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Synthesis of highly fluorescent coumarinyl chalcones derived from 8-acetyl-1,4-diethyl-1,2,3,4-tetrahydro-7*H*-pyrano[2,3-*g*]quinoxalin-7-one and their spectral characteristics

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ABSTRACT

A series of novel coumarin based chalcones were synthesized by the classical crossed aldol condensation reaction of 8-acetyl-1,4-diethyl-1,2,3,4-tetrahydro-7*H*-pyrano[2,3-*g*]quinoxalin-7-one and various substituted benzaldehydes. These novel ketocoumarin derivatives having a 1,4-diethyl-1,2,3,4-tetrahydroquinoxaline framework exhibited brilliant fluorescence. The novel chalcones absorbed in the range of 458–523 nm in various solvents. The wavelength of maximum absorption of these chalcones was found to be significantly longer than their simple acyl derivative known in the literature. The dyes displayed longer wavelength of absorption in the high polarity solvents compared to non-polar solvents. Thermogravimetric analysis of the chalcones revealed that the chalcones possess good thermal stability.

1. Introduction

Coumarins are one of the most important classes of organic heterocyclic molecules and possess versatile applications in various fields of science and technology. Due to inherent photochemical characteristics, reasonable stability, good solubility and relative ease of synthesis coumarin derivatives have been extensively investigated for electronic and photonic applications such as charge-transfer agents, solar energy collectors and nonlinear optical materials [1–3]. They are useful as optical brighteners, laser dyes, electroluminescent materials, two photon absorption (TPA) materials, as well as fluorescent labels and probes in biology and medicine [4–8]. It is well known that the property of fluorescence in the coumarin system is significantly altered by appropriate substituents at the 3- and the 7-position. Appropriately substituted coumarins find application as fluorescent dyes for synthetic fibres and as daylight fluorescent pigments, which impart vivid brilliance to paints and printing inks [9,10].

On the other hand, chalcones, the open chain molecules bearing a 3-aryl-2-propenoyl unit, are found to be effective photosensitive materials, and exhibit promising nonlinear optical properties [11]. Ketocoumarins are found to be highly efficient photosensitizers and photoinitiators in UV–vis curable systems [12]. Recent research suggests that the attachment of a 3-aryl-2-propenoyl unit to the coumarin ring appears quite promising for the synthesis of derivatives with enhanced TPA cross-sections [13].

Our research group was interested in preparing heteroaromatic derivatives, in particular, fluorescent coumarin derivatives, for various potential applications. We have reported the synthesis and spectroscopic properties of novel coumarin derivatives having a 1,4-diethyl-1,2,3,4-tetrahydroquinoxaline framework as an electron donating system [14]. These novel coumarin derivatives possessing a 1,4-diethyl-1,2,3,4-tetrahydroquinoxaline framework exhibited brilliant fluorescence, pronounced bathochromicity and good thermal stability. To extend our study on highly fluorescent compounds, one of these derivatives, 8-acetyl-1,4-diethyl-1,2,3,4-tetrahydro-7*H*-pyrano[2,3-*g*]quinoxalin-7-one, was utilized to synthesize chalcone derivatives by condensing it with various substituted benzaldehydes. In the present short paper a series of novel coumarinyl chalcones derived from 8-acetyl-1,4-diethyl-1,2,3,4-tetrahydro-7*H*-pyrano[2,3-*g*]quinoxalin-7-one is reported. The spectral properties of these novel chalcone derivatives were measured in various solvents differing considerably in polarity. The spectral properties of chalcones were compared with their analogues

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reported in the literature. Additionally, these ketocoumarins were subjected to thermogravimetric analysis in order to investigate their thermal properties.

2. Experimental

2.1. Materials and equipment

All melting points are uncorrected and are in °C. FT-IR spectra were recorded on a Bomem Hartmann and Braun MB-Series FT-IR spectrophotometer. ^{1}H NMR spectra were recorded using a Varian 300 MHz mercury plus instrument by dissolving the appropriate compound in deuterated chloroform. The chemical shifts are expressed in δ ppm using TMS as an internal standard. Microanalysis for C, H and N were performed on Thermo Finnigan Elemental analyzer. Electronic spectra were recorded on Spectronic spectrophotometer from dye solutions in DMF, acetonitrile, hexane, toluene, chloroform, ethyl acetate and methanol. The fluorescence spectra of the dyes were recorded on Jasco FP-1520 fluorimeter. The quantum yields were determined in chloroform using Rhodamine 6G as a standard according to the procedure reported in the literature [15,16]. Thermogravimetric analysis was carried out on SDT Q600 v8.2 Build 100 model of TA instruments. Common reagent grade chemicals were procured from s d fine-chem Ltd., Mumbai and were used without any further purification.

2.2. Synthesis of chalcone derivatives ***3(a–f)***

2.2.1. 1,4-Diethyl-1,2,3,4-tetrahydro-8-(3-phenylacryloyl)pyrano[3,2-g]quinoxalin-7-one ***3a***

8-Acetyl-1,4-diethyl-1,2,3,4-tetrahydro-7*H*-pyrano[2,3-*g*]quinoxalin-7-one **1** [14] (3.0 g, 0.01 mol) and benzaldehyde 1.06 g (0.01 mol) were dissolved in dry ethanol (20.0 mL). Piperidine (0.1 mL) was added and the reaction mixture was heated under reflux for 12 h. Ethanol was removed by distillation and the reddish crystals obtained were washed with water and dried. The crude dye **3a** thus obtained was further purified by column chromatography using neutral activated aluminium oxide (toluene:ethyl acetate 7:3), (3.3 g, 85%), m.p. 174–176 °C; IR (KBr) ν_{max} cm^{-1}: 2865–2979 (aliphatic C–H stretching), 3010–3100 (aromatic C–H stretching), 1701 (lactone carbonyl stretching), 1608, 1517 (aromatic C=C stretching), 1338 (lactone C–O stretching); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.22 (t, 7.1 Hz, 3H, CH_3), δ 1.27 (t, 7.1 Hz, 3H, CH_3), δ 3.20–3.23 (m, 2H), δ 3.33–3.38 (q, 7.0 Hz, 2H, CH_2), δ 3.39–3.44 (q, 7.0 Hz, 2H, CH_2), δ 3.53–3.57 (m, 2H), δ 6.42 (s, 1H, phenyl proton), δ 6.55 (s, 1H, phenyl proton), δ 6.82–6.92 (m, 5H, protons on phenyl ring), δ 7.77–7.81 (d, 15.9 Hz, 1H, –C=CH), δ 8.10–8.14 (d, 15.8 Hz, 1H, –CH=C), δ 8.55 (s, 1H, proton on lactone ring); *Anal.* Calcd. for $C_{24}H_{24}N_2O_3$: C, 74.21; H, 6.23; N, 7.21. Found: C, 74.29; H, 6.25; N, 7.30; MS $m/z = 389$ ($M^+ + 1$).

2.2.2. 8-(3-(4′-Methoxyphenyl)acryloyl)-1,4-diethyl-1,2,3,4-tetrahydropyrano[3,2-g]quinoxalin-7-one ***3b***

The procedure used to synthesize **3a** was followed using 4-methoxybenzaldehyde in place of benzaldehyde. The resulting compound **3b** was purified by column chromatography using neutral activated aluminium oxide (toluene:ethyl acetate 7:3), (3.4 g, 81%), m.p. 175–176 °C; IR (KBr) ν_{max} cm^{-1}: 2850–2970 (aliphatic C–H stretching), 3000–3100 (aromatic C–H stretching), 1703 (lactone carbonyl stretching), 1588, 1519 (aromatic C=C stretching),1172 (lactone C–O stretching); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.22 (t, 7.2 Hz, 3H, CH_3), δ 1.29 (t, 7.2 Hz, 3H, CH_3), δ 3.21–3.24 (m, 2H), δ 3.32–3.37 (q, 7.0 Hz, 2H, CH_2), δ 3.40–3.45 (q, 7.0 Hz, 2H, CH_2), δ 3.55–3.58 (m, 2H), δ 3.85 (s, 3H, $-OCH_3$), δ 6.40 (s, 1H, phenyl proton), δ 6.50 (s, 1H, phenyl proton), δ 6.90–6.92 (d, 8.5 Hz, 2H, protons on phenyl ring), δ 7.63–7.66 (d, 8.5 Hz, 2H, protons on phenyl ring), δ 7.79–7.83 (d, 15.9 Hz, 1H, –C=CH), δ 8.09–8.13 (d, 15.8 Hz, 1H, –CH=C), δ 8.52 (s, 1H, proton on lactone ring); *Anal.* Calcd. for $C_{25}H_{26}N_2O_4$: C, 71.75; H, 6.26; N, 6.69. Found: C, 71.79; H, 6.35; N, 6.65; MS $m/z = 419$ ($M^+ + 1$).

2.2.3. 8-(3-(4′-(Dimethylamino)phenyl)acryloyl)-1,4-diethyl-1,2,3,4-tetrahydropyrano[3,2-g]quinoxalin-7-one ***3c***

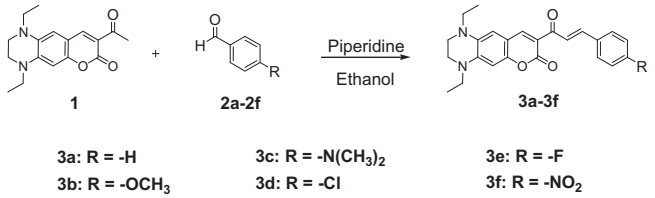
The procedure used to synthesize **3a** was followed using 4-N,N-dimethylaminobenzaldehyde in place of benzaldehyde. The resulting compound **3c** was purified by column chromatography using neutral activated aluminium oxide (toluene:ethyl acetate 4:1), (2.8 g, 65%), m.p. 238–240 °C; IR (KBr) ν_{max} cm^{-1}: 2800–2900 (aliphatic C–H stretching), 3000–3100 (aromatic C–H stretching), 1703 (lactone carbonyl stretching), 1596, 1521 (aromatic C=C stretching), 1338 (N–C stertching), 1164 (lactone C–O stretching); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.24 (t, 7.1 Hz, 3H, CH_3), δ 1.28 (t, 7.1 Hz, 3H, CH_3), δ 2.70 (s, 6H, $N(CH_3)_2$), δ 3.25–3.28 (m, 2H), δ 3.37–3.42 (q, 7.1 Hz, 2H, CH_2), δ 3.45–3.50 (q, 7.1 Hz, 2H, CH_2), δ 3.59–3.61 (m, 2H), δ 6.44 (s, 1H, phenyl proton), δ 6.58 (s, 1H, phenyl proton), δ 6.72–6.76 (d, 8.5 Hz, 2H, protons on phenyl ring), δ 7.63–7.66 (d, 8.52 Hz, 2H, protons on phenyl ring), δ 7.79–7.83 (d, 15.9 Hz, 1H, –C=CH), δ 8.09–8.13 (d, 15.8 Hz, 1H, –CH=C), δ 8.52 (s, 1H, proton on lactone ring); *Anal.* Calcd. for $C_{26}H_{29}N_3O_3$: C, 72.37; H, 6.77; N, 9.74. Found: C, 72.44; H, 6.71; N, 9.70; MS $m/z = 432$ ($M^+ + 1$).

2.2.4. 4 8-(3-(4′-Chlorophenyl)acryloyl)-1,4-diethyl-1,2,3,4-tetrahydropyrano[3,2-g]quinoxalin-7-one ***3d***

The procedure used to synthesize **3a** was followed using 4-chlorobenzaldehyde in place of benzaldehyde. The resulting compound **3d** was purified by column chromatography using neutral activated aluminium oxide (toluene:ethyl acetate 7:3), (3.7 g, 88%), m.p. 236–238 °C; IR (KBr) ν_{max} cm^{-1}: 2900–3000 (aliphatic C–H stretching), 3000–3100 (aromatic C–H stretching), 1701(lactone carbonyl stretching), 1600, 1521(aromatic C–H stretching), 1261(lactone C–O stretching); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.20–1.23 (t, 7.3 Hz, 3H, CH_3), δ 1.26–1.29 (t, 7.3 Hz, 3H, CH_3), δ 3.24–3.27 (m, 2H), δ 3.33–3.38 (q, 7.1 Hz, 2H, CH_2), δ 3.43–3.48 (q, 7.1 Hz, 2H, CH_2), δ 3.57–3.60 (m, 2H), δ 6.44 (s, 1H, phenyl proton), δ 6.55 (s, 1H, phenyl proton), 7.35–7.37 (d, 8.6 Hz, 2H, protons on phenyl ring), δ 7.60–7.62 (d, 8.7 Hz, 2H, protons on phenyl ring), δ 7.73–7.77 (d, 15.8 Hz, 1H, –C=CH), δ 8.18–8.22 (d, 15.7 Hz, 1H, –CH=C), δ 8.52 (s, 1H, proton on lactone ring); *Anal.* Calcd. for $C_{24}H_{23}ClN_2O_3$: C, 68.16; H, 5.48; Cl, 8.38; N, 6.62. Found: C, 68.24; H, 5.51; N, 6.63; MS $m/z = 424$ ($M^+ + 2$).

2.2.5. 8-(3-(4′-Fluorophenyl)acryloyl)-1,4-diethyl-1,2,3,4-tetrahydropyrano[3,2-g]quinoxalin-7-one ***3e***

The procedure used to synthesize **3a** was followed using 4-fluorobenzaldehyde in place of benzaldehyde. The resulting compound **3e** was purified by column chromatography using neutral activated aluminium oxide (toluene:ethyl acetate 4:1), (3.6 g, 88%), m.p. 206–208 °C; IR (KBr) ν_{max} cm^{-1}: 2900–3000 (aliphatic C–H stretching), 3000–3100 (aromatic C–H stretching), 1704 (lactone carbonyl stretching), 1610, 1510(aromatic C–H stretching), 1261 (lactone C–O stretching); ^{1}H NMR: δ 1.18–1.21 (t, 7.0 Hz, 3H, CH_3), δ 1.25–1.28 (t, 7.0 Hz, 3H, CH_3), δ 3.23–3.26 (m, 2H), δ 3.32–3.37 (q, 6.9 Hz, 2H, CH_2), δ 3.42–3.45 (q, 6.9 Hz, 2H, CH_2), δ 3.56–3.59 (m, 2H), δ 6.42 (s, 1H, phenyl proton), δ 6.52 (s, 1H, phenyl proton), 7.05–7.10 (d, 8.0 Hz, 2H, protons on phenyl ring), δ 7.65–7.69 (d, 8.0 Hz, 2H, protons on phenyl ring), δ 7.75–7.79 (d, 15.6 Hz, 1H, –C=CH), δ 8.16–8.18 (d, 15.5 Hz, 1H, –CH=C), δ 8.52 (s, 1H, proton on lactone ring); *Anal.* Calcd. for $C_{24}H_{23}FN_2O_3$: C, 70.92; H, 5.70; F, 4.67; N, 6.89. Found: C, 70.99; H, 5.74; N, 6.86; MS $m/z = 407$ ($M^+ + 1$).



Scheme 1. Synthetic pathway of coumarinyl chalcones **3a**–**3f**.

*2.2.6. 1,4-Diethyl-1,2,3,4-tetrahydro-8-(3-(4′-nitrophenyl)acryloyl) pyrano[3,2-g]quinoxalin-7-one **3f***

The procedure used to synthesize **3a** was followed using 4-nitrobenzaldehyde in place of benzaldehyde. The resulting compound **3f** was purified by column chromatography using neutral activated aluminium oxide (toluene:ethyl acetate 1:1), (4.4 g, 78.5%), m.p. 255–257 °C; IR (KBr) ν_{max} cm^{-1}: 2900–3000 (aliphatic C–H stretching), 3000–3100 (aromatic C–H stretching), 1697 (lactone carbonyl stretching), 1602, 1517 (aromatic C–H stretching), 1261 (lactone C–O stretching); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.19 (t, 7.0 Hz, 3H, CH_3), δ 1.23 (t, 7.0 Hz, 3H, CH_3), δ 3.24–3.27 (m, 2H), δ 3.33–3.38 (q, 7.1 Hz, 2H, CH_2), δ 3.43–3.48 (q, 7.1 Hz, 2H, CH_2), δ 3.57–3.60 (m, 2H), δ 6.43 (s, 1H, phenyl proton), δ 6.53 (s, 1H, phenyl proton), δ 7.90–7.92 (d, 8.7 Hz, 2H, protons on phenyl ring), δ 7.96–8.00 (d, 15.8 Hz, 1H, –C=CH), 8.27–8.29 (d, 8.6 Hz, 2H, protons on phenyl ring), δ 8.42–8.46 (d, 15.7 Hz, 1H, –CH=C), δ 8.52 (s, 1H, proton on lactone ring); *Anal.* Calcd. for $C_{24}H_{23}N_3O_5$: C, 66.50; H, 5.35; N, 9.69. Found: C, 66.57; H, 5.31; N, 9.65; MS $m/z = 434$ ($M^+ + 1$).

3. Results and discussion

3.1. Synthesis of coumarinyl chalcones

Typically the novel coumarinyl chalcones were prepared by classical crossed aldol condensation of 8-acetyl-1,4-diethyl-1,2,3,4-tetrahydro-7*H*-pyrano[2,3-*g*]quinoxalin-7-one **1** and substituted benzaldehyde derivatives **2a**–**2f** as shown in Scheme 1. 8-Acetyl-1,4-diethyl-1,2,3,4-tetrahydro-7*H*-pyrano[2,3-*g*]quinoxalin-7-one **1** was obtained according to our previously reported procedures [14]. To obtain chalcones **3a**–**3f**, a mixture of methylketone **1** and corresponding benzaldehyde derivative was heated under reflux in absolute ethanol containing a catalytic amount of piperidine. The structures of the chalcones were confirmed by FT-IR, ^{1}H NMR spectroscopy, mass spectrometry and elemental analysis. In the proton NMR spectra all the dyes showed characteristic one proton singlet at δ 8.52 ppm for the proton at the 4-position of coumarin ring. Two one proton singlets accounting for two protons on the coumarin phenyl ring were observed at around δ 6.4 and δ 6.5 ppm, respectively. The characteristic alkene protons on the chalcone unit appeared as doublets in the region 7.73–7.83 ppm and 8.09–8.22 ppm, respectively. These alkene protons showed a typical coupling constant value of 15.5 Hz confirming the *trans*-geometry of the alkene bond.

Table 1
Spectral properties of acetyl coumarin **1** and coumarinyl chalcones **3a**–**3f** in chloroform.

Dye no.	R	Absorption maxima λ_{max} (nm)	Emission maxima λ_{em} (nm)	Stokes shift	ε mol^{-1} dm^3 cm^{-1}	Quantum yield Φ
1	–	474	601	127	18,100	0.56
3a	–H	505	597	92	16,490	0.44
3b	$-OCH_3$	502	635	133	25,170	0.39
3c	$-N(CH_3)_2$	484	578	94	15,215	0.27
3d	–Cl	508	615	107	18,675	0.30
3e	–F	509	617	108	39,910	0.34
3f	$-NO_2$	520	598	78	13,856	0.12

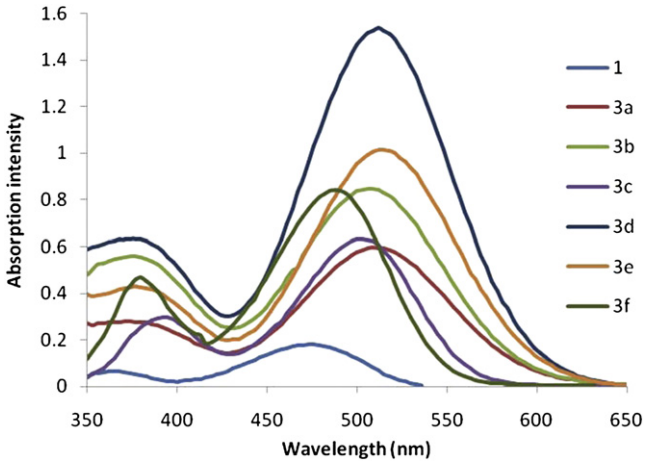


Fig. 1. Absorption spectra of acetyl coumarin **1** and coumarinyl chalcones **3a**–**3f** in chloroform[a]. [a]The concentrations of the dyes were in the range of 2.31–2.58 × 10^{-5} mol dm^{-3}.

3.2. Spectral characteristics of acetyl coumarin ***1*** and coumarinyl chalcones ***3a*–*3f***

The spectral characteristics of the compounds such as the absorption maxima (λ_{max}), emission maxima (λ_{em}), extinction coefficient (ε) and fluorescence quantum yield (Φ) were measured in chloroform and are presented in Table 1. The electronic absorption spectra of the acetyl coumarin **1** showed absorption maxima at 474 nm. The chalcones **3a**–**3f**, derived from **1**, displayed red-shift absorption maxima in the visible region from 484 to 520 nm, owing to their extended conjugation. In the case of dyes **3a**–**3f**, structural modification occurs only in the terminal phenyl ring where various substituents are attached at 4-position. Such substituents were expected to bring notable changes in the absorption and emission pattern of the dyes due to their different electron donating and accepting abilities. The dyes **3d**, **3e** and **3f** with electron accepting substituents showed a remarkable bathochromic shift in the absorption maxima. The dye **3f**, having the strong electron accepting nitro group, showed a well pronounced absorption band

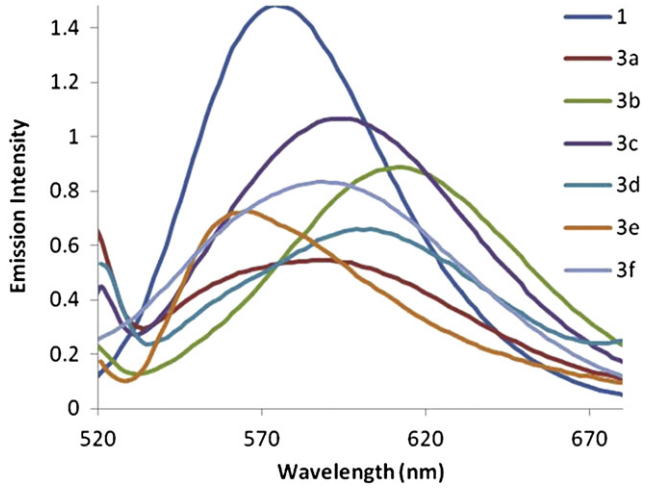


Fig. 2. Fluorescence spectra of acetyl coumarin **1** and coumarinyl chalcones **3a**–**3f** in chloroform.

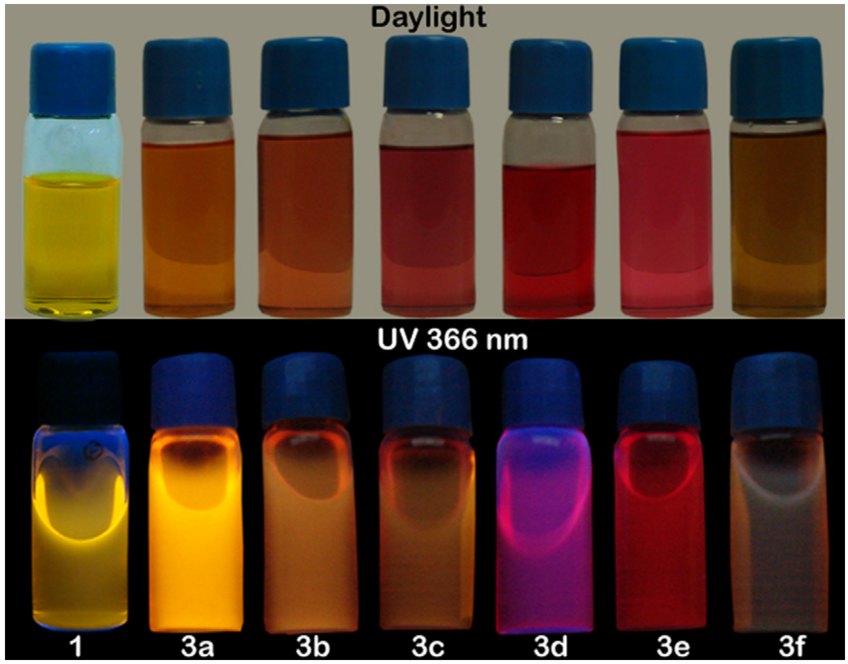


Fig. 3. Photograph of acetyl coumarin **1** and coumarinyl chalcones **3a**–**3f** in daylight and in UV light (366 nm).

at 520 nm. Dyes **3b** and **3c**, having the electron donating substituents, displayed absorption maxima at 502 and 484 nm, respectively. Dye **3c** with the strong electron releasing dimethylamino group showed the lowest absorption maxima among the chalcone derivatives. Fig. 1 presents absorption spectra of the dyes **1** and **3a**–**3f** in chloroform. All of the dyes displayed almost similar fluorescence spectra in the range of 578–635 nm as shown in Fig. 2. The dyes **1** and **3b** exhibited large Stokes shift of 127 and 133 nm, respectively, while dye **3f**, having nitro group, showed lowest Stokes shift of 78 nm. All dyes exhibited brilliant fluorescence. Fig. 3 shows photographs of the dyes in daylight as well as under UV light (366 nm). The fluorescence quantum yields (Φ) of the dyes were measured in chloroform using Rhodamine 6G as a standard [15,16]. All chalcones showed lower fluorescence quantum yield compared to their precursor, acetyl coumarin **1**. Among chalcone derivatives, the dye **3a** displayed highest quantum efficiency of 0.44 while dye **3f** displayed lowest quantum efficiency of 0.12.

To investigate the influence of solvents on the absorption maxima of compounds **1** and **3a**–**3f**, their absorption spectra were measured in a series of different solvents such as toluene, ethyl acetate, hexane, methanol, DMF, and acetonitrile. The solvents differ considerably in polarity and ability to form H-bonds. From the presented values in Table 2, it is apparent that in the polar solvents such as DMF, methanol and acetonitrile the dyes displayed a bathochromically shifted absorption maxima relative to those in non-polar solvents such as hexane and toluene. However, among polar solvents no appreciable solvatochromism was noted. It must be noted that the dyes did not show any dramatic changes in the fluorescence spectra recorded in different solvents.

The spectral properties in chloroform of some of the dyes were also compared with their 7-diethylaminocoumarin analogues reported in the literature [13] (Table 3). As expected, coumarins **1**, **3b**, and **3d** having rigid and strongly electron donating 1,4-diethyl-1,2,3,4-tetrahydroquinoxaline framework displayed a significant bathochromic shift in absorption maxima compared to the non-rigid coumarins **4a**–**4d** having a N,N-diethylamino group as an electron releasing moiety. The Stokes shift values of the reported dyes **4a**–**4d** were found to be lower than that of novel dyes **1** and **3b**–**3d**. Fluorescence quantum yields of the reported coumarins **4a**–**4d**, however, were significantly higher than that of the dyes **1** and **3b**–**3d**. Especially, the acetyl coumarin derivative **4a** showed remarkably high quantum yield of 0.95.

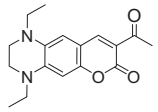
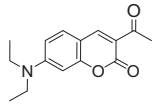
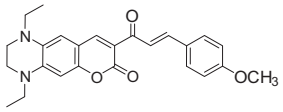
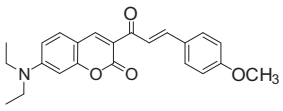
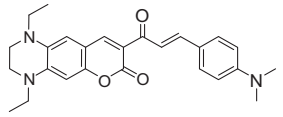
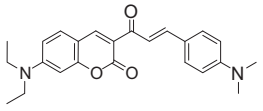
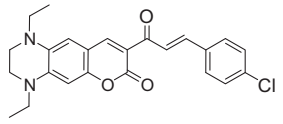
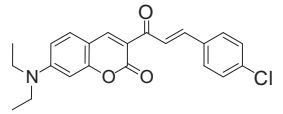
*3.3. Thermal characteristics of acetyl coumarin **1** and representative chalcone **3b***

The coumarinyl chalcone **3b** and its precursor, the acetyl coumarin **1** were subjected to thermogravimetric analysis in order to investigate their thermal stability. Stepwise isothermal ramping up to 600 °C at 10 °C/min was performed under a nitrogen

Table 2
Spectral properties of acetyl coumarin **1** and coumarinyl chalcones **3a**–**3f** in different solvents.

Dye no.	DMF		Methanol		Chloroform		Acetonitrile		Ethyl acetate		Toluene		Hexane	
	λ_{max} (nm)	ε mol^{-1} dm^3 cm^{-1}	λ_{max} (nm)	ε mol^{-1} dm^3 cm^{-1}	λ_{max} (nm)	ε mol^{-1} dm^3 cm^{-1}	λ_{max} (nm)	ε mol^{-1} dm^3 cm^{-1}	λ_{max} (nm)	ε mol^{-1} dm^3 cm^{-1}	λ_{max} (nm)	ε mol^{-1} dm^3 cm^{-1}	λ_{max} (nm)	ε mol^{-1} dm^3 cm^{-1}
1	481	18,066	477	15,600	474	18,100	475	16,785	469	22,000	465	14,711	458	16,869
3a	514	13,774	509	18,100	505	16,490	508	14,822	499	16,451	496	17,072	481	16,606
3b	511	20,386	498	25,651	502	25,170	505	23,490	496	24,395	493	24,912	478	21,938
3c	494	13,125	501	29,538	484	15,215	478	15,466	478	15,675	475	15,842	466	14,463
3d	514	12,760	513	36,450	508	18,675	508	16,731	502	17,703	498	18,675	484	18,844
3e	514	24,847	510	38,916	509	39,910	511	37,027	502	37,393	499	42,143	486	37,799
3f	523	10,652	515	28,600	520	13,856	520	14,289	508	13,423	511	13,077	493	14,289

Table 3
Comparison of photophysical properties[a] of chalcones with their reported analogues [13].

Structure of dye	Dye no.	Absorption maxima λ_{max} (nm)	Emission maxima λ_{em} (nm)	Stokes shift	ε mol^{-1} dm^3 cm^{-1}	Quantum yield Φ (%)
	**1**	474	601	127	18,100	0.56
	**4a**	435	463	28	57,453	0.95
	**3b**	502	635	133	25,170	0.39
	**4b**	456	497	43	56,234	0.50
	**3c**	484	578	94	15,215	0.27
	**4c**	489	552	63	69,183	0.32
	**3d**	508	615	107	18,675	0.30
	**4d**	459	505	46	57,453	0.41

[a] Photophysical properties of chalcones and their reported analogues were measured in chloroform.

atmosphere. The change in weight of the compound was measured as a function of temperature. Thermal stability is defined as the temperature up to which ~95% of the composition of the compound remains stable. The thermogravimetric analysis for the dyes **1** and **3b** showed a clear plateau up to ~250 °C followed by a sharp decomposition curve. For the acetyl coumarin dye **1**, 96.3% of the weight composition was stable up to 252 °C and underwent rapid thermal decomposition thereafter. The coumarinyl chalcone dye **3b** was found to be stable up to 294 °C.

4. Conclusion

In conclusion, the novel coumarin based chalcone derivatives **3a**–**3f** are valuable as new fluorescent chromophores having longer absorption and emission maxima than their precursor acetyl coumarin **1**. The dyes absorbed in the region 458–523 nm in different solvents. The dyes displayed longer wavelength of absorption in the high polarity solvents compared to non-polar solvents. These novel dyes however displayed lower fluorescence quantum yield with respect to the acetyl coumarin precursor. This may be attributed to the flexibility of the chalcone structure. The dyes showed good thermal stability. The novel dyes had bathochromically shifted λ_{max} relative to the reported 7-diethylaminocoumarin analogues owing to the rigid and highly electron donating 1,4-diethyl-1,2,3,4-tetrahydroquinoxaline framework, but also a decrease of fluorescence intensity, which may be due to the presence of additional electron donating N-ethyl unit.

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