Supporting Information

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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Preparation of KC

4-Diethylaminosalicyaldehyde (0.966g, 5.0 mmol) and dimethyl 1,3-acetonedicarboxylate (0.435g, 2.5 mmol) were dissolved in warm ethanol (25mL). Piperidine 1.25 mL was added, and the mixture was refluxed for 2 hours. The mixture was cooled to room temperature; the product was collected by filtration, washed with ethanol and recrystallized from ethanol. KC was obtained as a red solid with 70% yield (1.15 g). M. p 185.0–192.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (S,2H), 7.38 (7.38 (d, J=8Hz,6.61 (d, 2H J=8Hz), 6.49 (S,2H), 3.47 (m,8H,J=8Hz),1.25 (t,12H,J=8Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 188. 620, 160. 399, 158. 183, 152. 323, 145.761, 131. 09, 120. 382, 109.409, 108. 466, 97. 214, 45. 050, 12.48 ppm.

NMR spectrum

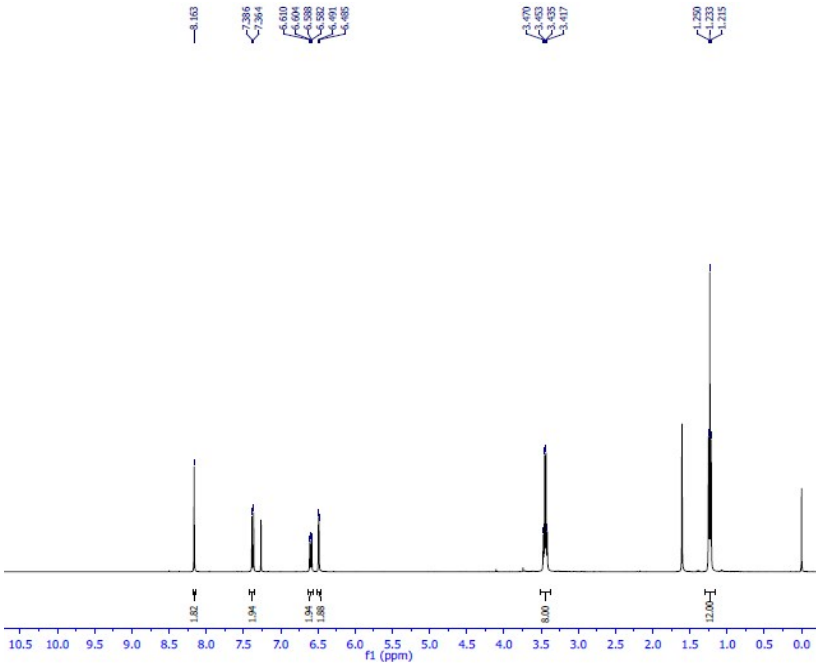


Fig. S1 ^{1}H NMR (400 MHz) spectrum of KC in $CDCl_3$-DMSO-d_6.

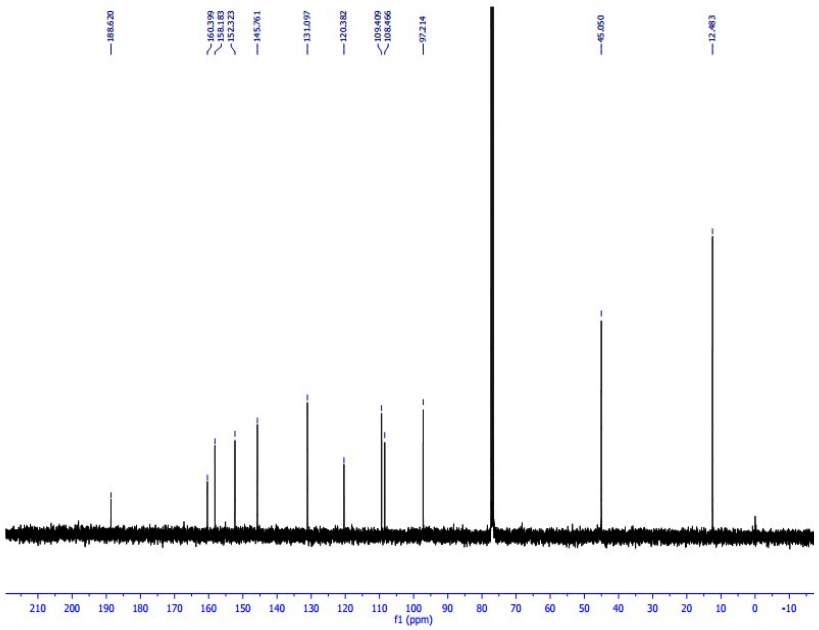


Fig. S2 ^{13}C NMR (100 MHz) spectrum of KC in $CDCl_3$-DMSO-d_6

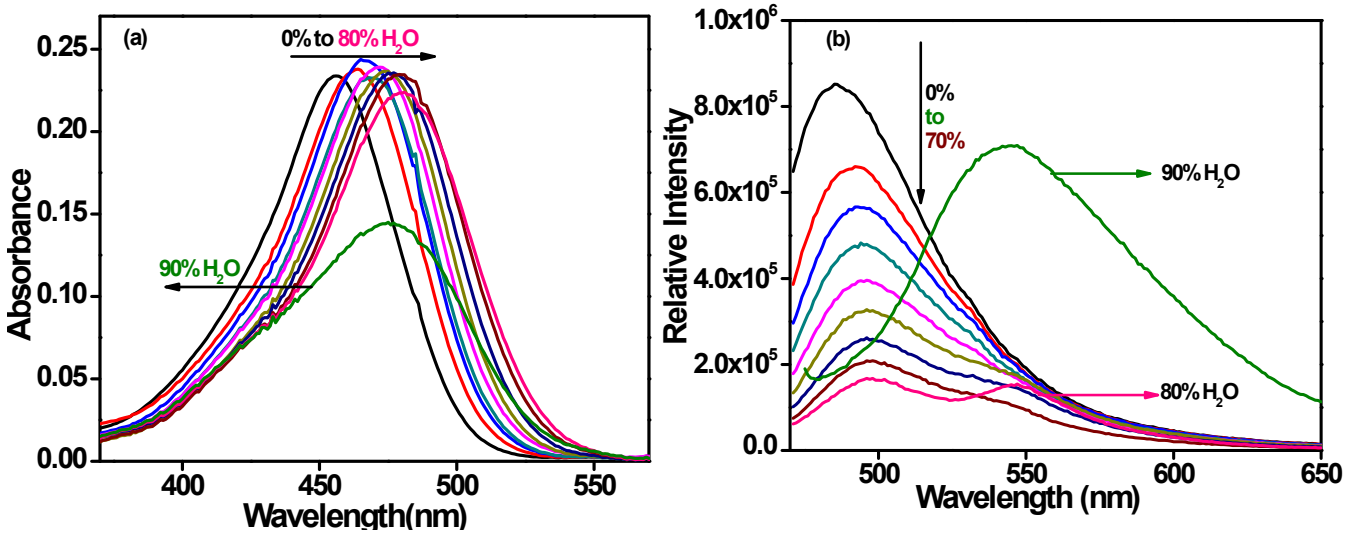


Fig. S3 Absorption (a) and Emission (b) spectra of KC in ethanol and ethanol: water mixtures. λ_{exc} 460 nm. The concentration of KC is 2.5388 X10^{-6}M.

Table S1 The absorption and emission properties of KC in Ethanol: water binary mixture.

% H_2O	Absorption λ_{max} (nm)	Emission λ_{max} (nm)	Stokes shift $\Delta\nu$ (cm^{-1})
0	456	487	1395
10	466	494	1216
20	467	494	1170
30	469	495	1120
40	473	497	1020
50	474	496	935
60	478	496	758
70	481	497	669
80	482	544	2364
90	475	544	2670

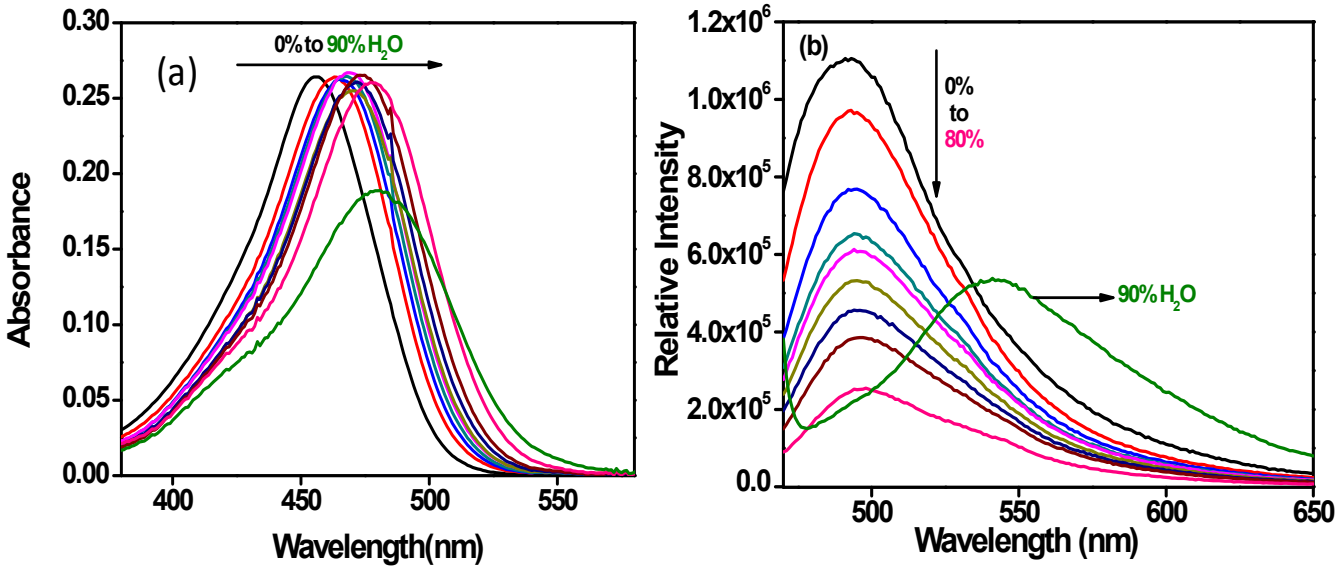


Fig. S4 Absorption (a) and Emission (b) Spectra of KC in n-proH and n-proH: water mixtures. λ_{exc} 460 nm. The concentration of KC is 2.7849 X10^{-6}M.

Table S2. The absorption and emission properties of KC in n-proH: water binary mixture.

% H_2O	Absorption λ_{max} (nm)	Emission λ_{max} (nm)	Stokes shift $\Delta\nu$ (cm^{-1})
0	455	493	1694
10	463	493	1314
20	465	495	1303
30	468	494	1124
40	468	496	1206
50	471	495	1010
60	472	497	935
70	473	497	669
80	474	545	2748
90	475	545	2734

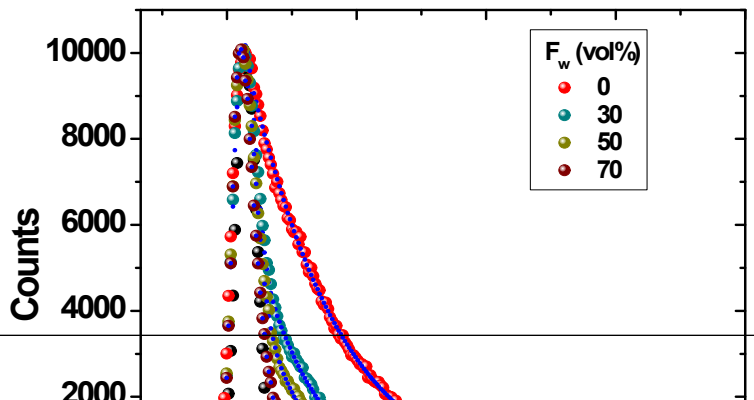


Fig. S5 Fluorescence decay of KC in THF:water mixture. Excitation wavelength is 445 nm.

Table S3 The fluorescence lifetime data of KC in THF: water mixture

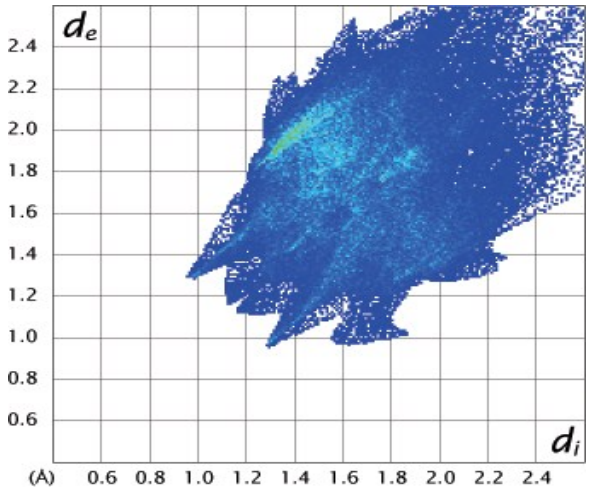
0% H_2O	τ_1[a] (ns)	τ_2[a] (ns)	B_1 (%)	B_2 (%)	χ^2
0	2.01	-	100	-	1.299
30	0.156	1.36	30.06	69.94	1.252
50	0.160	1.12	35.37	64.63	1.299
70	0.140	0.60	38.93	61.07	1.260

[a] Error in the lifetime ± 10%.

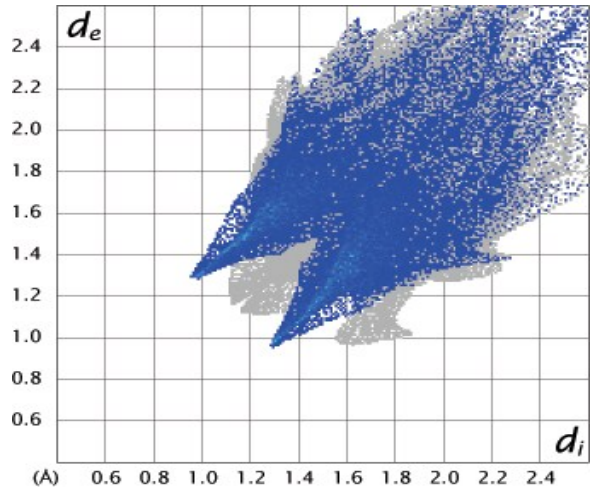
Table S4 Crystal data and structure refinement for KC

Empirical formula	**C_{28} H_{29} Cl_3 N_2 O_5**
CCDC	1819005
Formula weight	579.88
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pbca
Unit cell dimensions	**a = 11.7204(5) Å** a= 90°. **b = 17.1714(8)** b= 90°. **c = 28.6443(14)** g = 90°.
Volume	5764.8(5) $Å^3$
Z	8
Density (calculated)	1.336 Mg/m^3
Absorption coefficient	0.357 mm^{-1}
F(000)	2416
Crystal size	0.300 x 0.250 x 0.200 mm^3
Theta range for data collection	3.026 to 25.000°.
Index ranges	13<=h<=13, -20<=k<=20, -34<=l<=34
Reflections collected	76035
Independent reflections	5044 [R(int) = 0.0257]
Completeness to theta = 25.000°	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7459 and 0.7033
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5044 / 69 / 371
Goodness-of-fit on F^2	1.080
Final R indices [I>2sigma(I)]	R1 = 0.0506, wR2 = 0.1383
R indices (all data)	R1 = 0.0596, wR2 = 0.1525

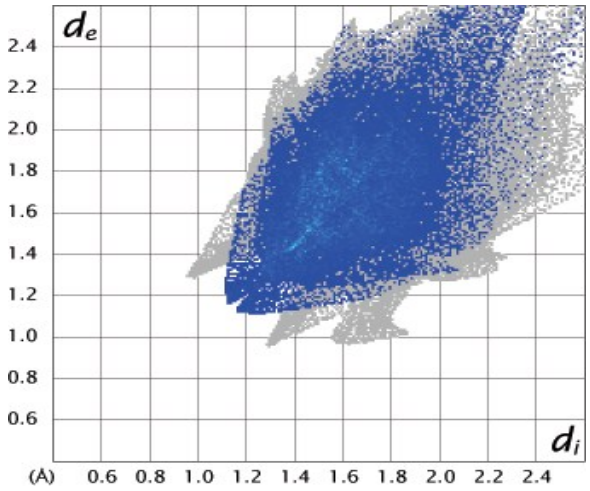
Extinction coefficient	n/a
Largest diff. peak and hole	0.327 and -0.364 e. Å^{-3}



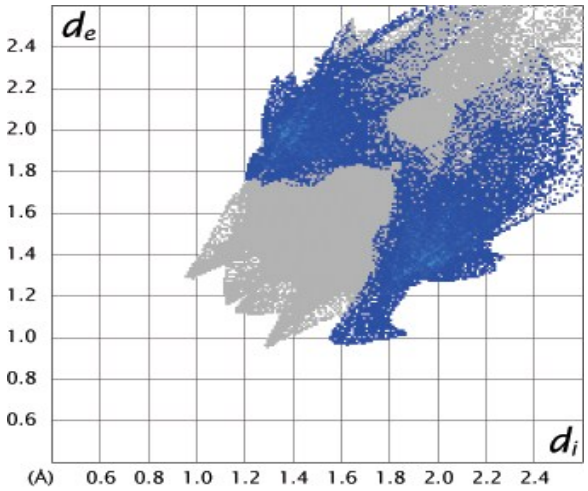
All intermolecular interaction



O...H interactions



H...H interactions



C...H interactions

- H-H interaction - 33%
- C-H interaction - 20.5%
- O-H interaction- 26.3%

Fig. S6 Hirshfeld surface 2D-fingerprint plots for the various intermolecular interaction in KC.

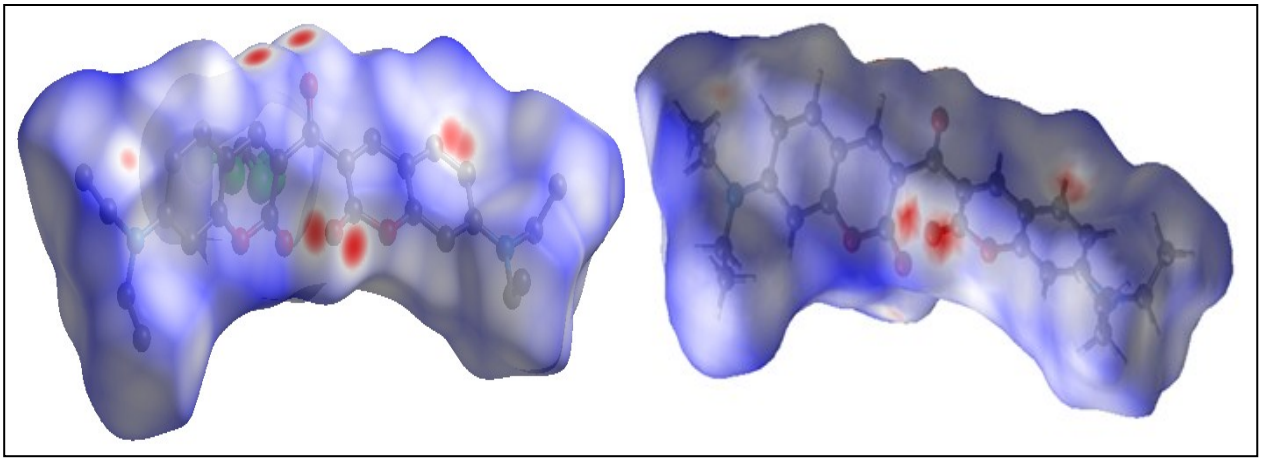


Fig. S7 Two views of the Hirshfeld surface mapped over d_{norm}.

Table S5 Total energies (hartree), (relative energies in kcal/mol) in the DFT optimized structures I,II, III of KC.

	B3LYP/6-31+G**	M052X/6-31+G**	BP86/def2-TZVP
I	-1531.4739504 (0.00)	-1531.293211 (0.00)	-1531.978670 (0.00)
II	-1531.4727957 (0.72)	-1531.292058 (0.72)	-1531.977639 (0.65)
III	-1531.4661384 (4.90)	-1531.284300 (5.59)	-1531.972253 (4.03)

Table S6 Bond lengths (in Å) of bridge carbonyl C10=O5 and the adjacent C8-C10 bonds predicted by the DFT methods and the XRD study.

	B3LYP/6-31+G**		M052X/6-31+G**		BP86/def2-TZVP		Expt. (XRD)	
	C10=O5	C8-C10	C10=O5	C8-C10	C10=O5	C8-C10	C10=O5	C8-C10
I	1.233	1.490	1.223	1.486	1.236	1.490	-	-
II	1.232	1.491	1.223	1.486	1.236	1.491	1.220	1.481
III	1.227	1.506	1.217	1.503	1.230	1.489	-	-