

Electronic Supplementary Information

Tailor made design of J- or H- aggregated Naphthalenediimide based gels and remarkable fluorescence turn on/off depending on solvents

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Experimental section and Instrumentation:

NMR experiments

All NMR studies were carried out on a Bruker DPX 500 MHz spectrometer at 300 K. Concentrations were in the range 1–10 mmol in CDCl₃ or DMSO-d₆.

Mass spectrometry

Mass spectra were recorded on a Q-ToF microTM (Waters Corporation) mass spectrometer by positive mode electro spray ionization process.

MALDI-TOF MS

MALDI-TOF MS analysis has been performed by using Applied Biosystems MALDI TOF/TOF Analyzer in dithranol as a matrix.

Morphological Studies

To study the morphology field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) were performed in dried gel state in aliphatic solvent (n-octane) and in aromatic solvent (toluene). Both of these microscopic studies revealed that these gels were composed of three dimensional nano-fibrillar assemblies. FE-SEM indicates that gel nanofibers obtained from n-octane gel range from 40 nm to 90 nm in width (Fig. S4a). Similarly, nanofibers obtained from toluene gel are ranged from 30 nm to 50 nm in width and these are several micrometers in length (Fig. S4b). TEM images (Fig. S5) also indicate nanofibrillar network structure of these two gels. Nano-fibers obtained from the n-octane and the toluene gels are very thin and their widths are ranged from 20 nm to 35 nm.

FE-SEM experiments were performed by placing a small portion of gel sample on a microscope cover glass. Then, these samples were dried first in air and then in vacuum and coated with platinum for 90 seconds at 10 kV voltages and 10 μ A 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.

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

X-ray diffraction study

X-ray diffraction 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 (Bruker AXS, Model No. D8 Advance). The instrument was operated at a 40 kV voltages and 40 mA current using Ni-filtered CuK α radiation and the instrument was calibrated with a standard Al₂O₃ (corundum) sample before use. For scan 1°-5°, the scintillation counts detector was used with scan speed 2s and step size 0.02°. In another scan 5°-50°, the LynxEye super speed detector was used with scan speed 0.3s and step size 0.02°.

UV/Vis spectroscopy

UV/Vis absorption spectra were recorded on a hewlett-packard (model 8453) UV/Vis spectrophotometer (varian carry 50.bio).

PL spectroscopy

Fluorescence studies were carried out in quartz cuvette in a Perkin Elmer LS55 Fluorescence Spectrometer instrument. The samples were excited at 340 nm wavelength and emission scans were recorded from 350 to 750 nm.

Rheological Study

The rheology experiments were performed by using an Anton Paar Modular Compact Rheometer MCR 302 at 25 °C. During the frequency sweep experiment the strain was kept constant at 0.1% while the angular frequency was kept constant at 1 rad/sec in the stress sweep experiment. The concentration was maintained at 12 mM for both n-octane and toluene gel.

FT-IR spectroscopy

All FT-IR spectra were recorded by using the KBr pellet technique in a Nicolet 380 FT-IR spectrophotometer (Thermo Scientific).

Solubility and Gelation Behaviour

The solubility of the molecule **1** is somewhat less in aliphatic solvents such as octane, cyclohexane, methylcyclohexane (MCH) and others. So, a small amount of chloroform (CHCl₃) was required to dissolve the compound and then aliphatic solvent was used in such a way that the ratio of the aliphatic solvent: CHCl₃ was kept constant at 95:5. After dissolving the compound **1** in required solvent mixture by heating (above gel melting temperature, T_{gel}) it was then slowly cooled down to room temperature to form a gel (Fig. 1a-i of main text). For gelation in aromatic hydrocarbon solvents, CHCl₃ was not required and after heating the compound **1** in the corresponding aromatic solvent it was allowed to cool down to room temperature to obtain a gel phase material (Fig. 1b-i – e-i of main text).

Determination of T_{gel}

Gel melting temperature determination was performed by heating gels in a thermostat controlled water bath at a heating rate of 2 °C/ 5 minute until the gel was melted. The calculated error range in T_{gel} determination was found to be ± 1 °C.

CD Spectroscopy

In CD spectra (Fig. S8, ESI[†]), two negative peaks at 379 nm and 358 nm with a small solder at 340 nm were observed in all aromatic solvents (including benzene, toluene, o-xylene and mesitylene), in which the gelator forms J-aggregates. Interestingly, the 379 nm peak shifts to shorter wavelength with the increase in electron donation capacity of solvents as it is evident from the CD plot. However, in aliphatic solvent like n-octane, in which the gelator forms H-aggregate, a sharp positive peak was found at 388 nm with two shoulders at 372 nm and 341 nm. This indicates that the chirality of J-aggregate and H-aggregate is different.

All spectra were recorded in a JASCO instrument, Model J-815–150S. Data were collected in a quartz cuvette with a path length of 1 mm.

Calculation of Binding Constant

The binding constants of the charge-transfer complex formed between the NDI-based compound **1** and the aromatic solvents have been calculated using the Benesi-Hildebrand method.^{1,2} The equation used in this method is

$$\frac{1}{\Delta A} = \frac{1}{b\Delta\epsilon[G]_0[H]_0K_a} + \frac{1}{b\Delta\epsilon[G]_0}$$

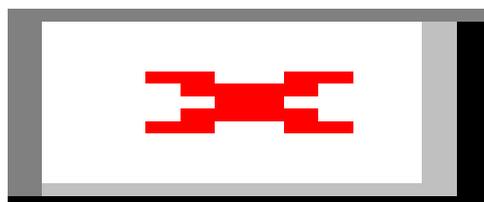
where $\Delta A = A - A_0$ (A_0 = absorbance of the guest, A = absorbance of the CT complex), $[G]_0$ and $[H]_0$ are the concentration of guest and host respectively, $\Delta\epsilon$ is the molar extinction coefficient of the CT complex, b is the path length of the cuvette used in the measurement of the absorbance and K_a is the binding constant.

To calculate the binding constant, concentration of compound **1** and concentration of aromatic solvent were taken as $[H]_0$ and $[G]_0$ respectively. Absorbance was measured keeping the volumes of the aromatic solvents constant and compound **1** was gradually added to it to obtain Fig. S14. Then $1/\Delta A$ is plotted against $1/[H]_0$ to get Fig. S15. Binding constants for each solvent (Table S2) is then calculated from the slope and intercept of each plot.

Materials:

L-Phenylalanine (Phe), dodecylamine (C_{12}) and 1,4,5,8-Naphthalenetetracarboxylic dianhydride (NDA) were purchased from Aldrich. 1-Hydroxybenzotriazole (HOBT), *N,N'*-Dicyclohexylcarbodiimide (DCC) and all gelling solvents were purchased from SRL, India.

Synthesis Procedures:



Scheme S1. Chemical structure and synthesis of the compound **1**.

Boc-Phe-C₁₂: 1.32 g (5 mmol) of Boc-Phe-COOH was dissolved in 10 ml of DMF in an ice water bath. 1.85 g (10 mmol) H₂N-(CH₂)₁₁CH₃ in 20 mL ethyl acetate was then added to the reaction mixture, followed immediately by 1.00 g (5 mmol) of DCC and 0.76 g (5 mmol) of HOBt. The reaction mixture was allowed to come to room temperature and stirred for 3 days. The residue was taken up in ethyl acetate (40 ml) and DCU was filtered off. The organic layer was washed with 1N HCl (3 × 30 ml), brine (1 × 30 ml), 1M sodium carbonate (3 × 30 ml) and brine (2 × 30 ml) and dried over anhydrous Na₂SO₄ and evaporated in *vacuum*. A white material was obtained.

Yield: 1.5 g (3.5 mmol, 70.0 %).

¹H NMR (500 MHz, CDCl₃): δ 7.31-7.19 (5H, aromatic Hs, m), 5.66 (1H, NH, br), 5.10 (1H, NH, br), 4.26-4.24 (1H, ^αH, m), 3.15-3.00 (4H, ^βHs and ^αCH₂, m), 1.65 (2H, ^βCH₂, s), 1.41(9H, Boc, s), 1.33-1.15 (18H, CH₂, m), 0.89-0.86 (3H, CH₃, m). ¹³C NMR (125 MHz, CDCl₃): δ 171.07, 129.46, 128.79, 127.05, 127.05, 39.64, 38.97, 32.06, 29.77, 29.72, 29.64, 29.48, 29.38, 28.44, 26.92, 22.82, 14.24. HRMS (m/z): 432.9029 [M+H]⁺, 454.8737 [M+Na]⁺, 470.8067 [M+K]⁺.

H₂N-Phe-C₁₂: To 1.5 g (3.5 mmol) of Boc-Phe-C₁₂, 4 ml of trifluoroacetic acid (TFA) was added and removal of Boc group was monitored by TLC. After 8 h, TFA was removed under *vacuum*. The residue was taken in water (20 ml) and covered with ethyl acetate (about 50 ml) and basified with a solution of NaHCO₃. The aqueous phase was extracted with ethyl acetate and this operation was done repeatedly. The ethyl acetate extracts were pooled, washed with water and dried over anhydrous Na₂SO₄ and evaporated in *vacuum*. A white material was obtained.

Yield: 0.73 g (2.2 mmol, 62.8 %).

¹H NMR (500 MHz, DMSO-D₆, 25 °C): δ 8.75 (1H, NH, br), 8.27-8.16 (5H, aromatic Hs, m), 4.35-4.33 (3H, ^αH and NH₂, m), 4.07-3.94 (4H, ^βH and ^αCH₂, m), 2.34-2.16 (20H, CH₂, m), 1.86-1.83 (3H, CH₃, m). ¹³C NMR (125 MHz, DMSO-D₆): δ 173.93, 138.71, 129.23, 127.98, 125.98, 56.26, 41.27, 40.02, 39.95, 39.85, 39.78, 39.69, 39.35, 39.19, 39.02, 38.27, 31.27, 29.02, 28.97, 28.72, 28.67, 26.30, 22.05, 13.90. HRMS (m/z): 333.3588 [M+H]⁺.

C₁₂-Phe-NDI-Phe-C₁₂ (1): H₂N-Phe-C₁₂ (0.36 g, 1.10 mmol) and NDA (0.130 g, 0.5 mmol) were placed in a round-bottomed flask along with dry DMF (15 ml) and the reaction mixture was stirred for 12 h at 140 °C under N₂ atmosphere. The heating was stopped and the solution was allowed to cool to room temperature and 30 mL ethyl acetate was added. The organic layer was washed with 1N HCl (3 × 30 ml), brine (3 × 30 ml) and dried over anhydrous Na₂SO₄ and evaporated in *vacuum*. The product was further purified by column chromatography by using silica gel as stationary phase and 3 % MeOH in CHCl₃ as eluent.

Yield: 0.15 g (0.16 mmol, 32 %).

^1H NMR (500 MHz, CDCl_3): δ 8.64 (4H, NDI, s), 7.26-7.10 (10H, aromatic Hs, m), 6.01-5.98 (2H, NH, t, $J = 8.0$), 5.76 (2H, $^{\alpha}\text{H}$, m), 3.68-3.49 (4H, $^{\beta}\text{Hs}$, m), 3.29-3.26 (4H, $^{\alpha}\text{CH}_2$, m), 1.65 (4H, $^{\beta}\text{CH}_2$, s), 1.47-1.44 (4H, CH_2 , m), 1.31-1.24 (32H, CH_2 , m), 0.89-0.86 (6H, 2CH_3 , m). ^{13}C NMR (125 MHz, CDCl_3): δ 168.29, 162.83, 136.97, 131.32, 129.07, 128.96, 127.28, 126.82, 126.54, 56.24, 40.18, 35.13, 32.06, 29.80, 29.78, 29.72, 29.67, 29.52, 29.49, 29.39, 26.98, 22.83, 14.24. MALDITOF MS: 919.738 $[\text{M}+\text{Na}]^+$.

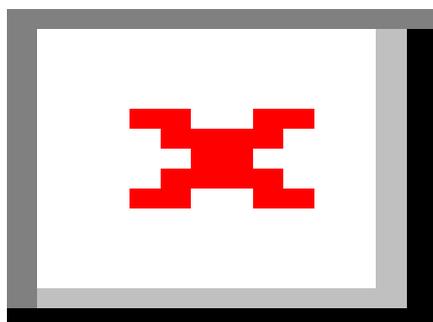


Fig. S1 MALDI TOF MS spectra of **1**.

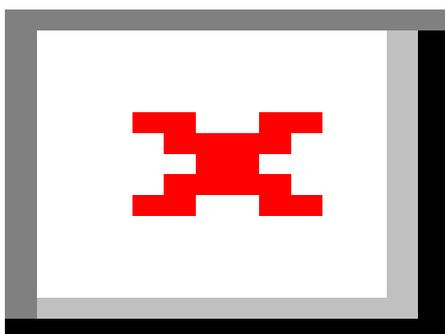


Fig. S2 ¹H NMR spectrum in CDCl₃ of **1** recorded in 500 MHz.

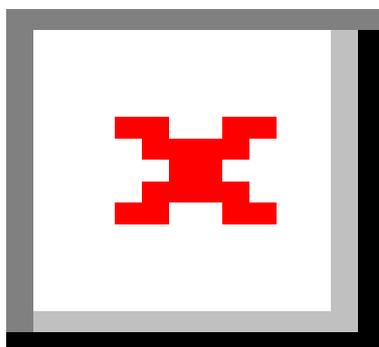


Fig. S3 ¹³C NMR spectrum in CDCl₃ of **1** recorded in 125 MHz.

Table S1 Gelation property of the gelator in different solvents.

Solvents	Gel Status	MGC (mM)	T_{gel} (°C)
n-Octane	Gel	2.5	95
Cyclohexane	Gel	2.9	93
Methyl cyclohexane	Gel	2.8	96
Benzene	-	-	-
Toluene	Gel	12	55
<i>o</i> -Xylene	Gel	11	51
Mesitylene	Gel	12	53

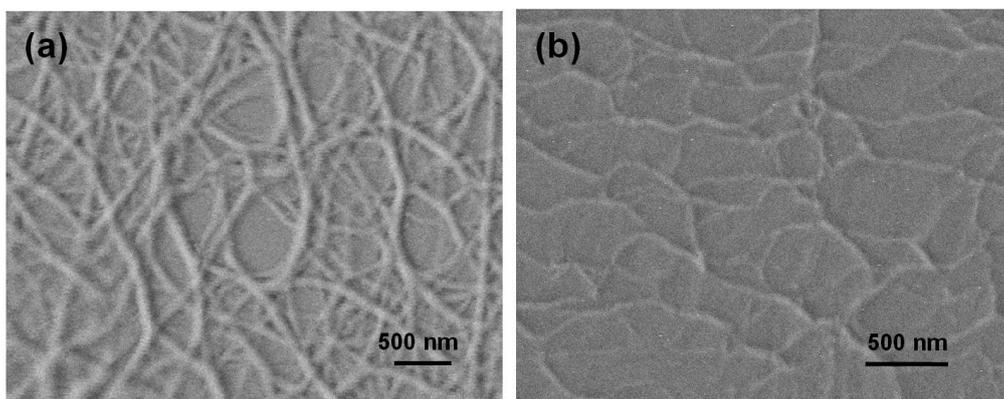


Fig. S4 The FE-SEM images obtained from (a) n-octane gel and (b) toluene gel.

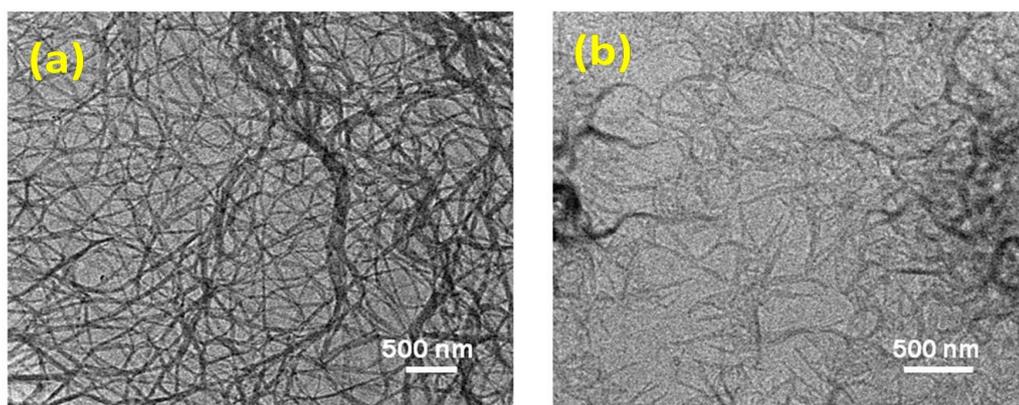


Fig. S5 The TEM image obtained from (a) n-octane gel and (b) toluene gel.

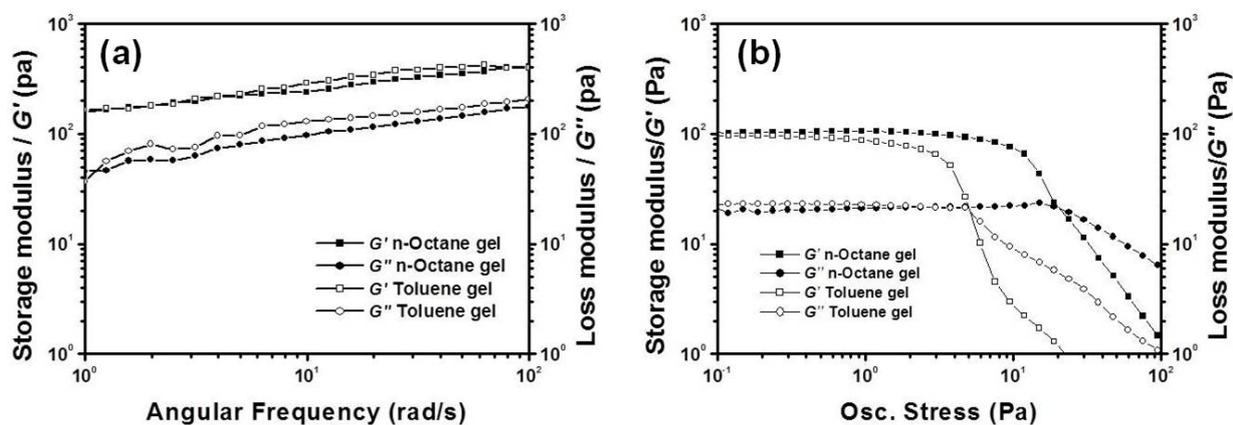


Fig. S6 (a) Frequency sweep experimental data showing no crossover point throughout the experimental region and (b) stress sweep experiment showing the yield stress were 20 Pa and 5 Pa for n-octane gel and toluene gel respectively.

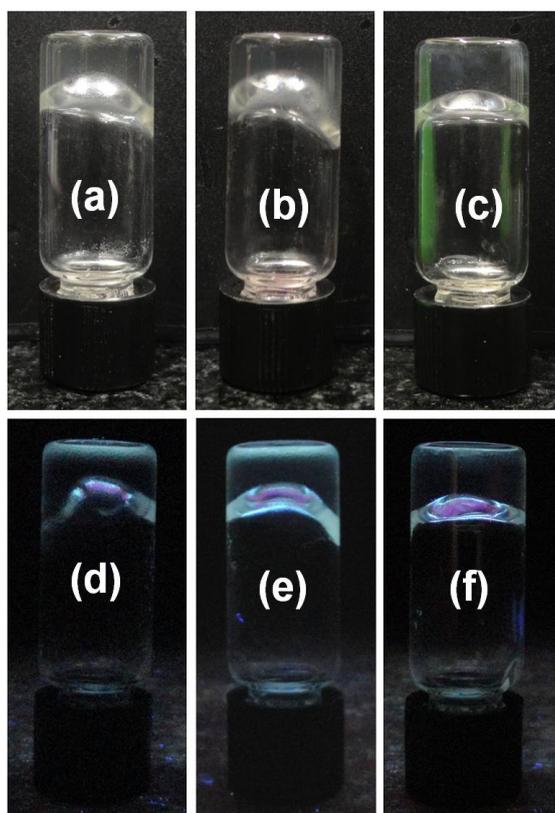


Fig. S7 The images of gels in (a) MCH, (b) cyclohexane and (c) n-heptane in daylight and in (d) MCH, (e) cyclohexane and (f) n-heptane under UV lamp obtained from gelator 1.

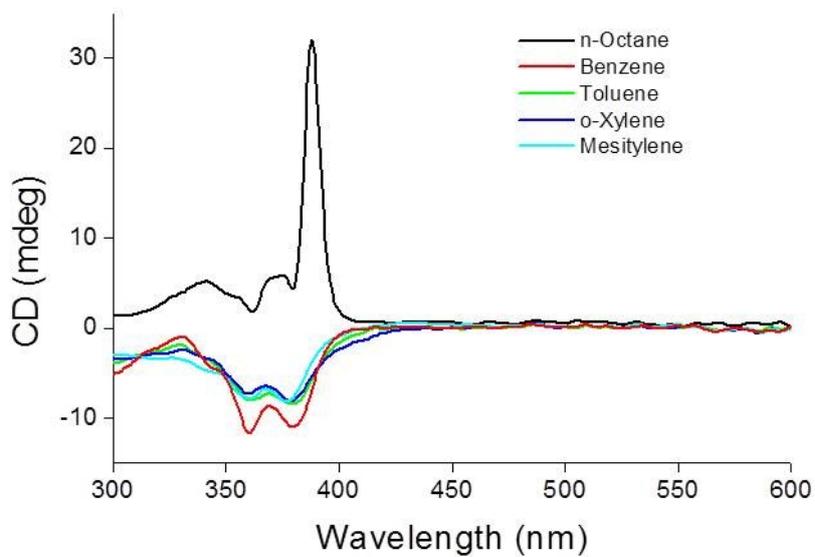


Fig. S8 CD plots obtained from different organic solvents of the gelator **1**.

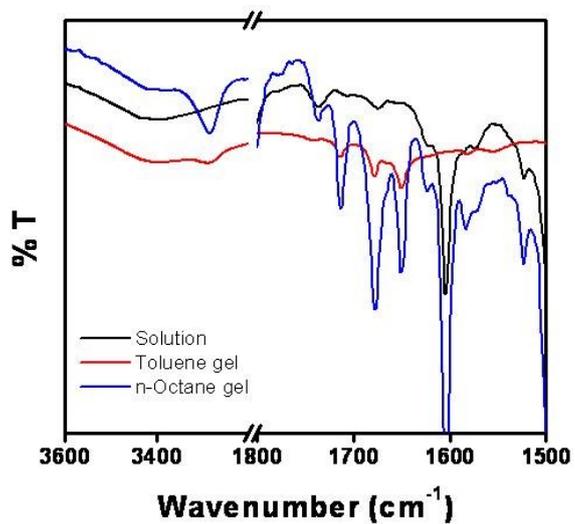


Fig. S9 FTIR spectra showing the characteristic H-bonded amide group (N–H) at 3285 cm^{-1} for both gels in n-octane and in toluene.

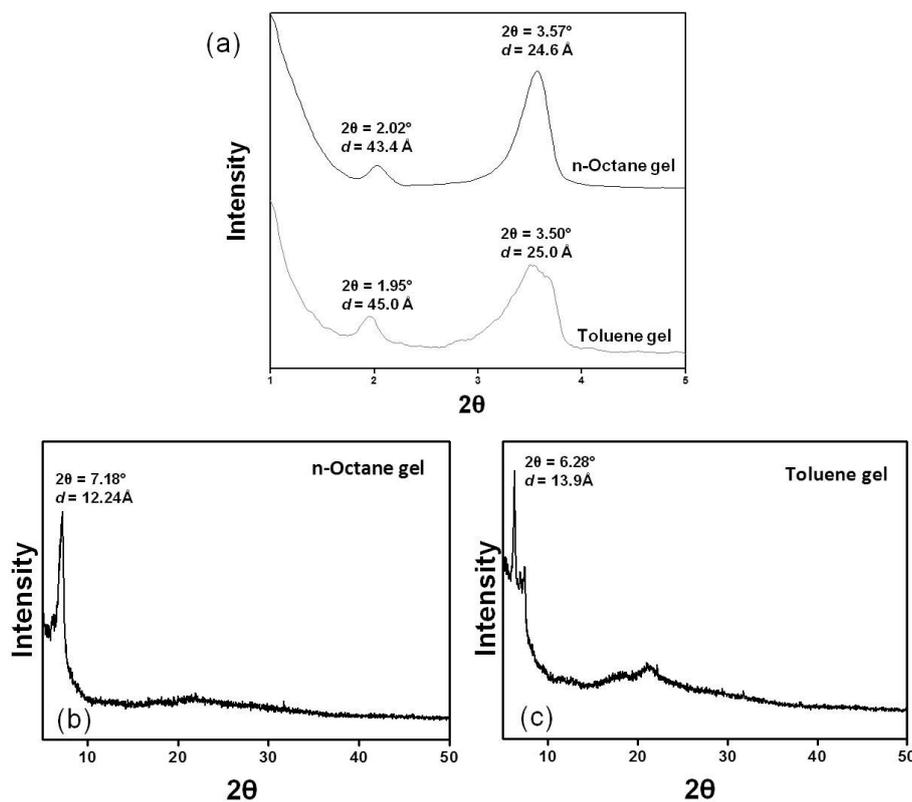


Fig. S10 (a) Low angle XRD pattern obtained from n-octane and in toluene gel. Wide angle XRD pattern in n-octane (b) and (c) toluene gel respectively.

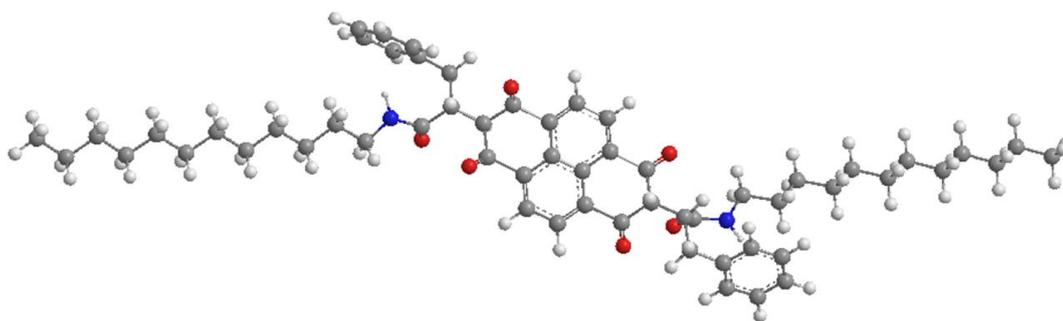


Fig. S11 The energy minimized structure of the gelator molecule **1**. The calculated molecular length was found 44.3 \AA .

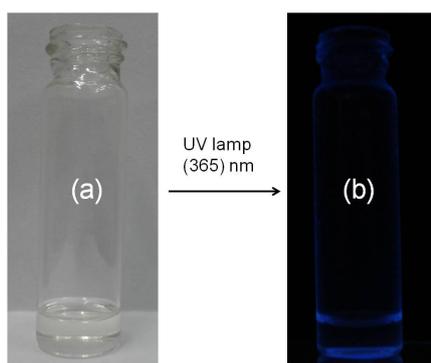


Fig. S12 The images of the solution of gelator **1** in chloroform under (a) daylight and (b) UV lamp showed no fluorescence.

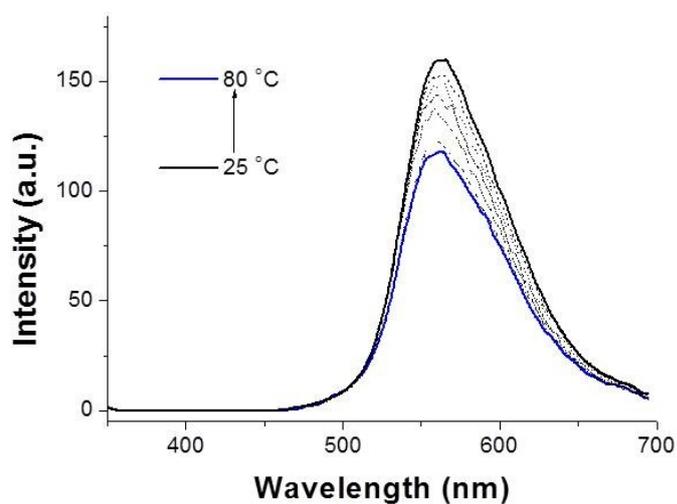


Fig. S13 The temperature dependent emission spectrum of gelator **1** in mesitylene showing no significant monomeric emission at high temperature (80 °C). This indicates strong CT interaction in mesitylene.

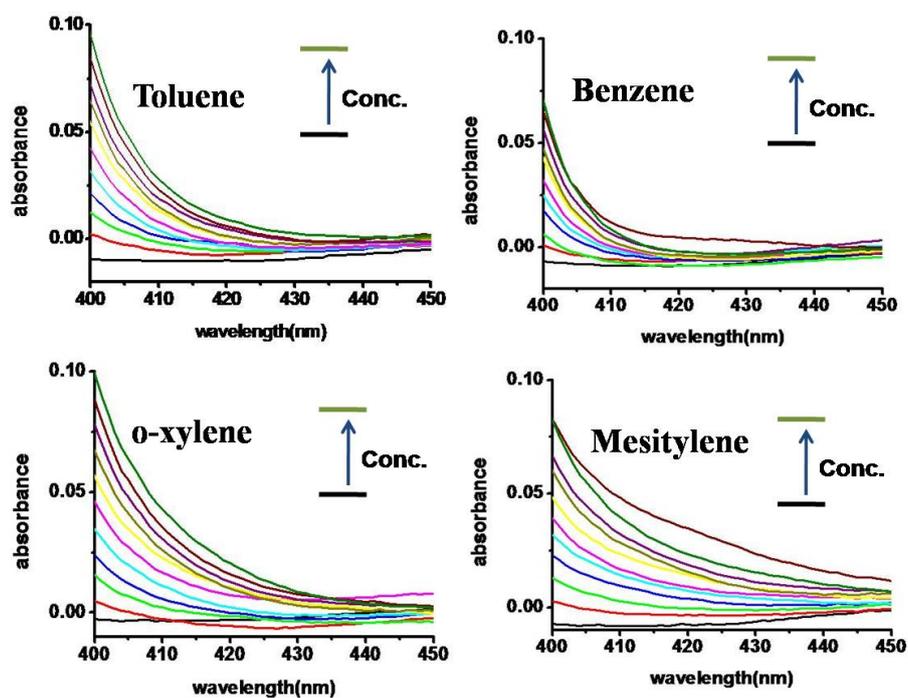


Fig. S14 Absorption spectra of charge-transfer complex for calculating binding constant.

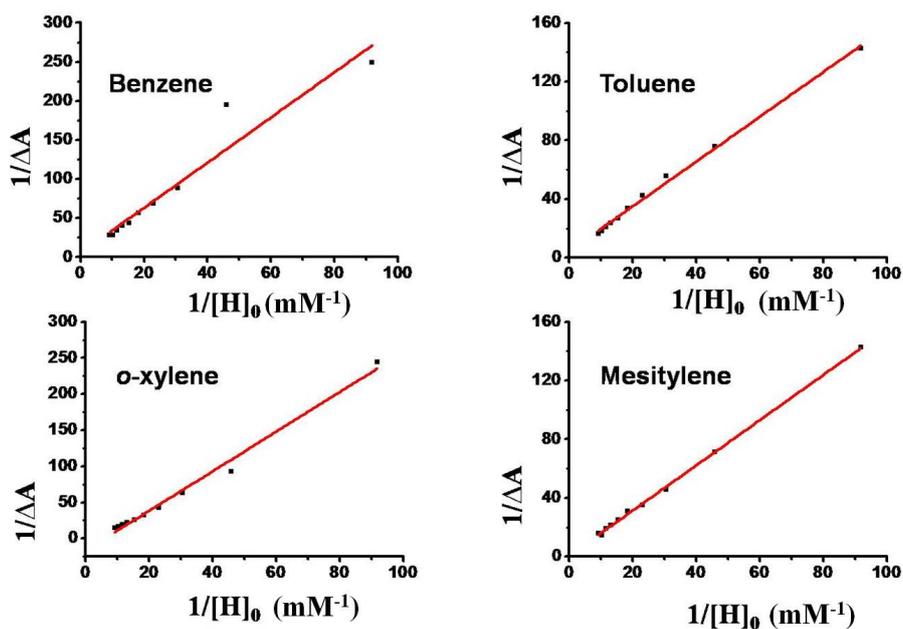


Fig. S15 $1/\Delta A$ vs $1/[H]_0$ plots of charge-transfer complex for calculating binding constant.

Table S2 Binding constants of each CT complexes.

Solvent	Binding Constant (K_a M⁻¹)
Benzene	1.90 x10 ³
Toluene	3.05 x10 ³
o-Xylene	5.90 x10 ³
Mesitylene	0.47 x10 ³

References

1. H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, 1949, **71**, 2703-2707.
2. E. V. Anslyn and D. A. Dougherty, *Modern Physical Organic Chemistry*, University Science Books, Sausalito, California, p-221.