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Synthesis, characterization, optical properties and theoretical calculations of 6-fluoro coumarin



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Yihui Bai*, Jinyan Du, Xuexiang Weng*

College of Chemistry and Life Sciences, Zhejiang Normal University, Jinhua, Zhejiang 321004, PR China

HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- Calculated IR spectra may reproduce the experimental results.
- Description of the largest vibrational contributed to the normal modes are given.
- Calculated ¹H NMR, ¹³NMR chemical shifts mainly agree with the experimental values.
- TD-DFT can be used to give precise simulation of the absorption and emission spectra.
- Theoretical B3LYP/6-311G(d,p)/ B3LYP/Aug-CC-Pvdz calculations are valid for the structural-similar compounds.

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ABSTRACT

6-Fluoro coumarin is synthesized and characterized by ¹H NMR and ¹³C NMR. The optical properties of the title compound are investigated by UV-vis absorption and fluorescence emission spectra, the results show the title compound can absorb UV-vis light at 319, 269 and 215 nm, moreover it exhibits blue-purple fluorescence emission at 416 nm. Theoretical studies on molecular structure, infrared spectra (IR), nuclear magnetic resonance (¹H NMR, ¹³C NMR) chemical shifts, UV-vis absorption and fluorescence emission of the synthesized compound have been worked out. Most chemical calculations were performed by density functional theory (DFT) method at the B3LYP/6-311G(d,p) level (NMR at B3LYP/Aug-CC-Pvdz level) using Gaussian 09 program. The compared results reveal that the scaled theoretical vibrational frequencies are in good accordance with the observed spectra; computational chemical shifts are consistent with the experimental values in most parts, except for some minor deviations; the UV-vis absorption calculated matches the experimental one very well, and the fluorescence emission spectrum is on good coincidences prove that the computational methods selected can be used to predict these properties of other similar materials where it is difficult to arrive at experimental results. © 2014 Elsevier B.V. All rights reserved.

Introduction

Coumarins, known for their pleasant odor, are widely used in perfumery, foods and beverage manufacture [1,2]. Also coumarin

derivatives can be used as intermediates in the manufacture of agrochemicals and pharmaceuticals with strong anti-bacterium, anti-cancer, anti-HIV activities, etc. [3–8]. Moreover, coumarins are known to be strongly fluorescent with absorption and emission phenomena, and can be used as photo luminescent materials [9,10]. With valuable biological activities, products that contain fluorinated heteroaromatic moieties get high priority research in

^{*} Corresponding authors. Tel.: +86 57982283702 (Y. Bai). E-mail addresses: baiyihui@zjnu.cn (Y. Bai), xuexian@zjnu.cn (X. Weng).

organofluorine chemistry [11,12]. 6-Fluoro coumarin could be very extensive in application with such a typical structure, which urges us to explore its chemical and optical behaviors.

Vibrational spectroscopy especially infrared resonance (IR) and nuclear magnetic resonance (NMR) techniques are the most powerful methods for the identifications of organic structural groups [13,14]. Experimental and theoretical studies on the vibrational spectra and NMR chemical shifts have been proven to be essential tools for interpretations and predictions of the chemical behaviors [14,15]. Moreover, the density functional theory (DFT) methods, combining the hybrid exchange–correlation functional Becke-3-Lee–Yang–Parr (B3LYP) with the standard 6-311G(d,p) basis set, yield good and consistent results in most organic molecular analyses [16–20], and the DFT B3LYP/Aug-CC-Pvdz method gives high accuracy in NMR simulation especially [21–24].

In this paper, 6-fluoro coumarin is synthesized and characterized by IR, ¹H NMR and ¹³C NMR. The optical properties of the title compound are investigated by UV–vis absorption and fluorescence emission spectra. Calculation on nuclear magnetic resonance (¹H NMR, ¹³C NMR) chemical shifts have been performed by using Gaussian 09 program [25] with DFT method at the B3LYP/Aug-CC-Pvdz level. Theoretical studies on molecular structure, IR, UV–vis absorption and fluorescence emission of the synthesized compound have been performed by using Gaussian 09 program with all the calculations performed by DFT at B3LYP/6-311G(d,p) level. By comparing the agreement between experimental and calculated results, we can check whether the selected methods are reliable to forecast the characteristics of other structural-similar compounds.

Synthesis and experimental methods

The general synthetic route is shown in Fig. 1. All the chemicals used were of analytical reagent grade obtained commercially and used as received without further purification, unless otherwise stated.

Synthetic steps [26]

0.01 mol of 4-fluorophenol, 0.01 mol of maleic anhydride and 1 mL of concentrated H₂SO₄ were mixed together. And the mixture was heated to 150 °C for 1.5 h. After cooling to room temperature, the reaction solution was diluted with 50 mL of water and extracted four times with 20 mL of ethyl acetate. The extracted liquid was dried with anhydrous magnesium sulfate, and then filtered and concentrated. The obtained crude product was further eluted and recrystallized from ethyl acetate for several times. Thus, we got 0.52 g 6-fluoro coumarin and the yield was 32%. ¹H NMR (DMSO, 600 MHz) δ : 6.58 (d, *J* = 9.6 Hz, 1H), 7.46(m,1H), 7.50(m,1H), 7.62(m, 1H); 8.04 (d, *J* = 9.6 Hz, 1H); ¹³C NMR (DMSO, 600 MHz) δ : 114.12, 114.29, 117.88, 118.69, 118.75, 119.56, 119.72, 120.13, 120.20, 143.83, 143.85, 150.34, 150.36,157.69, 159.28, 160.21; IR (KBr) υ : 584, 887, 916, 1055, 1274, 1261, 1441, 1485, 1568, 1591, 1724, 3074 cm⁻¹.



Fig. 1. The synthetic route of 6-fluoro coumarin.

Experiments

The FT-IR spectra of the title compounds diluted in the KBr pellets were recorded on a Thermo Electron Nexus 670 spectrophotometer in the range of 400–4000 cm⁻¹. The ¹H NMR measurements of 6-fluoro coumarin were carried out using a Bruker AV600 NMR spectrometer with tetramethylsilane (TMS) as an internal standard in dimethylsulfoxide-d6 (DMSO-d6). The UVvis absorption spectra were carried out on a Perkin Elmer Lambda 950 spectrometer using methanol (MeOH) as solvent, in the concentration of 10^{-5} g/mL. Fluorescence spectrum of 6-fluoro coumarin in methanol was recorded with a Perkin Elmer LS 55 fluorescence spectrometer with a concentration of 10^{-4} g/mL in MeOH, the range for recording fluorescence emission was from 360 to 800 nm, and the excitation wavelength was set at 357 nm. All these spectra were recorded at room temperature.

Computational details

Gaussian 09 software was used in the calculations of geometrical parameters, vibrational frequencies, chemical shifts, UV–vis absorption and fluorescence emission. All the calculations except NMR were performed by using DFT/B3LYP method with 6-311G(d,p) basis set in this study. There are no imaginary frequencies in the results of vibrational analyses, indicating that all the optimized geometry corresponds to the local minima on potential energy hypersurface. The calculated vibrational wavenumbers were scaled with the scale factors [27], yielding good agreements between calculated assignments and experimental data. Detailed assignments of the signals for each spectrum were made by employing the animate vibration function of the Gaussview program [28].

The calculations of potential energy distribution (PED) were done by Gaussian 09 software package with the key word: freq. intmodes. NMR chemical shifts were calculated at the B3LYP/Aug-CC-Pvdz level with the gauge including atomic orbital (GIAO) approach [29–31]. Absolute isotropic magnetic shielding constants were transformed into chemical shifts by referring to one of the standard compounds, TMS [32,33]. The calculated shielding constants of TMS is 31.78 ppm for ¹H NMR spectra and 192.72 for ¹³C NMR spectra.

The UV/vis spectra absorption are determined using the conventional Time-Dependent Density Functional Theory (TD-DFT) procedure on the ground state geometries [34–37]. The emission from the excited to the ground state, corresponding to a fluorescence process is computed with the same procedure but with the optimized excited-state structure. The solvent effect of methanol (MeOH) is incorporated by using the conductive polarized continuum model (CPCM) [38,39], comparing with the results of the calculated absorption and emission spectra of the hydrogen-bonded solute–solvent complex [40,41].

Results and discussion

Optimized structures

The optimized structural parameters of 6-fluoro coumarin are summarized in Table 1, and shown in Fig. 2, using a consistent atom numbering scheme.

As shown in Table 1, the ranges of C—C bond lengths of 6-fluoro coumarin are 1.349–1.460 Å. C11—C12 bond length is 1.460 Å, indicating that it is a single bond. The C—C bond lengths in the aromatic ring are 1. 378–1.406 Å, C9—C11 bond length is 1.349 Å, C4—C9 bond length is 1.441 Å, indicating that C9—C11 bond is a double bond, while C4—C9 is more like a single bond. The ester

Table 1			
Optimized	parameters	of 6-fluoro	coumarin.

Geometrical parameters B3LYP/6-311G(d,p)						
Bond length (Å)			Bond length (Å)			
R1	R(1,2)	1.388	R10	R(5,6)	1.378	
R2	R(1,6)	1.396	R11	R(5,10)	1.083	
R3	R(1,7)	1.083	R12	R(6,15)	1.354	
R4	R(2,3)	1.394	R13	R(9,11)	1.349	
R5	R(2,8)	1.083	R14	R(9,13)	1.085	
R6	R(3,4)	1.405	R15	R(11,12)	1.460	
R7	R(3,16)	1.365	R16	R(11,14)	1.081	
R8	R(4,5)	1.406	R17	R(12,16)	1.396	
R9	R(4,9)	1.441	R18	R(12,17)	1.202	
	Selected bond	angle (°)		Selected bond angle		
A1	A(1,2,3)	119.457	A7	A(5,4,9)	123.654	
A2	A(2,3,4)	121.171	A8	A(1,6,15)	118.573	
A3	A(3,4,5)	118.942	A9	A(5,6,15)	119.069	
A4	A(4,5,6)	118.931	A10	A(11,12,17)	126.183	
A5	A(2,3,16)	117.452	A11	A(16,12,17)	117.962	
A6	A(4,3,16)	121.378	A12	A(3,16,12)	122.862	
	Selected dihed	ral angle (°)		Selected dihedro	ıl angle (°)	
D1	D(1,2,3,4)	0.0001	D7	D(3,4,9,11)	0.0023	
D2	D(2,1,6,15)	180.000	D8	D(10,5,6,15)	0.001	
D3	D(1,2,3,16)	-180.000	D9	D(4,9,11,12)	0.011	
D4	D(2,3,16,12)	-180.008	D10	D(9,11,12,16)	-0.021	
D5	D(4,3,16,12)	0.006	D11	D(9,11,12,17)	180.029	
D6	D(4,5,6,15)	-180.000	D12	D(17,12,16,3)	179.973	



Fig. 2. The calculated molecular structure and atom numbering of 6-fluoro coumarin.

bonds C12—O16, C12—O17 are 1.396 Å and 1.202 Å, showing the latter is a double one. The range of C—H bond lengths are 1.083–1.085 Å. The C6—F15 bond lengths is 1.354 Å. The calculated values of the C—C—C angles in the aromatic ring are around the typical hexagonal angle of 120°. The calculated values of the dihedral angles of O17—C12—O16—C3, C4—C3—O16—C12 and C3—C4—C9

--C11, which are critical geometry parameters in the ground state, are --179.973°, 0.006°, and 0.002°, indicating that the benzene and pyran ring are almost at the same plane.

Vibrational assignments

The simulated spectra are shown in Fig. 3. Theoretical (unscaled and scaled) and experimental vibrational frequencies (cm^{-1}) , peak intensities (km mol⁻¹) and the corresponding assignments for the vibrational modes are gathered in Table 2.

According to Fig. 3, it is easy to discover that the main absorption peaks of the calculated spectrum are mainly in accordance with those of the experimental one, demonstrating that the calculated results are dependable. Taking into account the satisfactory agreement between theoretically predicted and experimental vibrational frequencies, it may be suggested that DFT method with hybrid B3LYP functional is quite reliable in the prediction of IR spectra of 6-fluoro coumarin and related compounds.

Phenyl ring vibrations

The C—H and C—C related vibrations can help to determine the existence of aromatic rings in a structure. The C—H stretching vibrations of aromatic structures often occur in the range of $3030-3100 \text{ cm}^{-1}$. The C—H in-plane bending vibrations often appear in the region $1000-300 \text{ cm}^{-1}$. And $650-900 \text{ cm}^{-1}$ is the C—H out-of-plane bending vibrational region. It is reported that the bands of the phenyl C–C stretching vibrations generally appear at 1450 cm^{-1} , 1500 cm^{-1} , 1580 cm^{-1} , and 1600 cm^{-1} in IR spectra with variable intensities [42].

For 6-fluoro coumarin, the aromatic C—H stretching vibrations appear at 3074 cm^{-1} in the IR spectrum with medium peaks, Scaled theoretical C—H stretching modes are found at 3065 cm^{-1} . In IR spectrum, the frequencies 1261 cm^{-1} are assigned to the C—H in-plane bending vibrations, and two intensive bands at 820 cm^{-1} and 887 cm^{-1} are expected to be the C—H out-of-plane bending vibrations. As shown in Table 2, the IR wave numbers 1441 cm^{-1} , 1485 cm^{-1} , 1568 cm^{-1} and 1591 cm^{-1} are assigned as the aromatic C—C semicircle stretching vibrations, they are in agreement with the calculated data except for 1589 cm^{-1} , there is no such vibration in calculated data, the most probable factor contribute to such a discrepancy is that this vibration is obscured by the intense (138.13) vibration at 1550 cm^{-1} . As shown in Table 2, the predicted vibrations assigned to phenyl ring vibrations are in good accordance with the experimental assignments.

C=*C* vibrations of pyran ring

The C=C stretching vibrations often occur in the range of 1620– 1680 cm⁻¹; The C-H stretching vibrations of alkene structures generally appear above 3000 cm^{-1} ; The bands at $800-840 \text{ cm}^{-1}$ attribute to the C-H in-plane bending vibrations; and



Fig. 3. Calculated and experimental IR spectra of 6-fluoro coumarin (A) (Exp.); (B) (Cal.).

Table 2

Comparison of theoretical and experimental vibrational parameters.

Exp. IR (cm^{-1})	Calculated (cm ⁻¹)			Assignments, PED ^b (>10%)
	Freq. (cm^{-1})		Inte. (km/mol)	
	Unscaled	Scaled ^a		
584	588	568	20.47	σring(90.5)
820	832	804	58.16	γring(11.7), γC—H(88.3)
864	885	856	50.82	γring(24.7), γC—H(74.4)
887	907	877	100.56	υC—O(13.2)
1055	1091	1055	104.39	vring(33.2)
1097	1130	1093	3.21	βC—H(11.6,12.0)
1138	1171	1132	29.34	βC—H(12.9,11.6)
1151	1187	1147	27.49	βC—H(9.8,11.7)
1261	1274	1231	62.16	υring(18.7), υC—F(6.3),
				β ring(26.8), β = C—H(19.5)
1274	1275	1232	102.11	β ring(18.1), β = C—H(54.0)
1441	1472	1423	70.84	υ C — C (Ph-ring) (16.1)
1485	1511	1461	57.26	υC—C(Ph-ring) (16.3)
1568	1603	1550	138.13	υC—C(Ph-ring) (36.8)
1591				
1624	1667	1611	15.53	υC—C(Ph-ring) (16.3)
1724	1806	1746	711.88	υC—C(11.9), υC=O(22.6)
3074	3170	3065	6.54	υ C —H(63.9,11.4)

^a With the scale factor of 0.9668.

^b υ , Stretching; β , in-plane-bending; γ , out-of-plane bending; and σ , scissoring.

 $675-730 \text{ cm}^{-1}$ is the C—H out-of-plane bending vibrational region of cis-alkenes.

For 6-fluoro coumarin, the IR wave number 1624 cm^{-1} is assigned to C=C stretching vibration of pyran ring, in accordance with predicted frequencies at 1611 cm^{-1} ; The C–H stretching vibrations of pyran ring are at about 3200 cm^{-1} with very low intensity; $820, 864 \text{ cm}^{-1}$ are assigned to the C–H in-plane bending vibrations, the calculated values are $804, 856 \text{ cm}^{-1}$ respectively. The experimental values match well with the theoretical data in Table 2.

O=*C*−*O* vibrations

The frequencies around $1050-1310 \text{ cm}^{-1}$ in IR spectrum are usually regarded as the C—O stretching band of the ester. For 6-fluoro coumarin, 1724 cm^{-1} is attributed to the C=O stretching band; 1274 cm^{-1} is assigned to C—O asymmetric stretching vibrations; C—O in-plane bending vibration is observed at 861 cm⁻¹. The theoretical values are 1746, 1232, 877 cm⁻¹ accordingly, which match well with the experimental data in Table 2.

C—F vibration

The C—F stretching vibrations of phenyl fluoride often happen in the range of $1100-1250 \text{ cm}^{-1}$ [43].

The strong vibration observed at 1261 cm^{-1} in IR spectrum is assigned as C—F stretching vibration. The theoretically computed value at 1231 cm^{-1} has fine consistency with the experimental result.

NMR chemical shifts

The experimental and calculated values together with the peak assignments of 6-fluoro coumarin for ¹H NMR chemical shifts

Table 3
Comparison of theoretical and experimental values of ¹ H NMR chemical shifts

Assignments (ppm)	13-H	8-H	7-H	10-H	14-H
Calc. ^a	8.31	7.74	7.73	7.68	6.80
Exp.	8.04	7.62	7.50	7.46	6.58

^a Reference: TMS B3LYP/Aug-CC-Pvdz GIAO/reference shielding: 31.78 ppm.

analyses are shown in Table 3, and ^{13}C NMR in Table 4. The observed ^{1}H NMR spectra are presented in Fig. 4, and ^{13}C NMR in Fig. 5

¹H NMR chemical shifts

The peaks with δ H of 2.51, 3.41 ppm in Fig. 4 is supposed to be related with the protons of the solvent DMSO-d6 and H₂O in it. The presence of other peaks suggests that there are five distinct types of protons in the compound. The peaks with δ H of 6.58 ppm in Fig. 4 are assigned to the proton of alkenyl at the 14-position of the coumarin, δ H of 8.04 ppm is assigned to the proton of alkenyl at the 13-position, they have the same coupling constant of 9.6 Hz. Normally, the protons on phenyl ring are expected to yield NMR signals in the δ H region of 6–8 ppm [43]. The substitution of fluorine atom in phenyl ring changes the chemical environment of the remaining aryl protons and generates coupling interaction to them. The peaks with δ H of 7.46 ppm, 7.50 ppm, 7.62 ppm in Fig. 4 are expected to be assigned to the protons of phenyl ring at the 10-, 7-, 8-position respectively.

Table 3 gives the comparison of theoretical and experimental values of ¹H NMR chemical shifts for the title compound. The results indicate that the calculated chemical shifts are in good agreement with the experimental data. However, there is an

Table 4	
Comparison of theoretical and experimental values of ¹³ C NMR chemical shif	ts.

Assignments (ppm)	12-C	6-C	3-C	9-C	4-C	1-C	2-C	11-C	5-C
^a Calc.	162.53	159.16	153.49	144.54	122.88	118.23	116.51	115.86	113.65
Exp.	160.21	159.28,	150.36	143.85,	120.20,	119.72,	118.75,	117.88	114.12,
		157.69	150.34	143.83	120.13	119.56	118.69		114.29

^a Reference: TMS B3LYP/Aug-CC-Pvdz GIAO/reference shielding: 192.72 ppm.



Fig. 4. Observed ¹H NMR spectrum of 6-fluoro coumarin.



Fig. 5. Observed ¹³C NMR spectrum of 6-fluoro coumarin.

obvious difference between the experimental and theoretical chemical shift values, that is none of the coupling constants can be given by computing. That is the limitation of theoretical model applied in the calculations.

¹³C NMR chemical shifts

The peaks with δ C of 40.11 ppm are supposed to be related with the carbons of the solvent DMSO-d6. Normally, the carbons on alkenyl are expected to yield NMR signals in the δ C region of 100–150 ppm [43].

The carbons on phenyl ring are supposed to give NMR signals in the region of 110–175 ppm. The substitution of fluorine atom in phenyl ring changes the chemical environment of the remaining aryl carbons and generates coupling interaction to them. ¹³C NMR signals of carbons in the ortho- or para- position to a fluoro substituent are significantly shifted to lower frequencies, whereas ipso C-atoms are characterized by a marked downfield shift [43,44].

Based on these, the peaks observed in Fig. 5 with δ C of 114.12/ 114.29 ppm, 118.69/118.75 ppm, 119.56/119.72 ppm, 120.13/ 120.20 ppm, 150.36/150.34 ppm and 157.69/159.28 ppm are expected to be assigned to the carbons of phenyl ring at 5-, 2-, 1-, 4-, 3-, 6-position respectively, each of them has coupling interaction with fluorine atom in some different degrees according to the distance to fluorine atom. δ C of 117.88 ppm is assigned to the carbon of alkenyl at the 11-position, and 143.83/143.85 ppm is assigned to the 9-carbon of alkenyl with a small coupling constant with fluorine atom. δC of 160.20 ppm is attributed to the carbon of acyl at the 12-position.

Table 4 gives the comparison of theoretical and experimental values of ¹³C NMR chemical shifts for the title compound. The results indicate that the calculated chemical shifts are in good agreement with the experimental data in most parts. However, there are some differences between the experimental and theoretical chemical shift values, the biggest one is that computing cannot give the coupling constants, it is because that the theoretical model applied in the calculations cannot simulate the coupling interaction.

UV-vis absorption and fluorescence spectra

Coumarins are known to be suitable photoluminescence materials for their strong fluorescence. Photo absorption and emission phenomena are vital for a photoluminescence material. TD-DFT method is often found efficient for evaluating the excited spectra of conjugated molecules [45–47].

Hydrogen-bonding interaction

In case of the solute molecules in the ground state can form hydrogen-bonded complexes with the solvent molecules, the hydrogen-bonding interactions can induce spectral shifts of some characteristic vibrational modes involved in the formation of hydrogen bonds [40,41]. In present work, the absorption and emission spectra are investigated in the hydrogen-donating solvent of methanol, we employ TD-DFT method for the calculations of the UV-vis absorption and fluorescence spectra of the isolated 6-fluoro coumarin with CPCM and the hydrogen-bonded (6-fluoro coumarin)-(methanol) complex to simulate the solvent effect. Since the C=O group is the most important site that is responsible for the hydrogen bond formation between 6-fluoro coumarin and methanol [41,48], and the C—F bond is capable of significant interactions with proton donors, although these are generally weak [49], the calculated geometric structure of the hydrogen-bonded complex in ground state shown in Fig 6 can be a good model for studying the hydrogen-bonding interactions between 6-fluoro coumarin and methanol. In Fig. 6, the length of the hydrogen bond C=O···H–O between H and O atom is 1.946 Å, the other hydrogen bond C—F···O—H has a hydrogen bond length of 2.252 Å. we can find that the lengths of the C=O, C-F and H-O bonds are all increased because of the formation of the hydrogen bonds. Compared to the structure in Fig. 2, the C=O bond length in Fig. 6 is increased to 1.211 Å from 1.202 Å, and the C-F bond length is increased to 1.364 Å from 1.354 Å. And the H–O bonds in C=O···H-O and C-F···O-H are increased to 0.970 Å and 0.963 Å from 0.961 Å (calculated in the same level), respectively. These suggest that the C=O and C-F bonds of 6-fluoro coumarin molecular can form hydrogen bonds with methanol moleculars, and the C=O group is more responsible for the hydrogen-bond formation.



Fig. 6. The calculated molecular structure of hydrogen-bonded (6-fluoro coumarin)-(methanol) complex.



Fig. 7. UV-vis absorption spectra of 6-fluoro coumarin in methanol ((A) observed, (B) calculated).

Absorption spectra

The UV/vis spectra absorption are determined using the conventional TD-DFT procedure on the ground state geometries. Experimental absorption spectrum of 6-fluoro coumarin in methanol, and the calculated absorption spectra of isolated 6-fluoro coumarin in CPCM and hydrogen-bonded (6-fluoro coumarin)-(methanol) complex are shown in Fig. 7. Theoretical and experimental values are listed in Table 5.

Results in Fig. 7 and Table 5 show that 6-fluoro coumarin has strong absorption at 319, 269, 215 nm in UV-vis region experimentally. For isolated 6-fluoro coumarin in CPCM, the calculated excitation energy (3.96 eV, 313 nm) with strong intensity (0.108) for the singlet state S_1 is close to the experimental absorption of 319 nm, the other higher energy absorption peaks calculated at 266 nm (4.66 eV) and 213 nm (5.81 eV) with large oscillator strength for S_3 and S_5 can be associated with the experimentally observed absorption of 269 and 215 nm. The simulated spectra exhibit only slightly blue-shifted compared with experimental ones. And as to the hydrogen-bonded complex, the absorption peaks calculated are at 308 nm (4.02 eV) for S₁, 269 nm (4.62 eV) for S₃, 214 nm (5.79 eV) for S₅, which are very close to the data of the isolated model. From that we can see that the theoretical absorption data of isolated 6-fluoro coumarin in CPCM are in good agreement with the experimental values, the influence of the hydrogen-bonding interaction between 6-fluoro coumarin and methanol is negligible in calculating the absorption spectrum of 6-fluoro coumarin.

Fluorescence spectra

Experimental fluorescence spectrum of 6-fluoro coumarin in methanol, and the simulated fluorescence spectra of isolated 6-fluoro coumarin with CPM and hydrogen-bonded (6-fluoro coumarin)-(methanol) complex are shown in Fig. 8. Theoretical and experimental values are listed in Table 6.

As shown in Fig. 8A, 6-fluoro coumarin has strong purple light emission at 416 nm in vis region, and the computed emission spec-

Table 5

Comparison of theoretical values of UV-vis absorption spectra of isolated 6-fluoro coumarin in CPCM and the hydrogen-bonded complex with experimental data.^a

State	$\lambda_{\text{Calc.}}(\text{nm})$	<i>E</i> (eV)	f	λ_{exp} . (nm)		
Isolated compound in CPCM						
<i>S</i> ₁	313	3.96	0.108	319		
S ₃	266	4.66	0.177	269		
S ₅	213	5.81	0.136	215		
Hydrogen-bonded complex						
<i>S</i> ₁	308	4.02	0.101	319		
S_4	269	4.62	0.214	269		
S ₉	214	5.79	0.097	215		

^a λ , Wavelength; *E*, electronic excitation energies; *f*, oscillator strengths; and *S_n*, low-lying singlets.

Table 6

Comparison of theoretical values of fluorescence emission spectra of isolated 6-fluoro coumarin in CPCM and the hydrogen-bonded complex with experimental data.

State	λ_{calc} . (nm)	<i>E</i> (eV)	f	$\lambda_{exp.}$ (nm)
Isolated co	mpound in CPCM			416
S_1	397	3.121	0.0694	
Hydrogen-l	bonded complex			
<i>S</i> ₂	405	3.061	0.0831	

tra in Fig 8B show that the calculated value for isolated 6-fluoro coumarin in CPCM is 397 nm (3.12 eV), which is basically consistent with the experimental data (416 nm). The calculated emission peak at 405 nm (3.05 eV) of hydrogen-bonded complex is closer to the experimental value compared with that of the isolated model. It is apparent that the hydrogen-bonding interaction between 6-fluoro coumarin and methanol affects the shift of simulated emission peak and should be considered in the simulation of fluorescence spectrum for 6-fluoro coumarin with methanol as solvent.



Fig. 8. Fluorescence spectra of 6-fluoro coumarin ((A) observed, (B) calculated).

Conclusions

In this study, we have synthesized 6-fluoro coumarin and characterized it by FT-IR and NMR. The geometric parameters have been optimized, vibrational frequencies and ¹H, ¹³C NMR chemical shifts of the title compound have been calculated using DFT/B3LYP method with the 6-311G(d,p) basis sets (NMR chemical shifts were calculated at the B3LYP/Aug-CC-Pvdz level). The theoretical vibrational frequencies and chemical shift values are in good agreement with the experimental findings. The major discrepancies between the experimental and theoretical chemical shift values are mainly due to the negligence the coupling interaction of the fluorine atom with carbon atom within the applied theoretical model. The optical properties of absorption and emission are also addressed theoretically and experimentally. TD-DFT method is used to calculate the absorption and emission spectra, the solvent effect of methanol is simulated by using the isolated 6-fluoro coumarin in CPCM and the hydrogen-bonded (6-fluoro coumarin)-(methanol) complex as models. Results show that the title compound has good absorption of UV light and can give purple light emission, which makes it a good candidate as a photo luminescent material. And the influence of the hydrogen-bonding interaction between 6-fluoro coumarin and methanol can be neglected on the calculated absorption values, but should be considered on the theoretical emission data. The theoretical absorption data of isolated 6-fluoro coumarin in CPCM together with the calculated emission values of hydrogenbonded (6-fluoro coumarin)-(methanol) complex are in good agreements with the experimental results. All these conclusions prove that the selected methods are feasible to predict the parameters and characteristics of structural-similar compounds. And we would like to mention in particular that although it is known that TD-DFT method overestimates energies of electronic transitions [50,51], but in this work, the method can give precise simulation of the fluorescence spectra of 6-fluoro coumarin, which is very useful to evaluate and design the optical properties for new photo luminescent materials from the structural-similar compounds.

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