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Four novel ketocoumarin-based chromophores: Synthesis, photoluminescent behaviors and theoretical studies

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ABSTRACT

Four novel coumarin derivatives were synthesized and characterized via MS, ¹H NMR, FT-IR, and UV-vis absorption spectra. The fluorescence behaviors of the compounds in DFM solutions were observed. The compounds exhibited strong blue and green emissions under ultraviolet light excitation. Calculations performed using a combined time-dependent density functional theory (TD-DFT) and conductor-like polarizable continuum model (C-PCM) reproduced the $\pi \rightarrow \pi^*$ type absorption bands of the four compounds. Resonance frequency calculations were also performed to study the IR spectra of the compounds. The calculated results are in good accordance with the experimental values.

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1. Introduction

Coumarins, representing an important class of organic heterocycles, have received considerable attention in the past few years. This compound group can be found in many natural or synthetic drug molecules and possess versatile biological and medical activities [1]. This compound group is used for the treatment of brucellosis, rheumatic disease and burns [2], and it also possesses anti-HIV [3], antiinflammatory [4], anticoagulant [5] and antimicrobial activities [6]. Moreover, coumarin derivatives exhibit unique photochemical and photophysical properties, including sufficient fluorescence in a visible light range, large Stokes shift, high quantum vield of photoluminescence and reasonable solubility [7–10], all of which make them useful in a variety of applications. These applications include optical brighteners, laser dyes, non-linear optical chromophores, solar energy collectors, fluorescent labels and probes in biology and medicine, as well as two-photon absorption (TPA) materials [11-13]. More importantly, coumarin dyes have also been used as blue, green, and red dopants in organic light-emitting diodes (OLEDs). For example, ketocoumarins, which belong to the highly fluorescent class of coumarin laser dyes, comprise a series of excellent fluorescent dopants and have been widely used as doped emitters in OLEDs. Many ketocoumarin-based electroluminescent (EL) materials have been developed at present [14-17].

In the current work, we report the synthesis, photophysical properties, and theoretical investigation of four novel ketocoumarin derivatives, 3a-3d, containing a series of substituents on the coumarin ring. These derivatives exhibit strong blue and green emissions under ultraviolet light excitation.

2. Experimental

2.1. Materials and methods

IR spectra (400-4000 cm^{-1}) were measured on a Nicolet 380 spectrophotometer. ¹H NMR spectra were obtained using a Varian Inova 500 spectrometer (at 500 MHz). Mass spectra were recorded on a micrOTOF-Q II mass spectrometer. Melting points were taken on a RY-1 micro melting apparatus; the thermometer was uncorrected. UV-vis absorption and emission spectra were recorded using a Thermo Evolution 300 spectrometer and a Carv Eclipse spectrometer, respectively. All the chemicals were commercially available and were used without further purification. All the solvents were dried using standard methods before use. The starting compounds 1a-1d were synthesized according to Refs. [18,19].

2.2. Synthesis and characterization of compounds 2a-2d and 3a-3d

The synthetic routes to compounds 2a-2d and 3a-3d are shown in Scheme 1.

The general process for the synthesis of compounds 2a-2d is as follows: in a reaction flask, 1 mol of compounds 1a-1d and 2 mol benzene-1,4-dicarboxaldehyde were dissolved in 200 mL glacial acetic acid. Three drops of piperidine were added as catalyst. The mixture was heated and refluxed for approximately 5 h, and then



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Scheme 1. Synthetic routes to compounds 3a-3d.

cooled to room temperature. The precipitate was collected via filtration and recrystallized twice in ethanol/acetonitrile.

2a: m.p. 204–205 °C. IR (KBr pellet cm⁻¹): 3040, 1720, 1690, 1670, 1560, 984 cm⁻¹. ¹H NMR (CDCl₃, δ , ppm): 10.049 (s, 1H), 8.631 (s, 1H), 8.078 (d, *J* = 16.0 Hz, 1H), 7.927 (d, *J* = 8.0 Hz, 2H), 7.871 (d, *J* = 15.5 Hz, 1H), 7.826 (d, *J* = 8.0 Hz, 2H), 7.686 (q, *J* = 13.3 Hz, 2H), 7.394 (m, 2H).

2b: m.p. 209–210 °C. IR (KBr pellet cm⁻¹): 3040, 1730, 1700, 1630, 1540, 982 cm⁻¹. ¹H NMR (CDCl₃, δ , ppm): 10.060 (s, 1H), 8.544 (d, *J* = 15.5 Hz, 1H), 8.108 (q, *J* = 7.8 Hz, 1H), 8.037 (d, *J* = 16.0 Hz, 1H), 7.947 (d, *J* = 8.0 Hz, 2H), 7.866 (d, *J* = 8.0 Hz, 2H), 7.720 (m, 1H), 7.350 (m, 2H).

2c: m.p. 203–204 °C. IR (KBr pellet cm⁻¹): 3050, 1720, 1690, 1660, 1610, 962 cm⁻¹. ¹H NMR (CDCl₃, δ , ppm): 10.048 (s, 1H), 8.600 (s, 1H), 8.078 (d, *J* = 16.0 Hz, 1H), 7.923 (d, *J* = 8.0 Hz, 2H), 7.865 (d, *J* = 16.0 Hz, 1H), 7.822 (d, *J* = 8.0 Hz, 2H), 7.253 (m, 3H), 4.008 (s, 3H).

2*d*: m.p. 205–206 °C. IR (KBr pellet cm⁻¹): 3090, 1750, 1700, 1621, 1600, 1060 cm⁻¹. ¹H NMR (CDCl₃, δ , ppm): 10.035 (s, 1H), 8.570 (s, 1H), 8.272 (d, *J* = 16.0 Hz, 1H), 7.905 (d, *J* = 8.0 Hz, 2H), 7.814(t, 3H), 7.442 (d, *J* = 9.0 Hz, 1H), 6.648 (q, *J* = 2.5 Hz, *J* = 2.5 Hz, 1H), 6.502 (d, *J* = 2.0 Hz, 1H), 3.479 (q, 4H), 1.261 (t, 6H).

The general process for the synthesis of compounds 3a–3d is as follows: a mixture of compounds 2a–2d (1 mol), cyanoacetic acid (1 mol), and piperidine (2 mL) in acetonitrile (200 mL) was placed in a three-necked flask under a nitrogen atmosphere and heated to reflux for approximately 1 h. After cooling, the precipitate was collected and recrystallized from acetonitrile to obtain the pure compounds 3a–3d.

3a: Yield: 52.4%. m.p. 204–205 °C. IR (KBr pellet cm⁻¹): 3442, 2366, 1729, 1606, 1177 cm⁻¹. ¹H NMR(DMSO, δ , ppm): 8.827 (s, 1H), 8.696 (s, 1H), 8.148 (s, 1H), 8.023 (d, *J* = 8.5 Hz, 2H), 7.942 (d, *J* = 7.5 Hz, 1H), 7.904 (d, *J* = 8.0 Hz, 2H), 7.766 (s, 2H), 7.743 (d, *J* = 8.5 Hz, 1H), 7.493 (d, *J* = 8.0 Hz, 1H), 7.430 (t, 1H). HRMS (ESI⁺): *m/z*: calcd. for C₂₂H₁₃NO₅: 394.0686 [M + Na⁺]; found: 394.0611.

3b: Yield: 49.1%. m.p. 279–280 °C. IR (KBr pellet cm⁻¹): 3424, 2363, 1709, 1613, 1433, 1276 cm⁻¹. ¹H NMR(DMSO, δ , ppm): 8.342 (t, 2H), 8.110 (d, *J* = 8.0 Hz, 2H), 8.023 (t, 2H), 7.936 (d, *J* = 7.5 Hz, 2H), 7.826 (t, 1H), 7.430 (t, 2H). HRMS (ESI⁺): *m/z*: calcd. for C₂₂H₁₃NO₆: 410.0635 [M + Na⁺]; found: 410.0614.

3c: Yield: 62.8%. m.p. 269–270 °C. IR (KBr pellet cm⁻¹): 3427, 1727, 1606, 1470, 1274, 1179 cm⁻¹. ¹H NMR(DMSO, δ , ppm): 8.664 (s, 1H), 8.332 (s, 1H), 8.087 (d, *J* = 8.0 Hz, 2H), 7.936 (d, *J* = 8.5 Hz, 2H), 7.775 (s, 2H), 7.473 (d, *J* = 7.5 Hz, 1H), 7.429 (d,

J = 7.5 Hz, 1H), 7.353 (t, 1H), 3.933 (s, 3H). HRMS (ESI⁺): *m*/*z*: calcd. for C₂₃H₁₅NO₆: 424.0792 [M + Na⁺]; found: 424.0711.

3*d*: Yield: 70.3%. m.p. 204–205 °C. IR (KBr pellet cm⁻¹): 1712, 1592, 1502, 1348, 1178, 1064 cm⁻¹. ¹H NMR(DMSO, δ , ppm): 8.595 (s, 1H), 8.273 (s, 1H), 8.056 (q, *J* = 1.5 Hz, *J* = 9.5 Hz, 3H), 7.877 (d, *J* = 8.5 Hz, 2H), 7.689 (d, *J* = 4.5 Hz, 1H), 7.664 (d, *J* = 2.0 Hz, 1H), 6.802 (q, *J* = 2.0 Hz, *J* = 2.0 Hz, 1H), 6.597 (d, *J* = 2.0 Hz, 1H), 3.493 (q, 4H), 1.141 (t, 6H). HRMS (ESI⁺): *m/z*: calcd. for C₂₆H₂₂N₂O₅: 465.1421 [M + Na⁺]; found: 465.1472.

2.3. Quantum chemical calculations

The full geometry optimization, resonance frequencies, lowest energy electronic transitions, and absorption spectra of compounds 3a–3d were calculated with the density functional theory (DFT) and the time-dependent DFT (TD-DFT) from Becke's three-parameter hybrid functional (B3LYP) [20] method using two different basis sets 6-311+G** and 6-31G*. The solvent polarity effects were included in the conductor-like polarizable continuum model (C-PCM) [21]. The solvent used in our calculations was N,N'-dimethylformide (DMF). All calculations were performed using the Gaussian 03 program.

3. Results and discussion

3.1. UV-vis absorption and fluorescence of compounds 3a-3d

The UV–vis absorption spectra of compounds 3a–3d in dilute DMF solutions are shown in Fig. 1. These molecules consist of a typical D– π –A structure, wherein 3-carbonylcoumarinyl, styryl, and cyanoacrylic acid groups act as donor (D), π -conjugated center (π), and acceptor (A) moieties, respectively. Structural modification only occurs in the coumarin moiety, where the 4-, 7-, and 8-positions are replaced with hydroxyl, diethylamino, and methoxyl groups, respectively. Such modifications are expected to change the electron-donating capability of the 3-carbonylcoumarinyl group, as well as cause red-shifts in the absorption and emission spectra.

The degree of red-shift in compound 3d is greater than that in compound 3c because the electron-repelling group at position 7 leads to electron displacement in the 3-carbonylcoumarinyl group (Fig. 2). This displacement enhances the electron-donating capability of the 3-carbonylcoumarinyl group. Although electron displacement occurs (Fig. 3) in the hydroxyl group at position 4 of



Fig. 1. UV-vis absorption spectra of compounds 3a–3d in DMF at room temperature. ($C = 5.00 \times 10^{-5}$ mol/L).



Fig. 2. Electron displacement in compound 3d.

compound 3b, a strong intramolecular hydrogen bond between the hydroxyl group and the ketonic oxygen weakens this interaction, which results in the maximum absorption peak in compound 3b similar to that in compound 3c.

The major absorption band of the four compounds corresponds to the intramolecular charge transfer from the 3-carbonylcoumarinyl group to the cyanoacrylic acid group in the whole electronic system. However, another minor absorption band is observed in the absorption spectrum of compound 3d, which is attributed to the $\pi \rightarrow \pi^*$ transition in the 3-carbonylcoumarinyl moiety. The main absorption band of compound 3d is red-shifted when the solvent polarity is increased. This result further shows the strong intramolecular charge transfer in the structure of compound 3d, which is in good agreement with the findings of a previous study (Fig. 4) [22].

Fig. 5 shows the photoluminescence spectra of compounds 3a– 3d. Compounds 3a–3c exhibit bright blue emissions with emission peaks at around 411, 439, and 432 nm, respectively. Compound 3d exhibits a bright green emission with a peak at 580 nm. The degree of bathochromic shift in compound 3d is greater than those of compounds 3b and 3c because the effect of electron displacement in the 3-carbonylcoumarinyl group causes a stronger intramolecular charge transfer. The emission band of compound 3d red¹-shifts and it gradually broadens with increasing solvent polarity. This result demonstrates that the compound also has an effective intramolecular charge transfer characteristic [23] (Fig. 6).

3.2. Quantum chemical calculations

Quantum chemical calculations were performed to further investigate the electronic and luminescent properties of compounds 3a-3d. The B3LYP method using two different basis sets, namely, 6-311+G** and 6-31G*, were used to obtain reliable spectral data to investigate the absorption spectra of the four compounds. The experimental and theoretical λ_{max} values of the four compounds are shown in Fig. 7. The error between the calculated and experimental results ranges from 17 nm to 22 nm for 6-311+G**, and 28 nm to 32 nm for 6-31G*. These values reveal that the 6-311+G** basis set is more suitable than the 6-31G* basis set for studying the absorption spectra of the four compounds. The results obtained with the introduction of the solvent reaction field and the individual combination of C-PCM and the 6-311+G** and 6-31G* basis sets are much closer to the experimental values. 6-311+G**/TD-DFT(C-PCM) and 6-311+G**(C-PCM)/TD-DFT(C-PCM) were determined using the optimized gas phase geometries and solvated geometries of the solvent, respectively. Similarly, 6-31G*/TD-DFT(C-PCM) and 6-31G*(C-PCM)/TD-DFT(C-PCM) were determined using optimized gas phase geometries and solvated geometries in the solvent, respectively. The λ_{max} optimized by 6-311+G^{**}(C-PCM)/TD-DFT(C-PCM) reduces the absolute deviation to 3 nm for compound 3a, 1 nm for compound 3b, 2 nm for compound 3c, and 6 nm for compound 3d. These results indicate that the accuracy remarkably increases when the solvent effects are taken into account because of the intermolecular hydrogen bonding interaction in the corresponding electronic excited state. The electronic transition energy from the ground state to the excited state generally decreases, which leads to a red-shift in the electronic spectrum because of strengthening of the excited hydrogen bond. In contrast, when the hydrogen bond is weakened in the excited state, the decrease in energy level of the excited state is less than that of the ground state. Thus, the electronic transition energy from the ground state to the excited state increases, which indicates an electronic spectral blue-shift because of weakening of the excited hydrogen bond [24].

The main orbital compositions of the computed lower-lying singlet excited states and the transition feature of compounds 3a-3d obtained at the 6-311+G**(C-PCM)/TD-DFT(C-PCM) level are listed in Table 1. The lowest energy absorption in the four compounds can be attributed to the electronic $\pi \rightarrow \pi^*$ transition from HOMO to LUMO. In addition, the calculated frontier orbitals of compounds 3a-3d are nearly the same. For example, the HOMO and LUMO diagrams (Fig. 8) of compound 3d show that it is likely to exhibit an efficient electron transfer from the 3-carbonylcoumarinyl group of the HOMO to the chalcone group of the LUMO if electronic transitions occur. The HOMO for the compound is localized at the 3carbonylcoumarinyl region, whereas the LUMO is located at the chalcone region. Therefore, when electrons transfer from HOMO to LUMO, the electron density significantly decreases in the electron-donating 3-carbonylcoumarinyl moiety, accompanied by an increase in the electron density of the electron-accepting chalcone moiety. This result indicates that the electrons transfer from the 3-carbonylcoumarinyl group to the cyanoacrylic acid group through the styryl group.

The resonance frequency calculation for compound 3d was conducted at the B3LYP/6-311+G^{**} level to perform a preliminary study of its IR spectra. The observed and calculated data of the IR spectra of compound 3d are given in Table 2. The calculated IR spectral data are slightly higher than the experimental values. A possible reason is that the result obtained from the calculation is that of the harmonic oscillator frequency, whereas the experimental value contains the frequency of an anharmonic oscillator. The data were modified using 0.9613 [25] as the frequency scaling factor. The consistent relation graph between the calculated and

¹ For interpretation of color in Figs. 1, 5 and 7–9, the reader is referred to the web version of this article.



Fig. 3. Electron displacement in compound 3b.



Fig. 4. Effect of the polarity of the solvent upon the absorption spectra of compound 3d. Solvents: Petroleum ether (a); cyclopentane (b); toluene (c); chloroform (d); N,N'-dimethylformide (e).



Fig. 5. Fluorescence emission spectra of compound 3a (λ_{ex} = 341 nm), compound 3b (λ_{ex} = 361 nm), compound 3c (λ_{ex} = 361 nm), and compound 3d (λ_{ex} = 465 nm) in DMF at room temperature ($C = 5.00 \times 10^{-5}$ mol/L).



Fig. 6. Effect of the polarity of the solvent upon the fluorescence emission spectra of compound 3d. Solvents: petroleum ether (a); cyclopentane (b); toluene (c); chloroform (d); N,N'-dimethylformide (e).



Fig. 7. Plot of experimental and theoretical λ_{max} of compounds 3a–3d in DMF.

Table 1			
Main orbital compositions	and excitation	energies of con	npounds 3a–3d.

Compounds	State	e Transition feature	6-311+G**/C-PCM	6-311+G**/C-PCM ^a			
			Transition character ^b	ΔE (eV)	ſ		
3a	^{1}A	$\pi \to \pi^*$	$H \rightarrow L (85.3\%)$	4.07	0.883		
3b	¹ A	$\pi \to \pi^*$	$H \rightarrow L (82.7\%)$	3.83	0.812		
3c	¹ A	$\pi \to \pi^*$	$H \rightarrow L (84.1\%)$	3.81	0.853		
3d	¹ A	$\pi \to \pi^*$	$\mathrm{H} \rightarrow \mathrm{L} \ (87.3\%)$	3.11	0.861		

^a Solvent is DMF solution.

 $^{\rm b}$ H and L stand for HOMO and LUMO, respectively, and the proportion of the main transition is given in the parentheses.

^c Oscillator strength coefficients.



Fig. 8. Sketch of the main molecular orbitals for compound 3d obtained at the $6-311+G^{**}(C-PCM)/TD-DFT(C-PCM)$ level.

 Table 2

 Comparison of the calculated and experimental infrared data of compound 3d.

_							
	No.	Exp.		Calcd.			Vibratory feature
		Freq. ^a	Int. (IR) ^b	Non scaled	Scaled ^c	Int. (IR)	
	1	1064	w	1113	1070	167.13	vC=C
	2	1178	m	1209	1163	271.98	vC=C
	3	1275	w	1347	1295	140.91	vC—N
	4	1348	m	1377	1324	205.42	vC=C
	5	1502	S	1581	1520	456.79	vC=C (CH=CH)
	6	1592	v	1642	1579	474.29	vC=0 (CO)
	7	1712	m	1824	1754	612.72	vC=0 (COO)
	8	2361	w	2436	2342	119.38	νC=N
	9	3432	w	3584	3446	150.98	<i>v</i> О—Н (СООН)

^a Frequencies in cm⁻¹.

^b m: middle, s: strong, v: very strong, w: weak.

^c Scaling factor using 0.9613.



Fig. 9. Consistency of the wavenumbers of the calculated and experimental IR spectra main peaks of compound 3d.

experimental data of compound 3d is shown in Fig. 9. It could be seen that the linear slope and intercept were 1.0433, 2.1998 for the non-scaled data and 1.0030, 1.9585 for the scaled, respectively. These results indicate that the description error clearly decreased after the introduction of the frequency-scaling factor, and the calculated data are in good agreement with the experimental value.

4. Conclusions

Four novel ketocoumarin derivatives (3a–3d) were successfully synthesized and their photophysical properties were investigated.

These derivatives exhibited strong blue and green emissions in dilute solutions. The 6-311+G**(C-PCM)/TD-DFT(C-PCM) method provided a reliable description of the molecular absorption characters and reproduced the $\pi \to \pi^*$ type absorption bands of the compounds. Resonance frequency calculation was also performed to study the IR spectra of the compounds, and the calculated results were consistent with the experimental values. Furthermore, the four compounds are potential candidates for use in opto- or optoelectronic blue and green-emitting devices. Their other characteristics will be further investigated in future studies.

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