Electronic Supplementary Information for

Cystine-derived Bis-naphthalimides as Stimuli-Responsive Fluorescent Gelators

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Details of synthesis, characterization of the ligands **L1** and **L2** (Figures S1-S4 to S6-S9, copies of the ^{1}H & ^{13}C NMR spectra), ES-MS (Figure S5, S10), along with the relevant UV-vis, fluorescence, FT-IR and ^{1}H NMR spectra (Figures S11-S24).

1. General experimental techniques.

All chemicals were commercially available from Sigma-Aldrich or Spectrochem (India) and used as received. Solvents for spectroscopic experiments were distilled under nitrogen atmosphere before use. All ^{1}H and ^{13}C NMR were measured on a 300 MHz Bruker spectrometer, and reported in δ/ppm. The electronic absorption spectra were recorded on a Shimadzu UV-VIS spectrophotometer.

2. Copies of $^{1}H/^{13}C$ NMR spectra for ND1, ND2, L1 and L2.

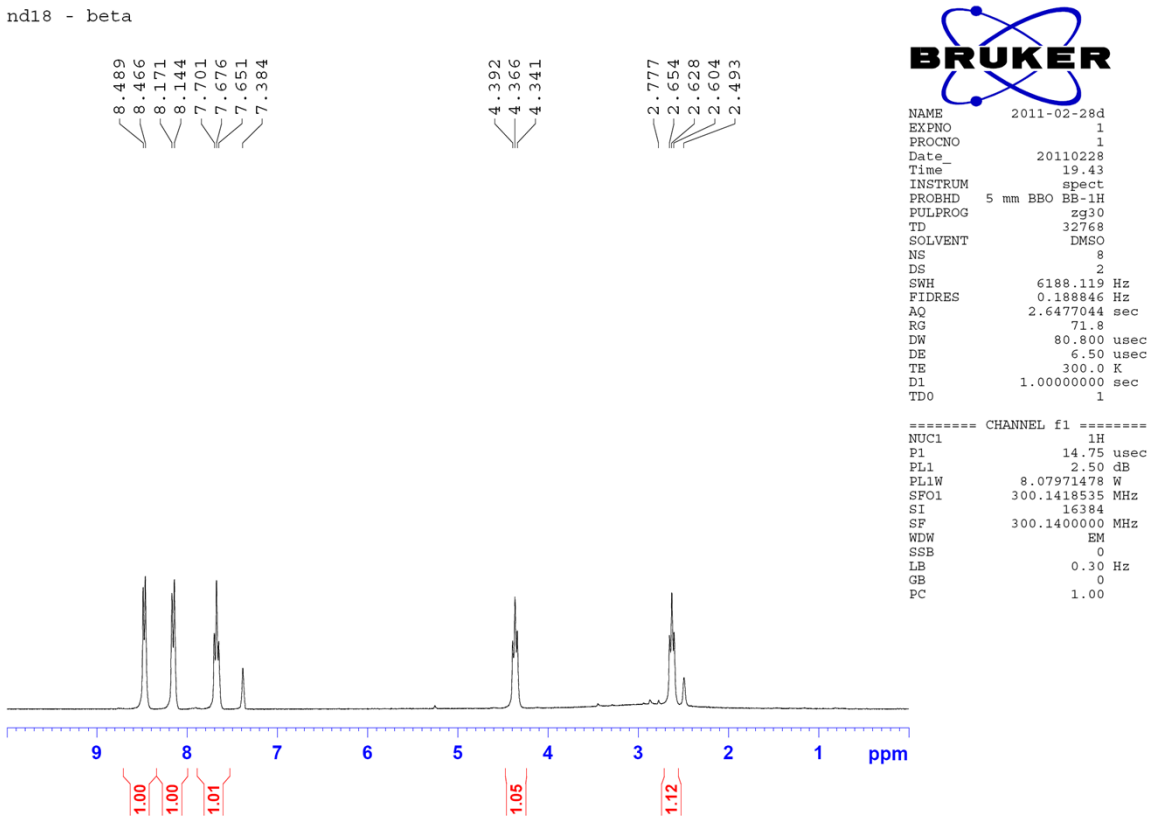

Figure S1: ^{1}H spectra of **ND1** in DMSO-d_6/$CDCl_3$

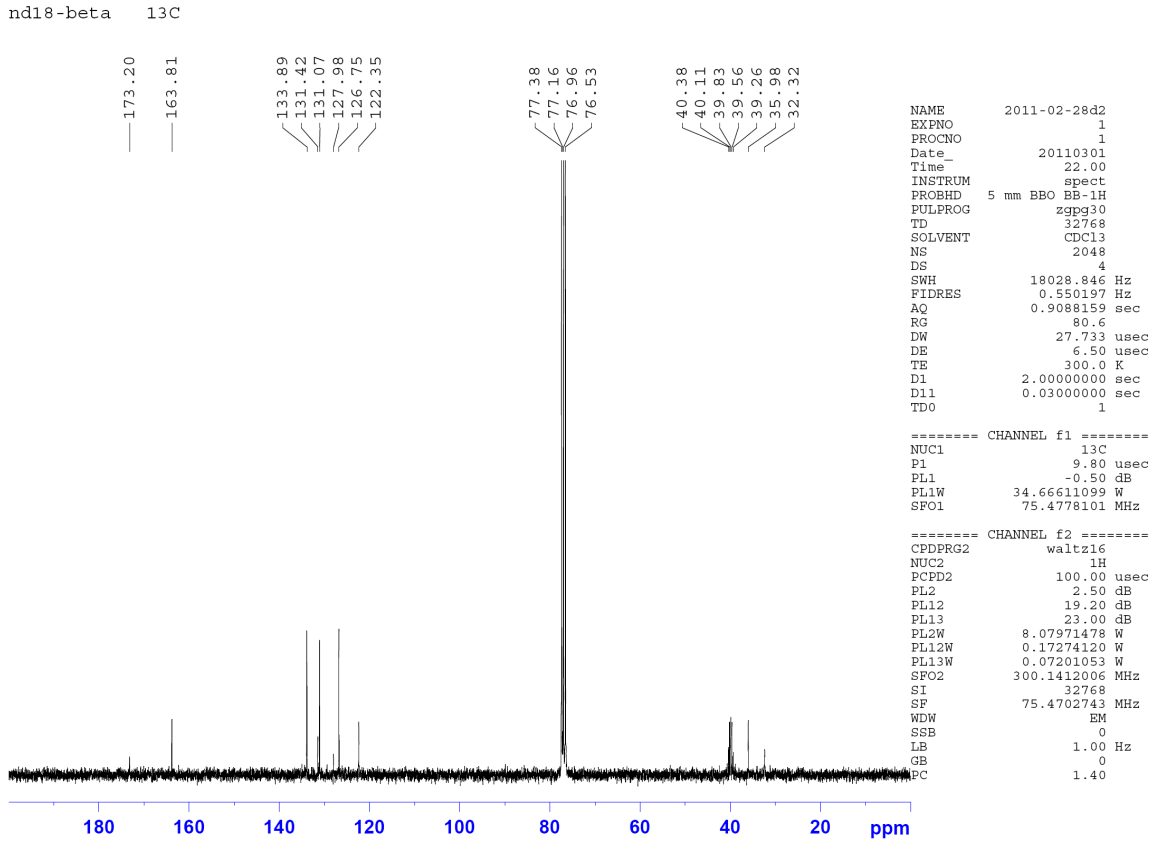

Figure S2: ^{13}C NMR spectra of **ND1** in DMSO-d_6/$CDCl_3$

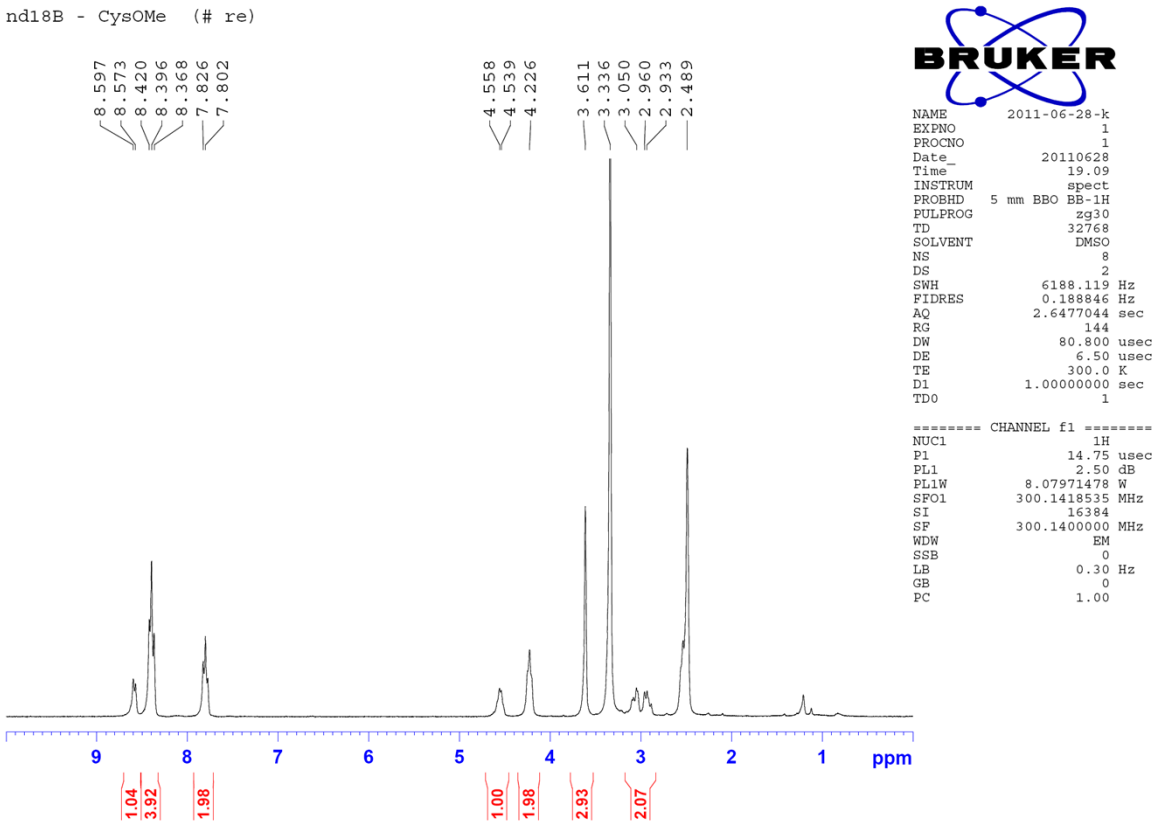

Figure S3: ^{1}H NMR spectra of **L1** in DMSO-d_6

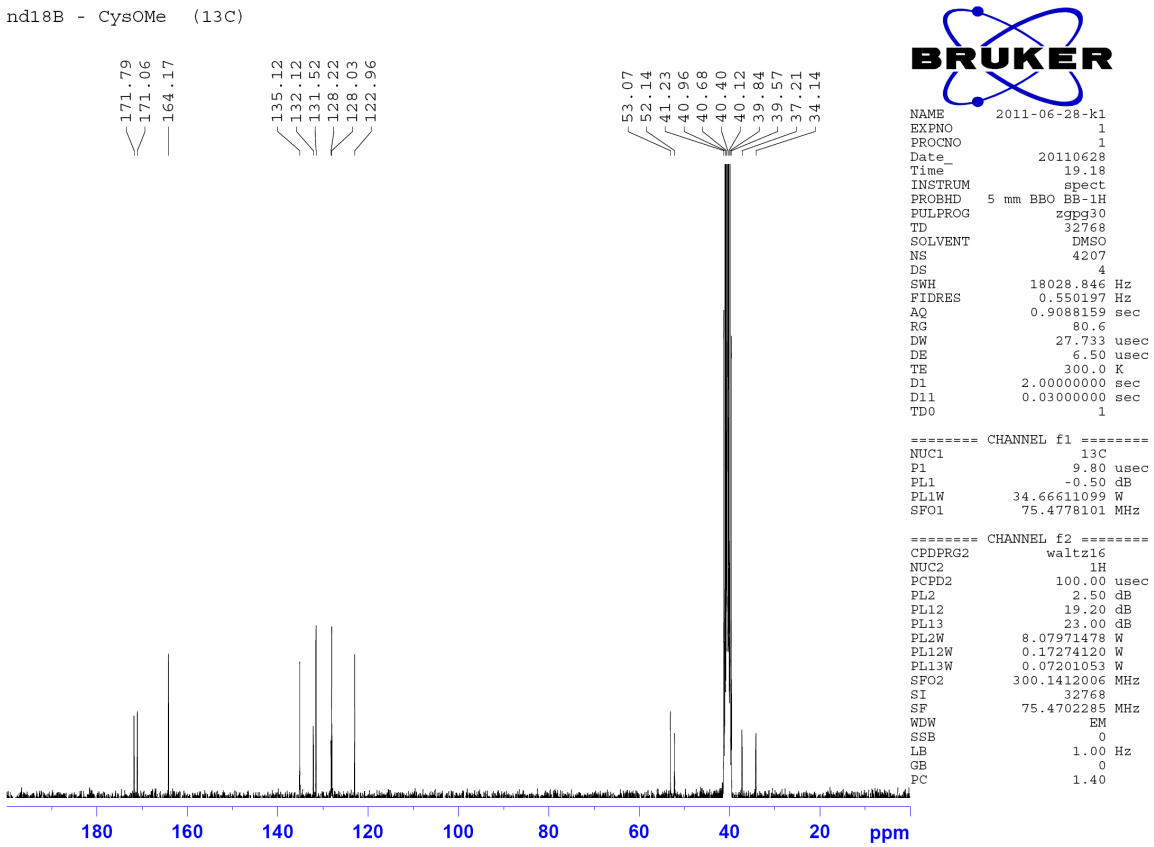

Figure S4: ^{13}C NMR spectra of **L1** in DMSO-d_6

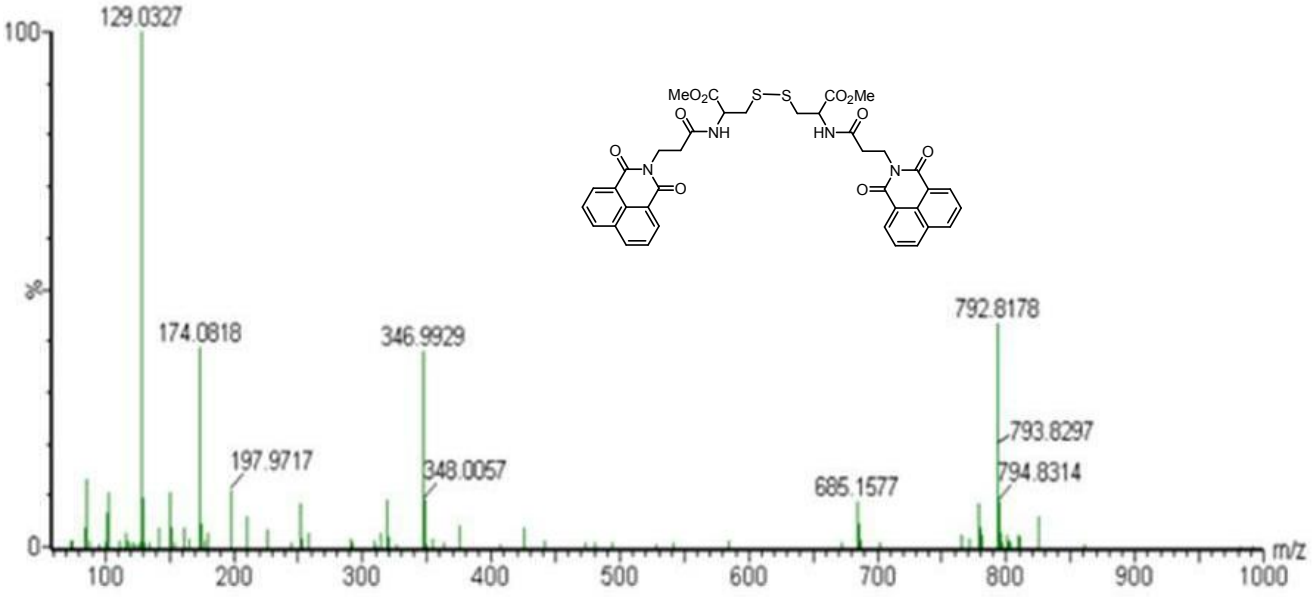

Figure S5: ES-MS of **L1** in MeCN (m/z = 793.81, calc. for M+Na^+)

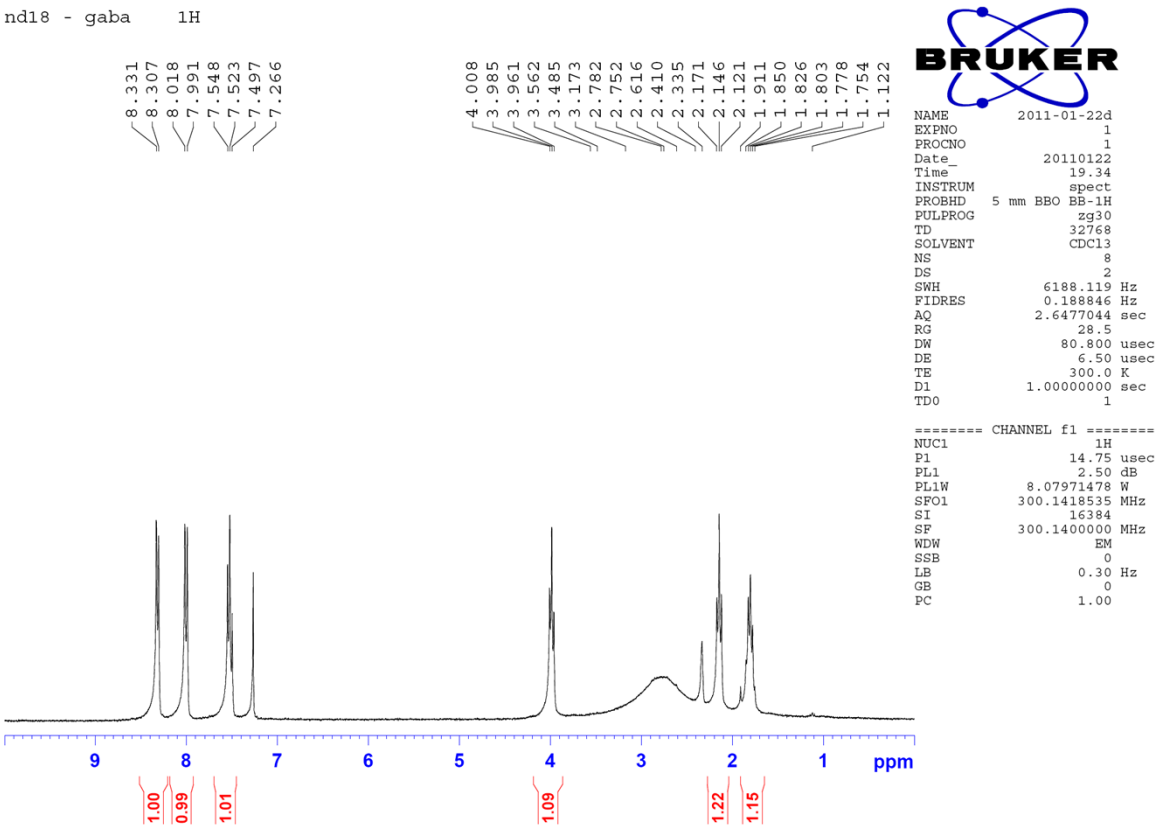

Figure S6: ^{1}H NMR spectra of **ND2** in DMSO-d_6/$CDCl_3$

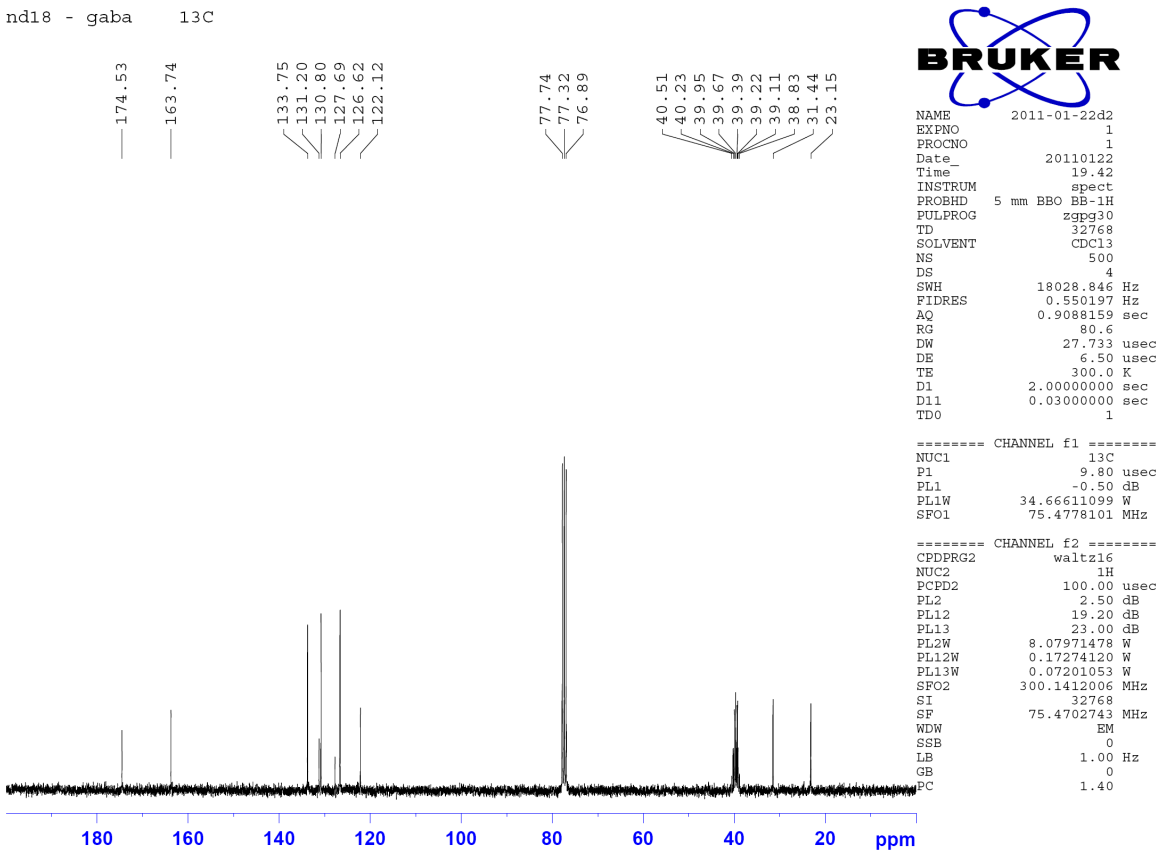

Figure S7: ^{13}C NMR spectra of **ND2** in DMSO-d_6/$CDCl_3$

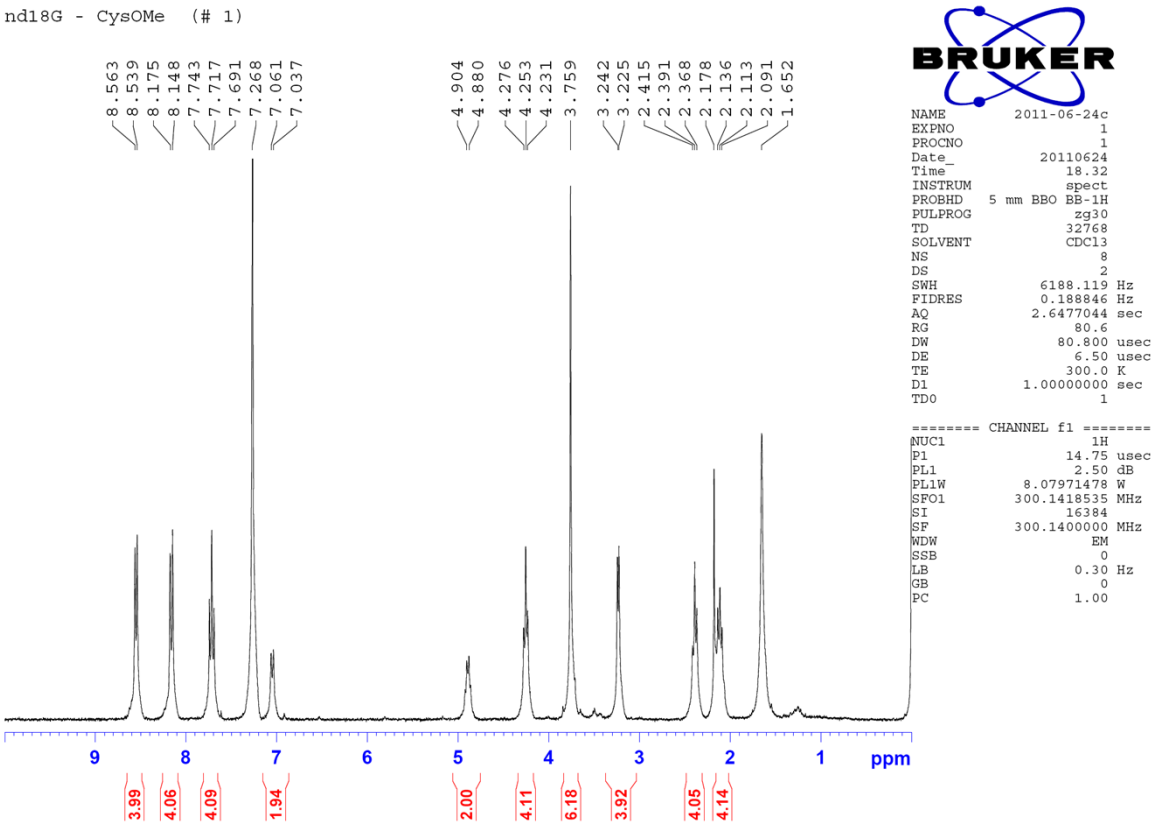

Figure S8: ^{1}H NMR spectra of **L2** in $CDCl_3$

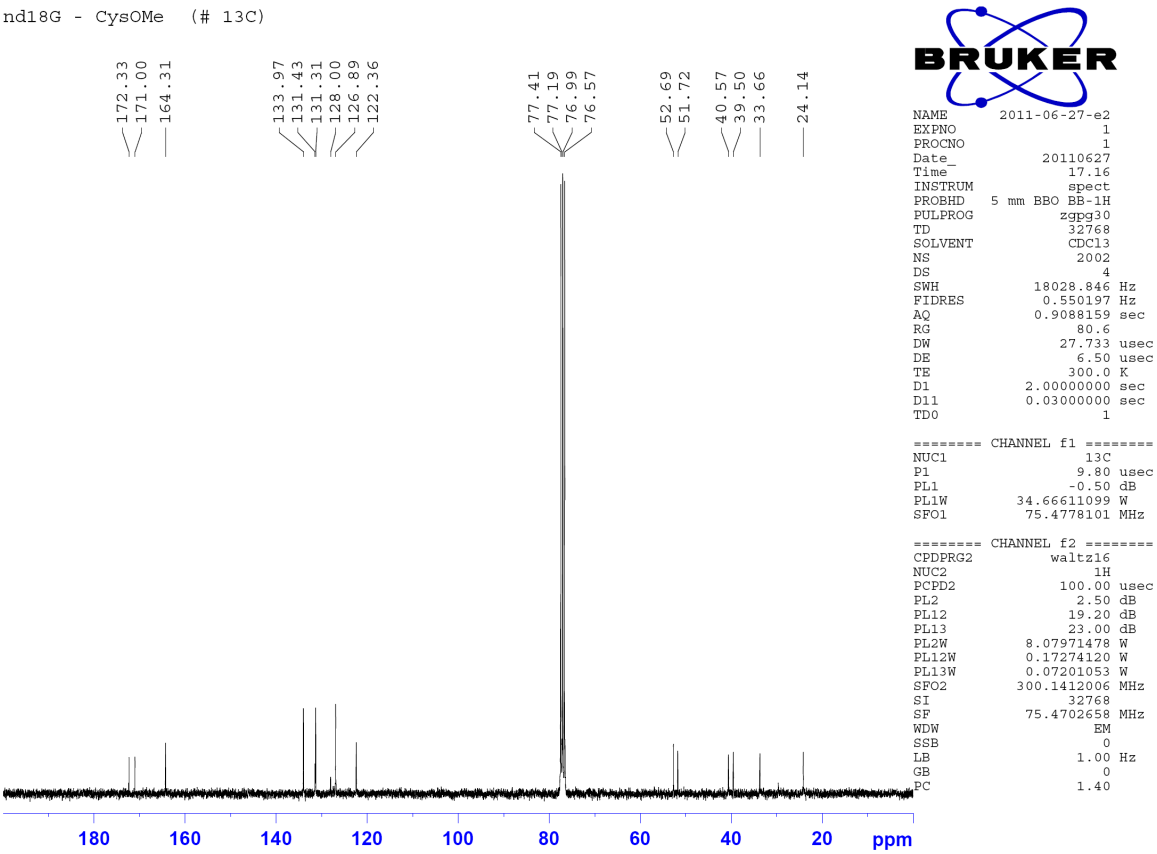

Figure S9: ^{13}C NMR spectra of **L2** in $CDCl_3$

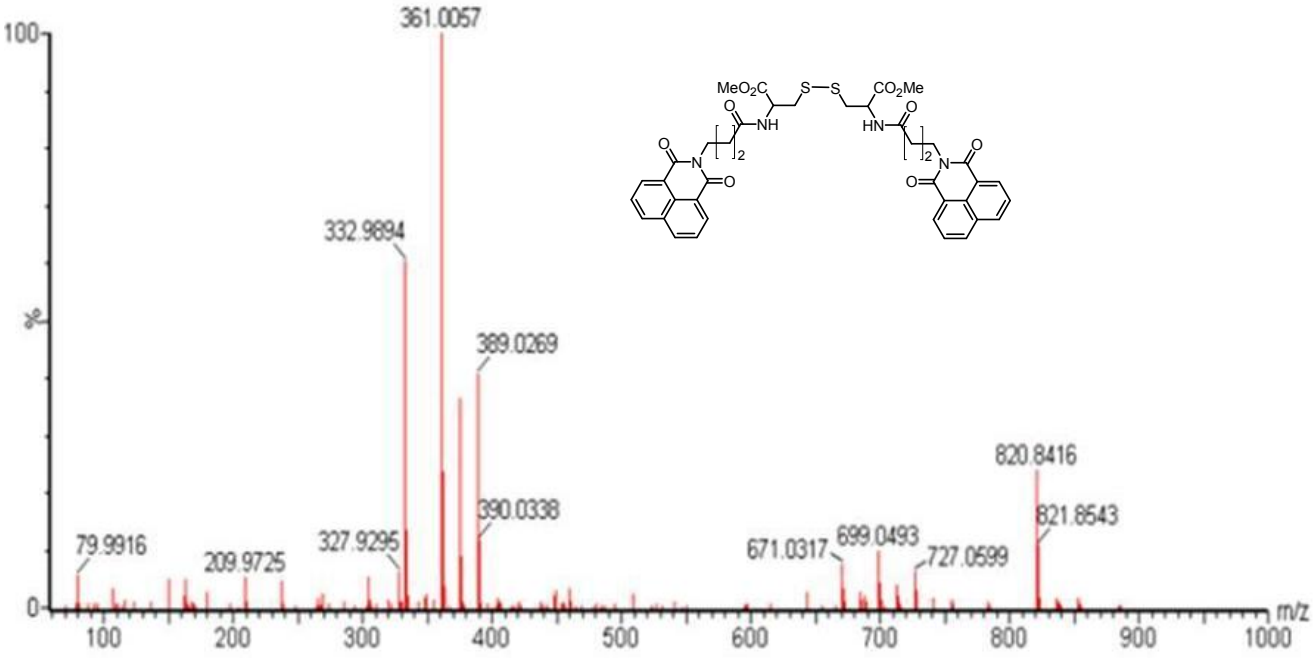

Figure S10: ES-MS of **L2** (m/z = 821.85, calc. for M+Na$^+$)

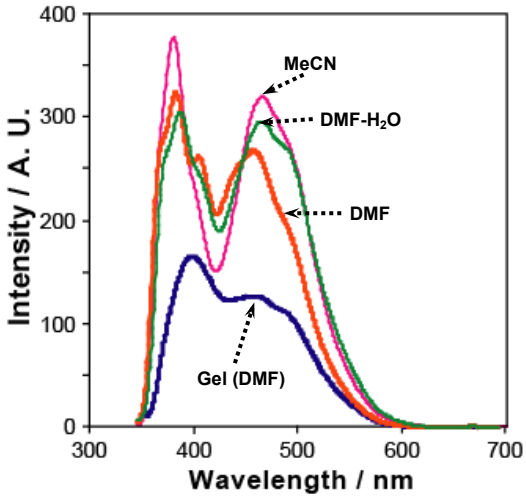

Figure S11: Solvent-dependent fluorescence emission spectra of **L2** (λ_{ex} 340nm).

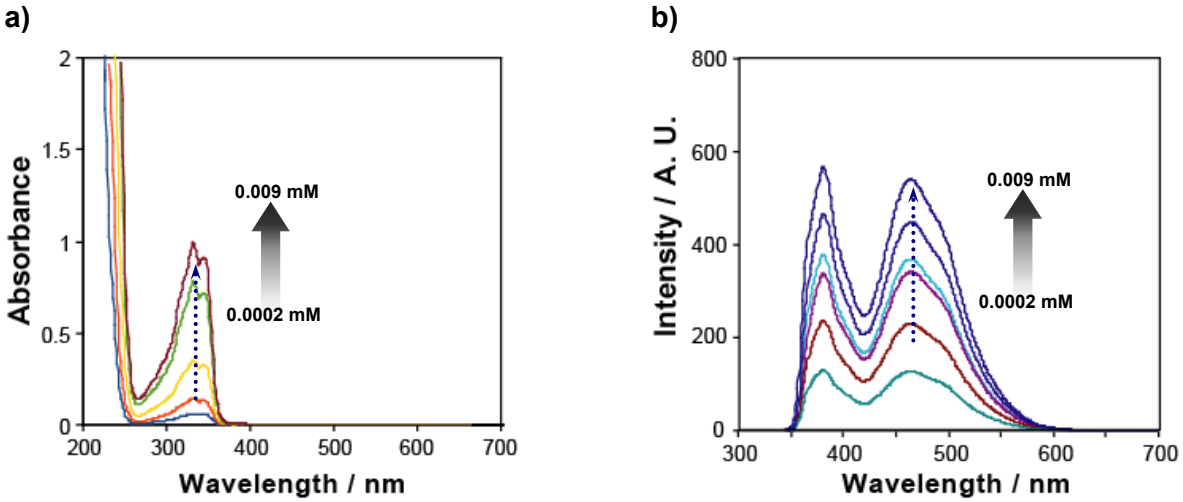

Figure S12: Concentration-dependent spectra of **L2** (in MeCN): (a) UV-visible, and (b) fluorescence emission (λ_{ex} 340nm); Note the monomer/excimer emission for **L2**.

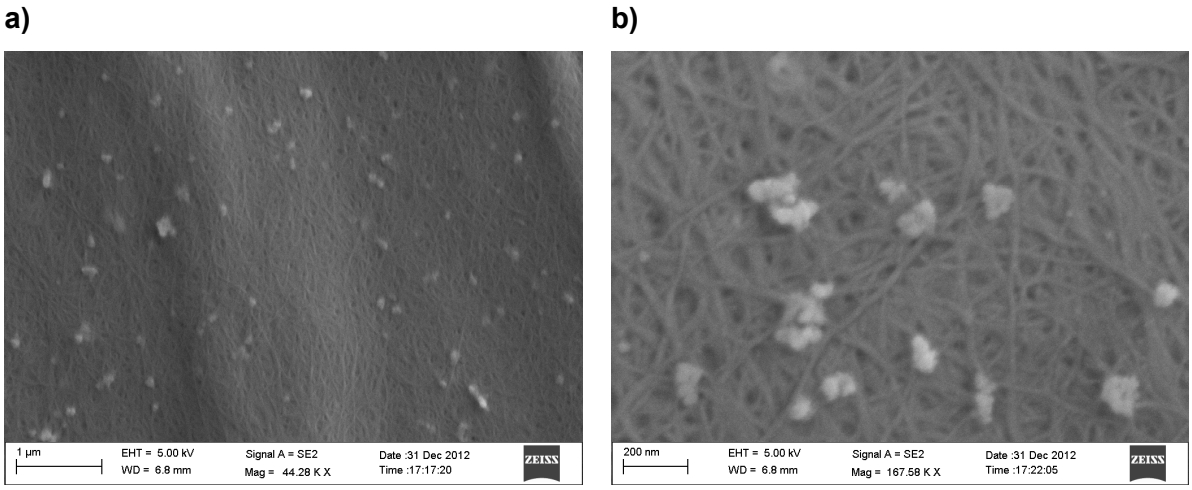

Figure S13. (a), (b) SEM images of the dried organogel obtained from **L1** in DMF (5mg/mL; the particles were initially formed due to spontaneous aggregation of the **L1** gelator (as tiny nucleation sites) while the formation of fibres was relatively slow (ageing 2-3 days).

Such features were not observed for **L2** in DMF, except at high concentration (>12mg/mL). It appears that the gelation of acetonitrile and DMF by **L1** and **L2** occurs due to hydrogen bonding between the amide NH groups and the solvent (immobilisation of the solvent molecules), with concomitant hydrophobic packing (stacking interactions) of the bis-naphthalimide motifs, which result in the formation of networks of self-assembled fibres.

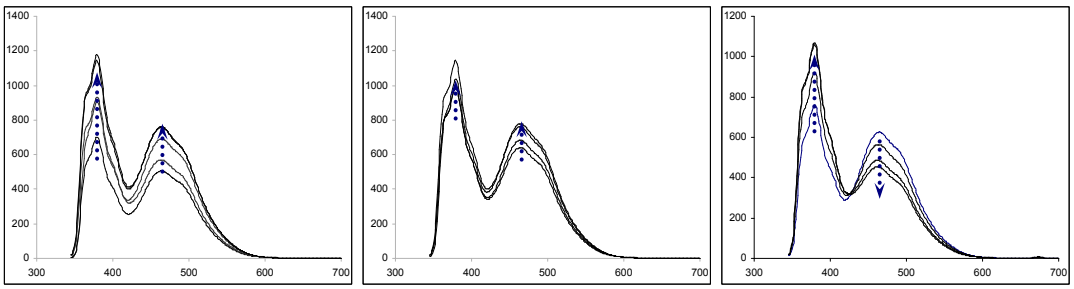

Figure S14. Fluorescence titration of **L1** with chloride, bromide and acetate anions in acetonitrile (10% water).

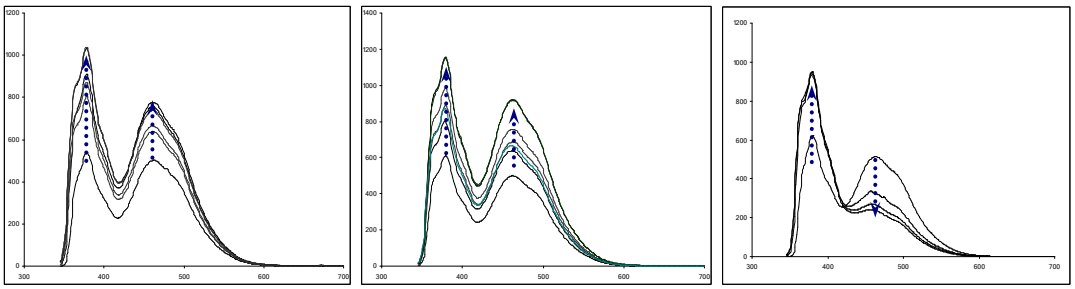

Figure S15. Fluorescence titration of **L2** with chloride, bromide and acetate anions in acetonitrile (10% water).

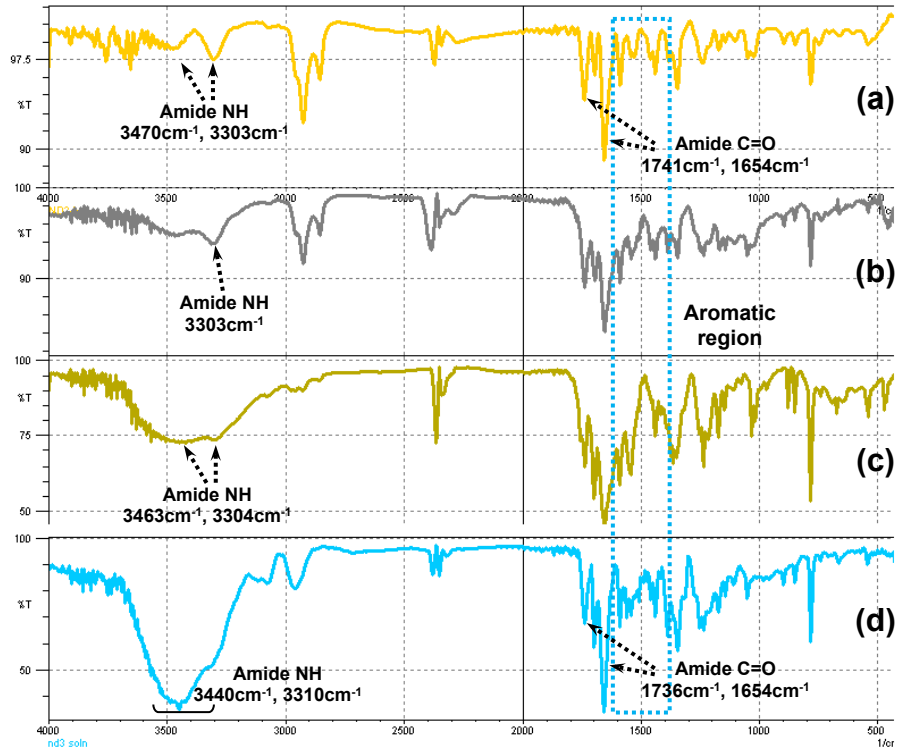

Figure S16. Comparative study of FT-IR spectra of **L2** under various conditions: (a) 0.1mg/mL in chloroform; (b) 1.0mg/mL in chloroform; (c) dried **L2**/acetonitrile gel, after removal of solvent; (d) **L2**/acetonitrile gel, when suspended in chloroform; the absorptions at 3303cm^{-1} in dilute solutions and in the aromatic region were distinct, of which the latter was apparently affected by changes in gelator concentration.

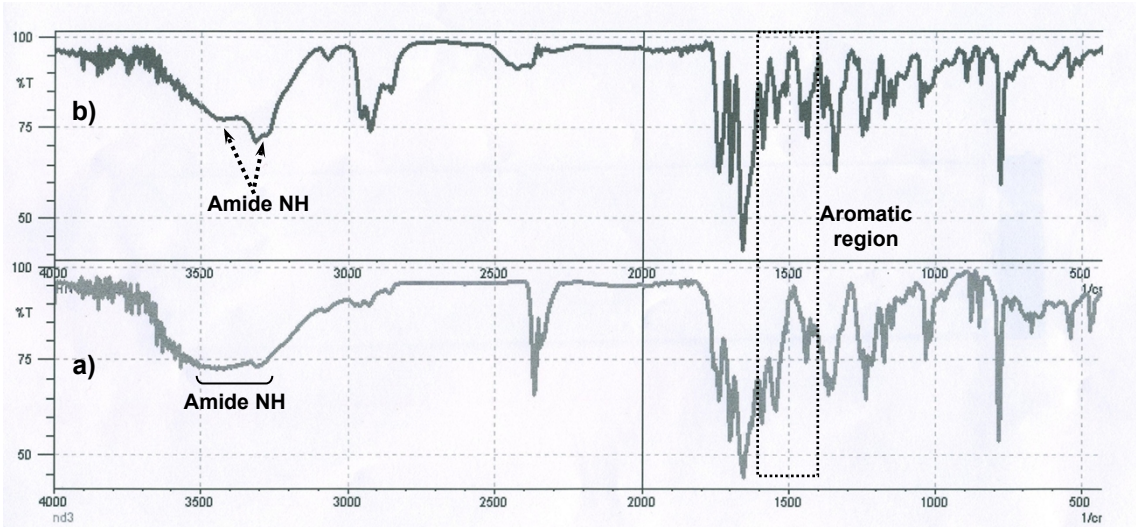

Figure S17. FTIR spectra of (**a**) **L2**/acetonitrile gel, and (**b**) upon addition of BF_4^- anions (**L2**/$NaBF_4$). Changes in the amide NH absorption and the aromatic region are noteworthy.

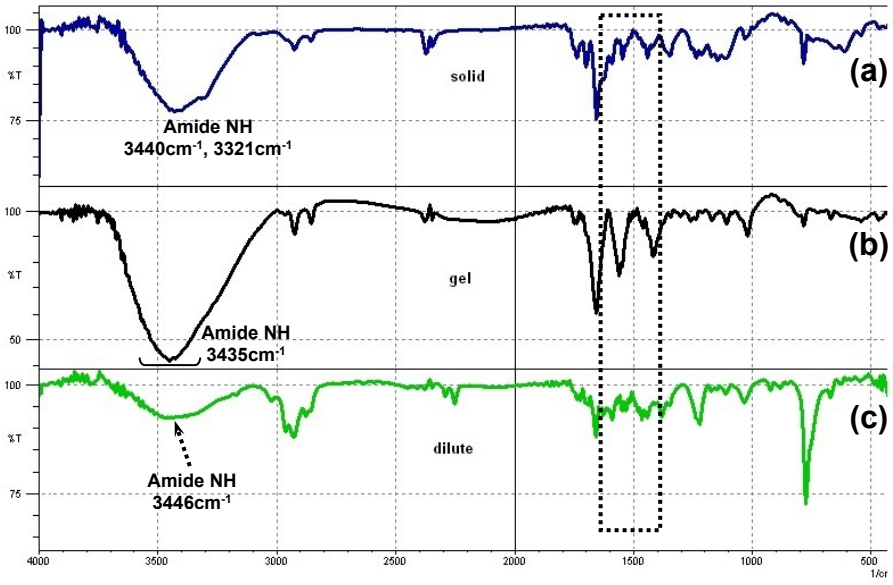

Figure S18. Comparative study of FT-IR spectra of **L1** under various conditions: (a) **L1**/DMF gel after removal of solvent; (b) **L1**/DMF, when suspended in chloroform ; (c) **L1** when suspended in acetonitrile; the absorptions at 3446 cm^{-1} in dilute solutions was affected by changes in gelator concentration.

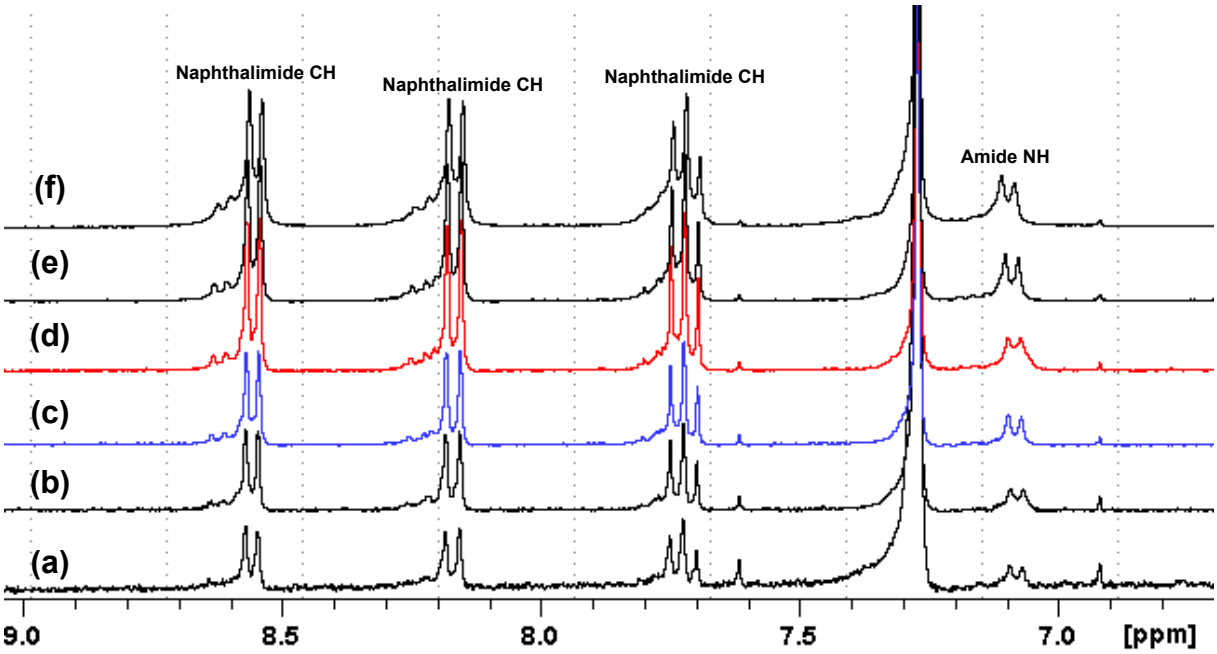

Figure S19. Concentration dependent ^{1}H NMR spectra of **L2** in $CDCl_3$: (a) 0.3mg/mL; (b) 1.0 mg/mL; (c) 2.0 mg/mL; (d) 4.0 mg/mL; (e) 6.0 mg/mL, with formation of partial gel; and (f) after the gelation process is complete. The amide NH resonance at 7.078ppm in dilute solutions, i.e. [**L2**] < 2mg/mL remains relatively unaffected by changes in gelator concentration. Beyond the critical gelation concentration of 6mg/mL, the amide NH resonances shifted downfield, to 7.082ppm, such that $\Delta\delta$ = 0.018ppm, indicating that H-bonding interactions were not dominant. However, the onset of gelation did cause the naphthalimide CH resonances to shift upfield by ~ 0.01ppm; for instance, from 7.723 (i.e. spectra '**a**') to 7.714 ppm (i.e. spectra '**f**'), and from 8.17ppm to 8.16ppm.

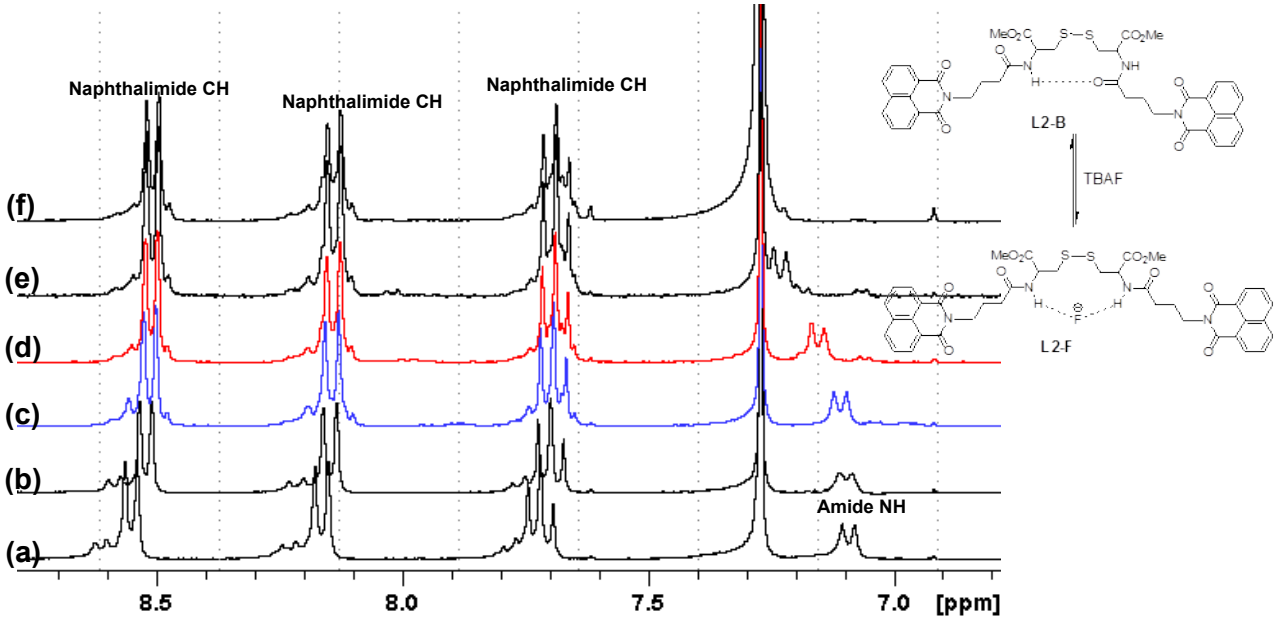

Figure S20. Partial 1H NMR spectra showing the effect of TBAF on **L2** (3.0 mg in 0.5mL chloroform-d), during the gel-to-sol transformation; (a) Partially formed **L2**/chloroform gel; (b) **L2**/chloroform gel; (c)-(f), after TBAF addition (0.5, 1.0, 2.0 and 3.0 equiv); (Inset: Plausible hydrogen bonding interactions of **L2** with fluoride anions, i.e. TBAF, in chloroform-d)

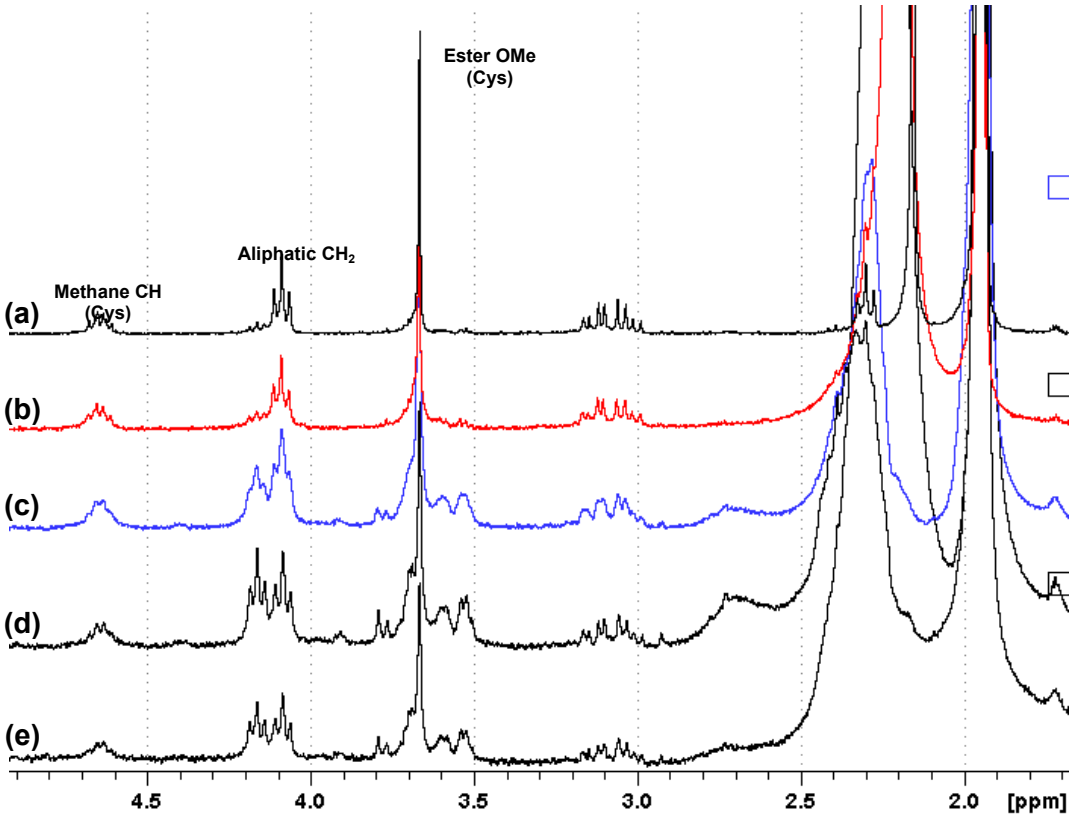

Figure S21. Partial 1H NMR spectra of **L2** showing the temperature-dependent variations of the naphthalimide CH and amide NH resonances in acetonitrile-d3: (a) 50°C; (b) 45°C; (c) 35°C; (d) 25°C; (e) 25°C after 12h. Splitting/broadening of the resonance due to the ester group (Cys) also indicated multiple interactions of this residue during the gel forming process.

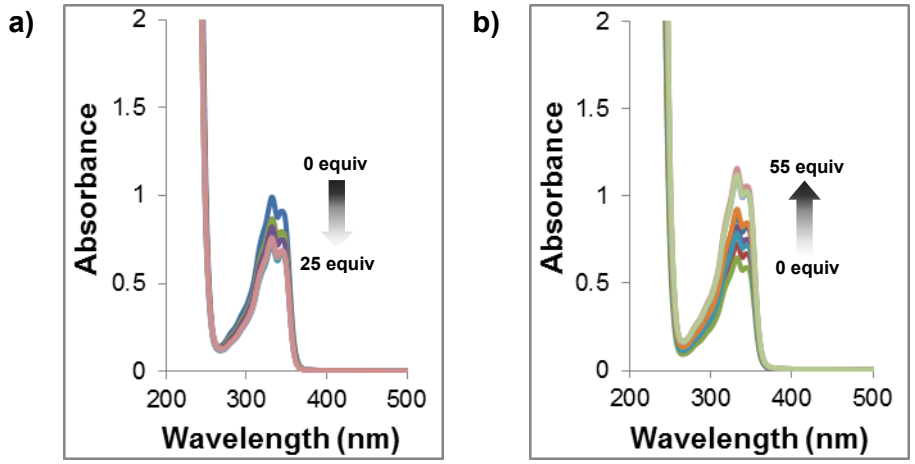

Figure S22. UV-vis spectra of **L2** in acetonitrile: (a) following the addition of fluoride anions (as TBAF, upto – equiv.); (b) and the addition of NaBF4 (upto – equiv.); [**L2**] = 0.001mM

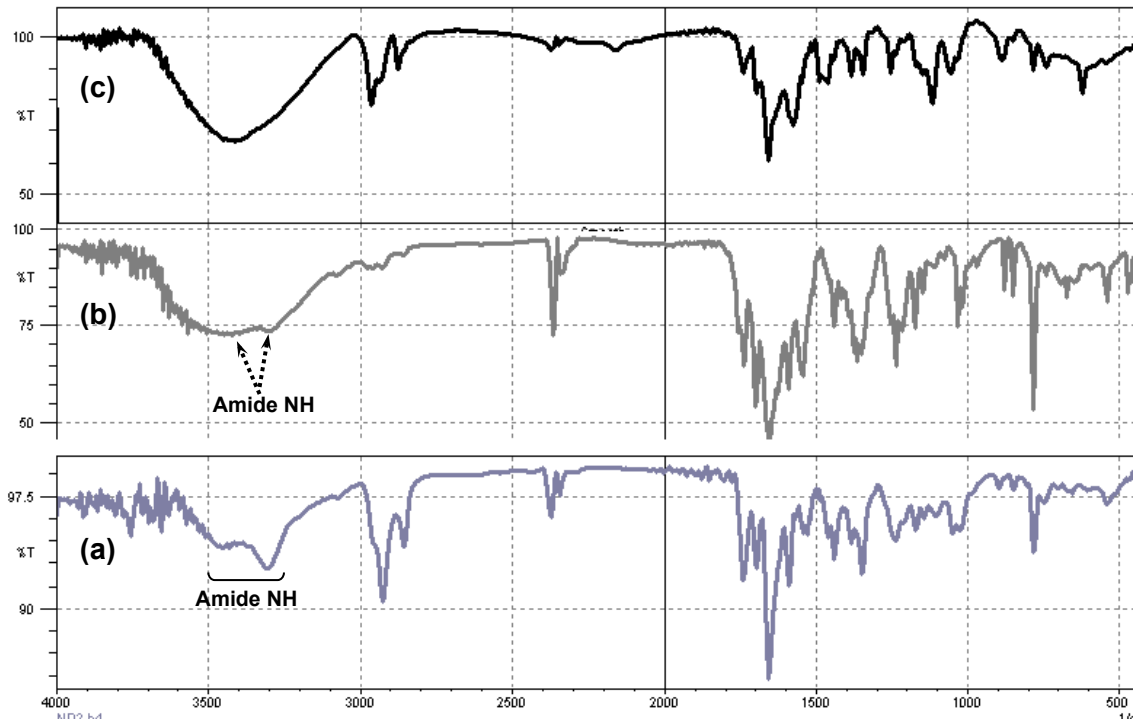

Figure S23. FTIR spectra of (**a**) **L2** (1.0mg/mL in chloroform); (**b**) **L2**/acetonitrile gel, after removal of solvent, and (c) upon addition of fluoride anions (as TBAF, ~ 20uL of 1mM stock); Changes in the amide NH absorption at 3304cm^{-1} and the aromatic region are noteworthy.

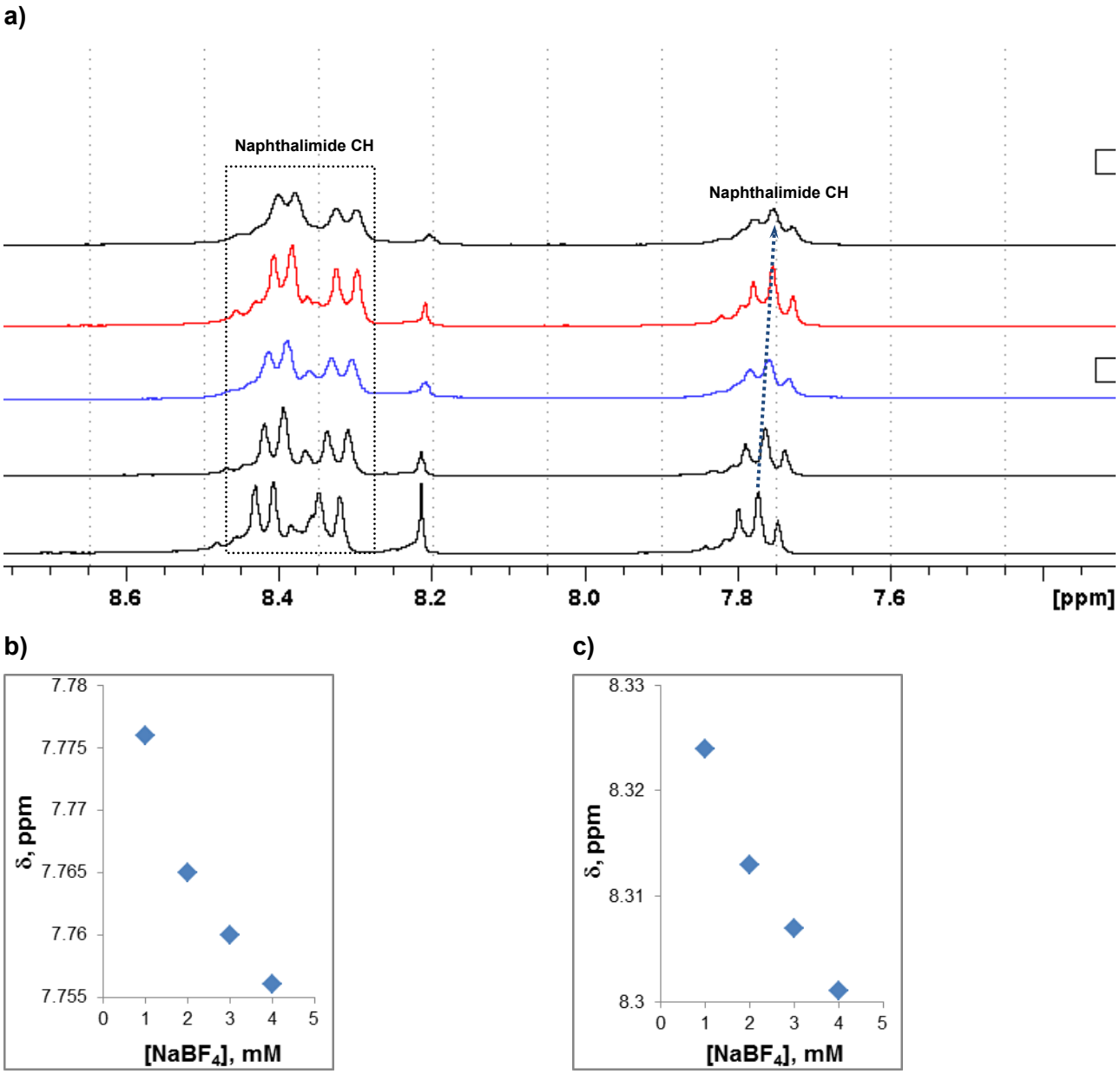

Figure S24. (a) Partial ^{1}H NMR spectra of **L2** (3mg in DMSO-d_6) following addition of BF_4^- anions (as $NaBF_4$). (b), (c) The chemical-shift changes for the naphthalimide CH resonances were noteworthy, which were indicative of anion-π interactions between the BF_4^- anions and the naphthalimide motif.