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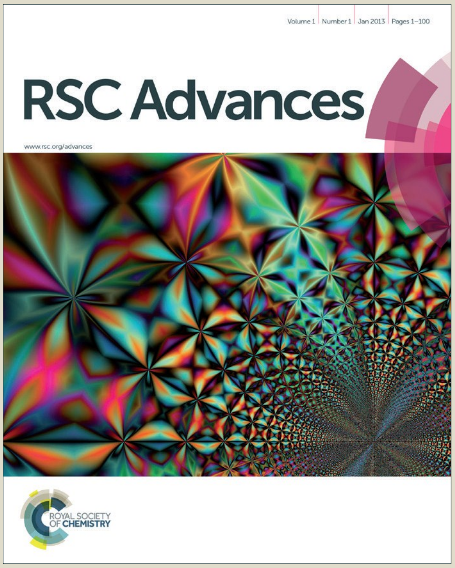

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High Quantum Yield and pH sensitive Fluorescence dyes Based on Coumarin Derivatives ： Fluorescence Characteristics and Theoretical Study

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ABSTRACT The fluorescence coumarin derivatives were synthesised by an efficient one-pot, three-component reaction in 80-90% yields. These fluorescence dyes exhibited high fluorescent intensity and quantum yield，which the compound **4e** with p-methyl substituted on the phenyl ring had the maximum fluorescence intensity and also the fluorescence quantum yield reached 0.83. These coumarin derivatives display the different fluorescence in acidity and alkaline conditions and the fluorescent colour changed from blue to yellow-green when the pH of solution turned acidic to alkaline. The pH sensitive fluorescence properties of the coumarin derivatives showed larger shift from 441 to 538 nm in wavelength. Experimental results have been confirmed with DFT and TDDFT calculations.

KEYWORDS: Fluorescent; Coumarin Derivatives; High Quantum Yield; Synthesis; DFT calculations;

INTRODUCTION

Coumarins consist of pyrone and benzene[1] which are considered with versatile applications in various fields of science and technology,[2] such as perfume,[3] cosmetic,[4] as a disperse dye,[5] cationic dye,[6] charge-transfer agent,[7] solar energy collectors[8] and potential application in organic light-emitting diodes (OLEDs)[9]etc. Besides, coumarin derivatives have played an important role in medicinal chemistry such as the platelet inhibition agent, antithrombus agent,[10] hepatoprotective and so on.

Coumarins are the well-known laser dyes for the bluegreen spectral region[11] whose derivatives is one of the most favorable fluorophore groups to develop fluorescence agent[12] because of its high quantum yields and high photostability.[13] It was reported[14] that the electron donating groups in the 7-position and electron-withdrawing groups in the 3-position can be able to enhance the fluorescence intensity of coumarins[15] based on an intramolecular charger transfer process.[16] Among different coumarin dyes , Xu's group reported that the 7-(N,N-diethylamino)coumarin-3-aldehyde were selected as fluorophore and ionphore for the construction of Cu^{2+} selective fluorescence sensors,[17] and in 2006 Li's group reported the 7-aminocoumarin derivatives dyes underwent change in their dipole moment on excitation from the ground to the excited S1 state transition.[18] Thus, these molecules are found to be suitable sensors in investigating many physical and physiochemical processes in the condensed phase,[19] making use of their fluorescence properties.

Optical methods[20] via fluorescent imaging and sensing are attracting attention for pH measurements due to its rapid response time,[21] simplicity, non-invasiveness and a good sensitivity.[22] Currently, a large number of fluorescence sensors for pH measurement have been reported in the literature and are commercially available due to its extensive applications. As an example, Liu[23] published coumarin sensors have optical responses in acid condition. Their studies disclosed that these coumarin derivatives could be used for quantitative fluorescence imaging in the detection of intracellular pH by the formation of an intramolecular charge transfer (ICT) platform in acidic environment, leading to colour changes. In addition, Oliveira's group[24] designed a new ratiometric fluorescent pH coumarin quinoline derivative sensor, whereas in acidic pH exhibits a strong fluorescence, being very useful for monitoring pH variations from neutral to acidic conditions in living cells.

To the best of our work, a series of high fluorescence quantum yield coumarin derivatives were synthesized in a very simple and facile economically cheap route which based on the literature from Ahmed' s group.[25] And the optical properties were investigated in the different conditions. There are high fluorescent intensity and quantum yield in DMSO. Moreover, we describe the different phenomenon between acid and alkaline in DMSO. Besides, we were using the DFT and TDDFT calculations to confirm the experimental results.

EXPERIMENTAL SECTION

General Methods.

All of the chemicals used in the current study were purchased from commercial vendors and used as received without further purification, unless otherwise noted. All solvents were purified and dried using standard methods prior to use. Nuclear magnetic resonance (^{1}H, ^{13}C) spectra were recorded on a Bruker AM 500 spectrometer with chemical shifts reported as ppm at 500, 125 MHz, respectively, (in DMSO and TMS as the internal standard). Fluorescence spectra were obtained with a F-7000 Fluorescence Spectrophotometer in a solution of 1.0×10^{-5} mol/L. UV-Vis absorption spectra were measured on a UV-2550. The absorption and emission studies at different pH were all measured in DMSO-water mixture (DMSO:H_2O=9:1).

General Procedure for the Synthesis of 4-aminocoumarin.

A mixture of well powdered 4-hydroxycoumarin (1.07 g, 0.0066 mol) and ammonium acetate (7.87 g, 0.100 mol) was melted in an oil bath (max. 130 ºC) and stirred for 3 h. After cooling to ambient temperature, water was added and the crude product was isolated as yellow crystals by simple filtration. 4-aminocoumarin was obtained by recrystallized from EtOH and water as yellow crystals (0.98 g, 92.2%).[25]

General Procedure for the Synthesis of compound 4a-4e.

A mixture of benzaldehyde (0.106 g, 1 mmol), 1,3-cyclohexanedione (0.112 g , 1 mmol) and 4-aminocoumarin(0.161 g, 1 mmol) in acetic acid (6 mL) was stirred for 2-3 h at 110 ℃ and complete reaction was detected by TLC analysis and then cooled to room temperature. Then, the reaction mixture was washed with H_2O (20 ml) and the crude product was recrystallized from DMSO to give product **4a** (0.295 g, 86.3 %) as light yellow solid.[25]

*7-phenyl-9,10,11,12-tetrahydro-6H-chromeno[4,3-b]quinoline-6,8(7H)-dione (**4a**)*

Light yellow solid. Yield 86%. Mp 296-298 □.^{1}H-NMR (DMSO, 500 MHz) δ (ppm): 9.76 (s,1H), 8.32 (d, *J* = 8.0 Hz, 1H), 7.62-7.65 (m, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 8.3 Hz, 1H), 7.11-7.24 (m, 4H), 7.09 (t, *J* = 7.2 Hz, 1H), 4.99 (s, 1H), 2.82-2.87 (m, 1H), 2.67-2.73 (m, 1H), 2.24-2.32 (m, 2H), 1.98-2.02 (m, 1H), 1.87-1.88 (m, 1H). ^{13}C NMR (DMSO, 125 MHz) δ (ppm): 194.93 (1C), 160.33 (1C), 152.02 (1C), 151.67 (1C), 145.90 (1C), 142.05 (1C), 131.92 (1C), 128.02 (2C), 127.65 (2C), 126.18 (1C), 123.97 (1C), 122.93 (1C), 116.85 (1C),113.03 (1C), 111.86 (1C), 101.78 (1C), 36.66 (1C), 34.12 (1C), 26.37 (1C), 20.71 (1C).

*7-(4-nitrophenyl)-9,10,11,12-tetrahydro-6H-chromeno[4,3-b]quinoline-6,8(7H)-dione(**4b**).*

Light yellow solid. Yield 90%. Mp 260-262 □. ^{1}H-NMR (DMSO,500 MHz) δ (ppm): 9.88 (s, 1H), 8.34-8.36 (m, 1H), 8.08-8.10 (m, 2H), 7.65-7.68 (m, 1H), 7.51-7.54 (m, 2H), 7.45-7.48 (m, 1H), 7.40 (t, J = 7.7 Hz, 1H), 5.11 (s, 1H), 2.87 (t, J=9.4Hz, 1H), 2.73 (t, J = 3.9 Hz, 1H), 2.27-2.33 (m, 2H), 1.98-2.02 (m, 1H), 1.88 (s, 1H). ^{13}C NMR (DMSO, 125 MHz) δ (ppm): 194.89 (1C), 160.21 (1C), 153.12 (1C), 152.31 (1C), 152.14 (1C), 145.94 (1C), 142.60 (1C), 132.22 (1C), 129.10 (2C), 124.06 (1C), 123.26 (2C), 123.12 (1C), 116.92 (1C), 112.83 (1C), 110.97 (1C), 100.63 (1C), 36.50 (1C), 34.96 (1C), 26.38 (1C), 20.61 (1C).

*7-(4-methoxyphenyl)-9,10,11,12-tetrahydro-6H-chromeno[4,3-b]quinoline-6,8(7H)-dione(**4c**).*

Light yellow solid. Yield 88%. Mp 276–278□. ^{1}H-NMR (DMSO,500 MHz) δ (ppm): 9.72 (s, 1H), 8.30-8.32 (m, 1H), 7.61-7.65 (m, 1H), 7.42-7.45 (m, 1H), 7.37 (t, J = 8.2 Hz, 1H), 7.13-7.14 (m, 2H), 6.75-6.77 (m, 2H), 4.93 (s, 1H), 3.66 (s, 3H), 2.81-2.86 (m, 1H), 2.65-2.72 (m, 1H), 2.24-2.32 (m, 2H), 1.98-2.03 (m, 1H), 1.84-1.90 (m, 1H). ^{13}C NMR (DMSO, 125 MHz) δ (ppm): 194.90 (1C), 160.32 (1C), 151.98 (1C), 151.32 (1C), 141.74 (1C), 138.23 (1C), 131.80 (1C), 128.59 (3C), 123.91 (1C), 122.86 (1C), 116.79 (1C), 113.38 (2C), 113.05 (1C), 112.09 (1C), 102.06 (1C), 55.99 (1C), 36.67 (1C), 33.19 (1C), 26.33 (1C), 20.74 (1C).

*7-(3-chlorophenyl)-9,10,11,12-tetrahydro-6H-chromeno[4,3-b]quinoline-6,8(7H)-dione (**4d**).*

Light yellow solid. Yield 82% . Mp 267–269 □. ^{1}H-NMR (DMSO,500 MHz) δ (ppm): 9.82(s, 1H), 8.33-8.35 (m, 1H), 7.46 (s, 1H), 7.39-7.41 (m, 1H), 7.36-7.38 (m, 3H), 7.28(m, 1H), 5.26 (s, 1H), 2.85-2.88 (m, 1H), 2.68-2.72 (m, 1H), 2.29-2.33(m, 2H), 2.00-2.02 (m, 1H), 1.83 (s, 1H). ^{13}C NMR (DMSO, 125 MHz) δ (ppm): 194.96 (1C), 160.30 (1C), 152.11 (1C), 149.12 (1C), 140.13 (1C), 133.39 (1C), 132.14 (1C), 131.21 (1C), 128.34 (1C), 126.83 (1C), 123.95 (1C), 121.08 (1C), 120.23 (1C), 116.82 (1C), 114.08 (1C), 113.04 (1C), 111.01 (1C), 101.09 (1C), 36.61 (1C), 33.93 (1C), 26.37 (1C), 20.65 (1C).

*7-(p-tolyl)-9,10,11,12-tetrahydro-6H-chromeno[4,3-b]quinoline-6,8(7H)-dione**(4e)**.* Light yellow solid. Yield 83%. Mp 304–305□.^{1}H-NMR (DMSO,500 MHz) δ (ppm) : 9.72 (s, 1H), 8.30-8.32 (m, 1H), 7.61-7.63 (m, 1H), 7.41-7.45 (m, 1H), 7.36 (t, *J* = 8.2 Hz, 1H), 7.12 (d, *J* = 8.05 Hz, 2H), 7.00 (d, *J* = 7.95 Hz, 2H), 4.95 (s, 1H), 2.82-2.86 (m, 1H), 2.69-2.71 (m, 1H), 2.18-2.31 (m, 2H), 2.19 (s, 3H), 2.0-2.02 (m, 1H), 1.82-1.89 (m, 1H). ^{13}C NMR (DMSO, 125 MHz) δ (ppm): 194.86 (1C), 160.28 (1C), 151.99 (1C), 151.40 (1C), 143.04 (1C), 141.87 (1C), 135.15 (1C), 131.81 (1C), 128.54 (2C), 127.52 (2C), 123.90 (1C), 122.87 (1C), 116.79 (1C), 113.02 (1C), 112.00 (1C), 101.91 (1C), 36.66 (1C), 33.66 (1C), 26.34 (1C), 20.72 (1C), 20.51 (1C).

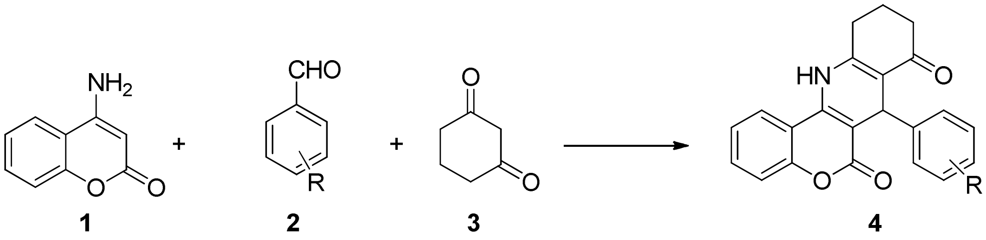
Computational Methodology.

All the structure optimization were based on density functional theory (DFT) with B3LYP functional and 6-311G basis set. For the fluorescence emission wavelength and the excitation wavelength of the compounds was calculated with the time-dependent density functional theory (TDDFT). All these calculations were performed with Gaussian 09W.[26]

RESULTS AND DISCUSSION

As shown in **Scheme 1**, the coumarin fused dihydropyridine derivatives **4** were synthesized by the efficient three-component reaction of 1,3-cyclohexadione, arylaldehydes and the product **4** were obtained in 86 % (**4a**), 90 % (**4b**), 88 % (**4c**), 82 % (**4d**), 83 % (**4e**) yields, respectively.

Para-nitro substituent on the benzene unit have the largest yields (90%) of the desired product was obtained. These compounds were all characterized by ^{1}H-NMR and ^{13}C-NMR.



4a R=H, 86%
4b R=4-NO$_2$, 90%
4c R=4-OMe, 88%
4d R=3-Cl, 82%
4e R=4-CH$_3$, 83%

Scheme 1. **Synthesis of coumarin fused dihydropyridine derivatives 4**.

UV-vis absorption and fluorescence emission spectra.

The absorption and fluorescence emission spectra of the coumarin fused dihydropyridine derivatives **4** was detected and summarized in **Fig. 1**. The fluorescence properties of the coumarin derivatives **4** were examined under different conditions such as: in different organic solvents and the different pH.

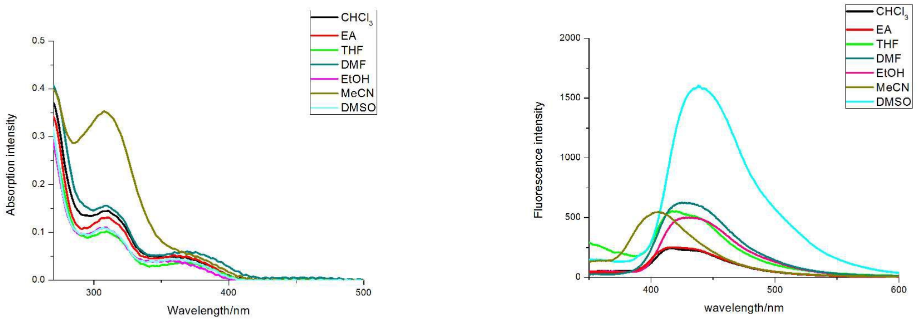


Fig. 1. Left: Absorption spectra of compound **4c** (1.0×10^{-5} mol/L) in different Solution (PMT Voltage: 900 V). Right: Fluorescence emission spectra of compound **4c** in different Solution (PMT Voltage: 500 V).

The solvent effect on the absorption and fluorescence properties of the 7-(4-methoxyphenyl)-9,10,11,12-tetrahydro-6H-chromeno[4,3-b]quinoline-6,8(7H)-dione(**4c**) were examined (**Fig. 1**, **Table 1**). As shown in **Fig. 1**, the coumarin **4c** showed a maximum sharp absorption peak at approximately 308 nm accompanied a shoulder peak at near 375 nm and were barely affected by solvent polarity. The molar absorption coefficient (ε) of **4c** underwent a slight change in different organic solvents and which in MeCN had the highest value.

Obviously, the compound **4c** shows the fluorescence emission wavelength at 438 nm with 375 nm as the excitation wavelength in the different organic solvents, excepted the slight blue shift in CH_3CN (410 nm). It's worth noting that the fluorescence intensity of the compound **4c** is much higher in DMSO than other solvents and thus we can anticipate the high fluorescence quantum yields in DMSO. Thus the Stokes shift is 63 nm in DMSO. So we selected DMSO as its best solvent for the study on the fluorescent properties of the compound **4**.

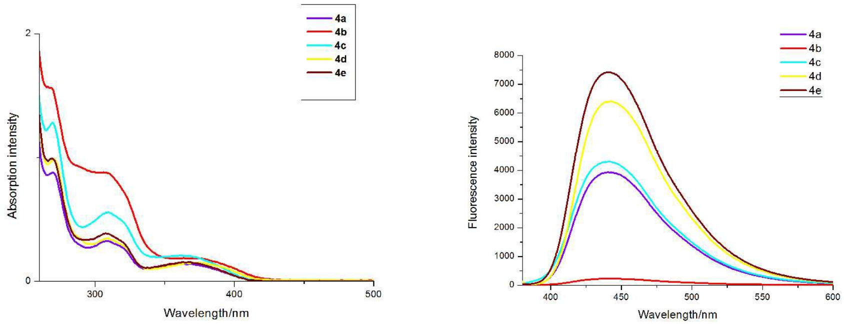


Fig.2. Left: Absorption spectra of different compounds (1.0×10^{-5} mol/L) in DMSO (PMT Voltage: 900 V). Right: Fluorescence emission spectra of different compounds **4a-4e** in DMSO (PMT Voltage: 600 V).

The absorption and fluorescence emission spectra of the compounds **4a-4e** in DMSO were shown in **Table 1** and **Fig. 2**. These compounds **4** showed the similar absorption, but a slight change in intensity with in the different substituted on the phenyl ring. Similarly, the fluorescence emission wavelength of **4** was at about 440 nm and showed a strong blue fluorescence, but the intensity of the fluorescence was significantly different with the different groups substituted on the phenyl ring of the coumarin fused dihydropyridine derivatives **4**. As shown in **Fig. 2**, the compound **4e** with p-methyl substituted on the phenyl ring had the maximum fluorescence intensity and also the fluorescence quantum yield reached 0.83. The compound **4a** (H), **4c** (4-OMe), **4d** (3-Cl) all had strong blue fluorescence and the fluorescence quantum yield is respectively 0.41, 0.26, 0.60. It is worth noting that compound **4e** shows unexpected high fluorescence quantum yields ($\Phi_F = 0.83$) than most of the fluorophores, and the Stokes shift of compound **4e** is 75 nm. The compound **4b** with p-nitro substituted on the phenyl ring displayed the maximum of absorption and the minimum of fluorescence intensity, so it’s fluorescence is weak and the fluorescence quantum yield is only 0.014. In addition, through the TD-DFT calculation, the HOMO–LUMO energy gap of compound **4b** is largest, which make the transition hard to happen. As shown in **Table 1**, the Stokes shift of the compound **4a, 4b, 4c, 4e, 4d** respectively were 72, 68, 80, 70, 75 nm in DMSO.

Table 1 Photophysical properties of compound 4a-4e.

compounds	λ^a_{abs}*(nm)*	λ^a_{em}*(nm)*	$\varepsilon(M^{-1}cm^{-1})$	Φ^a_F	SS^b*(nm)*
4a	368	440	14,000	0.41	72
4b	373	441	18,700	0.014	68

4c	361	441	20,800	0.26	80
4d	373	443	15,200	0.60	70
4e	366	441	15,300	0.83	75

[a]Measurements were performed in DMSO solvent. Fluorescence quantum yields were measured with quinine sulfate (Φ_F=54.6% in 0.05 M H_2SO_4) as the reference. [b]Stokes shift.

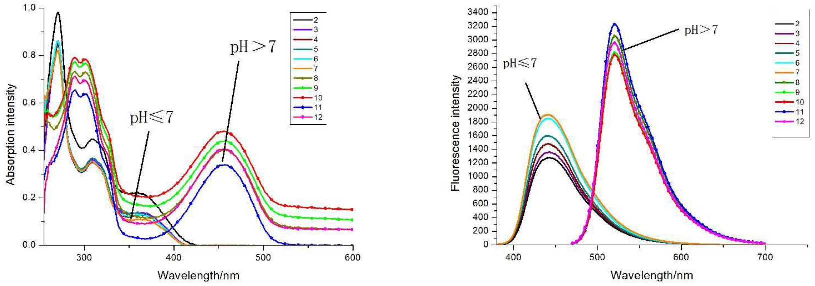


Fig. 3. Left: The absorption spectra of compound **4a** with different pH (1.0×10^{-5} mol/L) in DMSO-water mixture (DMSO:H_2O=9:1, PMT Voltage: 900 V). Right: Fluorescence emission spectra of compound **4a** (1.0×10^{-5} mol/L) with different pH in DMSO-water mixture (DMSO:H_2O=9:1, PMT Voltage: 500 V).

Fig. 4. Left: Compound **4a** (1.0×10^{-5} mol/L) under the visible light with different pH in DMSO-water mixture (DMSO:H_2O=9:1). Right: Compound **4a** (1.0×10^{-5} mol/L) under the UV lamp (365 nm) with different PH in DMSO-water mixture (DMSO:H_2O=9:1).

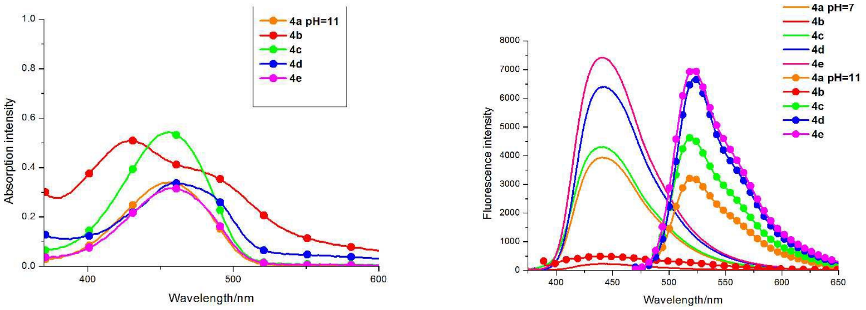


Fig. 5. Left: the absorption spectra of compound **4a-4e** (1.0×10^{-5} mol/L) with pH=11. Right: the fluorescence emission spectra of compound **4a-4e** (1.0×10^{-5} mol/L) with pH=7 and pH=11 in DMSO-water mixture (DMSO:H_2O=9:1, PMT Voltage: 550 V).

On the other hand, we also examined the absorption and fluorescence properties of the compound **4** under the different pH from 2 to 12 in DMSO-water mixture (DMSO:H_2O=9:1). As shown in **Fig.3** and **Fig.4** , the compound **4a** exhibited the different property of the UV-vis absorption and fluorescence spectra. A new absorption appeared at 455 nm which situated at visible region as the pH value gradually increased from 7 to 12 in DMSO-water mixture. It can be seen intuitively, the solution was colorless under acidic condition and lower yellow under basic condition. The fluorescence intensity of **4a** was obviously larger in the alkaline condition than in the acidic condition. The maximal emission wavelength of **4a** had an obvious red shift (103 nm) under the different pH conditions, which was displayed the blue fluorescence in 450 nm under acidic condition (pH: 2~7) and the yellow-green fluorescence in 553 nm under basic condition (pH: 7~12). This effect is brought about significant changes in fluorescence color, blue in acid solution and yellow green in the alkaline environment (**Fig. 4**). Moreover, the substituted compound **4c-4e** exhibited the same property accompanied by the change of pH value and the maximal absorption wavelength displayed a red shift from

375 nm to 450 nm with the solution from acid to alkaline. And then the fluorescence intensity varied with the pH obviously and the fluorescence intensity reached a maximum when the pH value of solution was reached to 11. However, the fluorescence emission wavelength of compound **4b** did not change significantly in alkaline condition. It happened due to the an intermolecular charger transfer (ICT) process.[27]

DFT calculations: rationalize the excitation and emission spectra. Recently theoretical calculations are becoming attractive for study of the fluorescence or molecular probes[26]. In older to support our assumptions we made the compounds geometry optimizations using the density functional theory (DFT) method as implemented in Gaussian 09W suits of the program employing basis sets B3LYP/6-311G (see **Fig.6**.). There are shown the most stable structures of compounds **4a-4e** and indicated that the precursor of these compounds containing a large conjugated system obviously.[28] Therefore, It is useful for the fluorescence properties.[29] However, the benzene ring which at the bottom of the pyridine do not in the same plane due to the steric effect of the carbonyl groups.

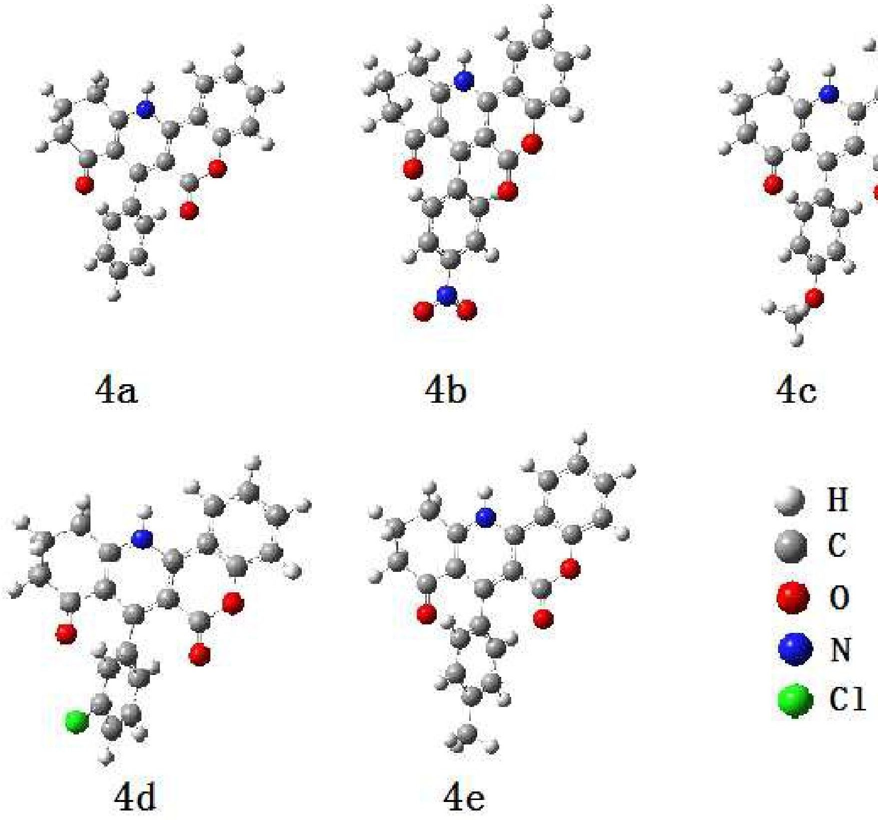


Fig.6 Optimized geometry of the compounds 4a-4e at B3LYP/6-311g level with Gaussian 09W.

TD-DFT calculations were performed at this study to further understand the mechanism of the fluorescence intensity with different groups by the energy and charge transfer model (see **Fig.7**). Besides, we calculated the fluorescence emission spectra and the HOMO–LUMO energy gap[30] by TD-DFT method as implemented(see **Table 2**). From this calculation, the compound **4b** is required more energy ($\Delta E = 0.66$ eV) to finish HOMO-LUMO transition and the compound **4e** is required least energy ($\Delta E = 0.31$ eV) to finish HOMO-LUMO transition on the contrary. Therefore, the photochemical property of the compound **4b (**$\Phi_F = 0.014$) is bad than the compound **4e (**$\Phi_F = 0.83$).

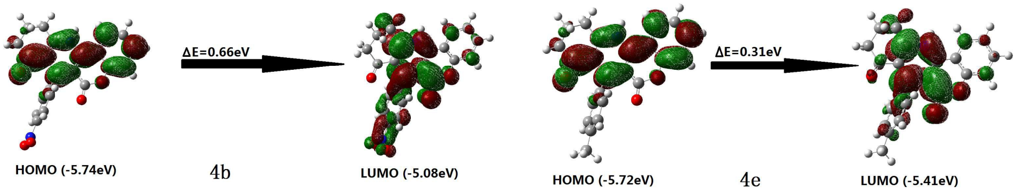


Fig.7 Frontier molecular orbitals of compound **4b** and **4e**

Table 2. Calculation data of compound 4a-4e.

compounds	λ^{a}_{cal} *(nm)*	λ^{b}_{exp} *(nm)*	λ^{c}_{cal} *(nm)*	λ^{d}_{exp} *(nm)*	f^{e}	*Transition character*	*Energy gap (eV)*
4a	450	440	372	368	0.0122	HOMO→LUMO	0.44
4b	473	441	375	373	0.0093	HOMO→LUMO	0.66
4c	455	441	368	361	0.0154	HOMO→LUMO	0.44
4d	447	443	373	373	0.0189	HOMO→LUMO	0.39
4e	459	441	367	366	0.0215	HOMO→LUMO	0.31

[a]theoretical calculations basis sets B3LYP/6-311G without solution (The calculated emission maximums). [b]λ_{max} in DMSO solvent (The experimental emission maximums). [c]theoretical calculations basis sets B3LYP/6-311G without solution (The calculated absorption maximums). [d]λ_{max} in DMSO solvent (The experimental absorption maximums). [e] Oscillator strength coefficients.

CONCLUSIONS

The coumarin fused dihydropyridine derivatives were prepared by an efficient one-pot, three-component reaction and obtained in good yield. The optical properties detection indicated that these coumarin derivatives had excellent fluorescence with high fluorescent quantum yield and exhibited significant emission change in fluorescence spectrum with the change of pH value. TD-DFT calculations were performed at this study to support our experiment results. Our findings will be useful for design of new pH probe fluorescent dyes with high fluorescent quantum yield and the chemical sensors for detecting pH environment.

Acknowledgement

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High Quantum Yield and pH sensitive Fluorescence dyes Based on Coumarin Derivatives：Fluorescence Characteristics and Theoretical Study

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ABSTRACT

The fluorescence coumarin derivatives were synthesised by an efficient one-pot, three-component reaction in 80-90% yields. These fluorescence agents exhibited high fluorescent intensity and quantum yield，which the compound **4e** with p-methyl substituted on the phenyl ring had the maximum fluorescence intensity and also the fluorescence quantum yield reached 0.83. These coumarin derivatives display the different fluorescence in acidity and alkaline conditions and the fluorescent colour changed from blue to yellow-green when the pH of solution turned acidic to alkaline. The pH sensitive fluorescence properties of the coumarin derivatives showed larger shift from 441 to 538 nm in wavelength. Experimental results have been confirmed with DFT and TDDFT calculations.