Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Tuning of multiple luminescence output and white-light emission from a single gelator molecule through ESIPT coupled AIEE process

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Materials and methods:

Unless otherwise stated, all reagents used for synthesis purpose were purchased from commercial suppliers, and used as such without further purification. Organic solvents were purified according to the standard procedure.[1] HPLC grade solvents were used for recording spectrometric data. FTIR spectra were recorded as KBr pellets in a cell fitted with a KBr window, using a Perkin-Elmer Spectra GX 2000 spectrometer. ^{1}H and ^{13}C NMR spectra have been recorded on a Bruker 200/400/500 MHz FT NMR (Model: Avance-DPX 200/500) and all spectra were calibrated against TMS. Mass spectrometric data were acquired by an electron spray ionization (ESI) technique on a Q-tof-micro quadruple mass spectrometer (Micro mass). High-resolution mass spectra were recorded on JEOL JM AX 505 HA mass spectrometer. Thermo-gravimetric analyses (TGA) were carried out on a TG50 analyzer (Mettler-Toledo) or a SDT Q600 TG-DTA analyzer under a N_2 atmosphere at a heating rate of $10^{\circ}C\ min^{-1}$ within a temperature range of 20–800 ^{o}C. UV-Vis spectra were recorded using a PerkinElmer Lambda-950 UV-Vis spectrometer equipped with a peltier system for variable temperature experiments, while fluorescence as well as fluorescence excitation spectra were recorded using Qunata Master 400, PTI spectrofluorometer. FESEM images were obtained using Nova Nano SEM 450 and Quanta™ Scanning Electron Microscope. TEM images were recorded using a FEI Tecnai G2 F20 X-TWIN TEM at an accelerating voltage of 200 kV. Rheology was performed using a TA-ARES rheometer equipped with a force rebalance transducer. X-ray powder diffraction (XRPD) of air dried THF gel of **1** were recorded on a Phillips PANalytical diffractometer for Cu K_{α} radiation (λ = 1.5406 Å).

General description of different experimental techniques:

UV-Vis and Fluorescence spectrum measurements: Stock solutions of both compounds (**1** and **2**) were made in THF (1.0 μM). An aliquot (0.5 mL) was taken and was added with an appropriate amount of THF and water (H_2O) to adjust the desired solvent composition and final concentration (10 μM). Each solution was allowed to equilibrate at room temperature for 1h before spectral measurements. For variable-temperature experiments compound-**1** solution in THF/Water (3:7) was heated from lowest to highest temperature and allowed to equilibrate for 15 min at the desired temperature before each measurement. All luminescence measurements were recorded using, λ_{Ext} = 365 nm and 306 nm for compound **1** and **2** respectively with an emission slit width of 2 nm. Fluorescence excitation spectra were recorded using the same solution used for fluorescence studies.

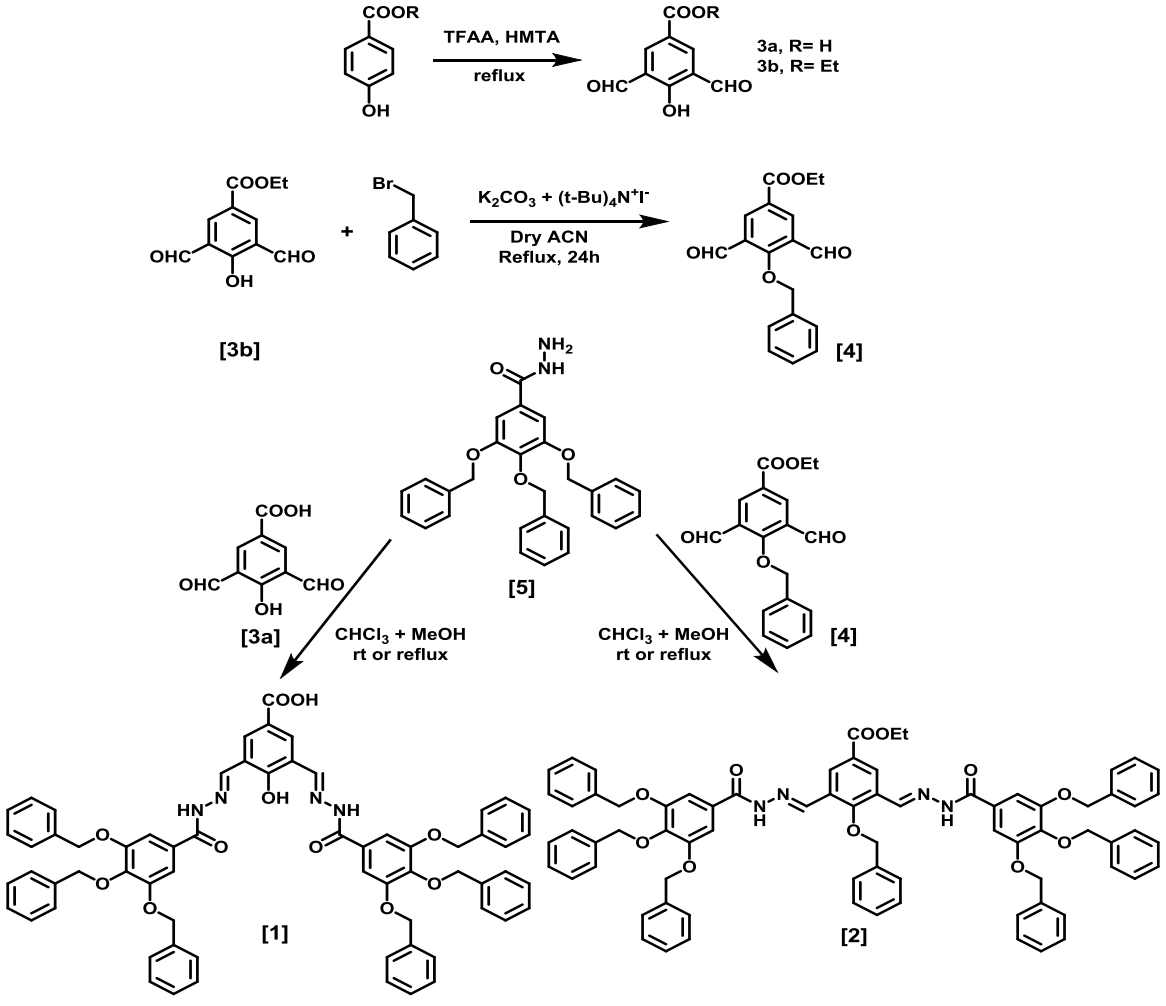
General procedure for gelation study: Due to the limited solubility of **1** in common organic solvent, gelation property of **1** was checked with three specified solvents, namely DMF, DMSO and THF. Compound **1** was highly soluble in DMF and DMSO, which were not suitable for studying the gelation phenomena. Whereas in case of THF solvent, A weighted amount **1** was dissolved in THF (1.0 mL) by heating in closed vials. The clear solution was left to cool down in air at 25^{o}C without any disturbance. The gel formation was confirmed by the failure of the soft mass to flow by inverting the glass vial.

Scanning electron microscopy (SEM): A solution of **1** (100 μM) in THF as well as in different composition of THF/water mixture were drop-casted on silicon wafer and allowed to air dry for 6-7 hrs in a dust free place. Finally it was dried under desiccator for overnight. Before taking images samples were coated with gold vapor.

Transmission Electron Microscopy (TEM): TEM samples were prepared drop-casting the 1.0 mM THF solution of **1** onto carbon coated copper grids (200 mesh). TEM images were obtained after drying the sample in vacuum for 24 hours.

Current (*I*) - voltage (*V*) measurements: The gel solution of **1** (10.0 mg/mL of THF) was drop-casted on indium tin oxide (ITO) coated glass surfaces and dried for 24 hrs at room temperature. *I-V* characteristic profile of this sample was measured in a two-probe electrode using a KEITHLEY 4200-SCS programmable electrometer instrument.

Synthetic scheme:



Sceme-1: Methodologies that were adopted for synthesis of **[1], [2], [3a & 3b], [4] and [5].**

Synthesis of [3a & 3b]: 3a and **3b** were synthesized following the previously reported procedure.[2]

Synthesis and characterization of [4]: In a 100 mL two neck RB 3,5-bisformyl-4-hydroxy ethyl benzoate **[3b]**[2] (200.0 mg, 0.9 mMol), commercially available benzyl bromide (169.5 mg, 0.99 mMol) , anhydrous K_2CO_3 were mixed in 20~25 mL dry acetonitrile (ACN) . Followed by a pinch of tertiary butyl ammonium iodide $(tBu)NH_4^+I^-$ was added and was reflux for 24 h under N_2 atmosphere. The reaction mixture was cooled to room temperature; solvent was then removed under reduced pressure using a rotary evaporator. Oily residue was taken in 80 mL of $CHCl_3$, and washed with distilled water (3 X 30 mL). Organic layer dried over anhydrous Na_2SO_4. Finally solvent was evaporated to get crude product as a color less oil. It was purified by column chromatography using silica gel as stationary phase and 25% ethyl acetate in hexane as eluent to obtain pure product as white solid. Yield = 35%, **^{1}H NMR** ($CDCl_3$, 200 MHz, TMS): δ (ppm) = 10.23 (2H, s, -CHO); 8.72 (2H, s, ArH); 7.41-7.36 (3H, m, ArH); 7.32-7.29 (2H, m, ArH); 5.24 (2H, s, $-CH_2$); 4.47-4.36 (2H, q, *J* = 7Hz, $-CH_2$ ester); 1.44-1.37 (3H, t, *J* = 7.2Hz, $-CH_3$ ester); **^{13}C NMR** ($CDCl_3$**,** 400 MHz, TMS): δ (ppm) = 14.72, 59.51, 61.84, 81.71, 127.52, 128.98, 129.06, 129.56, 130.57, 134.02, 138.35, 164.35, 165.81, 187.82; **HRMS (ESI):** m/z calculated for $C_{18}H_{16}O_5Na$ $[M + Na]^+$: 335.0890; found 335.0884.

Synthesis of [5]: Compound **[5]** was synthesized according to the previously reported procedure.[3]

Synthesis and characterization of [1] and [2]: Synthetic procedure of both compounds was followed according to reported procedure[3] with slide modification. A solution of compound **[3a]** (136.2 mg, 0.7 mMol) or **[4]** (219.1 mg, 0.7 mMol) in methanol was added drop wise to a $CHCl_3$ solution of compound **[5]** (638.0 mg, 1.4 mMol). The reaction mixture was stirred at room

temperature for 9~10 hour, resulting precipitate [for compound-**1** (yellow) and for compound-**2** (color less)] was filtered off using G4-gooch crucible. Washed with (1:1) $CHCl_3$/MeOH mixture several times, dried under desiccator to obtain the pure product.

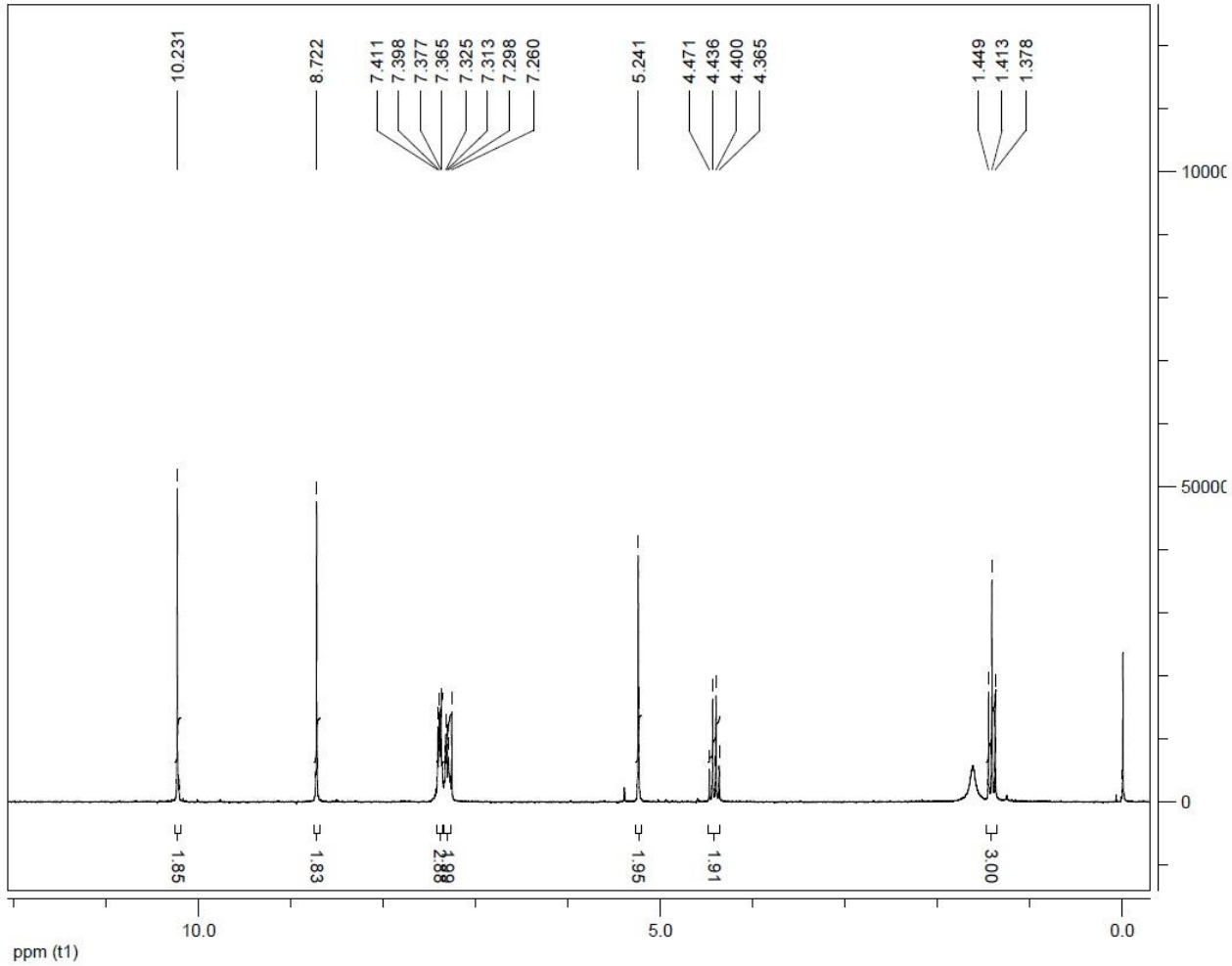
[1]: Yield = 90%; **^{1}H NMR** (DMSO-d_6, 500 MHz, TMS): δ (ppm) = 13.30 (1H, s, -COOH); 12.18 (2H, s, -NH); 8.82 (2H, s, -CH=N); 8.34 (2H, s, ArH); 7.51-7.49 (8H, d, *J* = 7Hz, ArH); 7.45-7.40 (12H, m, ArH); 7.37-7.36 (8H, m, ArH), 7.28-7.27 (6H, m, ArH); 5.22 (8H, s, $ArCH_2O$); 5.04 (4H, s, $ArCH_2O$); **^{13}C NMR** (DMSO-d_6, 400 MHz, TMS): δ (ppm) = 70.44, 74.22, 106.95, 120.23, 122.18, 127.65, 127.82, 127.91, 128.01, 128.11, 128.39, 130.84, 136.67, 137.30, 140.30, 145.15, 152.08, 159.82, 162.27, 166.37; **HRMS (ESI):** m/z calculated for $C_{65}H_{55}O_{11}N_4$ $[M + H]^+$: 1067.3862; found 1067.3861.

[2]: Yield = (84%); **^{1}H NMR** (DMSO-d_6, 400 MHz, TMS): δ (ppm) = 11.94 (2H, s, -NH); 8.75 (2H, s, -CH=N); 8.57 (2H, s, ArH); 7.56-7.54 (2H, m, ArH); 7.50-7.48 (6H, m, $ArCH_2O$);7.43-7.34 (26H, m, ArH); 7.29-7.27 (5H, m, ArH); 5.22 (8H, s, $ArCH_2O$); 5.04 (6H, s, $ArCH_2O$); 4.42-4.41 (2H, board, -CH_2 ester); 1.37 (3H, board, -CH_3 ester); **^{13}C NMR** (DMSO-d_6, 500 MHz, TMS): δ (ppm) = 14.22, 61.22, 70.48, 74.25, 78.44, 107.05, 126.56, 127.56, 127.87, 127.94, 128.05, 128.15, 128.34, 128.41, 128.58, 128.92, 129.20, 135.29, 136.71, 137.31, 140.25, 141.57, 152.07, 159.11, 162.80, 164.77; **HRMS (ESI):** m/z calculated for $C_{74}H_{65}O_{11}N_4$ $[M + H]^+$: 1185.4644; found 1185.4647.

References:

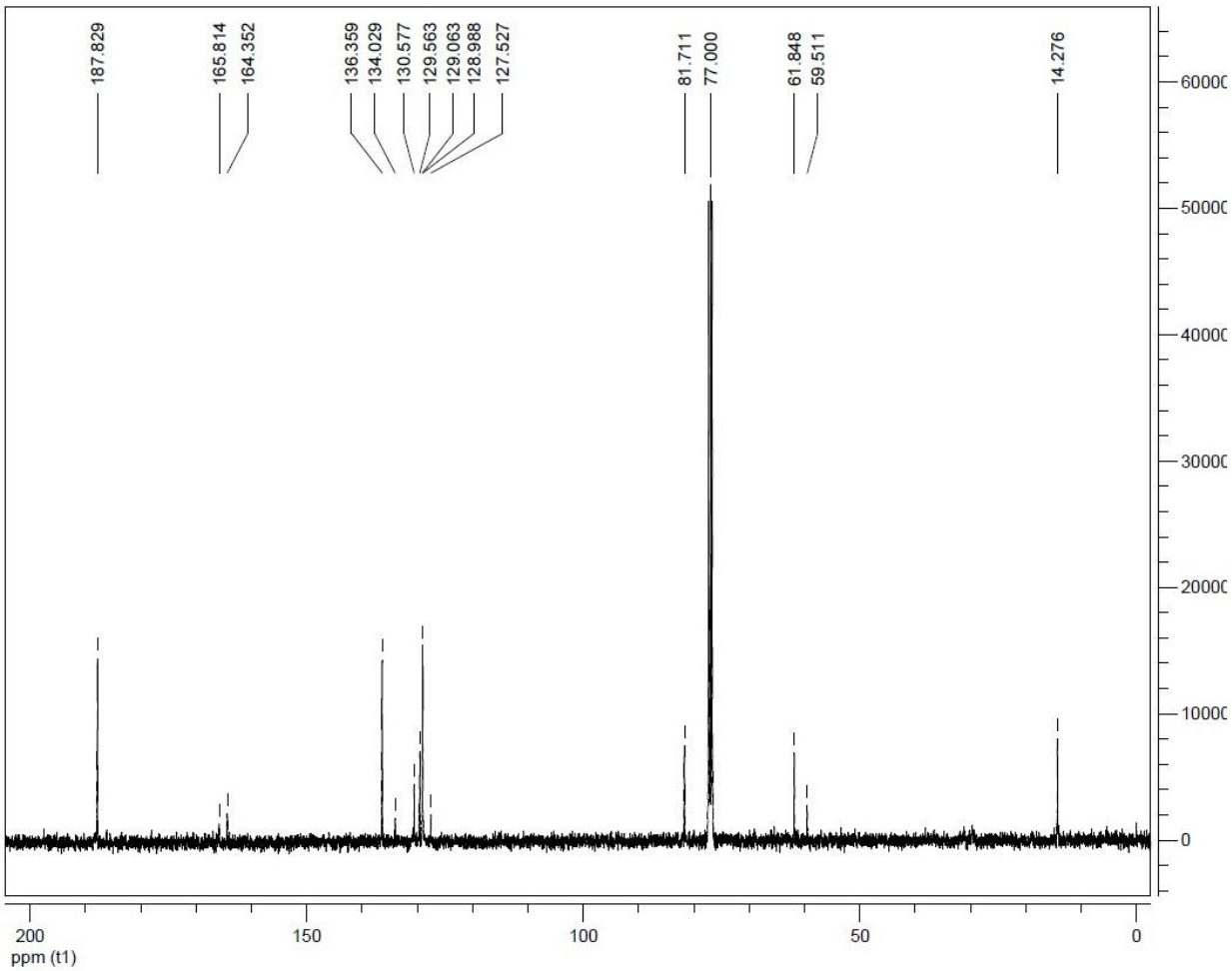
1. Perrin, D. D.; Armarego, W. L. F. Perrin, D. R. Purification of Laboratory Chemicals, 2nd ed., Pergamon, Oxford, 1980
2. Naama Karton-Lifshin, Lorenzo Albertazzi, Michael Bendikov, Phil S. Baran and Doron Shabat, *J. Am. Chem. Soc.*, 2012, **134**, 20412.
3. P. Rajamalli and E. Prasad, *Org. Lett.*, 2011. **13**, 3714.

[1]H NMR spectra of [4]:



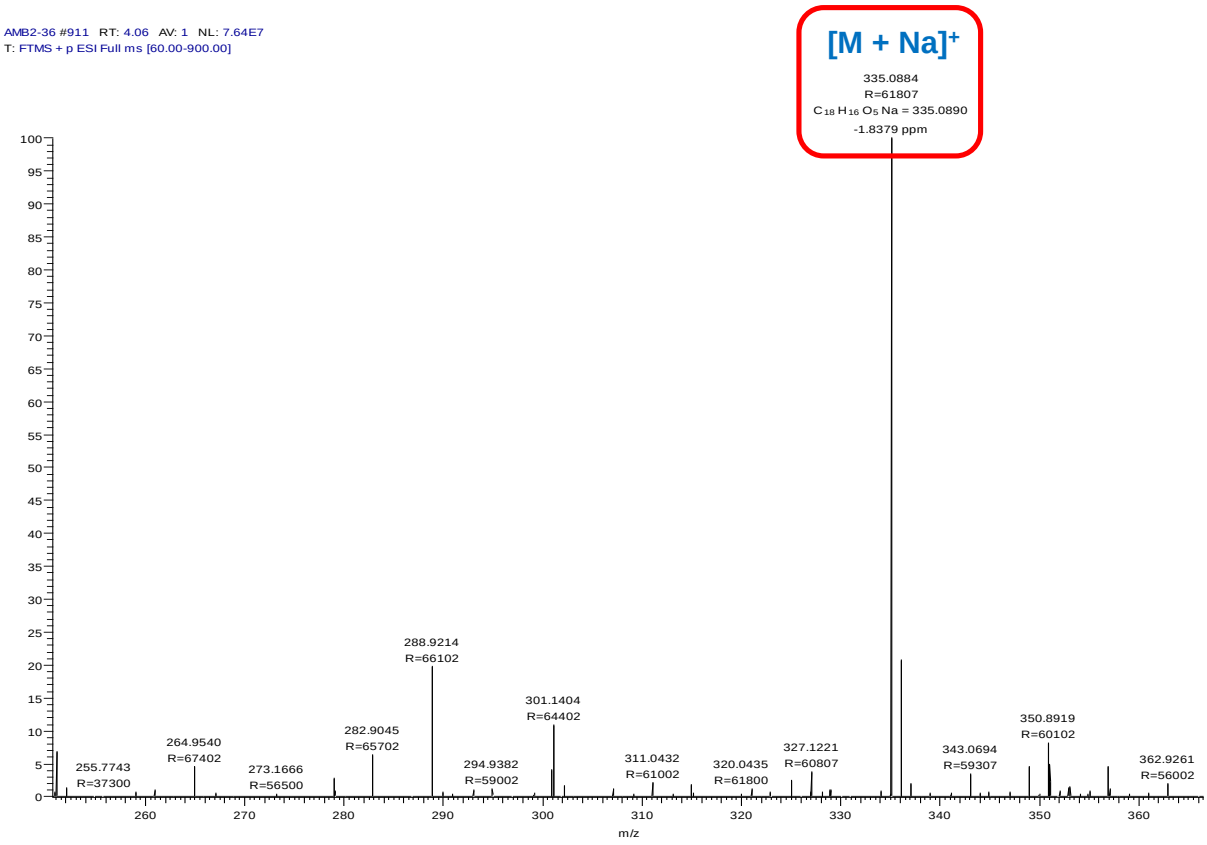
SI Fig.S1: ^{1}H NMR spectra of **[4]** in $CDCl_3$ recorded in 200 MHz.

^{13}C NMR spectra of [4]:



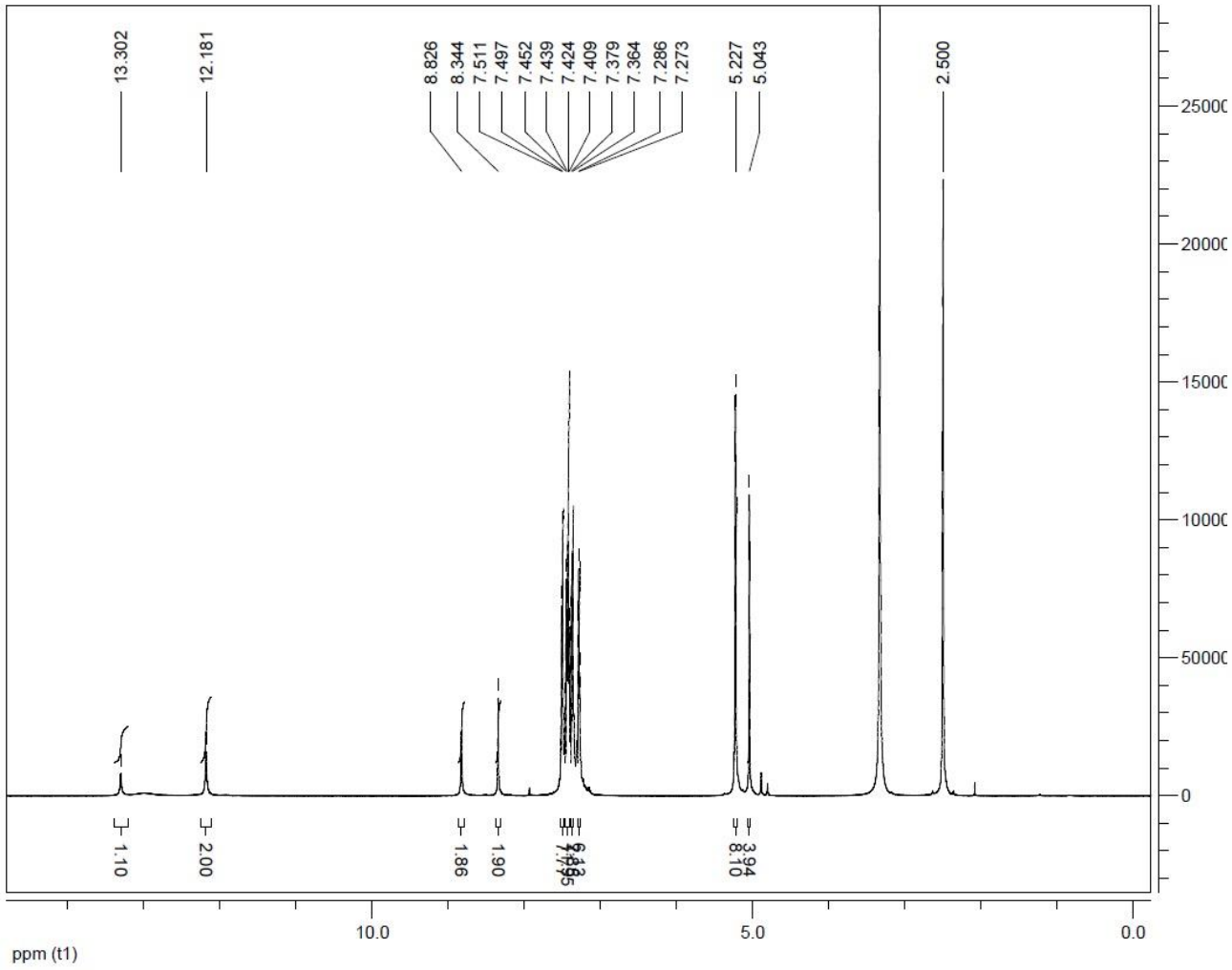
SI Fig.S2: ^{13}C NMR spectra of **[4]** in $CDCl_3$ recorded in 400 MHz.

Mass spectra of [4]:



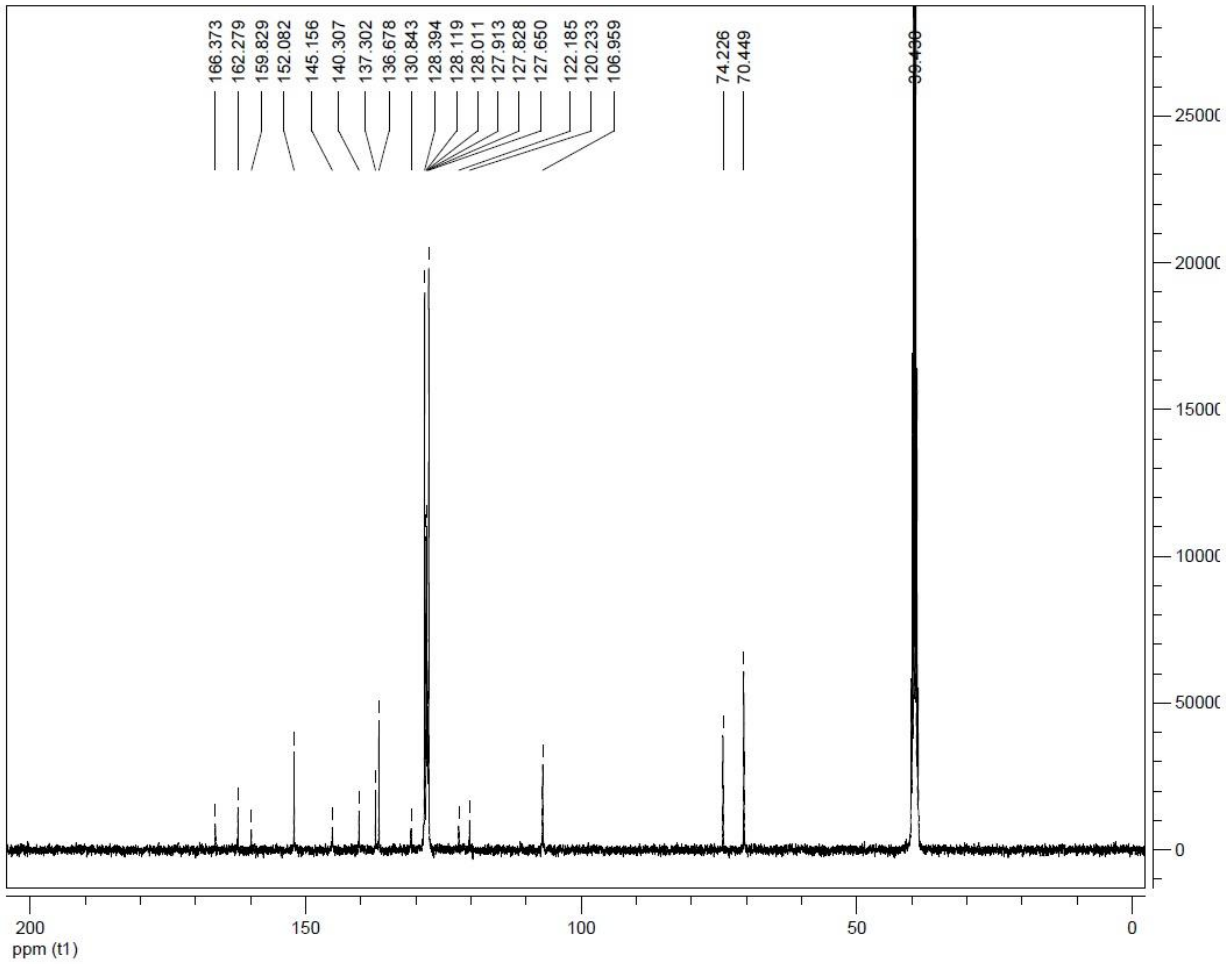
SI Fig.S3: HRMS spectrum of **[4]**.

[1]H NMR spectra of [1]:



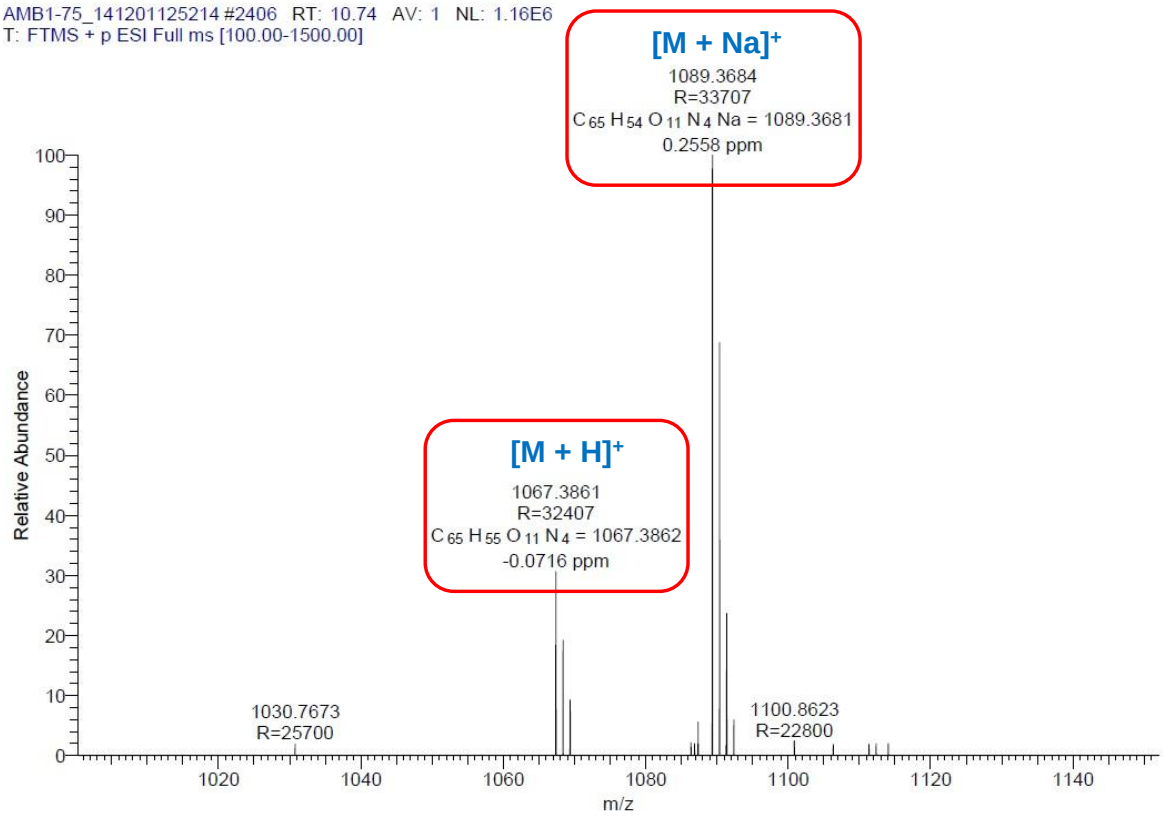
SI Fig.S4: ^{1}H NMR spectra of **[1]** in DMSO-d_6 recorded in 500 MHz.

^{13}C NMR spectra of [1]:



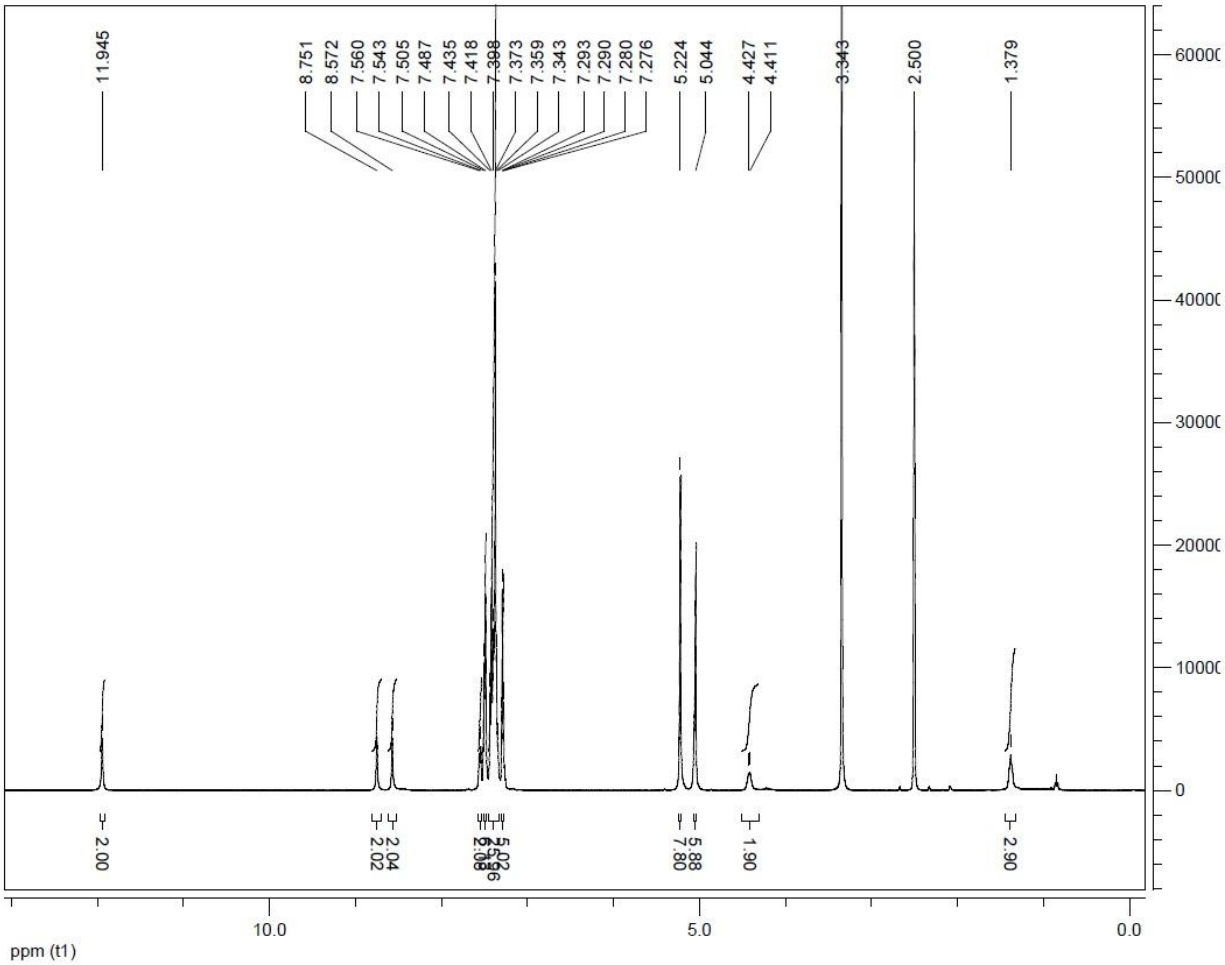
SI Fig.S5: ^{13}C NMR spectra of **[1]** in DMSO-d_6 recorded in 400 MHz.

Mass spectra of [1]:



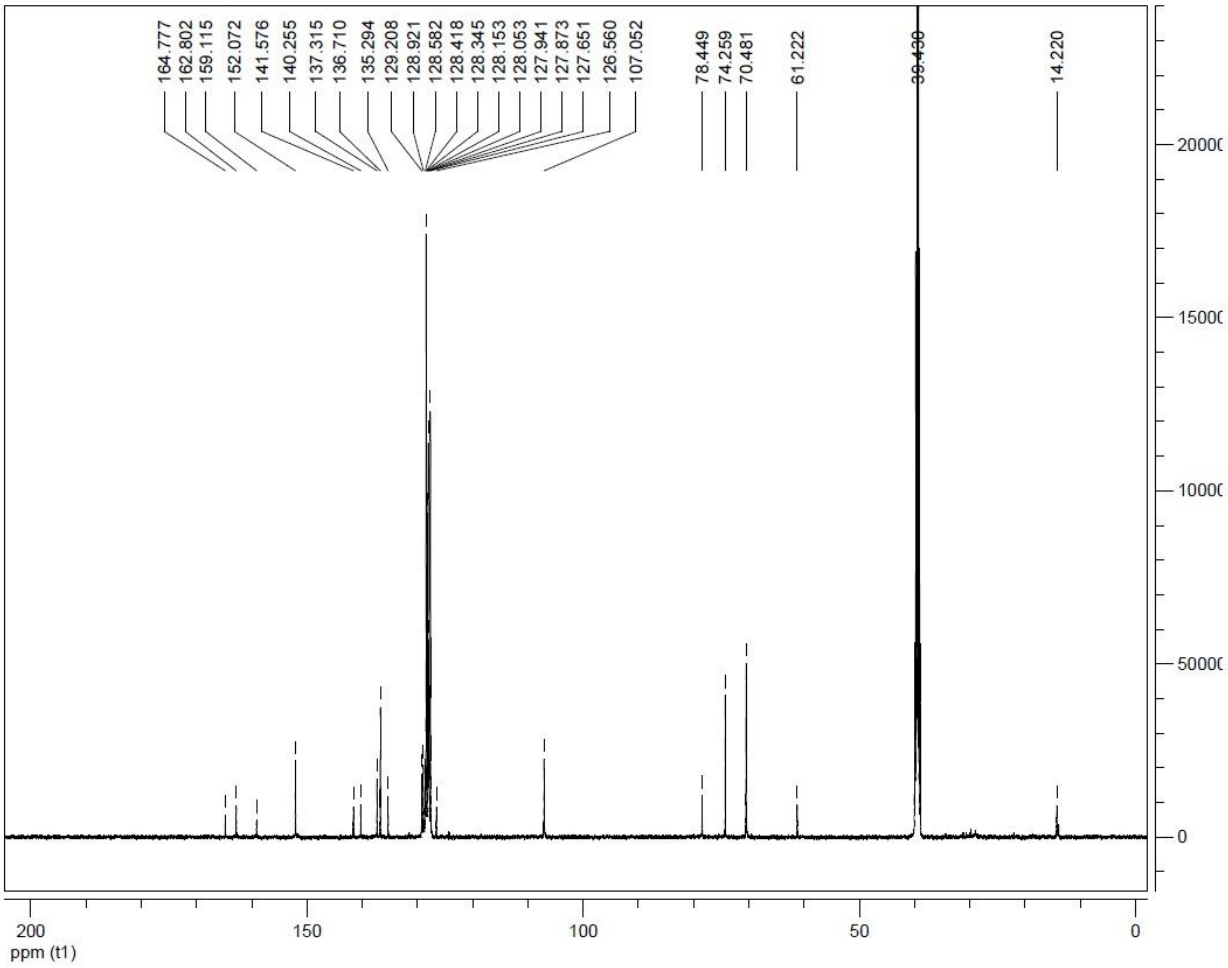
SI Fig.S6: HRMS spectrum of [**1**].

[1]H NMR spectra of [2]:



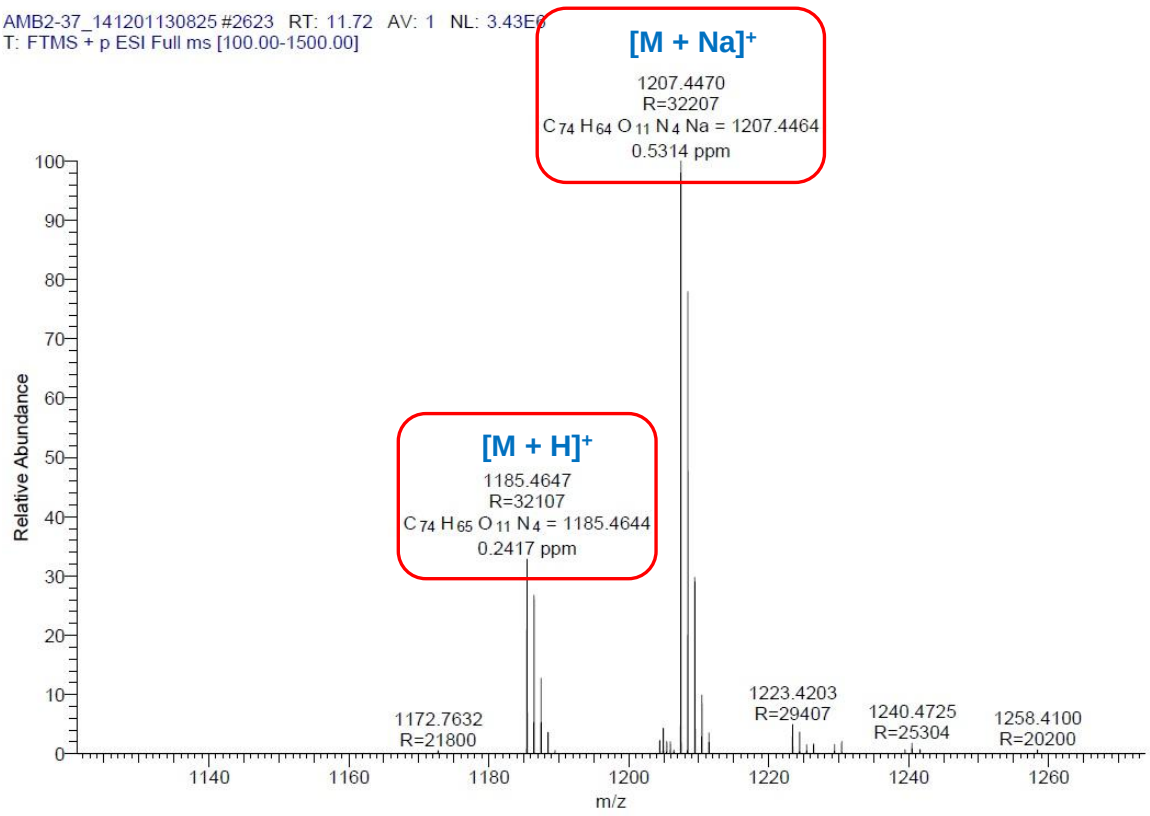
SI Fig.S7: [1]H NMR spectra of **[2]** in DMSO-d_6 recorded in 400 MHz.

^{13}C NMR spectra of [2]:



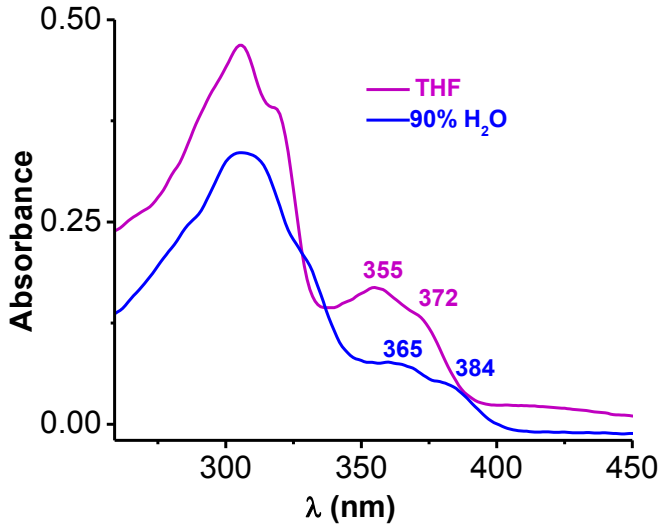
SI Fig.S8: ^{13}C NMR spectra of **[2]** in DMSO-d_6 recorded in 500 MHz.

Mass spectra of [2]:



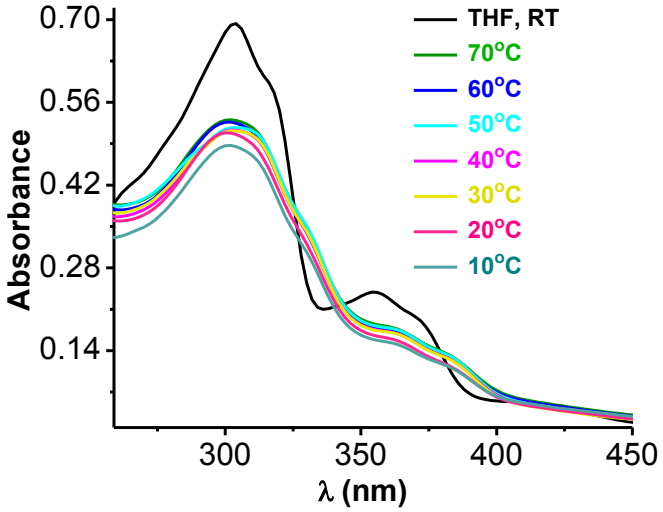
SI Fig.S9: HRMS Spectrum of **[2]**.

UV-Vis absorption spectra of [1]:



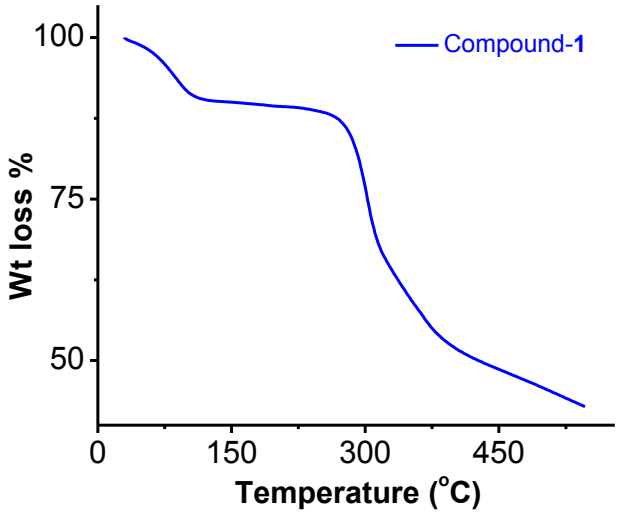
SI Fig.S10: Absorption spectra of **1** in pure THF and THF-water (1:9; v/v) mixture solution. Concentration used 10 μM.

Variable-temperature UV-Vis absorption spectra of [1]:



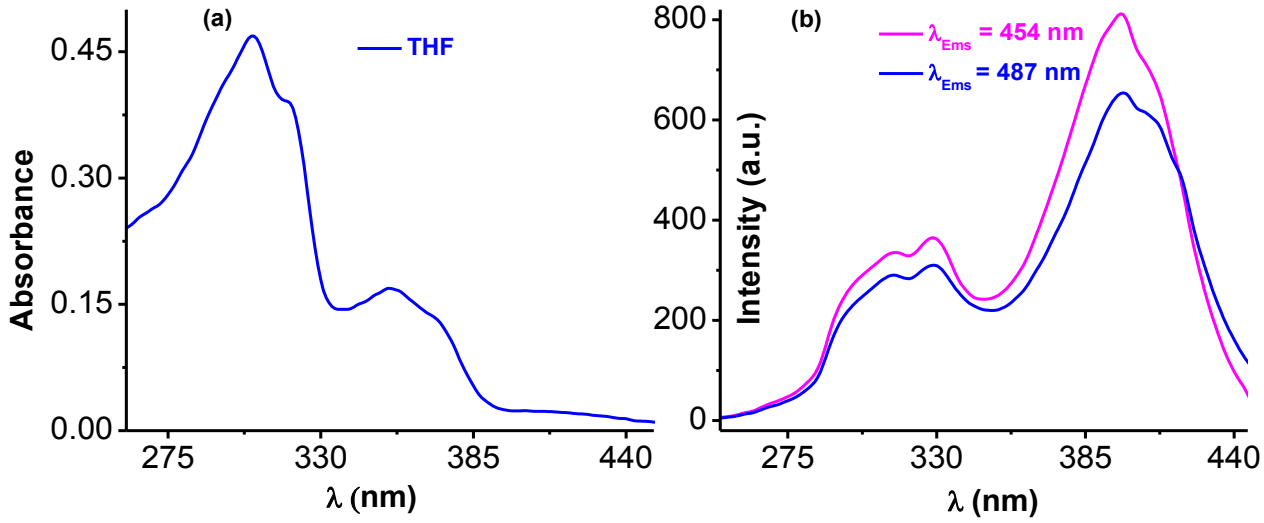
SI Fig.S11: Variable-temperature UV-Vis spectra of **1** (concentration used 10 μM) in THF-water (3:7; v/v). Temperature varied from 10-70°C.

Weight-loss profile (TGA plot) of [1]:

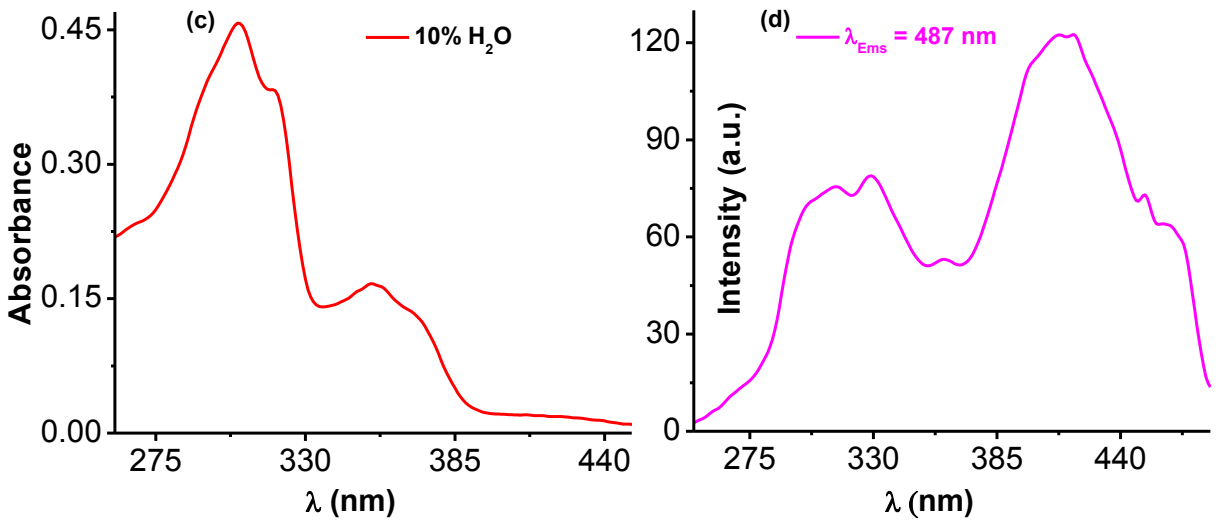


SI Fig.S12: Weight-loss profile for **1** obtained using thermogravimetric analysis (TGA).

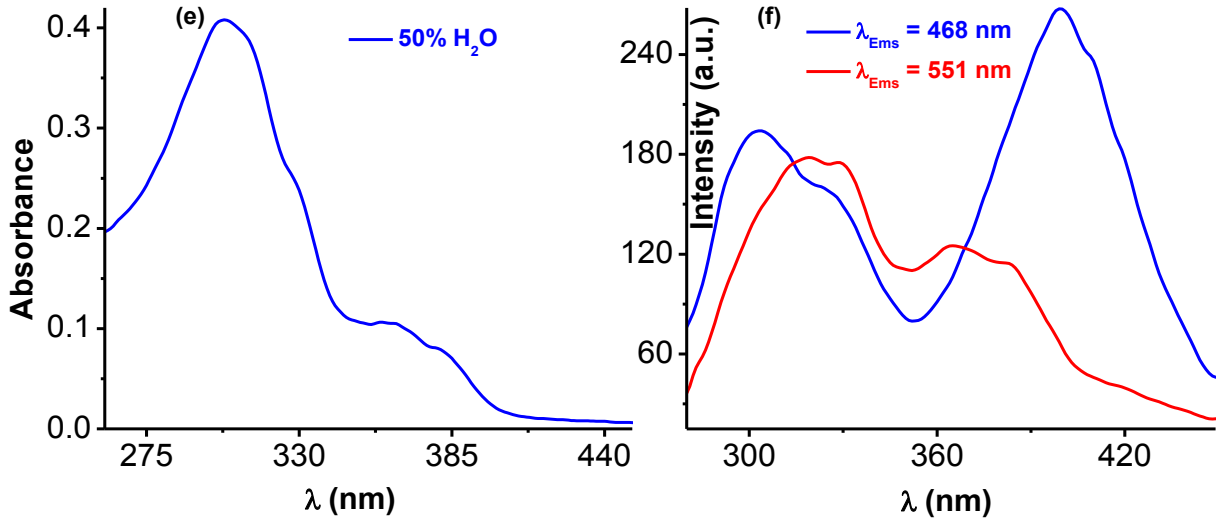
Comparisons between absorption and excitation spectra of [1]:



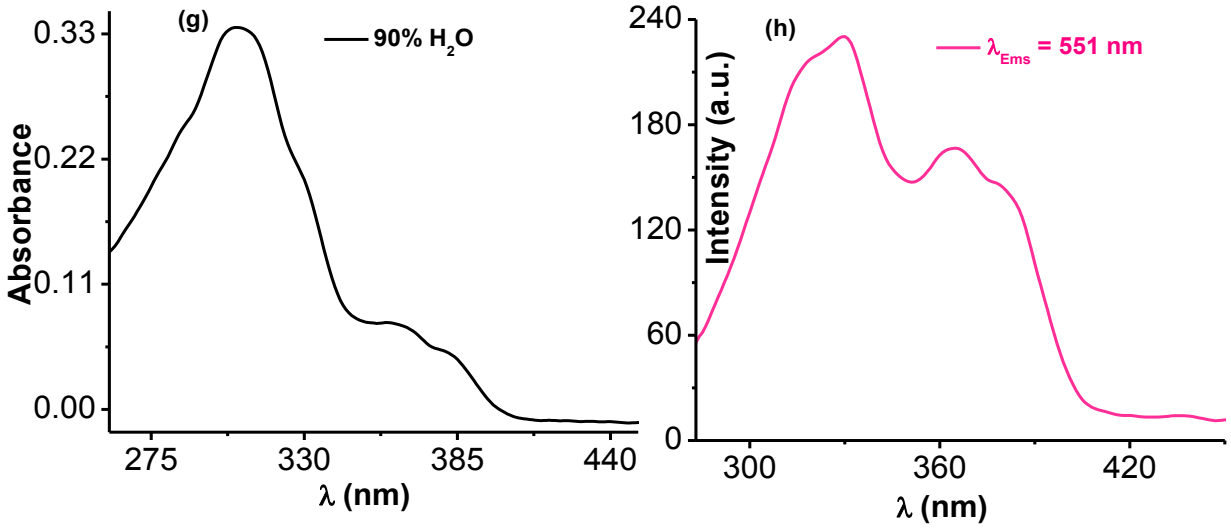
SI Fig.S13: a) Absorption and b) fluorescence excitation spectra (λ_{Ems} = 454 and 487 nm) of **1** in THF.



SI Fig.S14: a) Absorption and b) fluorescence excitation spectra (λ_{Ems} = 487 nm) of **1** in THF-water (9:1; v/v).

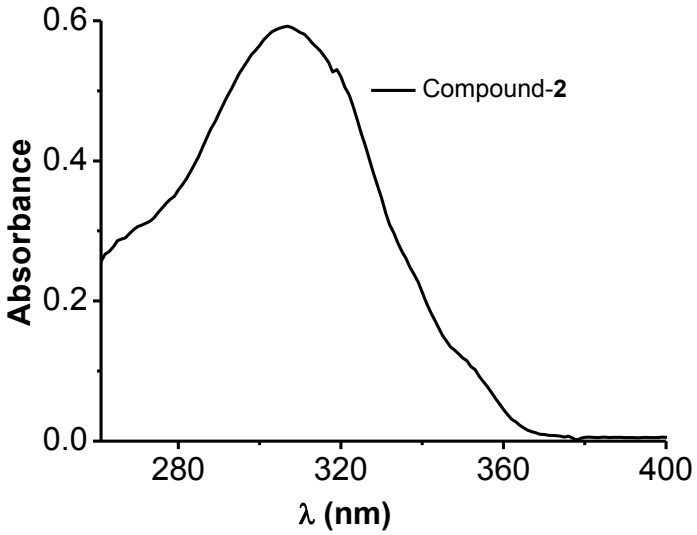


SI Fig.S15: a) Absorption and b) fluorescence excitation spectra (λ_{Ems} = 468 and 551 nm) of **1** in THF-water (1:1; v/v).



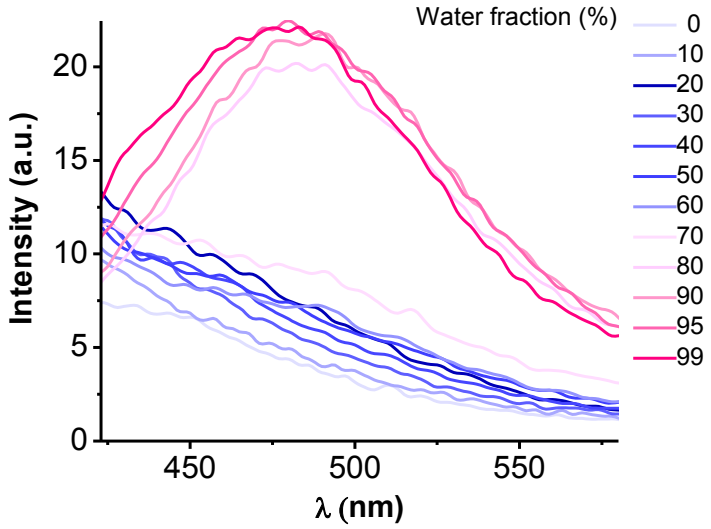
SI Fig.S16: a) Absorption and b) fluorescence excitation spectra (λ_{Ems} = 551 nm) of **1** in THF-water (1:9; v/v).

UV-Vis absorption spectra of [2].



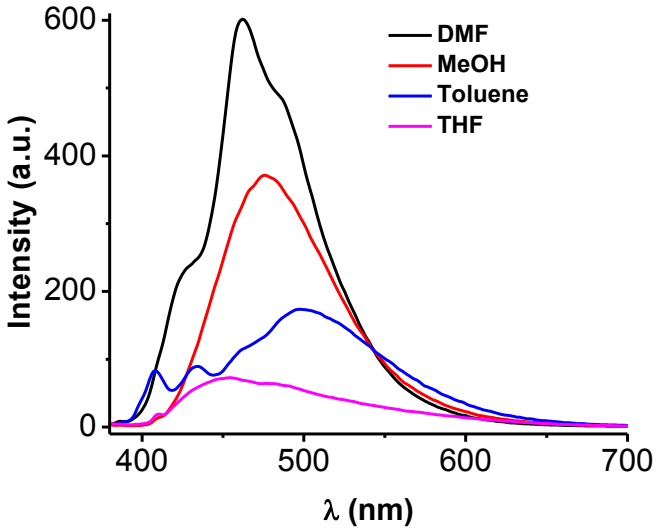
SI Fig.S17: Absorption spectra of **2** in pure THF. Concentration used 10 μM.

Solvent dependent emission spectra of [2]:



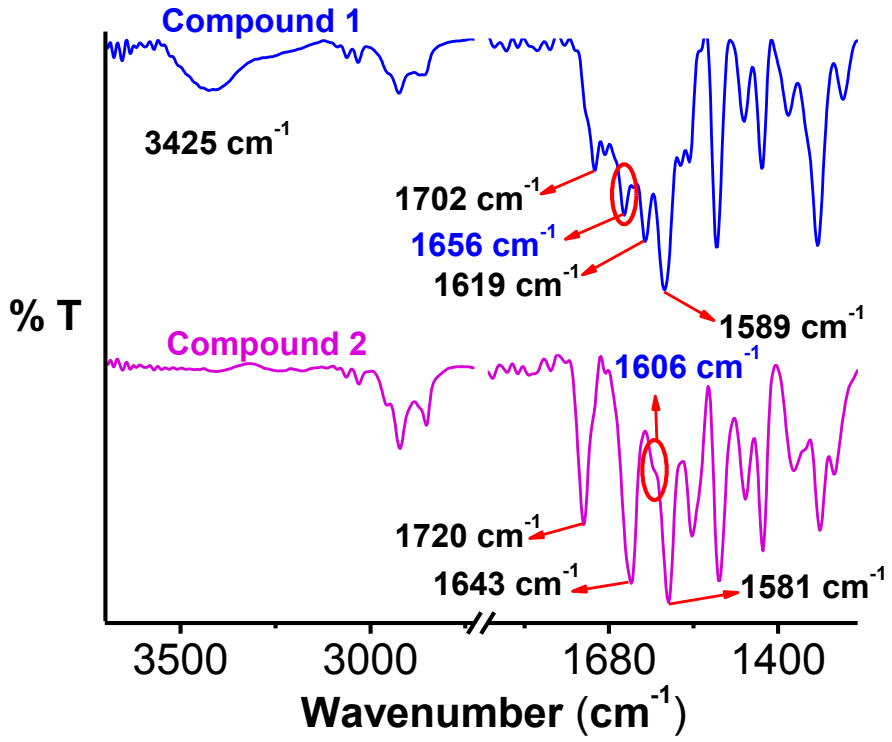
SI Fig.S18: luminescence spectra of **2** (10 μM) in THF and THF-water mixed solvent medium (λ_{Ext} = 306 nm was used for luminescence studies).

Emission spectra of [1] in different polarities of solvents:



SI Fig.S19: Emission spectra of **1** (1 μM) in DMF, MeOH, THF and Toluene. λ_{Ext} = 365 nm.

Comparisons of FT-IR spectrum between compound [1] and [2]:

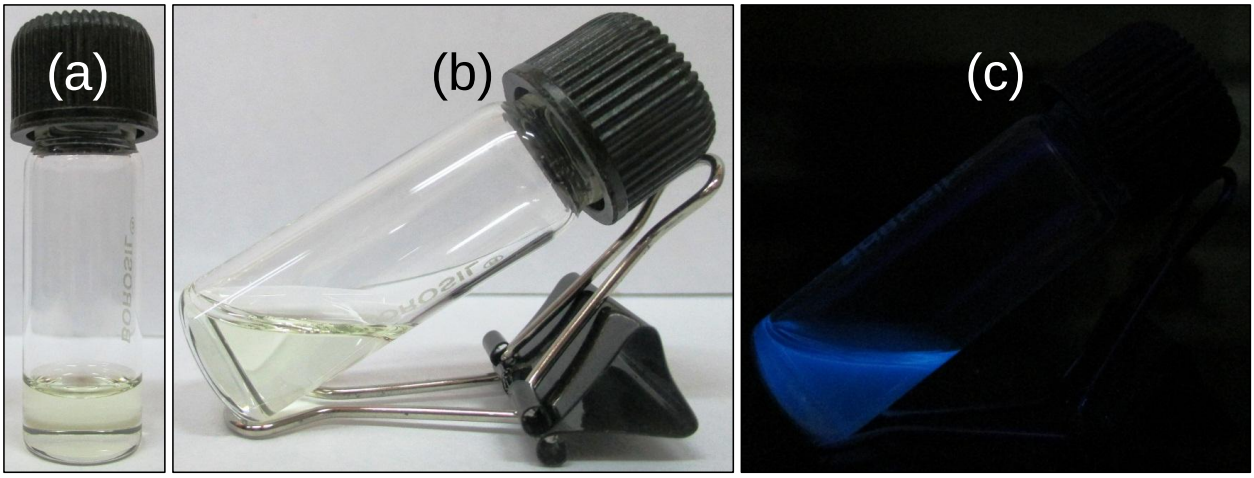


SI Fig.S20: Comparisons **of** FT-IR spectra of compound **1** and **2** at room temperature.

SI Table.S1: Important FT-IR frequency obtained from compound **1** and **2**.

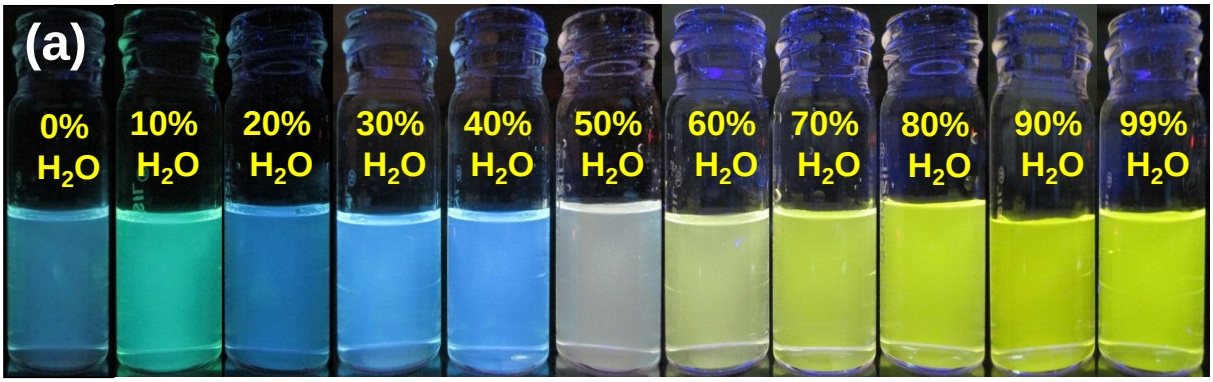
Compound-**1**	3425 cm^{-1} ($-OH_{hydrogen\ bonded}$), 1702 cm^{-1} ($-COOH_{str}$), 1656 cm^{-1} ($-C=N_{str}$), 1619 cm^{-1} ($-C=O_{amide,\ str}$), 1589 cm^{-1} ($-NH_{amide,\ str}$)
Compound-**2**	1720 cm^{-1} ($-COOEt_{str}$), 1643 cm^{-1} ($-C=O_{amide,str}$), 1606 cm^{-1} ($-C=N_{str}$), 1581 cm^{-1} ($-NH_{amide,str}$)

Gelation study of [2]:



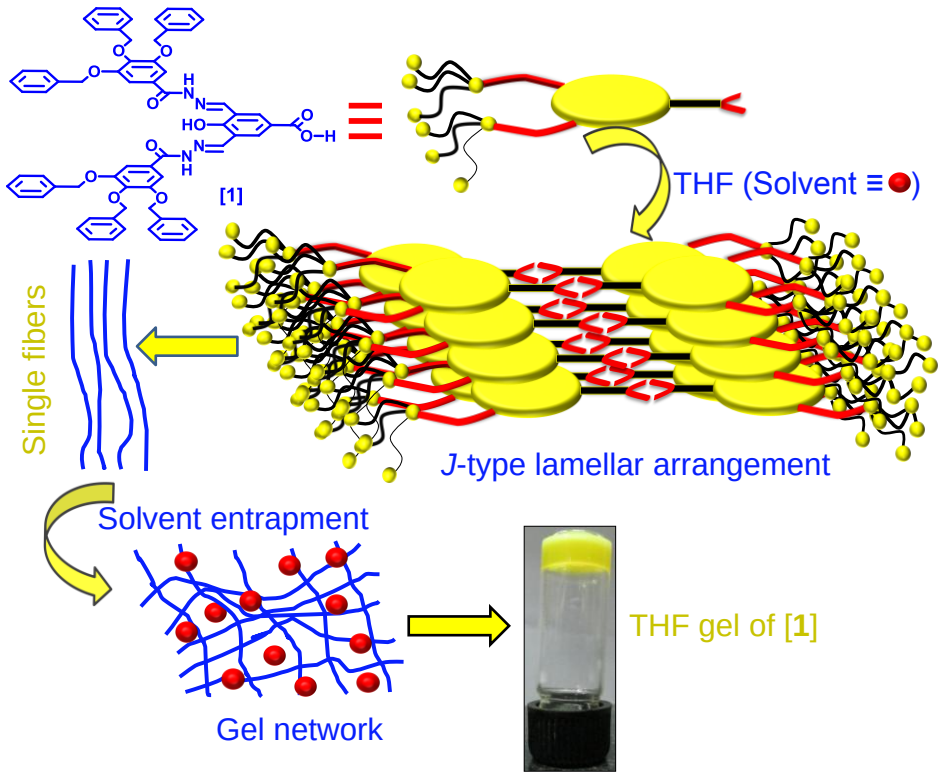
SI Fig.S21: Photographs of THF solution of compound 2 (a) immediately after dissolving the compound (16.0 mg/mL of THF) by gentle heating; (b) after 24 hrs upon cooling to room temperature; (c) under 365 nm UV light. Indicating Under identical condition or even higher concentration [compare to compound- 1 (10.0 mg/ mL of THF)] compound-2 is unable to give gel.

Photographs showing the changes of emission color of 1:



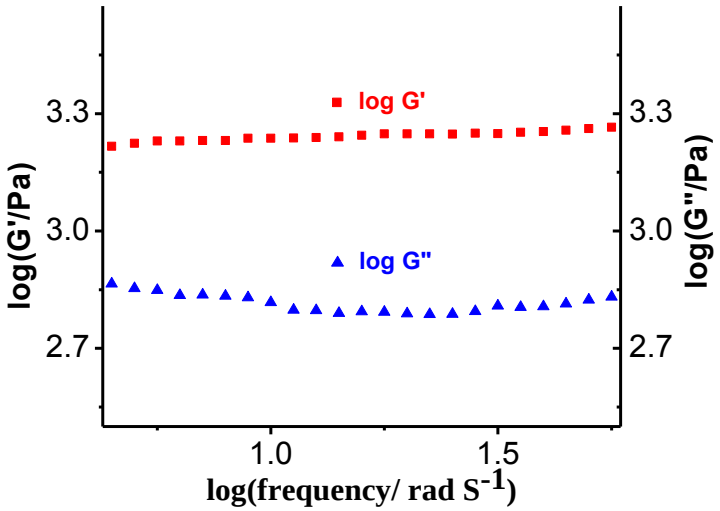
SI Fig.S22: (a) Photographs showing the changes of emission color with gradual increase of water (%) into THF solution of **1**.

Schematic route for gelation of [1]:



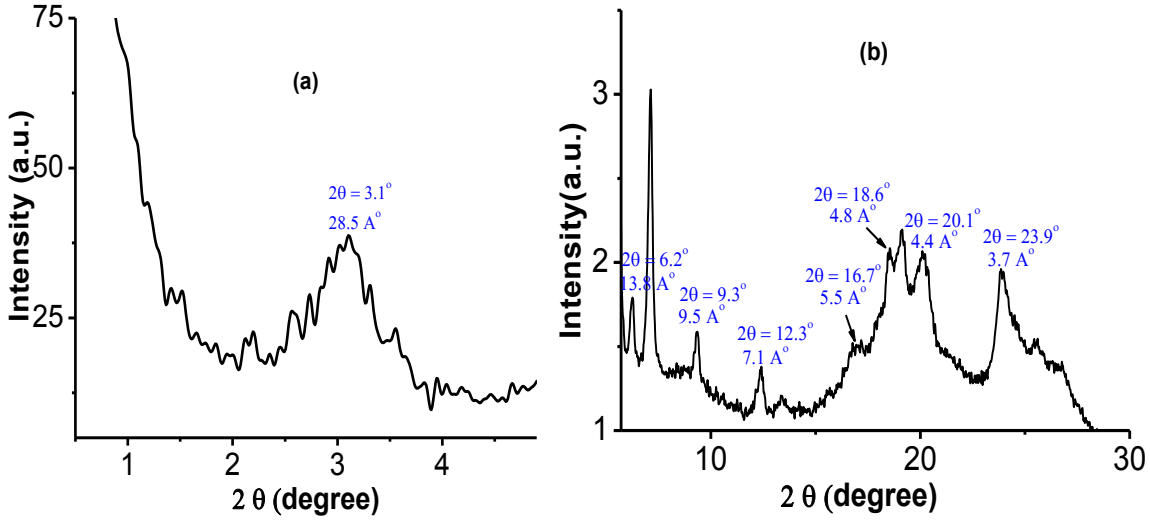
SI Fig.S23: A schematic route for the synthesis of THF gel of **1** and its molecular arrangement.

Rheological property of [1]:



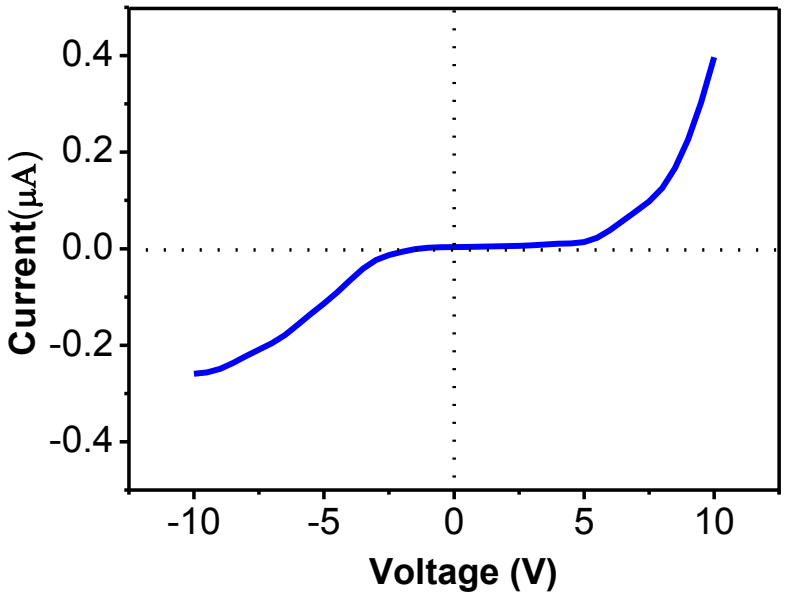
SI Fig.S24: Dynamic frequency sweep measurement of storage modulus (G´) and loss modulus (G´´) for THF gel (1.0 wt. %) of **1**. Strain used was 0.1%.

XRPD pattern of [1]:



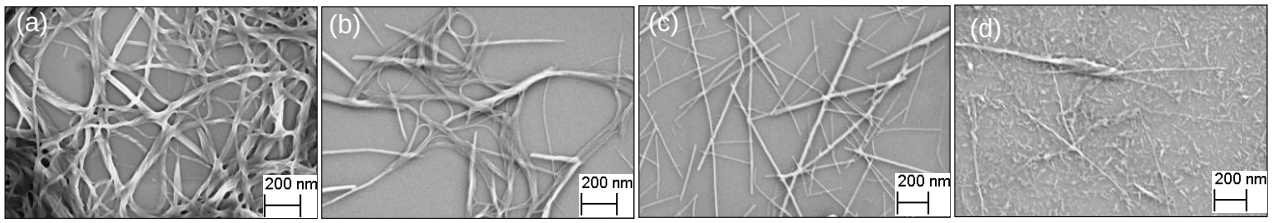
SI Fig.S25: (a) Small angle and (b) wide angle XRPD diffraction pattern of **1** in xerogel state.

***I-V* characteristic plot of [1]:**



SI Fig.S26: *I-V* characteristic plot obtained from **1.**

Solvent dependent FESEM images of [1]:



SI Fig.S27: Solvent dependent FESEM images of 1 having (a) 0, (b) 10, (c) 50 and (d), 90 % water content in THF. Concentration used was 100μM.