Supporting Information

Alkali base Triggered Homochiral Intramolecular Charge Transfer Metallogel based on symmetrical A-π-D-chiral-D-π-A type ligand

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Scheme S1. A synthetic strategy adopted for the precursor A, structural isomers (SI 1-3) and ligand (4)

	Isomer 1				Isomer2			Isomer 3			Ligand 4		
	Li ⁺	Na ⁺	K ⁺	NEt ₃ /NH ₃	Li ⁺	Na ⁺	K ⁺	Li ⁺	Na ⁺	K ⁺	Li ⁺	Na ⁺	K ⁺
DMSO	S	S	S	S	S	S	S	G	S	S	S	S	S
Acetonitrile	G	G	S	Ι	GP	S	S	G	S	S	Ι	Ι	Ι
Acetone	G	G	S	Ι	S	S	S	G	S	S	-	-	-
MeOH	S	S	S	Ι	S	S	S	G	S	S	S	S	S
Ethanol	S	S	S	Ι	S	S	S	G	S	S	S	S	S
Water	PS	PS	PS	Ι	PS	PS	PS	PS	PS	PS	-	-	-

Table S1: Gelation details isomer, cation and solvent*

*Where, S= solution, G= gel, GP= gelatinous precipetate, PS= partially soluble and I= Insoluble



Scheme S2. A schematic representation of gelation property of structral isomers 1-3 in presence of LiOH in various solvents. Isomer 3 is preeminent candidate for gelation in DMSO, acetone, acetonitrile, methanol and ethanol. While the isomer 1 does not form gel in DMSO but shows the gelation in acetonitrile as well as in acetone. On the other hand, isomer 2 forms the solution or gelatinous precipetate in DMSO and acetonitrile.



Figure S1. A complete summary of gelation property of isomers 1-3 and ligand 4 in various combinations of alkali base and solvent (A) Isomer 3, (B) Isomer 1, (C) Isomer 2 and (D) Isomer 4. Isomer 2 neither form gel nor produce any intense colour in comparison to isomer 1 and 3 while ligand 4 remain colourless after treatment with LiOH.

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Figure S2. Acetonitrile containing gel $(1+\text{Li}^+)$ in a vial inserted in water bath at 30 °C, gel started lifting up upon increasing the temperature and completely lifted at 75 °C. Notably, at 75 °C gel shows the distinct colour change and after cooling exhibits the more intense red colour than original gel. The experiment can be repeated more than 3 times. **Note:** The present gel is tight enough, that the acetonitrile vapour can not pass through the gel matrix resulting the gel lifted up with the help of pressure created by acetonitrile vapour. This experiment indicates stability of gel at elevated temperature 75 °C.



Figure S3. SEM images of isomer **3** and acetone containing dried gel/solution of showing the (A) well ordered long range fibrous in presence of LiOH, (A1) magnified image of A, (B) unique flower like aggregated growth in presence of NaOH, (B1) magnified image of B, (B2) EDX of B1, (C2) EDX of C1, (C) crystal growth in presence of KOH and (C1) magnified image of C.



Figure S4. SEM images of isomer **3** and acetonitrile containing dried gel/solution well supports results shown in the figure S3 (A) well ordered long range fibres in presence of LiOH, (A1) magnified image of A, (B) unique flower like aggregated growth in presence of NaOH, (B1) magnified image of B, (C) crystal growth in presence of KOH and (C1) magnified image of C.



Figure S5. SEM images of isomer **1** and acetonitrile/acetone containing dried gel/solution (A) fibrous in presence of LiOH, (B) twisted fibrous morphology in presence of NaOH and acetonitrile, (B1), (B2) and (B3) magnified image of B, (C) twisted fibrous morphology of xerogel of acetone containing gel, (C1) and (C2) magnified image of C (D) broken fibrous morphology in presence of KOH and (C1) magnified image of C.



Figure S6. SEM images of isomer **2** and acetonitrile containing dried solution (A) broken fibres in presence of LiOH, (A1) magnified image of A, (B) random fibres in presence of NaOH, (B1) magnified image of B, (C) no conclusive morphology in presence of KOH and (C1) magnified image of C.



Figure S7. UV-vis titration of isomer **3** ($1x10^{-5}$ M) in DMSO (blue line), upon addition of aqueous solution of (conc. $1x10^{-3}$ M) (A) NaOH and (B) KOH shows the gradual decrease in absorbance at 337 nm and appearance of a new band at 457 nm through a nice isosbestic point at 377 nm. (C and D) UV-vis titration of isomer **1** ($1x10^{-5}$ M) in DMSO (blue line), upon addition of aqueous solution of (conc $1x10^{-3}$ M) NaOH and KOH, respectively, shows the gradual decrease in absorbance at 292 nm and appearance of two new bands at 443 and 345 nm through a nice isosbestic point at 312 nm. The peak at 443 nm is because of the CT triggered by alkali base. The additional peak at 345 nm is because of the conformational change of gelator under the influence of alkali metal ion. (**E** and **F**) UV-vis titration of isomer **2** ($1x10^{-5}$ M) in DMSO (blue line), upon addition of aqueous solution of (conc $1x10^{-3}$ M) NaOH and KOH, respectively, shows the gradual decrease in absorbance at 345 nm is because of the conformational change of a new band at 345 nm through a nice isosbestic point at 312 nm. The peak at 443 nm is because are of isomer **2** ($1x10^{-5}$ M) in DMSO (blue line), upon addition of aqueous solution of (conc $1x10^{-3}$ M) NaOH and KOH, respectively, shows the gradual decrease in absorbance at 285 nm and appearance of a new band at 345 nm through a nice isosbestic point at 312 nm. The apearance of only one peak at 345 nm may be because of the conformational change in gelator under the influence of alkali base.



Figure S8. Plausible mechanism of presence and absence of charge transfer (A) isomer $1+K^+$ and (B) isomer $2+K^+$, respectively. The flow of charge density from amine N to – NO₂ group is feasible in case of isomer **1** and **3**, while in **2** does not because of lack of conjugative connectvity between ring and $-NO_2$ group. On the other hand, more precisely, the **1** will have a higher degree of charge delocalization in the ground state, which means that the actual UV-vis transition in fact should have smaller degree of CT character, it is already delocalized in the ground state. **2** with its insufficient electron delocalization in the ground state should give a transition that has more CT character, but it will have a lower oscillator strength and may be it is for this reason CT is less observed in 2 than 1 and 3.

Figure S9. Variable temperature UV-vis experiment on diluted gel (~ $5x10^{-5}$ M) shows the blue shift upon increasing the temperature from 30 –90 °C (A) 3+Li⁺ in acetonitrile; $\Delta\lambda$ = 63 nm and (B) 1+Li⁺ in acetonitrile; $\Delta\lambda$ = 60 nm.

Figure S10. UV-vis titration experiments- (**A**) The band at 457 nm of $3+Na^+$ (yellow line, $\sim 1x10^{-5}$ M, DMSO) corresponding to CT diminished upon treatment with [18]-crown-6 ($1x10^{-3}$ M) and apeared a new peak simultaneously at 337 nm through a nice isosbestic point correcsponding to isomer **3** demonstrate the removal of triggering unit Na⁺, in turn, amputate the charge transfer. However, the consumption of [18]-crown-6 is more (~ 1.5 times) in case of $3+Na^+$ than $3+K^+$ may be because of the more selectivity of [18]-crown-6 towards the K⁺ than Na⁺. (**B**) The band corrsponding to isomer **2**+**K**⁺ at 345 nm (blue line, $1x10^{-5}$ M, DMSO) shifted to 292 nm upon titration with [18]-crown-6 may be due to conformational reorganisation in gelator upon removal of K⁺. (C) Isomer 3 (337 nm) red shifted (473 nm, $\Delta\lambda$ = 136 nm) upon addition of TBAOH and further there is no significant change observed upoun treatment with excess [18]-crown-6.

Figure S11. A full spectrum of ¹H NMR titration of 3 (500 MHz, DMSO- d_6 , 300K) with LiOH.H₂O; (a) free of Li⁺ and (b) shows the deprotonation of labile protons of –NH and – OH upon addition of LiOH 0.36 equivalents while (c) shows the loss of peaks upon gelation.

Figure S12. Crystal lattice of **3** (A) H-bonded lattice between NH and O along 'a' axis (NH33...O3, 2.884 Å), (B) Water molecules connect the two molecule of **3** in a fashion of three centre two H-bond, (C) Role of $-NO_2$ group and ademine proton in crystal packing and (D) in zoom image of C. The interactions shown in C and D has already been demonstrated in NMR titration experiment.

Note: Crystallographic data and refinement parameters for **3**: Empirical formula C₉H₁₀ N₃O₅, Fw 240.20, T(K) 293(2), Wavelength 0.71073 (Å), monoclinic, *C*2, a = 15.791(3) Å, b = 5.0056(6) Å, c = 16.133(3) Å, $\alpha = \beta = 90$, $\gamma = 122.52(2)$, V = 1075.2(3) Å³, Z = 4, $\rho_{calcd} = 1.484 \text{ Mgm}^{-3}$, $\mu = 0.123 \text{ mm}^{-1}$, Reflections collected 1736, independent 1736, R1= 0.0554, wR2 = 0.1116 [I>2 σ]; R1 = 0.0860, wR2 = 0.1324 [all data], GOF = 1.038, ³Flack parameter = 0.23(3), CCDC 1445441.

H-bonds: O5...H44 2.781 Å, O3...H33 2.884 Å, O3...H66 2.844 Å.

Reference for unusual Flack parameter in case of L-tartaric acid: L. Jian, D. Chen, Y. Jiang, K. Yu and A. S. C. Chan, *Acta Cryst.*, 1999, **C55**, IUC9900053.

Figure S13. Powder X-ray diffraction pattern of gelator (isomer 3) black line and red line peaks for $3+\text{Li}^+$ containing xerogel indicating amorphous nature of gel, while $3+\text{Na}^+$ aggregate shows the crystalline nature in blue line. However the formation of minor proportion of crystals of corresponding carbonates (Li⁺/Na⁺ absorbs atmospheric CO₂) and LiOH/NaOH can not be ruled out.

Figure S14. A pictorial representation of plausible mechanism of gelation.