Asian Journal of Chemistry; Vol. 25, No. 8 (2013), 4481-4486

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.14025

Synthesis, Characterization, Optical Properties and Theoretical Calculations of Blue Light-Emitting 1-Alkyl-2-substituted Benzimidazoles

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(*Received*: 7 May 2012; *Accepted*: 15 February 2013) AJC-12993

A series of novel blue light-emitting 1-alkyl-2-substituted benzimidazoles (**4a-4g**) were synthesized by reactions of the 2-substituted benzimidazoles (**3a-3e**) with ethyl bromide or *n*-butyl bromide as electrophilic reagent. Compounds **3a, 3c, 3e** were synthesized by the condensation of **1a-1c** with 1,2-diamino benzene *o*-phenylene diamine using air as oxidizing agent and compounds **3b, 3d** were synthesized by the condensation of **2d-2e** with 1,2-diamino benzene *o*-phenylene diamine using phosphoric acid and polyphosphoric acid as catalyst. Their optical properties were investigated by UV-visible spectroscopy and photoluminescence techniques in solution. They emit violet-blue light (λ^{Em}_{max} = 380-440 nm) with fluorescence quantum yields of 0.43 to 0.92 while diluted in acetonitrile solution. In order to find the relationship between the structures and properties of compounds **4a-4g**, theoretical calculations using density functional theory at the B3LYP/6-31g* level were also studied.

Key Words: Benzimidazole, Synthesis, Optical property, Fluorescence, Theoretical calculation.

INTRODUCTION

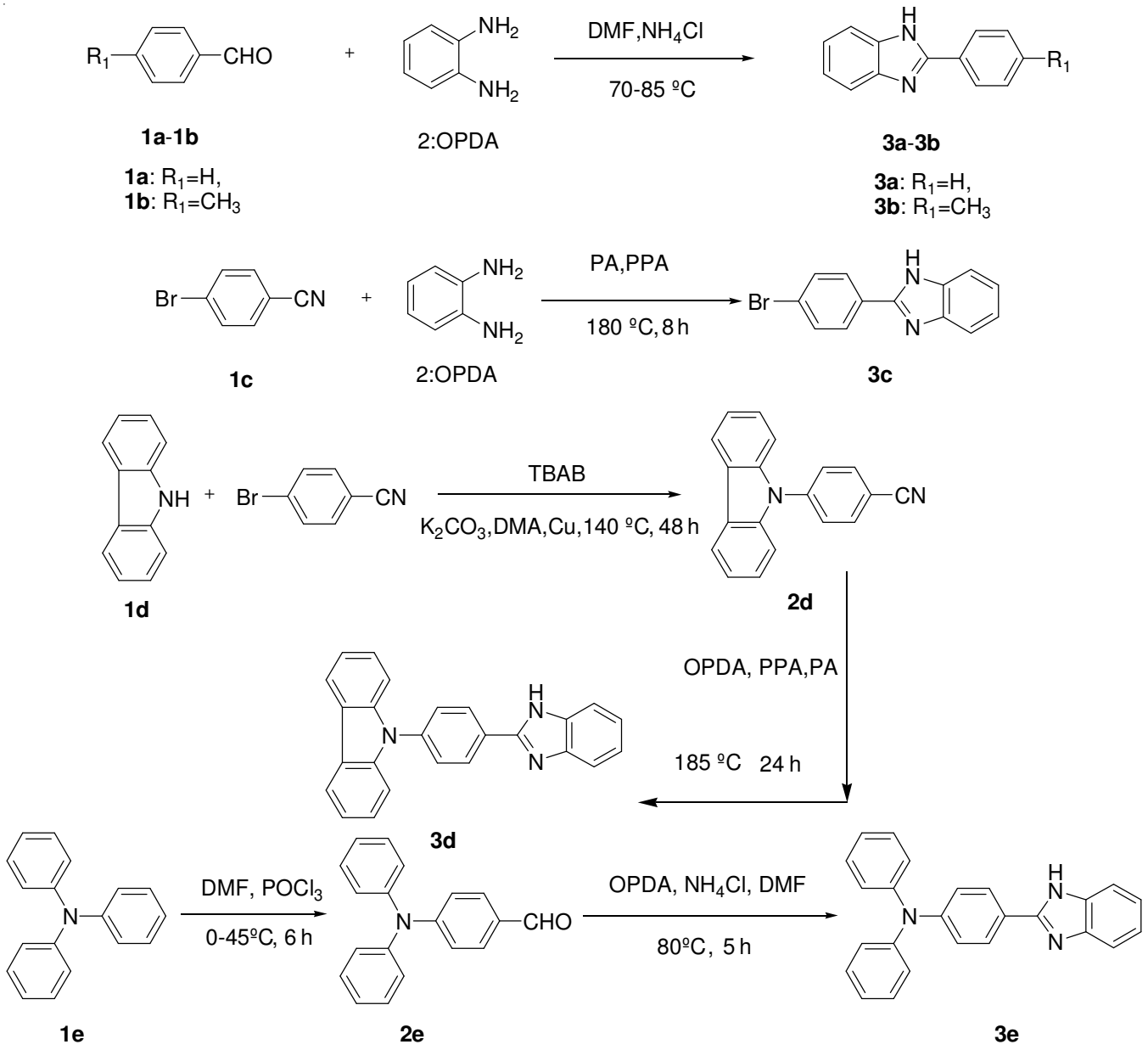
In recent years organic light-emitting diodes have attracted much interest due to their potential application in flat panel displays[1,2]. The blue light-emitting material is one of the important research subjects. Although great deals of blue light-emitting materials have been described in literature, the performance of their device leaves much to improve in colour purity, luminance efficiency and device stability[3,4]. The design and synthesis of blue emitters suitable for fabrication of stable organic light-emitting diode devices, however, remain major challenges for researchers.

Benzimidazole-based compounds were found to have intensive fluorescence and higher fluorescence efficiency and are widely used as fluorescence probes[5-7] fluorescent brightening agents[8] as components in organic light-emitting diodes[9] and in organic field effect transistors[10]. They also bear electron-withdrawing imine nitrogen (C=N) moieties, which behave as electron-accepting molecules that can facilitate electrochemical reduction, a feature that renders them suitable electron carriers[11]. In addition, for organic light-emitting diodes, the purity of materials directly affects the emission efficiency and operational stability. Small molecular organic materials have definite structures and can be purified by proper methods[12], which can solve the problems.

Many efforts have been taken to improve the characteristic of the benzimidazole-based compounds. Chih-Hsin *et al.*[13] designed benzimidazole compounds by introduction of benzene ring on N atom and the chromophores or auxochromes on 2 position of imidazole ring. Nomura *et al.*[14] reported novel substituted 2-(4-styrylphenyl)-1*H*-benzimidazole that could be used as multifunctional fluorescent materials. However, these compounds have the disadvantage of poor solubility because of the larger π-conjugated system. Our research group[15] reported several terphenyl-bridged *bis*benzimidazoles which obviously improved the solubility and exhibited satisfactory fluorescence properties. In this study, a series of novel small molecular benzimidazoles (**4a-4g**) were designed and synthesized (**Scheme-I and II**). For **4f** and **4g**, triphenylamine group and carbazole group were introduced because of their blue electroluminescent properties[16], high fluorescence quantum efficiency[17] and good hole-transporting abilities[18]. The optical properties of these compounds and theory calculation were also investigated.

EXPERIMENTAL

Melting points were measured on an X-4 microscope electrothermal apparatus (Taike) and remained uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on either a Bruker AV-500 spectrometer at 500 MHz or a Bruker AV-300



Scheme-I: Synthesis and molecular structure of 2-substituted benzimidazoles

spectrometer at 300 MHz, using DMSO-d_6 and $CDCl_3$ as the solvents, with tetramethylsilane (TMS) as the internal standard. Electrospray ionization-mass spectroscopy (ESI-MS) measurements were carried out with an Agilent 1100 series LC/MSD Trap SL mass spectrometer. Elemental analyses were performed with a Vario EL III elemental analyzer. Optical absorption spectra were obtained using an HP-8453 UV/VIS/near-IR spectrophotometer (Agilent). Photoluminescence spectra were carried out on an LS-55 spectrofluorometer (PerkineElmer).

All the chemicals for synthesis were purchased either from Sinopharm Chemical Reagent Co. Ltd. or from Shanghai Lingfeng Chemical Company and solvents were purified according to standard procedures. 4-(Carbazole-9-yl)benzonitrile (**2d**) was synthesized from carbazole and 4-bromobenzonitrile according to methods described in the literature[19]. 4-(*N,N*-diphenylamino)benzaldehyde (**2e**) was synthesized by formylation of *p*-phthalic acid (TPA) using *N,N*-dimethyl formamide (DMF) and $POCl_3$ according to the reported method[20].

Synthesis of 2-substituted-1*H*-benzimidazoles (3a-3e): 2-Substituted-1*H*-benzimidazoles (**3a-3e**) were synthesized by condensation of *o*-phenylenediamine with aromatic carboxylic aldehydes (**2a-2e**) in the presence of *N,N*-dimethylformamide (DMF) or in the presence of phosphoric acid and polyphosphoric acid according to the reported methods[21-23].

2-Phenyl-1*H*-benzimidazole (3a): Yield: 83.4 %; yellow crystals; m.p. 289-290 ºC [lit[24]]. 285-287 ºC).

2-(4-Methylphenyl)-1*H*-benzimidazole (3b): Yield: 77.6 %; blue crystals; m.p. 295-296 ºC [lit[24]].

2-(4-Bromophenyl)-1*H*-benzimidazole (3c): Yield: 87.7 %; white crystals; m.p. 293-295 ºC [lit[25]]. 296-298 ºC).

2-{4-(9H-carbazole-9-yl)phenyl}-1*H*-benzimidazole (3d): Yield: 58.9 %; light yellow crystals; m.p. > 300 ºC; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 7.25-7.18 (m, 2H, Ar-H), 7.33 (t, J = 7.32, 2H, Ar-H), 7.61-7.45 (m, 4H,Ar-H), 7.71-7.66

(m, 2H, Ar-H), 7.84 (d, *J* = 8.32 Hz, 2H, Ar-H), 8.27 (d, *J* = 7.76Hz, 2H, Ar-H), 8.47(d, *J* = 8.32 Hz, 2H, Ar-H), 13.1 (s, 1H, Ar-NH); ^{1}C NMR (DMSO-d_6, 300 MHz): δ 151.05, 140.36, 138.60, 129.57, 129.48, 122.68, 127.46, 126.90, 123.46, 121.09, 120.85, 110.31; Anal. calcd. for $C_{25}H_{17}N_3$: C, 83.54; H, 4.77; N, 11.69; Found: C, 83.57; H, 4.76; N, 11.60.

4-(1*H*-benzimidazol-2-yl)-*N,N*-diphenylbenzenamine (3e): Yield: 69.3 %; yellow crystals; m.p. > 300 ºC; ^{1}H NMR (DMSO-d_6, 300 MHz): δ 7.05 (d, 2H, *J* = 8.61 Hz), 7.18-7.10 (m, 8H, Ar-H), 7.37 (t, 4H, *J* = 7.38 Hz, Ar-NH), 7.74-7.56 (m, 2H, Ar-H), 8.05 (d, 2H, *J* = 8.61 Hz, Ar-NH), 12.71 (s, 1H, Ar-NH); ^{1}C NMR (DMSO-d_6, 300 MHz): δ 151.14, 148.65, 146.57, 139.65, 127.57, 124.82, 123.83, 123.31, 121.66, 121.57; Anal. calcd for $C_{25}H_{19}N_3$: C, 83.08; H, 5.30; N, 11.63; Found: C, 83.11; H, 5.28; N, 11.61.

Synthesis of (4a-4g): 1-Ethyl-2-phenylbenzimidazole (4a): 2-Phenyl-1*H*-benzimidazole (**3a**) (1.94 g, 10 mmol) and DMF (30 mL) were put into a 50 mL four-necked flask equipped with a temperature probe and magnetic stirrer and stirred to dissolve. The whole mixture was cooled to 0 ºC using ice bath. After adding NaH (1.44 g, 60 mmol), the mixture was warmed to room temperature and stirred for 1.5 h. Then ethyl bromide (1.31 g, 12 mmol) was added and the mixture was heat to 45 ºC. After reacting for 6-10 h at that temperature, saturated salt water (10 mL) was added dropwise and the reaction stopped. The mixture was extracted with ethyl acetate (3*10 mL), washed with saturated salt water and separated. The organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure to give **4a** with following properties: white crystal; m.p. 89-91 ºC (reference[26]): 88-88.5 ºC); Yield: 93.1 %. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 1.46 (t, *J* = 7.6 Hz, 3H, CH_3), 4.26 (q, *J* = 7.6 Hz, 2H, CH_2), 7.42-7.48 (m, 3H, Ar-H), 7.50-7.56 (m, 3 H, Ar-H), 7.71-7.81 (m, 3 H, Ar-H); Anal. calcd. for $C_{15}H_{14}N_2$: C 81.05, H 6.35, N 12.60; found C 81.09, H 6.33, N 12.58.

1-Ethyl-2-(4-methylphenyl)benzimidazole (4b): Following the same procedure described for the synthesis of **4a**, 2-(4-methylphenyl)-1*H*-benzimidazole (**3b**) and ethyl bromide were used to obtained product **4b**. Yield: 92 %; white crystals; m.p. 104-106 ºC; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 1.46 (t, *J* = 7.25 Hz, 3H, CH_3), 2.44 (s, 3H, CH_3), 4.28 (q, *J* = 7.25 Hz, 2H, CH_2), 7.33-7.29 (m, 4H, Ar-H), 7.43-7.40 (m, 1H, Ar-H), 7.62(d, *J* = 8.05 Hz, 2H, Ar-H), 7.84-7.81 (m, 1H, Ar-H); ^{1}C NMR ($CDCl_3$, 300 MHz): δ 152.60, 143.19, 139.83, 135.38, 129.40, 129.13, 127.65, 122.53, 122.26, 119.89, 109.81, 39.56, 21.40, 15.22; MS: *m/z* 237.1 ($M+H^+$), 238.1 ($M+2H^+$), 359.1 ($M+Na^+$); Anal. calcd. for $C_{16}H_{16}N_2$: C, 81.32; H, 6.82; N, 11.85; Found : C, 81.35; H, 6.78; N, 11.87.

1-Butyl-2-(4-methylphenyl)benzimidazole (4c): Compound 4c was obtained from 2-(4-methylphenyl)-1*H*-benzimidazole (**3b**) and *n*-butyl bromide. Yield: 91.4 %; white crystals; m.p. 62-63 ºC; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 0.87 (t, *J* = 7.35 Hz, 3H, CH_3), 1.31-1.25 (m, 2H, CH_2), 1.83-1.77 (m, 2H, CH_2), 2.44 (s, 3H, CH_3), 4.22 (t, *J* = 7.65 Hz, 2H, CH_2), 7.30-7.27 (m, 4H, Ar-H), 7.41-7.39 (m, 1H, Ar-H), 7.61 (d, *J* = 8.1 Hz, 2H, Ar-H), 7.83-7.81 (m, 1H, Ar-H); ^{1}C NMR ($CDCl_3$, 300 MHz): δ 153.77, 139.82, 135.56, 129.38, 129.29, 129.21, 127.61, 122.53, 122.28, 119.99, 119.79, 110.02, 44.53, 31.83, 21.41, 19.94, 13.52; MS: *m/z* 265.2 ($M+H^+$), 266.2 ($M+2H^+$); Anal. calcd. for $C_{18}H_{20}N_2$: C, 81.78; H, 7.63; N, 10.60; Found C, 81.75; H, 7.61; N, 10.63.

1-Ethyl-2-(4-bromophenyl)benzimidazole (4d): Compound **4d** was obtained from 2-(4-bromophenyl)-1*H*-benzimidazole (**3c**) and ethyl bromide. Yield: 94.8 %; yellow crystals; m.p.137-138 ºC; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 1.44 (t, *J* = 7.2 Hz,3H, CH_3), 4.25(q, *J* = 7.2 Hz, 2H, CH_2), 7.33-7.29 (m, 2H, Ar-H), 7.42-7.40 (m, 1H, Ar-H), 7.59 (d, *J* = 8.15 Hz, 2H, Ar-H), 7.65 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.83-7.81 (m, 1H, Ar-H); ^{1}C NMR ($CDCl_3$, 300 MHz): δ 152.15, 143.10, 135.36, 131.91, 130.66, 129.47, 124.20, 122.88, 122.47, 119.99, 109.88, 39.55, 15.18; MS: *m/z* 301.0 ($M+H^+$), 304.0 ($M+4H^+$), 323.0 ($M+Na^+$); Anal. calcd for $C_{15}H_{13}BrN_2$: C, 59.82; H, 4.35; N, 9.30; Found C, 59.86; H, 4.31; N, 9.35.

1-Butyl-2-(4-bromophenyl)benzimidazole (4e): Compound **4e** was obtained from 2-(4-bromophenyl)-1*H*-benzimidazole (**3c**) and *n*-butyl bromide. Yield: 93.3 %; yellow crystals; m.p. 81-83 ºC; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 0.88 (t, *J* = 7.35 Hz, 3H, CH_3), 1.31-1.24 (m, 2H, CH_2), 1.82-1.76 (m, 2H, CH_2), 4.21 (t, *J*= 7.65 Hz, 2H, CH_2), 7.33-7.29 (m, 2H, Ar-H), 7.47-7.40 (m, 1H, Ar-H), 7.58 (d, *J* = 8.3 Hz, 2H, Ar-H), 7.65 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.82-7.80 (m, 1H, Ar-H); ^{1}C NMR ($CDCl_3$, 500 MHz): δ 152.50, 143.05, 135.64, 131.96, 130.80, 129.65, 128.27, 124.23, 122.79, 120.01, 114.97, 110.14, 44.58, 31.86, 19.93, 13.51; MS: *m/z* 329.1 ($M+H^+$), 332.1 ($M+4H^+$), 351.0 ($M+Na^+$); Anal. calcd. for $C_{17}H_{17}BrN_2$: C, 62.02; H, 5.20; N, 8.51; Found C, 62.04; H, 5.19; Br, 24.23; N, 8.54.

1-Ethyl-2-{(4-(9*H*-carbazole-9-yl)phenyl}benzimidazole (4f): Compound **4f** was obtained from 2-{4-(9*H*-carbazole-9-yl)phenyl}-1*H*-benzimidazole (**3d**) and ethyl bromide. Yield: 88.7 %; yellow crystals; m.p. 166-168 ºC; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 1.58 (t, *J* = 7.25 Hz, 3H, CH_3), 4.45-4.40 (q, *J* = 7.25 Hz, 2H, CH_2), 7.38-7.30 (m, 4H, Ar-H), 7.51-7.43 (m, 5H, Ar-H), 7.76 (d, *J* = 8.35 Hz, 2H, Ar-H), 7.89-7.87 (m, 1H, Ar-H), 8.00 (d, *J* = 8.35 Hz, 2H, Ar-H), 8.16 (d, *J* = 7.7 Hz, 2H, Ar-H); ^{1}C NMR ($CDCl_3$, 300 MHz): δ 152.48, 140.57, 139.25, 135.47, 130.82, 129.35, 127.16, 126.13, 123.68, 123.02, 122.65, 120.41, 110.02, 109.73, 39.81, 15.40; MS: *m/z* 388.2 ($M+H^+$), 389.2 ($M+2H^+$), 410.2 ($M+Na^+$); Anal. calcd. for $C_{27}H_{21}N_3$: C, 83.69; H, 5.46; N, 10.84; Found C, 83.72; H, 5.44; N, 10.84.

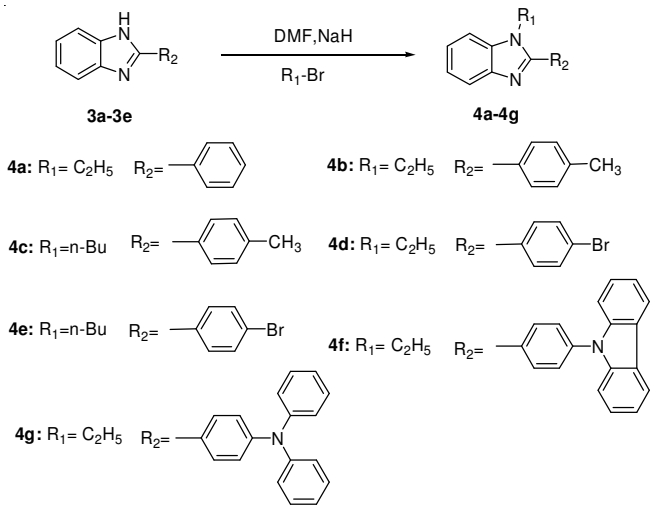
4-(1-Ethyl-1*H*-benzimidazol-2-yl)-*N,N*-diphenylbenzenamin (4g): Compound **4g** was obtained from 4-(*N,N*-diphenylaminophenyl)-1*H*-benzimidazole (**3e**) and ethyl bromide. Yield: 90.2 %; light yellow crystals; m.p. 170-172 ºC; ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 1.48 (t, *J* = 7.17 Hz, 3H, CH_3), 4.30 (q, *J* = 7.17 Hz, 2H, CH_2), 7.10-7.05 (m, 2H, Ar-H), 7.24-7.15 (m, 6H, Ar-H), 7.32-7.26 (m, 6H, Ar-H), 7.41-7.38 (m, 1H, Ar-H), 7.59 (d, *J* = 8.46 Hz, 2H, Ar-H), 7.81-7.78 (m, 1H, Ar-H); ^{1}C NMR ($CDCl_3$, 300 MHz): δ 130.02, 129.39, 125.10, 123.67, 123.35, 122.35, 122.14, 119.69, 109.71, 39.59, 15.23; MS: *m/z* 390.3 ($M+H^+$), 391.3 ($M+2H^+$), 412.3 ($M+Na^+$); Anal. calcd. for $C_{27}H_{23}N_3$: C, 83.26; H, 5.95; N, 10.79; Found C, 83.28; H, 5.90; N, 10.82.

Theory and computational details: Computations were performed using the Gaussian 03 simulation program[27] through the use of DFT based on Kohn-Sham approximations[28]. This method can determine molecular properties as a function of

electronic density when the molecules are in their ground state. Gaussian 03 has several functional options and basis sets which are available in its DFT module. The equilibrium geometry for each of the eight neutral molecules was found by using the hybrid B3LYP functional, which is a hybrid DFT functional that combines Becke's three parameter exchanges functional[29] with Lee-Yang-Parr's correlation functional[30]. 6-31g* basis set was also used. Equilibrium geometry was then calculated by using these sets.

RESULTS AND DISCUSSION

Synthesis and characterization: The synthesis of 1-alkyl-2-substituted benzimidazoles (**4a-4g**) is outlined in **Scheme-II**. Compounds **3a**, **3c**, **3e** were synthesized by the condensation of **1a-1c** with 1,2-diamino benzene *o*-phenylene diamine using air as oxidizing agent and compounds **3b, 3d** were synthesized by the condensation of **2d-2e** with 1,2-diamino benzene *o*-phenylene diamine using phosphoric acid and polyphosphoric acid as activator (**Scheme-I**). By alkylation reactions of the 2-substituted benzimidazoles (**3a-3e**) with ethyl bromide or *n*-butyl bromide as electrophilic reagent[31]. Compounds **4a-4g** were obtained. The yields were all 90 % above. ^{1}H NMR spectra, ^{13}C NMR spectra, mass spectra and elemental analyses of **4a-4g** confirmed the proposed structures and their purity. The crystal structure of **4g** monohydrate was revealed by X-ray crystallography[32].



Scheme-II: Synthesis and molecular structure of 1-alkyl-2-substituted benzimidazoles

Attention to the reaction of synthesis **4a-4g**, different reacting temperature of system (after adding C_2H_5Br) led to different yields. As seen from Table-1 (take **4a** as an example), when the reacting temperature was below 50 ºC, the yields changed little. However, when the temperature was above 50 ºC, the yields decreased. The higher the temperature, the lower the yields were. Therefore, considering this factor, 45 ºC of reacting temperature was chosen and the yields were all 90 % above.

Optical properties: The UV-visible absorption spectra of the 1-alkyl-2-substituted benzimidazoles in acetonitrile solution (10^{-5} mol L^{-1}) are displayed in Fig. 1 and their photophysical properties are summarized in Table-2. The lowest energy absorption bands are from the π-π* transitions by virtue of their large molar extinction coefficients (ε = 10^4 M^{-1} cm^{-1}). All eight compounds showed strong absorptions, with maximum wavelengths in the range of 290-334 nm. The increase in conjugation length and the increased electron density associated with carbazoleyl groups in **4f** and triphenylamine group in **4g** lead to a large bathochromic shift of absorption maximum in **4f** to 310 nm and in **4g** to 334 nm Ethyl and *n*-butyl had no influence on absorption maxima (λ^{Abs}_{max}). Compared to **4a** and **4d**, **4d** was red-shifted by 3 nm. This was due to the electron-withdrawing group bromide atom, which caused to produce intermolecular hydrogen bond (C-H···Br) with adjacent molecule and increased the coplanar degree of benzene ring and the benzimidazole ring. Optical band gaps (E_g^{opt}) determined from the absorption edge of the solution spectra[33] are also given in Table-2.

TABLE-1
INFLUENCE OF REACTION TEMPERATURE ON YIELD (TAKE **4a** AS AN EXAMPLE)

Reacting temperature (ºC) (after adding C_2H_5Br)	25	35	45	55	70	80
Yield (%)	92.4	93.1	93.1	92.2	89.6	84.8

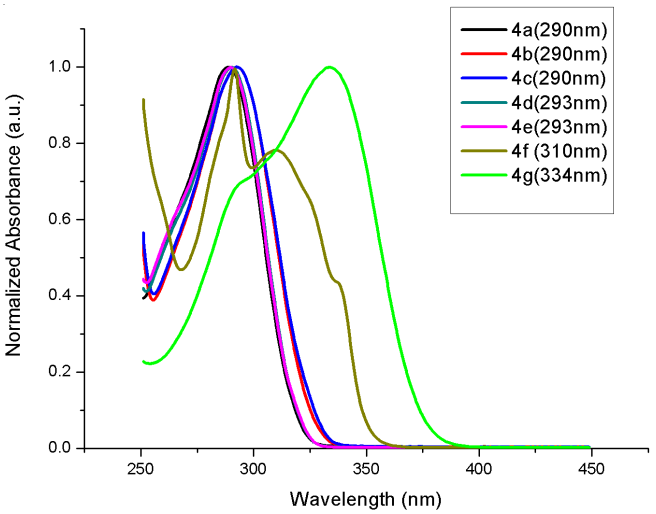


Fig. 1. UV-visible absorption spectra of the **4a-4g** in 10^{-5} acetonitrile solution

TABLE-2
PHYSICAL PROPERTIES OF **4a-4g**

Compound	ε (10^4 mol^{-1} cm^{-1})	λ^{Abs}_{max} (nm)	λ^{Em}_{max} (nm)	Stokes shift (nm)	ϕ_F [a]	Eg^{opt} (ev)[b]
4a	4.55	290	392	102	0.81	4.94
4b	4.71	290	391	101	0.85	4.88
4c	4.74	290	389	99	0.86	4.87
4d	3.12	293	401	108	0.43	4.92
4e	3.52	293	393	100	0.46	4.90
4f	4.88	310	412	102	0.89	4.77
4g	5.36	334	436	102	0.92	4.68

[a]Determined in CH_3CN solution (A<0.05) at room temperature using quinine sulfate (ϕ_F = 0.55 in 0.1 M H_2SO_4) as standard; [b]Estimated from the onset of absorption spectra (E_g^{opt} = 1240/λ_{onset})

The emission spectra of the eight 1-alkyl-2-substituted benzimidazoles (10^{-8} mol L^{-1}) in acetonitrile solution (λ_{ex} = $\lambda_{UV\text{-}max}$) are shown in Fig. 2. The fluorescence properties of

the compounds are also summarized in Table-2. All eight compounds have structured emission bands with the emission maximum in the 380-440 nm ranges. The excitation of these compounds at their respective absorption band maximum results in weak violet to blue luminescence, corresponding to a Stokes shift of 99-108 nm. Compared to **4c** and **4e**, **4c** was blue-shifted 3 nm while **4e** was red-shifted 1 nm. This may be due to the intermolecular hydrogen bond (C-H···Br) which increased the coplanar degree of the molecule. Compared to **4d** and **4e**, **4d** was red-shifted 9 nm while **4e** was red-shifted 1 nm. This is due to the steric effect of the *N*-alkyl chains. The effect will be more apparent with the increase of carbon atoms in the *N*-alkyl chains side chains.

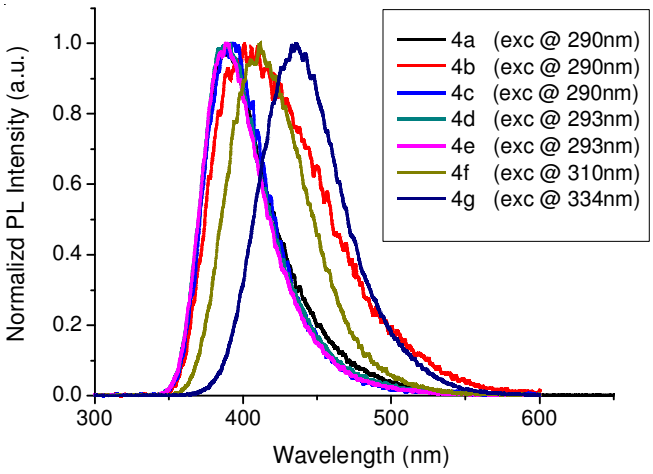


Fig. 2. Emission spectra of the **4a-4g** in acetonitrile solution ($\lambda_{ex} = \lambda_{UV\text{-}max}$)

The fluorescence quantum yields (ϕ_F) of these compounds in acetonitrile solution were determined by the standard method, using quinine sulfate (ϕ_F = 0.55 in 0.1 M H_2SO_4) as standard[34]. The fluorescence quantum yields were in the range from 0.43 for **4d** to 0.92 for **4g**. As can be seen from Table-2, with the increase in conjugation length, the fluorescence maximum shifted to longer wavelength and the fluorescence quantum yields also higher. It is noted that large p conjugated system can play important role in enhancing the quantum efficiency and decreasing the band-gap of chromophores. The fluorescence quantum yields of **4d** and **4e** were lower than other compounds, which is likely the results of competing $S_1 \rightarrow T_1$ intersystem crossing because of the internal heavy-atom effect[35].

Theoretical calculation: To gain insight into the electron properties and the geometries of the 1-alkyl-2-substituted benzimidazoles, quantum chemical calculations were performed. In the calculations, the ground state geometries of **4a-4g** were fully optimized using density functional theory (DFT) at the B3LYP/6-31g* level, as implement in Gaussian 03. DFT/B3LYP calculation of lowest excitation energies was performed at the optimized geometries of the ground states.

Frontier molecular orbitals and band energies: Because the relative ordering of the occupied and virtual orbitals provide a reasonable qualitative indication of the excitation properties[36], the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for these compounds are examined. The observed differences in the optical and chemical properties of these complexes rely mainly on the changes in the ground state electronic structures[37]. The HOMO-LUMO energy differences (energy band gaps, calculated Eg^{cal}) at DFT/B3YLP level of theory are presented in Table-3.

TABLE-3
ENERGY VALUES THEORETICAL CALCULATED FOR MOLECULES **4a-4g** IN GAS PHASE

Molecule	Energy (eV)		
	HOMO	LUMO	Eg^{cal}
4a	-5.74	-0.91	4.83
4b	-5.96	-1.17	4.79
4c	-5.94	-1.16	4.79
4d	-6.15	-1.50	4.66
4e	-6.14	-1.49	4.66
4f	-5.67	-1.51	4.17
4g	-5.31	-1.28	4.04

^{cal}: Energies theoretical calculated for gas phase by means of DFT B3LYP/6-31g*

The optimized structures of all the compounds showed the decrease of E_g when introduced conjugated groups, which is accord with the results obtained on the optical properties. Compared to **4c** and **4d**, the Eg both resulted in 4.79 eV, which indicated that *N*-alkyl chains have no influence on gap energy. For **4d** and **4f**, Eg resulted in 4.79 eV of **4d** and 4.65 eV of **4f**, respectively, which indicates that the electron acceptor groups make the E_g decreasing. For molecules **4f** and **4g**, HOMO resulted in -5.67 eV of **4f** and in-5.31 eV of **4g**, suggesting the electron-transporting properties in **4g** have been greatly improved. Compared to **4f** and **4g**, when phenylcarbazole group is replaced with triphenylamine group, HOMO is elevated, but LUMO is lowered, which facilitate both the hole and electron-transporting ability[38].

Charge-transporting abilities: The electrical and optical activity of electroluminescent materials relies on the ability of the materials to transport electrical charges. The molecules consisting of defined hole-transporting (donor) or electron-transporting (acceptor) segments are interesting because the electron and hole affinities can be enhanced simultaneously. Applications of such donor-acceptor copolymers to organic light-emitting diodes and to bulk heterojunction photovoltaic devices have recently been studied[39].

As can be seen from Fig. 3, the HOMO orbital of **4f** is localized mainly on the carbazole unit of the molecular, whereas the LUMO orbital is localized mainly on 2-phenyl-benzimidazole unit, which is different from **4g** and other compounds. This charge transfer implies that carbazole unit is a good electron-donating charge carrier and the 2-phenyl-benzimidazole unit serves as electron-accepting functionalities by the presence of the electron-withdrawing imine (C=N) nitrogen. This result will contribute to design the donor-acceptor conjugated copolymers for the future work.

Conclusion

A series of novel blue light-emitting 1-alkyl-2-substituted benzimidazoles were synthesized and characterized by UV-vis absorption and fluorescence emission spectroscopy. Fluorescence measurements showed that the compound emitted

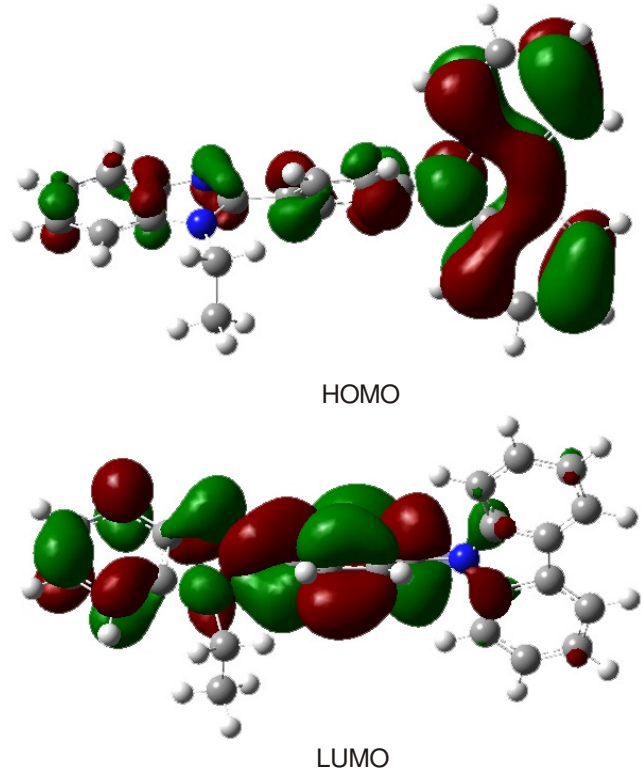


Fig. 3. HOMO and LUMO for molecules **4f** in gas phase

violet-blue light (λ^{Em}_{max} = 380-440) with fluorescence quantum yields of 0.43 to 0.92 while diluted in acetonitrile solution and **4g** had the best fluorescence quantum yields. Theoretical calculation results showed that **4g** has the better HOMO-LUMO ratio and **4f** is the best unit for the donor-acceptor conjugated copolymers that has the prospect to be studied for the future work.

ACKNOWLEDGEMENTS

The authors thank Linsen Zhou from School of Chemistry and Chemical Engineering, Nanjing University for help.

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