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ORIGINAL PAPER

Synthesis of Benzimidazoles Containing Pyrazole Group and Quantum Chemistry Calculation of Their Spectroscopic Properties and Electronic Structure

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Abstract Five benzimidazole compounds containing pyrazole group were synthesized *via* one-step reaction of *o*-phenylenediamine and 1-arylpyrazole-4-carbaldehyde in ethanol under mild conditions. The composition and structure of resultant benzimidazole compounds were analyzed by means of elemental analysis, mass spectrometry, ^{1}H-nuclear magnetic resonance spectroscopy and X-ray single crystal diffraction. The ultraviolet–visible light spectra and fluorescent spectra of the products were measured. Their ground-state (S_0) equilibrium geometries and vibrational frequencies were determined based on B3LYP method, and their first excited-state (S_1) geometries were fully optimized based on 6–31G (*d*, *p*) basis set of TD-B3LYP method. Besides, the spectroscopic properties of the products were computed based on cc-pVTZ basis set of TD-B3LYP method and compared with corresponding experimental data. It has been found that benzimidazole compounds containing pyrazole group can be readily synthesized in a high yield *via* one-step reaction of *o*-phenylenediamine and 1-arylpyrazole-4-carbaldehyde in ethanol solvent. The fluorescence properties of the five synthesized compounds are closely related to their molecular structure; and their computed fluorescence spectra well correspond to their experimental values. Moreover, they have stable structure and strong fluorescence, showing potential application in time-resolved fluoroimmunoassay and DNA probe.

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Introduction

Nitrogen-containing heterocyclic compounds like benzimidazole and pyrazole have been attracting extensive attention in pharmaceutics[1, 2] and organic synthesis[3, 4]. The derivatives of benzimidazole and pyrazole have found applications in diverse physiological and pharmacological areas such as anti-virals, anti-cancers, anti-fungals, anti-inflammatories, anti-oxidation, and treatment of hypoglycemia and physiological disorders [5–11]. In the meantime, benzimidazole and pyrazole possess excellent photoelectric properties and are widely used in photoelectric functional materials[12–15] and display device like organic light-emitting diode (OLED) [16, 17].

Usually, two traditional methods can be used to synthesize benzimidazoles and their derivatives[18, 19]. One is the coupling of phenylenediamines with carboxylic acids or their derivatives, which often needs harsh dehydrating condition. The other is a two-step procedure involving the oxidative cyclo-dehydrogenation of aniline Schiff base which is often generated in situ from the condensation of phenylenediamine and aldehyde. 2.3-dichloro-5,6-dicyanobenzoquinone (DDQ)[20, 21], MnO_2[22], $Pb(OAc)_4$[23], $Na_2S_2O_5$[24] and so on are the commonly used oxidants for the two-step process, but they bring about potential hazards and environmentally problematic by-products. To overcome those drawbacks, some researchers have made efforts to establish modified synthetic routes to synthesizing benzimidazoles and their derivatives[25–28]. Unfortunately, the modified synthetic methods still have disadvantages such as

often requiretadious work-up procedures and purifications or poor selectivity.

To our pleasure and surprise, when we intended to prepare a series of bis-Schiff base from *o*-phenylenediamine and 1-arylpyrazole-4-carbaldehyde, we obtained benzimidazole compounds containing pyrazole group by accident. Being advantageous over previous methods, the present procedure can be used to synthesize benzimidazole compounds in excellent yield under mild conditions and without use of any catalysts or promoting and dehydrating reagents. In this article we report the simple procedure for synthesizing benzimidazole compounds containing pyrazole group as well as characterization of their structure and evaluation of their fluorescent properties. The ground-state (S_0) equilibrium geometries and vibrational frequencies of the five compounds (determined by Becke's three parameter functional and the Lee-Yang-Parr functional method, B3LYP in short) [29, 30], their first excited-state (S_1) geometry (fully optimized based on the 6–31G (*d*, *p*) basis set of TD-B3LYP method), and their spectroscopic properties in relation to absorption and emission obtained based on cc-pVTZ basis set of TD- B3LYP method are also reported.

Experimental

General Procedure

Mass spectra were determined on an Agilent 1100LC-MS mass spectrometer. Nuclear magnetic resonance (^{1}H NMR) spectra were recorded on an INOVA-400 spectrometer in $CDCl_3$ or dimethyl sulphoxide (DMSO) in the presence of tetramethylsilane (TMS) as an internal standard. Elemental analysis was conducted with a PE2400 elemental analysis apparatus. The fluorescent properties of the products were evaluated using a Hitachi F-7000 apparatus (light source: Xe arc lamp; room temperature). Ultraviolet–visible light (UV–vis) absorption spectra of the products at room temperature were recorded using a Hitachi U-4100 apparatus. The equilibrium geometries and vibrational frequencies of the five compounds in their ground-states (S_0) were determined based on the 6–31G (*d*, *p*) basis set of B3LYP method. The first excited-state (S_1) structure of the five compounds was fully optimized also based on 6–31G (*d, p*) basis set of TD-B3LYP method. The spectroscopic properties of the five compounds in relation to their absorption and emission were investigated based on cc-pVTZ basis set of TD-B3LYP method. All calculations were implemented with Gaussian 09 program packages.

All chemicals and solvents are of commercial reagent grade and used without further purification. 1-phenylpyrazole-4-carbaldehydes were prepared according to published procedure [31, 32]. Known structures of synthesized products were verified by comparing their data with those reported in the literature.

1-phenylpyrazole-4-carbaldehyde: white solid, yield 57%. ^{1}H NMR ($CDCl_3$) δ: 2.41 (s, 3H. CH_3), 7.29(d, 2H, *J*=8 Hz, Ar-H), 7.59 (d, 2H, *J*=8.4 Hz, Ar-H), 8.15 (s, 1H, pyrazole-H), 8.40 (s, 1H, pyrazole-H), 9.95(s, 1H, CHO).

1-(*p*-tolyl)-pyrazole-4-carbaldehyde: pale-yellow solid, yield 57%. ^{1}H NMR ($CDCl_3$) δ: 2.41 (s, 3H, CH_3), 7.28–7.30 (d, 2H, *J*=8 Hz, Ar-H), 7.57–7.59 (d, 2H, *J*=8.4 Hz, Ar-H), 8.14 (s, 1H, pyrazole-H), 8.39 (s, 1H, pyrazole-H), 9.95 (s, 1H, CHO).

1-(4-chlorophenyl)-pyrazole-4-carbaldehyde: pale-yellow needle-like solid, yield 64%. ^{1}H NMR ($CDCl_3$) δ: 7.48 (d, 2H, *J*=8.8 Hz, Ar-H), 7.67 (d, 2H, *J*=8.8 Hz, Ar-H), 8.17 (s, 1H, pyrazole-H), 8.41 (s, 1H, pyrazole-H), 9.97 (s, 1H, CHO).

3,5-dimethyl-1-phenyl-pyrazole-4-carbaldehyde: pale-yellow solid, yield 54%. ^{1}H NMR ($CDCl_3$) δ: 2.53 (s, 3H, CH_3), 2.55 (s, 3H, CH_3), 7.41 (m, lH, Ar-H), 7.45 (m, 2H, Ar-H), 7.50 (m, 2H, Ar-H), 10.03 (s, lH, CHO).

5-chloro-3-methyl-1-phenylpyrazole-4-carbaldehyde: pale-yellow needle-like solid, yield 63%. ^{1}H NMR ($CDCl_3$) δ: 2.37 (s, 3H, CH_3), 7.28 (d, lH, *J*=7.2 Hz, Ar-H), 7.44 (t, 2H, *J*=7.4 Hz, Ar-H), 7.89 (d, 2H, *J*=7.6 Hz, Ar-H), 9.52 (s, lH, CHO).

General Procedure for Preparing Benzimidazoles

A certain amount of 1-phenylpyrazole-4-carbaldehydes (2 mmol) was dissolved in C_2H_5OH (EtOH, 20 mL), followed by dropwise addition of EtOH solution containing *o*-phenylenediamine (0.22 g, 2 mmol). Resultant mixture was refluxed in a water bath for 4 h before rotary evaporating to remove solvent and cooling to room temperature. As-separated crystalline precipitates were collected by filtration and recrystallized with EtOH.

2-(1-phenylpyrazol-4-yl)-benzimidazole (**1**): pale-yellow solid, yield 87%. APCI-MS (m/z) Calcd (M^+) 261.3, found: 261.1. ^{1}H NMR (DMSO-d_6) δ: 7.19 (m, 2H, Ar-H), 7.39 (t, 1H, *J*=7.4 Hz, Ar-H), 7.57 (t, 4H, *J*=7.6 Hz, Ar-H), 7.92 (d, 2H, *J*=8 Hz, Ar-H), 8.38 (s, 1H, pyrazole-H), 9.13 (s, 1H, pyrazole-H), 12.74 (s, 1H, NH). Anal. Calcd for $C_{16}H_{12}N_4$: C, 73.83; H, 4.65; N, 21.52. Found: C, 73.84; H, 4.65; N, 21.51.

2-(1-(*p*-tolyl)pyrazol-4-yl)-benzimidazole (**2**): pale-yellow solid, yield 91%. APCI-MS (m/z) Calcd (M^+) 275.3, found: 275.1. ^{1}H NMR (DMSO-d_6) δ: 2.37 (s, 3H, CH_3), 7.17–7.20 (m, 2H, Ar-H), 7.35 (d, 2H, *J*=8.4 Hz, Ar-H), 7.57 (m, 2H, Ar-H), 7.79 (d, 2H, *J*=8.4 Hz, Ar-H), 7.92 (d, 2H, *J*=8 Hz, Ar-H), 8.34 (s, 1H, pyrazole-H), 9.06 (s, 1H, pyrazole-H), 12.72 (s, 1H, NH). Anal. Calcd for $C_{17}H_{14}N_4$: C, 74.43; H, 5.14; N, 20.42. Found: C, 74.47; H, 5.13; N, 20.40.

2-(1-(*p*-chlorophenyl)pyrazol-4-yl)-benzimidazole (**3**): yellowish brown solid, yield: 89%. APCI-MS (m/z) Calcd (M^+) 295.7, found: 295.1. ^{1}H NMR (DMSO-d_6) δ: 7.20 (m, 2H, Ar-H), 7.57 (dd, 2H, J=3.2, 3.2 Hz, Ar-H), 7.62 (d, 2H, J=8.8 Hz, Ar-H), 7.96 (d, 2H, J=8.8 Hz, Ar-H), 8.40 (s, 1H, pyrazole-H), 9.16 (s, 1H, pyrazole-H), 12.72 (s, 1H, NH). Anal. Calcd for $C_{16}H_{11}N_4Cl$: C, 65.20; H, 3.76; N, 19.01. Found: C, 65.24; H, 3.78; N, 18.95.

2-(3,5-dimethyl-1-phenylpyrazol-4-yl)-benzimidazole (**4**): white solid, yield 85%. APCI-MS (m/z) Calcd (M^+) 289.4, found: 289.1. ^{1}H NMR (DMSO-d_6) δ: 2.50 (s, 3H, CH_3), 2.57 (s, 3H, CH_3), 7.17–7.21 (m, 2H, Ar-H), 7.45–7.49 (m, 1H, Ar-H), 7.57 (d, 6H, J=4.4 Hz, Ar-H), 12.13 (s, 1H, NH). Anal. Calcd for $C_{18}H_{16}N_4$: C, 74.98; H, 5.59; N, 19.43. Found: C, 74.94; H, 5.64; N, 19.43.

2-(5-chloro-3-methyl-1-phenylpyrazol-4-yl)-benzimidazole (**5**): pale-yellow solid, yield 86%. APCI-MS (m/z) Calcd (M^+) 309.8, found: 309.1. ^{1}H NMR (DMSO-d_6) δ: 2.57 (s, 3H, CH_3), 7.18 (d, 2H, J=4.8 Hz, Ar-H), 7.45–7.50 (m, 1H, Ar-H), 7.57 (t, 5H, J=7.6 Hz, Ar-H), 7.64 (s, 1H, Ar-H), 12.14 (s, 1H, NH). Anal. Calcd for $C_{17}H_{13}N_4Cl$: C, 66.13; H, 4.24; N, 18.15. Found: C, 66.14; H, 4.25; N, 18.13.

Results and Discussion

Synthesis

The route to synthesizing 2-(1-arylpyrazol-4-yl)-benzimidazoles (**1**–**5**) is outlined in Fig. 1.

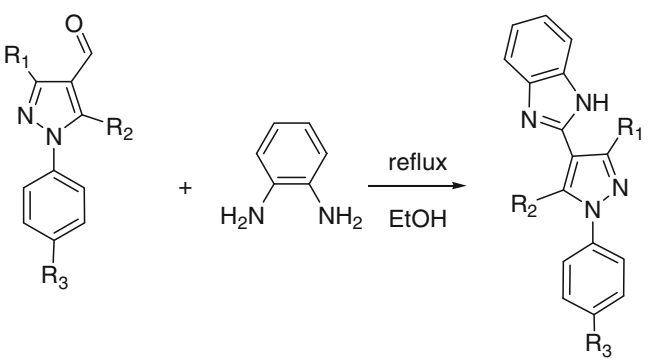
Usually, *o*-phenylenediamine yields a bis-Schiff base in the presence of aldehyde under normal circumstances. To our surprise, when we intended to synthesize a series of bis-Schiff base from 1-phenylpyrazole-4-carbaldehyde (4 mmol) and *o*-phenylenediamine (2 mmol), only mono-Schiff base intermediate was detected by MS during the course of the reaction, and a series of benzimidazoles were obtained as the final products. Even when reactant molar ratio was changed, a series of 2-(1-phenylpyrazol-4-yl)-benzimidazoles were still obtained in an isolated yield of 56%. This means that the reaction has a high selectivity, and the formation of the mono-Schiff base intermediate is the key step for preparing benzimidazoles, the products of thermodynamic control reaction with a better stability than Schiff base.

By adopting the simple synthetic route, we successfully prepared benzimidazole containing pyrazole group from equal molar amount of *o*-phenylenediamine and 1-phenylpyrazole-4-carbaldehyde under mild conditions. To extend the scope of the method, we had also examined a number of differently substituted 1-arylpyrazole-4-carbaldehydes. We were pleased to find that heteroaryl aldehydes bearing electron-donating and electron-withdrawing substituents gave desired benzimidazoles in excellent yields, and the substitutional groups in the pyrazole group had little impact on the formation of benzimidazoles. Besides, no 1,2-disubstituted benzimidazoles were separated at the end of the reaction, conforming to the finding that no bis-Schiff base intermediate was detected by MS during the course of the reaction.

Crystal Structure Description of the Products with a Bruker APEX-II CCD Detector

Suitable single crystal of the synthesized compounds with a dimension of 0.37 mm×0.26 mm×0.23 mm was mounted on a Bruker APEX-II CCD detector to identify the crystal structure (graphite monochromated Mo-$K\alpha$ radiation, λ= 0.71073 Å; 293(2) K; in a range of 1.81–25.50°). The crystal structure was solved by direct methods and refined using full-matrix least-square calculations in relation to anisotropic thermal parameters for all non-hydrogen atoms. All calculations were performed by using the SHELXTL-97 software package [33]. A summary of representative crystallographic information and selected bond lengths and angles are given in Tables 1 and 2.

The structure of the synthesized compounds is schematically shown in Fig. 2. One molecule of ethanol exists in the structure; and the bond distances and bond angles of the compound are within normal ranges reported in references [34–36]. The centroid to centroid distance between adjacent



ligand	R_1	R_2	R_3
1	H	H	H
2	H	H	CH_3
3	H	H	Cl
4	CH_3	CH_3	H
5	CH_3	Cl	H

Fig. 1 Route to synthesizing 2-(1-arylpyrazol-4-yl)-benzimidazoles

Table 1 Summary of crystallographic data for benzimidazole 1

Item	Data
Empirical formula	$C_{18}H_{17}N_4O$
Formula weight	305.360
Temperature/K	293(2)
Wavelength/Å	0.71073
Crystal system	orthorhombic
space group	P2(1)2(1)2(1)
a/Å	7.6078(8)
b/Å	14.2029(15)
c/Å	15.0102(15)
α/(°)	90.00
β/(°)	90.00
γ/(°)	90.00
Z	4
Density (calculated)/g·cm^{-3}	2.101
F(000)	644
Crystal size/mm^3	0.37×0.26×0.23
θ range for data collection/°	2.87 to 23.64
Limiting indices	$-8 \le h \le 9$, $-16 \le k \le 16$, $-15 \le l \le 17$
Reflections collected/unique	10350/2845 [*R*(int) = 0.0213]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2845/2/211
Goodness-of-fit on F^2	1.064
Volume/Å^3	1621.89
R_1 indices [$I > 2\sigma(I)$]	R_1 = 0.0471
wR_2 indices (all data)	wR_2 = 0.1400
Largest diff. peak and hole/(e·Å^{-3})	0.30 and −0.26

parallel aryl rings is 7.6078 Å, which indicates that no π-π stacking occurs in the framework of the title compounds. The three dimensional (3D) framework of the compounds is generated and stabilized through hydrogen bonds, as shown in Fig. 3; and corresponding data are listed in Table 2.

UV–Vis Spectra

Figure 4 shows the UV–vis spectra of benzimidazoles **1**–**5** in DMF. Within the tested wavelength range of 200–800 nm, they all had a remarkable absorption peak of π-π* transition and n-π* transition at 270–340 nm. Besides, the λ_{max} of **3** shows a bathochromic shift (2 nm) as compared to that of **1**, so does the λ_{max} of **5** as compared to that of **4**. The reason lies in that the introduction of the auxochrome group, Cl atom, enhances the operation scope of electrons, leading to shift of the absorption peaks towards long wavelength. However, compounds **1** and **2** have the same λ_{max}, which implies that the hyperconjugation effect of the electron donor group, methyl, is faint.

Fluorescent Spectra

The fluorescent spectra of five benzimidazole compounds (**1**–**5**) measured at room temperature are shown in Fig. 5; and corresponding data are listed in Table 3. In terms of the chemical structure, organic fluorescent compounds generally contain an aromatic ring, fused aromatic rings, or other conjugated ring systems along with plane rigid groups such as C = N, N = N in benzimidazoles [37, 38]. Besides, compound **1** has a good coplanarity, as evidenced by relevant crystal structure, so it possesses strong fluorescence and shows the maximum emission peak at 347.8 nm under excitation at 305 nm. Compounds **2** and **3** show the maximum emission peaks at 348.2 nm and 352.0 nm under the same condition. Moreover, compound **2** has much stronger fluorescence than **1**, but compound **3** has much weaker fluorescence than **1**, which is attributed to the introduction of the electron donor group and electron-withdrawing group, respectively. In addition, when compounds **4** and **5** were excited at 294 nm and 295 nm, they showed the maximum emission peaks at 345.2 nm and 345.8 nm, respectively.

Table 2 Selected bond lengths (Å) and angles (°) for benzimidazole 1

Bond	Length	Bond	Length	
N(1)—C(7)	1.362(3)	C(1)—C(2)	1.388(4)	
N(1)—C(1)	1.384(3)	C(1)—C(6)	1.392(3)	
N(2)—C(7)	1.317(3)	C(2)—C(3)	1.368(4)	
N(2)—C(6)	1.393(3)	C(3)—C(4)	1.391(5)	
N(3)—C(9)	1.325(4)	C(4)—C(5)	1.361(4)	
N(3)—N(4)	1.352(3)	C(5)—C(6)	1.388(4)	
N(4)—C(10)	1.347(3)	C(7)—C(8)	1.457(4)	
N(4)—C(11)	1.426(3)	C(8)—C(9)	1.394(4)	
C(11)—C(12)	1.391(4)	C(12)—C(13)	1.365(4)	
C(13)—C(14)	1.372(4)	C(14)—C(19)	1.374(4)	
C(16)—C(19)	1.380(4)	C(11)—C(16)	1.371(4)	
Bond	angle	Bond	angle	
C(7)—N(1)—C(1)	106.38(19)	C(7)—N(2)—C(6)	104.9(2)	
C(9)—N(3)—N(4)	104.3(2)	C(10)—N(4)—N(3)	111.3(2)	
C(10)—N(4)—C(11)	128.6(2)	N(3)—N(4)—C(11)	120.1(2)	
N(1)—C(1)—C(2)	132.6(2)	N(1)—C(1)—C(6)	105.9(2)	
C(2)—C(1)—C(6)	121.5(3)	C(3)—C(2)—C(1)	117.5(3)	
C(2)—C(3)—C(4)	121.3(3)	C(5)—C(4)—C(3)	121.3(3)	
C(4)—C(5)—C(6)	118.6(3)	C(5)—C(6)—C(1)	119.9(3)	
C(5)—C(4)—N(1)	130.6(2)	C(1)—C(6)—N(2)	109.5(2)	
N(2)—C(7)—N(1)	113.3(2)	N(2)—C(7)—C(8)	124.8(2)	
N(1)—C(7)—C(8)	121.9(2)	C(10)—C(8)—C(9)	103.5(2)	
C(10)—C(8)—C(7)	127.5(2)	C(9)—C(8)—C(7)	129.0(2)	
N(3)—C(9)—C(8)	112.8(2)	N(4)—C(10)—C(8)	108.2(20)	
C(16)—C(11)—C(12)	119.2(3)	C(16)—C(11)—N(4)	120.6(2)	
C(12)—C(11)—N(4)	120.0(2)	C(13)—C(12)—C(11)	119.8(3)	
C(12)—C(13)—C(14)	121.2(3)	C(13)—C(14)—C(19)	119.0(3)	
C(11)—C(16)—C(19)	120.3(3)	C(14)—C(19)—C(16)	120.5(3)	
Hydrogen bonds (Å) and angles (°)				
D-H···A	*d* (D-H)	*d* (H···A)	*d* (D···A)	∠(D-H···A)
O(1)-H(1)···N(2)	0.8200	1.9700	2.788(3)	172.60

Thus it can be concluded that the subsitituents on phenyl group and pyrazolyl group have different impacts on the maximum emission peak and stoke shift of the synthesized compounds.

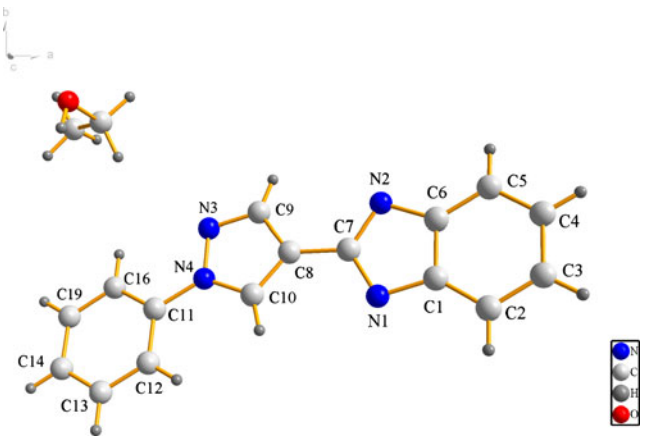


Fig. 2 Structure of the synthesized compounds

Theoretical Study of Electronic Structure and Spectroscopic Properties

Ground State Geometries and Electronic Structure Calculated at the B3LYP Level

Ground-State Geometries and Stabilities The molecular structures of the five compounds are depicted in Fig. 6, and their primary geometric parameters optimized with B3LYP and TD-B3LYP (bond lengths, bond angles, and dihedral angles) are summarized in Table 4. As shown in Fig. 6, the five benzimidazole compounds have the same matrix, i.e., compound **1**. In combination with the data listed in Table 4, it can be seen that their ground-state (S_0) geometric parameters, bond lengths and bond angles, are

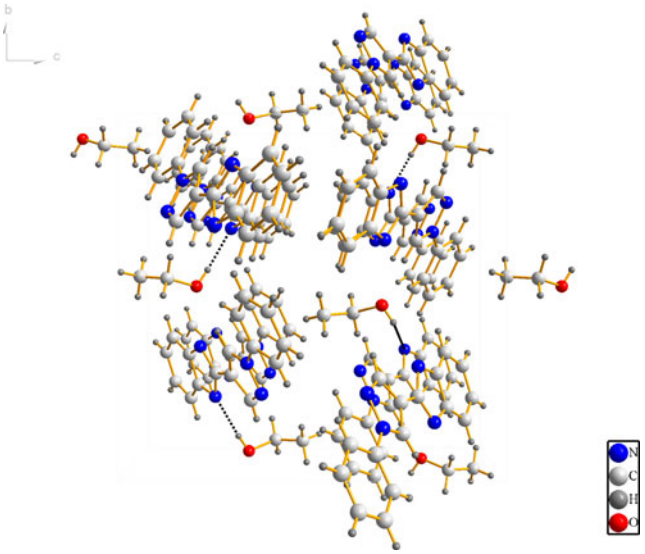


Fig. 3 Packing diagram of the compounds with hydrogen bonds shown in *dashed line*

very similar. In the meantime, compounds **1**, **2** and **3** with dihedral angles of 1.698°, 1.499°, and 2.031° in N(1)-C(7)-C(8)-C(10) as well as 158.0°, 156.5°, and 159.8° in C(10)-N(4)-C(11)-C(16) have better coplanarities than compounds **4** and **5** (4.914° and 13.99° in N(1)-C(7)-C(8)-C(10); 137.8° and 134.7° in C(10)-N(4)-C(11)-C(16)).

The calculated results reveal that all of the complexes have X^1A ground state. By comparing with the data shown in Table 1, we can see that the theoretically calculated structural parameters of **1** are in accordance with the experimental ones. Moreover, bond lengths of N(1)-C(7), N(2)-C(7), N(1)-C(1) and N(2)-C(6) in compound **1** are

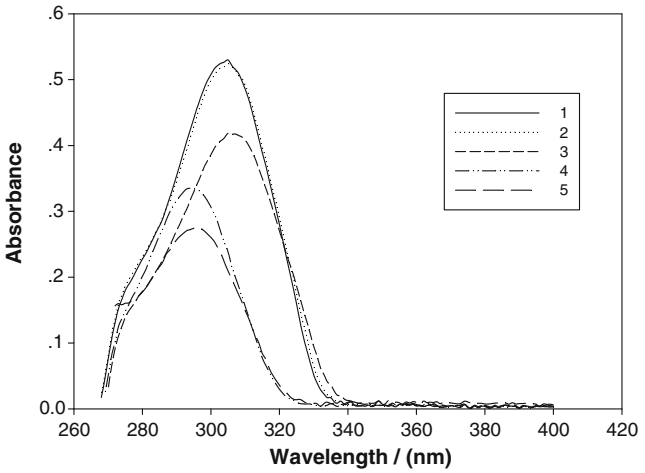


Fig. 4 UV–vis absorption spectra of benzimidazoles 1–5 in DMF solution (1×10^{-5} mol/L)

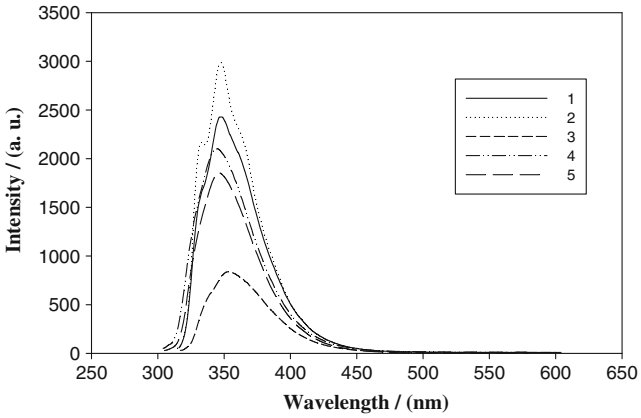


Fig. 5 The emission spectra of benzimidazoles 1–5 in DMF solution (1×10^{-6} mol/L)

1.318(1.317)[a] Å, 1.384(1.362)[a] Å, 1.384(1.393)[a] Å and 1.384(1.384)[a] Å, respectively, shorter than that of conventional N–C single bond (1.47 Å) but longer than that of conventional N = C double bond (1.28 Å). This indicates that the chemical bond linking imino and aromatic ring is partially a double bond in nature, due to π-conjugation involving the participation of N lone electron pair. For the same reason, bond lengths of N(3)-C(9) and N(4)-C(10) in pyrazole ring are 1.326(1.325)[a] Å and 1.360(1.347)[a] Å, respectively; and bond length of N(3)-N(4) (1.361(1.352)[a] Å) is shorter than that of N–N single bond. Furthermore, the bond length of the benzene ring connected with pyrazole N (4)-C(11) is 1.422(1.426)[a] Å, showing weaker double bond component.

In addition, frequency analyses based upon B3LYP/6-31G (*d*, *p*) vibrational calculations reveal that all the five synthesized compounds have stable structures on the potential energy curves, showing no imaginary frequency.

Electronic Structure The plots of the frontier molecular orbitals, the highest-occupied molecular orbital (HOMO) and lowest-unoccupied molecular orbital (LUMO), of compounds **1**–**5** in relation to their B3LYP-optimized geometries are shown in Fig. 7. Compounds **1**–**5** have the

Table 3 Fluorescent data of synthesized compounds

Compounds	$\lambda_{UV.\ max}$/nm	$\lambda_{FL.\ max}$/nm	Stokes shift/nm
1	305	347.8	42.8
2	305	348.2	43.2
3	307	352.0	45.0
4	294	345.2	51.2
5	295	345.8	50.8

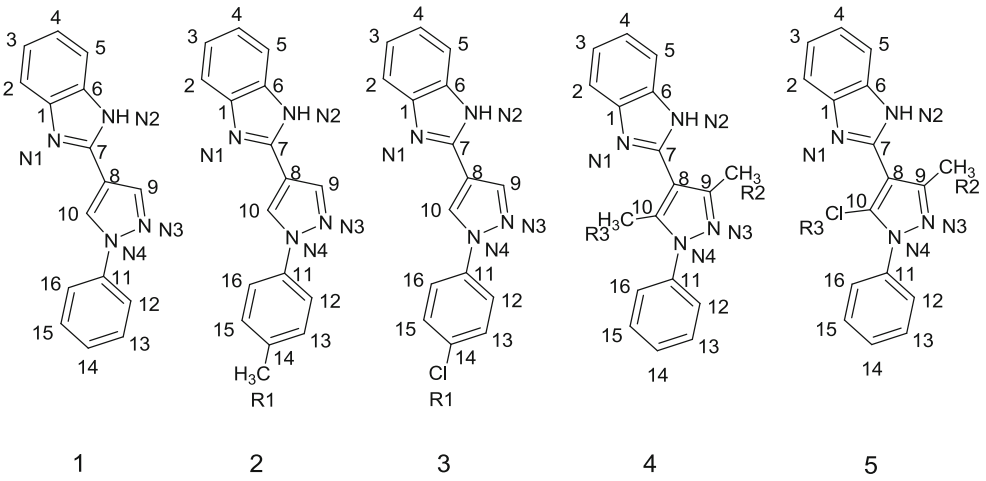


Fig. 6 Molecular structure of compounds **1**, **2**, **3**, **4** and **5**

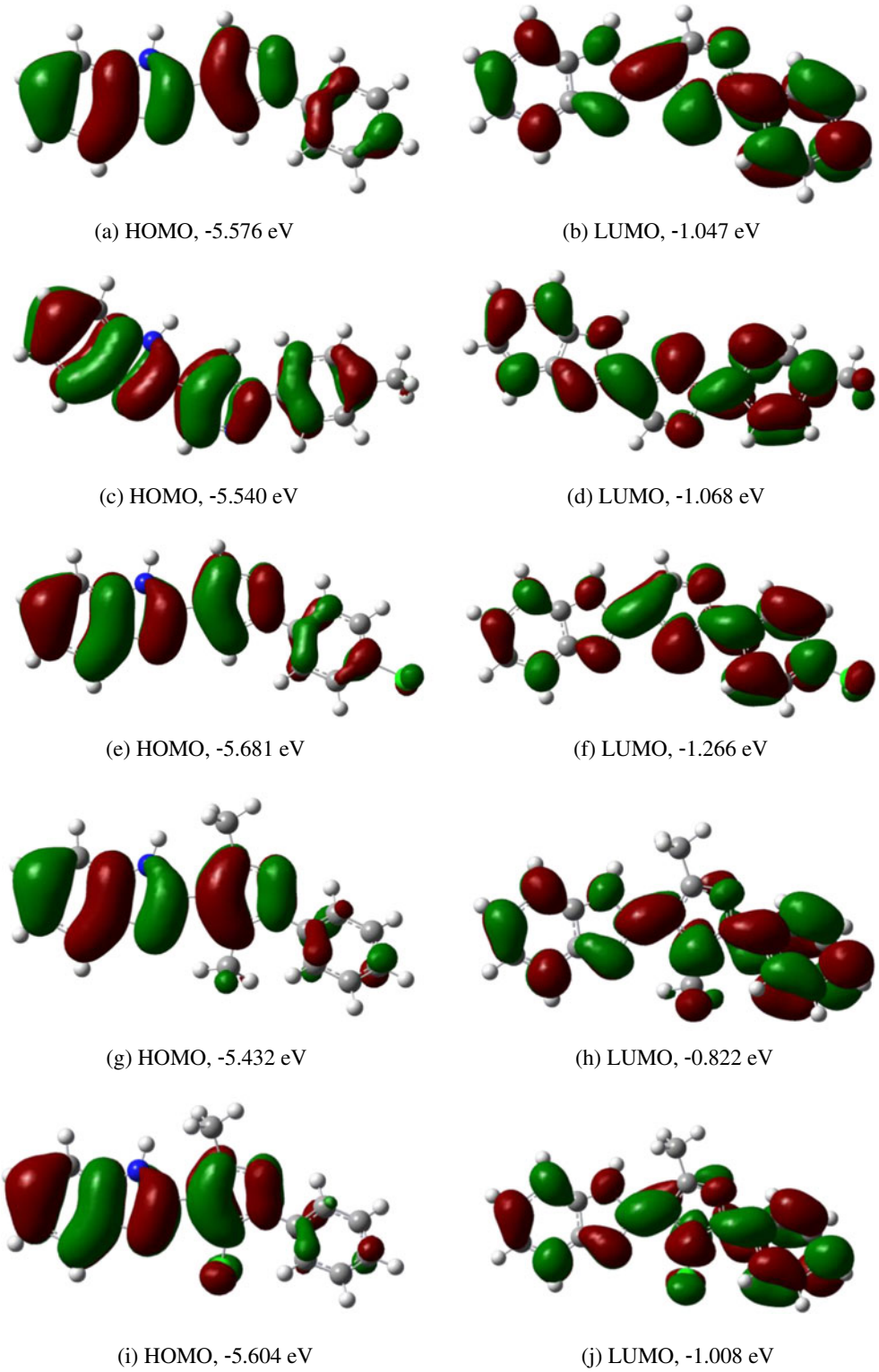
same electron density of LUMO. In the meantime, the electron density of HOMO in compound **1** is distributed over the whole molecules and has some delocalization along N(1)-C(7)-N(2), C(9)-C(8)-C(10), N(3)-N(4) and C(12)-C(11)-C(16), which are also observed in compounds **2** and **3**. However, in compounds **4** and **5**, the delocalization is distributed over C(11)-C(16) but not C(12)-C(11)-C(16).

The energies of frontier molecular orbitals of compound **1** are E_{HOMO} = −5.576 eV and E_{LUMO} = −1.047 eV, respectively, corresponding to ε-value of 4.529 eV which is a little bit larger than that of **2** and **3** (4.427 eV and 4.415 eV) but a little bit smaller than that of **4** and **5** (4.610 eV and 4.596 eV). For compounds **1**–**5**, conjugated π-electron systems, the smaller the energy gap *e*-value is,

Table 4 B3LYP-optimized primary geometric parameters of ground-states (S_0) of 1–5 and first excited state (S_1) of 1–4: bond lengths (in Å), bond angles and dihedral angles (in °)

Atom numbers	Primary geometric parameters									
	1		2		3		4		5	
	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
N(1)-C(7)	1.318(1.317)[a]	1.373	1.318	1.359	1.317	1.371	1.322	1.333	1.318	
N(2)-C(7)	1.384(1.362)[a]	1.384	1.385	1.397	1.384	1.382	1.387	1.396	1.388	
N(1)-C(1)	1.384(1.393)[a]	1.345	1.384	1.350	1.384	1.345	1.384	1.381	1.382	
N(2)-C(6)	1.384(1.384)[a]	1.383	1.383	1.376	1.383	1.383	1.383	1.379	1.382	
N(3)-C(9)	1.326(1.325)[a]	1.318	1.324	1.316	1.325	1.320	1.325	1.338	1.327	
N(4)-C(10)	1.360(1.347)[a]	1.360	1.364	1.373	1.361	1.356	1.369	1.363	1.365	
N(3)-N(4)	1.361(1.352)[a]	1.409	1.362	1.406	1.362	1.407	1.366	1.371	1.363	
N(4)-C(11)	1.422(1.426)[a]	1.393	1.420	1.384	1.419	1.394	1.424	1.426	1.427	
C(14)-R1			1.510	1.505	1.756	1.761				
C(9)-R2							1.499	1.500	1.499	
C(10)-R3							1.494	1.493	1.718	
C(1)-N(1)-C(7)	105.2(104.9)[a]	105.5	105.3	105.5	105.2	105.5	105.6	105.8	105.4	
C(6)-N(2)-C(7)	107.2(106.4)[a]	108.0	107.3	107.7	107.2	107.9	107.6	108.0	107.3	
N(1)-C(7)-N(2)	112.6(113.3)[a]	111.0	112.5	111.2	112.6	111.1	111.9	111.2	112.3	
C(10)-N(4)-N(3)	112.0(111.3)[a]	111.5	111.8	112.0	112.0	111.6	112.5	112.3	110.9	
N(4)-N(3)-C(9)	104.8(104.3)[a]	105.1	105.1	104.8	104.8	105.1	105.5	105.8	106.0	
N(1)-C(7)-C(8)-C(10)	1.698	0.019	1.499	0.679	2.031	0.020	4.914	4.940	13.99	
C(10)-N(4)-C(11)-C(16)	158.0	179.9	156.5	172.1	159.8	179.9	137.8	137.8	134.7	

[a] Experimental values



(a) HOMO, -5.576 eV (b) LUMO, -1.047 eV

(c) HOMO, -5.540 eV (d) LUMO, -1.068 eV

(e) HOMO, -5.681 eV (f) LUMO, -1.266 eV

(g) HOMO, -5.432 eV (h) LUMO, -0.822 eV

(i) HOMO, -5.604 eV (j) LUMO, -1.008 eV

Fig. 7 Schematic diagrams showing the frontier molecular orbitals of compounds 1–5: (**a** and **b**) 1; (**c** and **d**) 2; (**e** and **f**) 3; (**g** and **h**) 4; and (**i** and **j**) 5

the easier the delocalized π-electron is to be excited and the longer corresponding strongest absorption wavelength is. Therefore, the strongest absorption wavelength of compound **3** is the longest among the five compounds, as confirmed by relevant theoretical and experimental results (see Table 5).

Table 5 Calculated absorption wavelength of 1–5 as well as the emission wavelength of 1–4 at TD-B3LYP/cc-pVTZ level

Compounds	State	Transition	Absorption		Emission	
			λ/nm	f	λ/nm	f
1	X^1A	$(67a)^2(68a)^2(69a)^0$				
	2^1A	68a→69a	308.69(305)[a]	0.6537	359.02(347.8)[a]	0.6362
	5^1A	68a→71a	264.79	0.1649		
	19^1A	64a→70a	204.17	0.2203		
2	X^1A	$(71a)^2(72a)^2(73a)^0$				
	2^1A	72a→73a	310.65(305) [a]	0.9374	362.63(348.2) [a]	0.9840
	5^1A	72a→75a	265.34	0.1857		
	13^1A	72a→76a	223.89	0.2103		
	20^1A	66a→73a	203.55	0.2884		
3	X^1A	$(75a)^2(76a)^2(77a)^0$				
	2^1A	76a→77a	316.77(307) [a]	0.6601	366.96(352.0) [a]	0.6326
	5^1A	76a→79a	269.43	0.3677		
	13^1A	76a→80a	223.36	0.1916		
	21^1A	70a→77a	205.70	0.1859		
4	X^1A	$(75a)^2(76a)^2(77a)^0$				
	2^1A	76a→77a	301.90(294) [a]	0.6526	352.68(345.2) [a]	0.6524
	4^1A	76a→79a	271.18	0.1707		
	13^1A	76a→80a	223.75	0.3099		
5	X^1A	$(79a)^2(80a)^2(81a)^0$				
	2^1A	80a→81a	301.81(295) [a]	0.6381		
	4^1A	80a→82a	266.34	0.1810		
	13^1A	78a→82a	224.22	0.3562		

TD-B3LYP-Optimized Geometries of S_1 States (except for **5***)*

The geometries of the first excited state S_1 are optimized at TD-B3LYP/6-31G(*d*, *p*) level, and the primary geometrical parameters for compounds **1**–**4** are given in Table 4.

Since the lowest singlet transition of each compound refers to the transition from the HOMO and LUMO orbitals, the relaxation of bond length can be interpreted by analyzing the nodal patterns of the HOMO and LUMO orbitals (see Fig. 6). Taking compound **1** as an example, its HOMO orbitals involve N(1)-C(7) (1.318 Å) and N(3)-N(4) (1.361 Å) bonds, while its LUMO orbitals (1.373 Å and 1.409 Å, respectively) has nodes across these bonds, resulting in an extension of the N(1)-C(7) and N(3)-N(4) bonds (+0.055 Å and +0.048 Å, respectively). In addition, its HOMO has nodes in N(1)-C(1) (1.384 Å) and N(4)-C (11) (1.422 Å) bonds, but its LUMO (1.345 Å and 1.393 Å, respectively) has bonding at these regions. As a result, N (1)-C(1) and N(4)-C(11) bonds are shortened by −0.039 and −0.029 Å, respectively. A similar behavior has also been found for compounds **2**, **3** and **4**. Furthermore, by comparing the dihedral angles of S_0 and S_1 (see Table 4), we can infer that compounds **1**, **2** and **3** in S_1 state have a better coplanarity than in S_0 state; and in particular, compounds **1** and **3** are nearly co-planar. But the coplanarity of compound **4** keeps almost unchanged with varying state from S_1 to S_0.

Absorption Spectra

The absorption wavelengths (λ in nm) and oscillator strengths (f) of compounds **1**–**5** computed based on cc-pVTZ basis set of TD-B3LYP method are listed in Table 5 and shown in Fig. 8 for a direct comparison with relevant experimental results (see Table 3 and Fig. 4). Electron promotion from HOMO to LUMO gives rise to the most intense absorption in the UV region for every compound (see Table 5). By comparing with the experimental values in DMF solution, we can see that the theoretical absorption spectra values well correspond to the experimental ones.

In terms of the theoretical absorption spectra, all these observations agree well with relevant experimental results. As shown in Fig. 4, the UV–vis absorption spectra of benzimidazoles **1**–**5** in DMF solution, all emerging as single peaks, are located within 260–400 nm. However, as illustrated in Table 5 and Fig. 8, the theoretical calculations indicate that they have absorptions

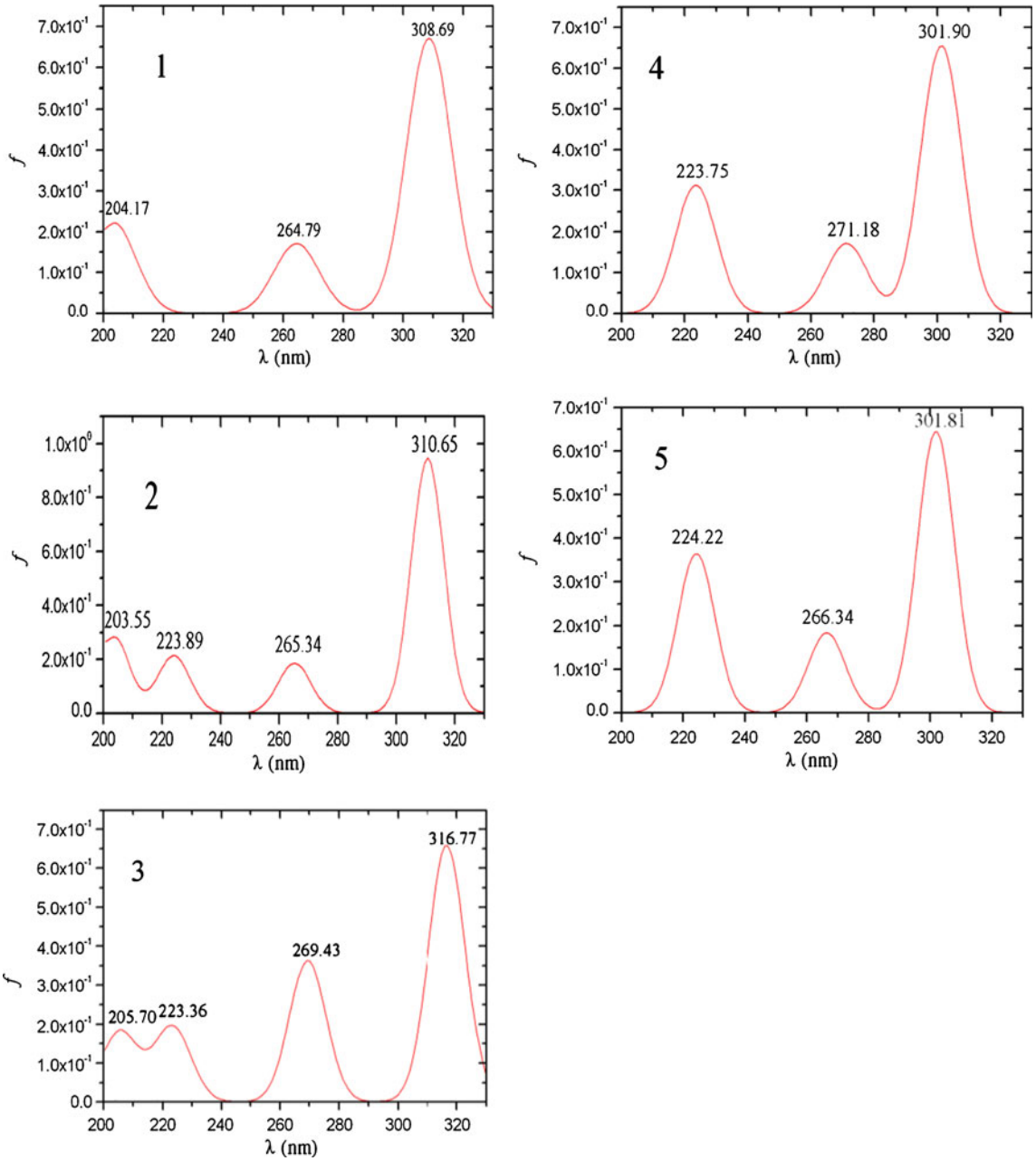


Fig. 8 Theoretical absorption spectra of 1–5

below 260 nm. For example, compound **1** has an X^1A singlet ground-state with an electronic configuration of $(67a)^2(68a)^2(69a)^0$ (see Table 2) and 2^1A second excited state derived from HOMO 68a to LUMO 69a orbitals; the absorption wavelength 308.69 nm corresponds to the largest f=0.6537, in good agreement with the experimental value of 305 nm. Nevertheless, with respect to the calculated electron excitations of 68a→71a leading to 5^1A state at 264.79 nm with f=0.1649 and of 64a→70a leading to 19^1A state at 204.17 nm with f=0.2203, no absorption was observed in the experiment.

Emission Spectra

The emission wavelengths (λ in nm) and oscillator strengths (f) of compounds **1**–**4** computed using the same TD-B3LYP method with the cc-pVTZ basis set, under the optimized geometries of S_1 state, are summarized in Table 5, where the experimental results at room temperature are also presented for a comparison. As it can be seen in Table 5, the calculated emission wavelengths of compounds **1**–**4** are 359.02 nm, 362.63 nm, 366.96 nm and 352.68 nm, respectively, in good agreement with corresponding experimental data of

347.8 nm, 348.2 nm, 352.0 nm and 345.2 nm. Besides, the emission spectra show noticeable red-shift as compared with corresponding absorption spectra, possibly due to relaxation of the excited state.

The B3LYP calculation shows that all the synthesized benzimidazole compounds (**1**–**5**) have stable S_0 and S_1 geometric configurations (excluding **5**) and C_S symmetry. Besides, compounds **1**, **2** and **3** have better coplanarities than **4** and **5** in S_0 state. In terms of the B3LYP-optimized geometries, the plots of the frontier molecular orbitals of compounds **1**–**5**, all being conjugated delocalized π-electron systems, have a sequence of $\varepsilon_3 < \varepsilon_2 < \varepsilon_1 < \varepsilon_5 \approx \varepsilon_4$, which implies that their UV–vis absorption spectra have a sequence of $\lambda_3 > \lambda_2 > \lambda_1 > \lambda_5 \approx \lambda_4$, as confirmed by relevant experimental observation and theoretical computation.

Summary

An efficient and facile method has been established for preparing 2-(1-arylpyrazol- 4-yl)-benzimidazoles. The method is dominated by simple procedure, mild condition, easy purification, and high efficiency and does not need any commercial oxidants/additives. Spectroscopic investigation indicates that the fluorescence spectra of the five synthesized compounds are closely related to their molecular structure. The data of quantum chemistry calculation of benzimidazole compounds correspond to the experimental values very well. Five benzimidazole compounds (**1**–**5**) have stable structure and strong fluorescence, showing potential applications in time-resolved fluoroimmunoassay and DNA probe.

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Supplementary material

The X-ray crystallographic file No. 769532 for compound **1**, in CIF format, is provided by the Cambridge Crystallographic Data Centre (CCDC). Copies of the file can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).