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 $\delta$/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-<em>d</em><sub>6</sub>/CDCl<sub>3</sub>

Figure S3: $^1$H NMR spectra of L1 in DMSO-<em>d</em><sub>6</sub>
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<sub>ex</sub> 340nm).
Figure S12: Concentration-dependent spectra of L2 (in MeCN): (a) UV-visible, and (b) fluorescence emission ($\lambda_{\text{ex}}$ 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 BF₄⁻ anions (L2/NaBF₄). 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 \(\Delta \delta = 0.018\)ppm, indicating that H-bonding interactions were not dominant. However, the onset of gelation did cause the naphthalimide CH resonances to shift upfield by \(\sim 0.01\)ppm; 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 L$_2$ (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.