, v/v) as a white solid.

9-Butylcarbazole (**7a**) yield 92%, m.p. $54\text{--}55^\circ\text{C}$, white powder, $^1\text{H NMR}$ (300 MHz, CDCl_3): $\delta = 8.21\text{--}8.24$ (m, 2H), 7.51–7.58 (m, 4H), 7.32–7.37 (m, 2H), 4.42 (t, $J = 6.3\text{ Hz}$, 2H), 1.93–2.02 (m, 2H), 1.49–1.54 (m, 2H), 1.06 (t, $J = 7.2\text{ Hz}$, 3H) ppm. HRMS M^+ : Calcd for $\text{C}_{16}\text{H}_{17}\text{N}$: 223.1361, Found: 223.1360.

9-Hexylcarbazole (**7b**) yield 92%, m.p. $64\text{--}65^\circ\text{C}$, white powder, $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 8.10$ (d, $J = 7.6\text{ Hz}$, 2H), 7.39–7.50 (m, 4H), 7.20–7.24 (m, 2H), 4.30 (t, $J = 6.8\text{ Hz}$, 2H), 1.81–1.91 (m, 2H), 1.28–1.40 (m, 6H), 0.86 (t, $J = 7.2\text{ Hz}$, 3H) ppm. HRMS M^+ : Calcd for $\text{C}_{18}\text{H}_{21}\text{N}$: 251.1674, Found: 251.1672.

2.5. 9-Butyl-carbazole-3-carbaldehyde (8)

Phosphorus oxychloride (caution: reacts violently with water; incompatible with many metals, alcohols, amines, phenol, DMSO, strong bases; 1.6 mL, 17 mmol) was added dropwise to DMF (1.5 mL, 20 mmol) at 0°C , and the mixture was stirred for 1 h at this temperature. 9-butylcarbazole **7a** (3.35 g, 15 mmol) was added and the reaction mixture was stirred at 100°C for 6 h. Then, the mixture was cooled to room temperature, poured into ice water and carefully neutralized with sodium hydroxide. The solution was extracted with dichloromethane ($3 \times 50\text{ mL}$). The organic phase was washed with water ($2 \times 50\text{ mL}$) and dried over anhydrous sodium sulfate. After filtration, the solvent was removed. The crude product was purified by silica gel column chromatography (ethyl acetate/petroleum ether, 1/10, v/v) to give **8** (2.63 g, 70%). m.p. $49\text{--}50^\circ\text{C}$, white powder, $^1\text{H NMR}$ (300 MHz, CDCl_3): $\delta = 10.04$ (s, 1H), 8.49 (s, 1H), 8.09 (d, $J = 7.8\text{ Hz}$, 1H), 7.96 (d, $J = 9.6\text{ Hz}$, 1H), 7.51 (t, $J = 7.5\text{ Hz}$, 1H), 7.27–7.39 (m, 3H), 4.18 (t, $J = 7.2\text{ Hz}$, 2H), 1.76–1.81 (m, 2H), 1.31–1.38 (m, 2H), 0.92 (t, $J = 7.2\text{ Hz}$, 3H) ppm. HRMS M^+ : Calcd for $\text{C}_{17}\text{H}_{17}\text{NO}$: 251.1310, Found: 251.1309.

2.6. 9-Butyl-carbazole-3,6-dicarbaldehyde (9)

This compound was prepared according to the general procedure for **8** by using 9-butylcarbazole **7a** (4.50 g, 20 mmol), phosphorus oxychloride (4.8 mL, 51 mmol), and DMF (4.5 mL, 60 mmol). The mixture was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether, 1/20, v/v) to afford **9** (3.80 g, 68%). m.p. $118\text{--}119^\circ\text{C}$, yellow powder, $^1\text{H NMR}$ (300 MHz, CDCl_3): $\delta = 10.15$ (s, 2H), 8.68 (s, 2H), 8.11 (d, $J = 8.7\text{ Hz}$, 2H), 7.58 (d, $J = 7.8\text{ Hz}$, 2H), 4.41 (t, $J = 6.3\text{ Hz}$, 2H), 1.89–1.92 (m, 2H), 1.43–1.45 (m, 2H), 0.99 (t, $J = 6.0\text{ Hz}$, 3H) ppm. HRMS M^+ : Calcd for $\text{C}_{18}\text{H}_{17}\text{NO}_2$: 279.1259, Found: 279.1260.

2.7. Bis[9-hexylcarbazol-3-yl] (12)

To a stirred solution of 9-hexylcarbazole **7b** (3.23 g, 11.6 mmol) in 50 mL chloroform under argon atmosphere was added iron(III) chloride (3.75 g, 23.2 mmol) at once. After stirring at room temperature during 16 h, 50 mL water was added. The organic layer was separated, dried over MgSO_4 , filtered and concentrated. The mixture was purified by column chromatography (ethyl acetate/petroleum ether, 1/8, v/v) to obtain **12** (2.34 g, 81%) as white crystals. m.p. $79\text{--}80^\circ\text{C}$, $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 8.46$ (s, 2H), 8.24 (d, $J = 7.6\text{ Hz}$, 2H), 7.88 (d, $J = 8.4\text{ Hz}$, 2H), 7.45–7.54 (m, 6H), 7.29 (t, $J = 7.6\text{ Hz}$, 2H), 4.35 (t, $J = 7.2\text{ Hz}$, 4H), 1.89–1.97 (m, 4H), 1.32–1.47 (m, 12H), 0.92 (t, $J = 7.2\text{ Hz}$, 6H) ppm. HRMS M^+ : Calcd for $\text{C}_{36}\text{H}_{40}\text{N}_2$: 500.3191, Found: 500.3190.

2.8. 9,9'-Dihexyl-3,3'-bicarbazole-6,6'-dicarbaldehyde (**13**)

This compound was prepared according to the general procedure for **8** by using **12** (5.00 g, 10 mmol), phosphorus oxychloride (2.8 mL, 30 mmol), and DMF (3.0 mL, 40 mmol). The mixture was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether, 1/4, v/v) to afford **13** (3.80 g, 68%). m.p. 138–139 °C, yellow powder, ¹H NMR (300 MHz, CDCl₃): δ = 10.11 (s, 2H), 8.89 (s, 2H), 8.47 (s, 2H), 8.05 (d, *J* = 6.3 Hz, 2H), 7.91 (d, *J* = 6.3 Hz, 2H), 7.57 (d, *J* = 6.3 Hz, 2H), 7.51 (d, *J* = 6.3 Hz, 2H), 4.37 (t, *J* = 5.4 Hz, 2H), 1.89–1.97 (m, 4H), 1.28–1.45 (m, 12H), 0.88 (t, *J* = 5.1 Hz, 6H) ppm. HRMS M⁺: Calcd for C₃₈H₄₀N₂O₂: 556.3090, Found: 556.3089.

2.9. 3-Bromo-9-butylcarbazole (**10**)

In a flask, covered with aluminum foil, a stirred solution of 9-butylcarbazole **7a** (4.46 g, 20.0 mmol) in CHCl₃ (100 mL) was cooled to 0 °C. NBS (3.56 g, 20.0 mmol) was added in small portions. The mixture was allowed to warm to room temperature overnight. CHCl₃ was evaporated and the crude product was purified by extraction with diethylether and water. After same work up as above, final product was obtained as colorless oil (4.23 g, 70%). ¹H NMR (400 MHz, CDCl₃): δ = 8.19 (s, 1H), 8.02 (d, *J* = 7.2 Hz, 1H), 7.36–7.53 (m, 3H), 7.23–7.26 (m, 2H), 4.23 (t, *J* = 6.8 Hz, 2H), 1.77–1.87 (m, 2H), 1.28–1.39 (m, 2H), 0.86 (t, *J* = 7.2 Hz, 3H) ppm. HRMS M⁺: Calcd for C₁₆H₁₆BrN: 301.0466, Found: 301.0464.

2.10. 9-Butylcarbazol-3-ylboronic acid (**11**)

A solution of 3-bromo-9-butylcarbazole **10** (3.03 g, 10.0 mmol) in anhydrous THF (50 mL) was cooled to –78 °C. *n*-BuLi (2.5 mol L⁻¹ in hexane, 4.8 mL, 12.0 mmol) was slowly added dropwise. After complete addition, the reaction mixture was stirred for another 1 h. Then, triisopropyl borate (3.5 mL, 15.0 mmol) was added at once. The mixture was allowed to warm to room temperature for 15 h. The reaction was finally quenched with HCl (2.0 mol L⁻¹, 40 mL) and the mixture was poured into a large amount of water. After extraction with CH₂Cl₂ (3 × 20 mL), the organic layer was washed with brine, dried over MgSO₄, concentrated. Further purification by silica gel column chromatography (petroleum ether/dichloromethane, 2/1, v/v) afforded **11** as a white solid (1.44 g, 54%). m.p. 148–150 °C, ¹H NMR (300 MHz, DMSO-*d*₆): δ = 8.59 (s, 1H), 8.11 (d, *J* = 7.5 Hz, 1H), 7.93 (s, 2H), 7.89 (s, 1H), 7.52–7.59 (m, 2H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 4.38 (t, *J* = 6.6 Hz, 2H), 1.71–1.76 (m, 2H), 1.25–1.32 (m, 2H), 0.87 (t, *J* = 7.5 Hz, 3H) ppm. HRMS M⁺: Calcd for C₁₆H₁₈BNO₂: 267.1431, Found: 267.1430.

2.11. 9-Butyl-6-iodo-carbazole-3-carbaldehyde (**14**)

Under heavy stirring and slightly warming, 5.02 g (20 mmol) of **8** was dissolved in 20 mL of glacial acetic acid. Then, 6.64 g (40 mmol) of KI and 12.84 g (60 mmol) of KIO₃ were added, and the reaction mixture was stirred for 3 h at 70 °C. After cooling, the salts were filtered off and washed thoroughly with water (50 mL) and dichloromethane (100 mL). The aqueous phase was extracted several times with dichloromethane. The combined organic phases were washed with a diluted ammonia solution until pH ≈ 8, with a NaHSO₃ solution, and with brine and dried over MgSO₄. After removal of the solvents, the crude compound was stirred for 15 min in 50 mL of boiling ethanol; the solution was cooled, and the pure product was isolated by filtration (5.65 g, 75%). m.p. 115–116 °C, yellow powder, ¹H NMR (300 MHz, CDCl₃): δ = 10.07 (s, 1H), 8.51 (s, 1H), 8.44 (s, 1H), 8.03 (d, *J* = 8.7 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.47

(d, *J* = 8.4 Hz, 1H), 7.24 (t, *J* = 8.4 Hz, 1H), 4.29 (t, *J* = 6.9 Hz, 2H), 1.84–1.87 (m, 2H), 1.37–1.41 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H) ppm. HRMS M⁺: Calcd for C₁₇H₁₆INO: 377.0277, Found: 377.0278.

2.12. 9,9'-Dibutyl-3,3'-bicarbazole-6-carbaldehyde (**15**)

Under a nitrogen atmosphere, a mixture of compound **14** (1.0 mmol), Pd(PPh₃)₄ catalyst (0.04 mmol) and the carbazole boronic acid **11** (1.0 mmol) was stirred in dry toluene (15 mL). Then, 2 mol L⁻¹ K₂CO₃ (aq) solution (2 mL) was added via syringe. The reaction mixture was heated to reflux for 36 h. After cooling, the product was extracted with dichloromethane, washed with water, dried over MgSO₄, filtered, concentrated and further purified by silica gel column chromatography (ethyl acetate/petroleum ether, 1/10, v/v). The pure compound **15** was obtained (0.31 g, 64%). m.p. 88–90 °C, yellow powder, ¹H NMR (300 MHz, CDCl₃): δ = 10.12 (s, 1H), 8.70 (s, 1H), 8.48 (s, 1H), 8.41 (s, 1H), 8.21 (d, *J* = 7.8 Hz, 1H), 8.05 (d, *J* = 8.7 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.7 Hz, 1H), 7.46–7.56 (m, 5H), 7.29 (s, 1H), 4.34–4.41 (m, 4H), 1.90–1.94 (m, 4H), 1.44–1.49 (m, 4H), 0.96–1.01 (m, 6H) ppm. HRMS M⁺: Calcd for C₃₃H₃₂N₂O: 472.2515, Found: 472.2514.

2.13. General procedure for the synthesis of the compounds (**16–19**)

A mixture of the corresponding aromatic aldehyde (1.0 mmol), 2-aminothiophenol (1.25 mmol, 1.25 equiv), and DMSO (30 mL) was heated in an oil bath to a bath temperature of 195 °C, held at that temperature for 2 h, and then poured into water. The separated solids were collected, reslurried in 1:4 acetic acid–water (50 mL), filtered, and washed with water and dilute sodium bicarbonate solution. These solids were recrystallized from ethanol to give compounds **16–19**.

3-Benzothiazolyl-9-butyl-carbazole (**16**): yield 82%, m.p. 121 °C, yellow powder, ¹H NMR (300 MHz, CDCl₃): δ = 8.85 (s, 1H), 8.18–8.21 (m, 2H), 8.06 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 7.5 Hz, 1H), 7.42–7.51 (m, 4H), 7.25–7.37 (m, 2H), 4.33 (t, *J* = 6.9 Hz, 2H), 1.86–1.90 (m, 2H), 1.41–1.43 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 169.7, 154.6, 142.3, 141.3, 135.1, 126.6, 126.4, 125.7, 124.8, 123.5, 123.1, 122.8, 121.7, 121.1, 120.2, 119.9, 109.4, 109.2, 43.2, 31.3, 20.8, 14.1 ppm. HRMS M⁺: Calcd for C₂₃H₂₀N₂S: 356.1347, Found: 356.1346.

9-Butyl-3,6-di-2-benzothiazolyl-carbazole (**17**): yield 80%, m.p. 189 °C, yellow powder, ¹H NMR (300 MHz, CDCl₃): δ = 8.93 (s, 2H), 8.26 (d, *J* = 7.8 Hz, 2H), 8.09 (d, *J* = 7.8 Hz, 2H), 7.93 (d, *J* = 6.6 Hz, 2H), 7.50–7.52 (m, 4H), 7.38–7.41 (m, 2H), 4.38 (s, 2H), 1.90–1.94 (m, 2H), 1.41–1.47 (m, 2H), 0.98 (s, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 169.2, 154.5, 142.8, 135.2, 126.5, 126.2, 125.7, 124.9, 123.5, 122.9, 121.8, 120.6, 109.7, 43.5, 31.3, 20.7, 14.1 ppm. HRMS M⁺: Calcd for C₃₀H₂₃N₃S₂: 489.1333, Found: 489.1331.

6-(2-Benzothiazolyl)-9,9'-dibutyl-3,3'-bicarbazole (**18**): yield 75%, m.p. 202 °C, yellow powder, ¹H NMR (300 MHz, CDCl₃): δ = 8.89–9.01 (m, 2H), 8.54 (s, 1H), 8.44 (s, 1H), 8.08–8.23 (m, 3H), 7.83–7.93 (m, 3H), 7.37–7.54 (m, 7H), 4.37–4.39 (m, 4H), 1.91–1.92 (m, 4H), 1.43–1.47 (m, 4H), 0.96–0.99 (m, 6H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 169.6, 154.6, 154.6, 148.1, 142.7, 140.5, 140.3, 140.2, 140.2, 135.1, 134.4, 133.1, 132.8, 128.7, 123.4, 123.4, 126.3, 125.6, 124.8, 124.7, 123.7, 123.6, 122.8, 121.7, 120.7, 119.4, 109.5, 109.2, 109.1, 43.3, 43.2, 31.5, 31.4, 20.8, 20.7, 14.1, 14.0 ppm. HRMS M⁺: Calcd for C₃₉H₃₅N₃S: 577.2552, Found: 577.2564.

6,6'-(Di-2-benzothiazolyl)-9,9'-dihexyl-3,3'-bicarbazole (**19**): yield 78%, m.p. 249 °C, yellow powder, ¹H NMR (300 MHz, CDCl₃): δ = 8.97 (s, 2H), 8.57 (s, 2H), 8.23 (d, *J* = 8.7 Hz, 2H), 8.09 (d, *J* = 8.1 Hz, 2H), 7.91 (d, *J* = 7.8 Hz, 4H), 7.47–7.57 (m, 6H), 7.37 (t, *J* = 7.5 Hz, 2H), 4.39 (t, *J* = 6.6 Hz, 4H), 1.94–1.98 (m, 4H), 1.34–1.46

(m, 12H), 0.89 (t, $J = 6.6$ Hz, 6H) ppm. ^{13}C NMR (75 MHz, CDCl_3): $\delta = 169.6, 154.5, 142.7, 140.4, 135.1, 133.8, 126.4, 126.2, 125.7, 124.7, 123.7, 123.6, 122.8, 121.7, 120.4, 119.4, 109.6, 109.3, 43.6, 31.8, 29.2, 27.2, 22.8, 14.3$ ppm. HRMS ($\text{M} + \text{H}^+$): Calcd for $\text{C}_{50}\text{H}_{46}\text{N}_4\text{S}_2$: 767.3243, Found: 768.3417.

2.14. 3-(4-(2-Benzothiazolyl)-phenyl)-9-butyl-carbazole (**20**)

Compound **20** was prepared according to the similar procedure for compound **15**: yield 61%, m.p. 169 °C, yellow powder, ^1H NMR (300 MHz, CDCl_3): $\delta = 8.39$ (s, 1H), 8.16–8.21 (m, 3H), 8.09 (t, $J = 8.1$ Hz, 1H), 7.76–7.94 (m, 4H), 7.37–7.53 (m, 5H), 7.27 (s, 1H), 4.35 (t, $J = 6.9$ Hz, 2H), 1.85–1.94 (m, 2H), 1.37–1.49 (m, 2H), 0.97 (t, $J = 7.2$ Hz, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3): $\delta = 168.3, 154.5, 144.9, 141.2, 140.5, 135.3, 131.7, 131.1, 128.2, 127.8, 126.5, 126.2, 125.3, 125.2, 123.7, 123.3, 123.1, 121.8, 120.7, 119.3, 119.1, 109.3, 109.1, 43.2, 31.4, 20.8, 14.2$ ppm. HRMS M^+ : Calcd for $\text{C}_{29}\text{H}_{24}\text{N}_2\text{S}$: 432.1660, Found: 432.1660.

2.15. General procedure for the synthesis of the compounds (**21–23**)

Compound **4** (2 mmol) and triethyl phosphite (caution: incompatible with strong oxidizing agents, strong bases; may

decompose on exposure to moist air or water; 3 mmol) were heated to reflux at 185 °C for 3 h with stirring. The resulting clear brown oil was then distilled under reduced pressure. Excess triethyl phosphite was collected at 69 °C (1.5 mm Hg) and **8** (2 mmol), **9** (1 mmol) or **13** (1 mmol) in dry DMF (5 mL) was added dropwise. NaOEt was added and the mixture was heated to 60 °C for 2 h. The mixture was cooled and quenched with EtOH. All solvents were then removed under reduced pressure. Solids were dissolved in CH_2Cl_2 , washed in distilled H_2O , dried over MgSO_4 and the solvent was removed. The residue was chromatographed on a silica gel column (petroleum ether/dichloromethane, 4/1, v/v) to afford the corresponding compounds.

(*E*)-3-(2-(4-(2-benzothiazolyl)-phenyl)-vinyl)-9-butyl-carbazole (**21**): yield 76%, m.p. 192 °C, yellow powder, ^1H NMR (300 MHz, CDCl_3): $\delta = 8.27$ (s, 1H), 8.09–8.15 (m, 3H), 7.90–7.96 (m, 2H), 7.66–7.72 (m, 2H), 7.39–7.50 (m, 6H), 7.17–7.26 (m, 1H), 6.88 (d, $J = 12.0$ Hz, 1H), 6.57 (d, $J = 12.3$ Hz, 1H), 4.32 (t, $J = 6.9$ Hz, 2H), 1.83–1.90 (m, 2H), 1.38–1.46 (m, 2H), 0.96 (t, $J = 7.2$ Hz, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 154.4, 141.1, 141.0, 140.7, 135.2, 132.1, 131.7, 128.3, 128.1, 126.8, 126.5, 126.1, 125.3, 125.0, 124.8, 123.5, 123.2, 123.0, 121.8, 120.6, 119.3, 119.2, 109.2, 109.1, 43.2, 31.3, 20.7, 14.1$ ppm. HRMS M^+ : Calcd for $\text{C}_{31}\text{H}_{26}\text{N}_2\text{S}$: 458.1817, Found: 458.1815.

(*E*)-3,6-di((2-(4-(2-benzothiazolyl)-phenyl)-vinyl)-9-butyl-carbazole (**22**): yield 73%, m.p. 280 °C, yellow powder, ^1H NMR

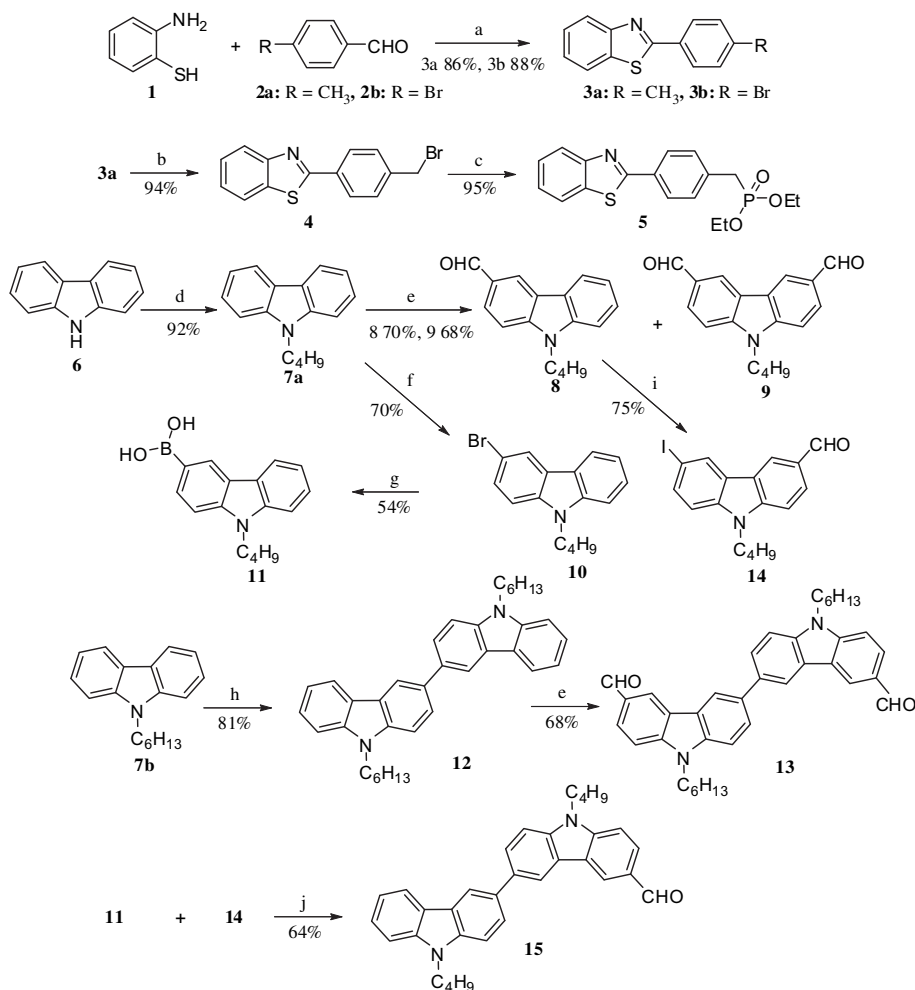


Fig. 1. Synthetic routines for the corresponding compounds. Reagents and conditions: (a) $\text{DMSO}/190^\circ\text{C}$; (b) $\text{NBS}/\text{CCl}_4/\text{reflux}$; (c) $\text{P}(\text{OEt})_3/\Delta$; (d) 1-bromobutane, KOH , TBAB , DMSO , 100°C ; (e) POCl_3/DMF ; (f) NBS , DMF , darkness, 0°C ; (g) *n*-BuLi (1.2 equiv), THF , -78°C , $(\text{CH}_3\text{O})_3\text{B}$ (1.5 equiv), $\text{H}_2\text{O}/\text{HCl}$; (h) $\text{FeCl}_3/\text{CHCl}_3$; (i) $\text{KI}/\text{KIO}_3/\text{HOAc}$; and (j) $\text{Pd}(\text{PPh}_3)_4$, 2 mol L^{-1} K_2CO_3 , toluene, 80°C .

(300 MHz, CDCl_3): δ = 8.31 (s, 1H), 8.10 (t, J = 8.4 Hz, 4H), 7.90 (d, J = 8.4 Hz, 1H), 7.67–7.73 (m, 4H), 7.37–7.51 (m, 6H), 7.19–7.24 (m, 2H), 4.32 (t, J = 7.2 Hz, 2H), 1.84–1.89 (m, 2H), 1.41–1.44 (m, 2H), 0.97 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 154.4, 152.2, 141.2, 140.9, 135.2, 132.2, 131.5, 129.5, 128.7, 126.9, 126.9, 126.5, 125.4, 125.3, 123.5, 123.4, 123.3, 121.8, 119.2, 109.5, 105.5, 40.3, 31.4, 20.7, 14.1 ppm. HRMS ($\text{M} + \text{H}$)⁺: Calcd for $\text{C}_{46}\text{H}_{35}\text{N}_3\text{S}_2$: 694.2351, Found: 694.2384.

(*E*)-6,6'-di((2-(2-benzothiazolyl)-phenyl)-vinyl)-9,9'-dihexyl-3,3'-bicarbazole (**23**): yield 62%, m.p. 258 °C, yellow powder, ^1H NMR (300 MHz, CDCl_3): δ = 8.47 (s, 2H), 8.37 (s, 2H), 8.06–8.12 (m, 6H), 7.86–7.91 (m, 4H), 7.66–7.70 (m, 6H), 7.35–7.53 (m, 11H), 7.19 (s, 1H), 4.35 (t, J = 7.2 Hz, 4H), 1.92–1.96 (m, 4H), 1.34–1.44 (m, 12H), 0.89 (t, J = 6.6 Hz, 6H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 154.4, 141.2, 135.2, 133.7, 132.3, 132.1, 131.7, 128.5, 128.3, 128.1, 126.8, 126.5, 126.0, 125.3, 125.1, 123.7, 123.3, 121.8, 119.4, 119.3, 109.9, 109.6, 109.5, 109.4, 109.3, 40.6, 31.8, 31.7, 29.3, 29.2, 27.2, 27.1, 22.8, 14.3, 14.2 ppm. HRMS ($\text{M} + \text{H}$)⁺: Calcd for $\text{C}_{66}\text{H}_{58}\text{N}_4\text{S}_2$: 971.4182, Found: 971.4222.

3. Results and discussion

Compound **3a/b** were prepared in high yield by stirring 2-aminothiophenol (**1**) and the corresponding aromatic aldehydes (**2**) in DMSO at 140 °C (Fig. 1) [43]. 2-(4-(Bromomethyl)phenyl)benzothiazole was prepared via free radical bromination of (**3a**) with NBS

(Fig. 1) and was reacted with triethylphosphite to yield phosphonium salt **5** via an Arbusov reaction [52]. Carbaldehydes (**8**, **9**, **13**) were obtained by a Vilsmeier formylation reaction of the corresponding carbazole (**7**) with DMF and POCl_3 (Fig. 1) [53] and subsequently condensed with 2-aminothiophenol using similar experimental conditions for compound **3a/b** and gave **16**, **17** and **19** (Fig. 2). Compound **18** was synthesized from the reaction between 2-aminothiophenol (**1**) and the intermediate aldehyde **15**, which was synthesized via a Pd(0) catalyzed Suzuki C–C coupling reaction [54]. Compound **20** was produced by another Suzuki C–C coupling reaction of **3b** with **11**. Compounds **21–23** were resulted from the Wittig–Horner condensation of the phosphonium salt **5** with corresponding carbaldehydes (**8**, **9**, **13**) in the presence of NaOEt as a base (Fig. 3). All of these new compounds were characterized by mass spectrometry and ^1H and ^{13}C NMR spectroscopy, which were shown detailed in experiment section and supporting information.

3.1. Thermal properties

The thermal properties of these compounds were examined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), and the detailed data are listed in Table 1. It should be pointed out that only **18**, **19** and **23** among these compounds exhibit glass transition temperatures during DSC analysis, which might be due to the bicarbazole units in these compounds. The other compounds in this study exhibit only single melting point

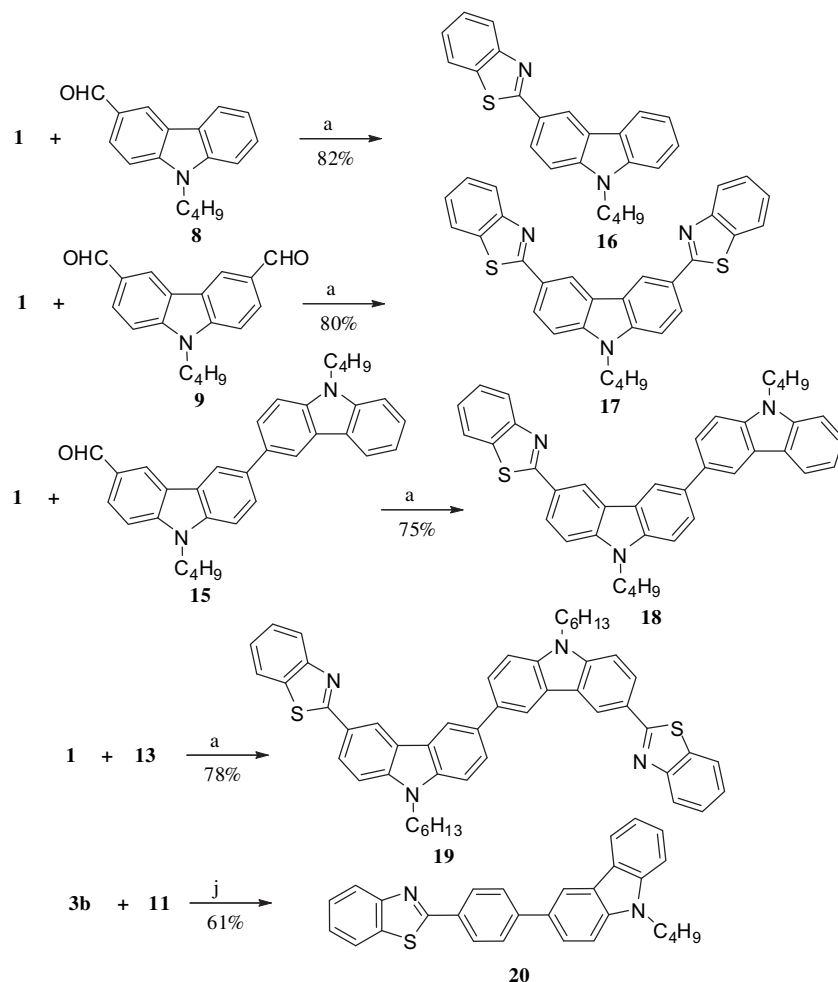


Fig. 2. Synthetic routines of **16–20**. Reagents and conditions: (a) DMSO/190 °C; and (j) $\text{Pd}(\text{PPh}_3)_4$, 2 mol L^{-1} K_2CO_3 , toluene, 80 °C.

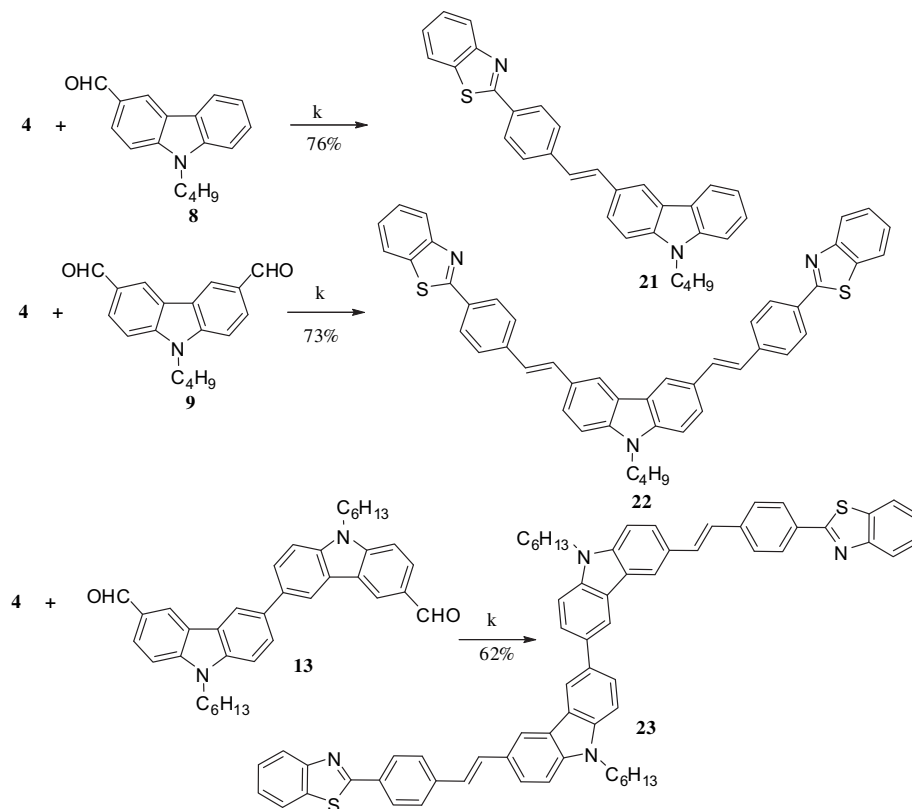


Fig. 3. Synthetic routines of **21–23**. Reagents and conditions: (k) NaOEt/DMF.

transitions. In addition, these compounds show high thermal stability with decomposition temperature (Td) from 255 to 400 °C. The incorporation of the carbazole units leads to the high thermal stabilities of these compounds, which are expected to be encouraging for the processing and longevity in a device application [46–49].

3.2. Optical properties

The absorption spectra of the compounds were measured in chloroform solutions and the results are shown in Figs. 4 and 5. All the compounds exhibit two absorption peaks attributed to carbazole moiety and the charge transfer associated with benzothiazole moiety (Table 1). The bands from 345 to 393 nm can be

attributed to the charge transfer (CT) type $\pi-\pi^*$ transition from the HOMO located at the electron-donating carbazole moiety to the LUMO located at the electron-accepting benzothiazole moiety, whereas the absorption bands from 290 to 318 nm should come from the locally excited (LE) $\pi-\pi^*$ transition at the carbazole moiety [55]. The CT absorption band of the compounds strongly depends on the conjugation length. As can be seen in Fig. 4, the largest red-shift of the CT band was observed at 393 nm for compound **23**, which possesses the longest conjugation length, relative to that of the other compounds. Whereas, compound **16**, having a shorter conjugation length (compared to **22** and **23**) exhibits a blue shifted absorption maximized at 345 nm. The explanation for such variations of the CT bands may be attributed to the difference in the steric hindrance imposed by the

Table 1
Optical, thermal, and electrochemical properties of the compounds **16–23**.

Compound	Abs. (nm)	em (nm)	Φ^a	Band gap ^b	HOMO/LUMO ^c (eV)	Eg ^c (eV)	Eox ^d (V)	Ered (V)	E _{HOMO} /E _{LUMO} ^e (eV)	Tm/Td/Tg ^f (°C)
16	346	400	0.73	3.98	−5.23/−1.25	3.04	0.90	0.60	−5.30/−2.26	121/255/— ^g
17	360	397	0.83	3.79	−5.28/−1.49	3.10	1.07	0.95	−5.47/−2.37	189/330/— ^g
18	352	452	0.31	3.67	−4.90/−1.23	2.97	1.08	0.79	−5.48/−2.51	202/340/−127
19	353	432	0.27	3.72	−5.01/−1.29	3.03	1.03	0.92	−5.43/−2.40	249/350/95
20	350	439	0.92	3.63	−5.16/−1.53	3.00	1.22	0.98	−5.62/−2.62	169/320/— ^g
21	381	475	0.31	3.15	−4.94/−1.79	2.79	1.03	0.77–1.11	−5.43/−2.64	192/355/— ^g
22	391	475	0.53	3.05	−4.93/−1.88	2.71	0.99	0.88–1.16	−5.39/−2.68	280/400/— ^g
23	394	492	0.53	3.05	−4.83/−1.78	2.70	0.96	0.79–1.24	−5.36/−2.66	258/380/132

^a The fluorescence quantum yields (Φ) were measured in CHCl₃ using quinine sulfate ($\Phi = 0.55$) as standard [54].

^b DFT/B3LYP calculated values.

^c Optical energy gaps calculated from the edge of the electronic absorption band.

^d Oxidation potential in DMF (10^{−3} mol L^{−1}) containing 0.1 mol L^{−1} (n-C₄H₉)₄NPF₆ with a scan rate of 100 mV s^{−1}.

^e E_{HOMO} was calculated by Eox + 4.4 V (vs NHE), and E_{LUMO} = E_{HOMO} − E_g.

^f Measured by TG-DTA analysis under N₂ at a heating rate of 10 °C min^{−1}.

^g Not determined.

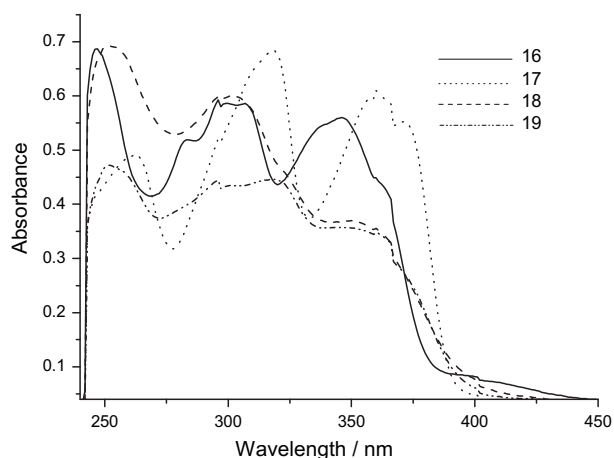


Fig. 4. The absorption spectra of compounds **16–19** (1×10^{-5} mol L⁻¹ in CHCl₃).

carbazole–benzothiazole, carbazole–benzothiazole and π -bridges, linkages and dihedral angles between two units that seem to affect the planarity of the molecules.

The lowest π – π^* energy gaps (E_g s) are noted for **21–23** (2.70–2.79 eV) whereas **16–19** (2.97–3.10 eV) showed higher band gaps as determined by the optical UV onset values (see Table 1). This result clearly indicates that the donor and acceptor interaction either in alternating fashion or discrete blocks within the molecules plays a significant role in modulating planarity and photophysical properties [40].

The fluorescence spectra for all compounds in CHCl₃ are shown in Fig. 6 and the data are listed in Table 1. With the increase in conjugation length, compounds **21**, **22** and **23** exhibit strong photoluminescent (PL) band at longer wavelength region. The PL bands are maximized at 472, 477 and 491 nm, respectively. A blue shift of 22 nm of the PL band occurs for **19**, compared to that of **18**. This is due to two electron-accepting benzothiazole moieties present in **19**. As suggested by Cao et al. [45], the benzothiazole moiety is also a conjugated delocalization system. The polarity, π -delocalization, and photoinduced charge transfer characteristics of a molecular system are basic structural factors in various branches of molecular non-linear optics, including TPA related photophysics. Similarly, **16** and **17** exhibit strong blue emission with PL maxima at 400 and 397 nm, respectively.

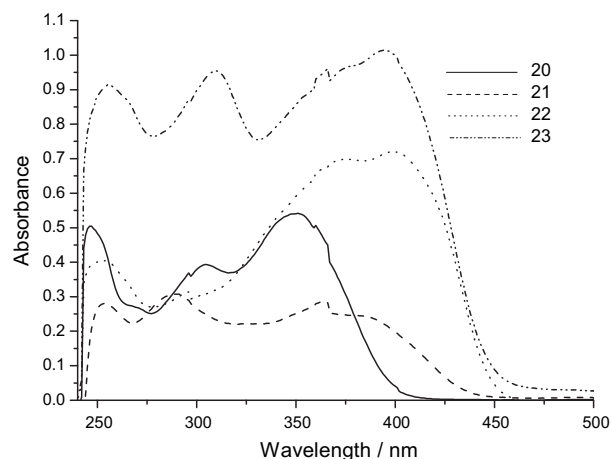


Fig. 5. The absorption spectra of compounds **20–23** (1×10^{-5} mol L⁻¹ in CHCl₃).

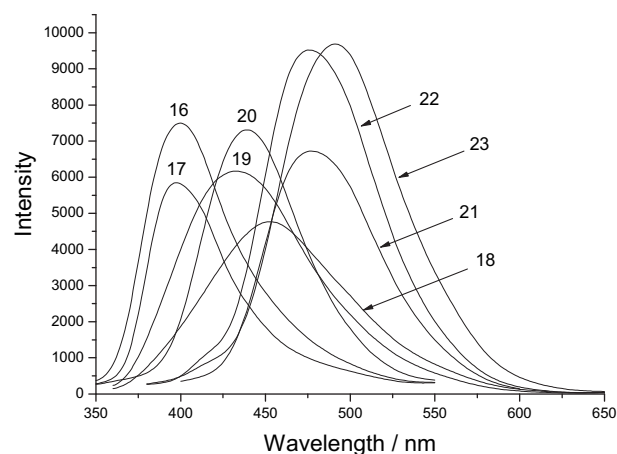


Fig. 6. The emission spectra of compounds **16–23** (1×10^{-5} mol L⁻¹ in CHCl₃).

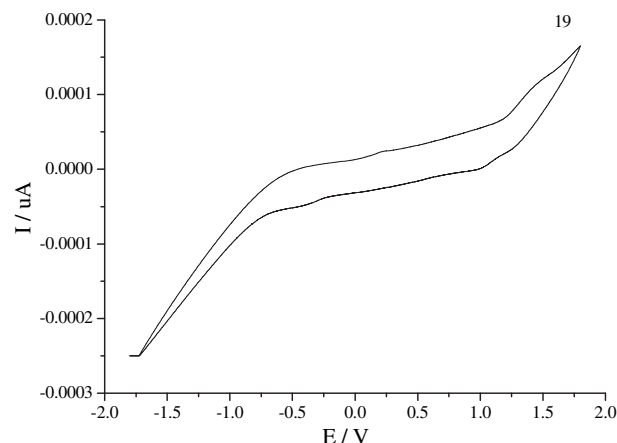


Fig. 7. Cyclic voltammogram of **19** (1×10^{-3} mol L⁻¹) as sample, in 0.1 mol L⁻¹ Bu₄NPF₆–CHCl₃, scan rate 100 mV/s.

The fluorescence quantum yields (Φ) were measured in CHCl₃ using quinine sulfate ($\Phi = 0.55$) as standard [56]. The photophysical data are summarised in Table 1. The Φ value of 0.92 was observed for **20**, which is higher than that of other compounds. This

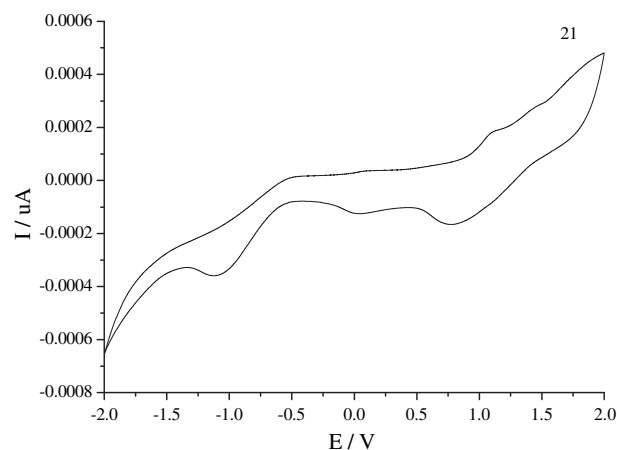


Fig. 8. Cyclic voltammogram of **21** (1×10^{-3} mol L⁻¹) as sample, in 0.1 mol L⁻¹ Bu₄NPF₆–CHCl₃, scan rate 100 mV/s.

might be due to the non-planar configuration of **20**, since the dihedral angle formed between the benzothiazole rings and carbazole rings of **20** is deduced to be 35.83° , the highest found within the compounds investigated here, based upon the quantum chemical calculations of the Gaussian 03. Both the steric hindrance and a non-planar configuration of the entire molecular structure contribute to hindering the compact π - π stacking interactions to some extent [57]. The PL quantum yields of the other compounds were in the range of 0.27–0.83, which became higher with increasing the number of benzothiazole units and the increase of the molecule length. This difference of quantum yields might be happened during the process of exciton migration [58] or might be due to the change of the molecular size [59].

3.3. Electrochemical properties

The electrochemical properties of compounds **16–23** were analyzed by cyclic voltammetry in CHCl_3 solution in the presence of tetrabutylammonium hexafluorophosphate (0.10 mol L^{-1}) as supporting electrolyte and the results are listed in the Table 1. All CV measurements were recorded at room temperature with a conventional three electrode configuration consisting of a platinum wire working electrode, a platinum counter electrode, and a saturated calomel electrode (SCE) reference electrode under argon. Electrochemical band gaps were calculated from onset potentials of the anodic and cathodic waves [60]. Compounds **16–20** show a reversible oxidation process associated with the

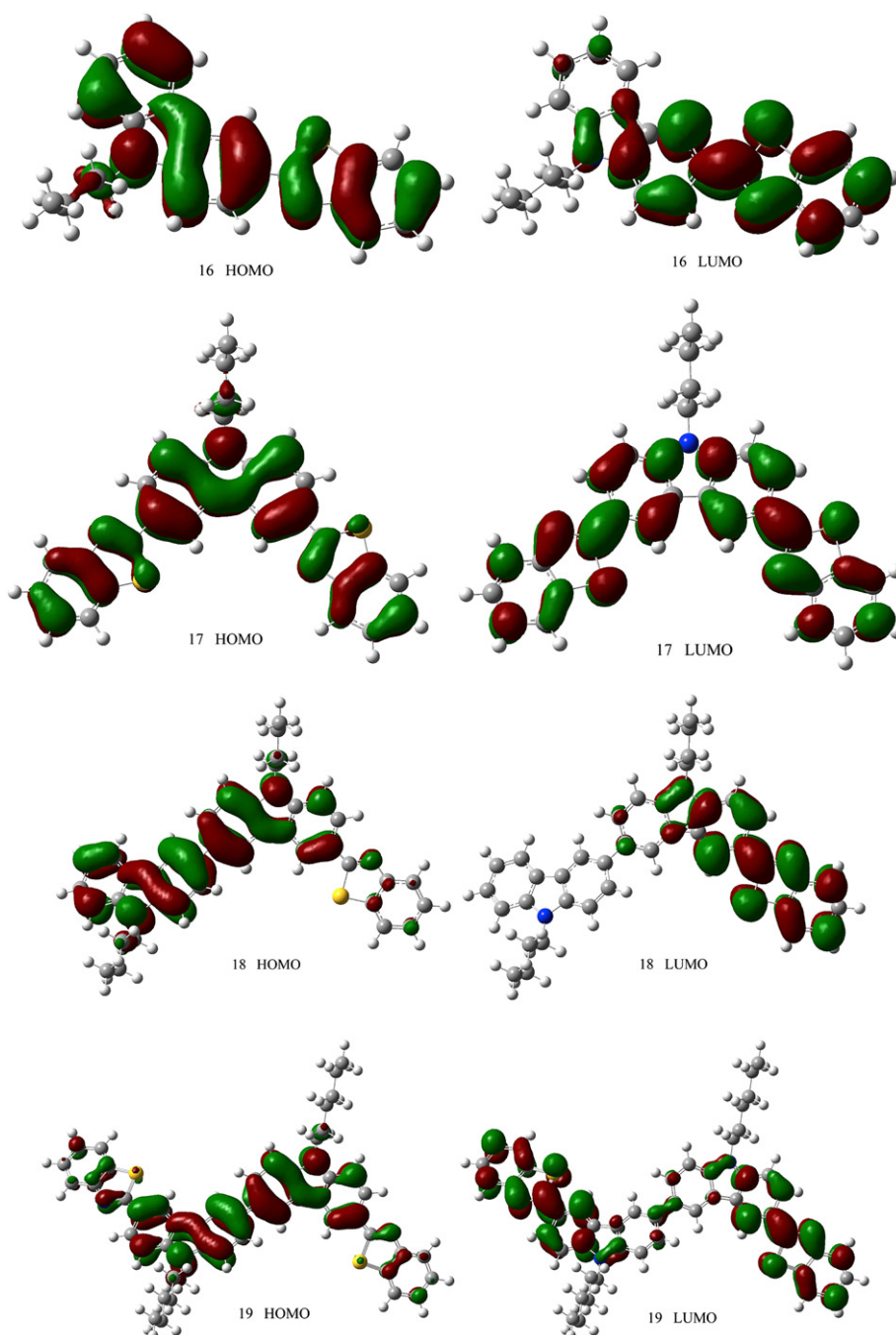


Fig. 9. Calculated spatial distributions of LUMO and HOMO of compounds **16–19**.

generation of the cation radical (Fig. 7). The CV of compounds **21–23** exhibit an irreversible cathodic wave (Ered) which shift positively from -1.24 to -1.11 V (Fig. 8). As shown in Table 1, the HOMO ranges are from -5.48 to -5.17 eV, while the LUMO ranges are from -2.68 to -2.10 eV, which are in agreement with the calculated values (-5.28 to -4.83 eV for the HOMO, and -1.88 to -1.23 eV for the LUMO of compounds). The HOMO and LUMO level are consistent with that of recently reported new bipolar host materials [55,57,61–63] and this might be beneficial for the hole-transport and electron-transport capacity. In all of the compounds, a decreased HOMO–LUMO gap was observed due to the increase in conjugation of styryl units. Therefore, these compounds might be used for hole-transporting and electron-transporting materials for OLEDs.

3.4. Theoretical calculation

The electronic configurations were further examined by theoretical models implanted in Gaussian 03 program [64]. Density functional theory (DFT) calculations (B3LYP; 6-31G*) were carried out to obtain information about the HOMO and

LUMO distributions of the compounds (Figs. 9 and 10). The theoretical model indicated the optimized dihedral angles formed between the benzothiazole rings and carbazole rings are 0.51° – 7.03° , which is nearly coplanar in all compounds except **20** (35.83°). In the case of **18**, **19** and **23**, the optimized dihedral angles formed between two carbazole moieties are about 38.55° , causing the whole molecule to adopt a non-planar configuration. Figs. 9 and 10 show that the HOMO is expected to lie on the electron-rich groups, affording an effective hole-transporting property. In fact, DFT studies of compounds clearly indicate that their LUMOs remain on the benzothiazole moiety with similar distributions to that of previous theoretical studies of dipolar molecules [65–67], whereas the HOMOs are localized only on the carbazole part. It is generally indicative of a HOMO/LUMO absorption transition bearing a significant charge transfer character. The lower calculated HOMO/LUMO energy levels relative to those estimated experimentally may be related with various effects such as conformation and solvation which were not taken into account. The predicted band gap calculated from DFT calculations and optical-electrochemical data shows similar trends.

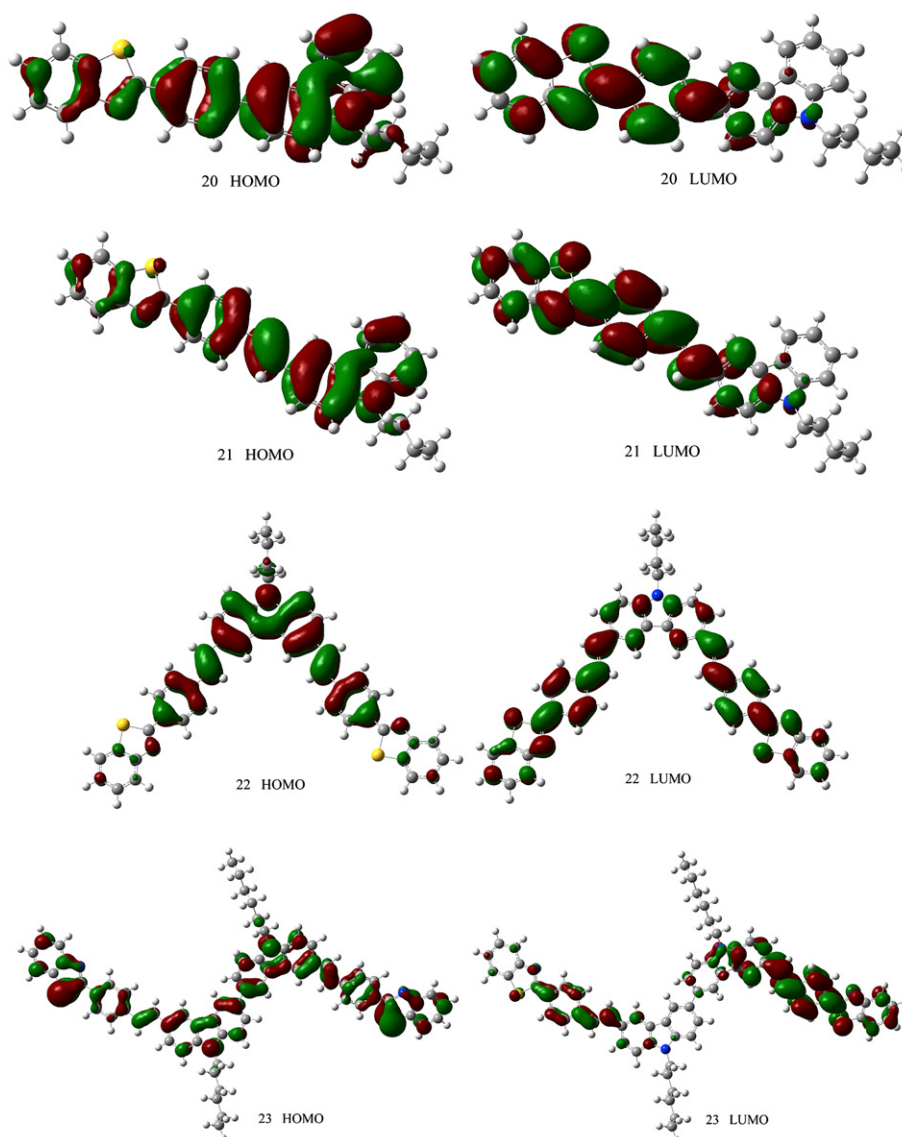


Fig. 10. Calculated spatial distributions of LUMO and HOMO of compounds **20–23**.

4. Conclusions

In summary, new bipolar host compounds based on benzo-thiazole moiety with attached carbazole groups were synthesized and their optical, electrochemical, and thermal properties were investigated. Optical spectra of these compounds imply that the increasing in conjugation styryl units length reduces the optical band gap up to 3.05 eV. Electrochemical data suggest the fine tuning of HOMO–LUMO values depends on conjugation length of the compounds. The electrochemistry and UV–vis spectroscopy were used to estimate the actual HOMO and LUMO levels, which showed good match with the data obtained from DFT calculations. Meanwhile, the electrochemical and fluorescence spectroscopy studies revealed that the new compounds would be promising in the application of OLEDs as a multifunctional material. Further synthesis and studies of using various donor–acceptors blocks based materials are in progress in our laboratory.

Acknowledgements

We are grateful to Prof. Ping Lu and Dr. Xiao-Peng Chen in the Department of Chemistry of Zhejiang University for computational assistance.

The work was partially supported by the National Natural Science Foundation of China (No. 20672079), Nature Science Key Basic Research of Jiangsu Province for Higher Education (No. 06KJA15007), Natural Science Foundation of Jiangsu Province (No. BK2006048), Nature Science of Jiangsu Province for Higher Education (No. 05KJB150116), the Specialized Research Fund for the Doctoral Program of Higher Education (No. 20060285001), and Key Laboratory of Organic Synthesis of Jiangsu Province (No. JSK008).

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