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Li⁺-induced selective gelation of discrete homochiral structural isomer derived from L-tartaric acid

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Experimental procedures

**Materials and Methods:** Common reagents and solvents were purchased from Merck, Qualigens or S.D. Fine Chem. Ltd, Mumbai, India and used as received without further purifications. The solvents were dried and distilled following standard procedures prior to their use. L-tartaric acid, 2-hydroxybenzaldehyde and 4-hydroxybenzaldehyde were purchased from Sigma Aldrich Chemical Co., USA and used as received.

Elemental analyses were acquired on an Exeter CHN Analyser CE-440 from the micro analytical laboratory of the Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi, India. FT-IR and electronic absorption spectra were obtained on a Perkin-Elmer 577 and Shimadzu UV-1601 spectrophotometers, respectively. $^1$H NMR spectra were obtained on a JEOL AL 300 FT-NMR and Bruker AVANCE III 400 spectrometer. Photoluminescence spectra were acquired on a PerkinElmer LS 55 spectrophotometer. High resolution mass spectra (HRMS) were obtained on Agilent 6520 Q-Tof mass spectrometer with a capillary voltage of 2.6–3.2 kV. Atomic force microscopy (AFM) images were captured using a NT-MDT Solver NEXT Russia. TEM and SEM images were captured using a 120 kV ultra modern Transmission Electron Microscope of FEI and Field Emission Gun-Scanning Electron Microscopes (FEG-SEM) model JSM-7600F respectively. CD spectra were recorded on a JASCO instrument, Model J-815-150S. Experiments were performed by purging dry N$_2$ gas continuously at 15 L min$^{-1}$ during data acquisition. Data were collected in a quartz cuvette with a path length of 1 mm between 200 and 400 nm. Powder XRD data was collected on Rigaku SmartLab between angle 20 = 5-60°. Solution electrical conductivity was measured on a Eutech Instruments CON 5/TDS 5 Conductivity Meter. The instrument was calibrated with standard solution and molar conductance was measured in methanol and found to be 550 ohm$^{-1}$ cm$^2$ mol$^{-1}$ which is in proximity for 4:1 electrolyte. Rheological experiments performed on Anton Paar Quality Control Rheometer RheolabQC Fluorescence quantum yield for isomer 1 and 2 were measured using quinine sulphate in 0.5M H$_2$SO$_4$ as a standard. The reported quantum yield for quinine sulphate is around 0.546. The lifetime measurements were made using a TCSPC system from Horiba Yovin (Model: Fluorocube-01-NL). The samples were excited at 325 nm using a picosecond diode laser (Model: Pico Brite-375L) and data analysis was performed using IBH DAS (version 6, HORIBA Scientific, Edison, NJ) decay analysis software.
Rheological Study: Measurements were performed using a stress-controlled rheometer (Anton Paar Quality Control Rheometer RheolabQC instrument) equipped with stainless steel parallel plates (20 mm diameter, 1.0 mm gap). Experiments were carried out on freshly prepared gels (0.7 % w/v). Linear viscoelastic regions of the gel samples were determined by measuring the storage modulus, $G'$ (associated with energy storage), and the loss modulus, $G''$ (associated with the loss of energy) as a function of stress amplitude (Dynamic oscillatory frequency of 10 rad s$^{-1}$). The following tests were performed: increasing amplitude of oscillation up to 100 % apparent strain on shear, time and frequency sweeps at 22 °C (20 min and from 0.1 to 10 rad s$^{-1}$, respectively), and a heating run to 100 °C at a scan rate of 5 °C min$^{-1}$. All these measurements were conducted in triplicate.

Theoretical Calculations: Quantum chemical calculations have been performed using a hybrid version of DFT and Hartree-Fock (HF) methods namely the B3LYP, where the exchange energy from Becke’s exchange functional is combined with exact energy from Hartree-Fock theory. Basis set 6-31G** has been used for C, H, N and O, which combines quasi-relativistic effective core potentials with a valence double basis-set. The geometry optimization and frequency calculations (to verify a genuine minimum energy structure) were performed by using the Gaussian 09 programme.

Synthesis and Characterization:

2,3-dihydroxysuccinohydrazide (DHSH). The precursor compound was synthesized by slight modification of the literature procedure. To a stirring solution of L-tartaric acid (1.00 g, 6.60 mmol) in methanol (25 mL) few drops of conc. sulphuric acid was added as a catalyst. The reaction mixture was refluxed for 18 hours and its volume was reduced in vacuo with mild heating (60 °C) to afford methyl tartarate as a clear oil with fruity smell. Methyl tartarate thus obtained was dissolved in methanol and hydrazine hydrate (0.80 g, 16.00 mmol) was added drop wise with continuous stirring at room temperature. The resulting clear colorless solution was refluxed for 7 hours. Upon slow cooling it afforded white crystals which were isolated by filtration, washed with diethylether and dried under reduced pressure. Yield 0.68 g (57 %). $^1$H NMR (300 MHz, D$_2$O, ppm): δ 4.49 (d, 2H, −CH), 2.09 (s, 4H, −NH$_2$), 1.96 (s, 2H, −NH), 1.87 (s, 2H, −OH). IR (KBr, cm$^{-1}$) $\nu$(NH$_2$)$_{sym}$ 3357, $\nu$(NH$_2$)$_{asym}$ 3412, $\nu$(NH)$_{sym}$ 3311, $\nu$(C=O) 1666 (s).

(10E,12E)-N1′,N4′-bis(2-hydroxybenzylidene)-2,3-dihydroxysuccinohydrazide(1). Methanolic solution of salicylaldehyde (0.68 g, 5.61 mmol) was added drop wise to a
solution of DHSH (0.50 g, 2.80 mmol) dissolved in water (10 mL) and resulting solution stirred for an additional 4 hours. It afforded a pale yellow solid, which was filtered, washed thoroughly with water, diethylether and dried under vaccuum. Yield 0.83 g (76 %). Anal. calcd for C_{18}H_{18}N_{4}O_{6}: C, 55.94; H, 4.69; N, 14.50. Found C, 56.11; H, 4.78; N, 14.40. Due to poor solubility of the neutral form, $^1$H NMR and UV-vis measurements were performed by dissolving the solid in methanol in presence of 6 eqv. of LiOH•H$_2$O. m/z (ESI−MS, [M+Li]$^+$, 393.14(calcd. 393.14). $^1$H NMR (400 MHz, D$_2$O, ppm): δ 8.32 (S, 2H, =CH), 7.39 (d, 2H, Ar), 7.06 (t, 2H, Ar), 6.54 (d, 2H, Ar), 6.46 (t, 2H, Ar), 4.32 (s, 2H, −CH). IR (KBr, cm$^{-1}$) $\nu$(NH) _sym 3294, $\nu$(C=O) 1673 (s), 1542. UV-Visible spectrum (methanol) [$\lambda_{max}$, nm ([ε, M$^{-1}$ cm$^{-1}$]): 325 (25400), 290 (45800), 280 (46100), 227 (36300).

(10E,12E)-N$_1'$,N$_4'$-bis(4-hydroxybenzylidene)-2,3-dihydroxyssuccinohydrazide(2). It was synthesized following the above procedure described for 1, using 4-hydroxy benzaldehyde in place of salicylaldehyde. Yield 0.78 g (72 %). Anal. calcd for C$_{18}$H$_{18}$N$_4$O$_6$: C, 55.94; H, 4.69; N, 14.50. Found C, 56.23; H, 4.82; N, 14.24. Due to poor solubility of the neutral form, $^1$H NMR and UV-vis measurements were performed by dissolving the solid in methanol in presence of 6 eqv. LiOH•H$_2$O. m/z (ESI−MS, [M+H]$^+$, 387.13(calcd. 387.13). $^1$H NMR (300 MHz, D$_2$O, ppm): δ 8.24 (s, 2H, =CH), 7.38 (d, 4H, Ar), 6.47 (d, 4H, Ar), 4.65 (d, 2H, −CH). IR (KBr, cm$^{-1}$) $\nu$(NH)$_{sym}$ 3339, $\nu$(C=O) 1607 (s), 1591. UV-Visible spectrum (methanol) [$\lambda_{max}$, nm ([ε, M$^{-1}$ cm$^{-1}$]): 310 (47300), 296 sh, 225 (30900).
Scheme S1. A synthetic strategy adopted for the precursor DHSH and structural isomers 1 and 2

Figure S1. Upper side figure shows the role of Li$^+$, Na$^+$, K$^+$ and Cs$^+$ ions in gelation with increasing size. In presence of Li$^+$ isomer 1 forms robust gel, Na$^+$ and K$^+$ gives the weak gel, while Cs$^+$ forms transparent yellow colored solution. Lower side figure (A) Freshly
prepared Li$^+$ containing gel in a vial at 20 °C, (B) gel containing vial inserted in a water bath at 75 °C, (C)-(E) gel started lifting up within 1 min. and completely lifted upto the neck within 2 min. at 75 °C. (F)-(G) upon cooling at room temperature the lifted gel comes down the bottom within 1 min. The experiment can be repeated more than 10 times.

**Note:** The present gel is tight enough, that the methanolic vapour can not pass through the gel matrix resulting the gel lifted up with the help of pressure created by methanolic vapour. This experiment indicates stability of gel at elevated temperature (75 °C) which is above the boiling point of methanol.

**Figure S2.** SEM images of dried gel showing the nano-grains aggregate into cluster like cauliflower.

**Figure S3.** TEM images of the diluted gel showing (A-B) aggregation of nano-grains where average size 200 nm measured for grains, (C) nano-grain clusters.
**Figure S4.** (A) AFM images of the diluted gel (1x10⁻³ M, MeOH), (B) Phase mode image, (C) Grain analysis of A shows the developing process of aggregation, (D) pieces of assembly of granular aggregates, (E) phase mode image of A clearly indicated aggregation of the grains, and (D) magnified image from D showing the granular morphology, diluted gel was spin-cast on mica before acquiring the AFM images.

**Figure S5.** (A) UV-vis spectrum of 1 (red line) and 2 (blue line) (deprotonated with LiOH, conc. 1x10⁻⁵ M) in methanol, (B) Variable temperature CD spectrum of diluted gel in methanol, where temperature ranges from 20-70 °C at 10 °C temperature gradient and (C) CD spectrum for isomer 2 in methanol.
Figure S6. Solution of 1 and 2 at the concentration 1x10^{-3} M in methanol (A) under naked eye, (B) under UV light 1 show the green-blue fluorescence like gel state while 2 non fluorescent nature, and (C) solution at the concentration 1x10^{-5} M in methanol under UV light 1 shows blue fluorescence while there is no change observed for 2.

Figure S7. Variable temperature fluorescence measurement of freshly prepared gel (A) Gel (0.4 % w/v; λ_{ex} = 325 nm at 15 °C) upon heating (5 °C interval, red line) intensity decreases gradually up to 70 °C with significant blue shift (Δλ = 14 nm). After cooling to 25 °C, it reversibly the fluorescence intensity resumes and (B) Primary axis: A change in intensity (200–1000) with increasing temperature (15–70 °C); Secondary axis: significant wavelength change Δλ = 14 nm (478–464 nm) with increasing temperature (15–70 °C), (C) Fluorescence decay curves of gel (red line, τ = 1.304 ns) and diluted gel (green line, τ = 0.948 ns, 1x10^{-5} M, MeOH).

Figure S8. FT-IR spectra of (A) gelator 1, and (B) its xerogel showing significant shift
of the band corresponding to >C=O.

Figure S9. ESI-MS (deprotonated with LiOH, MeOH) spectra of (A) isomer 1 molecular ion peak m/z, [M+Li]$^+$, 393.14(calcd. 393.14), and (B) isomer 2 molecular ion peak m/z [M+H]$^+$, 387.13(calcd. 387.13).

Figure S10. (A) $^1$H NMR spectra of isomer 1 (300 MHz, $d^6$-DMSO, 300K) and a sketch diagram of isomer 1 shows all the labile protons (Ar-OH, -NH, -OH) in red color, (B) The signals associated with the labile protons disapeared upon treatment with LiOH in the above solution of isomer 1, and (C) $^1$H NMR spectra of isomer 2 in presence of LiOH (300 MHz, D$_2$O, 300K) well supports structural formulation.

Figure S11. Powder X-ray diffraction pattern of gelator (isomer 1) without LiOH in black line and red line peaks for Li$^+$ containing xerogel indicating amorphous nature of gel.
Although, very less intense peaks corresponding to the crystals of Li$_2$CO$_3$ (Li$^+$ absorbs atmospheric CO$_2$) and LiOH indicates a tiny fraction of xerogel has crystalline nature.

Figure S12. (A) The optimized structure of isomer 1 shows bent structure with dihedral angle of 101.22° corresponding to two salen rings, where E = −37201.61 eV, upon Li$^+$ chelation with salen N, O donor the molecule changes conformation consequently became rigid and attains planar structure with dihedral angle of 169.12°, E = −37583.18 eV which may offer a nice platform for π−π stacking and lead to excellent J-aggregation. The molecular planarization of isomer 1 upon chelation with Li$^+$ as well aggregation led to rigidity towards rotation/vibration in molecular structure, strongly support the positive response towards gelation and enhancement of flourescence with such a simple system. No conformational changes are observed upon additional chelation of Li$^+$ with (nearby chiral centres) oxo donor atoms with dihedral angle 169.12°, where E = −37964.02 eV. (B) The optimized structure of isomer 2 shows bent structure with dihedral angle of 97.81° corresponding to two phenolic rings, where E = −37200.38 eV without significant changes upon treatment with Li$^+$ to all the donor sites, as a result, isomer 2 forms non-
fluorescent solution instead of fluorescent gel, where $E = -37960.75\text{eV}$.

**Figure S13.** A schematic route for the mechanism of gelation and its properties explored from various instrumental techniques as well as correlation with each other in logical steps; At the first isomer 1 undergoes planarization from bent structure in presence of Li$^+$. This conformational change was well supported by fluorescence (dilution & variable temperature), CD spectroscopy and structure optimization as well as comparative study of isomer 2. Further, the planar structure offers platform for $\pi-\pi$ stacking. Possibly, Li$^+$ will be in solvated form which may create various types of weak interactions. The chelation (CHEF) and aggregation (AIEE) are mainly responsible for the fluorescence enhancement. J-type aggregation is proved by fluorescence spectroscopy. Further, these J-aggregates assemble into nano-grains which further aggregate into nano-cluster. This nano-cluster traps the solvent and forms gel which after drying reveals the cauliflower like nano-cluster morphology. Based on structural characterization a sketch diagram inserted which shows the Li$^+$ ion binding.
Figure S14. (A) Dynamic shear stress of $G'$ and $G''$ for gel at frequency of 10 rad s$^{-1}$ and 22 °C, (B) Dynamic oscillation strain sweep of $G'$ and $G''$ for gel at frequency of 10 rad s$^{-1}$ and temperature at 22 °C, (C) Dynamic temperature ramp $G'$ and $G''$ for gel at a heating rate of 5°C min$^{-1}$, strain of 0.5 % and frequency of 10 rad s$^{-1}$ and (D) Dynamic temperature ramp of complex viscosity measurement at 5 °C min$^{-1}$.

References:
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