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Synthesis, photophysical and electrochemical properties and theoretical studies on three novel indolo[3,2-*b*]carbazole derivatives containing benzothiazole units

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ABSTRACT

Three novel indolo[3,2-*b*]carbazoles derivatives were successfully synthesized by condensation reaction and structurally characterized by elemental analysis, mass spectrometry and proton nuclear magnetic resonance spectroscopy methods, which belong to donor-π-acceptor systems comprising an indolo[3,2-*b*]carbazole group as an electron donor and two benzothiazole rings as electron acceptors. The thermal, electrochemical and photophysical properties of the compounds were characterized by thermogravimetric analysis combined with electrochemistry, UV–vis absorption spectroscopy and fluorescence spectroscopy. On the other hand, the geometries, molecular orbitals, charge-injection and transport properties were determined by quantum chemical calculations. The results show that the compounds synthesized exhibit good thermal stability and high fluorescence quantum yields, indicating the potential application as optoelectronic materials.

1. Introduction

Since Tang and Van Slyke demonstrated the use of hole-transporting layers (HTLs) for hole injection from the anodes into the light-emitting layer provides the significant improvement of the organic light-emitting diode (OLED) device performance,[1,2] much attention has been paid to OLED due to their potential applications in high-efficiency flat-panel displays and solid-state lighting.[3–7] To date, many types of high-performance materials have been fabricated.[8–10] Among them, indolo[3,2-*b*]carbazole and its derivatives are the most popular ones because these compounds comprise the large planar and rigid conjugated structures allowing efficient charge-injection and transfer with their proper molecular arrangement. In addition, the properties of this type of compounds can be greatly improved by derivatization with other functionalities. In 1999, Hu et al. reported the first indolo[3,2-*b*]carbazole derivative, 5,11-dihydro-5,11-di-1-naphthylindolo[3,2-*b*]carbazole, showing an unusual atropisomerism and excellent hole-transport properties in OLED.[11] Since then, the design and synthesis of novel derivatives based on indolo[3,2-*b*]carbazole have been booming. Wakim et al. successfully fabricated the first organic field-effect transistor (OFET) using 5,11-dioctyl-6,12-dimethylindolo[3,2-*b*]carbazole as an active layer in 2004.[12] Ong et al. developed *N*,*N*-disubstituted indolo[3,2-*b*]carbazoles and polyindolo[3,2-*b*]carbazoles as new classes of high-performance p-channel semiconductors, and these indolo[3,2-*b*]carbazole derivatives could be used to fabricate high-mobility organic thin-film transistor (OTFT).[13–15] Tao et al. synthesized three compounds based on indolo[3,2-*b*]carbazole, 2,8-bis(4-diphenylaminophenyl)-5,11-di-*n*-octylindolo[3,2-*b*]carbazole (BTOICZ), 2,8-bis(9,90-di-*n*-butylfluorenyl)-5,11-di-*n*-octylindolo[3,2-*b*]carbazole (BFOICZ) and 2,8-bis [*N*-(*n*-butyl)carbazolyl]-5,11-di-*n*-octylindolo[3,2-*b*]carbazole (BCOICZ) by Suzuki coupling reaction, these indolo[3,2-*b*]carbazole derivatives could be used as hole-transporting materials.[16]

Recently, the study of new indolo[3,2-*b*]carbazole derivatives continues to grow steadily. For instance, Lengvinaite et al. synthesized indolo[3,2-*b*]carbazole derivatives containing reactive oxetanyl groups, which could be used for preparation of cross-linked hole-transporting layers by photoinduced polymerization.[17] Pierre-Luc et al. synthesized new soluble materials based on the indolo[3,2-*b*]carbazole framework, which were particularly suitable for p-channel OFET.[18] Liu et al. developed a series of indolo[3,2-*b*]carbazole derivatives with donor-π-acceptor (D-π-A) systems.[19]

In view of the great potential applications in many fields of indolo[3,2-*b*]carbazole derivatives, the molecular design and synthesis of novel indolo[3,2-*b*]carbazole derivatives with D-π-A structure need to be further developed in order to improve their

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properties. In the present work, we synthesized three new indolo[3,2-*b*]carbazole derivatives by introducing different benzothiazole units to the 2,8-positions of indolo[3,2-*b*]carbazole, which contain an indolo[3,2-*b*]carbazole group as an electron donor and two benzothiazole rings as electron acceptors, namely 2,8-dibenzothiazolyl-5,11-dibutylindolo[3,2-*b*]carbazole (DDICZ), 2,8-bis((*E*)-2-(benzothiazolyl)vinyl)-5,11-dibutylindolo[3,2-*b*]carbazole (BBDICZ) and 2,8-bis((*E*)-2-(4-(benzothiazolyl)phenyl)vinyl)-5,11-dibutylindolo[3,2-*b*]carbazole (BBPDICZ). The structures of these derivatives were determined by elemental analysis, ^{1}H NMR, ^{13}C NMR and mass spectrometry. Their thermal, electrochemical and photophysical properties were characterized by thermogravimetric analysis combined with electrochemistry, UV–vis absorption spectroscopy and fluorescence spectroscopy. Their geometries, molecular orbitals, charge-injection and transport properties were determined by quantum chemical calculations.

2. Results and discussion

2.1. Synthesis

The molecular structures of three indolo[3,2-*b*]carbazole derivatives are shown in Fig. 1. As illustrated in Scheme 1, we carried out the synthesis of the key intermediate **4** for the whole procedure via a four-step reaction. The target compound DDICZ was formed by condensation reaction of **4** with 2-aminothiophenol in DMSO solution with 83% yield as light yellow solid. To gain BBDICZ, a two-step synthesis was carried out by lithiation of 2-methylbenzothiazole with *n*-butyllithium in THF solution followed by reaction with **4**, and then dehydration of the obtained product. BBDICZ was obtained as a greenish solid in an overall yield of 43%. To form the more extended conjugation molecule of BBPDICZ, a three-step synthesis was carried out by Wittig reaction of **4** with the corresponding phosphonium salt, which was obtained by bromination of 2-*p*-tolylbenzothiazole with NBS followed by reaction with PPh_3 in CCl_4. BBPDICZ was obtained as a greenish solid in an overall yield of 35%. All synthesized compounds were fully characterized by mass spectrometry and NMR methods. Details are given in experimental section.

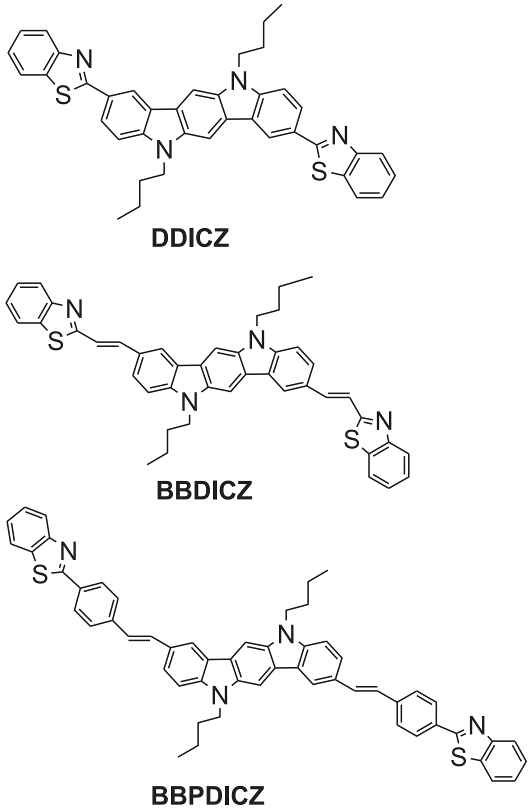


Fig. 1. The molecular structures of three indolo[3,2-*b*]carbazole derivatives.

2.2. Thermal stability

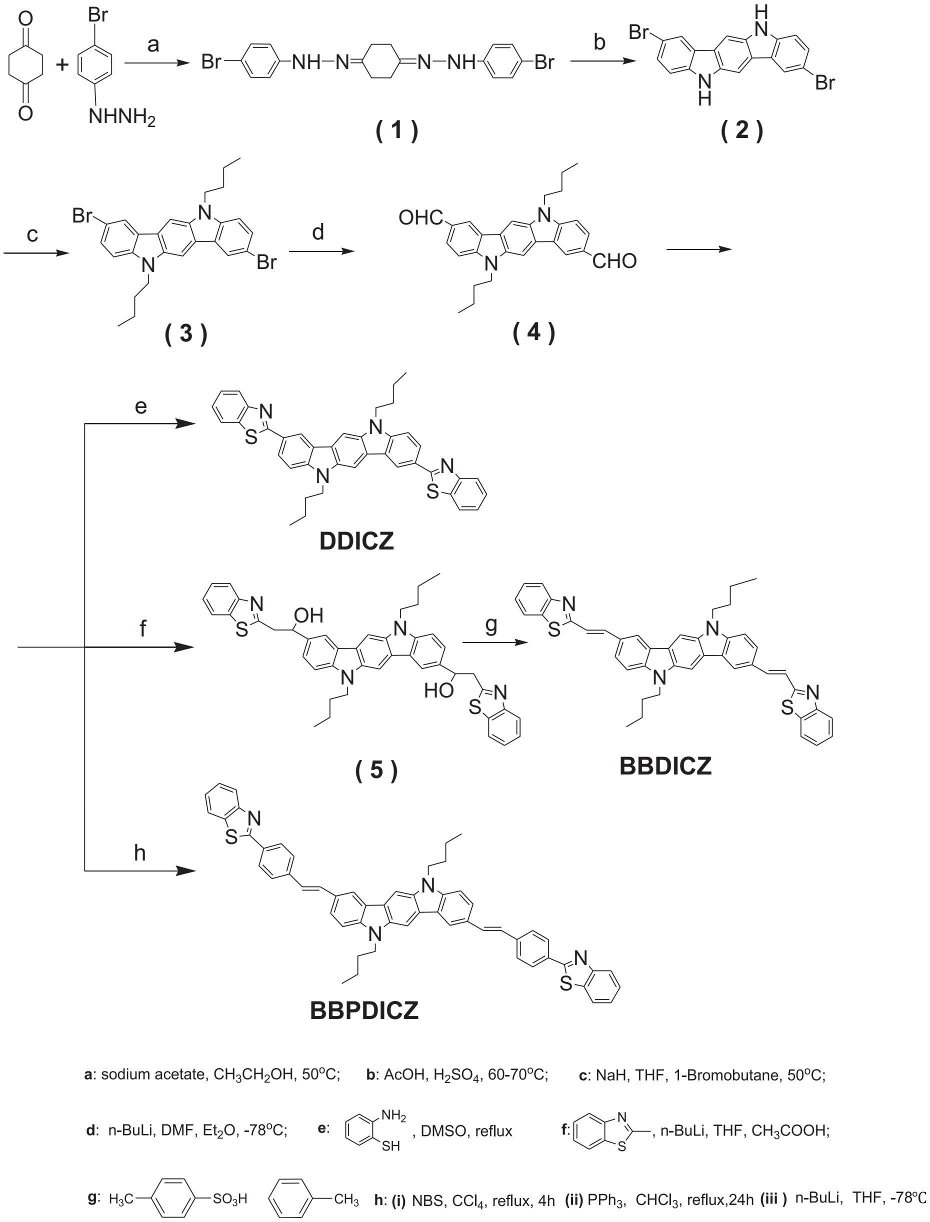
The thermal properties of three indolo[3,2-*b*]carbazole derivatives were determined by TGA, as shown in Supplementary data Fig. S1. DDICZ presents an onset degradation temperature (T_d) for 5% weight loss as high as 418 °C. Degradation temperature of BBDICZ and BBPDICZ is 331 °C and 390 °C, respectively. For comparison, the T_d data are listed in Table 1. Obviously, these derivatives exhibit good thermal stability, implying that incorporation of indolo[3,2-*b*]carbazole and benzothiazole units into the indolo[3,2-*b*]carbazole derivative is favorable to enhance the thermal stability. Furthermore, the different conjugate connection of benzothiazole units and indolo[3,2-*b*]carbazole has a significant effect on their thermal stability. Thus DDICZ has best thermal stability among these derivatives.

2.3. Quantum calculation

To understand the geometries and the electronic properties of DDICZ, BBDICZ and BBPDICZ, quantum chemical calculations were performed using the DFT/B3LYP/6-31G (d,p) method.

2.3.1. The geometries and frontier molecular orbitals. The optimized structures of the derivatives reveal that these molecules adopt planar conformations. Such structural characteristics can influence their electronic and physical properties as a result of an extension of the conjugation. Fig. 2 illustrates the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) of the obtained compounds. The election density of the HOMO of DDICZ is mostly localized on the central indolo[3,2-*b*]carbazole moiety, while that of LUMO is delocalized over indolo[3,2-*b*]carbazole core and benzothiazole terminals. Similar distribution of the election density of HOMO could be observed in BBDICZ and BBPDICZ as well, while the election density of LUMO of BBDICZ is mostly localized on vinyl linker segments and benzothiazoles and that of LUMO of BBPDICZ is mostly localized on styryl linker segments and benzothiazoles. The electron transitions of these derivatives from the ground to excited states are mainly from the indolo[3,2-*b*]carbazole ring to the benzothiazole rings, belonging to the intramolecular charge transfer (ICT) from electron donor to electron acceptors. The HOMO–LUMO energy gaps (E_g calcd) are calculated and presented in Table 1. The calculated values slightly deviate from those obtained from the experimental results (ca. 0.05–0.09 eV).

2.3.2. Charge-injection and transport properties. In order to understand the charge-injection and transport properties, the ionization potential (IP), electronic affinity (EA) and hole/electron reorganization energy of DDICZ, BBDICZ and BBPDICZ are calculated and displayed in Supplementary data Table S1. In general, the lower the IP, the easier the entrance of holes from ITO to hole-transport layer (HTL). The higher the EA, the easier the entrance of electrons from cathode to electron-transport layer (ETL). Furthermore, the charge transport rate can be represented by the Marcus electron-transfer theory,[20] and the charge transport rate is mainly decided by hole/electron reorganization energy according to this theory.[21] The calculated results show that DDICZ, BBDICZ and BBPDICZ have almost the same ionization potential but different electronic affinity and a small hole reorganization energy compared with electron reorganization energy, inferring their potential application as hole-transport materials.



a: sodium acetate, CH_3CH_2OH, 50°C; **b**: AcOH, H_2SO_4, 60-70°C; **c**: NaH, THF, 1-Bromobutane, 50°C;

d: n-BuLi, DMF, Et_2O, -78°C; **e**: , DMSO, reflux **f**: , n-BuLi, THF, CH_3COOH;

g: **h**: **(i)** NBS, CCl_4, reflux, 4h **(ii)** PPh_3, $CHCl_3$, reflux,24h **(iii)** n-BuLi, THF, -78°C

Scheme 1. The synthetic route of three indolo[3,2-*b*]carbazole derivatives.

Table 1
Experimental and theoretical data of three indolo[3,2-*b*]carbazole derivatives

Compounds	λ_{abs}[a] [nm]/ε_{max}	λ_{em}[b] [nm]	T_d[c] [°C]	F[d] (ϕ)	E_{ox}[e] [V]	E_{HOMO}[g] [eV] (E_{HOMO}[h] [eV])	E_{LUMO}[g] [eV] (E_{LUMO}[h] eV])	E_g[f] [eV] (E_g[h] [eV])
DDICZ	352 (65,300)	435, 465	418	0.38	0.88	−5.28 (−5.01)	−1.99 (−1.67)	3.29 (3.34)
BBDICZ	405 (32,320)	507	331	0.17	0.77	−5.17 (−4.95)	−2.03 (−1.71)	3.18 (3.24)
BBPDICZ	408 (38,110)	517	390	0.11	0.64	−5.04 (−4.81)	−2.14 (−1.82)	2.90 (2.99)

[a] Measured in a dilute THF solution (10^{-5} M).

[b] Excited at the absorption maxima.

[c] Obtained from TGA measurements with a heating rate of 10 °C/min under N_2.

[d] Fluorescence quantum yields (ϕ) in a dilute THF solution (10^{-6} M).

[e] E^{ox}_{onset}=onset oxidation potential; measured using a three-electrode system fitted with a glassy carbon working electrode, a platinum rod counter electrode, and Ag/AgCl reference electrode in degassed CH_3CN containing 0.1 M *n*-Bu_4NClO_4 as a supporting electrolyte at a scan rate of 50 mV/s.

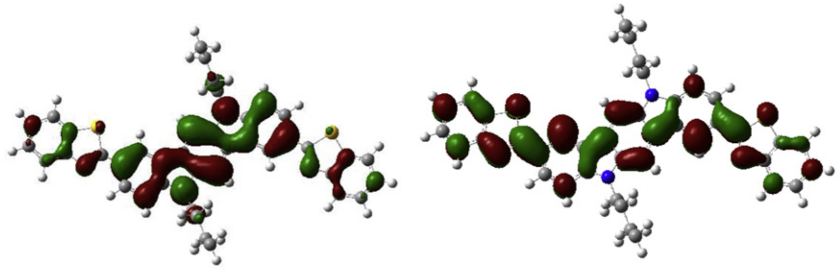
[f] Estimated according to the oxidation potential and the onset of the absorption spectra (E_g=1240/λ_{onset}).

[g] Calculated using the empirical equation: HOMO=(4.4+E_{onset}) and LUMO=HOMO+E_g.

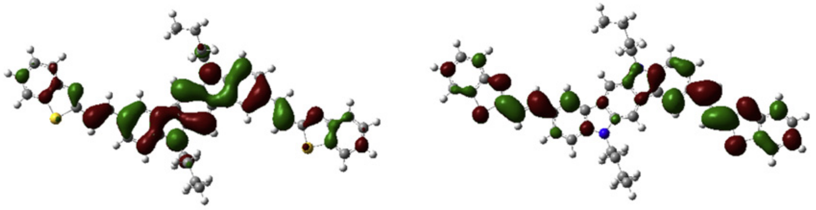
[h] Obtained from quantum chemical calculation using DFT/B3LYP/6-31G (d,p).

2.4. Photophysical properties

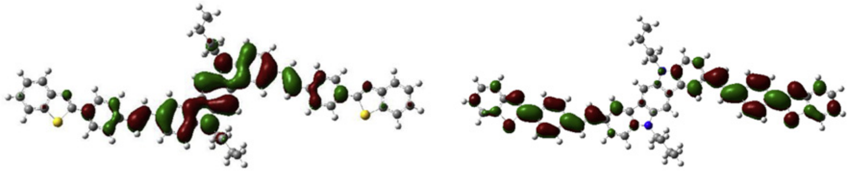
The UV–vis absorption spectra of the indolo[3,2-*b*]carbazole derivatives in several solvents (1×10^{-5} M) are illustrated in Fig. 3. The pertinent data are summarized in Table 1. All the derivatives exhibit two similar absorption bands, a high-energy absorption band at 300–370 nm and a low-energy absorption band at 370–480 nm, in which the high-energy absorption band is



HOMO of DDICZ **LUMO of DDICZ**



HOMO of BBDICZ **LUMO of BBDICZ**



HOMO of BBPDICZ **LUMO of BBPDICZ**

Fig. 2. The contour plots of HOMOs and LUMOs of three indolo[3,2-*b*]carbazole derivatives in the ground state.

attributed to π–π* transition of the indolo[3,2-*b*]carbazole backbone and the low-energy absorption band is attributed to π–π* transition of the intramolecular charge transfer (ICT) from the indolo[3,2-*b*]carbazole unit to the benzothiazole units. In addition, DDICZ, BBDICZ and BBPDICZ exhibit different maximum absorption wavelengths, varying from 355 nm to 363 nm and increasing with the elongation of the conjugated length of these molecules. Their HOMO–LUMO energy gaps (E_g) estimated from the onset of the absorption spectra are 2.96 eV for DDICZ, 2.89 eV for BBDICZ and 2.85 eV for BBPDICZ, respectively.

The normalized fluorescence spectra of the indolo[3,2-*b*]carbazole derivatives in several solvents (1×10^{-5} M) are illustrated in Fig. 4, respectively. The relevant data are also summarized in Table 1. DDICZ displays two emission bands, a high-energy emission band at 410–450 nm and a low-energy emission band at 450–650 nm in different solvents, in which the low-energy emission band is originated from π–π* transition of the intramolecular charge transfer (ICT) from the indolo[3,2-*b*]carbazole unit to the benzothiazole units, and the high-energy emission band is related to π–π* transition of DDICZ skeleton. BBDICZ and BBPDICZ exhibit mainly a broad emission band in several solvents except that hexane owe to overlap of π–π* transition of their skeletons and π–π* transition of the intramolecular charge transfer (ICT) from the indolo[3,2-*b*] carbazole unit to the benzothiazole units.

In order to further understand the emission property of these indolo[3,2-*b*]carbazole derivatives, their fluorescence quantum yields were measured in THF solvent (1×10^{-6} M) using quinine sulfate in 0.01 M H_2SO_4 solution as a standard at room temperature based on the literature.[22] The results are summarized in Table 1. Fluorescence quantum yields of DDICZ, BBDICZ and BBPDICZ are 0.38, 0.17 and 0.11, respectively. The results indicate that the direct attachment of the benzothiazole units to the indolo[3,2-*b*] carbazole unit in DDICZ raises the fluorescence quantum yield and the fluorescence quantum yields are reduced with the increase of the elongation of the conjugated length of BBDICZ and BBPDICZ as these two molecules become more planar and then the fluorescence of them is reduced by intermolecular π–π stacking.

2.5. Electrochemical properties

In order to investigate the redox properties of the indolo[3,2-*b*] carbazole derivatives and their HOMO and LUMO energy levels, cyclic voltammetry (CV) analysis was performed. The measurements were carried out in CH_3CN solution containing 0.1 M *n*-Bu_4NClO_4 as supporting electrolyte, using three-electrode systems under an argon atmosphere. The reference electrode was Ag/Ag^+. The results are shown in Supplementary data Fig. S2 and summarized in Table 1. The CV curves of these derivatives remain unchanged under successive oxidation, indicating their excellent stability against electrochemical oxidation. The onset oxidation potentials of DDICZ, BBDICZ and BBPDICZ are 0.88 V, 0.70 V and 0.64 V, respectively. The HOMO energy levels can be calculated by using the empirical equation $E_{HOMO}=-(E_{ox}+4.40)$ eV, where E_{ox} is the onset potentials for oxidation.[23] Therefore, the HOMO levels of DDICZ, BBDICZ and BBPDICZ are −5.28 eV, −5.17 eV and −5.04 eV, respectively. The LUMO energy levels can be calculated by using the equation $E_{LUMO}=E_{HOMO}-E_g$, where energy gap (E_g) is estimated from the onset of the absorption spectra for DDICZ, BBDICZ and BBPDICZ, respectively. The HOMO levels of the compounds increase whereas the LUMO levels of the compounds decrease with the extended conjugation. The HOMO levels are available to facilitate hole injection and transport from ITO (4.80 eV) to the emissive Alq_3 (5.80 eV), while the LUMO levels are available to facilitate electron injection and transport from cathode to the emissive Alq_3

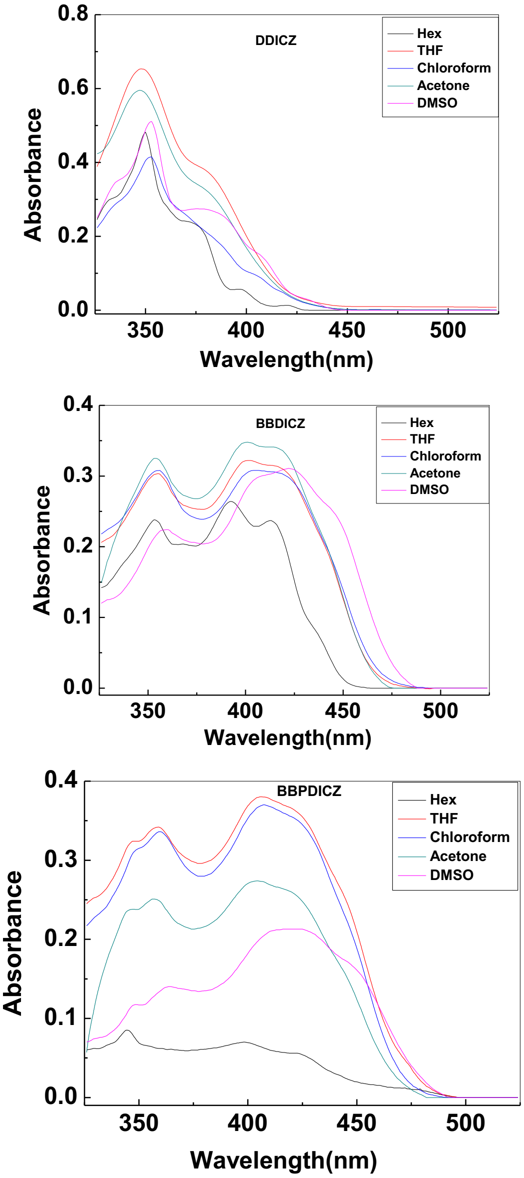


Fig. 3. UV–vis spectra of three indolo[3,2-*b*]carbazole derivatives in several solvents.

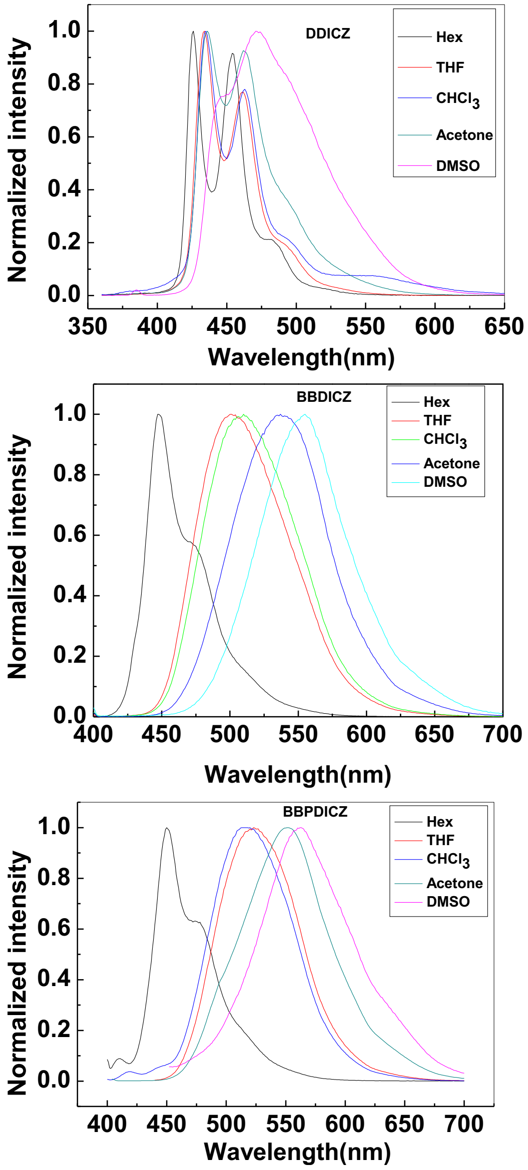


Fig. 4. The normalized fluorescence spectra of three indolo[3,2-*b*]carbazole derivatives in several solvents.

(5.80 eV).[24] The high-lying HOMO energy levels can be good and stable hole-transport and injection materials for fabrication of OLEDs. Therefore, incorporating both hole-transporting indole[3,2-*b*]carbazole unit and electron-transporting benzothiazole units into a structure can significantly tune electrochemical and transporting properties of the derivatives.

3. Conclusions

In this work, three novel compounds, namely 2,8-dibenzothiazolyl-5,11-dibutylindolo[3,2-*b*]carbazole(DDICZ), 2,8-bis((*E*)-2-(benzothiazolyl)vinyl)-5,11-dibutylindolo[3,2-*b*]carbazole (BBDICZ) and 2,8-bis((*E*)-2-(4-(benzothiazolyl)phenyl)vinyl)-5,11-dibutylindolo[3,2-*b*]carbazole (BBPDICZ), were successfully synthesized and structurally characterized by elemental analysis, NMR and MS methods. These compounds belong to donor-π-acceptor systems comprising an indolo[3,2-*b*]carbazole group as an electron donor and two benzothiazole rings as electron acceptors. Their properties were studied by the combination of experimental and theoretical methods. The results show that these compounds exhibit good thermal stability and high fluorescence quantum yields indicating the potential applications as optoelectronic materials.

4. Experimental

4.1. General procedure

The reagents, including 2-aminothiophenol, 4-bromophenylhydrazine hydrochloride, 1,4-cyclohexanedione, 2-methylbenzothiazole and 2-*p*-tolylbenzothiazole, were purchased from Alfa Aesar (Ward Hill, MA, USA) and used without further purification. All other reagents of analytical reagent grade or above from Beijing Chemical Plant (Beijing, China) were used as received. The solvents such as carbon tetrachloride, diethyl ether (Et_2O), *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), toluene, acetone and acetonitrile were treated according to the standard methods.

Elemental analyses were conducted on a PerkinElmer elemental analyzer (PerkinElmer. USA). ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 600 MHz NMR spectrometer (Bremen, Germany) with $CDCl_3$ or DMSO-d_6 as solvent. Mass spectra were recorded with the LC–MS system consisted of a Waters 1525 pump and a Micromass ZQ4000 single quadrupole mass spectrometer. UV–vis absorption spectra were conducted on a Shimadzu UV-2450 spectrophotometers. Fluorescence spectra were acquired on a Hitachi F-4500 spectrofluorometer (Tokyo, Japan). Fluorescence quantum yield was determined using the standard actinometric method. Quinine sulfate was the reference with a fluorescence quantum yield of 0.55 in 0.01 M H_2SO_4 and the sample was excited at 350 nm. The fluorescence quantum yield was calculated according to the following equation.

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

where φ is the fluorescence quantum yield, F is the integration of the emission intensity, 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 sample, respectively. The time-resolved photoluminescence measurements were performed on an Edinburgh FLS920 fluorescence lifetime spectrometer (Livingston, UK) operating in the time-correlated single photon counting mode. Differential scanning calorimetry (DSC) analysis and thermogravimetry analysis (TGA) were performed on a TA Instruments TGA 2050 thermogravimetric analyzer (New Castle, DE, USA) under nitrogen atmosphere at a heating rate of 10 °C/min from room temperature to 600 °C. Cyclic voltammetry experiments were performed on a CHI-600C electrochemical analyzer (Austin, TX, USA) using a three-electrode system comprising a glassy carbon working electrode, a platinum counter electrode and a Ag/AgCl reference electrode at a scan rate of 50 mV/s in acetonitrile under argon atmosphere. The concentrations of an analytical material and supporting electrolyte tetrabutyl ammonium hexafluorophosphate (n-Bu_4NPF_6) were 10^{-3} M and 0.1 M, respectively.

The ground state geometries of three derivatives and their ionic were fully optimized using density functional theory (DFT) at B3LYP level with 6-31G(d,p) basis set and 6-31G+(d,p), respectively.[25–27] The frontier molecular orbital characteristics were analyzed on the optimized neutral structures. The ionization potential (IP), electron affinity (EA) and reorganization energy of three compounds DDICZ, BBDICZ and BBPDICZ were calculated based on the optimized geometries of the neutral and ionic molecules. Solvent effect was also taken into account by using the polarized continuum model (PCM).[28,29] All calculations were carried out with the Gaussian 03 program package.[30] All the calculations were performed in supercomputing center of computer network information center of Chinese Academy of Sciences.

4.2. Synthesis and characterization

The synthesis of compounds cyclohexane-1,4-dione-bis(p-bromophenyl)-hydrazone (**1**), 2,8-dibromoindolo[3,2-*b*]carbazole (**2**) and 2,8-dibromo-5,11-dibutylindolo[3,2-*b*]carbazole (**3**) were performed according to or slightly modified literature procedures.[31]

*4.2.1. Synthesis of cyclohexane-1,4-dione-bis (p-bromophenyl)-hydrazone (**1**).* 1,4-Cyclohexanedione (5.62 g, 50 mmol) dissolved in absolute ethanol (EtOH) (100 mL) was added with stirring to a mixture of powdered 4-bromophenylhydrazine hydrochloride (22.4 g, 100 mmol), sodium acetate (8.2 g, 100 mmol) and absolute ethanol (200 mL) at room temperature. The mixture was quickly heated to 50 °C, and thereafter, the temperature was allowed to cool to 0 °C. A precipitate was filtered off, washed carefully with water to give **1** (yield 66%).

*4.2.2. Synthesis of 2,8-dibromoindolo[3,2-b]carbazole (**2**).* Compound **1** (10 g, 22 mmol) was added to a mixture of acetic acid (AcOH) (130 mL) and H_2SO_4 (32 mL) at 0 °C and stirred for 5 min. Afterward, the reaction mixture was stirred at 30 °C for 1 h. Thereafter, the mixture was further warmed up to 60–70 °C and stirred for 1 h. Subsequently cool down to room temperature and pour into ice water with stirring. The greenish solid was filtered off. Wash it with water and EtOH to neutral pH. Dried and pure 2,8-dibromoindolo[3,2-*b*]carbazole (**2**) (4.88 g, yield 52.8%) was obtained. Melting point (Mp) >300 °C. ^1H NMR (DMSO-d_6) δ 11.14 (2H, s, N–H), 7.1–8.24 (8H, m, Ar–H).

*4.2.3. Synthesis of 2,8-dibromo-5,11-dibutylindolo[3,2-b]carbazole (**3**).* Compound **2** (2.0 g, 4.8 mmol) was added to a suspension of NaH (0.35 g, 14 mmol) in THF (50 mL) under nitrogen flow. Thereafter, the mixture was stirred for 2 h at room temperature, and then the temperature was increased slowly to 50 °C. Keep at the uniform temperature for 4 h and cool to room temperature. 1-Bromobutane (1.91 g, 14 mmol) was added dropwise to the mixture with stirring continued for 50 min, and then the mixture was heated at 50 °C and maintained at this temperature for 24 h. Afterward, the solvent was evaporated and solid left. The solid was washed with water and two or three times each with acetone to afford the desired **3** (2.01 g, yield 79.5%). Mp: 271–274 °C. ^1H NMR ($CDCl_3$) δ 7.572–8.547 (8H, m, Ar–H), 4.359–4.383 (4H, t, –NCH_2–, J=7.2 Hz), 1.900–1.925 (4H, t, –CH_2–, J=7.5 Hz), 1.440–1.453 (4H, m, –CH_2–), 0.965–0.990 (6H, t, –CH_3, J=7.5 Hz).

*4.2.4. Synthesis of 5,11-dibutylindolo[3,2-b]carbazole-2,8-dicarbaldehyde (**4**).* To a well-stirred suspension of **3** (1.6 g, 3 mmol) in 80 mL of absolute ether under a nitrogen atmosphere at −78 °C was added 3.03 mL of a 2.5 mol solution of n-butyllithium. The resulting suspension was stirred for 4 h before adding dimethylformamide (DMF) (2.35 mL) at −78 °C. The mixture was allowed to warm to room temperature with stirring for 8 h and was then poured into ice water. After addition of a 10% aqueous hydrochloric acid solution to neutral pH, the precipitated solid was collected by filtration. The solid from the filtrate was separated, washed with water, ether and dried. Yellow crystals **4** was given (0.85 g, yield 67%). Mp: 282–284 °C. ^1H NMR ($CDCl_3$) δ 10.107 (2H, s, –CHO), 7.461–8.725 (8H, m, Ar–H), 4.400–4.448(4H, t, –NCH_2–, J=7.2 Hz), 1.928–1.978 (4H, t, –CH_2–, J=7.5 Hz), 1.428–1.903 (4H, m, –CH_2–), 0.965–1.013 (6H, t, –CH_3, J=7.2 Hz).

4.2.5. Synthesis of 2,8-dibenzothiazolyl-5,11-dibutylindolo[3,2-b]carbazole (DDICZ). A mixture of 2-aminobenzenethiol (300 mg, 2.4 mmol) and **4** (424 mg, 1 mmol) in 30 mL DMSO was refluxed at 195 °C for 2 h. Ice water was added after the mixture was cooled. The solid was filtered and added to acetic acid and water (50 mL, 1:4). The precipitate was filtered and washed with water and dilute $NaHCO_3$ solution. Recrystallized in ethanol to give 384 mg of DDICZ (yield 60.5%). Mp >300 °C. ^1H NMR ($CDCl_3$) δ 7.436–8.744 (16H, m, Ar–H), 4.557–4.605 (4H, t, –NCH_2–, J=7.2 Hz), 1.891–1.940 (4H, t, –CH_2–, J=7.3 Hz), 1.324–1.428 (4H, m, –CH_2–), 0.925–0.973 (6H, t, –CH_3, J=7.2 Hz). MS (m/z): 634.9213 (M^+). Anal. Calcd for $C_{40}H_{34}N_4S_2$: C, 75.68%; H, 5.40%; N, 8.83%; S, 10.10%. Found: C, 75.30%; H, 5.45%; N, 8.72%; S, 10.03%.

*4.2.6. Synthesis of 2,8-di(2-(benzothiazolyl)ethanolyl)-5,11-dibutylindolo[3,2-b] carbazole (**5**).* Under nitrogen, to a solution of 2-methylbenzothiazole (0.32 mL, 2.4 mmol) in 10 mL of anhydrous

THF at −78 °C was added dropwise, 2.5 M *n*-BuLi in hexane (0.56 mL, 1.4 mmol). The mixture was stirred at −78 °C for 30 min, then **4** (0.424 g, 1.0 mmol) in 15 mL of anhydrous THF was added dropwise. The reaction mixture 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 CH_2Cl_2. The solution was dried over $MgSO_4$, filtered and concentrated in vacuum. A yellow powder was obtained by recrystallization from ethanol (0.38 g, yield 53%). Mp 203–205 °C. ^1H NMR ($CDCl_3$) δ 7.258–8.341 (16H, m, Ar–H), 5.521–5.532 (2H, d, –CH–, *J*=6.6 Hz), 4.419–4.445 (4H, t, $-NCH_2-$, *J*=7.8 Hz), 3.622–3.654 (4H, t, $-CH_2-$, *J*=9.6 Hz), 1.994–2.018 (4H, t, CH_2-, *J*=7.2 Hz), 1.476–1.502 (4H, m, $-CH_2-$), 0.979–1.003 (6H, t, $-CH_3$, *J*=7.2 Hz).

4.2.7. Synthesis of 2,8-bis((E)-2-(benzothiazolyl)vinyl)-5,11-dibutylindolo[3,2-b] carbazole (BBDICZ). A mixture of 5 (0.29 g, 0.40 mmol) and *p*-toluenesulfonic acid monohydrate (0.304 g, 1.6 mmol) was added to 20 mL of toluene. The reaction mixture was heated at reflux for 3 h, then cooled to ambient temperature and concentrated in vacuum. The crude product was recrystallized from ethanol to give a yellow powder BBDICZ (0.125 g, yield 46%). Mp >300 °C. ^1H NMR ($CDCl_3$) δ 7.285–8.459 (20H, m, Ar–H), 4.437–4.463 (4H, t, $-NCH_2-$, *J*=7.8 Hz), 2.022–2.048 (4H, t, $-CH_2-$, *J*=7.8 Hz), 1.476–1.545 (4H, m, $-CH_2-$), 0.982–1.007 (6H, t, $-CH_3$, *J*=7.5 Hz). MS (*m*/*z*): 686.9402 (M^+). Anal. Calcd for $C_{44}H_{38}N_4S_2$: C, 76.93%; H, 5.58%; N, 8.16%; S, 9.34%. Found: C, 76.68%; H, 5.65%; N, 8.27%; S, 9.40%.

4.2.8. Synthesis of 2,8-bis((E)-2-(4-(benzothiazolyl)phenyl)vinyl)-5,11-dibutylindolo[3,2-b] carbazole (BBPDICZ)

4.2.8.1. 2-(4-(Bromomethyl)phenyl)benzothiazole. 2-*p*-Tolylbenzothiazole (2.71 g, 12 mmol) and *N*-bromosuccinimide (NBS) (2.14 g, 12 mmol) were dissolved in 50 mL of CCl_4. The solution was refluxed 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, yield 94%). Mp: 132–133 °C. ^1H NMR ($CDCl_3$) δ 7.928–8.132 (m, 8H, Ar–H), 4.550–4.622 (s, 2H, $-CH_2-$).

4.2.8.2. 4-(2-Benzothiazolyl)-benzyl triphenyl phosphonium bromide. A mixture of 2-(4-(bromomethyl)phenyl)benzothiazole (3.04 g, 10 mmol) and triphenylphosphine (2.62 g, 10 mmol) was added to $CHCl_3$ (50 mL) under N_2 flow. The mixture was heated up slowly to 60 °C and kept for 24 h. After that, it was cooled to room temperature, the solvent was removed under reduced pressure. The residue was recrystallized from Et_2O to give the white solid (4.98 g, yield 88%). Mp 295–297 °C. ^1H NMR ($CDCl_3$) δ 7.264–8.082 (m, 23H), 5.721–5.770 (s, 2H, $-CH_2-$).

4.2.8.3. 2,8-Bis((E)-2-(4-(benzothiazolyl)phenyl)vinyl)-5,11-dibutylindolo[3,2-b]carbazole (BBPDICZ). Under nitrogen atmosphere, a stirred slurry of 4-(2-benzothiazolyl)-benzyl triphenyl phosphonium bromide (0.566 g, 1 mmol) in 30 mL anhydrous THF was cooled to −78 °C, 0.40 mL of 2.5 M *n*-BuLi in hexane (1 mmol) was added and the mixture was warmed to room temperature over 2 h. Then a solution of compound **4** (0.21 g, 1.77 mmol) in 10 mL THF was added dropwise with vigorous stirring at −78 °C. The reaction mixture 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 powder BBPDICZ (0.16 g, yield 38%). Mp >300 °C. ^1H NMR ($CDCl_3$) δ 7.372–8.393 (28H, m, Ar–H), 4.422–4.447 (4H, t, $-NCH_2-$, *J*=7.5 Hz), 1.966–1.988 (4H, t, $-CH_2-$, *J*=6.6 Hz), 1.256–1.450 (4H, m, $-CH_2-$), 0.961–0.986 (6H, t, $-CH_3$, *J*=7.5 Hz). MS (*m*/*z*): 839.2037 (M+). Anal. Calcd for $C_{56}H_{46}N_4S_2$: C, 80.16%; H, 5.53%; N, 6.68%; S, 7.64%. Found: C, 80.46%; H, 5.41%; N, 6.39%; S, 7.40%.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2012.09.012. These data include MOL files and InChIKeys of the most important compounds described in this article.

References and notes

1. Tang, C. W.; Van Slyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913–915.
2. Yasuhiko, S. *J. Mater. Chem.* **2000**, *10*, 1–25.
3. Van Slyke, S. A.; Chen, C. H.; Tang, C. W. *Appl. Phys. Lett.* **1996**, *69*, 2160–2162.
4. Tullo, A. H. *Chem. Eng. News* **2000**, *78*, 11–12.
5. Tullo, A. H. *Chem. Eng. News* **2001**, *79*, 22–24.
6. Hung, L. S.; Tang, C. W. *Appl. Phys. Lett.* **1997**, *70*, 152–154.
7. Zhao, H. P.; Wang, F. Z.; Yuan, C. X.; Tao, X. T.; Sun, J. L.; Zou, D. C.; Jiang, M. H. *Org. Electron.* **2009**, *10*, 925–931.
8. Zhang, Q.; Chen, J.; Chen, Y.; Wang, L.; Ma, D.; Jing, X.; Wang, F. *J. Mater. Chem.* **2004**, *14*, 895–900.
9. Li, J.; Ma, C.; Tang, J.; Lee, C. S.; Lee, S. *Chem. Mater.* **2005**, *17*, 615–619.
10. Li, J.; Liu, D.; Li, Y.; Lee, C. S.; Kwong, H.; Lee, S. *Chem. Mater.* **2005**, *17*, 1208–1212.
11. Hu, N. X.; Xie, S.; Popovic, Z.; Ong, B. S.; Hor, A. M. *J. Am. Chem. Soc.* **1999**, *121*, 5097–5098.
12. Wakim, S.; Bouchard, J.; Simard, M.; Drolet, N.; Tao, Y.; Leclerc, M. *Chem. Mater.* **2004**, *16*, 4386–4388.
13. Wu, Y. L.; Li, Y. N.; Gardner, S.; Ong, B. S. *J. Am. Chem. Soc.* **2005**, *127*, 614–618.
14. Li, Y. N.; Wu, Y. L.; Gardner, S.; Ong, B. S. *Adv. Mater.* **2005**, *17*, 849–853.
15. Li, Y. N.; Wu, Y. L.; Ong, B. S. *Macromolecules* **2006**, *39*, 6521–6527.
16. Zhao, H. P.; Tao, X. T.; Wang, P.; Ren, Y.; Yang, J. X.; Yan, Y. X.; Yuan, C. X.; Liu, H. J.; Zou, D. C.; Jiang, M. H. *Org. Electron.* **2007**, *8*, 673–682.
17. Lengvinaite, S.; Grazulevicius, J. V.; Grigalevicius, S.; Gu, R.; Dehaen, W.; Jankauskas, V.; Zhang, B.; Xie, Z. *Dyes Pigments* **2010**, *85*, 183–188.
18. Boudreault, P. T.; Virkar, A. A.; Bao, Z.; Leclerc, M. *Org. Electron.* **2010**, *11*, 1649–1659.
19. Liu, Z.; Cao, D.; Chen, Y.; Fang, Q. *Dyes Pigments* **2010**, *86*, 63–67.
20. Marcus, R. A. *Rev. Mod. Phys.* **1993**, *65*, 599–610.
21. Coropceanu, V.; Cornil, J.; Demetrio, A.; Olivier, Y.; Silbey, R.; Brédas, J. L. *Chem. Rev.* **2007**, *107*, 926–952.
22. Dmas, J. N.; Crobys, G. A. *J. Phys. Chem.* **1971**, *75*, 991–1024.
23. Brédas, J. L.; Silbey, R.; Boudreaux, D. S.; Chance, R. R. *J. Am. Chem. Soc.* **1983**, *105*, 6555–6559.
24. Promaraka, V.; Ruchirawat, S. *Tetrahedron* **2007**, *63*, 1602–1609.
25. Hohenberg, P.; Kohn, W. *Phys. Rev. B* **1964**, *136*, 864–871.
26. Kohn, W.; Sham, L. J. *Phys. Rev. A* **1965**, *140*, 1133–1138.
27. Foresman, J. B.; Gordon, M. H.; Pople, J. A.; Frisch, M. J. *J. Phys. Chem.* **1992**, *96*, 135–149.
28. Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. *J. Chem. Phys.* **2001**, *114*, 5691–5701.
29. Cossi, M.; Scalmani, G.; Rega, N.; Barone, V. *J. Chem. Phys.* **2002**, *117*, 43–54.
30. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, T., Jr.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, B.; Rega, G. N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03. Gaussian: Pittsburgh PA, 2003.
31. Yudina, L. N.; Bergman, J. *Tetrahedron* **2003**, *59*, 1265–1275.