Stimuli responsive L-DOPA based supramolecular gel for detection of fluoride ion

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Electronic supplementary information (ESI)

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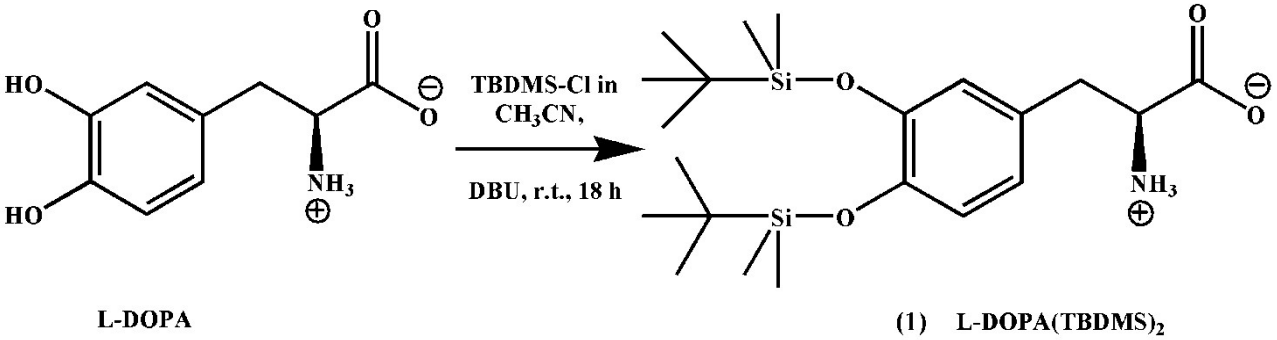

Scheme S1 Synthetic scheme for gelator **1**

Synthetic procedure of amphiphile 1 [*3,4-Bis(tert-butyldimethylsilyloxy)-L-phenylalanine*] i.e. [L-DOPA(TBDMS)$_2$]: 1.76 g (11.6 mmol) of tert-butyldimethylsilyl chloride (TBDMS-Cl) was taken in 10 ml of dry acetonitrile and 0.8 g (4 mmol) of L-DOPA was added to the solution. The suspension was stirred and cooled to 0°C, and 1.8 ml (12 mmol) of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was added to the suspension. Then the reaction mixture was stirred for 20 h at room temperature. A precipitate was obtained which was then filtered, dried at 50°C to yield L-DOPA(TBDMS)$_2$. Yield of the final product was 40%. The crude product was recrystallized from methanol/acetonitrile to obtain pure **1**.

Compound **1**. ^{1}H NMR (500 MHz, CD_3OD, rt) δ = 6.82 (m, 1H, aromatic H), 6.79 (m, 2H, aromatic H), 3.73 (m, 1H, α- CH_3), 2.91 (m, 2H, β-CH_2), 1.08 (s, 18H, $C(CH_3)_3$, 0.06 (s, 12H, Si-CH_3) MS (ESI): m/z calcd for $C_{21}H_{39}NO_4Si_2$: 425.2418 [M+], found: 426.2179 [M+1], 427.2158 [M+2], 428.2106 [M+3]; elemental analysis calcd. (%) for $C_{21}H_{39}NO_4Si_2$: C 59.25, H 9.23, N 3.29; found: C 59.31, H 9.29, N 3.23.

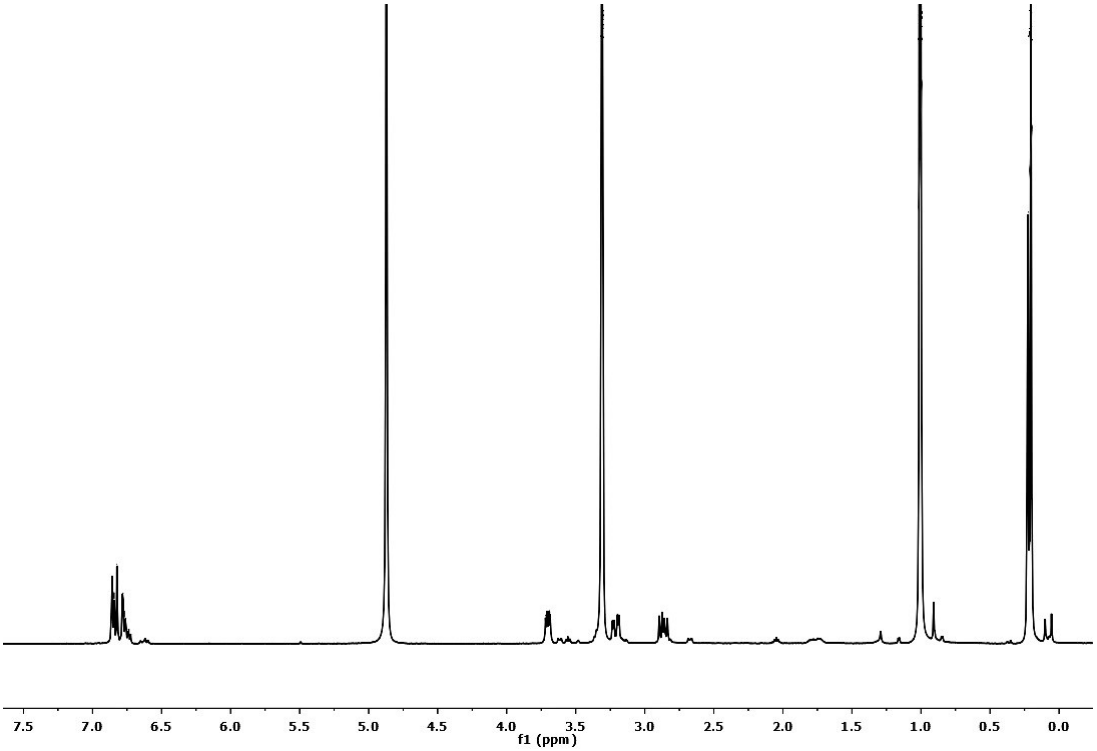

Fig. S1 NMR spectra of compound **1**

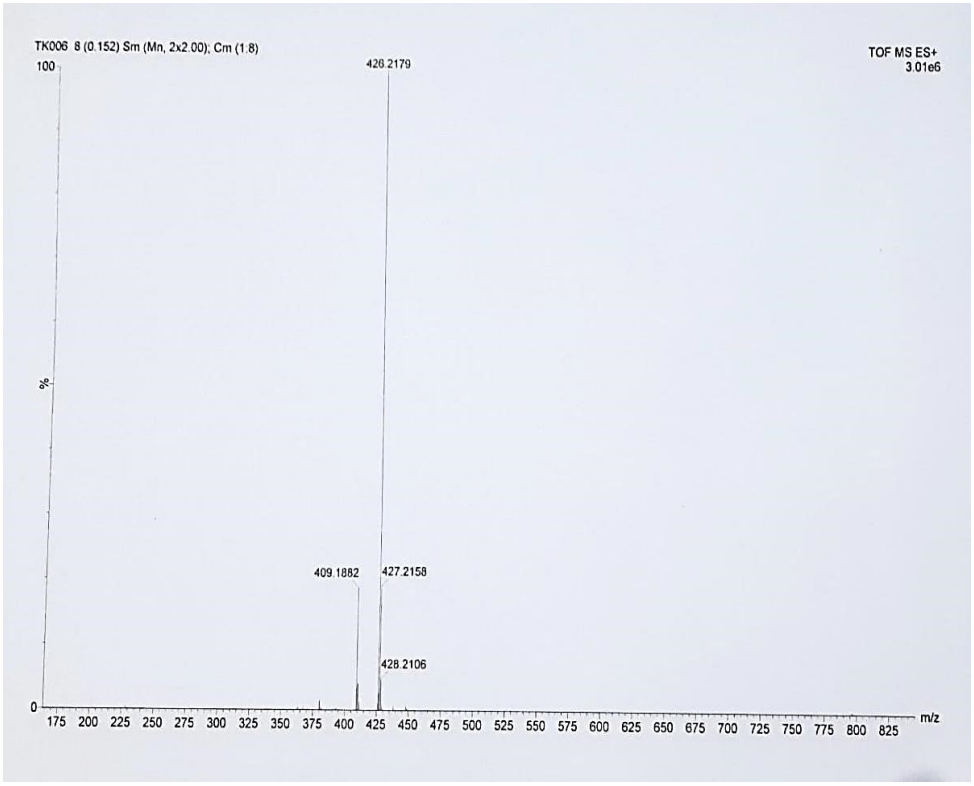

Fig. S2 Mass spectra of Compound **1**

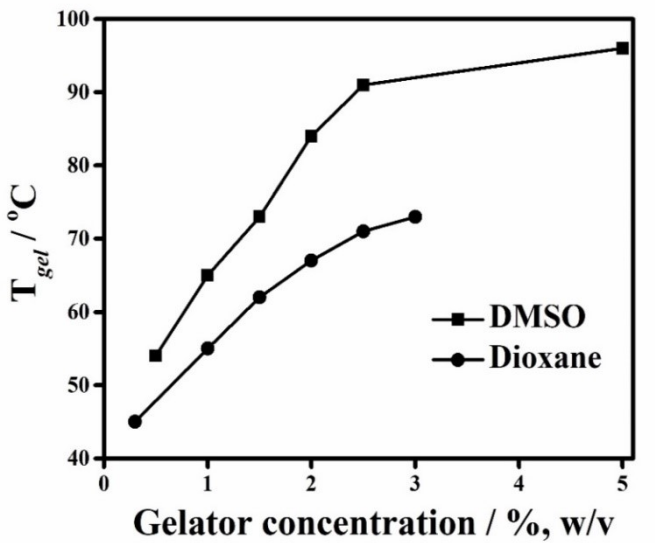

Fig. S3 Variation of T_{gel} with gelator concentrations (%, w/v) in DMSO and dioxane.

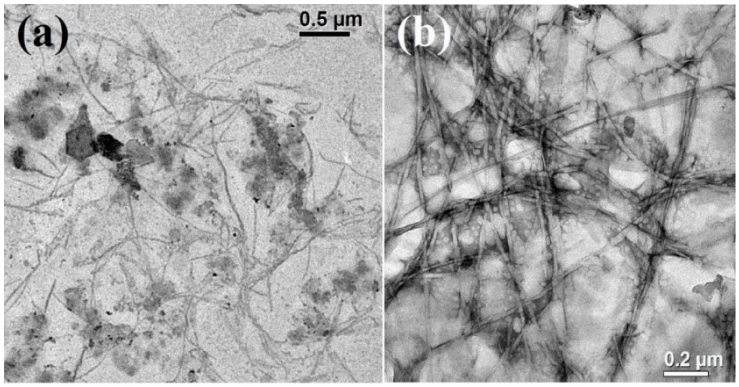

Fig. S4 TEM images of xerogels of **1** preraped from (a) DMSO, (b) dioxane.

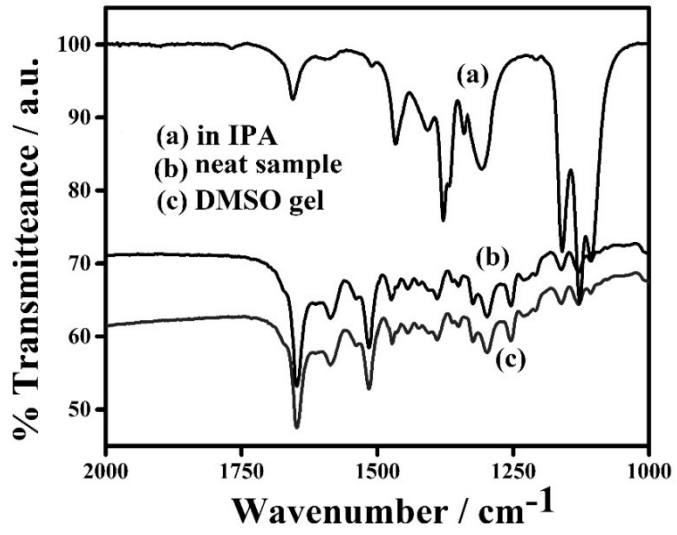

Fig. S5 FTIR spectra of **1** in (a) isopropanol, (b) solid sample, (c) DMSO gel.

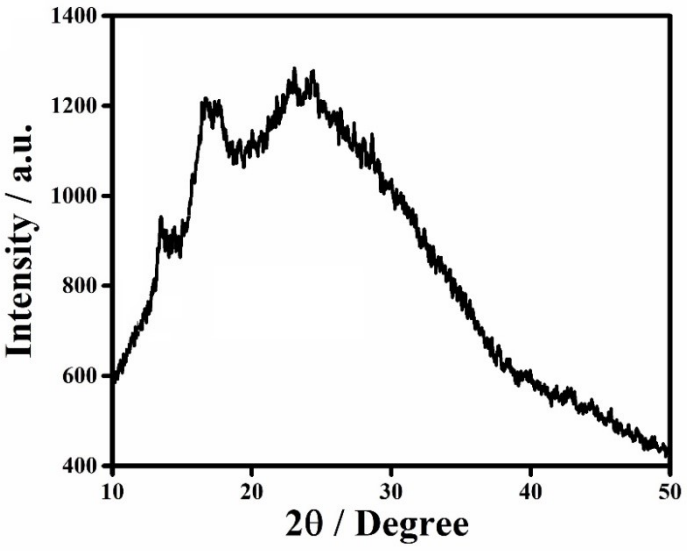

Fig. S6 XRD spectra of dried gel of **1** in DMSO.

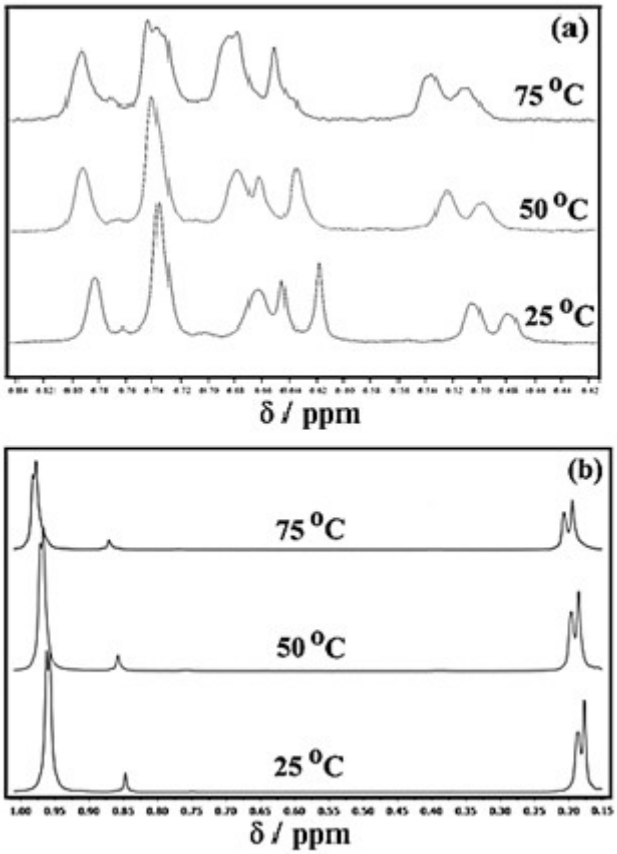

Fig. S7 Temperature dependent proton NMR spectra of gel of **1** in DMSO-d_6.

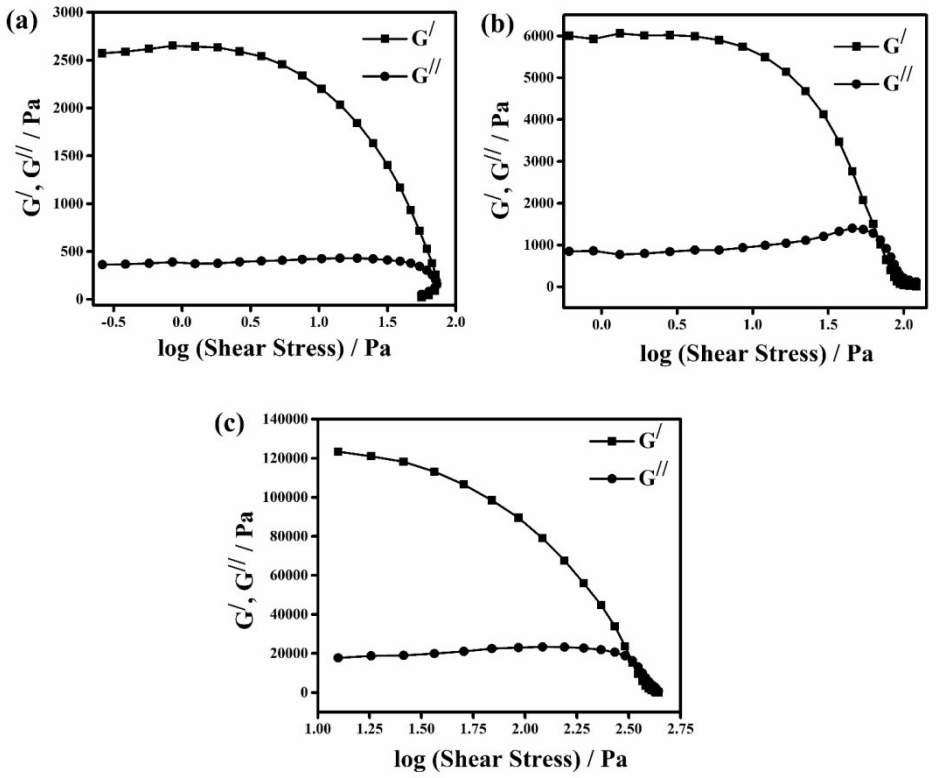

Fig. S8 Plots of G' and G'' of **1** in dioxane at gelator concentration (a) 1% w/v and (b) 2% w/v and (c) 5% w/v as a function of oscillatory stress.

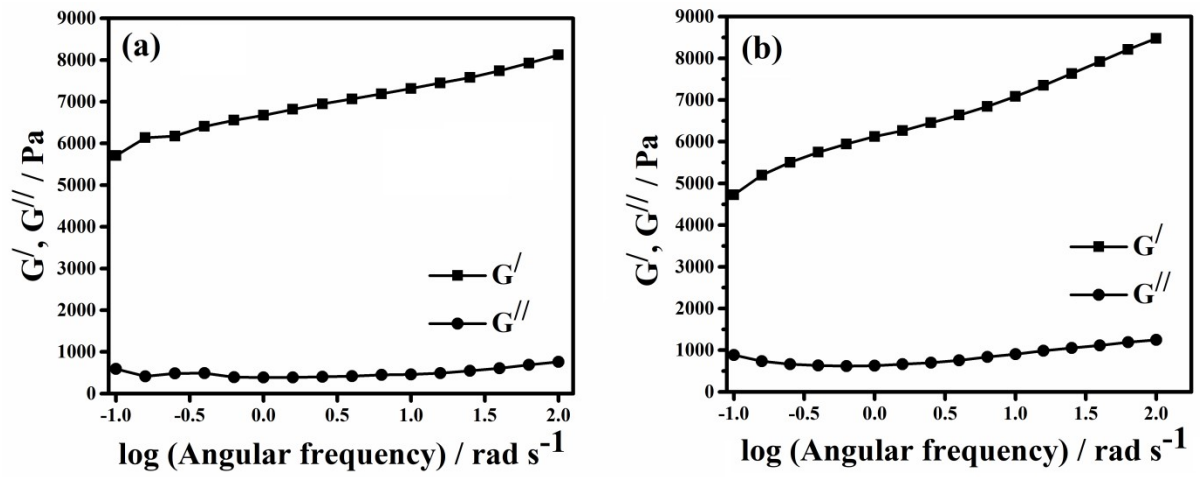

Fig. S9 Plots of G' and G'' of **1** (a) in DMSO at gelator concentration 2% w/v and (b) in dioxane at 2% w/v gelator concentration as a function of angular frequency.

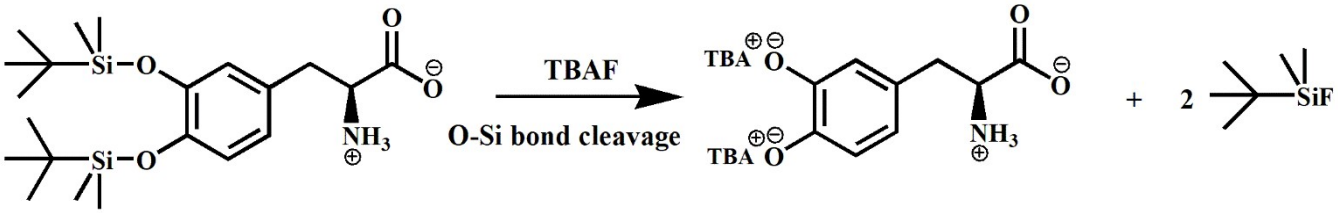

Fig. S10 Cleavage of Si-O bond to produce non gelating ditertiarybutyl ammonium salt of L-DOPA and tert butyldimethylsilyl fluoride.

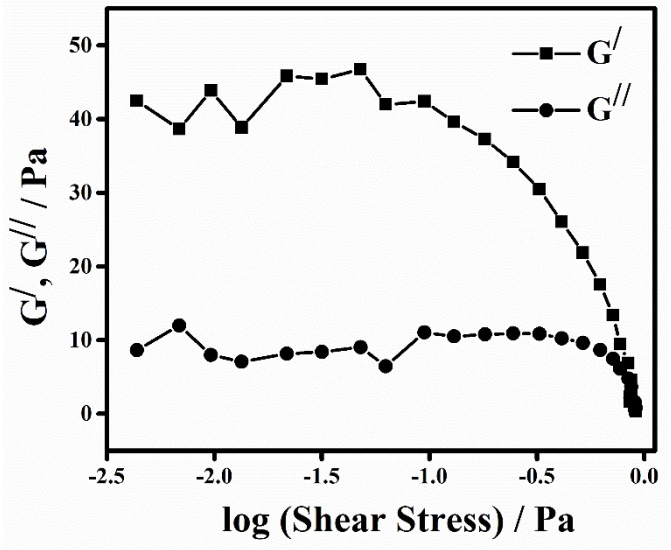

Fig. S11 Plots of G' and G'' of **1** at its MGC in DMSO in presence of 0.1 equiv. of TBAF as a function of oscillatory stress.

Table S1 Fluoride ion concentration (in equiv.) vs. gel degradation time in 30 °C and 45 °C temperature.

Fluoride equivalent	Degradation time at 30 °C (mean ± SD in second)	Degradation time at 45 °C (mean ± SD in second)
0.05	986±4.9	772±3.8
0.1	922±4.6	712±3.5
0.2	800±4.0	596±2.9
0.5	592±2.9	455±2.2
1.0	504±2.5	393±1.9
2.0	448±2.2	352±1.7
3.0	408±2.1	322±1.6
4.0	380±1.9	300±1.5
5.0	345±1.7	272±1.3

Table S2 Corresponding best fit equation for fluoride ion concentration vs. gel degradation time in sec. at 30 °C and corresponding R square value.

Equation	y = Intercept + B1*x^1 + B2*x^2 + B3*x^3 + B4*x^4		
Residual Sum of Squares	0.0724		
Adj. R-Square	0.99471		
		Value	Standard Error
B	Intercept	42.1928	7.3804
	B1	-0.19992	0.05055
	B2	3.52937E-4	1.2415E-4
	B3	-2.7335E-7	1.29683E-7
	B4	7.81543E-11	4.88294E-11

Table S3 Corresponding best fit equation for fluoride ion concentration vs. gel degradation time in sec. at 45 °C and corresponding R square value.

Equation	y = Intercept + B1*x^1 + B2*x^2 + B3*x^3 + B4*x^4		
Residual Sum of Squares	0.09188		
Adj. R-Square	0.99329		
		Value	Standard Error
B	Intercept	41.96347	8.19517
	B1	-0.24948	0.07159
	B2	5.48717E-4	2.24757E-4
	B3	-5.25746E-7	3.00666E-7
	B4	1.84503E-10	1.45124E-10