Electronic Supplementary Information

Selective Binding of Hydrogen Chloride and its Trapping through Supramolecular Gelation

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Experimental Section

Materials

Myristic acid, L-Ttyptophan and m-Aminopyridine were purchased from Aldrich. HOBt (1-hydroxybenzotriazole) and DCC (*N, N′*-dicyclohexylcarbodiimide) were purchased from SRL, India.

Methods

The amphiphile was synthesized by conventional solution phase methods using racemization free fragment condensation strategy. Couplings were mediated by DCC/HOBt. All compounds were purified by column chromatography using silica gel (100-200 mesh size) as stationary phase and chloroform and ethyl acetate as eluent.

Instrumentation

NMR experiments: All 500 MHz NMR studies were carried out on a Bruker DPX 500 MHz spectrometer at 300 K using cryo probe in $CDCl_3$ and DMSO-d_6 maintaining the concentration 4–10 mM.

Mass spectrometry: Mass spectra were recorded on a Qtof Micro YA263 high-resolution mass spectrometer.

Field emission scanning electron microscopic (FESEM) study: FE-SEM experiment was performed by placing a small portion of gel sample on a microscope cover glass. Then, the sample was dried first in air and then in vacuum and coated with platinum for 90 seconds at 10 kV voltages and 10 μA current. The average thickness of the coating layer of platinum was 3 to 4 nm. After that, micrographs were taken by using a Jeol Scanning Microscope JSM-6700F.

Transmission electron microscopy (TEM): A drop of dilute solution of the gel was placed on carbon-coated copper grid (300 mesh) and dried by slow evaporation. Each grid was then allowed to dry in a vacuum for two days. TEM images were recorded on a JEM 2010 electron microscope at an accelerating voltage of 200 KV.

FT-IR Spectroscopy: FT-IR spectroscopy was performed using Nicolate 380 FT-IR spectrophotometer (Thermo Scientific). All reported FT-IR spectra were taken using the spectroscopic cell with CaF_2. During the recording of IR spectra using the CaF_2 cell 100 scans were performed.

XRD study: XRD study of the xerogel was carried out by placing the sample on a glass plate. Experiments were carried out by using an X-ray diffractometer (Seifert XDAL 3000). Scan speed was 2s and step size was 0.02°.

Rheology: The rheology experiment was performed by using an Advanced Rheometer AR 2000 (TA Instruments) at 25 °C.

NMR Titration: For the calculation, chemical shift values were taken upto their respective saturation and these values were fitted by using WINEQNMR software to calculate the binding constant.

Amphiphile synthesis

(1) C_{14}-Trp-OMe

Myristic acid (2.28 g, 10 mmol) in DMF (10 mL) was cooled in an ice-water bath. H-Trp-OMe was isolated from the corresponding methyl ester hydrochloride (5.1 g, 20 mmol) by neutralization, subsequent extraction with ethyl acetate and concentrate to 10 mL. Then it was added to the reaction mixture, followed immediately by DCC (2.06 g, 10 mmol) and HOBt (1.53 g, 10 mmol). The reaction mixture was stirred for three days. The reaction mixture was taken in ethyl acetate (60 mL) and the DCU was filtered off. The organic layer was washed with 1M HCl (3×50 mL), brine (2×50 mL), 1M sodium carbonate (1×50 mL), and brine (2×50 mL) and then dried over anhydrous sodium sulfate and evaporated in vacuum to yield peptide as a white solid. Purification was done by silica gel column (100–200 mesh) using chloroform and ethyl acetate as eluent.

Yield: 3.3 g (7.8 mmol, 78 %).

H^1 NMR (500 MHz, $CDCl_3$, TMS, 25 °C) δ 8.29 (NH, 1H, s), 7.54–6.96 (Aromatic Hs, 5H, m), 6.02-6.00 (NH, 1H, d, J = 7.6), 4.99–4.95 ($C^{\alpha}H$, 1H, m), 3.69 (OCH_3, 3H, s), 3.33–3.31 ($C^{\beta}H$, 2H, m), 2.16–2.12 ($^{\alpha}CH_2$, 2H, t, J = 7.6), 1.58–1.55 ($^{\beta}CH_2$, 2H, m), 1.32-1.24 ($10CH_2$, 20H, m), 0.90–0.87 (CH_3, 3H, t, J = 7). C^{13} NMR (125 MHz, $CDCl_3$, 25°C): δ 173.07, 172.65, 136.26, 127.86, 122.82, 122.35, 119.79, 118.68, 111.42, 110.23, 53.04, 52.43, 36.71, 32.04, 29.80, 29.76, 29.73, 29.58, 29.47, 29.44, 29.34, 27.80, 25.60, 22.80, 14.22. HRMS: (m/z) 429.0173 $[M+H]^+$, 451.0047 $[M+Na]^+$, 466.9285 $[M+K]^+$.

(2) C_{14}-Trp-OH

C_{14}-Trp-OMe (3.3 g, 7.8 mmol) was dissolved in MeOH (20 mL) and then 2M NaOH (10 mL) was added. The reaction mixture was stirred and the progress of saponification was monitored by thin layer chromatography (TLC). After 10 h methanol was removed under vacuum, the residue was taken in 50 mL of water, washed with diethyl ether (2×50 mL). Then the pH of the aqueous layer was adjusted to 2 using 1M HCl and it was extracted with ethyl acetate (3×50 mL). The extracts were dried over anhydrous sodium sulfate, and evaporated in vacuum to yield as a white solid sample.

Yield: 3.0 g (7.2 mmol, 92 %).

H^1 NMR (500 MHz, DMSO-d_6, 25 °C) δ 12.54 (COOH, 1H, br), 10.81 (NH, 1H, s), 8.04–8.01 (NH, 1H, d, J = 7.92), 7.53–6.94 (Aromatic Hs, 5H, m), 4.51–4.43 ($C^{\alpha}H$, 1H, m), 3.19–2.94 ($C^{\beta}H$, 2H, m), 2.07–2.02 ($^{\alpha}CH_2$, 2H, t, J = 7.32), 1.42–1.37 ($^{\beta}CH_2$, 2H, m), 1.29-1.17 ($10CH_2$, 20H, s), 0.87–0.82 (CH_3, 3H, t, J = 6.58). C^{13} NMR (125 MHz, DMSO-d_6, 25°C): δ 173.60, 172.17, 136.08, 127.22, 123.46, 120.83, 118.26, 111.33, 110.02, 52.83, 35.09, 31.31, 29.06, 28.94, 28.83, 28.74, 28.57, 27.14, 25.16, 22.11, 13.94. HRMS: (m/z) 415.1390 $(M+H)^+$, 437.0984 $[M+Na]^+$, 453.0745 $[M+K]^+$.

(3) C_{14}-Trp-m-aminopyridine

C_{14}-Trp-OH (3.0 g, 7.2 mmol) in DMF (10 mL) was cooled in an ice-water bath. m-aminopyridine (0.7 g, 7.5 mmol) was added to the reaction mixture, followed immediately by DCC (1.48 g, 7.2 mmol) and HOBt (1.1 g, 7.2 mmol). The reaction mixture was stirred for three days. The reaction mixture was taken in ethyl acetate (60 mL) and the DCU was filtered off. The organic layer was washed with 1M HCl (2×50 mL), brine (2×50 mL), 1M sodium carbonate (1×50 mL), and brine (2×50 mL) and then dried over anhydrous sodium sulfate and evaporated in vacuum to yield peptide as a white solid. Purification was done by silica gel column (100–200 mesh) using chloroform and ethyl acetate as eluent.

Yield: 2.5 g (5.1 mmol, 70 %).

H^1 NMR (500 MHz, DMSO-d_6, 25 °C) δ 10.81 (Trp-NH, 1H, s), 10.29 (Aromatic H, 1H, s), 8.73 (Aromatic H, 1H, s), 8.26-8.25 (Aromatic H, 1H, d, *J* = 4.0), 8.16-8.15 (NH, 1H, d, *J* = 7.5), 8.02-8.00 (NH, 1H, d, *J* = 8.5), 7.64-7.62 (Aromatic H, 1H, d, *J* = 8.0), 7.34-7.30 (Aromatic H, 2H, m), 7.16 (Aromatic H, 1H, s), 7.06-6.94 (Aromatic H, 2H, m), 4.74–4.70 ($C^{\alpha}H$, 1H, m), 3.19-2.99 ($C^{\beta}H$, 2H, m), 2.10–2.06 ($^{\alpha}CH_2$, 2H, m), 1.44–1.40 ($^{\beta}CH_2$, 2H, m), 1.28-1.17 ($10CH_2$, 20H, m), 0.86–0.84 (CH_3, 3H, t, *J* = 6.75). C^{13} NMR (125 MHz, DMSO-d_6, 25 °C): δ 172.89, 172.00, 144.86, 141.63, 136.63, 136.16, 127.85, 126.89, 124.19, 121.45, 119.10, 118.75, 111.84, 110.41, 54.53, 35.69, 31.88, 29.63, 29.49, 29.36, 29.29, 29.13, 28.43, 25.75, 22.67, 14.53. HRMS: (m/z) 490.1024 $[M+H]^+$, 513.0737 $[M+Na]^+$.

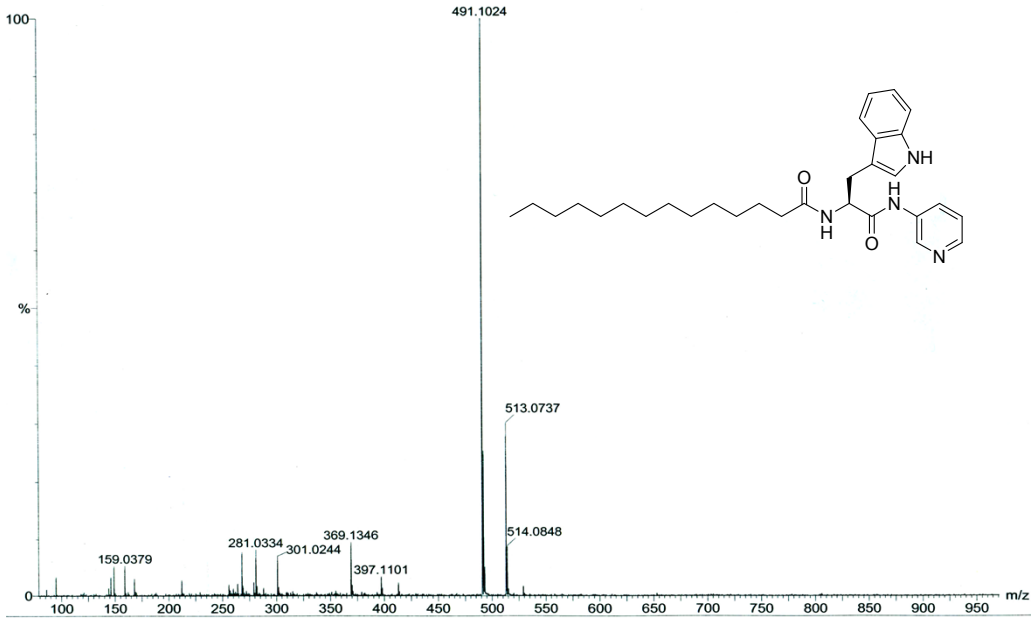

Fig. S1 Mass spectrum of **1**.

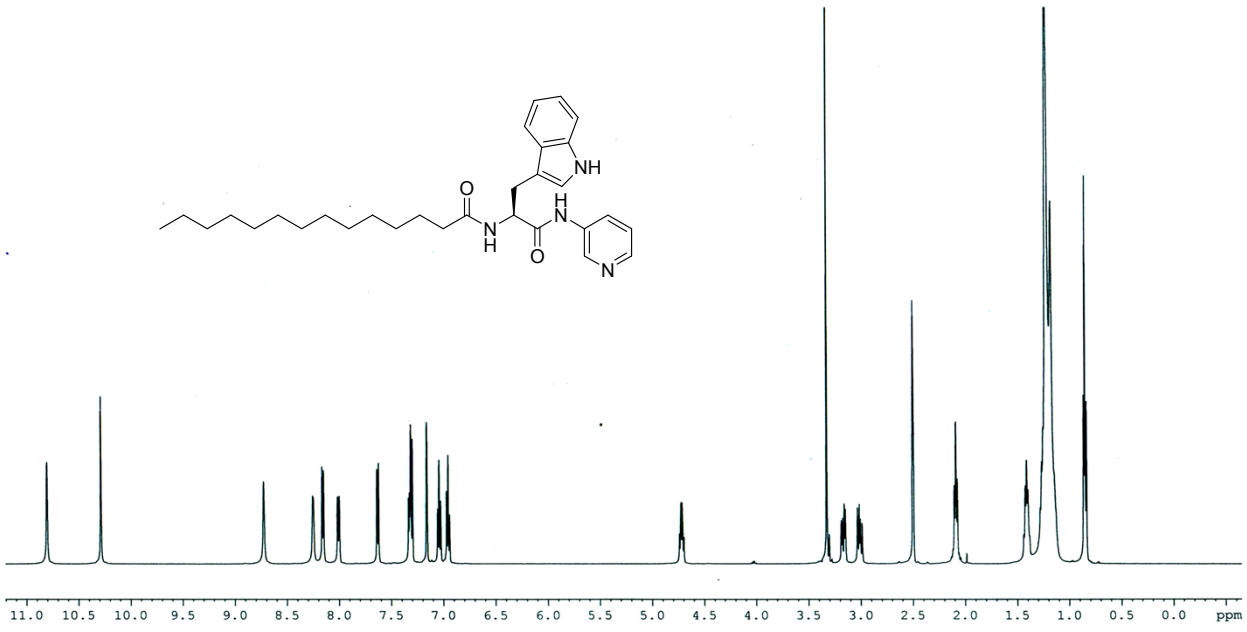

Fig. S2 H^1 NMR of **1** (500 MHz) in DMSO-D_6.

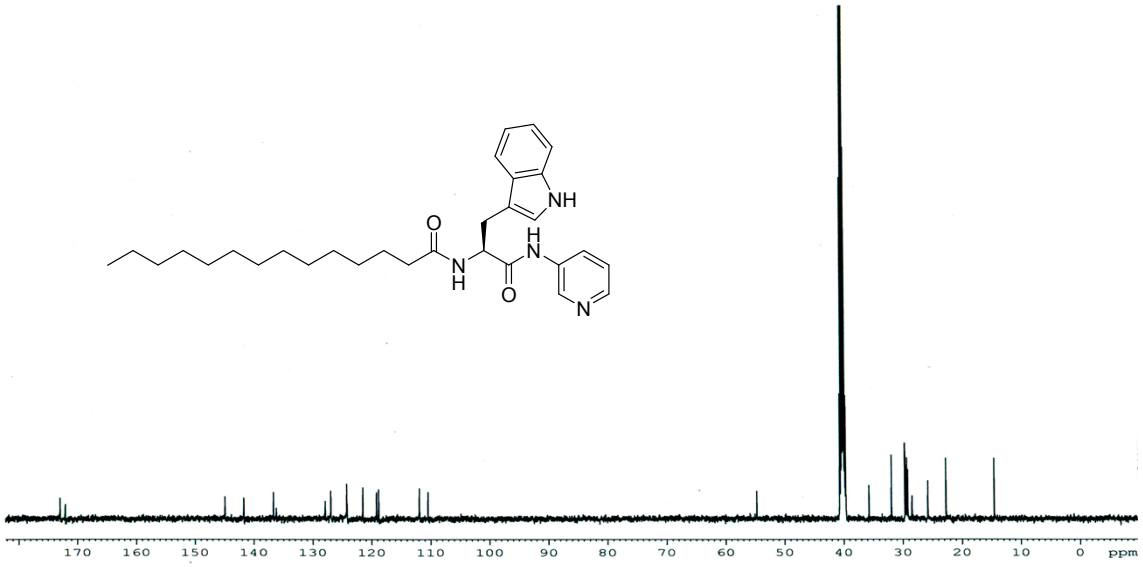

Fig. S3 C^{13} NMR of **1** (500 MHz) in DMSO-D_6.

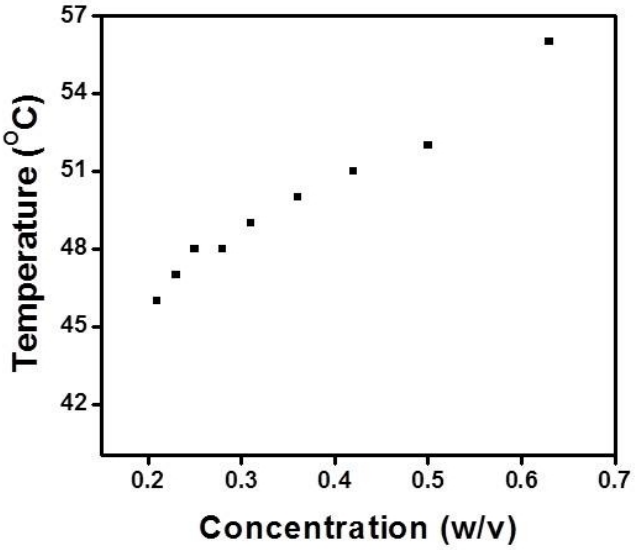

Fig. S4 Plot of gel melting temperature vs. gels obtained in different concentration of gelator **1**.

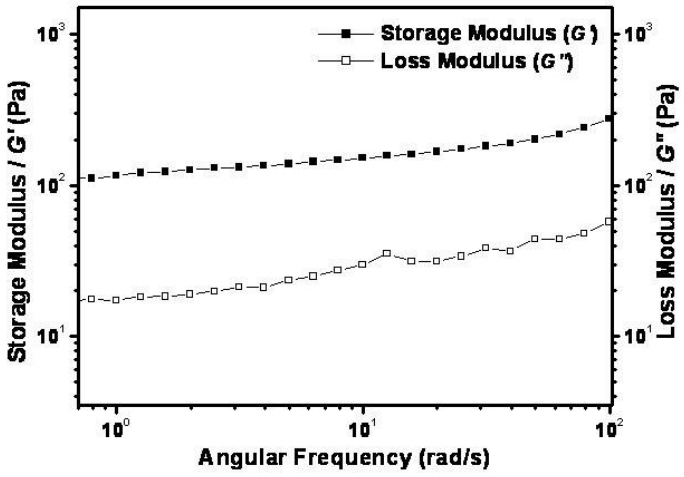

Fig. S5 The frequency sweep experimental data showing no crossover point throughout the experimental region for the gel phase material.

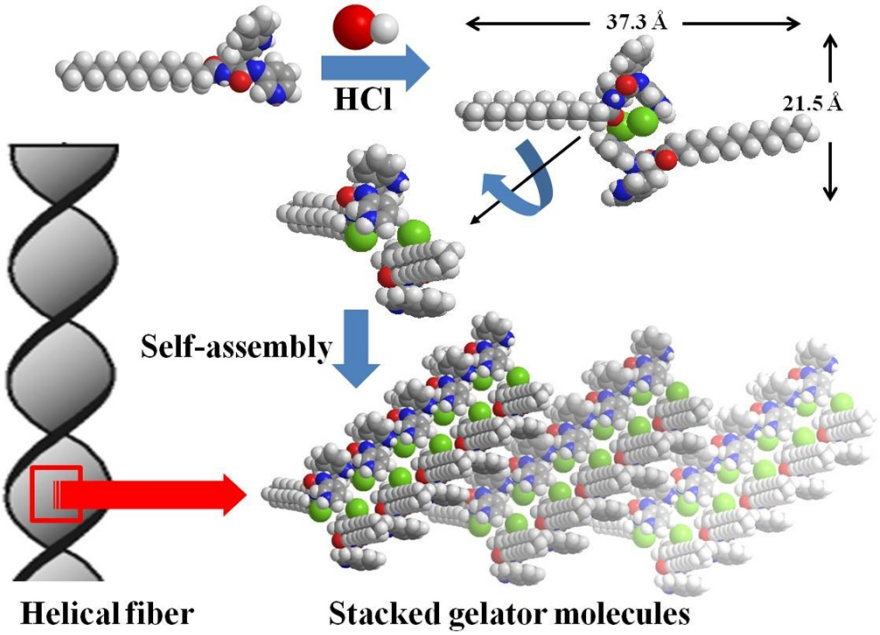

Fig. S6 The probable stacking formed in the gel state. A probable unit is showing the involvement of two gelator molecules and HCl molecule. This further self-assembles to form higher order structures that can be responsible for gelation. The distances which are marked by the double headed arrows were obtained from XRD patterns of the xerogel in presence of HCl.

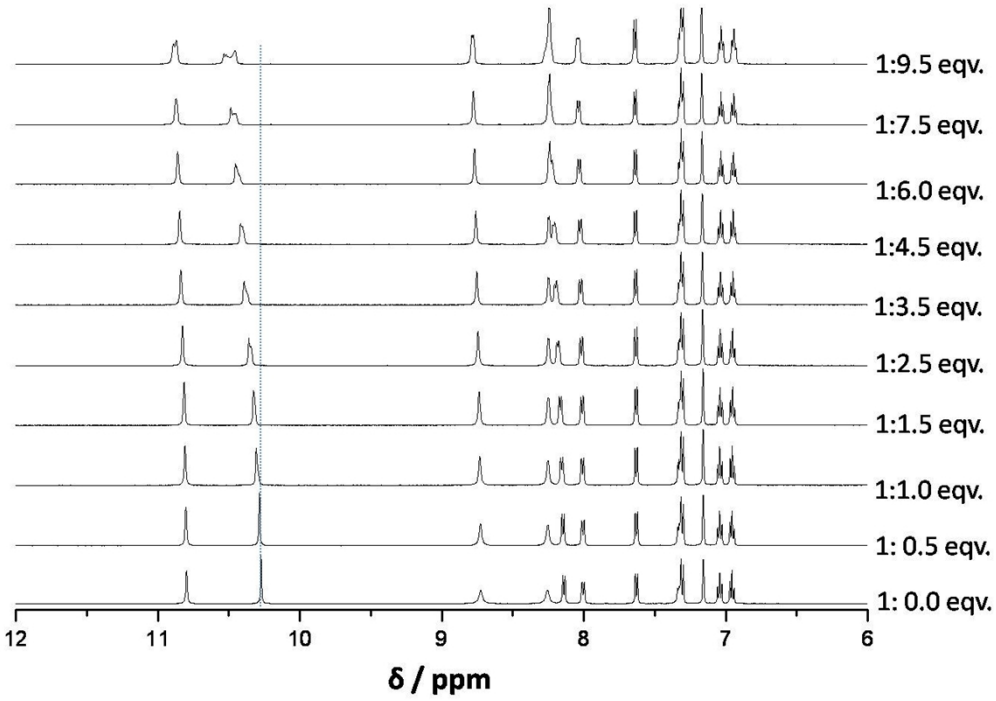

Fig. S7 Gradual addition of tetrabutylammonium chloride (TBA chloride) into the gelator solution within the NMR tube shows the NMR titration. Dotted line indicates the shifting of the pyridinium hydrogen upon the gradual addition of TBA chloride suggesting the binding of chloride ions with gelator molecules. A solution of the host species of concentration (10 mM) was prepared in an NMR tube using DMSO-d_6 (0.5 ml). The TBA chloride in DMSO-d_6 was added in 10 µl aliquots, representing 0.5 equivalents of the guest with respect to the gelator.