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Hydrogen bonded dimers of ketocoumarin in solid state and alcohol: water binary solvent by fluorescence spectroscopy, crystal structure and DFT investigation.

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Abstract:

The photophysical properties of 3,3' Carbonylbis (7-diethylamino)-2H-chromen-2-one (Ketocoumarin) was investigated in solid state, different solvents and alcohol: water binary mixture using steady state, time-resolved fluorescence spectroscopy, XRD studies and DFT calculations. In neat solvents ketocoumarin (KC) shows small Stokes shift as compared to other 7-diethylaminocoumarin dyes (7-DEC) and is due to the π - π * electronic transitions involving the bridge keto group. In aqueous alcoholic solution, the fluorescence maximum of KC depends on the percentage of water and a new emission at 550 nm with large Stokes shift is observed at 90% water content. The solid state fluorescence and XRD crystal structure analysis revels that the new decay component with lifetime 2.71 ns and new emission maximum in alcohol: water mixture is due to the intermolecular hydrogen bonding [HB] interaction between KC molecules in alcohol: water binary mixture. XRD structure reveals that the two modes of intermolecular CH...O=C hydrogen bonding (HB) which lead to two dimeric forms of KC, D1 and D2. The emission wavelength dependent excitation spectrum in solid state and alcohol: water binary mixture confirms the H-type nature of dimer D1 and J-type nature of dimer D2. The timeresolved fluorescence studies indicates the new decay component with lifetime 2.71 ns is due the dimer D1 and new emission with maximum at 550 nm is assigned to dimer D2. Density

functional theory (DFT) analysis confirms that the KC dimers are stabilized by hydrogen bonding and other non-covalent interactions. The hydrogen bonded KC dimers are responsible for the anomalous fluorescence behavior of KC in alcohol: water binary mixture and bright yellow fluorescence from solid state.

1. Introduction

Coumarin and its derivatives are important class of organic heterocyclic systems and are widely used in the different fields of science and technology. They can be found in natural and synthetic drug molecules and exhibit wide variety of pharmacological activities such as anticoagulant,¹anti-bacterial,² anticancer³ and specific inhibitor activitities. Coumarins constitute the largest class of laser dyes in the "blue-green" region.⁴⁻⁷ 7-aminocoumarin is one of the well documented candidate from this family due to its excellent photophysical and photochemical properties such as large Stokes shift with environmental sensitivity,⁸⁻⁹ high fluorescence quantum yield¹⁰, reasonable solubility,¹¹ excited state electron donor and acceptor capability , excited state conformational change¹² and photoionization¹³. These properties make them useful in a wide variety of applications such as fluorescent probes,¹⁴ sensors,¹⁵ optical brighteners,¹⁶ laser dyes, solar energy collectors¹⁷ and dopants in organic light emitting diodes.¹⁸

The unusual photophysical properties of 7-aminocoumarins in different solvent environments have been reported recently and are due to i) presence of different conformations and ii) intermolecular interactions.¹⁹⁻²⁰ In non-polar solvents, 7-aminocoumarins adopt nonplanar conformation and the fast flip-flop motion of the 7-amino group introduces additional non-radiative decay channel, which is absent in the planar conformation present in moderate to highly polar solvents.¹⁹ In the case of 7- N,N-dialkylamino substituted coumarin dyes such as Coumarin-481 and coumarin-152 in highly polar solvents, the planar fluorescent ICT

2 3 4 5 6 7 8 9 10 11 12 AB1 MO1 23 population of the second secon 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60

(Intramolecular charge transfer) is converted to non-fluorescent TICT (Twisted intramolecular charge transfer) state and there is unusual decrease in fluorescence quantum yield and lifetime.²⁰ Poonom et.al reported the formation of H-aggregate and H-dimer in the aqueous solution of Coumarin-481 through steady state and time resolved fluorescence techniques.²¹ They also found that the aggregates are emissive in nature. These aggregates are also formed in high polar solvents such as ethanol and acetonitrile when increasing the concentration of the coumarin.

KC is an important member of coumarin dyes and has a carbonyl group attached to the 3position in the coumarin structure through a single bond. The coumarin-3-carboxylic acid and coumarin-343 also belong to the family of ketocoumarin dves.²² ketocoumarins have very high singlet-triplet intersystem crossing quantum yield and serve as a new class of triplet sensitizer.²³ The intersystem quantum yield increases on replacing the hydroxyl group by alkyl/aryl group in coumarin -3-carboxylic acids. Xiaogang Liu et.al reported the origin of dye aggregation and complex formation in 7-(diethylamino)-coumarin-3-carboxylic acid [DCCA] and in coumarin -The formation of J-aggregates was understood from photophysical and TD-DFT 343.24 calculations. The formation of H-aggregates in cholesterol substituted ketocoumarin was reported in pluronic surfactant based polymeric micelles.²⁵ The intermolecular interaction induced polymorphism and concentration dependent fluorescence emission of ketocoumarins such as 7-(Diethylamino)coumarin-3-aldehyde [DCA] and DCCA was recently reported by Rong Rong Cui et.al.²⁶ Ketocoumarins are widely used for the sensitization of semiconductor nanoparticles and studies related to aggregation are quite important for the construction of dyesensitized solar cells and other optoelectronic devices.²⁷

Aggregate formation is governed by weak intermolecular interactions which are noncovalent in nature. Hydrogen bonding (HB) interactions^{28,29} and London dispersion

interactions³⁰ are predominant noncovalent interactions operating in large organic and biological systems. HB interactions are electrostatic in origin whereas the dispersion interactions arise due to induced dipole-induced dipole interactions.³⁰ The dispersion interaction contributes to stability in all systems, in principle and has a significant role in stabilizing weak van der Waals dimers.³¹⁻³⁴ Different studies show that the dispersion interactions play a major role in stabilizing sterically crowded inorganic, organic and biological systems, guest–host complexes etc.³⁵ In large molecular systems, the DFT-D3 method developed by Grimme based on the atom-pair wise potential is a convenient tool to study the dispersion interaction.³⁶

In the present study the photophysical properties of KC was studied and the role of aggregation was investigated. This KC has very small Stokes shift and low fluorescence quantum yield in both polar and non-polar solvents (Scheme-1). In non-polar solvents, KC shows strong triplet-triplet absorption with triplet lifetime of several microseconds.²³ KC acts as a heavy-atom free triplet sensitizer used for variety of applications such as photocatalysis³⁷, photodynamic therapy³⁸ and triplet-triplet annihilation up conversion. The two photon absorption cross-section of KC two to three orders of magnitude larger than that of the coumarin dyes.³⁹ Numerous studies report the application of KC as photosensitizer or photoinitiators for one and two photon polymerization. KC based OLED's and electroluminescent materials have been reported recently.⁴⁰ In polar solvents, the triplet yield decreases with decrease in the fluorescence quantum yield. The unusual photophysical properties of KC such as small Stocks shift and low fluorescence quantum yield in polar and non-polar solvents are not understood fully. We have investigated the photophysical properties of KC in solid state and alcohol: water binary mixture using steady state, time-resolved fluorescence spectroscopy. In alcohol: water binary mixture, KC shows new fluorescence maximum with large Stokes shift. This observation is similar to the

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emission behavior from the single crystal of KC. The origin of anomalous bright yellow emission in solid state and alcohol: water binary mixture is explored using x-ray diffraction and DFT studies.



Scheme 1. Structure of KC

2. Experimental section

Materials

4-Diethylaminosalicyaldehyde and dimethyl 1,3-acetonedicarboxylate were purchased from Sigma Aldrich. Piperidine were purchased from spectrochem. All the solvents used in this study are HPLC quality obtained from Fisher Scientific. The spectroscopic grade solvents like 1,4 dioxane, toluene, tetrahydrofuran (THF), chloroform (CHCl₃), 1,2-dichloromethane (DCM), methanol (MeoH), ethanol (EtoH), n-propanol, acetonitrile (ACN), *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and water (H₂O) were used after proper distillation as needed.

General techniques

The ¹H and ¹³C NMR spectra of KC compound were recorded on a Bruker- Avance at 400 MHz and 100 MHz NMR instruments using CDCl₃ and DMSO- d_6 as solvents containing tetramethylsilane (TMS) as an internal standard. Absorption spectra of the KC were recorded using an Agilent 8453 UV-visible diode array spectrophotometer. The fluorescence spectral measurements were carried out using Fluoromax-4 spectrophotometer (Horiba Jobin Yvon). The fluorescence quantum yield of KC was calculated using a single point method. The coumarin-

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153 in ethanol was used as reference. The quantum yield of coumarin-153 is 0.544 at 422 nm excitation⁴¹. The quantum yield of KC was calculated using the following equation

$$\Phi_f = \varphi_r \, x \frac{I_s}{I_r} x \frac{A_r}{A_s} x \frac{\eta_s^2}{\eta_r^2}$$

where φ_f refers to the quantum yield of KC and I, η and A is the measured integrated emission intensity (area under the curve), refractive index and absorption at 422nm respectively. The subscript r and s refers to the reference coumarin-153 and KC respectively. An excitation slit width of 4 nm and emission slit width of 2 nm was used to record the fluorescence spectra in the wavelength range of 440-700 nm. The refractive index of the methanol: water mixture was obtained from the literature and used in the quantum yield calculation.⁴²

Time-resolved fluorescence decays were obtained by the time correlated single-photon counting (TCSPC) technique with microchannel plate photomultiplier tube (Hamamatsu, R3809U) as detector and femtosecond laser as an excitation source. The 425 nm output from the mode-locked femtosecond laser (Tsunami, Spectra physics) was used as the excitation source. The instrument response function for TCSPC system is ~50 ps. The data analysis was carried out by the software provided by IBH (DAS-6), which is based on a deconvolution technique using nonlinear least-squares methods. Femtosecond fluorescence decays were recorded using fluorescence up-conversion technique as reported elsewhere.¹³ The fluorescence decays were fitted using a Gaussian shape for the excitation pulse with FWHM of 200 fs. The femtosecond fluorescence decay was analyzed using IGOR software. All the fluorescence lifetime measurements were carried out for at least three times and error in the fitted lifetime values is well within 5%.

X-ray structure analysis and refinement

Single crystal X-ray diffraction data of KC were collected from Bruker AXS Kappa Apex2 CCD diffractometer at room temperature, (SAIF-IIT Madras) using graphite monochromated Mo K α (λ =0.71073 Å) radiation. For data reduction SAINT/XPREP program was used and for cell refinement APEX2/SAINT program was used. The structures were resolved by direct methods and refined by full-matrix least-squares on F² (SHELXL97). The positions of all the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were placed at ideal positions and included in the refinement. The Hirshfeld surfaces represented by d_{norm}, shape index and 2-D fingerprint plots were calculated using Crystal Explorer 3.1.⁴³ For each point on the Hirshfeld surface, two parameters are defined. d_e is the distance from the point to the nearest nucleus external to the surface and d_i is the distance from the point to the nearest nucleus internal to the surface. The normalized contact distance, d_{norm}, based on both d_e and d_i, and the vdW radius of the atom, ⁴⁴ is given by the equation:

$$d_{norm} = \frac{d_{i} r_i^{vdW}}{r_i^{vdW}} + \frac{d_{e} r_e^{vdW}}{r_e^{vdW}} \dots 1$$

Here, r_i^{Vdw} and r_e^{Vdw} are the internal and external van der Waals radii of the atom. The combination of de and d_i in the form of a 2-D fingerprint plot provides summary of intermolecular contacts in the crystal.

Computational method

The molecular and electronic structures of KC in different geometrical arrangements were studied in the gas-phase by performing complete structural optimization using the density functional theory (DFT) methods B3LYP.^{45,46} M052X⁴⁷ and BP86.^{48,49} The relative energies of the low-energy structures of KC by the above DFT methods were compared. Intermolecular interaction energies (IE) between two KC molecules were computed at two different dimer

structures **D1** and **D2**, which were characterized from the XRD structure of the single crystal. The stability of the dimer was examined by single-point energy calculations using the DFT methods M052X³ and M062X-D3⁵⁰⁻⁵² that are suitable to study noncovalent interactions.⁵³⁻⁵⁶ Benchmark analysis of Goerigk and Grimme reveals that the M062X-D3 method yield reliable predictions of the dispersion energy in varied types of systems. The IE is computed from the total energy in the dimer (E_{total} (dimer)) and the total energy in the monomer (E_{total} (monomer)) using the equation:

$$IE = E_{total}(dimer) - 2E_{total}(monomer).$$

The B3LYP and M052X calculations were performed by the Gaussian 03 software.⁵⁷ Pople's extended basis set including polarization and diffuse functions⁵⁸, 6-31+G**, was used in the B3LYP and M052X study. The BP86 and M062X-D3 calculations were carried out by the ORCA4.0.1 software^{59,60} making use of the extended triple-zeta basis set def2-TZVP and auxiliary coloumb fitting def2/J and RI-JK basis sets.^{61,62}

3. Results

3.1 Stationary absorption and emission spectral studies of KC in different solvents:

The steady state absorption and fluorescence spectra of KC were recorded in different solvents. The absorption maximum of KC in different solvents was complied in **Table 1**. The UV–Vis absorption spectra of KC in different solvents is shown in (**Fig. 1a**). On increasing solvent polarity, the absorption maximum of KC is found to be red shifted. KC has non-bonding electron, π electrons and electron donor and acceptor groups. The long wavelength electronic absorption may be due to i) $n - \pi^* 2$ $\pi - \pi^*$ and 3) ICT transition. The effect of the solvent on the absorption spectra confirms that the long wavelength absorption of KC is not due to $n - \pi^*$ transition. The molar extinction coefficient of KC was determined in methanol and non-

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polar toluene solvent and was found to be 0.911×10^5 and 1.014×10^5 M⁻¹cm⁻¹ respectively. The higher molar extinction coefficient value further indicates the $\pi - \pi^*$ nature of the long wavelength absorption band.

The fluorescence spectra of KC in different solvents is shown in (Fig. 1b). The fluorescence maximum is shifted to red on increasing the solvent polarity. The fluorescence maximum and Stokes shift of KC in different solvents is given in **Table 1**. The Stokes shift is independent of solvent polarity and was found to be in the range of 900 cm⁻¹ to 1300 cm⁻¹. The smaller stokes shift observed in KC confirms that the emission is not due to ICT excited state. In KC, the nature of the electronic transition is completely different from the other 7-aminocoumarin dyes due to the presence of bridge carbonyl group. The steady state absorption and fluorescence studies confirm that long wavelength absorption and fluorescence of KC is due to the π - π * electronic transition in all the solvents studied.



Fig. 1 a) Absorption Spectra of KC in different solvents. b) Emission Spectra of KC in different solvents.

Solvents	ε ^a	$\lambda_{ab}(nm)$	$\lambda_{em}(nm)$	$\Delta v (cm^{-1})$	$\Phi_{\rm f}$
1,4 Dioxane	2.25	447	468	1004	0.0017
Toluene	2.35	449	473	1130	0.015
EA	6.02	448	471	1070	0.016
THF	7.58	449	474	1174	0.024
n-ProH	20.0	455	493	1695	0.01
EtoH	24.55	456	487	1496	0.006
МеоН	32.7	458	486	1258	0.004
DMF	36.7	461	492	1366	0.0056
ACN	37.5	457	490	1473	0.0053
DMSO	46.58	466	495	1251	0.0054

 Table 1 Photophysical data of KC in different solvents.

3.2 Steady-state absorption and emission spectra of KC in alcohol: water binary mixture:

The absorption and fluorescence spectra of KC were investigated in methanol and methanol: water binary mixtures to understand the nature of the ground and excited state. The absorption and fluorescence maximum of KC in methanol: water binary mixture is presented in **Table 2**. The effect of water addition on the absorption and fluorescence spectrum of KC in methanol is shown in (**Fig. 2a and 2b**). Upto 70% addition of water to methanol, the absorption maximum of KC shift to longer wavelength from 458 nm to 480 nm without noticeable change in absorption. Further addition of water, the absorption maximum of KC was blue shifted with increase in full width half maximum and decrease in the absorption. The absorption maximum of KC in 90% methanol: water mixture was found to be at 469 nm.

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The fluorescence maximum of KC in neat methanol was observed at 486 nm. On addition of water to methanol up o 70%, the fluorescence intensity was guenched with red shift in the fluorescence maximum. The fluorescence maximum of KC at 70% methanol: water is found to be at 502. Further increase in water percentage, the KC fluorescence maximum shifted towards red with increase in fluorescence intensity. The fluorescence maximum of KC in 90% water is found to be at 551 nm. At higher water content, the KC shows new emission maximum with large Stokes shift compared to methanol. The KC fluorescence with small Stokes shift in methanol is assigned to $\pi \to \pi^*$ excited state. The new fluorescence maximum with large Stokes shift of KC at higher water content may be due to the ICT state induced by the specific solvent effect such as hydrogen bonding/aggregation of hydrophobic KC in aqueous environment. The steady state photophysical properties of KC in methanol: water mixtures confirm general solvent effect up to 70% H₂O and specific solvent effect beyond 70% H₂O. The fluorescence quantum yield of KC in methanol was found to be 0.0040. On increasing the water percentage upto 70% H_2O_2 , the fluorescence quantum yield decreases to 0.0013. Further increasing water percentage to 80% and 90%, the fluorescence quantum yield value increases to 0.0054. The new emission maximum with high quantum yield may be due to specific solvent effect between the KC and solvent or hydrophobicity induced intermolecular interactions such as dimer/aggregate formation , brings back the ICT absorption and emission in KC, similar to other 7-DEC dyes.

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Fig. 2 Absorption (a) and Emission (b) spectra of KC in methanol and methanol: water mixtures. λ_{exc} 460 nm. The concentration of KC is 4.4 X10⁻⁶M.

The photophysical properties of KC was studied in ethanol: water and propanol: water binary mixture. The absorption and fluorescence spectra of KC in ethanol: water and propanol water: binary mixture was shown in the **Fig. S3 and S4 (ESI†)** respectively. Absorption and fluorescence spectra of KC in ethanol : water mixture and propanol: water mixture were similar to methanol: water mixture. The absorption and fluorescence maximum of KC in ethanol: water and propanol: water mixture is presented in **Table S1 and S2 (ESI†)**. Upto 70% addition of water to ethanol and propanol results in the shift in the absorption and fluorescence maximum to longer wavelength with decrease in the fluorescence emission with maximum at 545 nm, similar to methanol: water mixture. The intensity of new emission was found to be more in methanol : water mixture when compared to ethanol and propanol: water mixture. On increasing alcohol chain length the new emission intensity decreases. Methanol is more hydrophilic solvent compared to ethanol and n-propanol. The decrease in the new emission intensity on increasing

hydrophobicity of alcohols, indicate the role of environment hydrophobicity on the new emission intensity. This is further confirmed from the photophysical studies of KC in THF :water binary mixture. The steady state photophysical properties of KC in methanol: water mixture confirms the operation of general solvent effect upto 30:70 (v/v) methanol: water mixture and operation of specific solvent effect beyond 30.70 (v/v) methanol: water mixture.

% H ₂ O	$\lambda_{ab}(nm)$	λ_{em} (nm)	Δv(cm ⁻¹)	$\Phi_{ m f}$
0	458	486	1258	0.0040
10	464	493	1268	0.0031
20	468	497	1247	0.0025
30	473	499	1101	0.0020
40	475	500	1052	0.0019
50	478	500	920	0.0014
60	480	502	913	0.0016
70	479	502	956	0.0013
80	477	546	2649	0.0014
90	469	551	3173	0.0054

Table 2 The absorption and emission properties of KC in methanol: water binary mixture.

3.3 Steady-state absorption and emission spectra of KC in THF: water binary mixture.

The origin of new emission observed in KC at higher water may be due to any one of the following i) aggregation ii) excited state reaction and iii) conformational change. The absorption and fluorescence spectrum of KC was recorded in THF: water mixtures to understand the origin of new emission of KC in methanol: water mixture. THF: water mixture is

well known for promoting aggregation induced emission.⁶³ The absorption and fluorescence spectrum of KC in THF: water mixture is shown in (Fig 3a and 3b). On increasing water percentage, both the absorption and fluorescence maxima of KC are red shifted. At higher water content the absorption spectrum of KC is red-shifted more as compared to the fluorescence spectrum. The absorption and fluorescence maxima of KC in THF and THF:water mixture is shown in **Table 3.** On addition of water to THF upto 90% (v/v), the fluorescence intensity was quenched with red shift in the fluorescence maximum. The fluorescence maximum of KC at 90% THF: water is found to be at 496 nm. Further increase in water percentage results in the precipitation of KC with new emission maximum at 531 nm. The reprecipitation of KC was observed from 92% water: THF and results in the formation of needle like crystals. Due to the precipitation, the absorbance of KC decreases drastically at high water content (above 92%). In alcohols the new emission with large Stokes Shift was observed from the water content greater than 70% and there is no re-precipitation of KC was observed upto 90% water. The decrease in the fluorescence intensity on the addition of water is due to additional non-radiative relaxation such as the non-emissive TICT state formation in the excited state.64



Fig. 3 Absorption (a) and Emission (b) spectra of KC in THF and THF:water mixtures. Insert shows the fluorescence spectrum of KC in 90, 92, 94, 96 and 98 % of water in THF. λ_{exc} 450 nm. The concentration of KC is 1.811 X10⁻⁶M.

% H ₂ O	$\lambda_{ab}(nm)$	λ_{em} (nm)	Δv (cm ⁻¹)
0	449	471	1040
10	455	482	1231
20	457	484	1220
30	460	485	1120
40	463	488	1106
50	464	488	1059
60	468	490	959
70	472	491	819
80	477	494	721
90	481	496	628
92	474	500	1097
94	475	529	2149

Table 3 The absorption and emission properties of KC in THF: Water binary mixture.

96	475	530	2184
98	475	530	2184

3.4 Time-resolved fluorescence studies

Fluorescence decay of KC was recorded in methanol: water mixture using time correlated single photon counting technique. The time resolved fluorescence decay of KC in methanol: water mixture was monitored at 490 nm and 550 nm by exciting at 425 nm. In both methanol and methanol water mixture, the fluorescence decay curves of KC dye do not obey single exponential fit, but they are satisfactorily fitted by the biexponential and triexponential function according to the equation

$$I(T) = B_1 \exp(-t/\tau_1) + B_2 \exp(-t/\tau_2) - - -1$$
$$I(T) = B_1 \exp(-t/\tau_1) + B_2 \exp(-t/\tau_2) + B_3 \exp(-t/\tau_3) - - -2$$

where B_1 , B_2 and B_3 are the pre-exponential factors, τ_1 , τ_2 and τ_3 are fluorescence lifetimes. The fractional intensity contribution of each decay component in the multiexponential decay towards the total steady state intensity is given by the relative amplitude and is calculated from the pre-exponential factor and decay time as follows

$$A_i = \frac{B_i \tau_i}{\sum_j B_j \tau_j}$$

The typical fluorescence decay of KC in different percentages of methanol: water mixture is shown in (**Fig. 4a and 4b**). The fluorescence lifetime data of KC in different percentage of water in methanol are compiled in **Table 4**. The fluorescence decay of KC in methanol shows bi-

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exponential nature with one short and long component. In neat methanol, the decay time of the short component was found to be around 85 ps (35.52%), whereas the long component decay time was found to be 1.4 ns (64.48%), which are found be independent of emission wavelength. On increasing water percentage in methanol, decay time of both short and long component decreases for decays monitored at both 490 and 550 nm. A new decay component with decay time of 2.71 ns was observed from 30% water addition to methanol. The relative amplitude of the new decay component observed at 490 nm increases with increasing water percentage in methanol. The lifetime of the new decay component is fixed. In the free fitting this decay component is varying from 2.4 -2.9 ns and this variation influence the relative amplitudes of the short decay components particularly in the decay monitored at 550 nm at higher water content.

The decay time τ_2 and it relative amplitude remains constant at higher water percentage (> 70%) for the fluorescence decay curves monitored at 490 nm. There is a noticeable difference in the amplitude of the decay component τ_2 and τ_3 at higher water percentage for fluorescence decay of KC monitored at the new emission maximum (550 nm). As the water percentage increases above 70% the relative amplitude of τ_2 increases with decrease in the relative amplitude of the τ_3 decay component. This indicates that the new emission maximum observed at 550 nm at higher water percentage is not due to the new decay component τ_3 with decay time 2.71 ns. The higher relative contribution of τ_2 decay component at 550 nm confirms that the new emission maximum is due to the presence of this decay component. At 90% water, the fluorescence decay monitored at 490 nm and 550 nm is tri-exponential with decay time constants $\tau_1 \approx 45$ ps and $\tau_2 \approx 300$ ps and $\tau_3 = 2.71$ ns. At water content >70%, the decay component τ_2 is constant with higher contribution for intensity monitored at 550 nm and confirms that the decay

component τ_2 corresponds to the new emission maximum. The time-resolved fluorescence results clearly suggest that there are three emitting species present in the aqueous solution of KC.



Fig. 4 Fluorescence decays of KC in different percentage of methanol: water mixture.

The fluorescence decay of KC was recorded in THF: water mixture using time correlated single photon counting technique. The time resolved fluorescence decay of KC in THF: water mixture was monitored at 490 nm by exciting at 445 nm. The typical fluorescence decay of KC in different percentages of THF: water mixture is shown in **Fig. S5**. The fluorescence lifetime data of KC in different percentage of water in THF are compiled in **Table S3**. The fluorescence decay of KC in THF is single-exponential with decay time of 2.01 ns. On addition of water to THF, the fluorescence decay of KC is biexponential with a two decay times τ_1 (130 -160 ps) and τ_2 . The decay time and relative amplitude of the long component decreases with increasing water percentage. In THF: water mixture, there is no formation of additional decay component τ_3 (2.71 ns) when compared to alcohol: water mixture. The absence of new decay component in THF: water mixture confirms the role of hydrophilicity of the medium and preferential solvation on

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intra and intermolecular interactions which effects the photophysical properties of KC. This study also confirms that the decay component with lifetime 2.71 ns is not due to the solute-solvent hydrogen bonding promoted intramolecular charge transfer state.⁶⁵

In neat methanol and in presence of water, the fluorescence decay of KC exhibits ultrafast decay component close to the time resolution of the TCSPC setup. Investigation of the ultrafast excited state dynamics of KC in femtosecond time domain in methanol: water binary mixture provides information on the excited state dynamics of the KC. The femto up-conversion fluorescence decay of KC in methanol: water mixture is recorded at 490 nm and 550 nm and the ultrafast decay time constants are presented in the Table 5. Femtosecond fluorescence decay of KC in methanol: water mixture is shown in (Fig. 5a and 5b). The femtosecond fluorescence decay of KC shows bi-exponential emission decay behavior in methanol: water mixture at both 490 nm and 550 nm. In methanol, the ultrafast fluorescence decay of KC monitored at 490 nm and 550 nm follows bi exponential with two ultrafast components τ_1 =555 fs, τ_2 =2 ps and τ_1 =1.10 ps, $\tau_2=3$ ps respectively. Addition of water to methanol, the ultrafast decay time constant τ_1 monitored at 490 nm decreases to157 fs at 90% water. At higher water content 70% and 90% of water, the τ_2 lifetime increases to 6ps. The absence of rise component in the ultrafast fluorescence decay of KC monitored at the new emission maximum in methanol: water mixture leads to the conclusion that the new emission maximum is not due to the ultrafast excited state reactions. The new emission maximum of KC at higher water percentage is due to the ground state phenomenon such as dimerization or conformational change or inter and intramolecular interactions. The time-resolved fluorescence results clearly suggest that there are three emitting species present in the aqueous solution of KC.

%		H	Emission wavel	ength (nm)		
H ₂ O		490 nm			550 nm	
	τ_1^a ps	τ_2^a ns	τ_3^a ns	τ_1^a ps	τ_2^a ns	τ_3^a ns
	(A ₁ %)	(A ₂ %)	(A ₃ %)	(A ₁ %)	(A ₂ %)	(A ₃ %)
0	85 (35.52)	1.43 (64.48)	-	88 (33.94)	1.33 (66.10)	-
10	75 (45.03)	1.22 (54.94)	-	81 (47.10)	1.15 (52.90)	-
20	70 (52.52)	1.06 (47.48)	-	68 (59.20)	1.06 (40.80)	-
30	61 (47.09)	0.71 (26.64)	2.71 (26.27)	58 (54.58)	0.70 (23.01)	2.71 (23.72)
40	57 (49.44)	0.71 (24.25)	2.71 (26.31)	53 (57.38)	0.63 (21.63)	2.71 (22.23)
50	55 (46.15)	0.60 (20.81)	2.71 (33.04)	53 (55.26)	0.55 (15.62)	2.71 (30.46)
60	51 (48.14)	0.49 (15.78)	2.71 (36.08)	52 (58.84)	0.48 (14.28)	2.71 (27.22)
70	49 (50.85)	0.34 (11.38)	2.71 (37.77)	50 (55.62)	0.31 (12.95)	2.71 (28.29)
80	49 (50.56)	0.29 (12.42)	2.71 (37.03)	50 (55.56)	0.28(17.61)	2.71 (22.93)
90	45 (46.43)	0.29(12.12)	2.71 (41.44)	65 (34.30)	0.30(49.45)	2.71 (6.47)

Table 4 The fluorescence lifetime data of KC in methanol: water mixture

^a Error $\pm 10\%$ (reported for lifetime only).

	490 nm						550 nm	
% H ₂ O	$\begin{array}{c c} \tau_1^a \\ (fs) \end{array}$	$\begin{array}{c c} \tau_2^a \\ (ps) \end{array}$	A ₁ %	A ₂ %	τ_1^a (fs)	$\begin{array}{c c} \tau_2^{a} \\ (ps) \end{array}$	A ₁ %	A ₂ %
0	574	2.0	54.37	45.63	1105	3.0	68.04	31.95
10	550	2.0	58.46	41.54	910	3.5	64.27	35.72
30	360	2.3	53.98	46.02	560	1.8	44.94	55.05
50	253	2.2	60.09	39.91	440	1.9	51.74	48.25
70	182	6.7	20.17	79.84	300	7.1	7.66	92.33
90	157	4.15	20.15	79.75	1000	6.0	8.86	91.13

Table 5 Femtosecond fluorescence decay parameters of KC in methanol: water mixture .

^aError $\pm 10\%$ (reported for lifetime only).



Fig. 5 Femtosecond fluorescence decay profile of KC in different percentage of methanol: water mixture.

3.5 Photophysical properties of the KC in the solid state

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The solid absorption and fluorescence spectrum of KC was recorded and is shown in **Fig. 6.** The absorption and emission maximum of KC in solid state was found to be at 462 and 549 nm respectively. The solid state absorption and fluorescence spectrum of KC is similar to 90% methanol: water mixture. The fluorescence spectrum of a fluorophore in dilute solution reflect mainly its single molecular characteristics, while the fluorescence spectrum in solid state results from the interaction of large numbers of molecules. This confirms that intermolecular interactions between the KC molecules are responsible for the new emission observed at 550 nm. Solid state KC possesses strong absorption in the UV-A region and yellow emission under UV-A excitation (Fig. 6 (b)). To resolve all these ambiguities in the fluorescence behavior of KC in the solid state and alcohol: water binary mixture, a detailed investigation on the crystal structure, solid state packing and the active intermolecular interactions in the crystalline state was carried out.



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Fig. 6 (a) Normalized absorption and emission spectra of KC in 90% methanol: water mixture and solid state. **(b)** Photographs of solid state fluorescence of KC under UV (365nm) excitation. **(c)** Photographs of solid state KC under room light.

3.6 Crystal structure analysis of KC

The crystallization of KC in alcohols such as methanol, ethanol etc., did not yield single crystals suitable for X-ray crystal analysis. Single crystals of KC for X-ray crystal analysis were prepared by slow evaporation from CHCl₃ solution. Single crystal of KC belongs to an orthorhombic crystal system, space group Pcab with unit cell dimensions of a = 11.7204(5) Å, $\alpha = 90^{\circ}$; b = 17.1714(8)Å, $\beta = 90^{\circ}$ and c = 28.6443(14)Å, $\gamma = 90^{\circ}$. The crystal structure of KC is given in (Fig. 7). The crystal data and experimental details are shown in Table S4 (ESI[†]). In KC, two 7-N,N-diethylaminocoumarin units are connected by the bridge >C=O group at the 3position. The bridge carbonyl group is shared by the two coumarin units A and B. The KC molecule is not planar as a whole. The two coumarin rings are planar and the angle between the planes of the two coumarin rings is 55.31°. The XRD structure of KC shows that the orientation of the donor diethyl amino group is different in the two coumarin units. In the coumarin unit A, the two ethyl groups in the diethylamino substituent are in eclipsed arrangement. In the second coumarin unit **B** two ethyl groups adopt staggered arrangement. In coumarin **A** the plane containing the atoms C24-N1-C26 deviate from the plane of the coumarin ring by 1.26°. On the other hand in coumarin ring **B**, the corresponding angle between the plane containing C20-N2-C22 and plane of coumarin ring is 11.06°.

Hirshfeld surface analysis is an effective tool for exploring packing modes and intermolecular interactions in KC crystals, as they provide a visual picture of intermolecular interactions and of molecular shapes in a crystalline environment. Hirshfeld surfaces comprising

 d_{norm} surface and fingerprint plots were generated and analysed for the title compound in order to explore the packing modes and intermolecular interactions. The two dimensional fingerprint plots from Hirshfeld surface analyses are shown **Fig. S6 (ESI**†). From the 2D-fingerprint plot and crystal packing analysis of KC, it is very clear that the nonbonded H...H (33%) and O...H (26.3%) intermolecular interactions are the prime interactions in stabilizing the packing in the solid state. This intermolecular contact is highlighted by conventional mapping of d_{norm} on molecular Hirshfeld surfaces and is shown in **Fig. S7 (ESI**†). The red spots over the surface indicates that the strong intermolecular interactions through hydrogen bonding.

The XRD structure reveals the presence of intermolecular C-H...O interactions between two KC molecules. These HB interactions between the KC molecules in the crystal were analyzed using mercury software. Two modes of HB interactions between two KC molecules are identified from the crystal structure depending on the type of the hydrogen bond acceptor, C=O as seen from Fig. 8. The ring carbonyl group present in the coumarin unit A, wherein the two ethyl groups are eclipsed, and the bridge carbonyl group that connects the two coumarin units in KC participate as intermolecular HB acceptors. The CH groups in the coumarin rings adjacent to the bridge carbonyl group behave as HB donors. The details of the intermolecular HB interactions between two KC molecules are given in **Table 6**. The HB interactions between the acceptor C9=O4 and donor C-H groups are illustrated using the expansion contacts between four KC molecules in the crystal packing and is shown in **Fig. 8a**. The carbonyl oxygen O4 in the coumarin ring A of KC-1 forms HB with the C-H hydrogens, C3-H3 and C7-H7, present in the coumarin ring A' of KC-2 molecule. Similarly the O4 atom of KC-2 establishes HB with the C3-H3 and C7-H7 hydrogens of KC-3. This mode of HB interactions leads to dimer, trimer and higher order aggregates. The higher order aggregates are formed in the supramolecular structure,

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which is possible only in the solid state. However, in aqueous solution this mode of HB interaction leads to the dimer **D1**. The HB interactions between the bridge carbonyl acceptor and the C-H donor groups are illustrated using the expansion contacts between two KC molecules in the crystal packing and is shown in the **Fig. 8b.** The oxygen atom O5 present in the bridge carbonyl of KC-1 molecule forms hydrogen bonds with C15-H15 and C16-H16 present in the coumarin ring **B'** of KC-2 molecule. Similarly the O5 atom of KC-2 establishes the HB interaction with the C15-H15 and C16-H16 of KC-1. The one to one hydrogen bonding interaction between the O5 and C15-H15 and C16-H16 leads to the dimer **D2**. The two modes of HB interactions described above leading to the dimers **D1** and **D2** are responsible for the anomalous fluorescence from the solid state and aqueous solutions of KC.

Table 6 Hydrogen bond parameters and symmetry operations in XRD structure of KC

D-HA	D-H(Å)	HA(Å)	DA(Å)	D-HA(°)
C3-H3O4 ⁱ	0.93	2.41	3.207 (2)	144
C7-H7O4 ⁱ	0.93	2.39	3.192 (2)	144
C15-H15O5 ⁱⁱ	0.93	2.43	3.296 (2)	156
C16 -H16O5 ⁱⁱ	0.93	2.78	3.564 (2)	141

Symmetry codes : (i) -1/2+x, 1/2-y,-z, (ii) 1-x, -y, -z.







Fig. 8 Two modes of intermolecular HB interactions observed from the XRD structure. (a) Intermolecular HB formation between ring carbonyl group of coumarin **A** with ring CH in Coumarin A' (**D1**). (b) intermolecular HB formation between bridge carbonyl group in KC-1with ring CH in Coumarin B' in KC-2 and vice-versa (**D2**).

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The optimized structures I, II and III of KC in the gas-phase are shown in Fig. 9a. In I, the N, N- diethyl groups in the coumarin units B1 and B2 exhibit staggered arrangement and this structure is predicted to be the lowest energy structure. In the structure II, the N.N-diethyl groups in the coumarin A are in eclipsed arrangement while they are staggered in coumarin B. This structure (II) is about 0.7 kcal/mol higher in energy than that of I. It is seen that in the crystal, KC monomer possesses the structure II as evidenced from its XRD structure (Fig. 7). The relative orientations of both the coumarin units with reference to the bridge carbonyl group are similar in the structures I and II as seen from the dihedral angle C8C10C11C12 of about -34° (Fig. 9a). However in III, the coumarin B2 is rotated with reference to the C10-C11 bond that is adjacent to the bridge carbonyl, though the N,N-diethyl groups adopt staggered arrangement as observed in structure I. It is found that the structure III of KC is about 5 kcal/mol higher than the structure I. Similar trend in the relative stability of the KC structures is predicted by the M052X³ and BP86^{48,49} methods Table S5 (ESI⁺). The C=O length for the bridge carbonyl bond and the adjacent C-C length given in **Table S6 (ESI**⁺) show the values are similar in the structures I and II. The values predicted by the M052X method for the C=O and C8-C10 in structure II (1.223) and 1.486 Å) are in good agreement with the XRD values of 1.220 and 1.481 Å, respectively. To understand the nature of electronic transitions in KC, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of structures I, II and III were examined and are depicted in (Fig. 9b). The HOMO and LUMO are π -molecular orbitals that are delocalized over the two coumarin units in the two lowest energy structures I and II. Thus the lowest energy excited states in these structures are generated by $\pi - \pi^*$ transition. However as seen from Fig. 9b, the electronic structure differs in III, as the HOMO is delocalized over the coumarin **B2** while the LUMO is delocalized over the coumarin **B1**. It is observed that the HOMO has significant contribution from the amino nitrogen in coumarin B2 and there is an increase in the contribution of bridge carbonyl oxygen in the LUMO. This analysis demonstrates that the change in the molecular geometry leads to significant change in the electronic structure and thus the nature of electronic transition.



Fig. 9 (a) B3LYP/6-31+G** optimized geometries of KC structures **I**, **II** and **III**. The total energies (TE) in hartree and relative energies in kcal/mol (inside parenthesis) are given.(b) HOMO and LUMO in the KC predicted at B3LYP/6-31+G** optimized geometries **I**, **II** and **III**.

3.8 Stabilization of the dimers of KC and their electronic structures

The XRD structure of the single crystal of KC (Fig. 7) reveals the existence of intermolecular C-H...O HB interactions^{28,29} between the carbonyl oxygen atom in one of the KC

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molecules with the ring C-H in the neighbouring molecule. These HB interactions are arche types of weak HBs and their role in the formation of supramolecular assemblies is well recognized.²⁸ Recent studies using accurate wave function methods predict a stability of ~1 kcal/mol due to each CH...O interaction at coupled cluster singles, doubles and perturbative singles CCSD(T) level using complete basis set limit.^{66,67} The HB interactions in two dimer arrangements **D1** and **D2** of KC which are characterised from the XRD structure are shown in Fig. 8a and 8b. In the dimer D1 there are two bifurcated CH...O interactions between the ring carbonyl oxygen of coumarin unit A' with the two CH hydrogens which are adjacent to the ring carbonyl in coumarin unit A (Fig. 8a). These HBs have lengths 2.406 and 2.391 Å and angles 144.2° (Table 6). D2 possesses centre of symmetry and is formed by HBs between the bridge carbonyl group in one KC with two ring CH in **B** (**B'**) which are adjacent to bridge keto group (C15-H15 and C16-H16) in the second KC and *viceversa*. The HB parameters are listed in **Table** 6. Thus it is seen that there are two CH...OHBs in dimer D1 while D2 possesses 4 CH...O HBs. In addition to these weak HBs, other noncovalent interactions⁵³⁻⁵⁶ also contribute to stability in the dimers.

It is seen from **Table 7** that the interaction energies in the dimers **D1** and **D2** are, respectively, -10.38 and -5.80 kcal/mol at the M052X/6-31+G** level. The more reliable M062X-D3/def2-TZVP calculations yield IEs of -11.59 and -6.39 kcal/mol, respectively, in **D1** and **D2**. The above results demonstrate that the dimer **D1** is more stable than **D2** by \sim 5.2 kcal/mol at the M062X-D3 level. From the number of hydrogen bonds we estimate that **D1** and **D2** possess HB energy of \sim -2 and -4 kcal/mol, respectively. The dispersion interaction energy as shown in **Table 8** is -3.48 and of -1.92 kcal/mol, respectively, in **D1** and **D2**. Clearly the dispersion interaction energy is more significant than the HB energy in the dimer **D1**. The

present analysis reveals that the sum of the remaining interaction terms, such as the induction energy and first- and second-order exchange interactions,⁶⁸⁻⁷¹ is -0.47 kcal/mol in **D2** but it amounts to -6.11 kcal/mol in **D1** at M062X-D3/def2-TZVP level.

 Table 7 Total energy TE (hartree) and interaction energy IE (kcal/mol) in the dimers D1 and D2 of KC generated from the XRD structure.

Method		IE			
	КС	D1	D2	D1	D2
M052X/6- 31+G**	-1530.847315	-3061.711174	-3061.703878	-10.38	-5.80
M062X/def2 -TZVP-D3	-1530.906156	-3061.830788	-3061.822489	-11.59	-6.39

Table 8 Dispersion energy (kcal/mol) and dispersion interaction energy IE_{disp} (kcal/mol) in the dimers **D1** and **D2** of KC generated from the XRD structure.

Method	Dispersion energy			IE _{disp}	
	КС	D1	D2	D1	D2
M062X/def2- TZVP-D3	-2.54	-8.56	-7.00	-3.48	-1.92

The HOMO and the LUMO in the dimers **D1** and **D2** as predicted at the B3LYP/6-31+G** level are depicted in **Fig. 10a and 10b**, respectively. It is evident that there is considerable reorganization in the electronic distribution in the two structures **D1** and **D2**. **Fig. 10a** shows that the HOMO of **D1** is a π -MO localized largely on the coumarin unit **A'** of the

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second molecule. The LUMO is a π^* -MO delocalized over the first KC involving both **A** and **B**. In **D2**, the HOMO is a π -MO delocalized over the two KC molecules involving coumarin units **B** and **B'** where in the N,N-diethyl groups adopt the staggered arrangement. It is seen that the nitrogen atoms in **B** and **B'** have significant contribution in the HOMO. The LUMO is essentially a π^* -MO delocalized over the coumarin units **A** and **A'** wherein the N,N-diethyl groups are eclipsed. It is observed that LUMO has larger contribution on the bridge carbonyl oxygen atoms as compared to that in the HOMO. Interestingly, the electronic nature of the HOMO and LUMO of **D2** is closely related to that of KC structure III but having contributions from both the molecules simultaneously. It is obvious that the electronic excitation from the two dimers **D1** and **D2** will result in different types of excited states.



Fig. 10 HOMO and LUMO predicted at B3LYP/6-31+G** level in the KC dimer(a) D1; (b)D2

4. Discussion

The KC molecules exhibit less Stokes shift in both polar and aprotic solvents when compared to the 7-DEC.⁷² It is well known that 7-DEC dye shows ICT absorption in the visible region and is due to the transfer of charge density from electron donor N_N diethylamino group to electron acceptor ring carbonyl group. The absorption and fluorescence maximum of 7-DEC dve were red shifted on increasing solvent polarity. In alcoholic solvents, hydrogen bonding interactions between the alcohol and 7-DEC dye cause extra red shift in the absorption and fluorescence spectra as compared to other solvents.⁷² On excitation, 7-DEC dye undergoes ICT from the electron donating amino group to the electron withdrawing ring carbonyl group. The more polar ICT excited state is stabilized more in polar solvents and this results in larger Stokes shift. The Stoke shift reported for 7-DEC dyes in polar solvents is greater than 3000 cm⁻¹. In KC, two 7-N, N-diethylaminocoumarin dyes are connected by >C=O group at the 3-position. Both the ring carbonyl groups and the bridge carbonyl group act as electron acceptors. The bridge carbonyl group is shared by the two coumarin units in the KC. The steady state absorption and fluorescence studies confirm the $\pi - \pi^*$ nature of the electronic transition in KC. This is further supported by the theoretical calculations. The lowest energy structures (I and II) of KC, the HOMO is π molecular orbital delocalized over both coumarin rings. The LUMO is a π * molecular orbital which is also delocalized over both coumarin rings. In 7-DEC, the electronic transition is $\pi - \pi^*$ involving the coumarin ring and ring carbonyl group. In 7-DEC, the hydrogen bonding interaction between the solvent and ring carbonyl bringing the ICT transition and exhibits large Stokes shift. The small Stokes shift in KC in both aprotic and protic solvents is due the $\pi - \pi^*$ electronic transition involving the coumarin ring and bridge carbonyl group. The ketocoumarin monomer, exhibits $\pi - \pi^*$ transition.

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The addition of water up to 70% to methanol leads to the decrease in the fluorescence intensity with red shift in the absorption and emission maxima. The red shift in the absorption and fluorescence maxima on the addition of water is due to the general solvent effect on the $\pi - \pi^*$ electronic transition of KC monomer.⁶⁴ The decrease in the fluorescence intensity is explained based on the TICT model, considering only general solvent effect. The hydrogen bonding effect on the photophysical properties of 7-Aminocoumarian dyes have studied extensively by several research groups.73-75All these studies focused the intermolecular hydrogen bonding between 7-AC in protic solvents.⁷⁶ The different hydrogen bonds have been proposed for 7-AC in protic solvents. In alcoholic solvents, the hydrogen bond interaction between the solvent and amino group stabilize the ground state and leads to the blue shift in the absorption maximum. In alcohol, the N,N diethyl group of KC interact with the alcohol through specific hydrogen bonding interaction, which slowdown the TICT formation from the ICT state.⁶⁴ On the addition of water, the alcohol molecules present in the solvation shell is replaced by the water molecules. The repulsion of water molecules by the N,N-diethylamino group results in the increase in the non-radiative relaxation to TICT state through flip-flap or umberla-like motion. This non-radiative relaxation increases k_{nr} values in water than in alcohols and result in the decrease in the fluorescence intensity. At higher water percentage, decrease in the absorption with blue shift indicates the formation of dimer/aggregates. The new emission with 550 nm at water percentage greater than 70% is assigned to dimer/aggregates.

On the addition of water to methanol, the new decay component (τ_3) with lifetime 2.71 ns was observed from the 30% of water addition to methanol. H. N. Ghosh et.al reported the triexponential fluorescence decay of DCCA in water and is due to the barrierless non-radiative transition to non-emissive TICT state.⁷⁷ The quenching of the decay component τ_1 and τ_2 on the

addition of water to methanol is assigned due to the increase in the non-radiative relaxation on increasing the water percentage. On going from alcohol to water red shift in the absorption and emission maximum with increase in the fluorescence lifetime is assigned due to the hydrogen bonding interaction between the ring carbonyl oxygen and solvent. The formation of new decay component (τ_3) may be due to the i) solute-solvent hydrogen bonding promoted intramolecular charge transfer state ii) dimer/aggregation of KC on the addition of water. The ultrafast fluorescence decay measurements confirm the absence of excited state reaction in the formation of new emission at higher water percentage.

The fluorescence spectrum of KC at higher water content is similar to the solid state fluorescence spectra of KC. This result indicates that the new decay component (τ_3) observed in moderate to higher water content is not due to the solvent solute hydrogen bonding promoted ICT state. The hydrogen bonding interactions between the KC molecules is observed from the XRD analysis. From the XRD structure of KC in the solid state we obtained two hydrogen bonded dimer structures **D1** and **D2**. The DFT calculations indicate that dimer **D1** is more stable than dimer **D2**. The dimer **D1** has HB interactions between the ring carbonyl oxygen (O4) of coumarin A and C3-H3, C7-H7 of coumarin ring A'. The participation of ring carbonyl oxygen in the HB interactions leads to stabilization of ground state with increase in the fluorescence lifetime of coumarin dyes. Based on this discussion we assigned that decay component τ_3 with lifetime 2.71 ns is due to the dimer **D1**. At higher water content, the KC molecules come together and form dimer **D2**, which involves 1:1 hydrogen bonding between O5 and C15-H15, C16-H16. The 550 nm emission corresponds to **D2** dimer. At higher water content, the decay monitored at 550 nm shows maximum amplitude for the decay component τ_2 with decay time 300 ps and is assigned to dimer **D2**. This is further supported by the increase in the relative amplitude of this

decay component on increasing water percentage from 70% to 90% in the decay monitored at 550nm. The presence of ultrafast decay component in the aqueous solution concludes the presence of KC monomer. The time-resolved fluorescence studies confirm the presence of three emitting species in aqueous solution of KC. On addition of water to alcohol upto 70%, the KC monomer and dimer **D1** are present in the ground state. Above 70% water content all three species, namely, KC monomer, **D1** and **D2** exist in the ground state. This is further confirmed by solid state time-resolved fluorescence measurements.

The time resolved fluorescence decay of KC in solid state was recorded at two different emission wavelength corresponding to KC monomer and dimer emission maximum (490 and 560 nm) on exciting at 445nm. The fluorescence decay of KC in solid state monitored at 490 and 560 nm is shown **fig.11**. The fluorescence lifetime data of KC in solid state compiled in **Table 9.** The fluorescence decay of KC in solid state monitored at both 490 and 560 nm follows tri-exponential with decay times $\tau_1 \sim 100$ ps , τ_2 = 400-500 ps and τ_3 = 2.47-2.59 ns. This time constant are similar to those observed in fluorescence decay of KC at higher water content. The ultrafast decay component (τ_1) is correspond to monomer emission. The decay component τ_2 with lifetime 400-500ps is assigned to dimer D2. The higher amplitude of the τ_2 decay component monitored at 560 nm emission wavelength confirms that this decay component is responsible for the 560 nm emission maximum. The decay component τ_3 is assigned to the dimer D1.



Fig.11 Fluorescence decays of KC in solid state recorded using 445 nm excitation.

Table.9 The fluorescence l	ifetime da	ata of KC	in solid sta	ite
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Emission	$\tau_1^a ps$	τ_2^a ns	τ_{3}^{a} ns	χ2
wavelength (nm)	(B ₁ %)	(B ₂ %)	(B ₂ %)	
490	93(84.57)	0.411(12.40)	2.47(3.04)	1.311
560	115 (67.51)	0.511 (24.39)	2.59(8.09)	1.328

^a Error in the lifetime $\pm 5\%$.

The excitation spectra of KC in neat methanol and different percentage of methanol water mixture were recorded by monitoring the emission at 450, 490 and 550 nm and is shown in **Fig.12**. In neat methanol, the excitation spectrum monitored at 450 nm, shows excitation maximum at 430 nm. On increasing water percentage the excitation intensity decreases with blue shift in the excitation maximum. On increasing water percentage above 80% H_2O results in blue shift in the excitation spectrum with maximum at 400 nm region along with Raman scattering. This excitation maximum is assigned to dimer **D1**. The dimer **D1** has absorption in the 380 to 400 nm region which is also shifted towards blue region when compared to KC monomer

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absorption. This concludes that dimer **D1** is also H-type dimer. Due to the very less population of this dimer, it cannot be resolved in the absorption spectrum.

In neat methanol, the excitation spectrum monitored at 490 nm with shows maximum at 440 nm. On increasing water percentage the excitation intensity decreases with small red shift in the excitation maximum. On further increasing water percentage above 80% H₂O results in the excitation spectrum with maximum at 447 nm region and is due to the KC monomer.

In neat methanol, the excitation spectrum monitored at 550 nm , with shows excitation maximum at 440 nm. On increasing water percentage the excitation intensity decreases with red shift in the excitation maximum. On increasing water percentage above 80% H₂O results in red shift in the excitation maximum to 458 nm. This excitation maximum is assigned to dimer D2 and red shift in the excitation maximum indicates the J-type nature of dimer D2. The 350 nm shoulder in the excitation spectrum of 90% water: methanol mixture monitored at 550 nm confirms the absorption of dimer D2 350 nm to 470 nm region. Due to the very less population of this dimer, it cannot be resolved in the absorption spectrum.

The excitation spectra of KC was recorded in solid state by monitoring the emission intensity at 450, 490 and 570 nm and is shown in **Fig.13**. The solid state excitation spectra is similar the excitation spectrum of KC in water rich alcohol mixture. The emission wavelength dependent solid state excitation spectrum confirms the presence of KC monomer, dimer D1 and D2 in solid state. The solid state excitation spectrum of KC monitored at 560 nm shows excitation maximum at 370 and 520 nm. This confirms that the dimer D2 is J-type dimer. The nature of electronic transition in KC monomer and KC dimer is π - π * and ICT respectively, which is confirmed by the theoretical calculations. In dimer **D1**, the ICT transition involves the

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transfer of electron density from one 7-AC ring to another 7-AC in molecule involving bridge carbonyl group. This is similar to the KC monomer structure III in which the coumarin ring **B** is rotated with reference to the C-C bond that is adjacent to the bridge carbonyl and is the low energy ICT state. In dimer **D2**, the ICT transition involves transfer of π electron density from one KC molecule to another KC molecule and this requires more energy which is further confirmed in excitation spectrum.



Fig.12 Excitation spectra of 2.55µM concentration of KC in different percentage of methanol: water binary mixture.



Fig.13 Solid excitation spectra of KC monitored at 460nm, 490 nm and 570 nm.

The fluorescence spectra of KC was recorded at different excitation wavelengths in methanol, 70% and 90% water methanol mixture. Three different excitation wavelengths, 350 nm, 430 nm and 460 nm were selected. The fluorescence spectrum of KC in different excitation wavelengths is shown in Fig. 14. On excitation at 350, 430 and 460 nm, there is no change in the fluorescence maximum of KC in neat methanol. This confirms the presence of KC monomer in neat methanol. In solvents such as neat protic and aprotic solvents, KC exist as monomer and exhibit $\pi - \pi^*$ electronic transition. In 70% water methanol mixture, 350 nm excitation results in fluorescence spectrum with maximum at 450 nm, whereas 430 and 460 nm excitations leads to fluorescence with maximum at 490 nm. These results confirm the presence of KC monomer and dimer D1 in 70% water methanol mixture. In 90% water methanol mixture, 350 nm excitation results in fluorescence spectrum with dual emission maxima at 450 and 550 nm whereas 430 and 460 nm excitations give rise to the fluorescence with maximum at 550nm along with a shoulder at 490 nm. The 350 nm excitation selectively excites the dimer D1, which is absent in neat solvents. This is further supported by the absence of 450 nm emission in neat methanol. The KC monomer is preferentially excited at 430 nm excitation and the emission with maximum at 490 nm confirms the presence of KC monomer in all the three environments. The dimer D2 was excited preferentially by exciting at 460 nm, and 550 nm emission observed in 90% water: methanol mixture confirms the presence of dimer D1, at higher water content. The dual emission maximum of KC on excitation at 350 nm in 90% water methanol mixture further confirms the absorption of both D1 and D2 dimer at this excitation wavelength. In solid state, the fluorescence maximum of KC was found to be at 550 nm on excitation from 350-520 nm. The emission maximum of KC in solid state is independedent of excitation wavelength. The strong absorption of UV-A radiation by solid state KC may be dye to the absorption of both dimer D1 and D2 and

intense yellow fluorescence (fig. 6 (b)) displayed by the solid state KC is may due to the dimer D2. Both direct population and ultrafast excitation energy transfer from D1 to D2 may be responsible for the intense yellow fluorescence from solid state. To explore the application of solid state KC in the field of "Laser Activated Remote Fluorescer" a latest lighting technology, ultrafast fluorescence spectroscopy of KC in the solid state will be carried out in future.



Fig. 14 Emission spectra of 2.25 μ M concentration of KC (a) 0% H₂O, (b) 70% H₂O, (c) 90% H₂O in methanol recorded at different excitation wavelength.

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Conclusions

In this study, we presented detailed photophysical studies of KC in different solvents and alcohol: water binary mixture and solid state. In neat solvents, KC exist as monomer and the nature of electronic transition is $\pi - \pi^*$ which results in smaller Stokes shift when compared to other 7-AC dyes. The addition of water to alcohol leads to increase in the hydrophilicity of the environment and results in the conformational relaxation and dimerization of hydrophobic KC. The XRD structure of the KC crystal reveals two modes of weak CH...O hydrogen bonds. Two dimers of KC are characterized from the XRD structure. The intermolecular HB interactions between the KC molecules lead to the formation of dimers. The HB interactions in the KC crystal were explored using XRD crystal structure analysis. The carbonyl oxygen atoms O4 and O5 present in the KC are involved in weak CH--O HB interactions and lead to the dimers **D1** and **D2**. The fluorescence and excitation spectral studies conclude the presence the two different dimers in the aqueous solution of KC which in turn depend on the water percentage. At moderate water percentage (<70%) water) the KC monomer and dimer **D1** are present which is further confirmed by the timeresolved fluorescence measurements. At higher water percentage, the dimer D2 co-exist with the KC monomer and dimer **D1**. The new emission maximum (550 nm) with large Stokes shift observed at higher water percentage is due to the dimer **D2**. The H-type nature of dimers **D1** and J-type nature **D2** was confirmed by the wavelength dependent excitation spectral studeies. The new knowledge gained in this study is important to extent application of solid state KC as "Laser Activated Remote Fluorescer" in laser diode based lighting technology and other optoelectronic materials.

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Graphical Abstract

Hydrogen bonded dimers of Ketocoumarin in solid state and alcohol: water binary solvent by Fluorescence spectroscopy, crystal structure and DFT investigation.

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Fluresence emission spectrum of ketocoumarin dimers in alcohol:water binary mixture and solid

state