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Synthesis, crystal structures and photoluminescence of 7-(*N*,*N*′-diethylamino)-3-phenylcoumarin derivatives

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ABSTRACT

Two new coumarin derivatives, 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin and 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin, were synthesized successfully. Their structures were verified by single crystal X-ray crystallography. The UV–vis absorption and fluorescence of the compounds were discussed. The compounds exhibit strong blue emission under ultraviolet light excitation. The molecular structures, the lowest energy transitions and the UV–vis spectra of 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin and 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin have been studied with density functional theory (DFT) and time-dependent density functional theory (TD-DFT) at B3LYP/6-31G(d) level.

1. Introduction

Coumarin and its derivatives exist widely in plant, and have been broadly studied due to their applications in biological, chemical and physical fields. For example, they have wonderful biological and medical activity [1–3], such as antitumor and anticoagulant effect [4]. Furthermore, this series of compounds has prominent optical properties, such as an extended spectral range, large Stokes shifts, high quantum yields, superior photostability and good solubility in common solvents [5–9]. As a result, the coumarin derivatives are widely used as laser dyes [10,11], ionophores, colorants, non-linear optical chromophores [12], fluorescent probes [13] and fluorescent whiteners [14]. Since Tang et al. [15] first used 3-(2-benzothiazolyl)-7-diethylaminocoumarin (coumarin 6) as an electroluminescent (EL) material successfully, coumarin dyes have attracted much interest owing to their potential application in organic light-emitting diodes (OLEDs) [6,16–20].

Although several coumarin derivatives which possess good photoluminescence and electroluminescence properties were investigated in our laboratory [5–9], there remain some interests in the molecular design and synthesis of new coumarin derivatives with high quantum yield of fluorescence and greater stability. The present work is a continuation of our search for high efficient emitting fluorescent materials, two new coumarin derivatives, 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin and 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin, were synthesized. They contained electron-releasing moieties (i.e., diethylamino) in 7-positions, but the difference between them is that in 3-position of 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin is phenol moiety, in the same position of 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin is bromophenyl moiety. These moieties could increase the conjugative effect and surely benefit the fluorescence of the compounds. We synthesize them in order to understand the effect of substituents in coumarin skeleton on the photoluminescent properties of coumarin.

2. Experimental

2.1. Materials and methods

4-(*N*,*N*′-Diethylamino)salicylaldehyde from Zhejiang Huadee Dyestuff Chemical Co. Ltd. (China) was recrystallized from ethanol. 4-Hydroxyphenylacetonitrile was purchased from Jinan Haohua Industrial Co. Ltd. (China). 4-Bromophenylacetonitrile was analytical grade reagent from Alfa Aesar China (Tianjin) Co. Ltd. The other solvents were analytical grade reagents.

IR spectra (400–4000 cm^{-1}) were measured on a Shimadzu IRPrestige-21 FT-IR spectrophotometer. ^1H NMR spectra were obtained on Unity Varian-500 MHz. C, H, and N analyses were obtained using an Elemental Vario-EL automatic elemental

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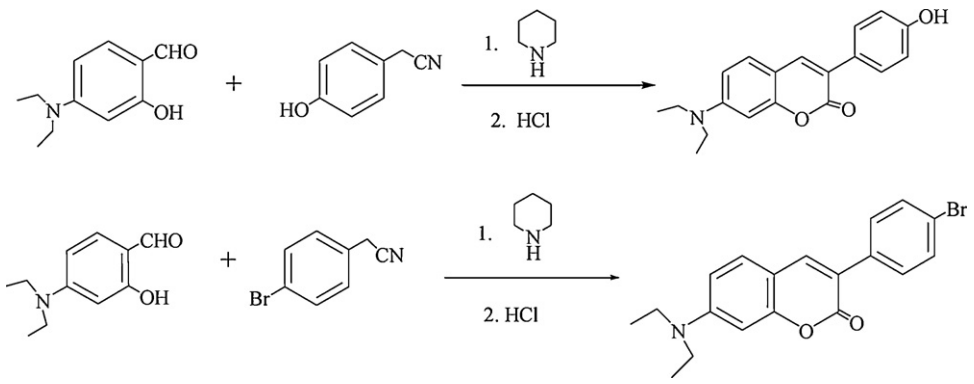

Scheme 1. Synthetic route of 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin and 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin.

analysis instrument. UV–vis absorption and photoluminescent spectra were recorded on a Shimadzu UV-2550 spectrometer and Perkin Elmer LS-55 spectrometer, respectively.

2.2. Synthesis and characterization of 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin and 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin

The synthetic routes were shown in Scheme 1.

7.2 g (37.6 mmol) of 4-(*N*,*N*′-diethylamino)salicylaldehyde and 5.0 g (37.6 mmol) of 4-hydroxyphenylacetonitrile were dissolved in 30 mL of ethanol at room temperature and treated with piperidine (0.5 mL). The reaction mixture was held for 24 h at 80 °C, treated with HCl (50 mL, 7%) and boiled for 8–10 h to hydrolyze the iminocoumarin. After the reaction was finished, the acidic solution was neutralised with aqueous ammonia until the pH was 7. Some of solvent was removed by rotary evaporation and the resulting mixture was poured into 100 mL water and extracted with dichlormethane (3× 60 mL). The organic phase was washed with water (2× 50 mL) and dried over anhydrous $MgSO_4$. After filtering, the filtrate was evaporated to dryness under reduced pressure. The crude was purified by chromatography on silica gel using ethyl acetate/petroleum ether (1:5, v/v) as the eluent to give 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin (6.16 g, 53.4%). m.p. 187–189 °C. IR (KBr pellet, cm^{-1}): 3298 (ν_{O-H}, phenol), 1714 ($\nu_{C=O}$, lactone), 1618 ($\nu_{C=C}$), 1519, 1520, 1355, 1235. ^1H NMR (Actone-D6, δ, ppm): 8.415 (s, 1H, 4-H), 7.839 (s, 1H, –OH), 7.604 (d, J = 7.2 Hz, 2H, Aryl-H), 7.460 (d, J = 8.8 Hz, 1H, Aryl-H), 6.868 (d, J = 7.2 Hz, 2H, Aryl-H), 6.734 (d, J = 8.8 Hz, 1H, Aryl-H), 6.525 (s, 1H, Aryl-H), 3.525 (m, 4H, N-CH_2), 1.219 (t, J = 6.8 Hz, 6H, CH_3). Anal. Calc. for $C_{19}H_{19}NO_3$ (%): C, 73.77; H, 6.19; N, 4.53. Found: C, 74.20; H, 6.30; N, 4.23.

5.0 g (25.9 mmol) of 4-(*N*,*N*′-diethylamino)salicylaldehyde, 5.2 g (26.5 mmol) of 4-bromophenylacetonitrile were placed into a round bottom flask (100 mL) and dissolved in 50 mL of ethanol. 2 mL of piperidine was added into the mixed reaction, and then the mixture was refluxed with stirring for 48 h. After the reaction was complete, 10 mL of aqueous solution of HCl was added into reaction, and then the mixture was refluxed with stirring for 24 h. The resulting solution was evaporated to dryness under reduced pressure. The precipitate was recrystallized from ethyl acetate, and 6.01 g of brown crystal was 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin obtained (yield 63%). m.p.: 159–160 °C. IR (KBr pellet, cm^{-1}): 3421(ν_{N-H}), 1716 ($\nu_{C=O}$), 1128 (ν_{C-O-C}), 719 (ν_{C-Br}). ^1H NMR (500 MHz, $CDCl_3$, δ, ppm): 7.472–7.678 (m, 4H, phenyl-H), 7.261–7.315 (t, 1H, coumarin skeleton), 6.514–6.610 (m, 3H, coumarin skeleton), 3.364–3.450 (m, 4H, CH_2), 1.167–1.236 (m, 6H, CH_3). Anal. Calc. for $C_{19}H_{18}NO_2Br$ (%): C, 61.30; H, 4.87; N, 3.76. Found: C, 61.83; H, 4.60; N, 3.43.

2.3. Crystallography

Suitable single crystal of 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin and 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin were obtained by evaporation of ethyl acetate solution, respectively. The diffraction data were collected with a Bruker Smart Apex CCD area detector using a graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 20 °C. The structures were solved by using the program SHELXL and Fourier difference techniques, and refined by full-matrix least-squares method on F^2. All hydrogen atoms were added theoretically. The crystal and experimental data of 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin and 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin are shown in Table 1. The selected bond lengths and bond angles of the compounds are listed in Tables 2 and 3, respectively.

2.4. Quantum chemical calculations

The structure of 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin and 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin were optimized by semi-empirical density functional theory (DFT) using a B3LYP/6-31G(d) basis set. The structural energies of the compounds were calculated at B3LYP/6-31G(d) levels. The structure optimizations and energy calculations were performed with the GAUSSIAN 98 program.

3. Results and discussion

3.1. X-ray crystal structures

The structure of 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin and 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin were measured by X-ray crystallography. Their crystal structures and packing diagrams are given in Figs. 1–4 , respectively. The crystal data and experimental details are shown in Table 1. The selected bond lengths and bond angles of the compounds are listed in Table 2.

The crystal of 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin belongs to the triclinic space group *P*-1. As shown in Fig. 1, there is an asymmetric unit consisted of two molecules in crystal structure of the compound due to the different space configuration of hydroxy groups in 4′-position of benzene ring, these two molecules are space conformers. In every molecule, the phenol ring is not coplanar with the coumarin ring and the dihedral angle is 38.13°. As shown in Fig. 2, the distance of the coumarin rings between two adjacent molecules along *a*-axis in crystal lattice is about 3.8 Å, which means weak intermolecular π–π stacking interaction between 7-(*N*,*N*′-diethylamino)-3-(4-

Table 1
Crystallographic data for 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin (I) and 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin (II).

Compound	I	II
Empirical formula	$C_{19}H_{19}NO_3$	$C_{19}H_{18}BrNO_2$
Formula weight	309.35	372.25
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	*P*-1	$P2_1/c$
Unit cell dimensions		
a (Å)	10.071(2)	16.2673(19)
b (Å)	11.670(3)	12.5722(15)
c (Å)	13.869(3)	8.2004(10)
α (°)	92.707(4)	90
β (°)	101.863(3)	104.60(3)
γ (°)	97.796(4)	90
Volume (Å^3), *Z*	1575.7(6), 4	1623.0(3), 4
Density (calculated) (g/cm^3)	1.304	1.523
Absorption coefficient (mm^{-1})	0.088	2.542
F (0 0 0)	656	760
Crystal size (mm)	0.45 × 0.28 × 0.21	0.42 × 0.29 × 0.05
θ range for data collected (°)	1.50–25.75	2.07–26.08
Limiting indices	$-12 \le h \le 11$, $-12 \le k \le 14$, $-15 \le l \le 16$	$-19 \le h \le 20$, $-15 \le k \le 15$, $-8 \le l \le 10$
Reflections collected	8698	8888
Independent reflections	5882 (R_{int} = 0.0157)	3211 (R_{int} = 0.0252)
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9821 and 0.9612	0.8728 and 0.4170
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5882/0/421	3211/0/210
Goodness-of-fit on F^2	1.040	1.035
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0626, wR_2 = 0.1682	R_1 = 0.0384, wR_2 = 0.0957
R indices (all data)	R_1 = 0.0835, wR_2 = 0.1894	R_1 = 0.0606, wR_2 = 0.1059
Largest diff. Peak and hole (eÅ^{-3})	0.642 and −0.354	0.590 and −0.295

Table 2
Experimental and calculated structural parameters of 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin (I) and 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin (II).

	I			II	
	Exp.	Calcd.		Exp.	Calcd.
Bond length (Å)			Bond length (Å)		
C(1)–O(1)	1.377(2)	1.3676	Br(1)–C(1)	1.902(3)	1.9130
C(7)–O(2)	1.385(2)	1.3973	C(7)–O(1)	1.205(3)	1.2109
C(7)–O(3)	1.206(2)	1.2108	C(7)–O(2)	1.383(3)	1.3972
C(15)–O(2)	1.382(2)	1.3637	C(11)–O(2)	1.378(3)	1.3633
C(13)–N(1)	1.366(3)	1.3729	C(13)–N(1)	1.374(3)	1.3784
C(16)–N(1)	1.459(3)	1.4634	C(16)–N(1)	1.461(3)	1.4625
C(18)–N(1)	1.468(3)	1.4629	C(18)–N(1)	1.459(3)	1.4630
Bond angles (°)			Bond angles (°)		
C(6)–C(1)–O(1)	121.71(19)	122.797	C(2)–C(1)–Br(1)	120.4(2)	119.486
O(1)–C(1)–C(2)	118.78(19)	117.649	C(6)–C(1)–Br(1)	119.29(19)	119.684
O(3)–C(7)–O(2)	115.63(19)	116.171	O(1)–C(7)–C(8)	127.2(2)	126.959
O(3)–C(7)–C(8)	126.8(2)	126.897	O(1)–C(7)–O(2)	115.01(19)	116.195
O(2)–C(7)–C(8)	117.52(18)	116.932	O(2)–C(7)–C(8)	117.80(19)	116.846
O(2)–C(15)–C(10)	119.67(19)	120.175	C(11)–O(2)–C(7)	122.98(17)	123.719
C(14)–C(15)–O(2)	117.05(19)	117.074	O(2)–C(11)–C(10)	119.7(2)	120.164
C(7)–O(2)–C(15)	122.98(16)	123.677	C(12)–C(11)–O(2)	116.6(2)	117.139
C(13)–N(1)–C(16)	121.1(2)	120.863	N(1)–C(13)–C(12)	121.3(2)	121.293
C(13)–N(1)–C(18)	122.2(2)	121.150	N(1)–C(13)–C(14)	121.4(2)	121.236
N(1)–C(13)–C(14)	121.8(2)	121.378	C(13)–N(1)–C(16)	122.4(2)	122.071
N(1)–C(13)–C(12)	121.3(2)	121.325	C(13)–N(1)–C(18)	121.2(2)	121.703
C(16)–N(1)–C(18)	116.7(2)	117.853	C(18)–N(1)–C(16)	115.5(2)	116.223
N(1)–C(16)–C(17)	113.8(3)	114.972	N(1)–C(16)–C(17)	113.3(2)	113.889
N(1)–C(18)–C(19)	114.4(2)	115.025	N(1)–C(18)–C(19)	113.9(2)	113.920
Hydrogen bonds					
D–H···A	d(D–H)	d(H···A)	d(D···A)		
O(1)–H(1)···O(6)[a]	0.82	2.00	2.790(2)		
O(4)–H(4)···O(1)[b]	0.82	1.93	2.739(3)		

[a] Symmetry transformations used to generate equivalent atoms: $x+1, y+1, z$.
[b] Symmetry transformations used to generate equivalent atoms: $-x+2, -y+1, -z+2$.

Table 3
Absorption spectra data of 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin and 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin.

Compound	Transition character	OSC[a]	$\lambda_{max,\,cal.}$ (nm)	$\lambda_{max,\,exp.}$ (nm)[b]	Transition feature
1	HOMO → LUMO	0.7848	356.31	397	$\pi \rightarrow \pi^*$
	HOMO → LUMO + 3	0.1526	244.30	268	$\pi \rightarrow \pi^*$
2	HOMO → LUMO	0.9542	372.07	403	$\pi \rightarrow \pi^*$
	HOMO − 2 → LUMO + 1	0.3392	204.06	273	$\pi \rightarrow \pi^*$

[a] Oscillator strength coefficients (*f*).
[b] λ_{max} in dichlormethane solvent.

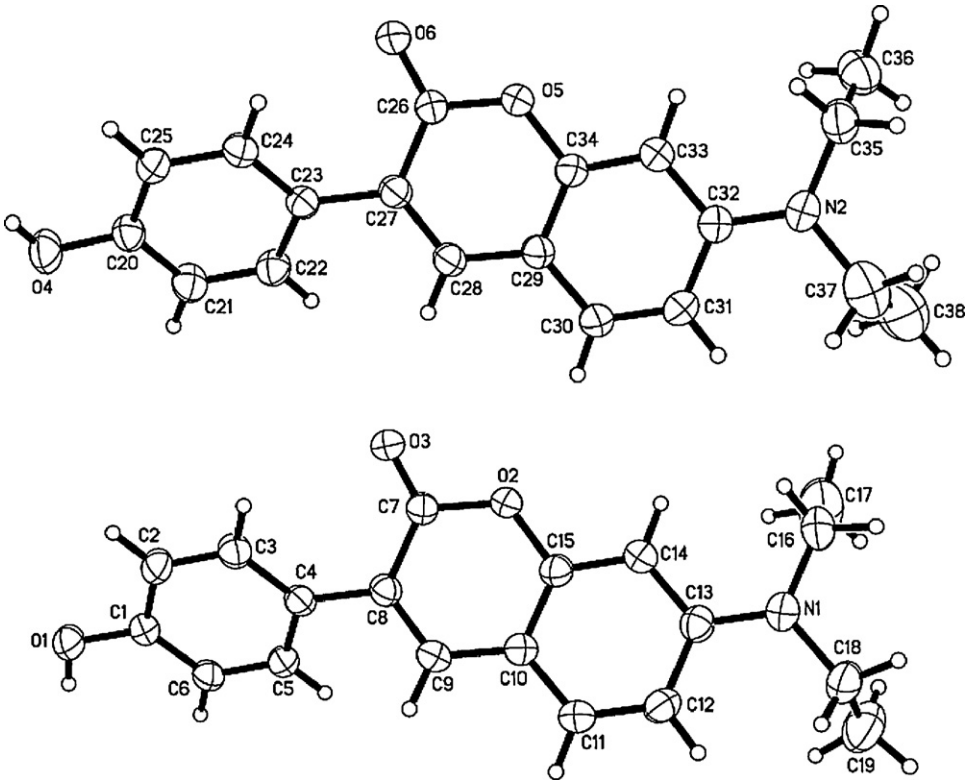

Fig. 1. Crystal structure of 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin.

hydroxyphenyl)-coumarin molecules in crystal lattice. In addition, there are the formation of hydrogen bonds between molecules in the crystal of 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin (Table 2).

Compared with 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin, the crystal of 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin belongs to the monoclinic space group $P2_1/c$ (Fig. 3). In the molecule, the phenol ring is also not coplanar with the coumarin ring and the dihedral angle is 31.28°. As shown in Fig. 4, the distance of the coumarin rings between two adjacent molecules along *c*-axis in crystal lattice is about 3.5 Å, which means strong intermolecular π–π stacking interaction between

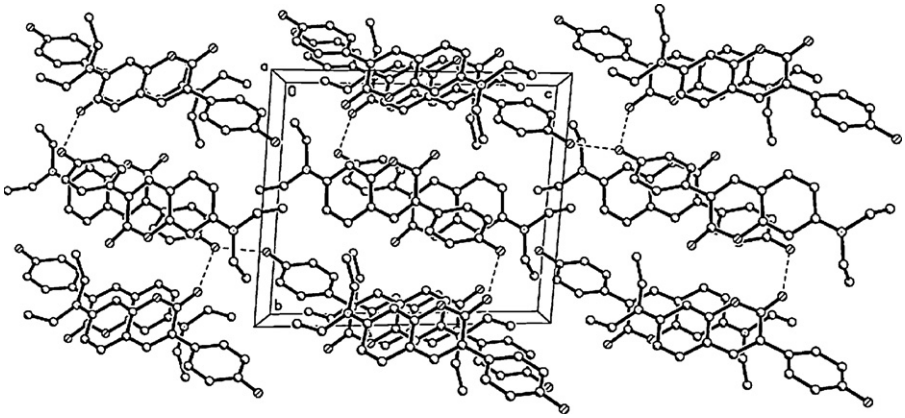

Fig. 2. Packing diagram of 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin along *a*-axis. H atoms are omitted for clarity.

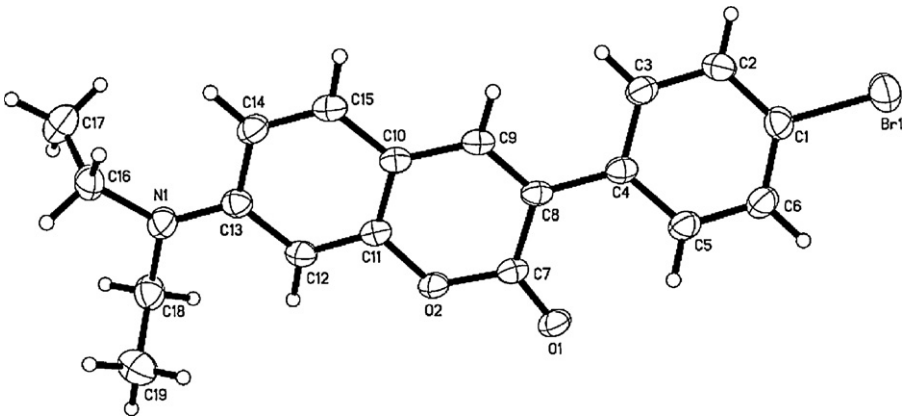

Fig. 3. Crystal structure of 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin.

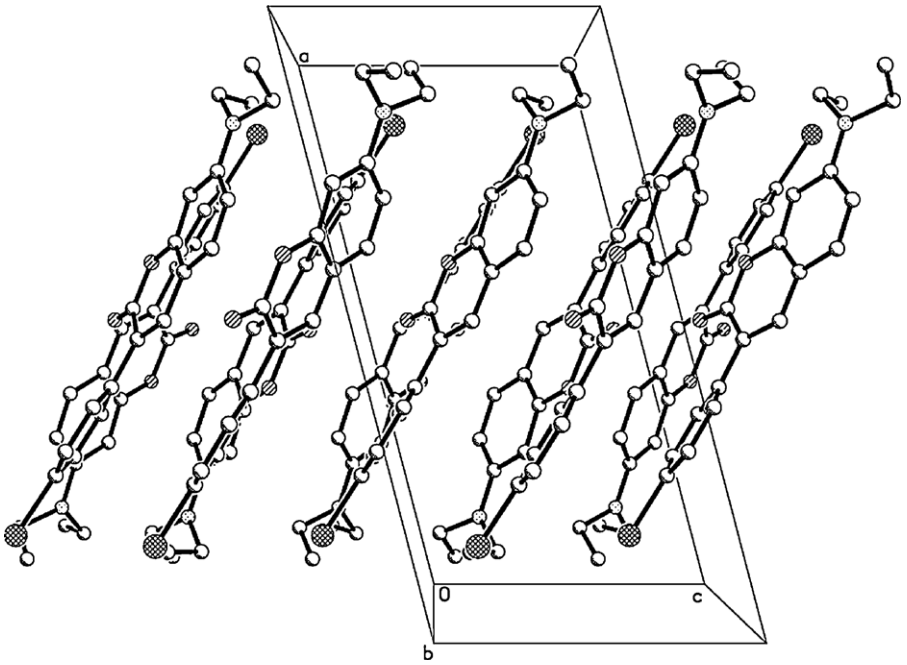

Fig. 4. Packing diagram of 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin along *c*-axis. H atoms are omitted for clarity.

7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin molecules in crystal lattice.

3.2. UV–vis absorption and photoluminescence

UV–vis absorption and photoluminescent spectra of 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin and 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin in diluted dichloromethane solutions are shown in Fig. 5. The absorption spectrum of coumarin was reported to have two peaks at 281 and 320 nm [21], while 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin has absorption peaks at 268 and 398 nm, respectively. The second absorption band at 398 nm presents bathochromic shift as the result of the electron-releasing diethylamino substituent in 7-position and a phenol group in 3-position which can increase conjugative effect of the molecule. The absorption spectrum of 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin is similar to that of 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin, there are two absorption at 273 and 403 nm.

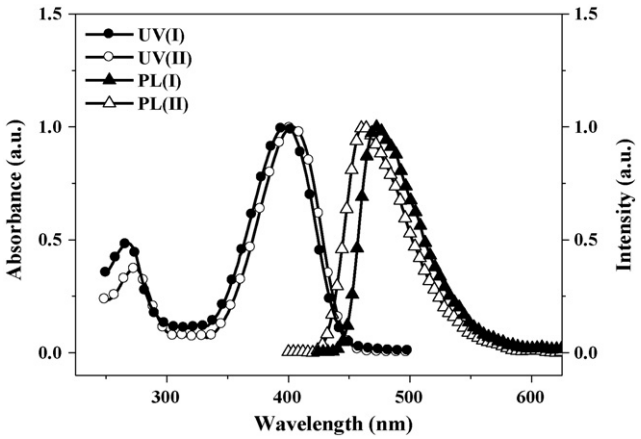

Fig. 5. UV–vis absorption spectrum (5×10^{-5} mol/L) and fluorescence spectrum (1×10^{-5} mol/L) of 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin (I) and 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin (II).

Fig. 5 also shows the photoluminescent spectra of 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin and 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin in dilute dichloromethane solutions. They all exhibit bright blue emission, and the emission peaks of the compounds locate at around 472 and 462 nm, respectively. The emission peak of 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin was red-shifted by 10 nm with respect to that of 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin, it can be generally deduced that the conjugative effect of the phenol derivative is larger than that of the bromophenyl derivative.

3.3. Fluorescence quantum yield of the compounds (Φ_F)

Fluorescence quantum yields of 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin and 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin in chloroform solution were checked with anthracene, respectively. The quantum yield (Φ_F) were calculated according to the relationship [22,23]:

$$\Phi_F = \Phi_F^S \frac{\int_0^\infty I_F(\tilde{\nu})d\tilde{\nu}}{I_F^S(\tilde{\nu})d\tilde{\nu}} \left(\frac{1-10^{-A^S}}{1-10^{-A}}\right)\left(\frac{n}{n^s}\right)^2$$

where Φ_F^S is the quantum yield of anthracene as standard, which was assumed to be 0.25 for all environments [23]. The integral $\int_0^\infty I_F(\tilde{\nu})d\tilde{\nu}$ and $\int_0^\infty I_F^S(\tilde{\nu})d\tilde{\nu}$ are the areas under the emission curves of the investigated and standard compound, respectively. A and A^S are the absorbances at the wavelength of excitation, n and n^S are the refractive indices for the investigated and standard, respectively. In the research, the Φ_F of 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin and 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin are 0.49 and 0.52, respectively. Fluorescence quantum yields of coumarin 6 in acetonitrile is 0.63 [24]. Fluorescence quantum yields of 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin and 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin are slightly lower than that of coumarin 6.

3.4. Quantum chemical calculations

B3LYP/6-31G(d) optimized structure of 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin and 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin are close to their X-ray crystal structures, B3LYP/6-31G(d) optimized geometrical data of them are in good agreement with the X-ray crystallographic data as listed in Table 2, the average discrepancy of the selected bond lengths between theoretical and experimental data is less than ±0.02 Å, and the average discrepancy of the selected bond angles is less than ±1.1°.

The orbital energy levels of HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) of 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin and 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin were deduced using the DFT method as shown in Figs. 6 and 7, respectively. It can be seen that E_{HOMO} and E_{LUMO} values of 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin are −5.011 and −1.278 eV, respectively. The energy gap between HOMO and LUMO is about 3.733. For 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin, the HOMO level of is −5.251 eV and the LUMO level is −1.625, the energy gap between HOMO and LUMO is about 3.626.

The UV–vis absorption spectra of 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin and 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin were also calculated by the time-dependent density functional theory (TD-DFT) at the same level. The experimental and calculated λ_{max} (nm) for the lower-lying singlet states of the compounds are listed in Table 3. As shown in Table 3, there are some discrepancies between theoretical and experimental data due to several influencing factors, such as solvent effect and intermolecular interaction,

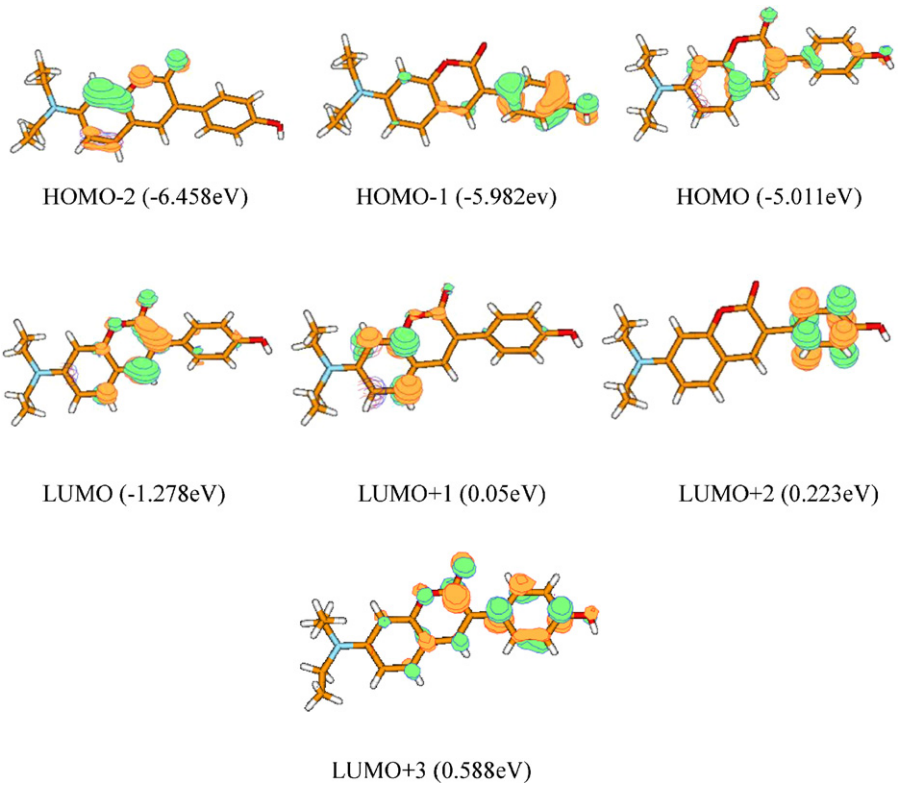

Fig. 6. Frontier molecular orbitals of 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin.

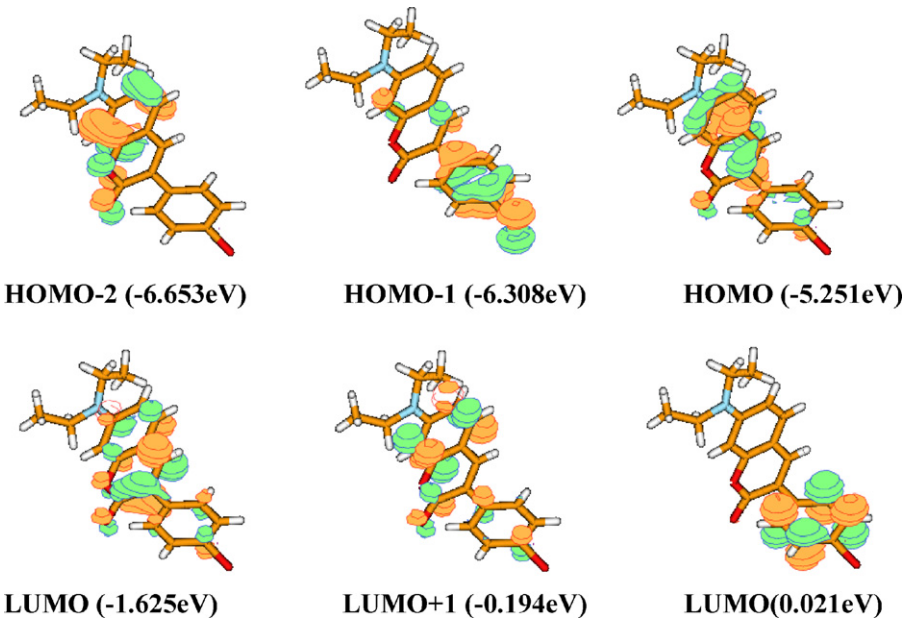

Fig. 7. Frontier molecular orbitals of 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin.

etc. It has been found that the lowest energy absorption at 397 nm for 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin or 403 nm for 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin is an excitation from the HOMO to the LUMO. The transition occurring at 268 nm for 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin is attributed to the electronic $\pi \rightarrow \pi^*$ transition from the HOMO to the LUMO + 3. Similarly, the transition occurring at 273 nm for 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin is attributed to the electronic $\pi \rightarrow \pi^*$ transition from the HOMO − 2 to the LUMO + 1.

4. Conclusions

Two new coumarin derivatives, 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin and 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin, were successfully synthesized and verified by means of IR, ^{1}H NMR and single crystal X-ray crystallography. With the diethylamino moiety, both the peak of absorption and emission were shifted to long wavelength. The HOMO and LUMO levels of the compounds and the lowest energy transition have been studied with density functional theory (DFT) and time-dependent density functional theory (TD-DFT) at B3LYP/6-31G(d) level, showing that the calculation outcomes are in good agreement with experimental data.

Supplementary material

The crystallographic data (excluding structure factors) of 7-(*N*,*N*′-diethylamino)-3-(4-hydroxyphenyl)-coumarin and 7-(*N*,*N*′-diethylamino)-3-(4-bromophenyl)-coumarin have been deposited with the Cambridge Crystallographic Center as supplementary publication number CCDC 733175 and number CCDC 735343, respectively.

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