

Synthesis and characterization of indolo [2, 3-a] carbazole-based novel luminescent materials

MINXIN YANG^{a, b}, GUIJIE MAO^a, LULU WANG^{a, b}, JINCHANG TIAN^{a, b}, XIN HUANG^{a, b}, YONG YANG^{a, b}, WENYI CHU^{a, b*}, ZHIZHONG SUN^{a, b*}

^aSchool of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, P. R. China

^bKey Laboratory of Chemical Engineering Process and Technology for High-efficiency Conversion, College of Heilongjiang Province, Harbin 150080, P. R. China

A series of novel indolo [2,3-a] carbazole derivatives as small molecule luminescent compounds were successfully synthesized by bromination and Suzuki coupling reaction, and characterized by thermal analysis, UV absorption spectra, fluorescence emission spectra and quantum calculation textng. These compounds have a high decomposition temperature ($T_d=317-369^\circ\text{C}$) and good thermal stability. They exhibit stable blue light emitting both in dilute solutions and solid films. By density functional theory (DFT) calculations, these compounds have wide energy levels, good electron injection and transport capability.

(Received February 26, 2016; accepted April 05, 2016)

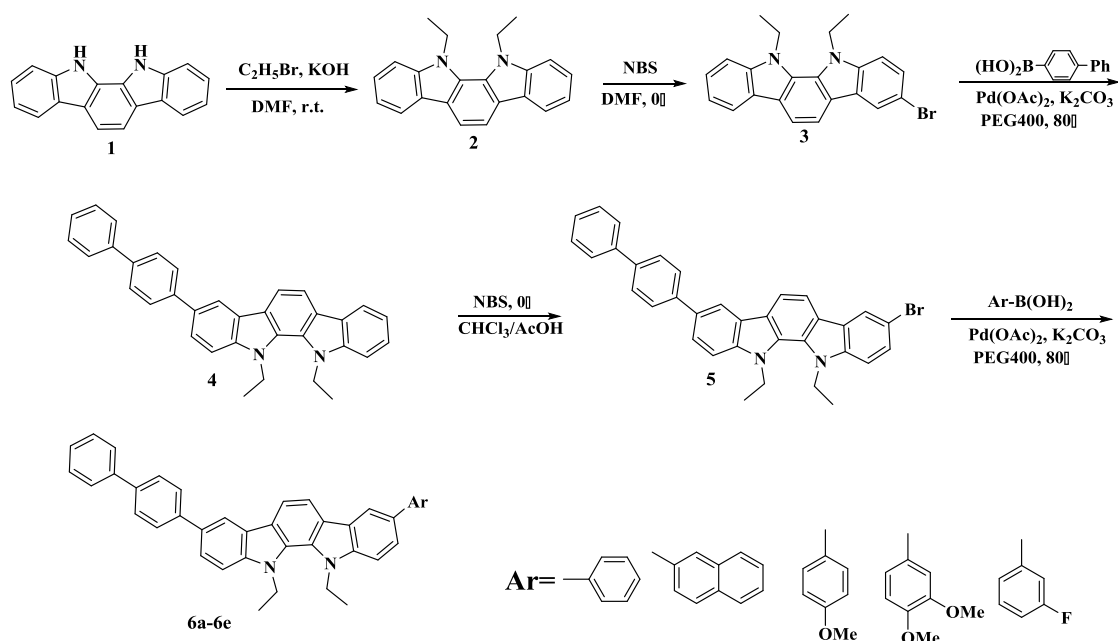
Keywords: Indolo [2,3-a] carbazole derivatives, Suzuki coupling reaction, Thermal stability, Blue light emitting

1. Introduction

In recent years, small organic molecules emitting materials as new generation of display and lighting technology has attracted wide attention because of their simple structure, fast response, high resolution, low driving voltage, and anti-shock resistance. These materials can be made into large size and flexible ultra-thin panels. These fluorescent materials are not only used in organic light-emitting diodes (OLED) but also in fluorescent probes[1], solar cells[2], printing inks[3] and so on. They have an important application in the field of biology[4], medical[5], materials science[6], environmental science [7], and the defense sector[8]. Numerous building blocks such as anthracene[9,10], fluorine[11,12], pyrene[13,14], carbazole[15,16] and triphenylamine[17] are designed as main structures. As we know, indolo[3,2-b]carbazole (ICZ) moiety[18] is recently widely used as a building block for the design and synthesis of charge-transporting materials for (opto)electronics because of the interesting electrical and optical properties of ICZ-based compounds. However, few of indolo[2,3-a]carbazole as building block for luminescent materials have been reported. Its structure is similar with ICZ. Therefore, indolo[2,3-a]carbazole derivatives have attracted much attention owing to their favorable properties such as good planarity, high thermal stability and excellent photophysical properties. In this article, five kinds of small molecule luminescent compounds containing indolo[2,3-a] carbazole were

designed and synthesized by using indolo[2,3-a]carbazole as a raw material through two brominations and two Suzuki coupling reactions with different aryl boronic acid. These compounds are 3-([1,1'-biphenyl]-4-yl)-11,12-diethyl-8-phenyl-11,12-dihydroindolo[2,3-a]carbazole(**BPPIC**), 3-([1,1'-biphenyl]-4-yl)-11,12-diethyl-8-(naphtha-ene-2-yl)indole-11,12-dihydro[2,3-a]carbazole (**BPNIC**), 3-([1,1'-biphenyl]-4-yl)-11,12-diethyl-8-(4-methoxyphenyl)-11,12-dihydroindolo[2,3-a] carbazole (**BPMPI**), 3-([1,1'-biphenyl]-4-yl)-8-(3,4-dimethoxyphenyl)-11,12-diethyl-11,12-dihydro-indolo[2,3-a] carbazole (**BDMPIC**), 3-([1,1'-biphenyl]-4-yl)-11,12-diethyl-8-(3-fluorophenyl)-11,12-dihydroindolo[2,3-a]carbazole (**BPFIC**), respectively. Structures of these compounds were confirmed by ¹H NMR, ¹³C NMR and high resolution mass spectrometry (HRMS). Characteristics of these compounds were investigated by thermal analysis, UV absorption spectra, fluorescence emission spectra and quantum calculation textng.

In this study, 11,12-dihydroindolo[2,3-a]carbazole (1) was used as starting material to obtain indolo[2,3-a] carbazole-based derivatives via N-ethylation reaction, brominations and Suzuki coupling reactions. Main synthetic routes of indole[2,3-a] carbazole-based derivatives were shown in Scheme 1.



Scheme 1. Synthetic route of indolo[2, 3-a]carbazole derivatives.

2. Experimental

2.1 Material and methods

All starting materials were purchased from TCI; the reagents were obtained from J&K Chemical Company and used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX 400 MHz and 100 MHz spectrometer in CDCl_3 or DMSO. High resolution mass spectra were recorded on Agilent 1100 (VL) mass spectrometer. Experimental process was monitored by thin layer chromatography (TLC). Column chromatography was carried out on silica gel (200 ~ 300 mesh).

Thermogravimetric (TGA) measurements were performed on Shimadzu DTG-60A thermal analyzers at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ under nitrogen atmosphere. UV-visible spectra and photoluminescence (PL) spectra were measured by Shimadzu UV-2501PC UV-visible spectrophotometer and Shimadzu RF-5301PC fluorescence spectrophotometer, respectively. Density functional theory (DFT) calculations have been applied to characterize the frontier molecular orbital energy levels of the compounds at the B3LYP/6-31G (d) level by using the Gaussian 03 program. Melting points were measured on a digital melting point apparatus without correction. Infrared spectroscopy (IR) was measured by SP-100 Fourier transform infrared spectroscopy.

2.2 Synthesis

11,12-diethyl-11,12-dihydroindolo[2,3-a]carbazole(2). $\text{C}_2\text{H}_5\text{Br}$ (3.2 mL, 42.92 mmol) was added dropwise to a suspension of 11,12-dihydroindolo[2,3-a]carbazole (5.00 g, 19.51 mmol) and KOH (2.74 g, 48.77 mmol) in DMF (75 mL) at room temperature. It was dropped slowly within 30

minutes. After being continually stirred for an additional 10 hours, the mixture was poured into cold water. Finally, the pale yellow solid was collected by filtration and washing with ethanol and water. Yield: 5.63 g (92.45%). ^1H NMR (400 MHz, CDCl_3) δ 8.12 (d, $J = 7.7$ Hz, 2H), 7.95 (s, 2H), 7.57 (d, $J = 8.2$ Hz, 2H), 7.47 (ddd, $J = 8.2$, 7.2, 1.2 Hz, 2H), 7.33-7.27 (m, 2H), 4.62 (q, $J = 7.1$ Hz, 4H), 1.34 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.98, 143.34, 130.99, 128.93, 125.70, 125.52, 122.63, 122.05, 120.67, 120.04, 117.08, 111.73, 111.20, 108.49, 43.33, 43.03, 13.85, 13.78. HRMS (EI) calcd for $\text{C}_{22}\text{H}_{20}\text{N}_2$ ($[\text{M}+\text{H}]^+$): 313.1704. Found: 313.1732. Anal. calcd for $\text{C}_{22}\text{H}_{20}\text{N}_2$: C, 84.58; H, 6.45; N, 8.97. Found: C, 84.56; H, 6.46; N, 8.98. m.p.: 194-197 $^\circ\text{C}$.

3-bromo-11,12-diethyl-11,12-dihydroindolo[2,3-a]carbazole (3). A solution of 11,12-diethyl-11,12-dihydroindolo[2,3-a] carbazole (4.89 g, 15.65 mmol) in DMF (85 mL) was stirred at $0\text{ }^\circ\text{C}$. NBS (2.79 g, 15.65 mmol) was added in small portions. The mixture was stirred for 7 hours. The reaction mixture was poured into cold water, pale yellow solid was precipitated. The solid was filtered and washed with water and ethanol, and dried to give a pale yellow solid. Yield: 5.63 g (92.45%). ^1H NMR (400 MHz, CDCl_3) δ 8.94 (d, $J = 8.0$ Hz, 1H), 8.11-8.06 (m, 2H), 7.61 – 7.48 (m, 4H), 7.39 – 7.30 (m, 2H), 4.67 – 4.56 (m, 4H), 1.22 (dt, $J = 11.8$, 7.1 Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.98, 143.34, 130.99, 128.93, 126.02, 125.87, 125.70, 125.63, 125.52, 122.63, 122.05, 120.67, 120.25 120.04, 117.08, 111.73, 111.20, 108.49, 43.33, 43.03, 13.85, 13.78. HRMS (EI) calcd for $\text{C}_{22}\text{H}_{19}\text{BrN}_2$ ($[\text{M}+\text{H}]^+$): 391.0810. Found: 391.0851. Anal. calcd for $\text{C}_{22}\text{H}_{19}\text{BrN}_2$: C, 67.53; H, 4.89; Br, 20.42; N, 7.16. Found: C, 67.56; H, 4.85; Br, 20.47; N, 7.12. m.p.: 122-126 $^\circ\text{C}$.

3-([1,1'-biphenyl]-4-yl)-11,12-diethyl-11,12-dihydroindolo[2,3-a]carbazole (4 BPIC). A mixture of 3-bromo-11,12-diethyl-11,12-dihydroindolo[2,3-a]carbazole (5.31 g, 13.57 mmol), 4-biphenyl boronic acid (4.03 g, 20.35 mmol), Pd(OAc)₂ (0.61 g, 2.71 mmol), and K₂CO₃ (1.16 g, 8.40 mmol) in PEG400 (50 mL) was heated at 80 °C under an argon atmosphere for 24 hours. After completion, the mixture was cooled to room temperature and extracted with ethyl acetate (50 mL×3). The organic extracts were dried with anhydrous Na₂SO₄, filtered and concentrated by rotary evaporation. The crude residue was purified by column chromatography (eluent: petroleum ether and ethyl acetate) to obtain the pure product as a white powdery solid **BPIC**. Yield: 4.84 g (76.83%). ¹H NMR (400 MHz, CDCl₃) δ 8.08 (t, J = 9.6 Hz, 1H), 7.78 (td, J = 13.1, 6.4 Hz, 7H), 7.58 (t, J = 9.2 Hz, 2H), 7.53 – 7.46 (m, 4H), 7.40 (t, J = 7.3 Hz, 2H), 7.30 (t, J = 7.4 Hz, 1H), 7.02 (t, J = 7.5 Hz, 1H), 4.65 (dq, J = 13.6, 6.8 Hz, 4H), 1.33 (q, J = 6.7 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 144.04, 143.57, 141.00, 139.88, 130.51, 130.21, 130.16, 128.86, 127.30, 127.13, 127.01, 126.09, 125.42, 124.93, 124.52, 122.28, 122.08, 120.43, 119.96, 119.84, 114.53, 111.55, 111.14, 43.33, 42.97, 14.14, 14.11. HRMS (EI) calcd for C₃₄H₂₈N₂ ([M+H]⁺): 465.2330. Found: 465.2341. Anal. calcd for C₃₄H₂₈N₂: C, 87.90; H, 6.07; N, 6.03. Found: C, 87.92; H, 6.04; N, 6.04. m.p.: 198–200 °C. IR (KBr, cm⁻¹): 2973.78, 1595.38, 1558.06, 1479.89, 1440.80, 1383.68, 1265.33, 1210.18, 843.20, 739.38, and 699.31.

3-([1,1'-biphenyl]-4-yl)-8-bromo-11,12-diethyl-11,12-dihydroindolo[2,3-a]carbazole(5). A mixture of 3-([1,1'-biphenyl]-4-yl)-11,12-diethyl-11,12-dihydroindolo [2,3-a]carbazole (4.56 g, 9.81 mmol) in CHCl₃/AcOH (300/60 mL) was stirred at 0 °C. NBS (1.75 g, 9.81 mmol) was added in small portions. After being stirred for 7 hours, the mixture was poured into cold water. The pink precipitate was filtered off and washed with ethanol to give a white solid. Yield: 4.46 g (83.6%). ¹H NMR (400 MHz, CDCl₃) δ 9.02 (d, J = 8.1 Hz, 1H), 7.84 (dd, J = 15.6, 7.8 Hz, 4H), 7.63 (d, J = 8.4 Hz, 1H), 7.53 (dt, J = 10.3, 6.4 Hz, 6H), 7.38 (dt, J = 13.8, 7.3 Hz, 3H), 6.94 (t, J = 7.6 Hz, 1H), 6.72 (d, J = 8.0 Hz, 1H), 4.65 (dq, J = 14.3, 7.0 Hz, 4H), 1.19 (dd, J = 6.9, 4.7 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 144.17, 144.06, 140.82, 139.61, 130.77, 130.44, 130.36, 129.08, 128.85, 127.33, 127.15, 126.72, 126.11, 125.78, 125.45, 124.18, 123.14, 122.63, 122.27, 120.38, 120.33, 111.59, 110.28, 43.28, 13.62. HRMS (EI) calcd for C₃₄H₂₇BrN₂ ([M+H]⁺): 543.1436. Found: 543.1457. Anal. calcd for C₃₄H₂₇BrN₂: C, 75.14; H, 5.01; Br, 14.70; N, 5.15. Found: C, 75.12; H, 5.03; Br, 14.73; N, 5.12. m.p.: 205–208 °C.

3-([1,1'-biphenyl]-4-yl)-11,12-diethyl-8-phenyl-11,12-dihydroindolo[2,3-a]carbazole (6a BPPIC). A mixture of 3-([1,1'-biphenyl]-4-yl)-8-bromo-11,12-diethyl-11,12-dihydroindolo[2,3-a]carbazole (810.00 mg, 1.49 mmol), phenylboronic acid (272.57 mg, 2.24 mmol), K₂CO₃ (411.94 mg, 2.98 mmol), Pd(OAc)₂ (66.92 mg, 298.06 μmol) and PEG400 (10.0 mL) was stirred at 80 °C under

an argon atmosphere for 24 hours. After being cooled to room temperature, the mixture was poured into water and extracted with ethyl acetate (3×50 mL). The organic extracts were dried with anhydrous Na₂SO₄, filtered and concentrated by rotary evaporation. The crude residue was purified by column chromatography (eluent: petroleum ether and ethyl acetate) to obtain the pure product as a white solid **BPPIC**. Yield: 4.84 g (76.83%). ¹H NMR (400 MHz, CDCl₃) δ 7.68 (d, J = 7.4 Hz, 2H), 7.57 (d, J = 8.0 Hz, 4H), 7.45 (t, J = 7.6 Hz, 2H), 7.39–7.27 (m, 10H), 6.91 (d, J = 6.5 Hz, 2H), 6.82 (d, J = 7.9 Hz, 1H), 6.68 (d, J = 7.9 Hz, 1H), 4.67 (s, 4H), 1.35 (t, J = 7.0 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 144.16, 140.86, 139.83, 138.83, 131.35, 130.90, 129.19, 128.74, 127.96, 127.14, 126.92, 126.62, 126.40, 124.88, 123.02, 122.30, 122.25, 119.96, 111.23, 43.21, 14.12. HRMS (EI) calcd for C₄₀H₃₂N₂ ([M+H]⁺): 541.2643. Found: 541.2684. Anal. calcd for C₄₀H₃₂N₂: C, 88.85; H, 5.97; N, 5.18. Found: C, 88.82; H, 5.99; N, 5.19. m.p.: 152–154 °C. IR (KBr, cm⁻¹): 2972.59, 2931.03, 1600.10, 1575.36, 1455.41, 1424.48, 1364.57, 1330.24, 1169.25, 1079.21, 1024.88, 849.95, and 746.90.

3-([1,1'-biphenyl]-4-yl)-11,12-diethyl-8-(naphthalen-2-yl)-11,12-dihydroindolo[2,3-a]carbazole (6b BPNIC). **BPNIC** was synthesized in a manner similar to that of **BPPIC**. The pure product was obtained as a white powdery solid **BPNIC**. Yield: 751.90 mg (85.4%). ¹H NMR (400 MHz, CDCl₃) δ 7.85–7.78 (m, 2H), 7.72 (dd, J = 9.3, 7.1 Hz, 2H), 7.63–7.54 (m, 4H), 7.51 (dd, J = 5.3, 2.3 Hz, 2H), 7.48–7.28 (m, 10H), 6.92 (t, J = 7.3 Hz, 1H), 6.80 (t, J = 7.2 Hz, 2H), 6.61 (d, J = 7.9 Hz, 1H), 4.69 (d, J = 5.6 Hz, 4H), 1.35 (t, J = 6.9 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 144.17, 140.77, 138.87, 133.34, 132.27, 131.48, 131.10, 129.72, 129.42, 129.31, 128.68, 128.13, 127.75, 127.45, 126.91, 126.51, 126.47, 125.69, 125.55, 124.94, 123.10, 122.33, 120.05, 111.26, 43.24, 14.09. HRMS (EI) calcd for C₄₄H₃₄N₂ ([M+H]⁺): 591.2800. Found: 591.2831. Anal. calcd for C₄₄H₃₄N₂: C, 89.46; H, 5.80; N, 4.74. Found: C, 89.42; H, 5.83; N, 4.75. m.p.: 165–168 °C. IR (KBr, cm⁻¹): 2970.74, 2930.66, 1599.73, 1517.68, 1453.39, 1300.14, 1238.04, 1024.14, 746.70, and 695.86.

3-([1,1'-biphenyl]-4-yl)-11,12-diethyl-8-(4-methoxyphenyl)-11,12-dihydroindolo[2,3-a]carbazole (6c BPMPIC). **BPMPIC** was synthesized in a manner similar to that of **BPPIC**. The pure product was obtained as a white powdery solid **BPMPIC**. Yield: 691.52 mg (81.3%). ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, J = 8.3 Hz, 2H), 7.58 (t, J = 8.9 Hz, 4H), 7.46 (t, J = 7.6 Hz, 2H), 7.36 (dd, J = 12.3, 6.0 Hz, 5H), 7.21 (d, J = 8.5 Hz, 2H), 6.98–6.89 (m, 2H), 6.85 (d, J = 8.6 Hz, 2H), 6.82–6.76 (m, 2H), 4.67 (dd, J = 13.9, 6.9 Hz, 4H), 3.82 (s, 3H), 1.35 (t, J = 7.0 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 158.24, 140.89, 138.76, 131.33, 128.83, 128.77, 127.56, 127.38, 127.15, 127.05, 126.93, 126.44, 124.87, 122.32, 119.98, 113.41, 111.22, 55.13, 43.21, 14.21. HRMS (EI) calcd for C₄₁H₃₄N₂O ([M+H]⁺): 571.2749. Found: 571.2763. Anal. calcd for C₄₁H₃₄N₂O: C, 86.28; H, 6.00; N, 4.91. Found: C, 86.24; H, 6.01; N, 4.90. m.p.: 229–231 °C. IR (KBr, cm⁻¹):

2969.65, 2928.61, 1607.13, 1557.93, 1513.02, 1462.35, 1428.37, 1330.97, 1244.03, 1171.07, 1076.53, 1030.06, 750.61, and 703.15.

3-([1,1'-biphenyl]-4-yl)-8-(3,4-dimethoxyphenyl)-11,12-diethyl-11,12-dihydroindolo[2,3-a]carbazole (6d BPDMPIC). BPDMPIC was synthesized in a manner similar to that of BPPIC. The pure product was obtained as a white powdery solid BPDMPIC. Yield: 747.69 mg (83.51%). ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, J = 8.5 Hz, 2H), 7.59 (t, J = 8.9 Hz, 4H), 7.46 (t, J = 7.6 Hz, 2H), 7.41 – 7.31 (m, 5H), 6.90 (dd, J = 12.9, 5.2 Hz, 4H), 6.86 – 6.80 (m, 3H), 4.67 (d, J = 6.6 Hz, 4H), 3.90 (s, 3H), 3.69 (s, 3H), 1.35 (dd, J = 13.3, 6.9 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 148.40, 147.62, 144.19, 144.13, 140.87, 139.17, 138.94, 132.21, 131.36, 131.24, 129.25, 129.18, 129.14, 129.04, 128.78, 127.18, 126.97, 126.62, 126.59, 126.40, 124.91, 123.29, 123.14, 122.99, 122.47, 122.32, 120.03, 114.37, 111.25, 111.19, 110.65, 55.82, 55.72, 43.19, 14.16, 14.09. HRMS (EI) calcd for C₄₂H₃₆N₂O₂ ([M+H]⁺): 601.2855. Found: 601.2885. Anal. calcd for C₄₂H₃₆N₂O₂: C, 83.97; H, 6.04; N, 4.66. Found: C, 83.93; H, 6.05; N, 4.68. m.p.: 153-155 °C. IR (KBr, cm⁻¹): 2973.63, 2932.19, 1606.38, 1516.09, 1453.79, 1330.17, 1233.06, 1136.69, 1028.06, 844.86, 747.72, and 692.63.

3-([1,1'-biphenyl]-4-yl)-11,12-diethyl-8-(3-fluorophenyl)-11,12-dihydroindolo[2,3-a]carbazole (6e BPFIC). BPFIC was synthesized in a manner similar to that of BPPIC. The pure product was obtained as a white powdery solid BPFIC. Yield: 664.78 mg (79.84%). ¹H NMR (400 MHz, CDCl₃) δ 7.71-7.68 (m, 2H), 7.62 – 7.56 (m, 4H), 7.46 (t, J = 7.6 Hz, 2H), 7.41 – 7.33 (m, 5H), 7.28 (dd, J = 11.0, 4.8 Hz, 1H), 7.11 (d, J = 7.6 Hz, 1H), 7.06 – 6.91 (m, 4H), 6.81 (d, J = 7.8 Hz, 1H), 6.73 (d, J = 7.8 Hz, 1H), 4.68 (q, J = 7.0 Hz, 4H), 1.35 (t, J = 7.1 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 163.79, 161.34, 144.09, 142.12, 140.74, 139.05, 138.60, 131.24, 131.18, 129.44, 129.35, 129.31, 129.16, 128.84, 128.77, 127.22, 126.93, 126.80, 126.58, 126.49, 126.26, 125.03, 122.89, 122.63, 122.26, 122.04, 120.08, 118.02, 117.81, 113.74, 113.53, 111.34, 111.27, 43.21, 14.10. HRMS (EI) calcd for C₄₀H₃₁FN₂ ([M+H]⁺): 559.2550. Found: 559.2549. Anal. calcd for C₄₀H₃₁FN₂: C, 85.99; H, 5.59; F, 3.40; N, 5.01. Found: C, 85.95; H, 5.57; F, 3.46; N, 5.02. m.p.: 172-174 °C. IR

(KBr, cm⁻¹): 2972.61, 2932.63, 1610.44, 1581.09, 1441.59, 1373.98, 1332.20, 1227.68, 1169.99, 844.38, 779.48, 746.91, and 697.10.

3. Results and discussion

3.1 Thermal properties

The thermal properties of BPPIC, BPNIC, BPPMIC, BPDMPIC and BPFIC were investigated through thermogravimetric analysis (TGA). As shown in Fig. 1, their thermal decomposition temperatures (T_d, corresponding to 5% weight loss) were 317, 336, 351, 318 and 369 °C, respectively. The thermal data were summarized in Table 1.

TGA studies showed that all the compounds exhibited good thermal stabilities with decomposition temperatures in the range of 317-369 °C. Excellent thermal and chemical stabilities of indolo[2,3-a]carbazole unit is strongly beneficial to the thermal stability[19]. Different functional groups caused T_d value difference. The order of their T_d levels is BPPIC < BPDMPIC < BPNIC < BPPMIC < BPFIC (see Fig. 1 and Table 1).

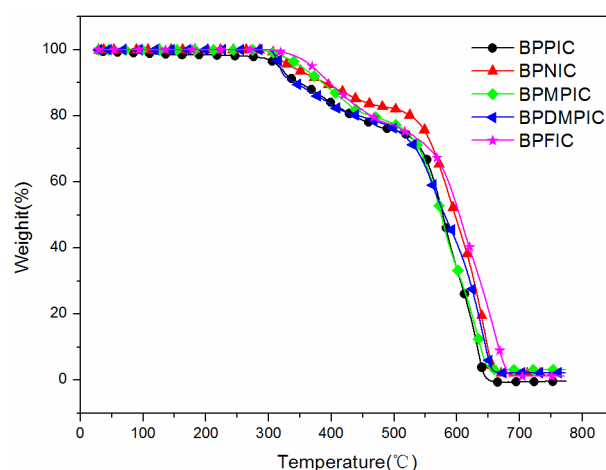


Fig. 1. TGA graphs of target compounds recorded.

Table 1. Physical properties of target compounds

Compound	T _d ^a (°C)	λ _{max} (nm)	Abs ^b		λ _{max} PL(nm)	HOMO ^d (eV)	LUMO ^d (eV)	E _g (eV)	T _m (°C)
			Solution ^b	Film ^c					
BPPIC	317	266,293,327	407	420	-4.72	-0.98	3.74	152-154	
BPNIC	336	265,293,326	407	420	-4.72	-0.99	3.73	165-168	
BPPMIC	351	267,294,329	409	421	-4.65	-0.97	3.68	229-231	
BPDMPIC	318	266,294,329	408	424	-4.63	-0.96	3.67	153-155	
BPFIC	369	265,292,327	405	422	-4.77	-1.00	3.77	172-174	

^a Obtained from TGA measurements with a heating rate of 10 °C/min under N₂. ^b Measured in a dilute CH₂Cl₂ solution (10⁻⁵ M). ^c Measured in thin neat films. ^d Obtained from quantum chemical calculation using DFT/B3LYP/6-31G (d).

3.2 Photophysical properties

Photophysical properties of **BPPIC**, **BPNIC**, **BPMPIIC**, **BPDMPIC** and **BPFIC** were analyzed via ultraviolet-visible (*UV-Vis*) and photoluminescence (PL) spectrometers. Spectrums of these compounds were shown in Fig. 2, and their key photophysical parameters were listed in Table 1. The **BPPIC**, **BPNIC**, **BPMPIIC**, **BPDMPIC** and **BPFIC** in 10^{-5} M CH_2Cl_2 solutions exhibited three similar UV absorption bands: 260-280, 285-305 and 320-340 nm (Fig. 2a). The 285-305nm, 320-340nm absorption bands were attributed to the $\pi-\pi^*$ transition of the indolo[2,3-a]carbazole ring, and the 260-280 nm absorption band was attributed to the $\pi-\pi^*$ aromatic terminals [20]. PL spectrum of five compounds in dilute 10^{-5} M CH_2Cl_2 solution exhibited similar

emission peaks at a wavelength of approximately 407 nm (Fig. 2b). The PL spectrum of their solid films exhibited blue emission with the peak maxima at 420-424 nm (Fig. 2c). All compounds exhibited blue light emission. The order of the emission wavelength of PL spectrum is similar to the absorption wavelength of UV spectrum. Red shifts of the emission wavelength occurred between solutions and solid films of these compounds, because molecular vibrations in the solutions are easier than those in solid films, and molecular collisions caused by molecular vibrations will decrease the emission wavelength [21]. The emission images of five compounds in CH_2Cl_2 under irradiation at 365 nm at room temperature are shown in Fig. 2d. Thus, **BPFIC** showed blue violet. The other compounds can exhibit blue light emission stably in dilute solutions.

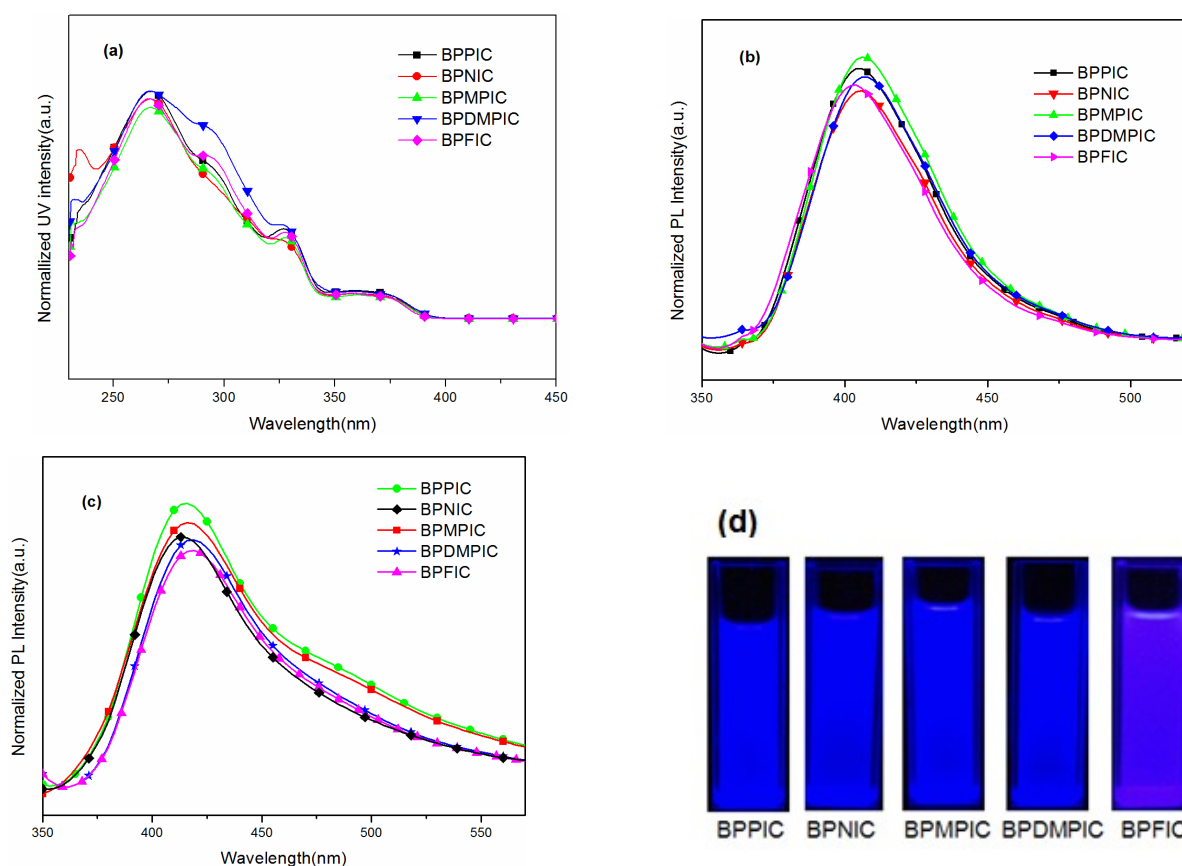


Fig. 2. (a) *UV-Vis* absorption in CH_2Cl_2 solution (10^{-5} M). (b) PL spectra in CH_2Cl_2 solution (10^{-5} M). (c) PL spectra in solid films. (d) The emission images at 365 nm UV.

3.3 Theoretical calculations

To understand the structure-property relationship of the compounds at the molecular level, density functional

theory (DFT) calculations were performed for these molecules using B3LYP hybrid functional theory with Gaussian 03[22]. Calculated density surfaces of the highest occupied molecular orbital (HOMO) and the

lowest unoccupied molecular orbital (LUMO) are shown in Fig. 3. Their computed frontier orbital energies are shown in Table 1.

The LUMO of five compounds were mostly localized over indolo[2,3-a] carbazole core and 3-substituted biphenyl groups, while HOMO mainly distributes on the whole molecule. Meanwhile, the planar structure of molecules could affect their electronic properties and

physico-chemical properties (Fig. 3). The HOMO and LUMO energy levels of **BPPIC**, **BPNIC**, **BMPIC**, **BDMPIC** and **BPFIC** ranged from -4.63 to -4.77 eV and -0.96 to -1.00 eV, respectively (Fig. 3 and Table 1). The calculated HOMO-LUMO energy gaps for these materials were 3.74, 3.73, 3.68, 3.67 and 3.77 eV, respectively. Such wide energy gap can be beneficial to electronic transfers and transports [23].

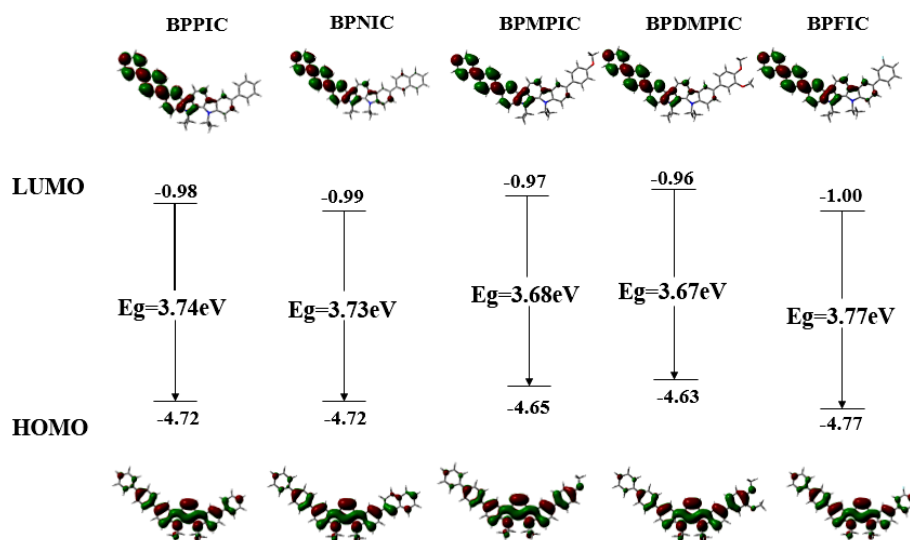


Fig. 3. Spatial distributions of frontier orbitals of target compounds.

4. Conclusion

In summary, a series of novel small molecule luminescent compounds containing indolo[2,3-a]carbazole have been successfully synthesized and characterized. These new compounds have a high decomposition temperature ($T_d = 317\text{--}369\text{ }^\circ\text{C}$) and good thermal stability. These compounds exhibit similar UV absorption wavelength and stable blue light emitting either in dilute solutions or solid thin-film states. By density functional theory (DFT) calculations, these compounds have wide energy levels and favor the electron injection and transport. Further research about these new compounds used as fluorescent materials is ongoing in our laboratory.

Acknowledgments

This work was supported by Fund of Natural Science Foundation of Heilongjiang Province of China (No. B201207).

References

- [1] N. Gandra, C. Portz, L. Tian, R. Tang, B. Xu, S. Achilefu, S. Singamaneni, *Angew. Chem.*, **53**, 866 (2014).
- [2] J. Chang, Y. Ning, S. Wu, W. Niu, S. Zhang, *Adv. Funct. Mater.*, **23**, 5910 (2013).
- [3] E. Molnár, S. Kuntam, P. K. R. Cingaram, B. Peksel, B. Suresh, G. Fabian, L. Z. Feher, A. Bokros, A. Medgyesi, F. Ayaydin, L. G. Puskas, *Molecules*, **18**, 9999 (2013).
- [4] G. W. Doorley, C. K. Payne, *Chem. Commun.*, **48**, 2961 (2012).
- [5] L. Cui, Y. Zhong, W. Zhu, Y. Xu, X. Qian, *Chem. Commun.*, **46**, 7121 (2010).
- [6] C. W. Freudiger, W. Yang, G. R. Holtom, N. Peyghambarian, X. S. Xie, K. Q. Kieu, *Nat. Photonics*, **8**, 153 (2014).
- [7] L. D. Mafu, T. A. M. Msagati, B. B. Mamba, *Environ. Sci. Pollut. Res.*, **20**, 790 (2013).
- [8] H. F. W. Shu, *Prog. Chem.*, **11**, 14 (2009).
- [9] I. Cho, S. H. Kim, J. H. Kim, S. Park, S. Y. Park, *J. Mater. Chem.*, **22**, 123 (2012).
- [10] S. R. S. Sarsah, M. R. Lutz, M. Zeller, D. S. Crumrine, D. P. Becker, *J. Org. Chem.*, **78**, 2051 (2013).
- [11] Y. Wei, C. T. Chen, *J. Am. Chem. Soc.*, **129**, 7478 (2007).
- [12] Z. F. Li, B. Jiao, Z. X. Wu, P. Liu, L. Ma, X. Lei, D. Wang, G. Zhou, H. Hu, X. Hou, *J. Mater. Chem. C*, **1**, 2183 (2013).
- [13] K. R. J. Thomas, N. Kapoor, M. N. K. P. Bolisetty, J.

- H. Jou, Y. L. Chen, Y. C. Jou, *J. Org. Chem.*, **77**, 3921 (2012).
- [14] X. Feng, J. Y. Hu, H. Tomiyasu, N. Seto, C. Redshaw, M. R. J. Elseqood, T. Yamato, *Org. Biomol. Chem.*, **11**, 8366 (2013).
- [15] B. J. Moon, K. S. Yook, J. Y. Lee, S. Shin, S. H. Hwang, *J. Lumin.*, **132**, 2557 (2012).
- [16] L. J. Deng, J. Y. Li, G. X. Wang, L. Z. Wu, *J. Mater. Chem. C*, **1**, 8140 (2013).
- [17] R. R. Reghu, J. Simokaitiene, J. V. Grazulevicius, S. Raisys, K. Kazlauskas, S. Jursenas, V. Jankauskas, A. Reina, *Dyes Pigments*, **115**, 135 (2015).
- [18] (a) N. X. Hu, S. Xie, Z. Popovic, P. Ong, A. M. Hor, *Am. Chem. Soc.*, **121**, 5097-5098(1999). (b) Y. Wu, Y. Li, S. Gardner, B. S. Ong, *J. Am. Chem. Soc.*, **127**, 614(2005). (c) H. Shi, J. Dai, X. Wu, L. Shi, J. Yuan, L. Fang, Y. Miao, X. Du, H. Wang, C. Dong, *Org. Electron.*, **14**, 868 (2013). (d) H. Shi, J. Yang, X. Dong, L. Fang, C. Dong, M. M. F. Choi, *Synthetic Met.*, **179**, 42 (2013).
- [19] C. H. Jun, Y. J. Pu, M. Igarashi, T. Chiba, H. Sasabe, J. Kido, *Chem. Lett.*, **43**, 1935 (2014).
- [20] R. A. Irgashev, A. Y. Teslenko, E. F. Zhilina, A. V. Schepochkin, O. S. El'tsov, G. L. Rusinov, V. N. Charushin, *Tetrahedron*, **70**, 4685 (2014).
- [21] R. Kim, X. Liu, S. G. Lee, J. Lee, Y. H. Kim, *Synthetic Met.*, **197**, 68 (2014).
- [22] H. Shi, J. Yang, X. Dong, L. Fang, C. Dong, M. M. F. Choi, *Synthetic Met.*, **179**, 42 (2013).
- [23] Y. Zhang, S. L. Lai, Q. X. Tong, M. F. Lo, T. W. Ng, M. Y. Chan, Z. C. Wen, J. He, K. S. Jeff, X. L. Tang, W. M. Liu, C. C. Ko, P. F. Wang, C. S. Lee, *Chem. Mater.*, **24**, 61 (2012).

*Corresponding author: wenyichu@hlju.edu.cn