

Supporting Information.

Evidence of Aggregation Induced Emission Enhancement and Keto-enol-tautomerism in a Gallic acid derived Salicylideneaniline Gel

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a) Physical measurements and instrumentation.

Gelation studies. The gelation test of **1** was performed in various organic solvents. A weighed amount of a compound **1** was taken in a sealed glass vial and heated to get a clear solution. The solution was then left to cool to room temperature. After 0.5 h the stability of the gel was checked using inverse flow method and each experiment was performed in duplicate. If a gel was formed, it was evaluated quantitatively by determining the minimum gelator concentration (MGC) which has been defined as the minimum amount of gelator required to immobilize 1 mL of a particular solvent. When the compound did not dissolve completely, it was labelled as “insoluble” where as “precipitation” indicates that after initial solubilization, a precipitation occurred during cooling.

¹H-NMR. Temperature-dependent ¹H-NMR spectra of gel of **1** were recorded on a Bruker-400 Avance NMR spectrometer using C₆D₆ as the solvent.

FT-IR spectroscopy. As prepared organogel of **1** was drop cast on the NaCl cell and dried under vacuum and the spectra were recorded in Perkin Elmer Spectrum BX FT-IR system.

UV-Vis and Fluorescence Spectroscopy. The UV-Vis and fluorescence Spectroscopy of gel and solution of gelator **1** were recorded on a Shimadzu model 2100 spectrophotometer and Hitachi F-4500 spectrofluorimeter.

Scanning electron microscopy. The toluene gel of compound **1** was carefully scooped onto the brass stub and was allowed to freeze-dry overnight. The sample was then coated with gold vapour and analyzed on a Quanta 200 SEM operated at 15 kV.

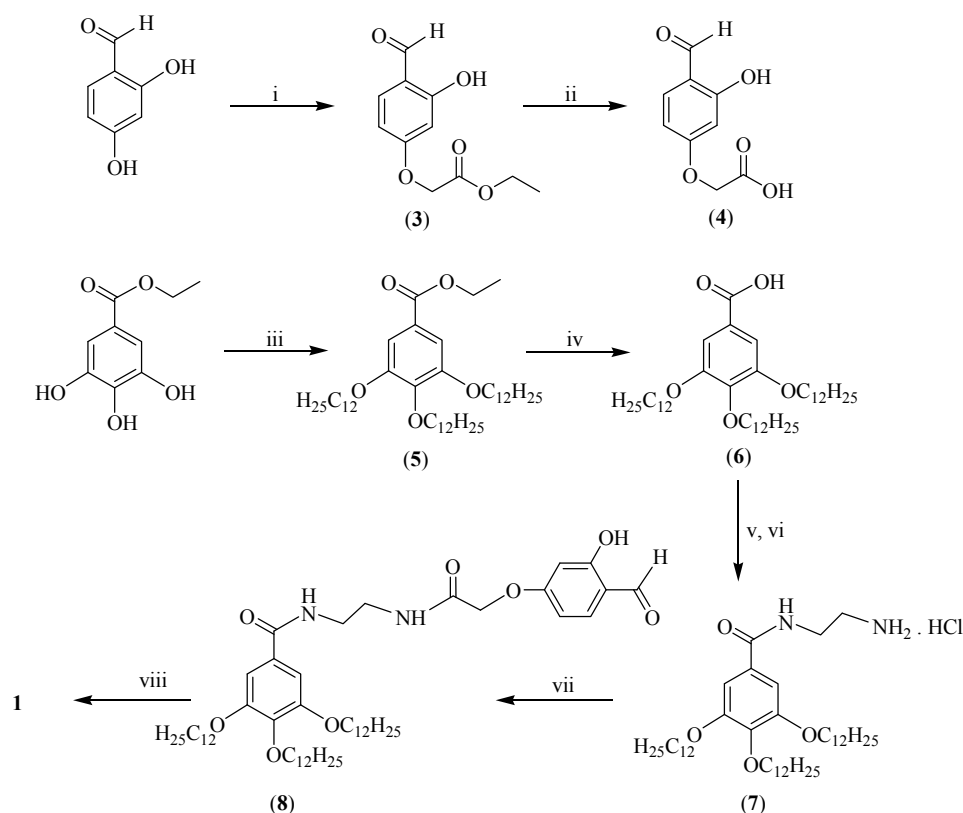
Small-angle X-ray diffraction. Toluene gel of compound **1** was scooped onto either scotch tape/glass slide and dried under vacuum for the corresponding small-angle XRD measurements. SAXD measurement was recorded on a Bruker Nanostar-SAXS instrument using the X-ray beam generated with rotating Cu anode at the wavelength of K α beam at 1.5418Å.

b) Materials and Methods.

All chemicals, solvents and silica gel for TLC and column chromatography were obtained from well-known commercial sources and were used without further purification, as appropriate. Solvents were distilled and dried by standard procedure before use. Melting

points was measured in open capillaries and were uncorrected. FT-IR studies were performed on a Perkin-Elmer FT-IR Spectrometer BX model by incorporating the samples in KBr disk and were reported in wave numbers (cm^{-1}). $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded in Bruker-400 Avance NMR spectrometer. Chemical shifts were reported in ppm downfield from the internal standard tetramethylsilane (TMS). MALDI-TOF experiments were performed in Ultraflex MALDI TOF (Bruker Daltonics). Elemental analysis was recorded in Thermo Finnigan EA FLASH 1112 SERIES.

c) Scheme S1.



(i) NaHCO_3 , dry DMF, ethyl bromoacetate, 70°C , 48 h, yield = 70%; (ii) aq. NaOH (1M)/EtOH(1:1), reflux at 80°C , 3 h, yield = quantitative; (iii) $n\text{-C}_{12}\text{H}_{25}\text{Br}$, K_2CO_3 , TBAB, CH_3CN , reflux for 72 h, yield = 85%; (iv) aq. NaOH (1 M)/EtOH (1:1), reflux for 3 h at 80°C , yield = 98%; (v) SOCl_2 , Dry CH_2Cl_2 , 3 h, rt, yield = quantitative; (vi) Ethylenediamine, dry THF, 0°C to rt, yield = 50%; (vii) DCC, DMAP, Pyridine, CH_2Cl_2 , 0°C to rt, 24 h, yield = 70%; (viii) o -phenylenediamine, ethanol, glacial AcOH (cat. amount), 80°C , reflux for 3 h, yield = 82%.

d) Synthetic procedure and characterization data.

Synthesis. Compound **1** was synthesized according to the reaction scheme 1 and was characterized by ^{13}C -NMR, ^1H -NMR, FTIR and MALDI-TOF mass spectrometry and elemental analysis. Compound **3**, **4** and **6** were prepared as described earlier.^{1,2}

8. 3, 4, 5-(Tri-dodecyloxy)benzoylaminoethyl amide (0.715 g, 1.019 mmol) and 2-hydroxy-4-carboxymethoxybenzaldehyde (0.2 g, 1.0195 mmol) were dissolved in dry CH_2Cl_2 (10 ml) containing dry pyridine (0.1317 ml, 1.529 mmol). The solution was cooled to 0 °C. Catalytic amount of DMAP (0.012 g, 0.1019 mmol) and DCC (0.252 g, 1.22 mmol) were added to the mixture and stirred for 24 h at room temperature. White precipitate of DCU was removed by filtration. The filtrate was diluted with CH_2Cl_2 . The organic layer was washed with 2N HCl and water. After drying over Na_2SO_4 , solvent was evaporated under reduced pressure and the resultant residue was purified by column chromatography ($\text{CHCl}_3/\text{MeOH}$ 9:1) on silica gel to get a white solid. Yield: 70 %; IR (KBr): 3648, 3269, 2954, 2850, 1743, 1635, 1583, 1496, 1467, 1435, 1424, 1386, 1374, 1344 cm^{-1} ; ^1H -NMR (400 MHz, CDCl_3 , TMS, rt): δ (ppm) 0.87 (t, 9H), 1.26–1.46 (m, 54H), 1.68–1.93 (m, 6H), 3.62 (s, 4H), 3.97–4.01 (m, 6H), 4.52 (s, 2H), 6.48 (s, 1H), 6.59 (d, 1H), 6.93 (s, 1H), 6.99 (s, 2H), 7.39 (s, 1H), 7.44 (d, 1H), 9.73 (s, 1H), 11.41 (s, 1H); Elemental analysis: calculated for $\text{C}_{54}\text{H}_{90}\text{N}_2\text{O}_8$: C, 72.44; H, 10.13; N, 3.13; Found: C, 72.43; H, 10.11; N, 3.15.

1. A solution of **8** (0.5 g, 0.558 mmol) and *o*-phenylenediamine (0.03 g, 0.279 mmol) in ethanol was heated to reflux for 3 h in presence of cat. amount of glacial AcOH and cooled to room temperature. The precipitate was collected filtration and washed by hexane thoroughly to obtain yellow solid; Yield: 80 %; mp = 111–112 °C; IR (KBr): 3261, 2922, 2851, 1672, 1622, 1582, 1541, 1500, 1467, 1425, 1389, 1340 cm^{-1} ; MALDI-TOF: m/z calcd for $[\text{M}+\text{H}]^+$: 1863.71; found 1863.88; ^1H -NMR (400 MHz, CDCl_3 , TMS, rt): δ (ppm) 0.87 (t, 18H), 1.25–1.43 (m, 108H), 1.63–1.76 (m, 12H), 3.61 (s, 8H), 3.95–3.99 (m, 12H), 4.49 (s, 4H), 6.50 (m, 4H), 6.99 (s, 4H), 7.12 (s, 2H), 7.22–7.24 (m, 4H), 7.31 (m, 4H), 8.51 (s, 2H), 13.68 (s, 2H); ^{13}C -NMR (400 MHz, CDCl_3 , TMS, rt): δ (ppm) 14.09, 22.68, 26.08, 26.10, 29.35, 29.38, 29.42, 29.59, 29.65, 29.68, 29.70, 29.74, 30.32, 31.91, 39.68, 40.86, 67.07, 69.23, 73.48, 102.14, 105.53, 106.77, 114.65, 127.90, 128.74, 133.74, 135.21, 140.63, 153.07, 160.83, 163.09, 164.27, 168.08, 169.22; Elemental analysis: calculated for $\text{C}_{114}\text{H}_{184}\text{N}_6\text{O}_{14}$: C, 73.51; H, 9.96; N, 4.51; Found: C, 73.54; H, 9.94; N, 4.50.

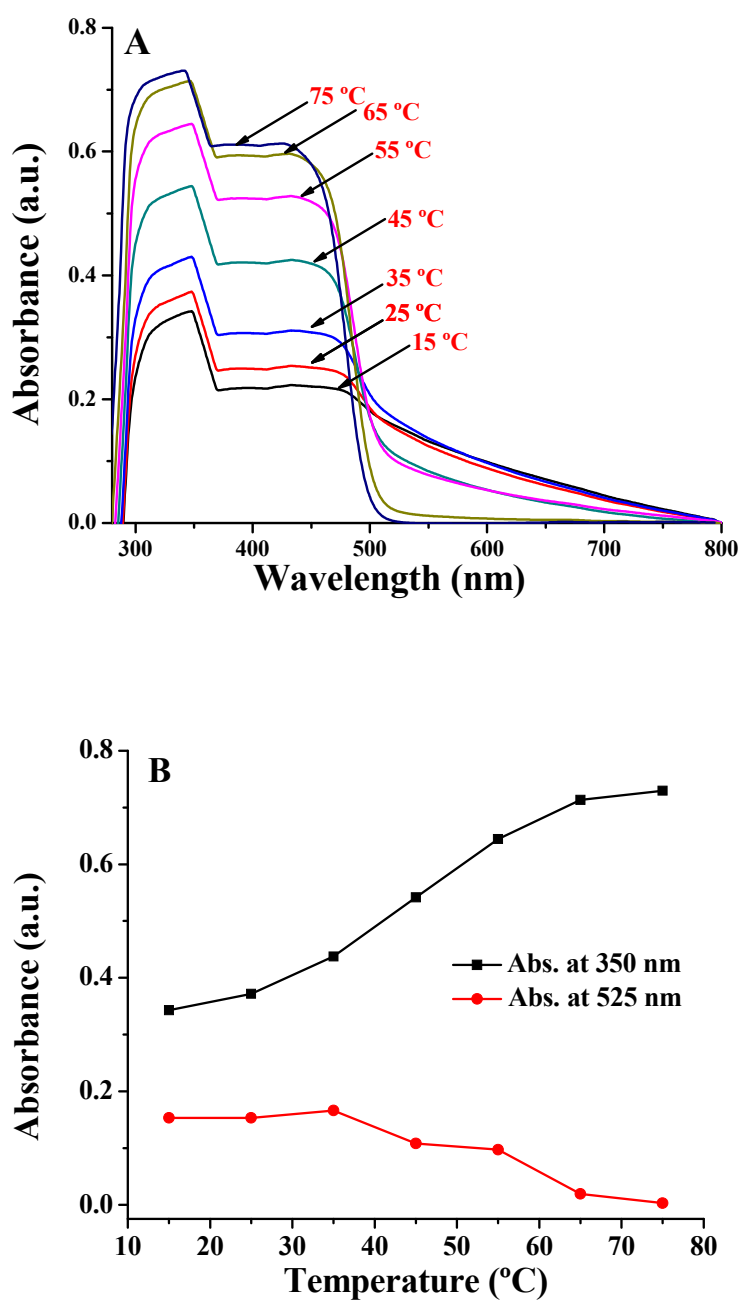


Figure S1. (A) Temperature-dependent UV-Vis spectra of gelator **1** in toluene at 2 mM. (B) Plot of the absorption intensity at 350 nm and 525 nm vs. temperature.

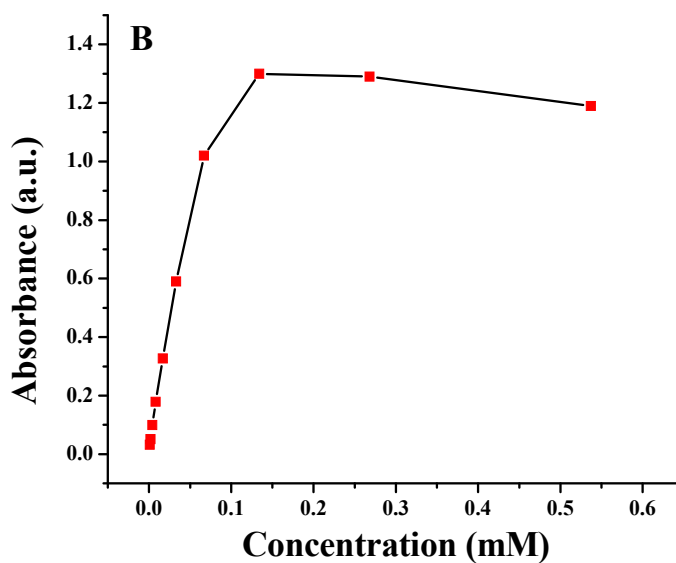
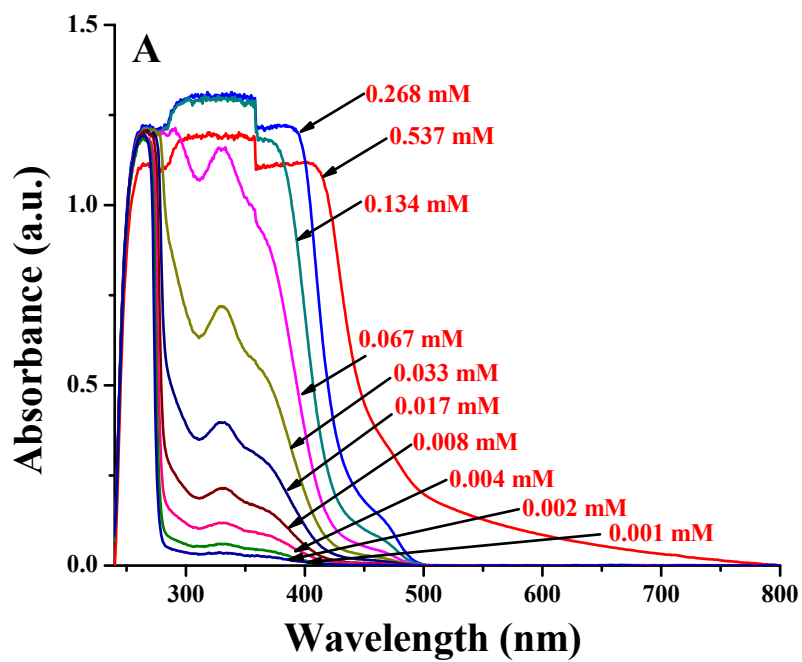


Figure S2. (A) Concentration-dependent UV-Vis spectra of gelator 1 in toluene at 25 °C. (B) Plot of the absorption intensity at 350 nm vs. concentration.

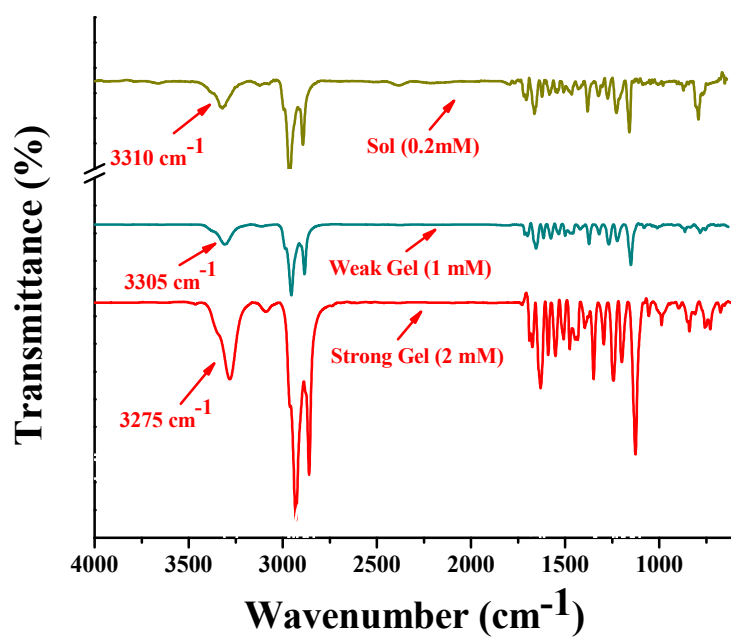


Figure S3. Concentration-dependent IR-spectra of gelator 1 in toluene.

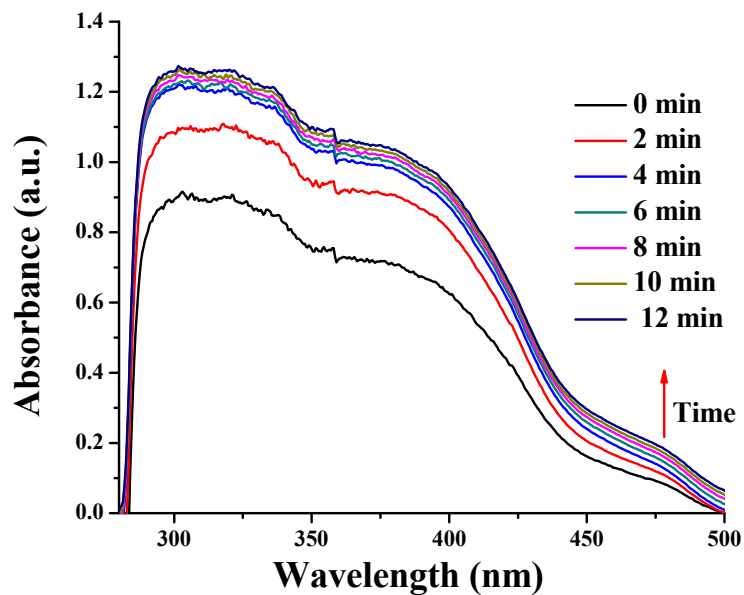


Figure S4. Changes in the UV-Vis spectra of gelator 1 in toluene at the concentration of 0.27 mM while warming from 77 K to 298 K naturally.

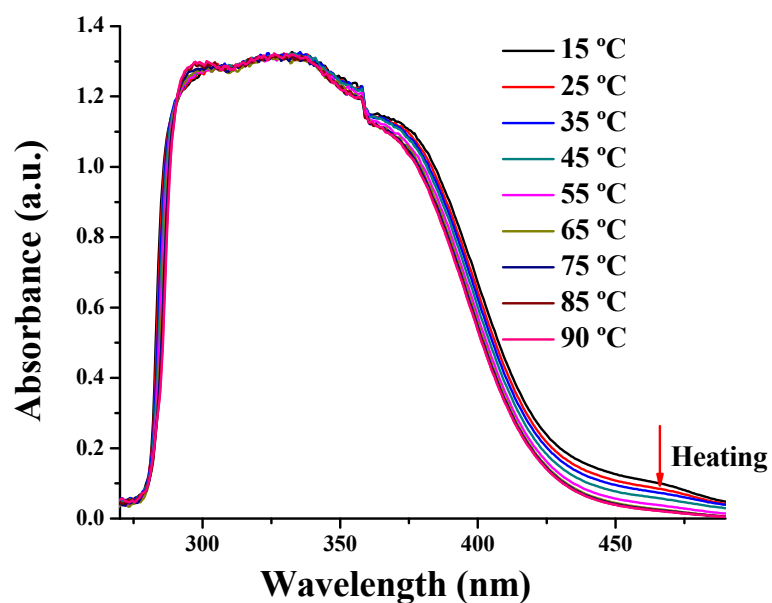


Figure S5. Temperature-dependent UV-Vis spectra of gelator **1** in toluene at the concentration of 0.27 mM.

References.

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