Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Developement of a rhodamine-benzimidazol hybrid derivative as a novel FRET based chemosensor selective for trace level water†

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1. Materials and physical methods

1.1 General Procedures

2-amino phenyl benzimidazole was purchased from Sigma Aldrich (India) and rhodamine B and solvents (spectroscopic grade) were purchased from E. Merck. Other chemicals were of analytical reagent grade and used without further purification except when specified. Milli-Q, 18.2 MΩ cm^{-1} water was used throughout all experiments. A Shimadzu (model UV-1800) spectrophotometer was used for recording electronic spectra. Liquid IR spectra were recorded using prestige-21-shimadzu FTIR spectrometer. ^{1}HNMR and ^{13}CNMR spectrum of organic moiety was obtained on a Bruker 300 MHz spectrometer using DMSO-d_6 solution. Electrospray ionization (ESI) mass spectra were recorded on a Qtof Micro YA263 mass spectrometer. Steady-state fluorescence emission and excitation spectra were recorded with a Perkin Elmer LS 55 spectrofluorimeter. Time-resolved fluorescence lifetime measurements were performed using a HORIBA JOBIN Yvon picosecond pulsed diode laser-based time-correlated single-photon counting (TCSPC) spectrometer from IBH (UK) at λ_{ex}= 340 nm and 560 nm, and MCP-PMT as a detector. Emission from the sample was collected at a right angle to the direction of the excitation beam maintaining magic angle

polarization (54.71). The full width at half-maximum (FWHM) of the instrument response function was 250 ps, and the resolution was 28.6 ps per channel. Data were fitted to multiexponential functions after deconvolution of the instrument response function by an iterative reconvolution technique using IBH DAS 6.2 data analysis software in which reduced w2 and weighted residuals serve as parameters for goodness of fit.

1.2 General method of UV-vis and fluorescence titration

Path length of the cells used for absorption and emission studies was 1 cm. For UV-vis and fluorescence titrations, stock solution of **L** was prepared in different spectroscopic grade pure solvents at 25 °C. Fluorescence measurements were performed using 10 nm x 5 nm slit width. All the fluorescence and absorbance spectra were taken after 20 minutes of mixing of **L** (in different pure solvent) and water**.**

2. Preparation

2.1. Synthesis of the probe (**L**)

The organic probe **(L)** was prepared following a common procedure as stated below. At first rhodamine B acid (1.34 g, 3.0 mmol) was activated by phosphorous oxychloride (460 mg, 3.0 mmol) in dry dichloroethane and stirred for 2 h. After that 2-amino phenyl benzimidazole (837 mg, 3.5 mmol) in dry acetonitrile and 2-3 drops of Et_3N were added to it dropwise and reflux for 32 h. Evaporated to a small volume, cooled, add 30 ml water and extracted 5 times by dichloroethane. Next evaporated to dryness and a reddish colored mass obtained which was recrystallized from pure dry acetonitrile **(Scheme 1)**.

$C_{41}H_{39}N_5O_2$: Anal. Found: C, 77.82; H, 6.03; N, 11.19; Calc.: C, 77.70; H, 6.20; N, 11.05. Liquid IR titration (acetonitrile and water as background, cm^{-1}): $\nu_{OH,}$ 3449; $\nu_{NH,}$ 3188.54; $\nu_{C=C(aromatic)}$, 2926; $\nu_{C=O}$, 1752; ν_{C-O}, 1181; $\nu_{C=N}$, 1590. ^{1}H NMR (δ, ppm in dmso-d_6): 12.64 (1H, s); 7.96 (m, 1H,); 7.83-7.60 (m, 4H); 7.48 (d, 1H, J = 7.5); 7.25-7.10 (m, 4H); 6.81(d, 1H, J = 8.4); 6.62 (t, 1H J = 7.8); 6.42 (s 6H) 3.25 (8H); 1.07 (m, 12H).

^{13}C NMR (δ, ppm in dmso-d_6): (125 MHz, DMSO-d6): 170.03, 150.06, 149.35, 148.77, 133.56, 133.34, 132.44, 132.34,132.0, 131.72, 130.43, 129.77, 129.48, 129.35, 129.08, 128.80, 127.28, 125.84, 124.94, 124.78, 124.09, 116.74, 108.90, 70.32, 44.55-44.74, 12.58-12.81.

^{1}H NMR (δ, ppm in dmso-d_6 and D_2O): 7.94 (1H, d, J = 6.9); 7.73-7.59 (m, 4H,); 7.48 (d, 1H, J = 6.9); 7.16-7.11 (m, 4H); 6.78 (d, 1H, J = 9); 6.64 (t, 1H, J = 7.2); 6.52-6.48 (m, 6H); 3.34 (d, 8H, J = 6.9); 1.16-1.03 (m, 12H).

ESI-MS (in dry acetonitrile): $[M + H]^+$, m/z, 634.31 (100 %) (calcd.: m/z, 634.3104); where M = molecular weight of **L**], $[M + Na]^+$, m/z, 656.33 (13%) (calcd.: m/z, 656.3004). Yield: 66%.

3. Spectral Characteristics

3.1 Emission study

Organic moiety (**L**) shows emission spectrum at around (570-575) nm in different dry organic solvents with increasing water content (25 °C λ_{ex} = 350 nm). Fluorescence quantum yields (Φ) were estimated by integrating the area under the fluorescence curves with the equation:

$$\Phi_{sample} = \Phi_{ref} \times \frac{OD_{ref} \times A_{sample} \times \eta^2_{sample}}{OD_{sample} \times A_{ref} \times \eta^2_{ref}}$$

Where A is the area under the fluorescence spectral curve and OD is optical density of the compound at the excitation wavelength, 350 nm, η is the refractive index of the solvent used. The standard used for the measurement of fluorescence quantum yield was rhodamine-B (Φ = 0.7 in ethanol).

3.2 Calculation of the energy transfer based on the Förster equation:[1,2]

$$\mathbf{E = R_0^6/(R_0^6 + R^6)}$$

Where R_0 is the Förster distance; R is the distance between energy donor dye and energy acceptor dye. The Förster critical distance (R_0) of **L** was calculated to be 52 Å by the simplified equation below:

$$\mathbf{R_0 = 0.211\ [\ k^2\, n^{-4}\, \Phi_D\, J_{DA}\ ]^{1/6} = 0.211\ [\ k^2\, n^{-4}\, \Phi_D \int_0^\infty I_D(\lambda)\, \varepsilon_A(\lambda)\, \lambda^4\, d\lambda\ ]^{1/6}} \quad \textbf{(in Å)}$$

Where n is the refractive index (n = 1.33 in water); Φ_D is the quantum yield of the donor; k denotes the average squared orientational part of a dipole-dipole interaction, typically k^2 =2/3;[3] J_{DA} expresses the degree of spectral overlap between the donor emission and the acceptor absorption; $I_D(\lambda)$ is the normalized fluorescence spectra of the donor; $\varepsilon_A(\lambda)$ is the molar absorption coefficient of the acceptor.

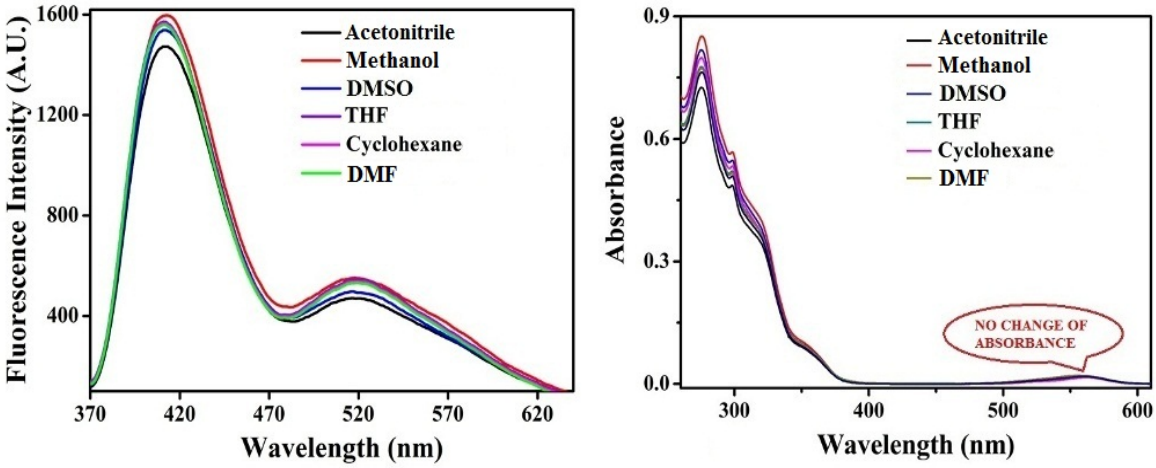

Fig.S1 Fluorescence (left) and absorption (right) study of L in different dry HPLC grade pure solvents.

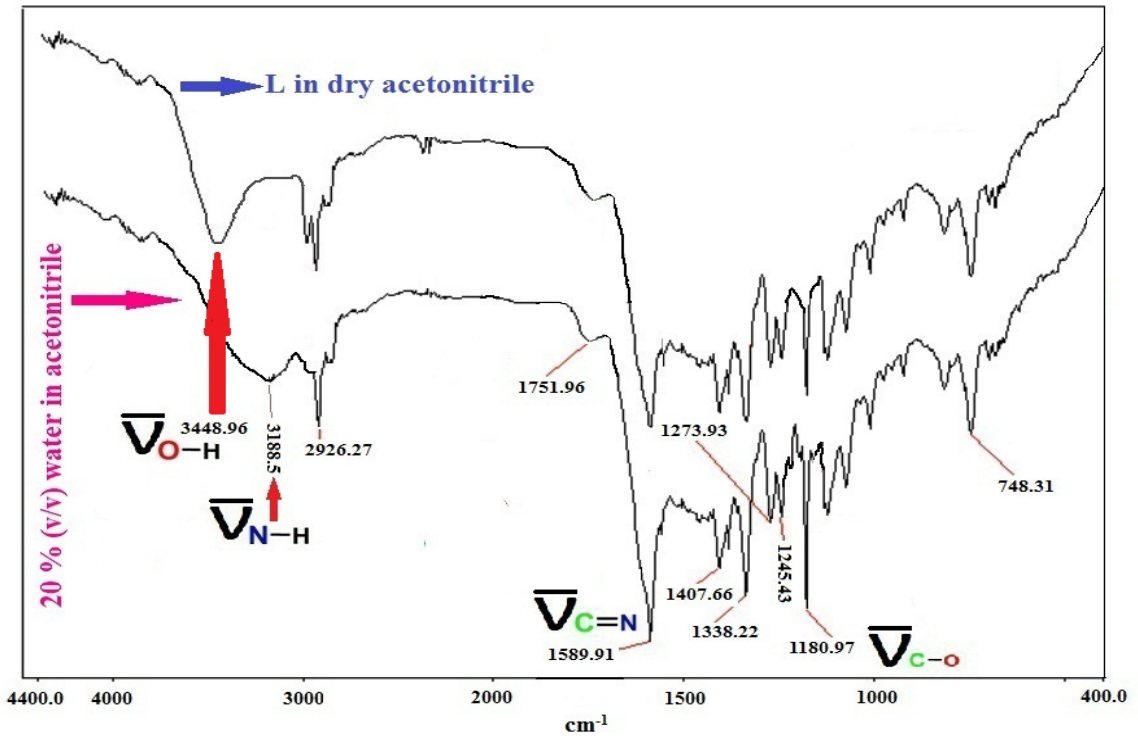

Fig. S2 Liquid IR titration of **L**

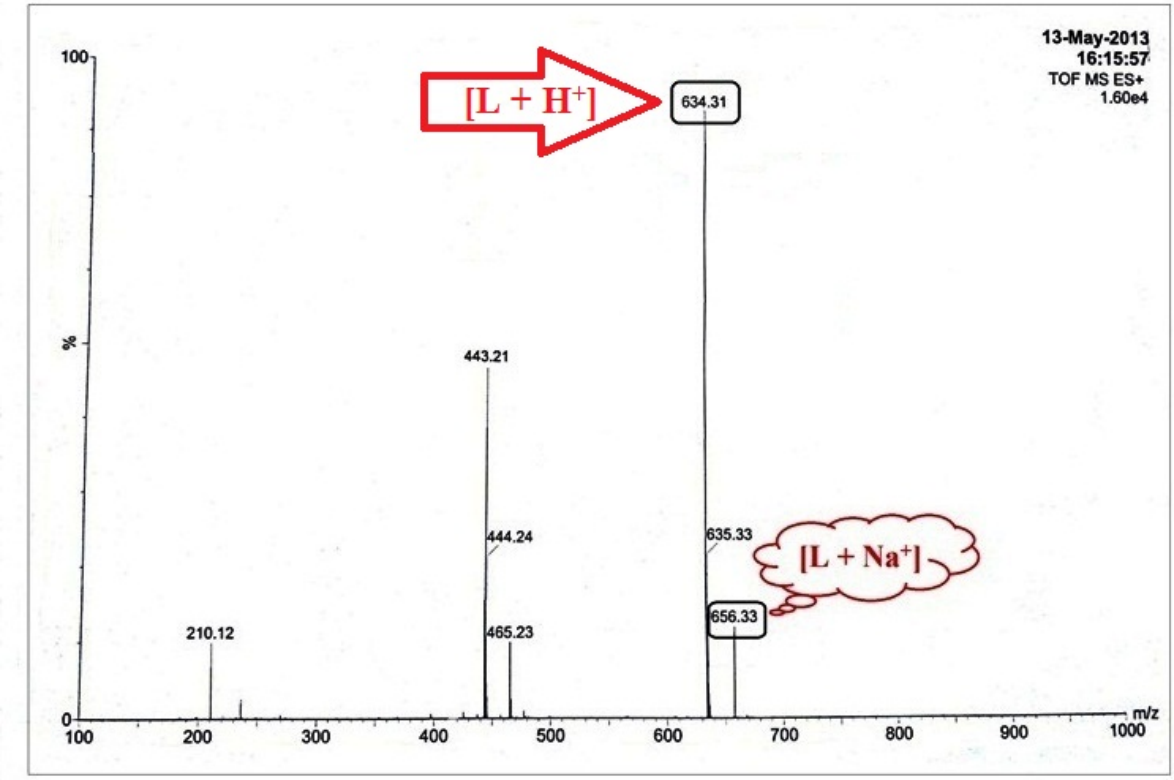

Fig. S3 ESI-MS spectrum of probe (**L**)

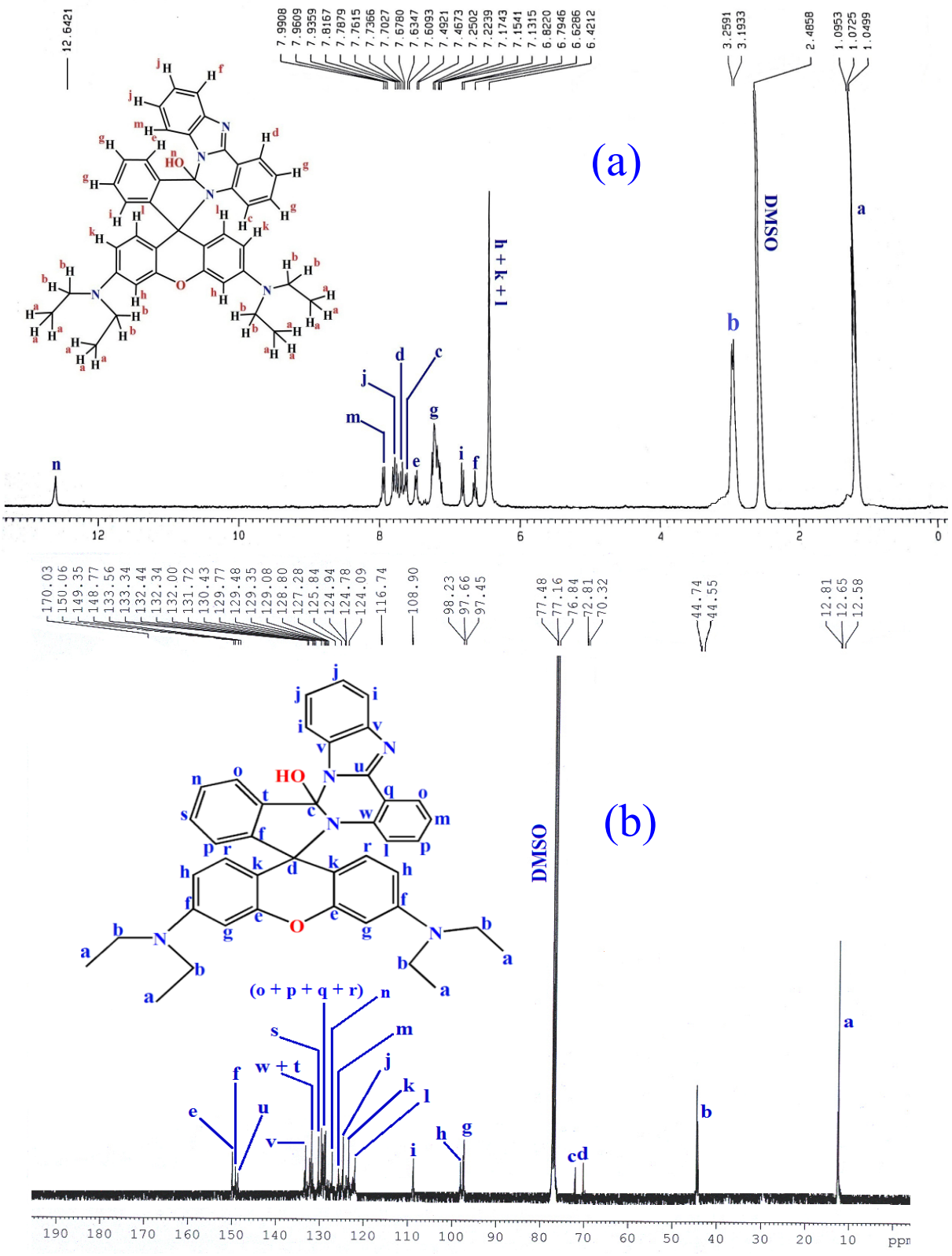

Fig. S4 (a) ^{1}H NMR and (b) ^{13}C NMR of the probe (**L**) in dmso-d_6

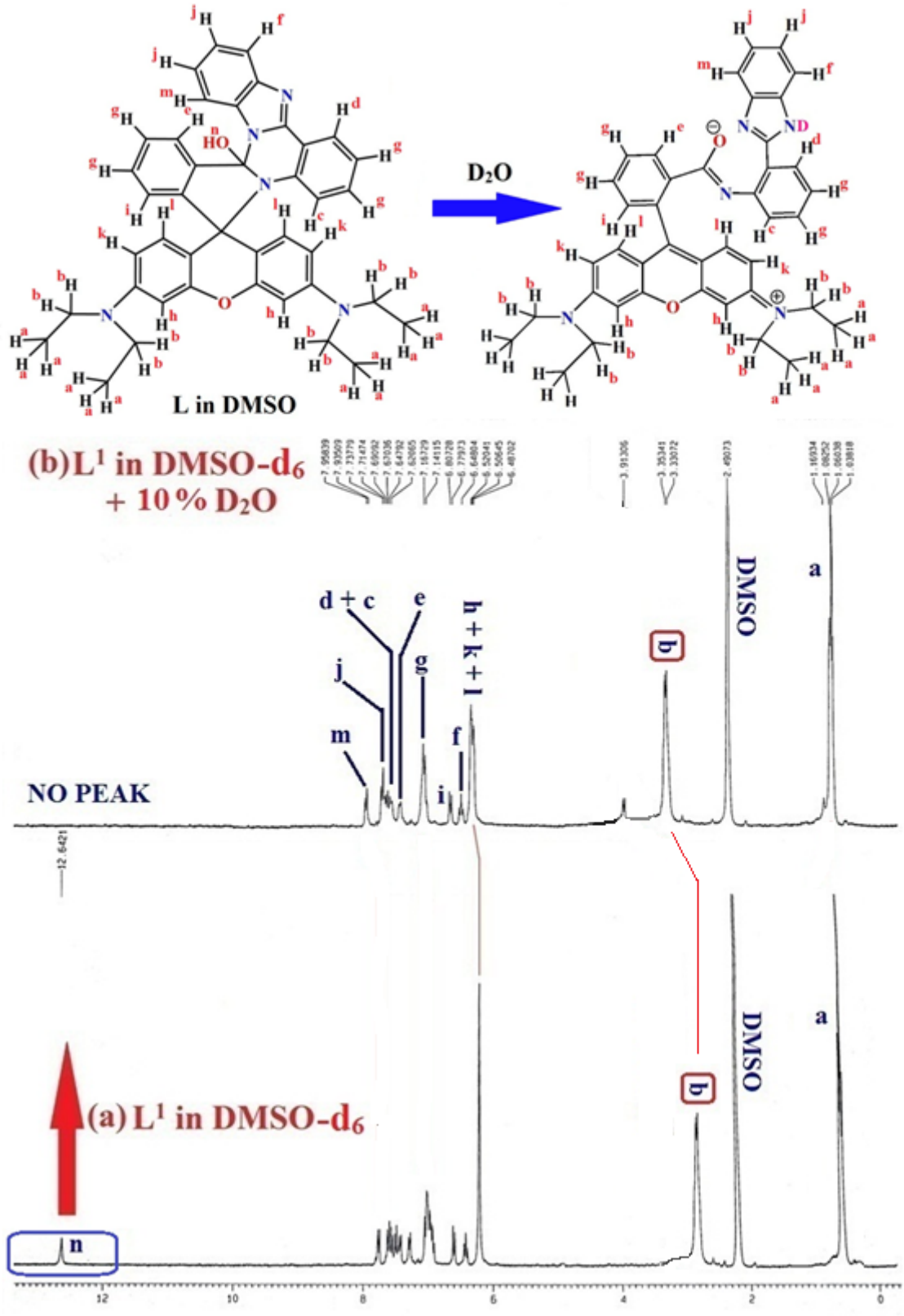

Fig. S5 ^{1}H NMR spectra of **L (a)** in DMSO-d_6 and (b) DMSO-d_6 containing 10% D_2O.

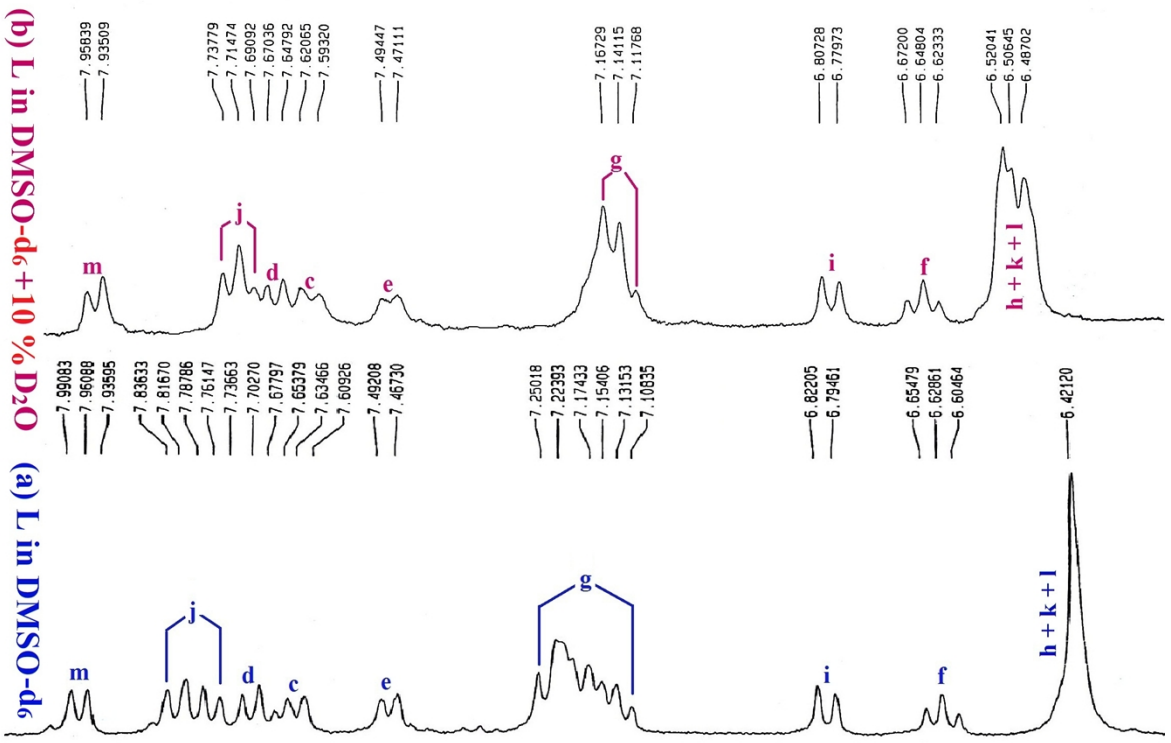

Fig. S6 Expanded ^{1}H NMR spectra of **L (a)** in DMSO-d_6 and (b) DMSO-d_6 containing 10% D_2O (in the aromatic range)

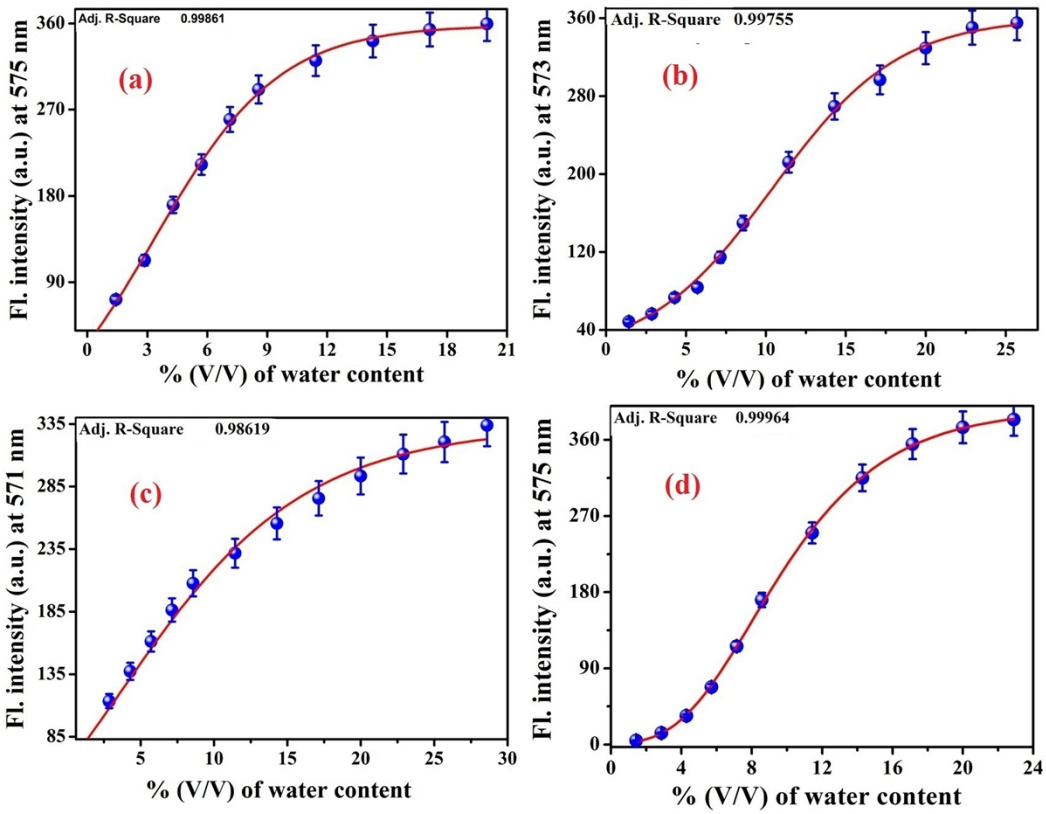

Fig. S7 Fluorescence intensity of **L** at around 574 nm (λex = 350 nm) as a function of water content in (a) acetonitrile, (b) methanol, (c) DMSO and (d) THF

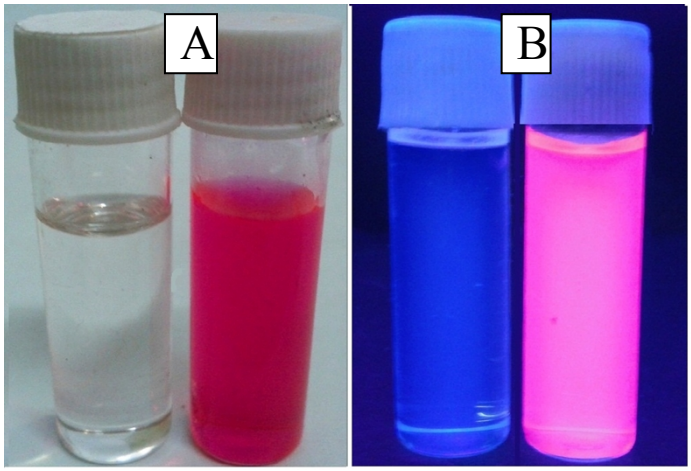

Fig. S8 (A) Visual and (B) fluorescence color change of probe **L** in dry solvent (left) and in 30 % (v/v) water containing solvent (right)

Table S1 Life time detail of **L** at 420 nm

	B_1	B_2	T_1(ns)	T_2(ns)	T_{av}(ns)	χ^2
Probe (L) in Dry DMSO	15.85	84.15	1.29	4.57	4.05	1.05
DMSO + 5 %(v/v) water	17.45	82.55	1.34	4.51	3.96	1.08
DMSO + 10 %(v/v) water	20.67	79.33	1.37	4.46	3.83	1.03
DMSO + 15 %(v/v) water	37.77	62.23	1.26	4.95	3.56	1.04
DMSO + 30 %(v/v) water	42.22	57.78	1.34	5.09	3.51	1.07

References

1 J.R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Springer 2006.

2 N.J. Turro, *Modern Molecular Photochemistry*; Benjamin/ Cummings Publishing Co., Inc.: Menlo Park, CA, 1978.