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Photophysical investigation of 3-substituted 4-alkyl and/or 7-acetoxy coumarin derivatives—A study of the effect of substituents on fluorescence

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ABSTRACT

In the present work an array of novel substituted 2H-chromen-2-one (coumarin) derivatives has been subjected to photophysical analysis. Though the influence of the electron-donating groups such as amino, substituted amino, hydroxyl, alkoxy groups, etc. at position 7 of the coumarin ring system has been extensively studied, the luminescent properties of the coumarin moieties with an acetoxy substituent have not been explored. Herein it is attempted to study the variation of fluorescence behavior of substituted coumarin derivatives with change of nature and position of the substituents on the 2H-chromen-2-one skeleton. Effect of a methyl substituent at position 4 which imposes abnormal photophysical behavior to the chromenone unit has also been briefly described.

1. Introduction

During the last few years there has been a remarkable growth in the use of fluorescence in biological sciences especially in biochemistry and biophysics. Fluorescence also finds application in environmental monitoring, clinical chemistry, DNA sequencing and genetic analysis by fluorescence *in situ* hybridization (FISH). In molecular biology, fluorescence is used for cell identification and sorting in flow cytometry, and in cellular imaging to reveal the localization and movement of intracellular substances by means of fluorescence microscopy. Because of the high sensitivity of fluorescence detection, there is continuing development of medical tests based on the phenomenon of fluorescence. These tests include the widely used enzyme linked immunoassays (ELISA) and fluorescence polarization immunoassays.

Coumarin derivatives are the subject of photophysical studies during the last few decades as they are highly fluorescent molecules. The nature and position of the substituents on coumarin ring has profound importance in deciding the photophysical behavior of the substituted coumarin compounds. Coumarins substituted at position 7 with an electron-donating group are known to exhibit strong fluorescence [1]. As 7-aminocoumarins are highly fluorescent, they have been used as optical brighteners and fluorescent probes. Substituted 7-aminocoumarins also form an important class of laser dyes for the blue-green region. The photophysical properties of these compounds depend on the nature and position of a substituent group in the parent molecule and also vary with surrounding media. Coumarins are used as non-linear optical chromophores and as an excellent probe to study solvation dynamics in homogeneous solutions as well as organized media [2–8]. In the recent past, numerous coumarin heteroderivatives have been synthesized and the possibility of their applications as laser dyes, organic scintillators and triplet sensitizers have been explored [9–13]. In a series of earlier works the effect of solvents, substituents and temperature on the various photophysical properties of coumarin compounds have been reported [14–19]. It is found that the nature of solvents and substituents bring about changes in the values of fluorescence wavelength maxima, quantum yield, lifetime, polarization and excited-state dipole moment of the coumarins [18]. A systematic study of fluorescence quenching of 4- and 7-substituted coumarins by halide ions in aqueous media has also been conducted previously [3,19]. Recently, photochromic and redox properties of a series of 2H-pyrano[3,2-c]chromen-5-one derivatives were investigated by the UV/vis absorption spectroscopy [20].

The influence of the alkoxy substituent at position 7 and alkyl group at position 4 of the coumarins has been investigated by Diehl et al. [15]. The spectroscopic properties of 7-dialkylamino and 3-styryl substituted coumarins have been studied by Raju and Varadarajan [16]. The solvent effect on the absorption and fluorescent spectra of some 6-alkylamino-7-alkyl coumarin derivatives

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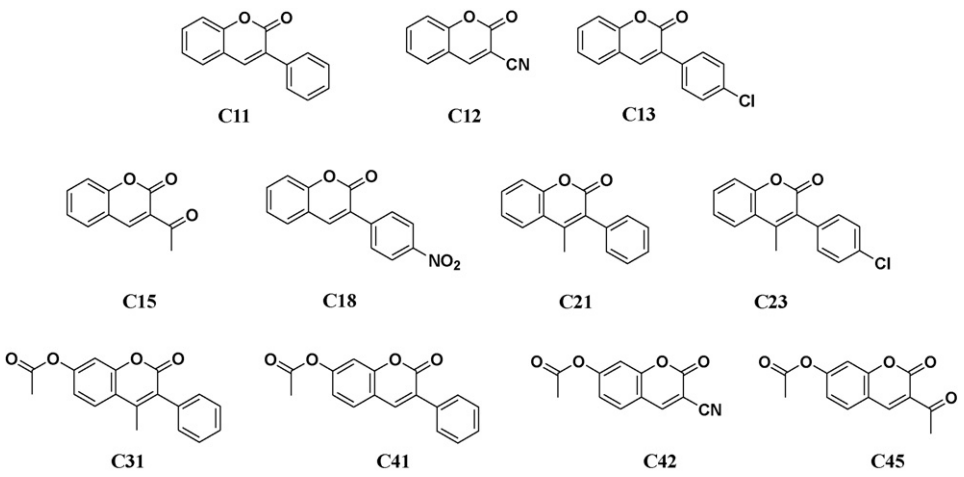

Fig. 1. Substituted coumarin derivatives under study.

have been reported recently [17]. The spectroscopic analyses of coumarins with bulky groups such as phenyl, phenylthio, benzylthio, etc. substituted at position 3 were reported in solvents of different viscosity and polymer matrices [2]. The dependence of various photophysical parameters on concentration [18], polarity and viscosity of the solvents and effect of various substituents on some biscoumarins [21], cyclopentacoumarins [11], aminocoumarins [22], etc. have been reported in the subsequent years. Recent reports by Zhao et al., on coumarin chromophores demonstrated with the support of theoretical and experimental studies that the hydrogen-bonding dynamics can strongly facilitate the ultrafast radiationless deactivation process, such as internal conversion and intermolecular photoinduced electron transfer in fluorophores [23–25]. In a different study, Liu and co-workers investigated theoretically the electronic excited-state hydrogen-bonding dynamics of photoexcited coumarin chromophore in hydrogen-donating aniline solvent [26].

In the present work an array of substituted 2H-chromen-2-one derivatives has been subjected to photophysical analysis. Although the influence of the electron-donating groups such as amino, substituted amino, hydroxy, alkoxy groups, etc. at position 7 of the coumarin ring system has been extensively studied, the luminescent properties of the coumarin moieties with an acetoxy substituent have not been explored. Hence our interest was to exploit the luminescence of these coumarins to find application in industries and biological field. Nowadays coumarins are used in dye-laser techniques [27,28], transcription assays [29], intrinsic probe for labeling peptides [30], etc. To know the applicability based on fluorescence of any molecule, the knowledge of photophysical parameters and the factors governing it are essential. Therefore the aim of the present study is to determine the basic spectroscopic and photophysical data for the compounds given in Fig. 1 and analyze the variation of their properties in the presence and absence of certain functional groups.

2. Materials and methods

2.1. General

All the chemicals used are of synthetic grade and purified before use. The melting points are determined using a GUNF melting point apparatus and are uncorrected. IR spectra are measured on a JASCO FT/IR-4100 spectrophotometer by KBr pellet method, NMR spectra recorded on a BRUKER AVANCE DPX 300 MHz spectrometer using TMS as internal standard and mass spectra on a SHIMADZU GC-MS-QP 2010 mass spectrometer. Microwave irradiation is done using a modified microwave assisted reacting system, MARS 1505 (CEM corporation, USA).

2.2. General synthetic procedure for coumarin derivatives [31]

Substituted 2-hydroxybenzaldehydes/2-hydroxyacetophenone (10 mmol), substituted acetic acid/derivatives (10 mmol), triethylamine (0.7 ml, 5 mmol) and acetic anhydride (5 ml) are taken in a 50 ml stoppered flask, mixed well and irradiated under 120 W microwave for 5 min intermittently. The reaction mixture is poured into ice-cold water, stirred for half an hour at low temperature (0–10 °C), the separated solid is washed repeatedly with dilute $NaHCO_3$ solution and distilled water, dried and re-crystallized to more than 90% purity from ethanol. The final purification is done with chromatography using a 100–200 mesh silica gel column with light petroleum-ethyl acetate as the eluent by gradient elution technique. The yield is 65–88%.

2.3. Electronic spectral measurements

Electronic absorption spectra were recorded on a Shimadzu UV-3101 PC UV/VIS/NIR scanning spectrophotometer or SYSTRONIC double beam UV/VIS spectrophotometer. The emission spectra were recorded on a SPEX-Fluorolog F112x spectrofluorimeter. The absorption measurements were carried out using 1 mm cuvette and fluorescence measurements were carried out using 1 cm × 1 cm cuvette. The fluorescence quantum yields of all the coumarin derivatives in DMSO were estimated by comparison with quinine sulfate in 0.1 M sulfuric acid ($\Phi_F = 0.546$) as the standard reference [32].

2.4. Fluorescence lifetime measurements

Fluorescence lifetimes were measured using IBH (FluoroCube) time-correlated picoseconds single-photon counting (TCSPC) system. Solutions were excited with a pulsed diode laser (<100 ps pulse duration) at a wavelength of 375 nm (NanoLED-11) with a repetition rate of 1 MHz. The detection system consisted of a microchannel plate photomultiplier (5000U-09B, Hamamatsu) with a 38.6 ps response time coupled to a monochromator (5000 M) and TCSPC electronics (Data station Hub including Hub-NL, NanoLED controller and preinstalled fluorescence measurement and analysis studio (FMAS) software). The fluorescence lifetime values were obtained using DAS6 decay analysis software. The quality of the fit has been judged by the fitting parameters such as χ^2 (<1.3) as well as the visual inspection of the residuals.

Table 1
Photophysical parameters of coumarin derivatives.

Entries	λ_A (nm)	ε_A (M^{-1} cm^{-1})	λ_F (nm)	Stokes Shift ν_S (cm^{-1})	Φ_F	τ_{av} (ns)	k_R (10^7 s^{-1})	k_{NR} (10^7 s^{-1})
C11	304	11,601	404	6922	0.060	0.95	6.32	98.94
	326	12,431	421			1.36	4.41	95.59
C12	358	1573	435	4944	0.006	3.74	0.16	99.83
C13	326	14,938	405	5984	0.153	0.50	30.41	168.39
	304	13,300	423			0.41	37.05	205.08
C15	300	9800	435	6862	0.003	3.66	0.08	27.24
	345	6200						
C18	343	19,657	435	6166	0.002	2.48	0.08	40.32
C21	285	11,600	406	7115	0.003	3.09	0.11	32.25
	317	9980						
C23	286	14,600	403	6932	0.007	0.98	0.72	101.85
	319	12,500						
C31	288	14,136	431	8344	0.006	2.56	0.23	38.83
	317	11,900						
C41	328	13,400	428	7124	0.250	2.22	11.26	33.78
C42	298	7700	408	9048	0.024	0.80	3.00	122.00
	329	6800						
C45	301	8600	466	11,764	0.040	3.25	1.23	29.53
	339	8400						

3. Results and discussions

The optical properties are investigated in detail by measuring the UV/vis absorption (as expressed by the molar absorption coefficient, ε_A), steady state and time resolved fluorescence. The photophysical parameters like extinction coefficient (ε_A), quantum yield (Φ_F), lifetime values (τ_F) radiative (k_R) and non-radiative (k_{NR}) decay constants form a basic set of data characterizing a luminescent molecule. An analysis on the correlation between the optical properties and structural characteristics of newly synthesized coumarin derivatives reveals some interesting results.

3.1. Absorption and emission properties of coumarin derivatives

All the measurements have been made in the polar solvent, dimethyl sulfoxide (DMSO), as it is the only solvent in which all the compounds are soluble. The absorption maxima (λ_A), and the molar extinction coefficients (ε_A) and absorption spectra are shown in Table 1 and Fig. 2 respectively.

It is known that the spectral shifts result from the general effect of solvent polarity whereby the energy of the excited-state decreases with increasing solvent polarity. However, spectral shifts also occur due to specific fluorophore–solvent interactions caused by charge separation in the excited state. Hence emission from fluorophores generally occurs at wavelengths, which are longer than those at which absorption takes place. This loss of energy is also due to various dynamic processes, which occurs following the light absorption [32].

Coumarins are polar in nature and hence display large sensitivity to the solvent polarity. Solvent polarity and the local environment have profound effects on the emission spectra of polar fluorophores. Previous studies demonstrated that substituted coumarin molecules exhibit solvatochromic effect in different solvents with varying polarity due to internal charge transfer (ICT) [16,17]. However, in the current investigation the solvatochromic effect of all the coumarin derivatives in different solvents could not be studied due to the solubility problem. The emission maxima (λ_F) and emission spectra are shown in Table 1 and Fig. 3 respectively.

The Stokes shift (ν_S) calculated for all the coumarin derivatives are given in Table 1. The Stokes shifts are expressed in wave number

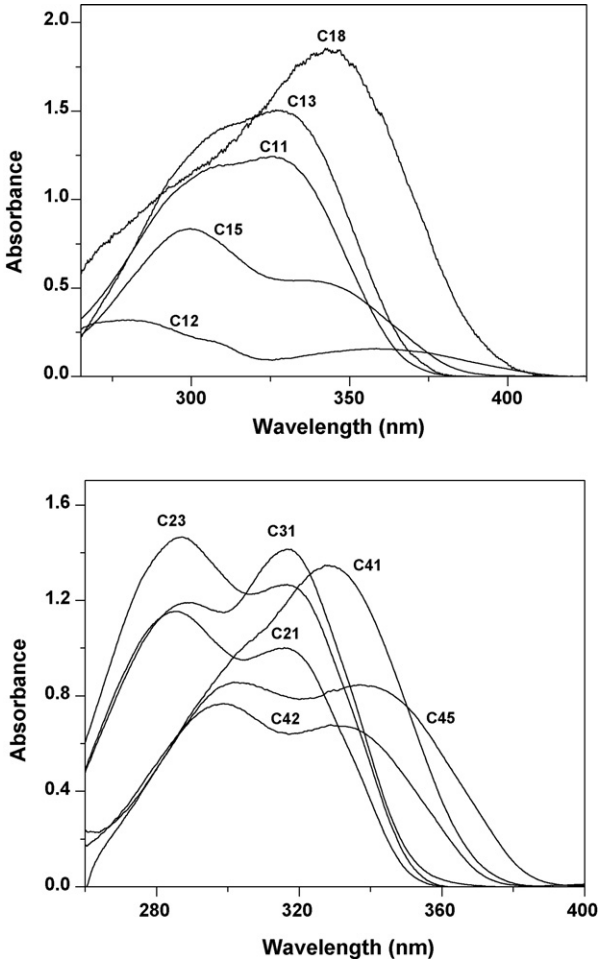

Fig. 2. Absorption spectra of coumarin derivatives.

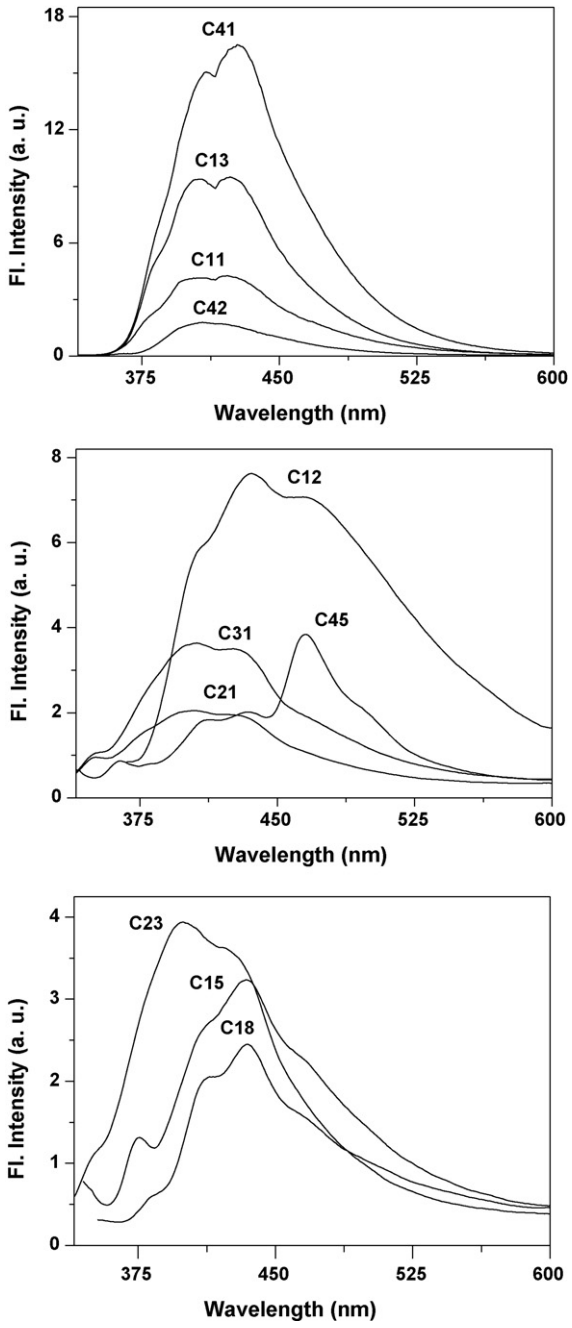

Fig. 3. Emission spectra of coumarin derivatives.

and are calculated from the experimental parameters by taking the difference between absorption and emission maxima expressed in wave number using the equation [32]:

Stokes shift, $\nu_S = (\bar{\nu}_A - \bar{\nu}_F) \times 10^7\ \mathrm{cm}^{-1}$,

where

$$\bar{\nu}_A = \frac{1}{\lambda_A}\,(\mathrm{nm})$$

and

$$\bar{\nu}_F = \frac{1}{\lambda_F}\,(\mathrm{nm})$$

The moderately high Stokes shift observed for all coumarin derivatives are ascribed partly to the polarity of the solvent, DMSO. The relatively long timescale of fluorescence allows ample time for the solvent molecules to reorient around the excited-state dipole, which lowers its energy and shifts the emission to longer wavelengths. This process of solvent relaxation results in substantial Stokes shift.

3.2. Quantum yield

Quantum yield of a molecule is a direct measure of its luminescent property. If the absolute fluorescence efficiency of one substance (reference Φ_r) is known, then that of the other (sample Φ_s) can simply be calculated. Quinine sulfate in dilute H_2SO_4 (0.1 M) has been used as a standard substance for quantum yield measurements. The quantum yield of a solution of quinine sulfate in 0.1 M H_2SO_4 is known to be 0.546 and hence the quantum yield values of the coumarin derivatives are calculated knowing the other parameters [32]. The experiments were done using optically matching solutions and the quantum yield is calculated using the following equation:

$$\Phi_s = \Phi_r \left[\frac{A_r F_s}{A_s F_r}\right] \left[\frac{\eta_s{}^2}{\eta_r{}^2}\right]$$

where A_r and A_s are the absorbance of the 'reference standard' and 'sample' respectively at the excitation wavelength, F_r and F_s are the relative integrated fluorescent intensities (area under the fluorescence curve, peak area) of the reference and samples respectively. η_r and η_s are respectively the refractive indices of the solvents in which the reference standard and samples are prepared.

A general trend of decrease in quantum yield is observed for all these compounds in DMSO (Table 1). This is presumably due to the solvent relaxation resulting from the excited-state internal charge transfer (ICT) of fluorophores. The large Stokes shift of these fluorophores also point towards an ICT emission in highly polar solvents. In addition to specific solvent–fluorophore interactions and ICT state formation, the fluorophores can also form a twisted internal charge-transfer (TICT) state.

A keen examination of the quantum yields also reveals some interesting results regarding the influence of substituents on the pyrone ring as well as the aromatic ring. The presence of electron-withdrawing groups (–CN, $-COCH_3$, *p*-NO_2-phenyl) at position 3 of the benzopyrone ring is found to decrease the fluorescence quantum efficiency whereas electron-donating functionalities (phenyl, *p*-Cl-phenyl) cause an increase in quantum yield of the molecules. Another observation is that an acetoxy group at position 7 of the coumarin ring increases the fluorescence of the coumarins. These results are in conjunction with those reported literatures [21,22].

3.3. Abnormal photophysical behavior of coumarin derivatives with a methyl substituent at position 4

On a perusal of the photophysical values of the coumarin derivatives under investigation (Table 1), the noteworthy observations that could be made is that, when an alkyl group (methyl) is present at position 4 of the benzopyrone ring, the fluorescence of the compound is diminished to a great extent, which is different from the earlier reports [15]. This is discussed in detail in view of the photophysical properties of the representative compounds C41 (Φ_F = 0.25) and C31 (Φ_F = 0.006) (Table 1).

Compounds C41 and C31 differ only by a methyl group at position 4 (Fig. 1). But the quantum yield of C31 is found to be 40 times lesser than that of C41. One of the possible explanations for the discrepancy could be that, the electron-donating ability of methyl group on the benzopyrone ring of the compound C31 can lead to an enhanced donor–acceptor capability compared to C41, which eventually helps the molecule to form a better internal charge transfer state (ICT) upon excitation.

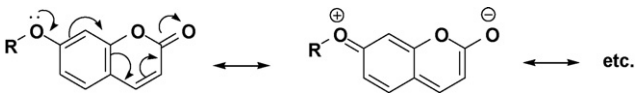

Fig. 4. Electron displacement in 7-hydroxy/7-acetoxy coumarin.

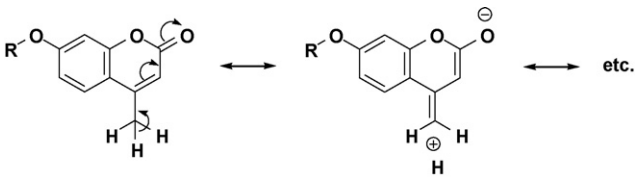

Fig. 5. Electron displacement in 7-hydroxy/7-acetoxy coumarin in the presence of a methyl group at position 4.

Another reason for a reduced fluorescence in the presence of a methyl group at position 4 could be suggested on the basis of the following electron displacement mechanism that can happen in the coumarin structure. Generally in 7-hydroxy/7-acetoxy coumarin, the electron displacement that will results the polarity at carbonyl carbon can be represented as in Fig. 4.

Similarly the electron interaction in the presence of a methyl group at position 4 of the coumarin ring is as shown in Fig. 5.

In the case of 7-acetoxy-4-methyl coumarin derivatives the decreased fluorescence observed could be attributed in part to the competitive electronic interactions of the two substituents with the lactone carbonyl group. Thus the effect of the acetoxy group at position 7 is reduced and hence the fluorescence. In addition to these, the methyl group at position 4 of the coumarin may have a major impact on the conformation of phenyl ring at position 3. During photo excitation, because of the steric effect of the methyl substituent, a geometric twist can occur by the rotation of phenyl ring through C–C bond at position 3, which can make the molecule as whole nonplanar. This twisted state may disrupt the π-conjugated bridge that connects the donor with the acceptor and can subsequently result in a drastic change on their fluorescence quantum yields presumably via a TICT mechanism. Under this condition, the excited-state dipole moment of the compound C31 would be high

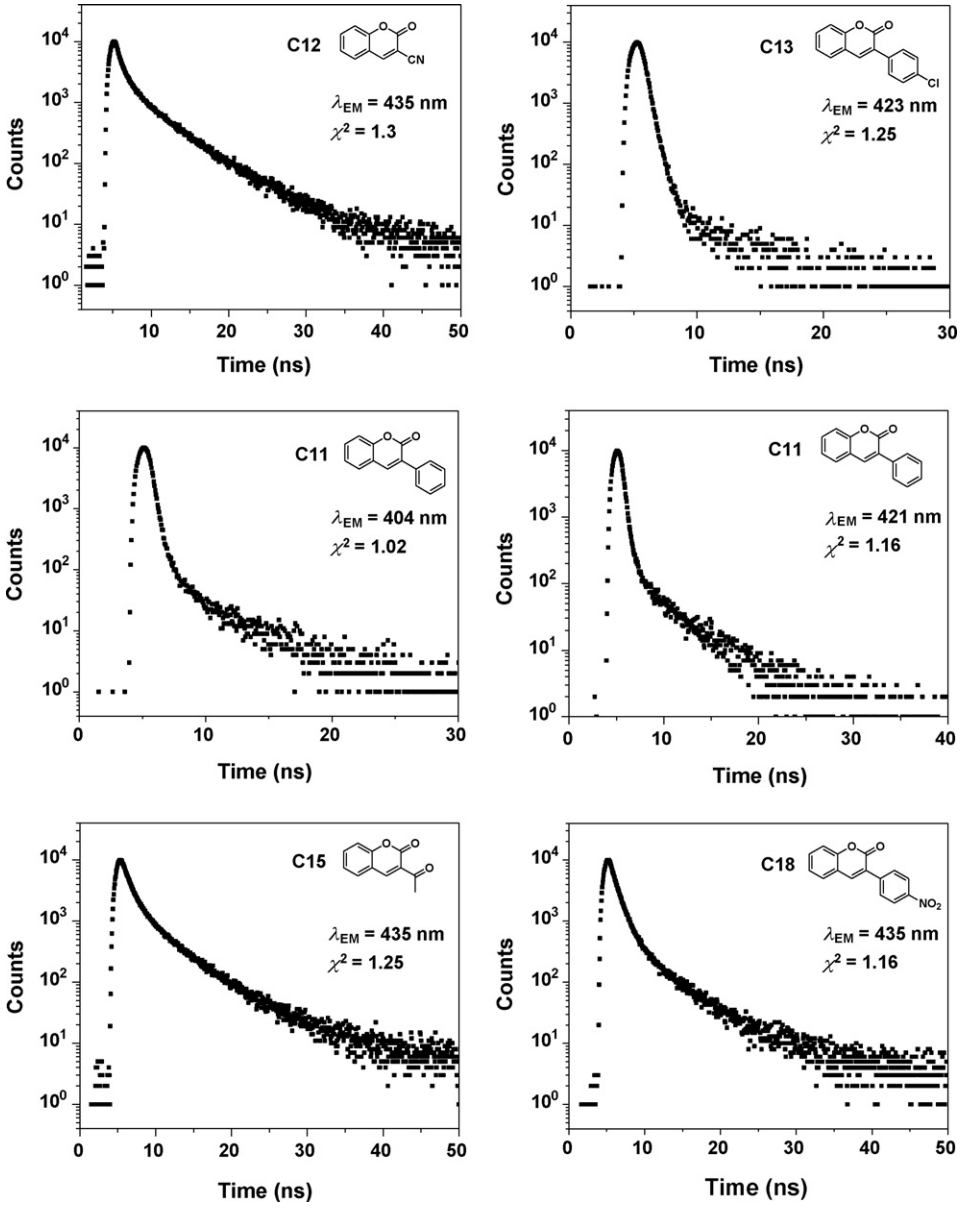

Fig. 6. Fluorescent lifetime decays of compounds C11, C12, C13, C15, and C18. λ_{EM} is the emission wavelength at which fluorescent lifetime is monitored.

compared to that of C41 and may result in a higher stabilization of the excited state of C31 by solvent relaxation. This argument is supported by the higher Stokes shift and lower radiative decay values of C31 ($\nu_S = 8344\,cm^{-1}$, $k_R = 0.23 \times 10^7\,s^{-1}$) when compared that of C41 ($\nu_S = 7124\,cm^{-1}$, $k_R = 11.26 \times 10^7\,s^{-1}$).

Apart from the above mentioned reasons, on the basis of the recent literature [25], it can also be proposed that the fluorescence quenching of C31 is feasible by an intermolecular electron transfer from the solvents to the fluorophore, especially when the donor-acceptor capability of C31 became increased by an electron-donating methyl group at position 4 of benzopyrone ring (Fig. 5). Although it could not be established due to the insolubility of present coumarin derivatives in protic solvents, there is a possibility of a hydrogen-bonding dynamics in fluorescence quenching by the ultrafast radiationless deactivation process [23–26].

Similarly, a marginal decrease in the fluorescent property with the presence of a methyl group is observed in the case of compounds C13 ($\Phi_F = 0.153$) and C23 ($\Phi_F = 0.007$) (Fig. 1; Table 1). Compounds C11 ($\Phi_F = 0.06$) and C21 ($\Phi_F = 0.003$) are considered as less emissive species in DMSO on the basis of the quantum yield values. Even in this case also a well defined trend in decrease of fluorescence in the presence of methyl group is apparent. The quantum yield value of the C21, which is having a methyl group at position 4 is nearly 20 times less than that of the compound C11 that lacks it (Fig. 1; Table 1).

3.4. Fluorescent lifetime studies

The fluorescent decay of all the substituted coumarin derivatives have been measured and plotted in Figs. 6 and 7.

From these figures, it is obvious that all the compounds follow a characteristic bi-exponential fluorescent decay, which reveals the existence of two different emissive states for the molecule, which could be the locally excited state (LE, Franck-Condon state) and charge transfer state (CT). The χ^2 values, which are known as the

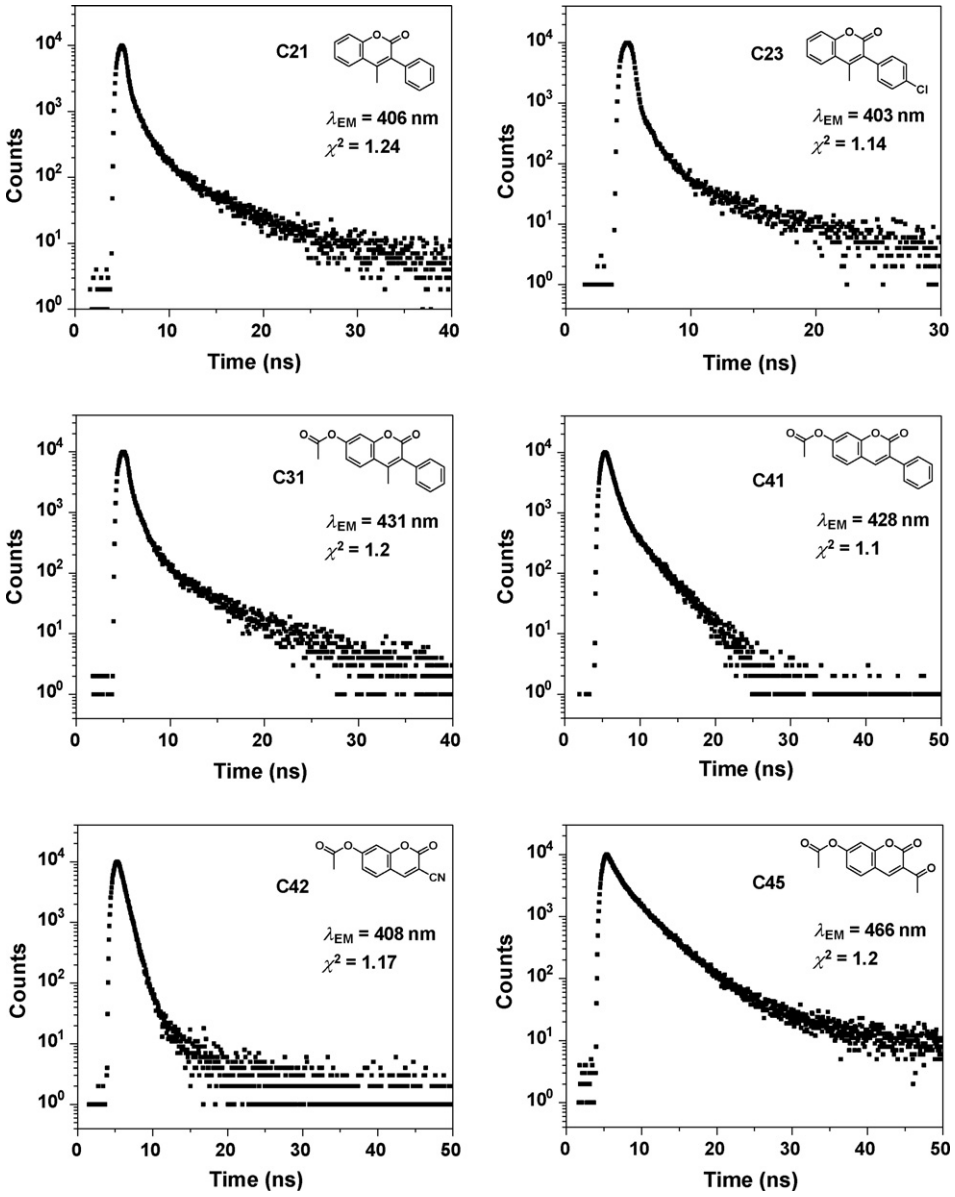

Fig. 7. Fluorescent lifetime decays of compounds C21, C23, C31, C41, C42, and C45. λ_{EM} is the emission wavelength at which fluorescent lifetime is monitored.

fitting parameter, determine fine fit for the bi-exponential decay and are found to be <1.3 and the average lifetime (τ_{av}) is calculated using the following equation [32]:

$$\tau_{av} = \frac{\alpha_1\tau_1^2 + \alpha_2\tau_2^2}{\alpha_1\tau_1 + \alpha_2\tau_2}$$

where τ_1 and τ_2 are the lifetime values of the two emissive states and α_1 and α_2 are called the pre-exponential factors, which give the abundance of each emissive state. The average lifetime values of all coumarin derivatives are summarized in Table 1.

3.5. Radiative and non-radiative decay constants

The fluorescence emission is a random process and occurs by a unimolecular process. The radiative lifetime of the excited state may be defined in terms of a first order decay process. The radiative decay constant (k_R) and non-radiative decay constant (k_{NR}) can be calculated by knowing the quantum yield (Φ_F) and lifetime values (τ), which are related by the equation [32]:

$$k_R = \frac{\Phi_F}{\tau} \quad \text{and} \quad k_{NR} = \tau^{-1} - k_R$$

The calculated values of the k_R and k_{NR} are shown in Table 1. Most of the compounds have significant k_{NR} values. It may be ascribed to the vibrational relaxation during the charge transfer process. The high k_{NR} values for few molecules (C13, C14, and C42) are apparently due to the torsional vibrations of the substituents on the coumarin ring in addition to the vibrational relaxation during the charge transfer.

4. Conclusions

In the present study the luminescence parameters of some novel acetoxy coumarin derivatives have been reported for the first time and a study of the variation of photophysical properties in the presence of substituents on the coumarin chromophore has been carried out. Most of the results obtained here for the substituents effect on luminescence are in close agreement with the earlier reports that an electron-donating substituent at position 3 of the coumarin ring increases the fluorescence and an electron-withdrawing group at position 3 decreases the same [2,21,22]. However some interesting results are emerged from the present study. An electron-donating acetoxy group at position 7 seems to enhance the luminescent property of coumarin derivatives to high extent. An extraordinary decline in the fluorescence of coumarin derivatives are observed when a methyl group is present at position 4, which differ from the report of an enhanced quantum efficiency of the coumarin molecules with the presence of alkyl group at position 4 [15]. This discrepancy in fluorescence with the presence of a methyl group requires an extensive experimental investigation with the support of a theoretical evaluation. Thus it is evident that depending upon the need for its application, the photophysical properties can be varied suitably by incorporating electron donating or withdrawing substituents at different positions of the coumarin scaffold. An examination of the feasibility to use some of the acetoxy coumarin compounds in cell imaging and dye-laser techniques is in progress.

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