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Multifunctional hexacatenar mesogen exhibiting supergelation, AIEE and its ability as a volatile acid sensor

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Supporting information

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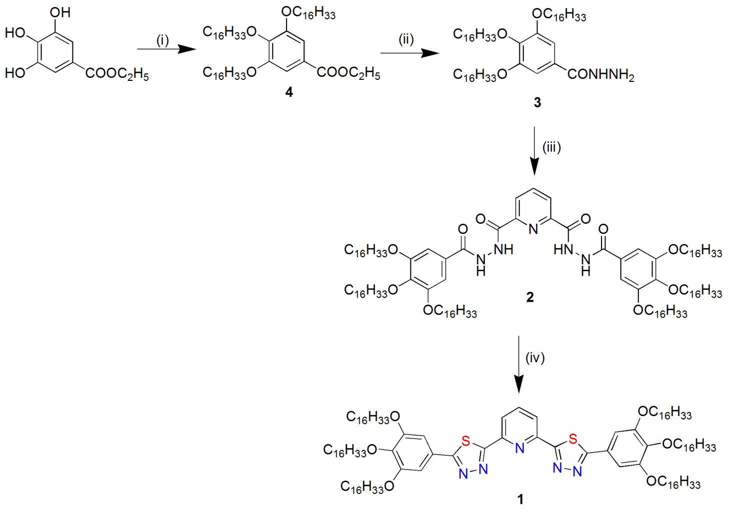
(i) Materials and methods

All commercially obtained chemicals were used as received. As required the solvents were dried as per the standard protocols. Silica gel or neutral alumina used as stationery phase for column chromatography. Alluminium sheets coated with silica gel were used for thin layer chromatography (TLC) to monitor the reactions and column purifications. Infrared spectra were measured on a Perkin Elmer IR spectrometer at room temperature by preparing the KBr pellet. ^{1}H and ^{13}C NMR spectra were recorded using Varian Mercury 400 MHz (at 298K) or Bruker 600 MHz NMR spectrometer. Mass spectrometry was carried out using MALDI-TOF mass spectrometer or High Resolution Mass Spectrometer. Polarizing optical microscope (POM) (Nikon Eclipse LV100POL) in conjunction with a controllable hot stage (Mettler Toledo FP90) was used for the characterization of mesogens. The phase transitions, associated enthalpy changes were obtained by differential scanning calorimeter (DSC) (Mettler Toledo DSC1). X-ray diffraction (XRD) studies were carried out using image plate and a detector. This setup had Cu Kα (λ =0. 15418 nm) radiation from a source (GeniX3D, Xenocs) operating at 50 kV and 0.6 mA in conjunction with a multilayer mirror was used to irradiate the sample. Glass capillaries containing the sample were used for the measurements. Thermogravimetric analysis (TGA) was accomplished with a thermogravimetric analyser (Mettler Toledo, model TG/SDTA 851 e).Perkin-Elmer Lambda 750, UV/VIS/NIR spectrometer was used to obtain UV-Vis spectra, while Fluoromax-4 fluorescence spectrophotometer and Perkin Elmer LS 50B spectrometer were used to obtain emission spectra in solution state and solid thin film state respectively. The xerogel of the compounds were prepared from gel state, evaporating the solvent first in air for 2-3 days followed by vacuum. Then, the morphologies of the xerogel were examined by Atomic Force Microscopy (AFM) and field emission scanning electron microscopy (FE-SEM). Atomic Force microscopy (AFM) images were obtained for the spin-coated films using Agilent 5500-STM instrument. Field Emission Scanning Electron Microscope (FESEM) images were recorded on Zeiss Sigma microscope at an accelerating voltage of 2-8kV.

(ii) Synthetic Scheme



Scheme 1. Synthesis of hexacatenar **1**. Reagents and conditions (yield): (i) *n*-Bromoalkanes, anhydrous K_2CO_3, DMF, 80 ^oC, 24 h (85%); (ii) $NH_2NH_2.H_2O$, n-butanol, reflux, 48 h (78%); (iii) (a) 2,5-pyridine dicarboxyllic acid, $SOCl_2$, reflux, 8h; (b) **3**, THF, triethylamine, 12h, reflux; (iv) Lawesson's reagent, toluene, reflux, 17 h (65%).

(iii) Experimental Section

Procedure for the synthesis of ethyl 3,4,5-tri(hexadecyloxy) benzoate (**4**)[1]

A mixture of ethyl gallate (10.1 mmol, 1equiv.), anhyd. K_2CO_3 (66.6 mmol, 6.6 equiv.), n-bromohexadecane (33.3 mmol, 3.3 equiv.) were taken in dry DMF (20 ml) and heated at 80 ^oC for 17 h under nitrogen atmosphere. Then the reaction mixture was poured into ice-water and extracted with CH_2Cl_2. The combined extract was washed with water, brine, and then dried over anhyd. Na_2SO_4 and concentrated. The crude product was purified by column chromatography on neutral alumina. Elution with hexanes followed by 2 - 5% EtOAc-hexanes yielded the desired product.

R_f = 0.81(10% EtOAc-hexanes); white solid, m.p.: 54-56^oC; yield: 85%; IR (KBr pellet): ν_{max} in cm^{-1} 2922.08, 2850.18, 1716.36, 1583.80, 1468.54, 1426.93, 1331.02, 1218.57, 1110.30; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.25 (s, 2H, H_{Ar}), 4.35 (q, 2H, J = 7.2 Hz, $COOCH_2$), 4.01 (t, 6H, 3 × OCH_2), 1.25-1.82 (m, 84H, 42 × CH_2), 0.87(m, 12H, 4 × CH_3), ^{13}C NMR ($CDCl_3$, 100 MHz): 166.70, 153.04, 142.61, 125.28, 108.29, 73.72, 69.44, 61.17, 33.05, 32.16, 30.56, 29.94, 29.89, 29.87, 29.80, 29.63, 29.60, 29.57, 26.32, 26.29, 22.92, 14.63, 14.33. HRMS (ESI+) exact mass calculated for $C_{57}H_{107}O_5$ ($M+H^+$): 871.8113, Found: 871.8121.

Procedure for the synthesis of 3,4,5-tri-*n*-hexadecyloxy benzhydrazide (**3**)[1]

A mixture of ethyl 3,4,5-tri-*n*-hexadecyloxybenzoate (9.2 mmol, 1equiv.), excess hydrazine hydrate (18.4 mL), *n*-butanol (20 mL) was refluxed for 40 h. Water (100 mL) was added and resulting precipitate was collected, dried under vacuum, and recrystallized from ethanol to yield pure **3** as a white solid.

R_f = 0.52 (20% EtOAc-hexanes); white solid, m.p.: 102-104°C; yield: 78%; IR (KBr pellet): ν_{max} in cm^{-1} 3448.94, 3248.41, 2921.55, 2850.68, 1635.32, 1579.85, 1466.26, 1427.84, 1238.90, 1122.06; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.22 (br s, 1H, CONH), 6.92 (s, 2H, H_{Ar}), 4.07(s, 2H, NH_2), 3.99(m, 6H, 3 × OCH_2), 1.26 – 1.80(m, 84H, 42×CH_2), 0.88(m, 9H, 3×CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz): 168.70, 153.54, 141.92, 127.68, 105.74, 69.60, 30.53, 29.97, 29.95, 29.88, 29.60, 26.30, 22.92, 14.33; HRMS (ESI+) exact mass calculated for $C_{55}H_{105}N_2O_4$ (M+H$^+$): 857.8069, Found: 857.8070.

Procedure for the synthesis of 2,6-bis(5-(3,4,5-tris(hexadecyloxy)phenyl)-1,3,4-thiadiazol-2-yl)pyridine (**1**)

Pyridine dicarboxyllic acid (0.8 mmol) in 3.6 ml of thionyl chloride and DMF (2 - 3 drops) was heated under reflux for 8 h. The excess of thionyl chloride was removed by distillation; the crude product (pyridine diacidchloride) was dried in vacuo and used for the next reaction without further purification and characterization. The solution of pyridine diacidchloride (0.7 mmol, 1equiv.) in THF was added dropwise to a solution of solution of 3,4,5-tri-*n*-hexadecyloxy benzhydrazide (1.4 mmol, 2.05 equiv.) and triethylamine (2.1 mmol, 3 equiv.) in THF (20 mL). The reaction mixture was stirred at 55 °C for 12 h. After cooling, THF was removed through distillation and the residue was extracted with EtOAc. The extract was washed with water and brine. Dried over Na_2SO_4 and concentrated. The resulting crude product (**3**) was directly used for next reaction.

The solution of crude product **2** (0.5mmol, 1equiv.) in dry toluene (8 mL) was added dropwise to a solution of Lawesson's reagent (1.2 mmol, 2.4 equiv.) in toluene at room temperature under Argon atmosphere and refluxed for 24 h. After the reaction, toluene was evaporated under reduced pressure. After removal of solvent *in vacuo*, the crude product was further purified through column chromatography on neutral alumina. Elution with DCM followed by 5-10% EtOAc-hexanes yielded the desired product. Again, the product was recrystallized with DCM-Ethanol system (1:2).

R_f = 0.6 (DCM); white solid, yield: 65%; IR (KBr pellet): ν_{max} in cm^{-1} 3438, 2950, 2917, 2849, 1585, 1432, 1331, 1124, 813, 773; ^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.46(d, 2H, *J* =12Hz, H$_{Ar}$), 8.04(t, 1H, H$_{Ar}$), 7.28(s, 4H, H$_{Ar}$), 4.10(t, 8H, 4× OCH$_2$), 4.05(t, 4H, 2× OCH$_2$), 1.75 – 1.88(m, 12H, 6 × CH$_2$), 1.35 – 1.53(m, 12H, 6 × CH$_2$), 1.25 – 1.29(m, 144H, 72 × CH$_2$), 0.87 (m, 18H, 6 × CH$_3$); ^{13}C NMR (CDCl$_3$, 150 MHz): 169.11, 166.76, 153.83, 141.37, 131.55, 130.29, 130.12, 127.27, 124.93, 106.80, 73.89, 69.65, 32.15, 30.56, 29.94, 29.88, 29.81, 29.64, 29.59, 26.32, 22.91, 14.32; MALDI TOF MS: m/z for $C_{117}H_{206}N_5O_6S_2$ [M+H$^+$], calculated: 1841.5410, Found: 1841.835.

(ii) NMR spectra

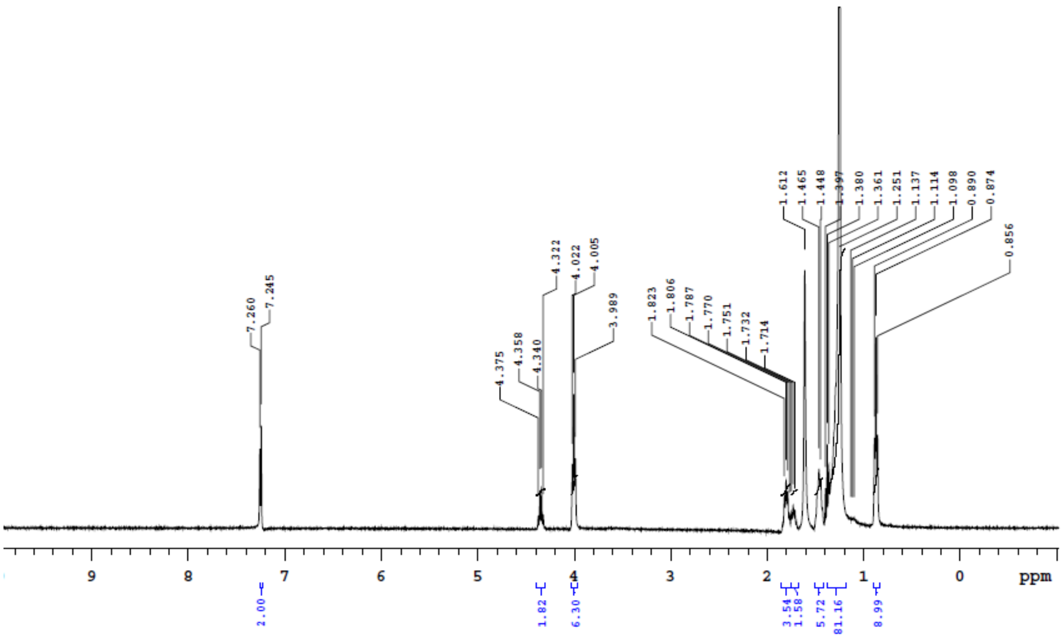


Figure S1. ^{1}H NMR (400 MHz) spectrum of **4** in $CDCl_3$

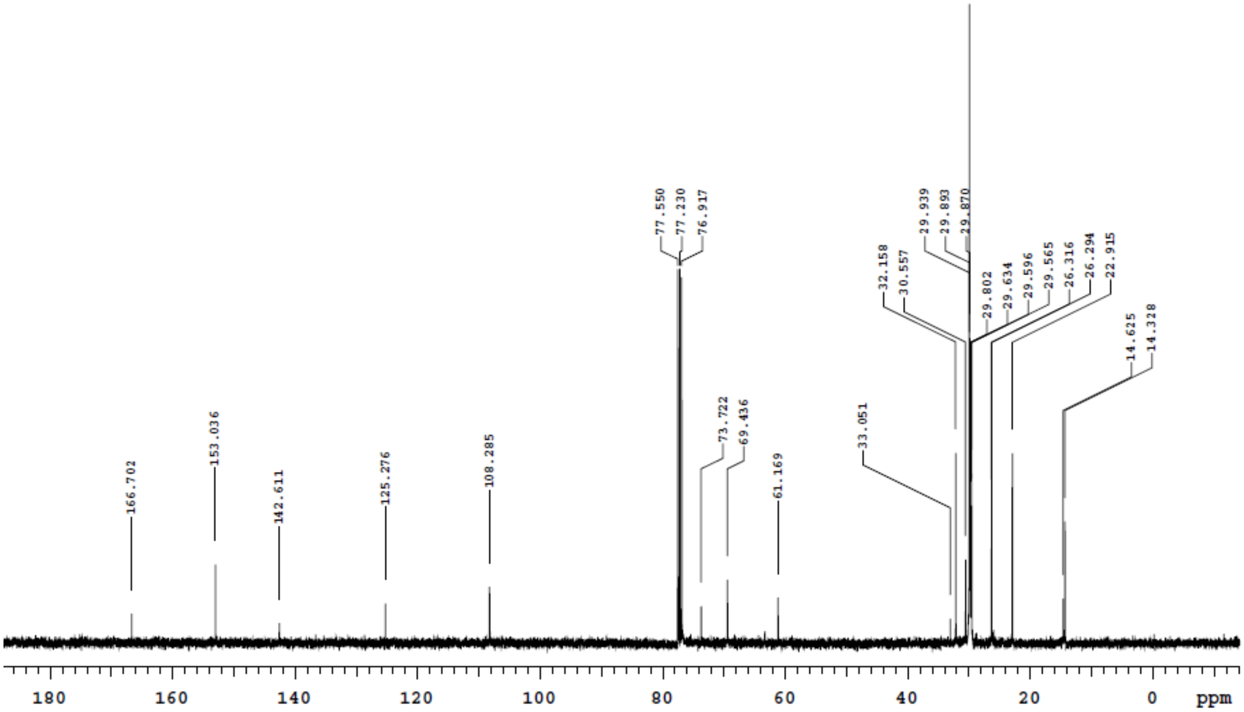


Figure S2. ^{13}C NMR (100 MHz) spectrum of **4** in $CDCl_3$

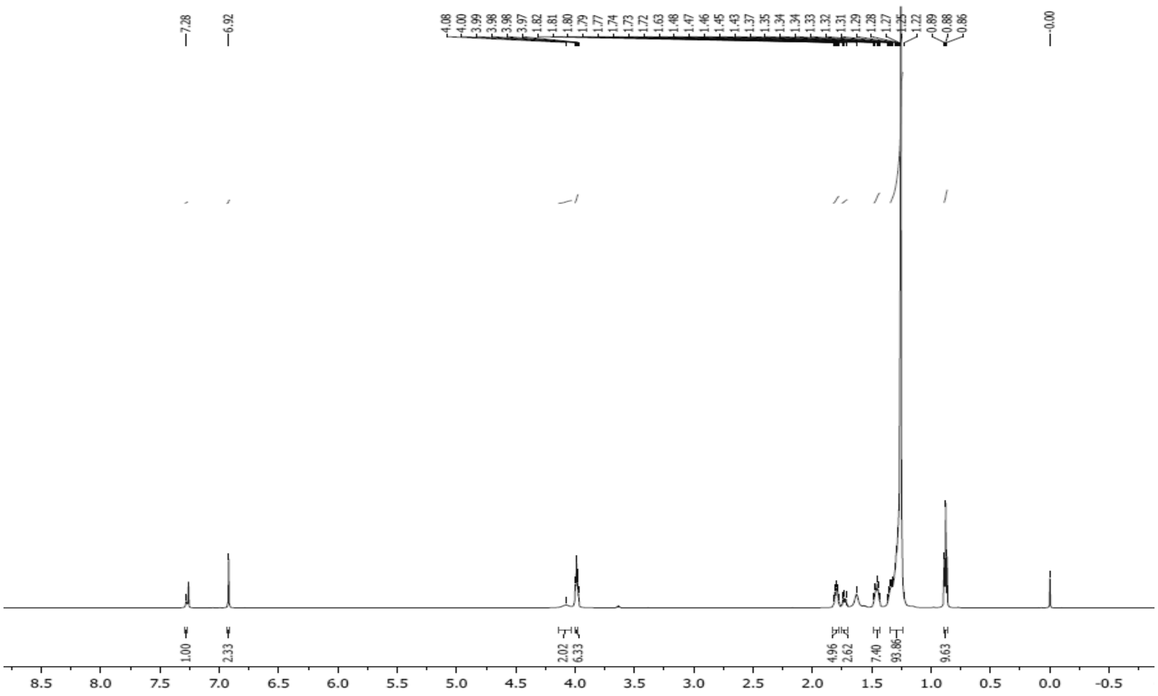


Figure S3. ^{1}H NMR (600 MHz) spectrum of **3** in $CDCl_3$

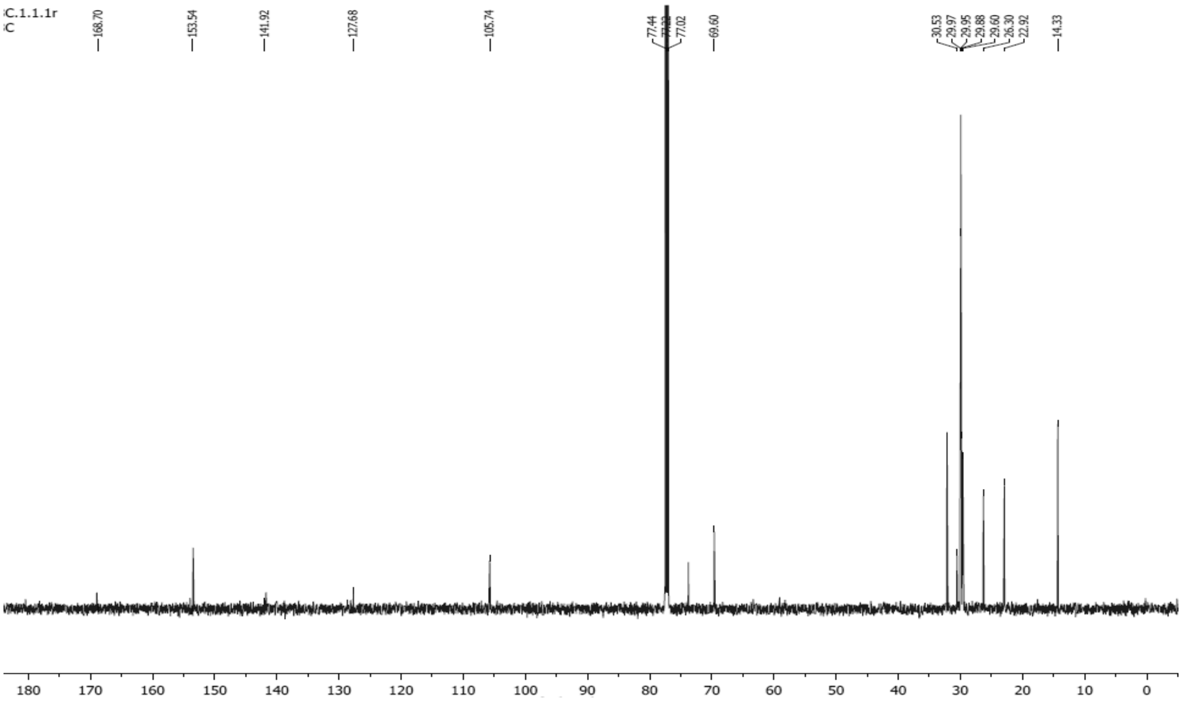


Figure S4. ^{13}C NMR (150 MHz) spectrum of **3** in $CDCl_3$

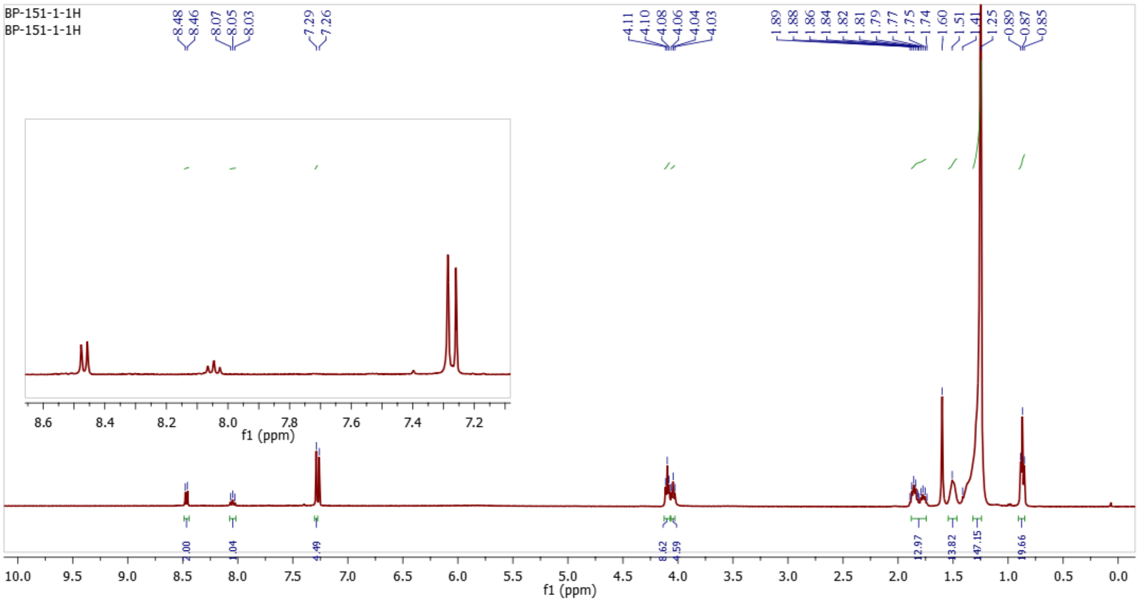


Figure S5. ^{1}H NMR (600 MHz) spectrum of **1** in $CDCl_3$

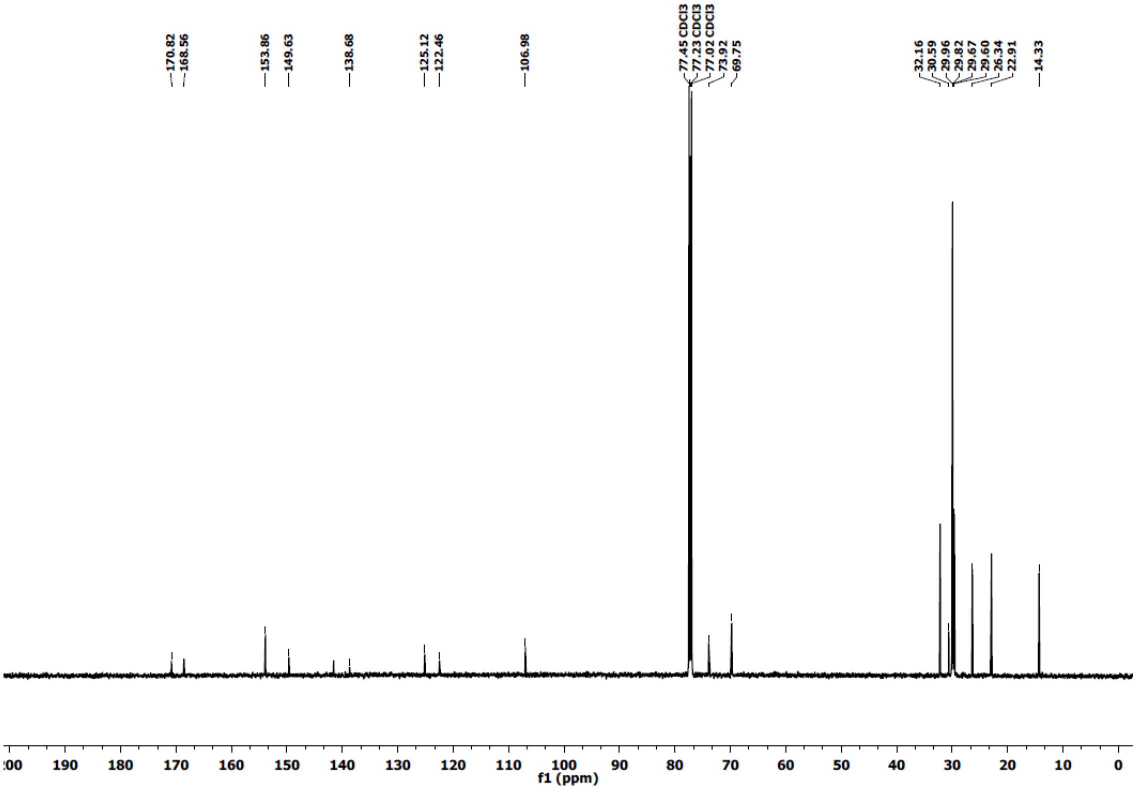


Figure S6. ^{13}C NMR (150 MHz) spectrum of **1** in $CDCl_3$

(v) Thermogravimetric Analysis

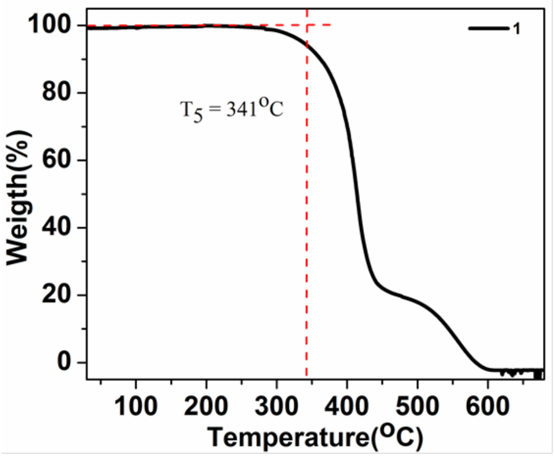


Figure S7. TGA profile compound **1** carried out at a rate of 5°C/min under nitrogen atmosphere.

(vi) X-ray Diffraction studies

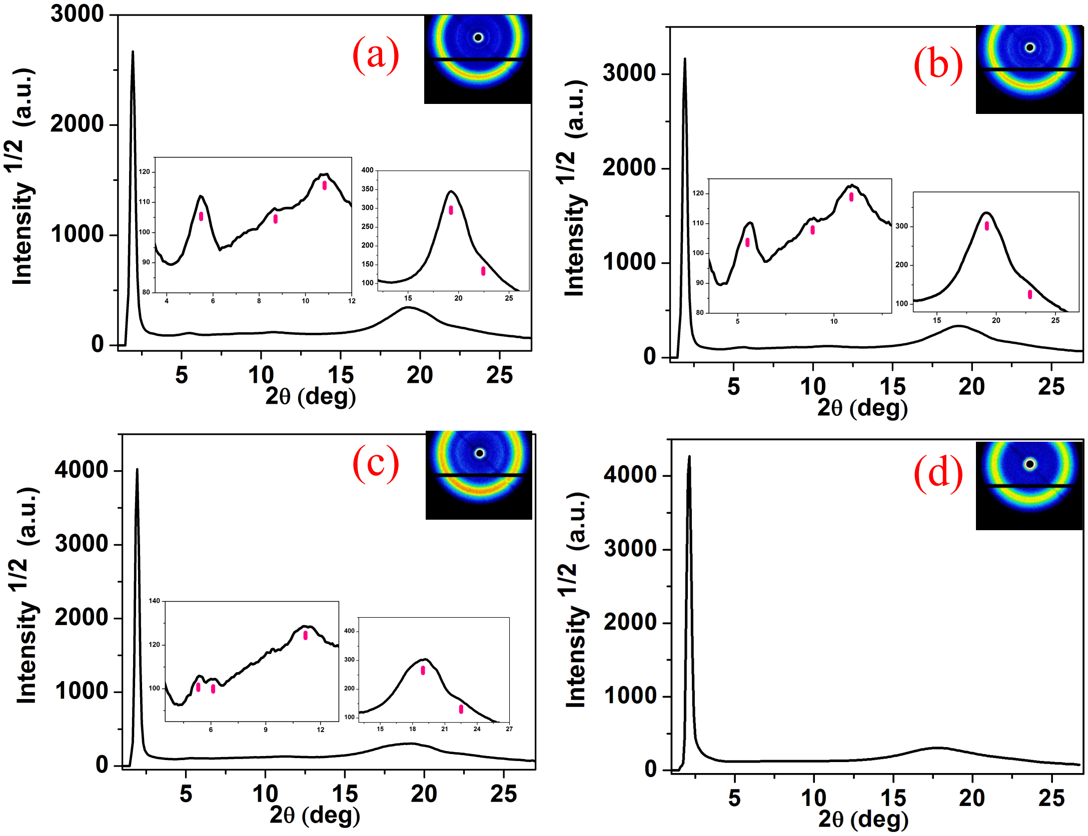


Figure S8. XRD profiles depicting the intensity against the 2θ obtained for the Col$_{r2}$ phase of compound **1** at 25°C (a); Col$_{r2}$ at 45°C (b); Col$_{r1}$at 65°C (c); Col$_{h}$ phase at 90 °C (d) (inset shows the XRD image pattern obtained).

Table 1. Results of (hk) indexation of XRD profiles of the compound **1** at a given temperature (T) of mesophase.

Compounds (D/Å)	Phase/ symmetry (T/^{o}C)	d_{obs} (Å)	d_{cal}(Å)	Miller indices hk	Lattice parameters (Å), Lattice area S (Å^2), Molecular volume V (Å^3)
1 (61.06)	Col$_h$ / p6mm (90)	41.48 4.99(h_a)	41.48	10	a = 47.87, c = 4.99, S = 1984.47, V = 9902.51, Z = 3.2
	Col$_r$ / p2mm (65)	45.52 16.52 14.25 7.95 4.63(h_a) 4.33(h_c)	45.52 16.52 14.21 7.96	03 11 15 25	a = 16.64, b = 136.56, c = 4.33, S = 2272.36, V = 9839.32, Z = 3.2
	Col$_r$ / p2mm (45)	45.52 15.69 9.88 8.09 4.63(h_a) 4.31(h_c)	45.52 15.69 9.78 8.10	01 22 42 52	a = 43.32, b = 45.52, c = 4.31, S = 1971.93, V = 8499.02, Z = 2.78
	Col$_r$ / p2gg (25)	45.52 16.24 10.21 8.09 4.61(h_a) 4.35(h_c)	45.52 16.24 10.20 8.09	02 20 33 41	a = 32.48, b = 91.04, c = 4.35, S = 2957, V = 12863, Z = 4.2

(vii) Photophysical properties

Table 2. Photophysical properties of compound **1**in solution and film state.

Entry	Solution State					Thin film State		
	Absorption (nm)	Emission^b (nm)	Stokes shift (nm)	λ_{onset} (nm)	$\Delta E^{c,d}_{g,\ opt}$	Absorption (nm)	Emission^b (nm)	Stokes shift (nm)
1	343	473	130	401	3.1	359	451	92

^{a}micromolar solutions in THF; ^{b}excited at the respective absorption maxima; ^{c}Band gap determined from the red edge of the longest wave length (λ_{onset}) in the UV-vis absorption spectra; ^{d} In volts (V).

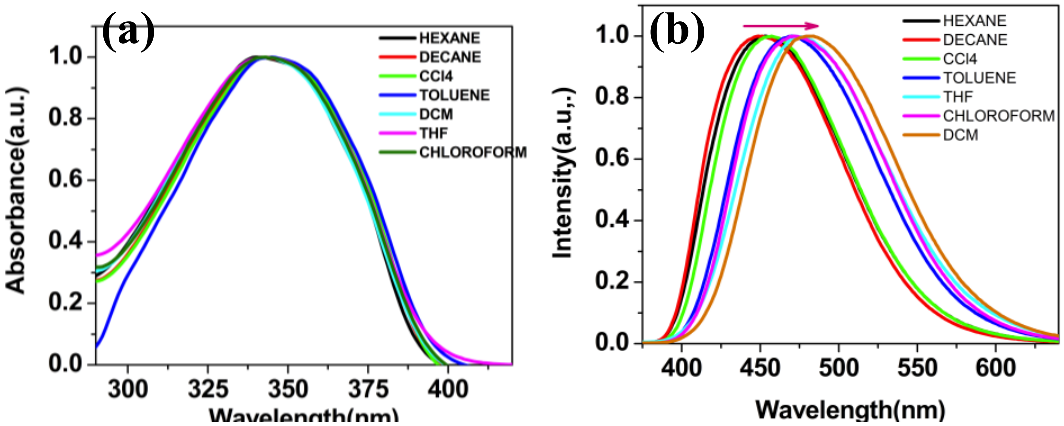


Figure S9. Normalized absorption spectra (a); normalized emission spectra of **1** in different solvents (20micromol) (b).

Table 3. Photophysical properties[a] of compound **1** in different solvents.

Solvent	Absorption (nm)	Emission[b] (nm)	Stokes shift(nm)
Hexane	343	453	110
Decane	343	449	106
CCl_4	343	457	114
THF	343	473	130
Toluene	343	471	128
$CHCl_3$	343	472	129
DCM	343	484	141
[a]micromolar solutions in different solvents; [b]excited at the respective absorption maxima.			

(viii) Gelation studies

Table 4. Gelation properties of compound **1** in different solvents.

Sl. No.	Solvent	1		
		Properties	CGC (wt.%)	T_{gel} (^{O}C)
1	Hexane	G(O)	0.56	43
2	Decane	G(O)	0.50	47
3	Dodecane	G(O)	0.48	52
4	Hexadecane	G(O)	0.41	56
5	Toluene	S	----	---
6	Benzene	S	----	---
7	*m*- xylene	S	----	---
8	DCM	S	----	---
9	Chloroform	S	----	---
10	THF	S	----	---
11	*n*- butanol	P	----	---
12	Ethanol	P	----	---
13	Methanol	P	----	----
14	DMSO	I	----	---
15	DMF	I	----	----

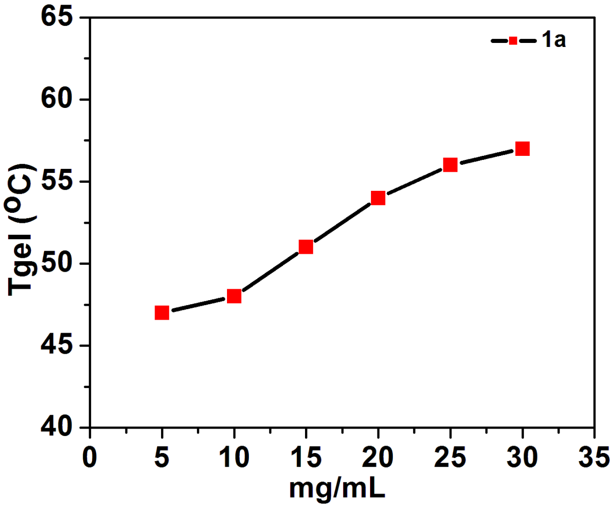


Figure S10. Plots of T_{gel} vs. concentration for compound **1.**

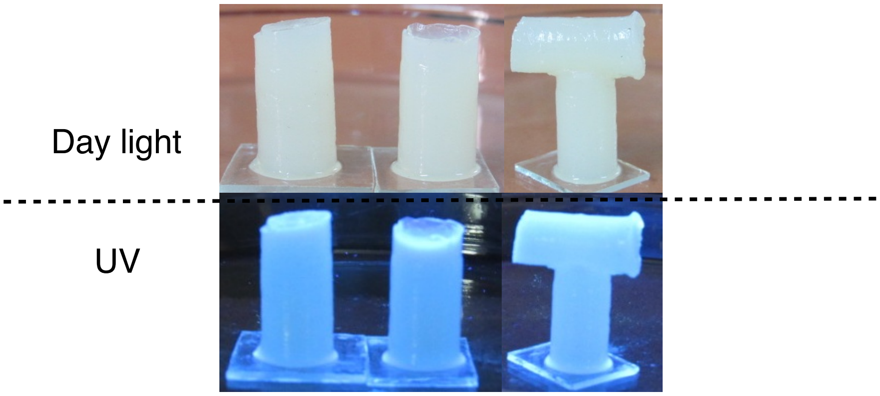


Figure S11. Images of self standing moldable gel of compound **1** (Concentration:0.8 wt% in decane).

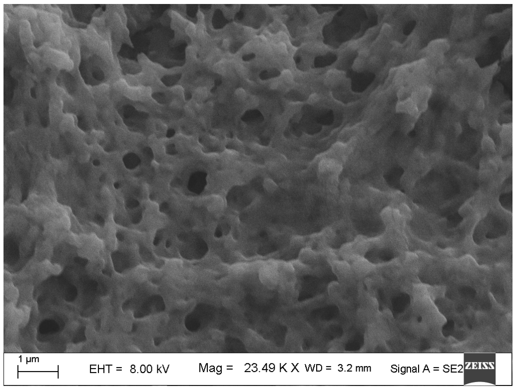


Figure S12. SEM images obtained for compound **1** at 5 x 10^{-6} M decane solution**.**

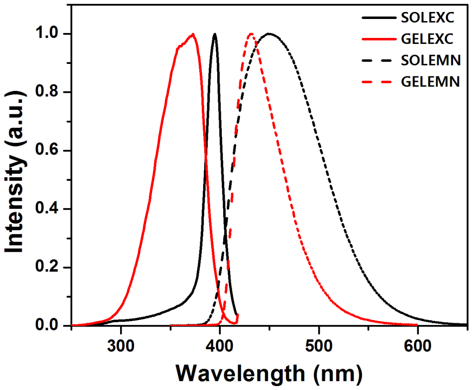


Figure S13. Excitation and emission spectra of compound **1** in solution and gelation state.

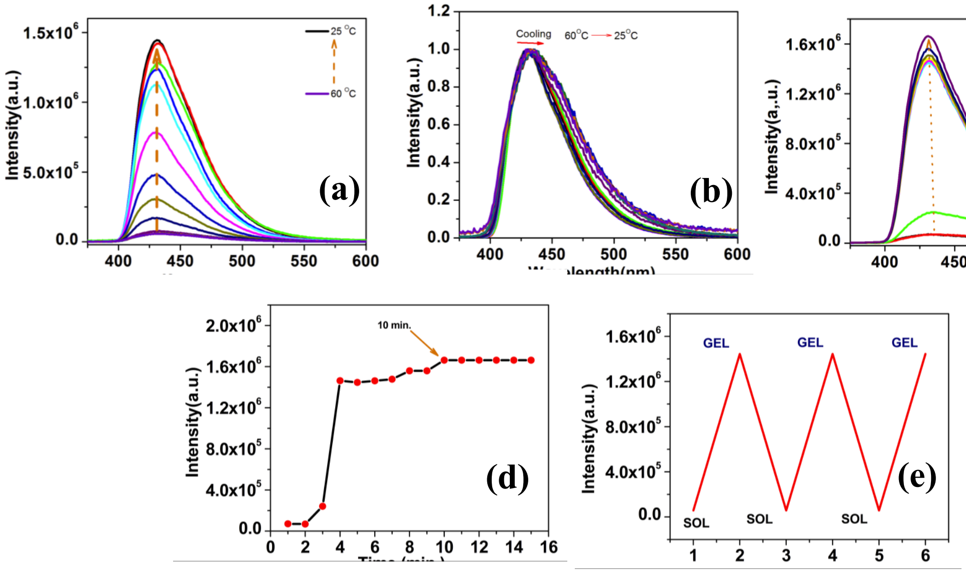


Figure S14. Emission spectra of compound **1** in decane (0.27 mmol) on cooling from 60 °C to 25 °C (a); Normalized emission spectra on cooling from 60 °C to 25 °C (b); Emission spectra obtained as a function of time (c); Plot showing the emission intensity at 431 nm as a function of time (d); Reversible change in the emission intensity at 431nm by repeated sol-gel transition (e).

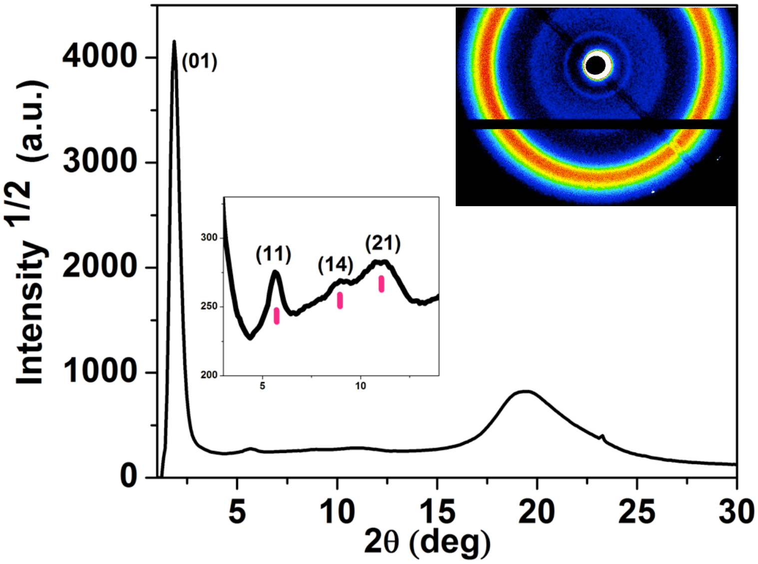


Figure S15. XRD profiles depicting the intensity against the 2θ obtained for the Col$_r$ phase of compound **1** in xerogel state at 25^{o}C (inset shows the XRD image pattern obtained).

Table 5. Results of (hk) indexation of XRD profile of the compound **1** xerogel at room temperature (RT).

Compounds (state)	Phase/ symmetry (T/°C)	d_{obs} (Å)	d_{cal}(Å)	Miller indices *hk*	Lattice parameters (Å), Lattice area S (Å^2), Molecular volume V (Å^3)
1 Xerogel[a]	Col$_r$ / p2mm (RT)	47.95 15.69 9.89 8.04 4.58(h_a) 3.82(h_c)	47.95 15.69 9.72 8.18	01 11 14 21	a = 16.60, b = 47.95, c = 3.82, S = 795.97, V = 3040.61, Z = 1

[a] At the first stage, we have prepared gel of compound **1** in decane at CGC. Then we placed the gel in a clean glass slide carefully. After the solvent evaporation of the gel in glass slide in air for 2-3 days, followed by vacuum evaporation for several hours, we scratched out the xerogel film from the glass slide and filled the powder into a capillary tube for XRD analysis.

(ix) Acidochromic properties

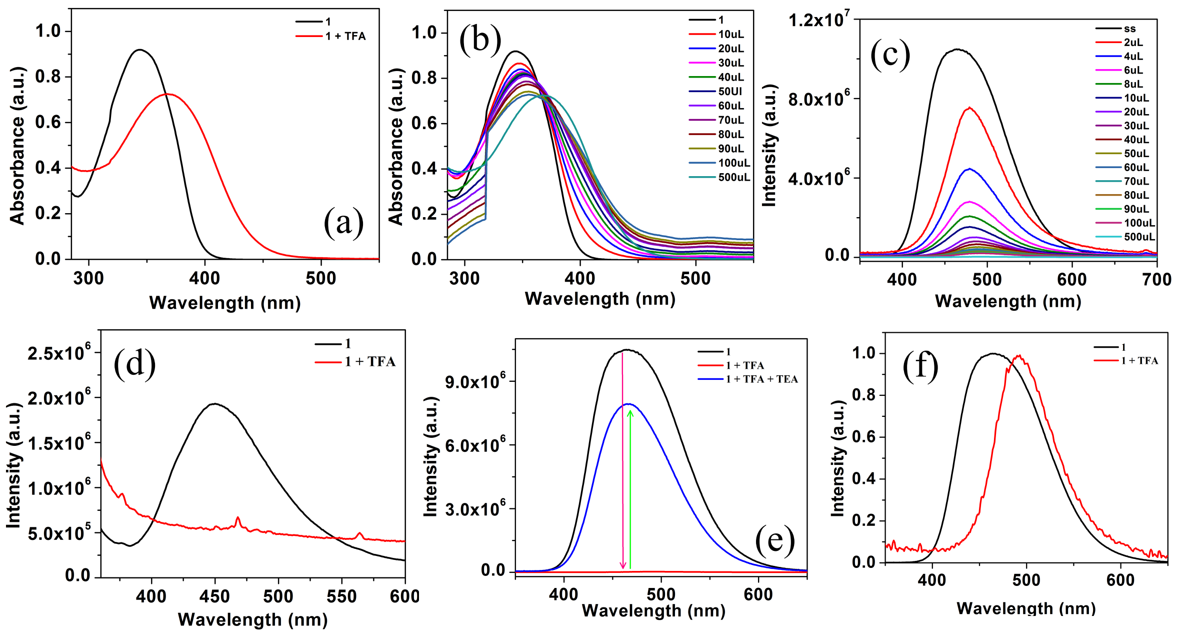


Figure S16. Absorbance spectra of compound **1** in chloroform before and after addition of TFA (a); Absorbance spectra (b); Emission spectra of compound **1** in chloroform upon gradual addition of TFA (c); Emission spectra of thin film of compound **1** before and after addition of TFA (d); Emission spectra of compound **1** in chloroform before and after addition of TFA and TEA (e); Normalized emission spectra of compound **1** in chloroform before and after addition of TFA (f).

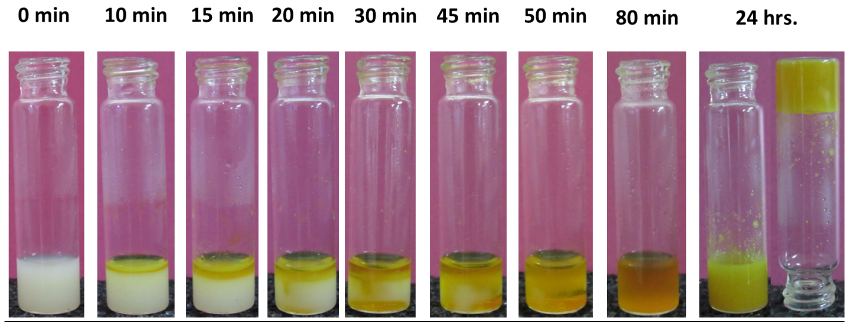


Figure S17. Photographs of compound **1** in gel state after exposing to TFA vapour as a function of time.

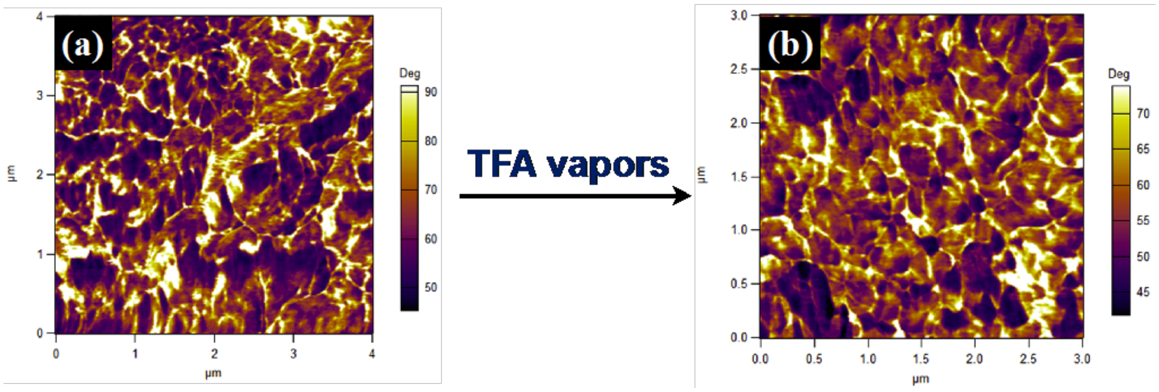


Figure S18. AFM image of compound **1** in gel state before and after exposing to TFA vapour.

(x) Calculation of Detection Limit[2]

For calculating detection limit, different samples of compound **1** (20 µM) each containing TFA solution (0 µM, 3.25 µM, 6.5 µM, 9.75 µM and 13 µM) in 2 ml $CHCl_3$ were prepared separately and fluorescence spectrum was then recorded for each sample by exciting at 343 nm. The detection limit plot for TFA was obtained by plotting change in the fluorescence intensity *vs*. the concentration of TFA. The curve demonstrates a linear relationship and the correlation coefficient (R^2) via linear regression analysis were calculated to be 0.9845. The limit of detection (LOD) was then calculated using the equation 3σ/K, where σ signifies the standard deviation for the intensity of compound **1** in the absence of TFA and K denotes slope of the equation.

$LOD = 3 \times \sigma / K$

$LOD = 3 \times 25087.88 / 2 \times 10^{11}$

$= 37.63 \times 10^{-8}$ M (85ppb)

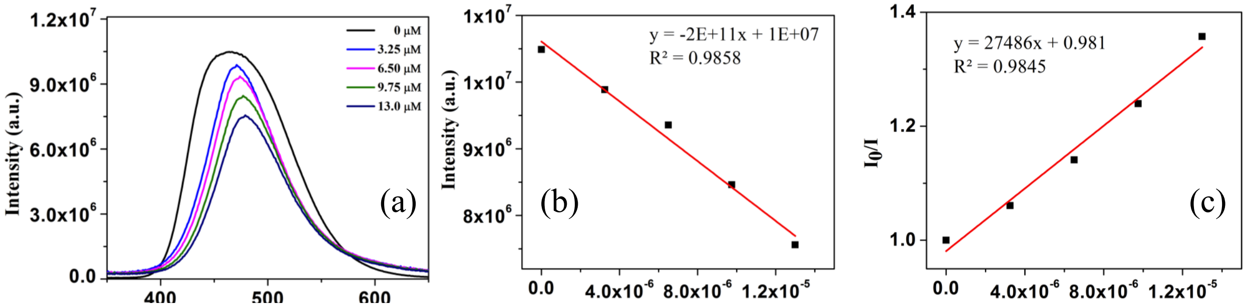
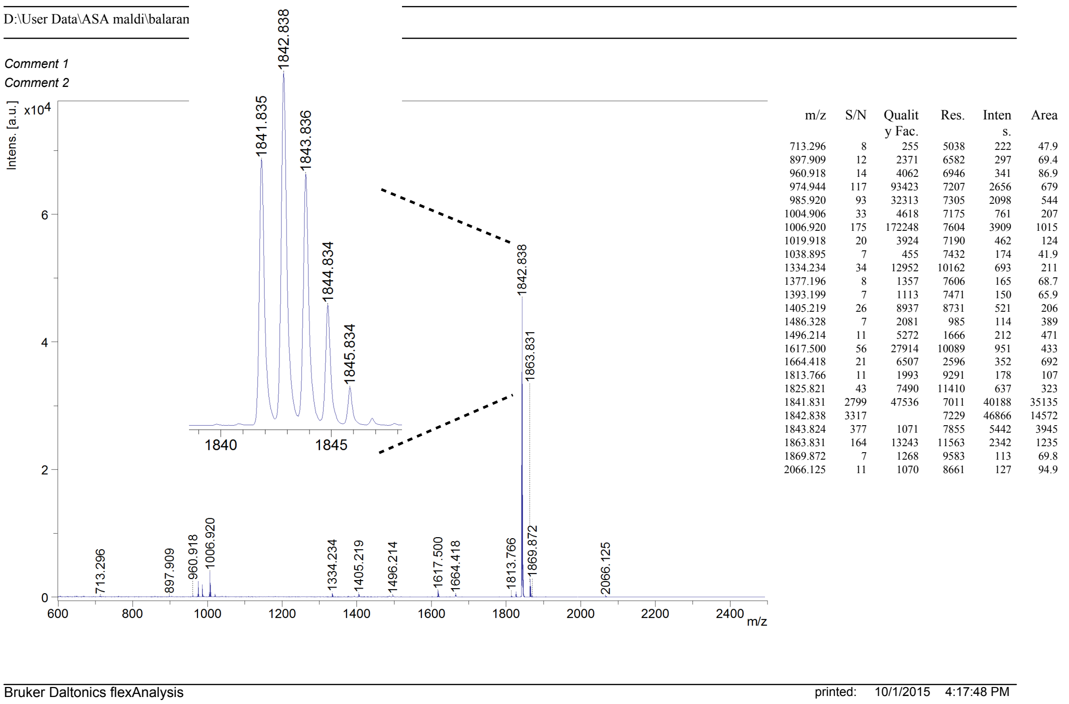


Figure S19. Fluorescence response of compound **1** (20 µM) in chloroform toward TFA solution (a); Fluorescence intensity of compound **1** (20 µM) taken in chloroform as a function of TFA concentration (b); Stern−Volmer plot for TFA (c).

Table 6. Comparison of the reported acidochrmic systems with the present work

Publication	Properties of the materials	Force of interaction / specific functional group for gelation	State of matter used for sensing	Reversibility of state of matter shown	Supporting data for sensing
Present work	Liquid crystal, Organogel	π-π interaction/ Protonation of heteroatom	Wet gel, Xerogel, Thin LC film, Solution	In all cases (TFA and TEA)	^{1}H NMR, Absorbance, Fluorescence.
Soft Matter, **2015**, 11, 9179-9187	Organogel	π-π interaction	Thin film	In thin film (TFA and TEA)	Fluorescence
J. Mater. Chem. C, **2015**, 3, 8888-8894	Organogel	π-π interaction	Wet gel, Thin film	Not available	Fluorescence
Chem. Eur. J., **2015**, 21, 4712-4720	Organogel	H-bonding/amide group	Wet gel, Thin film	In thin film (TFA and TEA)	Fluorescence
Chem. Eur. J., **2015**, 21, 17508-17515	Organogel	H-bonding/amide group	Wet gel, Thin film, Solution	Not available	Fluorescence
J. Mater. Chem. C, 2015, **3**, 10225−10231	Chromophore	Protonation of heteroatom	Solution	Solution (TFA and NH_3)	Fluorescence
J. Mater. Chem. A, 2015, **3**, 22441–22447	Photochromic molecule	Protonation of heteroatom	Solution and thin film on PDMS	Heating and UV irradiation	Absorbance
Dyes and Pigments, **2016**, 130, 233-244	Chromophores	Dipole-dipole interactions, intermolecular π-π stacking	Solution	Solution (TFA and TEA)	Fluorescence

(xi) Mass spectrometry



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Comment 1
Comment 2

m/z	S/N	Quality Fac.	Res.	Intens.	Area
713.296	8	255	5038	222	47.9
897.909	12	2371	6582	297	69.4
960.918	14	4062	6946	341	86.9
974.944	117	93423	7207	2656	679
985.920	93	32313	7305	2098	544
1004.906	33	4618	7175	761	207
1006.920	175	172248	7604	3909	1015
1019.918	20	3924	7190	462	124
1038.895	7	455	7432	174	41.9
1334.234	34	12952	10162	693	211
1377.196	8	1357	7606	165	68.7
1393.199	7	1113	7471	150	65.9
1405.219	26	8937	8731	521	206
1486.328	7	2081	985	114	389
1496.214	11	5272	1666	212	471
1617.500	56	27914	10089	951	433
1664.418	21	6507	2596	352	692
1813.766	11	1993	9291	178	107
1825.821	43	7490	11410	637	323
1841.831	2799	47536	7011	40188	35135
1842.838	3317		7229	46866	14572
1843.824	377	1071	7855	5442	3945
1863.831	164	13243	11563	2342	1235
1869.872	7	1268	9583	113	69.8
2066.125	11	1070	8661	127	94.9

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Figure S20. MALDI-TOF mass spectrum obtained for compound **1**

(xii) References

1. B. Pradhan, S. K. Pathak, R. K. Gupta, M. Gupta, S. K. Pal and A. S. Achalkumar, *J. Mater. Chem. C.*, 2016, **4**, 6117-6130.
2. G. Yang, W. Hu, H. Xia, G. Zou and Q. Zhang, *J. Mater. Chem. A*, 2014, **2**, 15560-15565.