Supporting Information

Counteranion Driven Homochiral Assembly of a Cationic C_3-Symmetric Gelator through Ion-Pair Assisted Hydrogen Bond

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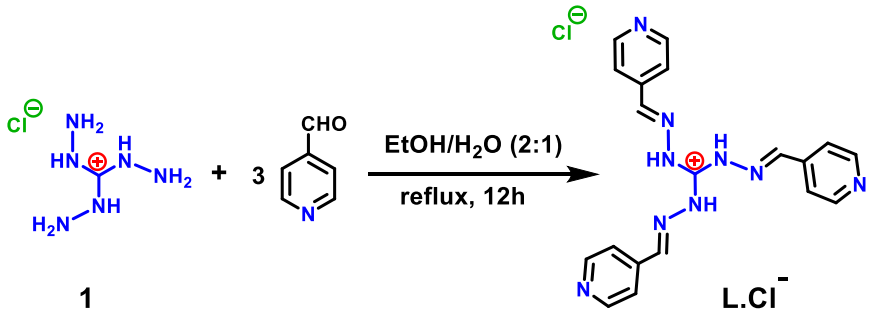
1. Materials and Methods

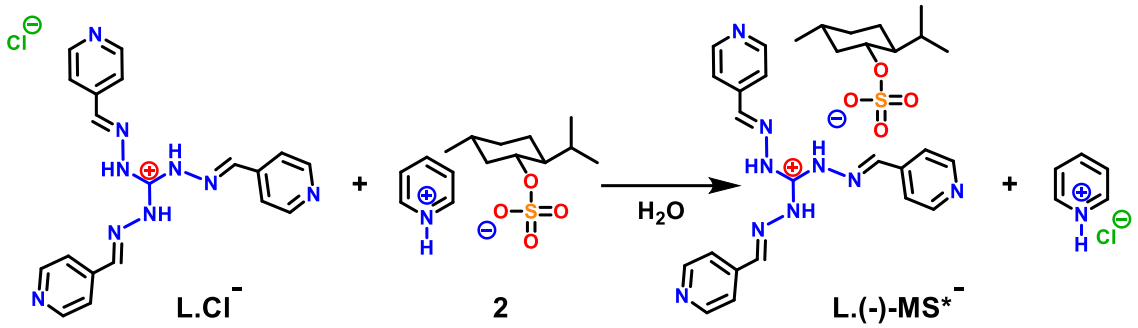
Unless otherwise stated, all reagents and organic solvents used for synthesis purpose were purchased from commercial suppliers, and used as such without further purification. Fresh double distilled water was used throughout the experiment. HPLC grade solvents were used for recording spectrometric data. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 400/500 MHz FT NMR (Model: Avance-DPX 400/500). Chemical shifts are reported in ppm using tetramethylsilane (TMS) as the internal standard. High-resolution mass spectra (HRMS) were recorded on JEOL JM AX 505 HA mass spectrometer. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Optics ALPHA-E spectrometer with a universal Zn-Se ATR (attenuated total reflection) accessory in the 600−4000 cm^{-1}. UV−Vis absorption spectra were measured with a Perkin Elmer Lambda 950 UV-Vis spectrophotometer equipped with a peltier system. Circular dichroism (CD) spectra were recorded on a JASCO model type J-815 spectropolarimeter. SEM images were obtained with a Zeiss DSM 950 scanning electron microscope a with tungsten filament as electron source operated at 10 kV.

2. Synthesis

Compounds **1**[S1]and pyridinium salt of **(+)- or (–)-menthylsulfate (MS*⁻) 2**[S2] were prepared according to previously reported procedures.



Tris(4-pyridinecarboxaldehyde)triaminoguanidinium chloride (L.Cl⁻). To an aqueous solution (15 mL) of **1**[S1] (500 mg, 4.76 mMol), a mixed solution of 4-pyridinecarboxaldehyde (1.35 mL, 14.34 mMol) and ethanol (30 mL) was slowly added. The resulting solution was refluxed for 12 hours and then cooled to ambient temperature. A yellow colour gelatinous precipitated was obtained within 3-4 hours. The precipitate was filtered off, washed initially with ice-cold water (two times) and then with 10 mL of ethanol/ether (2:8) solution. Finally the desired product (**L.Cl⁻**) was collected and dried under reduced pressure. Yield: 1.56 g (~80%). ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 8.71~8.70 (d, J = 6 Hz, 6H), 8.58 (s, 3H), 8.00~7.99 (d, J = 6 Hz, 6H). ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) 159.43, 151.03, 150.29, 150.06, 149.92, 148.39, 147.51, 147.05, 142.74, 122.15. MS (ESI): *m/z* calcd. for $[M\text{-}Cl^-]^+$ $(C_{19}H_{18}N_9)^+$: 372.167; found: 372.168.



L.(–)-MS*⁻. To an aqueous solution (35 mL) of **L.Cl⁻** (250 mg, 0.61 mMol), an aqueous solution (2.5 mL) of **(–)-2**[S2] (290 mg, 0.92 mMol) was added drop wise. During the course of (–)-**2** addition, a yellow colour precipitate was obtained. To complete the reaction, it was stirred for another 5 hours at room temperature. The product was filtered off and washed thoroughly with water and dried under desiccator for overnight to obtain ~95 % isolated yield. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 8.72~8.71(d, J = 6 Hz, 6H), 8.57 (s, 3H), 8.02~8.01 (d, J = 6 Hz, 6H), 2.26~2.24 (d, J = 12 Hz, 1H), 2.09~2.06 (m, 1H), 1.55~1.49 (m, 2H), 1.25~1.24 (broad, 1H), 1.06~1.01 (m, 1H), 0.91~0.88 (m,1H), 0.81~0.76 (m, 8H), 0.68~0.67 (d, J = 7 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 179.02, 175.16, 173.79, 169.09, 142.89, 84.89, 77.02, 52.05, 49.78, 46.58, 42.64, 33.06, 32.71, 29.07, 28.95, 21.47, 21.20, 18.81, 18.64, 18.02, 17.85, 16.41, 16.37. MS (ESI): *m/z* calcd. for $[M-H]^-$ $(C_{29}H_{36}O_4N_9S)^-$: 606.26; found 606.26.

L.(+)-MS*⁻. The title compound was prepared using **(+)-2**[S2] isomer following the same procedure as that employed for the preparation of **L.(–)-MS*⁻**in a ~92% yield.

3. Characterization

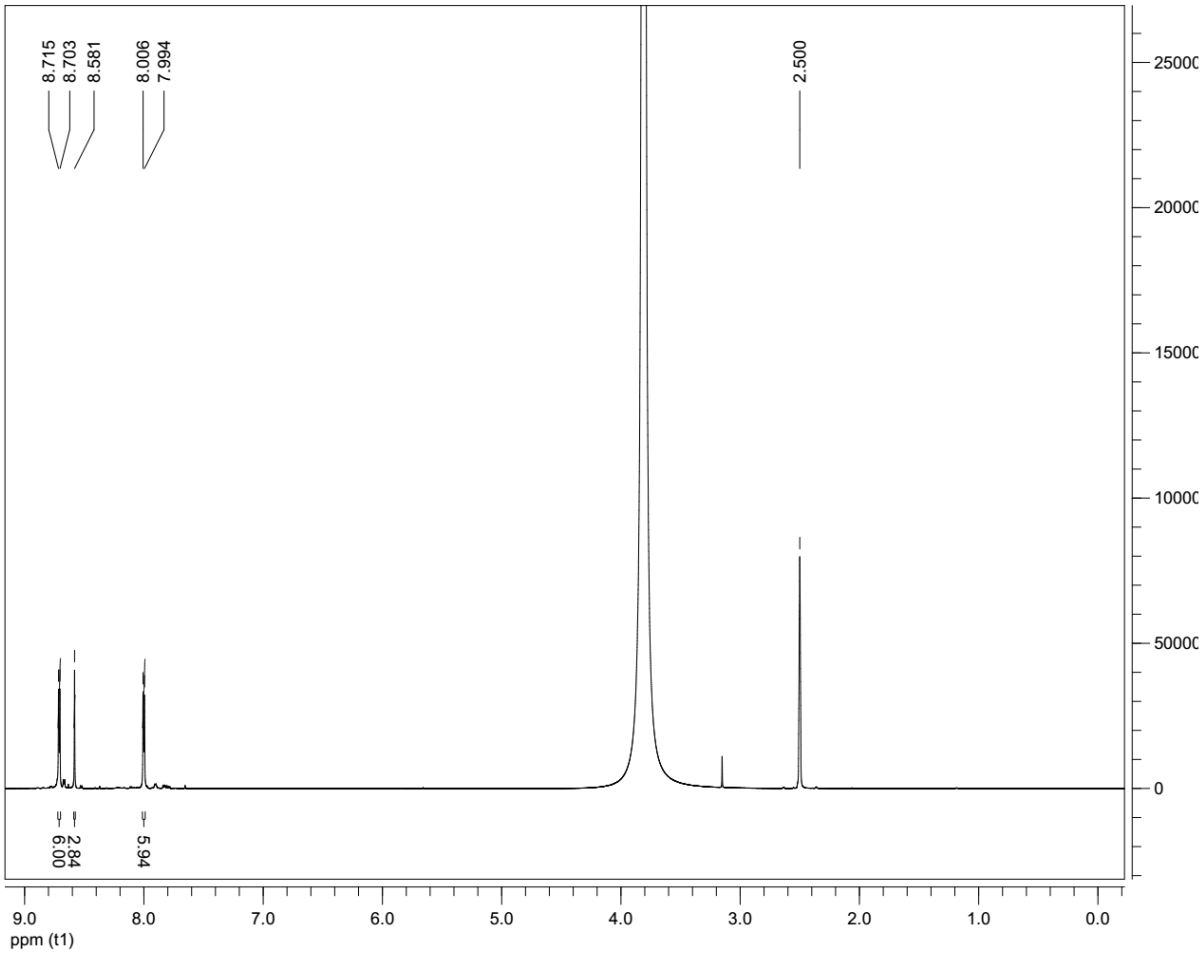


Figure S1. ^{1}H NMR spectrum (500 MHz) of **L.Cl**$^{-}$ in DMSO-d_6.

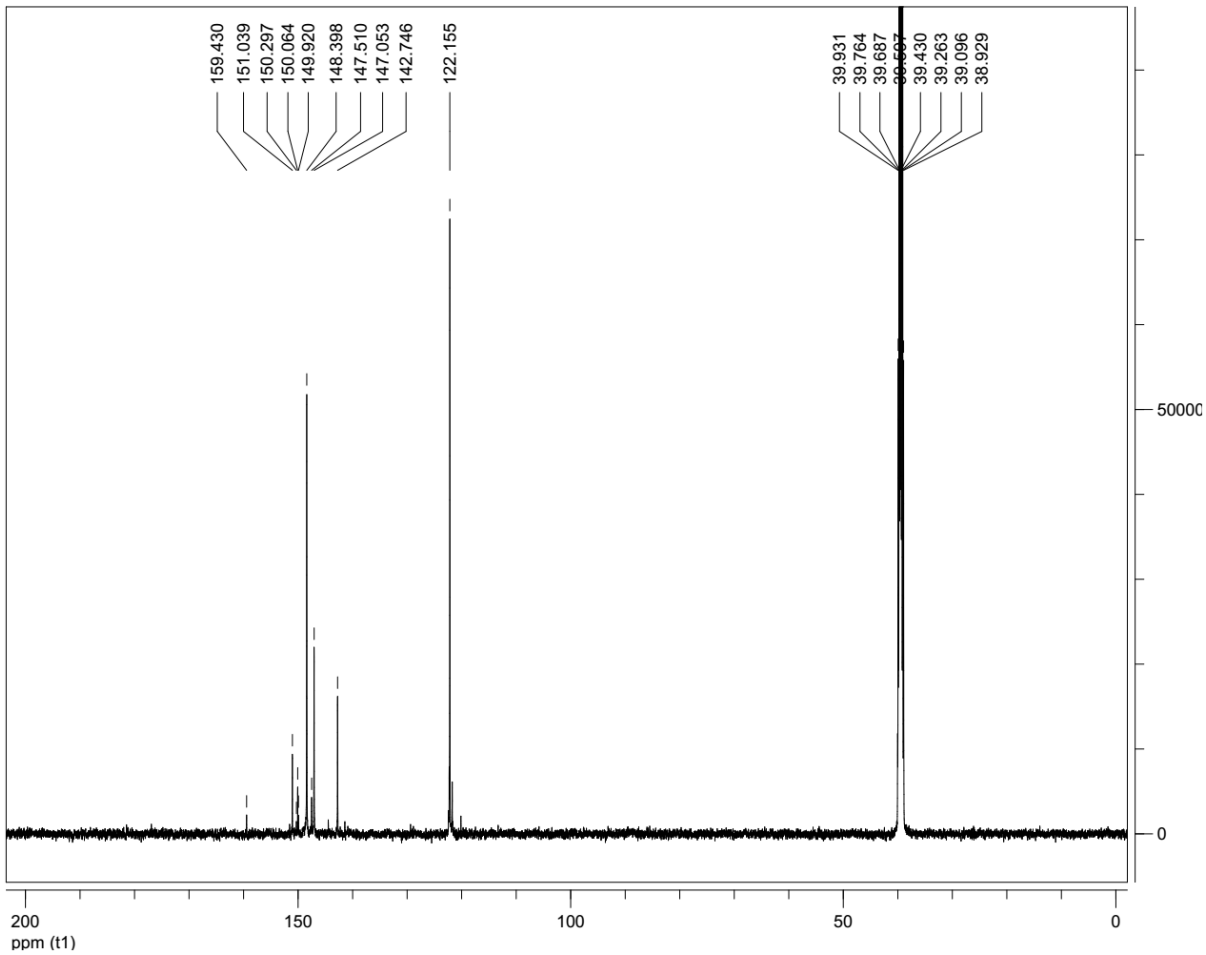


Figure S2. ^{13}C NMR spectrum (125 MHz) of **L.Cl**$^{-}$ in DMSO-d_6.

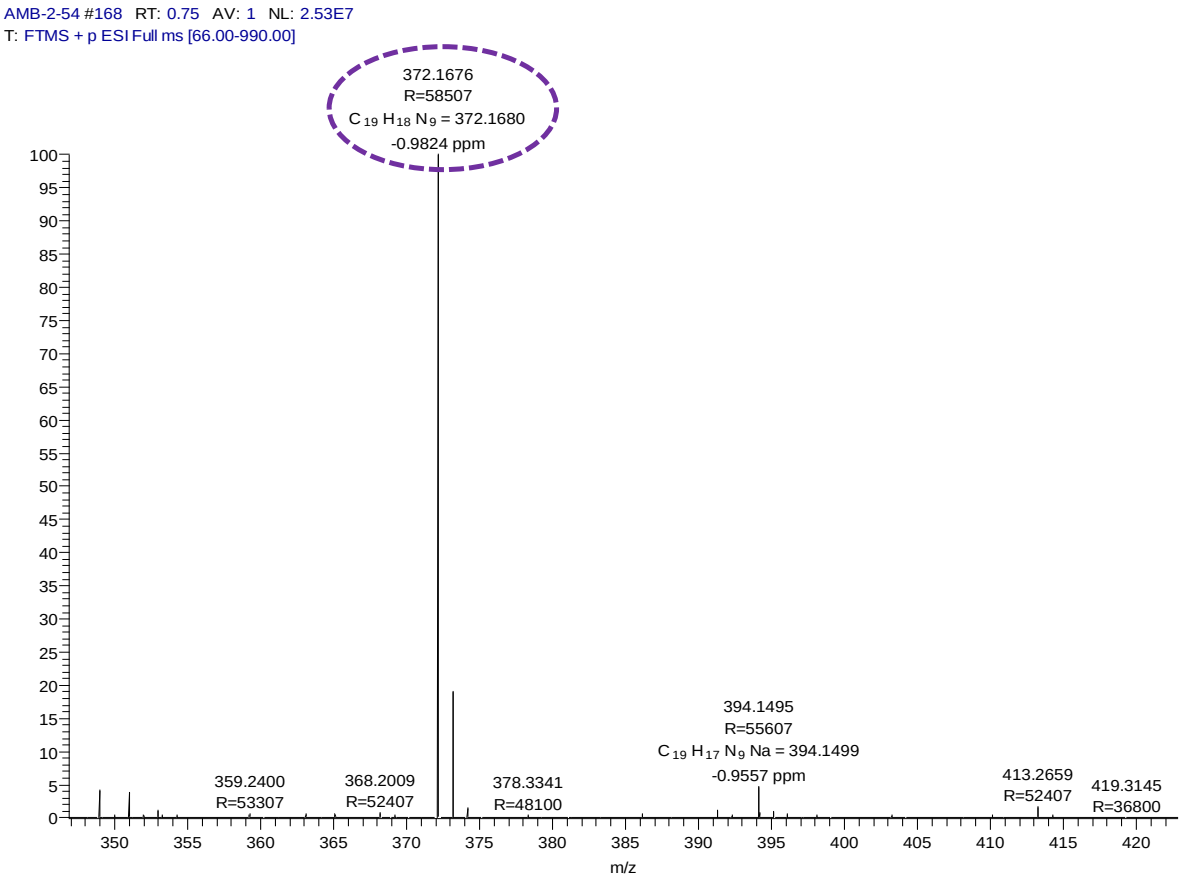


Figure S3. ESI-MS spectrum of **L.Cl**$^{-}$.

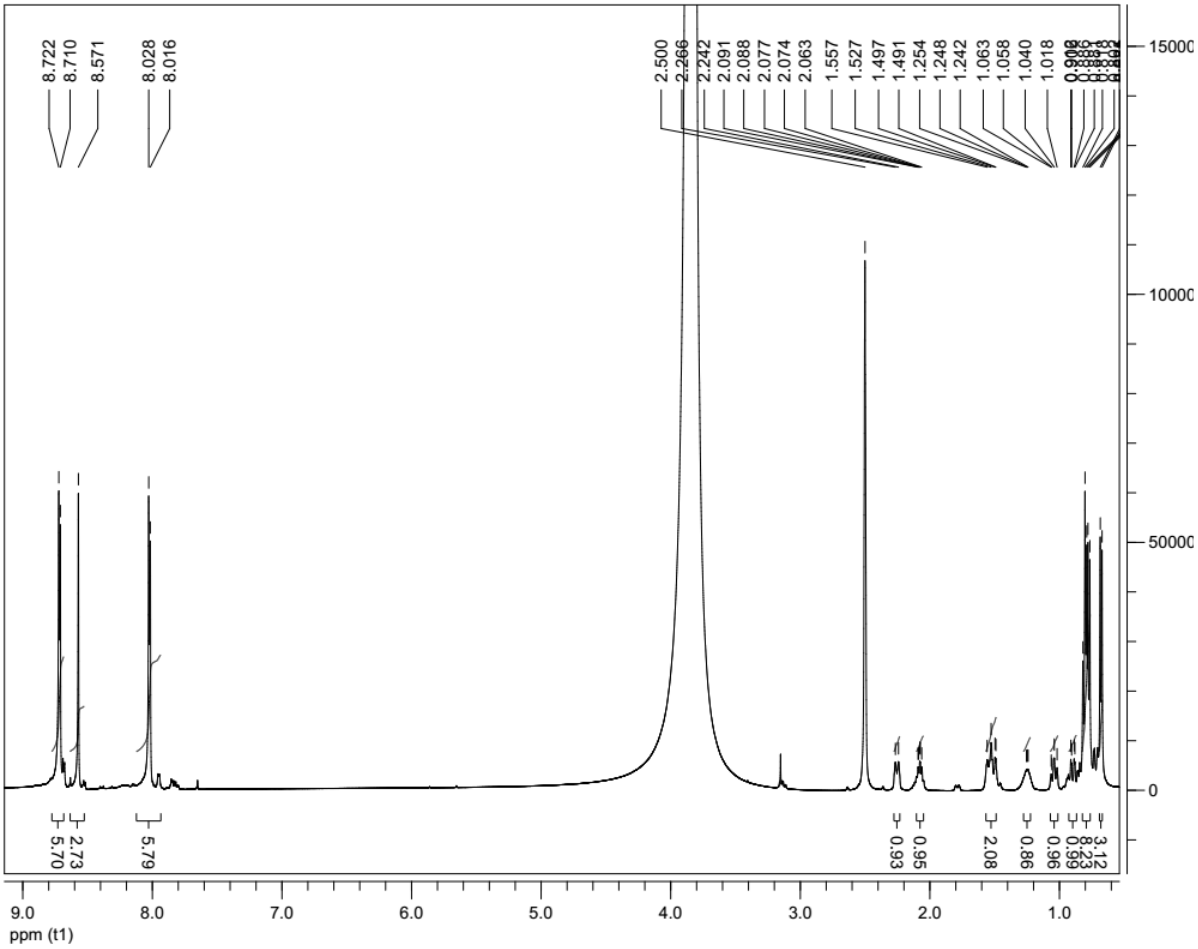


Figure S4. ^{1}H NMR spectrum (500 MHz) of **L.(–)-MS*⁻** in DMSO-d_6.

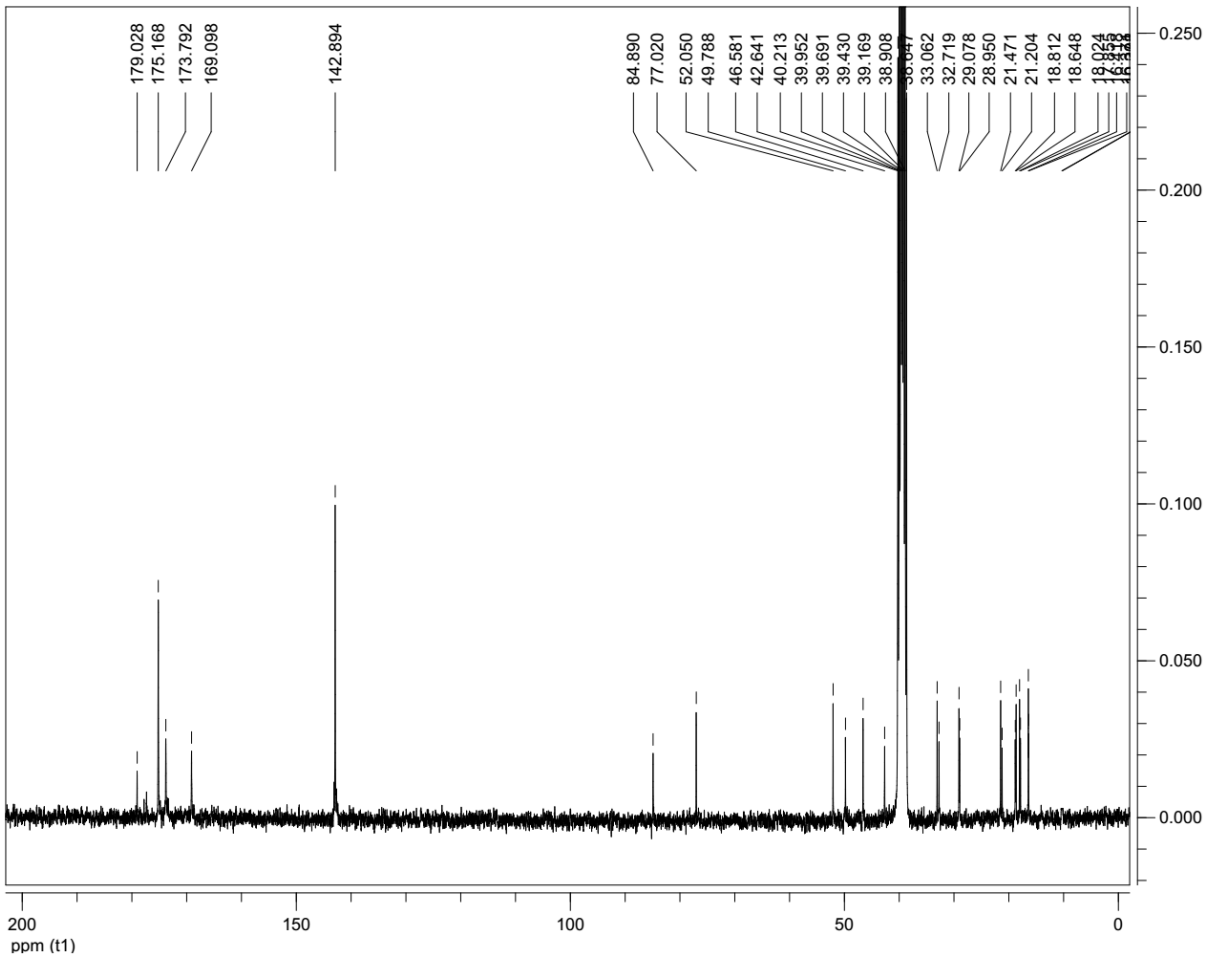


Figure S5. ^{13}C NMR spectrum (100 MHz) of **L.(–)-MS*⁻** in DMSO-d_6.

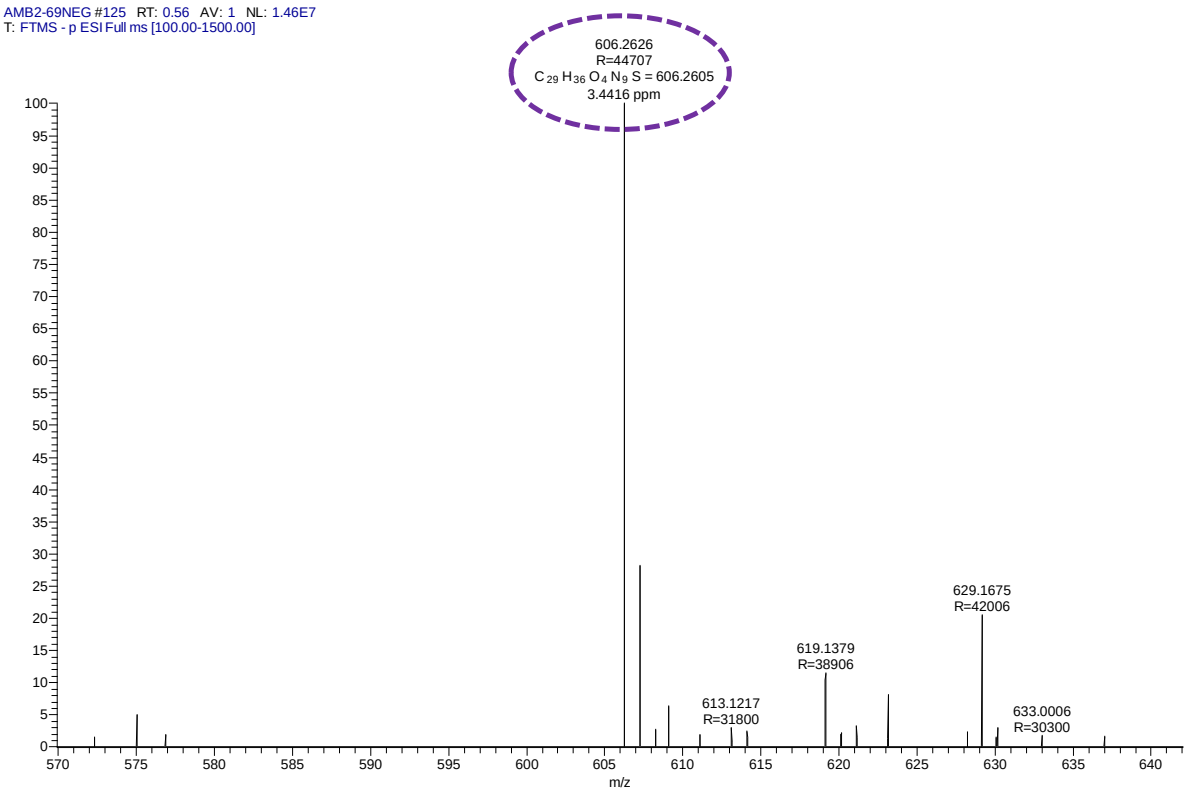


Figure S6. ESI-MS spectrum of **L.(–)-MS*⁻**.

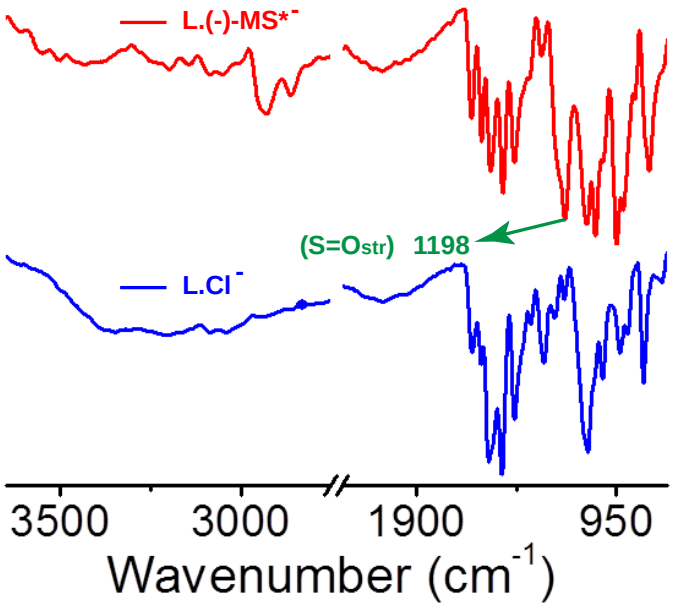


Figure S7. Comparison of IR spectra of **L.Cl⁻** and **L.(–)-MS*⁻**, indicating that the **Cl⁻** counteranion of **L** was exchanged successfully by **MS*⁻**.

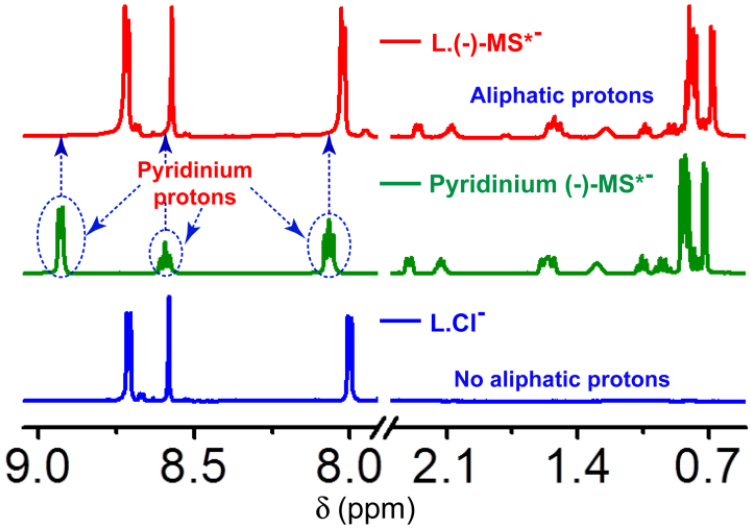


Figure S8. Comparison of ^{1}H NMR spectra (in DMSO-d_6) of **L.Cl⁻**, pyridinium **(–)-MS*⁻** and **L.(–)-MS*⁻** demonstrating the successful exchange of Cl⁻ counteranion of L with chiral MS*⁻.

Formation of the counteranion exchanged compound **L.(–)-MS*⁻** was confirmed by comparison of the ^{1}H NMR spectra (in DMSO-d6). ^{1}H NMR spectra of **L.Cl⁻** lacks protons in the aliphatic region whereas the pyridinium **(–)-MS*⁻** ion displays aliphatic protons along with three sets of pyridinium protons (encircled peaks) in the aromatic region. However in the final compound **L.(–)-MS*⁻**, appearance of multiple sets of aliphatic protons (corresponds to MS*⁻ protons) and complete disappearance of pyridinum protons strongly support that the anion exchange reaction has taken place.

4. General Description of Different Experimental Techniques

Gelation. Synthesized compounds **L.Cl⁻**, **L.(–)-MS*⁻** and **L.(+)-MS*⁻** were taken in 1 mL of MeOH/H_2O (1:1, *v/v*) at their minimum gelation concentration, and dissolve completely by heating in three different closed glass vial. The clear solution was left to cool down in ambient temperature without any disturbance. A stable gel was obtained instantly from **L.(–)-MS*⁻** and **L.(+)-MS*⁻**, whereas it took 3-4 hours for **L.Cl⁻**. The gel formation was confirmed by the failure of the soft mass to flow by inverting the glass vial.

UV-Vis and Circular Dichroism (CD) Spectroscopy. **L.Cl⁻** was dissolved in MeOH/H_2O (1:1, *v/v*) to a concentration of 15 mg/mL. Then, a 60 µL of this resulting solution was placed on a circular quartz plate (20 mm diameter × 1 mm thick) and allowed to air dry for ~6-7 hours in a dust free place, leads to a uniform transparent thin film. Both UV-Vis and CD spectrum was then recorded. For **L.(–)-MS*⁻** and **L.(+)-MS*⁻** same procedure was followed to prepare the film, but concentration was used 4 mg/mL. CD spectra of **L.Cl⁻** in the crystalline phase were recorded on KBr pallet containing crystalline sample.[S3]

Scanning Electron Microscopy (SEM). Small portion of the prepared gels (of **L.Cl⁻**, **L.(–)-MS*⁻** and **L.(+)-MS*⁻)** was scooped out and diluted with MeOH/H_2O (1:1, *v/v*). Resulting solutions are drop-casted on silicon wafer and allowed to air dry for 5 hours in a dust free place. Finally it was dried under desiccator for overnight. Before taking images samples were coated with gold vapour.

Crystallization Procedure. 20 mg of **L.Cl⁻** was dissolved in 1 mL of MeOH/H_2O (1:1, *v/v*) and taken in a screw capped vial. The solution was gently heated, then kept it in closed condition with no mechanical disturbance for allowing the crystals of **L.Cl⁻** to grow. After ~4-5 days high quality rod shaped yellow coloured crystals were obtained, which was used for X-ray diffraction mediated characterization. For **L.(–)-MS*⁻** and **L.(+)-MS*⁻**, 15 mg of weighted corresponding compound taken in two different glass vial and dissolved with 1 mL of slight acidic MeOH (prepared by mixing 4 µL of CH_3COOH with 1 mL MeOH). When diethyl ether vapor was allowed to diffuse slowly at 25°C into the prepared **L.(–)-MS*⁻** or **L.(+)-MS*⁻** solutions, X-ray quality crystals were obtained within 48 hours. These crystals are immediately used for single crystal X-ray diffraction (SC-XRD).

5. Supplementary Figures

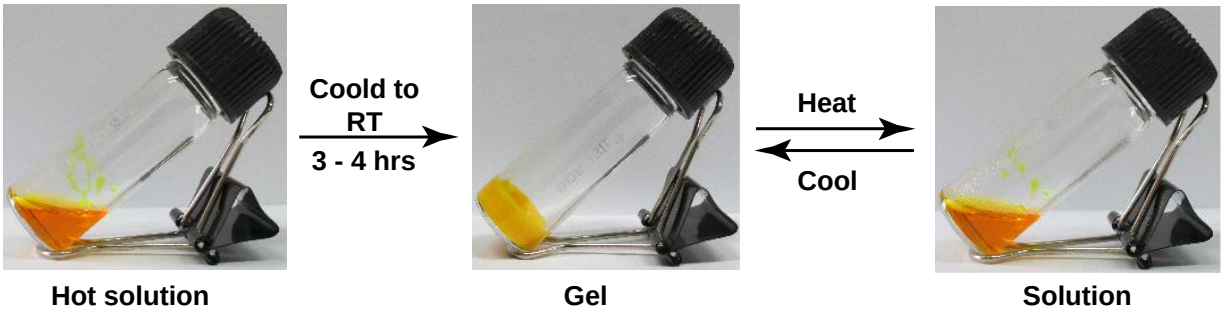


Figure S9. Photographs of the yellow colour opaque gels formed by **L.Cl⁻** in MeOH/H_2O (1:1, v/v) and the reversible gel-sol transition by temperature. Critical gel concentration (CGC) is 6.2 wt%.

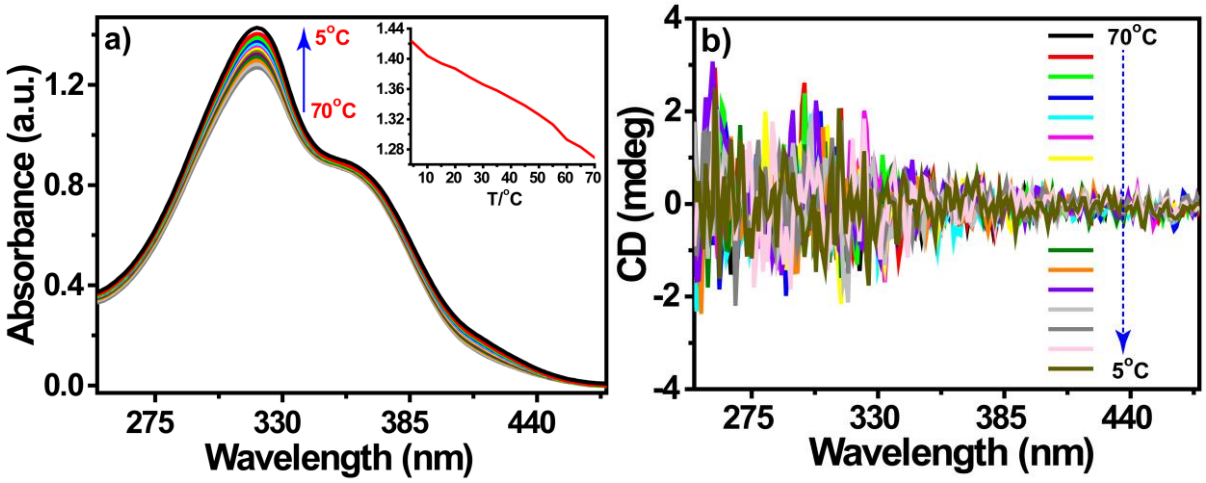


Figure S10. Variable temperature (a) UV-Vis and (b) CD spectra of **L.Cl**$^{-}$ (c = 1.0×10^{-4} Mol in 1:1 MeOH/H_2O, l = 10 mm) from 70 to 5 °C. Inset of (a) shows variation of absorbance at 319 nm with temperature.

By cooling from 70 to 5°C, no distinct UV-Vis spectral change is observed, except slight increase in absorption intensity at 319 nm (Fig S10a). Moreover, characteristic aggregation features such as an isosbestic point or a shift in the absorption maximum are also missing. The slight increase in absorption intensity with decreasing the temperature could be due the planarized structure of **L.Cl**$^{-}$ from its initial propeller shape.[S4] Hence the temperature dependent UV-Vis spectra clearly indicates that gelator **L.Cl**$^{-}$ molecule either as monomer or as optically silent minor aggregates at lower concentration. As a result, no CD signal is identified in solution (Figure S10b).

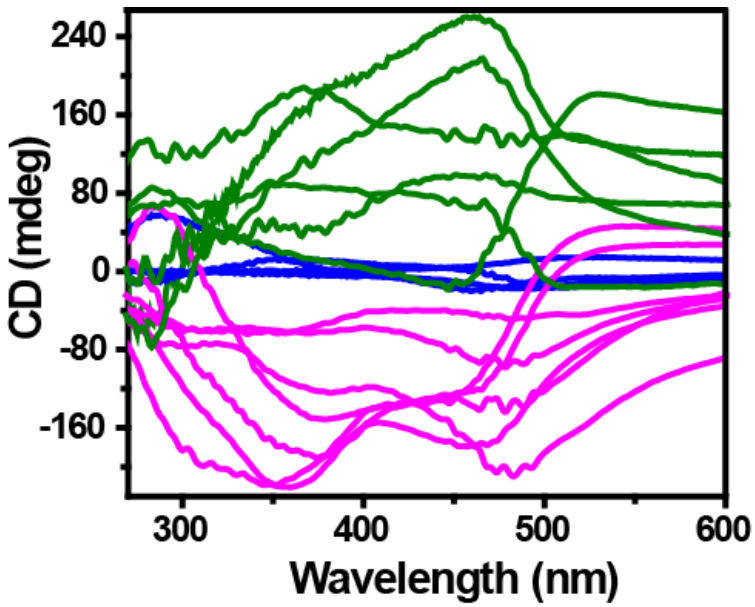


Figure S11. CD spectra of different batches of **L.Cl**$^{-}$ thin films showing random cotton effect. (Concentration used to prepare film, C = 15 mg/mL in MeOH/H_2O (1:1, v/v) mixture).

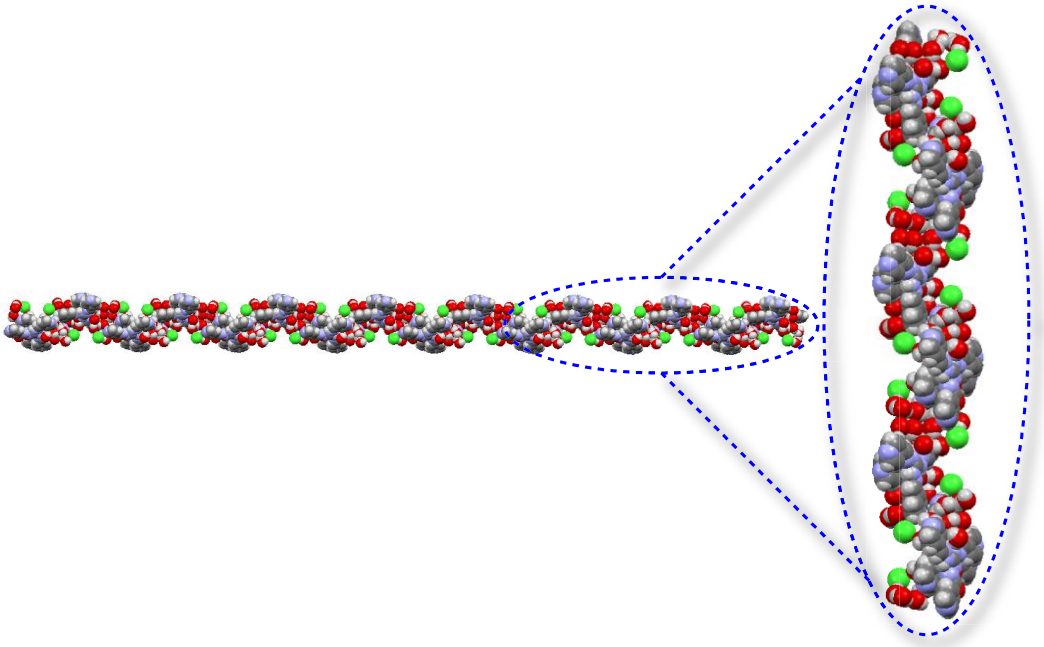


Figure S12. One dimensional (1D) left-handed helical arrangement of **L.Cl**$^{-}$ by H-bonding interaction between **L**, hydrated **Cl**$^{-}$ and water molecule.

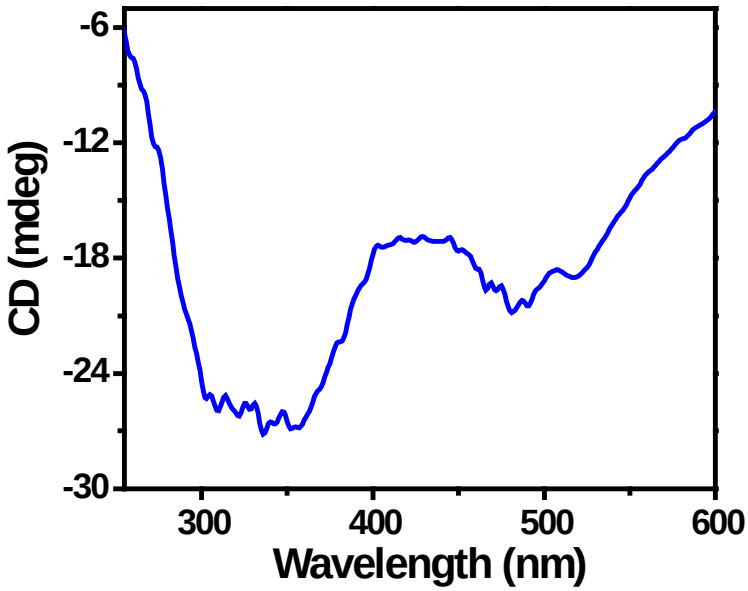


Figure S13. CD spectra of **L.Cl**$^{-}$ in the crystalline phase.

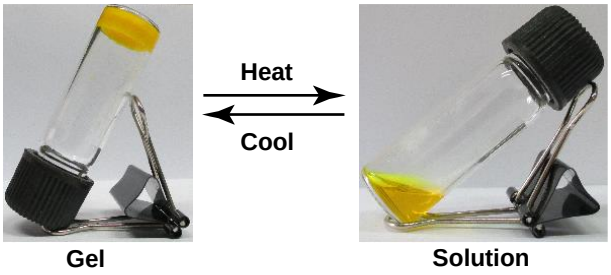


Figure S14. Photographs showing thermal reversibility of **L.(–)-MS*⁻** gel prepared in MeOH/H_2O (1:1, v/v). Gel prepared from **L.(+)-MS*⁻** is also thermo reversible. CGC for the both gelator is 0.7 wt%.

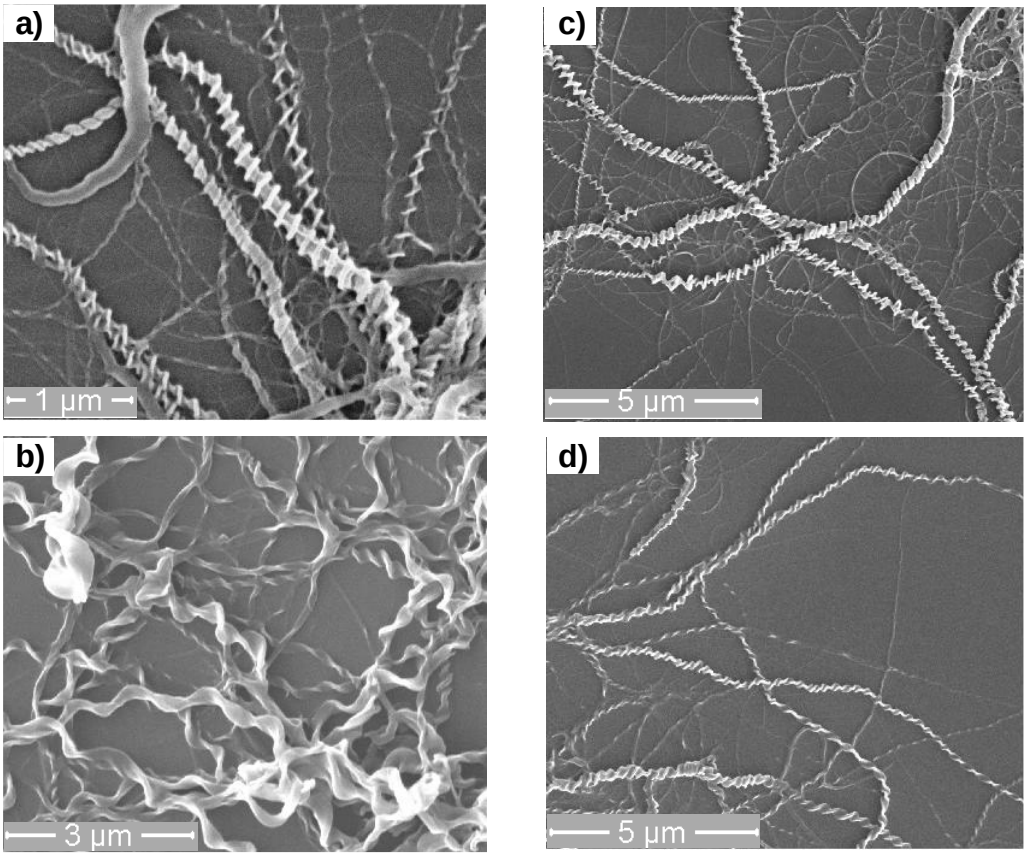


Figure S15. (a, b) SEM images of **L.(+)-MS*⁻** showing *P* twists and (c, d) the SEM images of **L.(–)-MS*⁻** showing *M* twists. Centration used [$C = 0.5 \times 10^{-5}$ Mol, for (a, c)] and [$C = 1.0 \times 10^{-4}$ Mol for (b, d)] respectively.

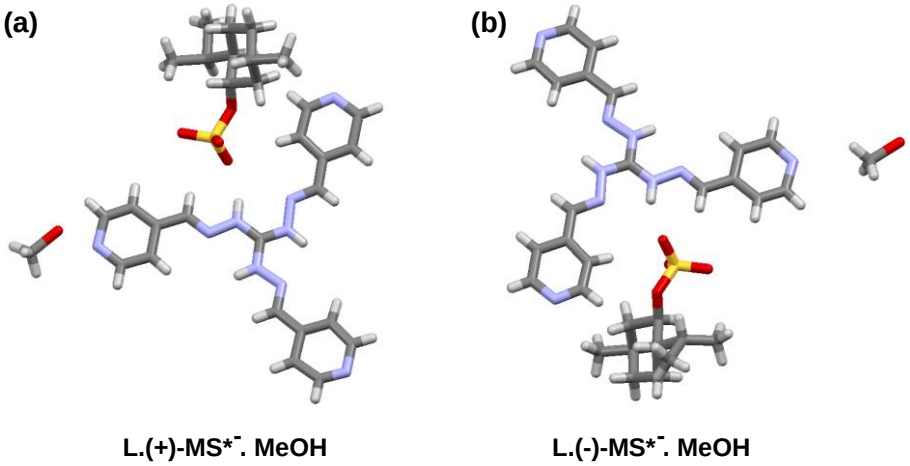


Figure S16. (a) and (b) crystal structure of both **L.(+)-MS*⁻** and **L.(–)-MS*⁻** gelators respectively in capped sticks model.

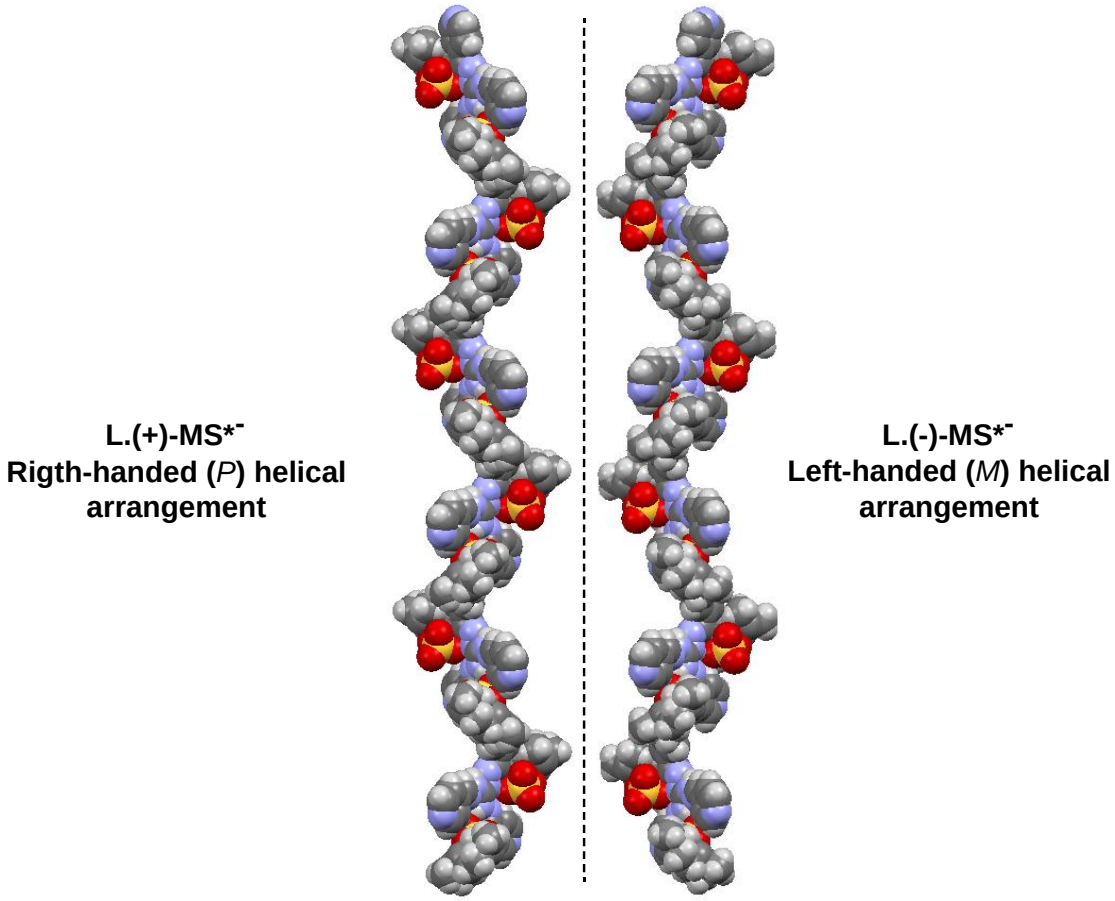


Figure S17. Right (*P*) and Left (*M*) handed helix like assembly of **L.(+)-MS*⁻** and **L.(–)-MS*⁻** in crystallographic state through Ion-Pair Assisted Hydrogen (IPA-H) bonds.

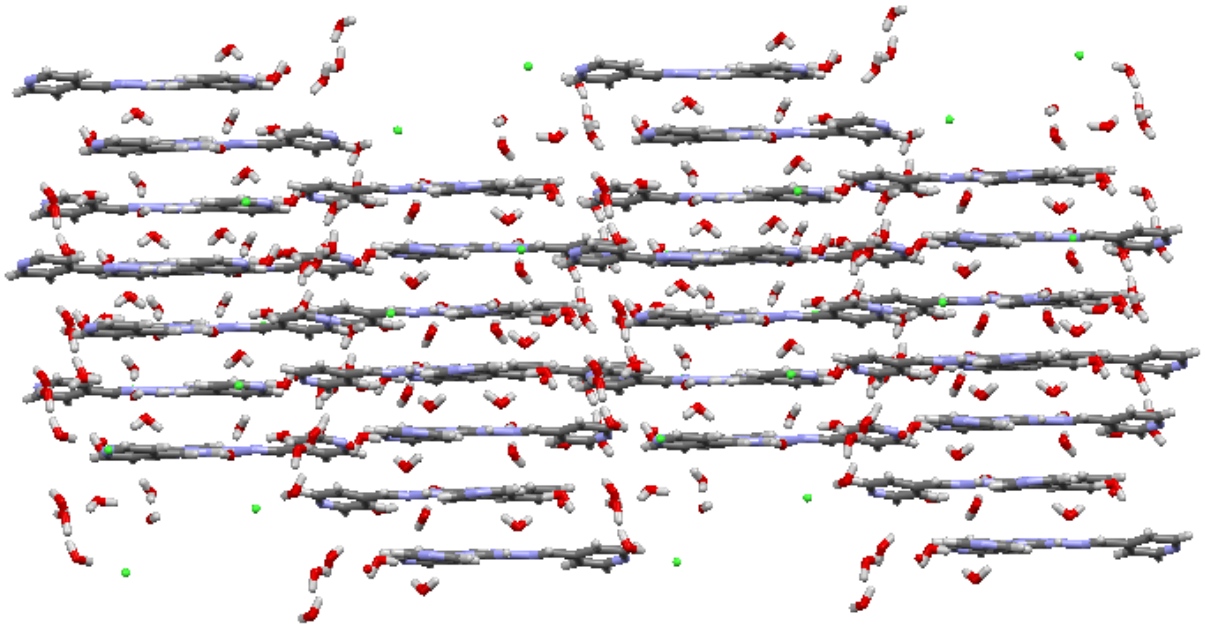


Figure S18. Crystal packing of **L.Cl**$^{-}$.

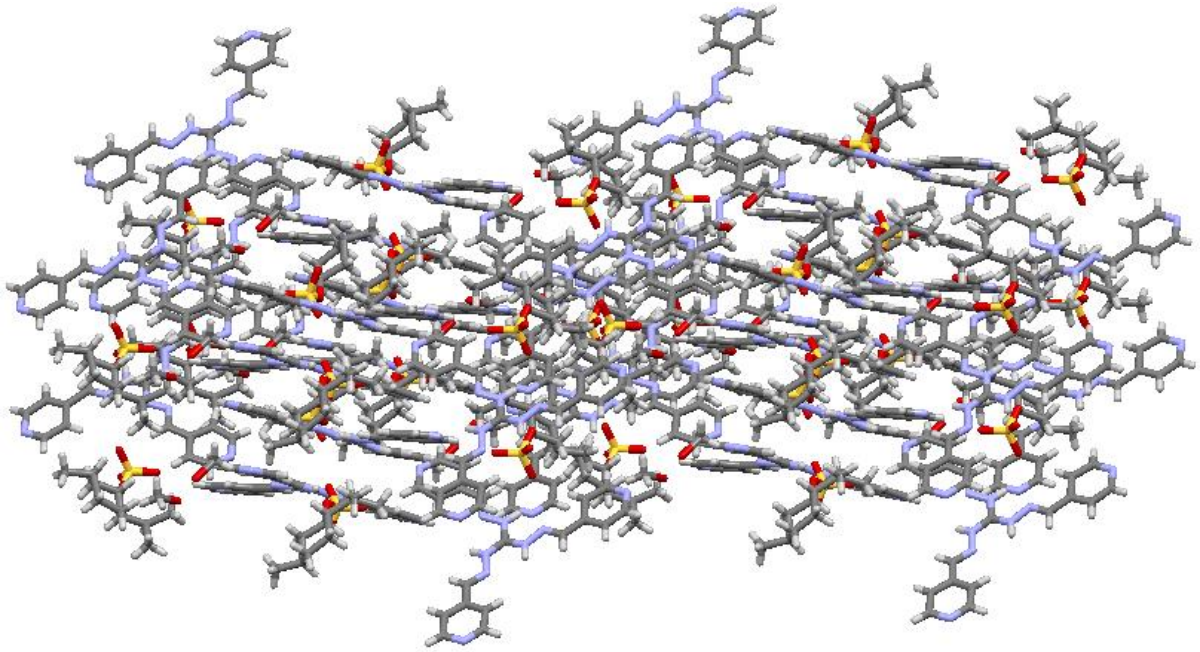


Figure S19. Crystal packing of **L.(+)-MS***$^{-}$.

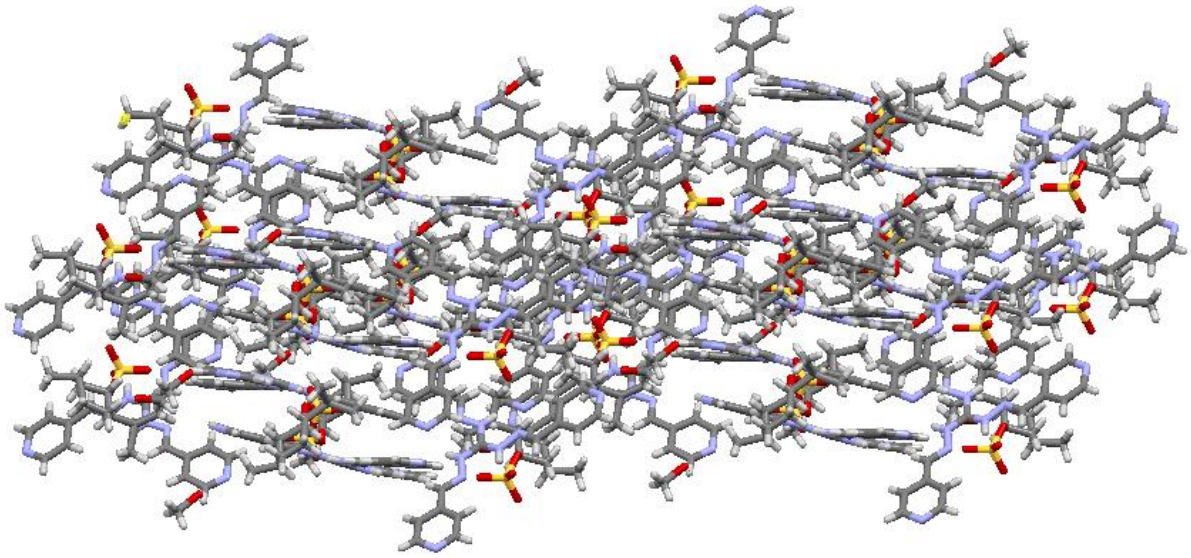


Figure S20. Crystal packing of **L.(–)-MS*⁻**.

6. Single crystal X-ray diffraction studies and details

Crystallographic refinement details. The intensity data were collected using a Bruker SMART APEXII CCD diffractometer, equipped with a fine focus 1.75 kW sealed tube CuK\α radiation (λ = 1.54178 Å) at 298(2) K, with increasing ω (width of 0.3° per frame) at a scan speed of 3 s per frame . The SMART software was used for data acquisition. Data integration and reduction were undertaken with SAINT and XPREP[S5] software. Multi-scan empirical absorption corrections were applied to the data using the program SADABS.[S6] Structures were solved by direct methods using SHELXL-2014 refined with full-matrix least squares on F^2 using SHELXL-2014.[S7] The hydrogen atoms attached to all the carbon atoms were geometrically fixed and the positional as well as temperature factors are refined isotropically. Structural illustrations have been drawn with Mercury for Windows.[S8] In all cases, non-hydrogen atoms are treated anisotropically. In other cases, the hydrogen atoms are geometrically fixed. PLATON/SQUEEZE[S9] was performed for complex **L.(+)-MS*⁻ (2)** and **L.(–)-MS*⁻ (3)** to remove disordered un assignable solvent molecules.

Table S1. Crystal structure details of L.Cl^{-} (1), L.(+)-MS*$^{-}$(2) and L.(–)-MS*$^{-}$(3).

Objects	**L.Cl^{-} (1)**	**L.(+)-MS*$^{-}$ (2)**	**L.(–)-MS*$^{-}$ (3)**
CCDC	1485416	1485417	1485418
Formula	C19 H36 Cl N9 O9	C30 H40 N9 O5 S	C30 H40 N9 O5 S
Fw	570.02	638.77	638.77
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P 21/c	P 21/n	P 21/n
a/Å	10.7037(4)	18.376(5)	18.411(4)
b/Å	28.6071(10)	7.384(2)	7.3949(16)
c/Å	9.3466(3)	26.915(7)	26.935(6)
α/deg	90.00	90.00	90.00
β/deg	104.8260(10)	104.570(17)	104.741(12)
γ/deg	90.00	90.00	90.00
V/Å^3	2766.66(17)	3534.5(16)	3546.4(14)
Z	4	4	4
Dc/g cm^{-3}	1.368	1.200	1.196
μ Mo Kα/mm^{-1}	1.773	1.219	1.215
T/K	298(2)	298(2)	298(2)
θ max.	68.37	59.75	64.57
Total no. of reflections	53881	39790	37796
Independent reflections	5082	6286	5767
Observed reflections	4595	3163	2640
Parameters refined	345	350	350
R_1,I>2σ(I)	0.0722	0.2114	0.1932
wR_2 (all data)	0.2170	0.5381	0.5230
R(int)	0.0379	0.2347	0.1652
GOF (F^2)	1.003	1.415	1.617

Table S2. Hydrogen bonding contacts of L.Cl^{-} (1), L.(+)-MS*$^{-}$(2) and L.(–)-MS*$^{-}$(3).

Complex	D−H···A	d(H···A)/Å	d(D···A)/Å	<D-H··· A/º
L.Cl^{-} (1)	O1···Cl1		3.088(2)	
	O7−H7A··· Cl1	2.383	3.229(1)	173.66
	O2···Cl1	-	3.084(3)	-
	O5−H5B···Cl1	2.167	3.145()	160
	C11−H11···Cl1	2.715	3.546(1)	149
	C17−H17···Cl1	2.774	3.667(1)	160
L.(+)-MS*$^{-}$ (2)	C5−H5···O1	2.334	3.228(1)	161
	N7−H7···O2	2.058	2.881(1)	160
	C10−H10···O2	2.460	3.384(1)	172
	C14−H14···O2	2.444	3.245(1)	144
	N1−H···O3	2.283	2.993(1)	140
	C2−H2···O3	3.208	2.481(1)	135
	C19−H19···O3	2.532	3.434(1)	163
	C10−H10···O4	2.646	3.340(1)	131
L.(–)-MS*$^{-}$ (3)	C6−H6···O1	2.335	3.234(1)	162
	N4−H4···O2	2.306	3.031(1)	142
	C2−H2···O2	2.547	3.263(1)	132
	C10−H10···O2	2.502	3.406(1)	164
	N1−H···O3	2.017	2.839(1)	159
	C8−H8···O3	2.350	3.160(1)	145
	C16−H16···O3	2.529	3.454(1)	173
	C16−H16···O4	2.665	3.363(1)	132

7. Supporting References

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