Supporting Information

Differential response of cholesterol based pyrimidine systems with oxyethylene type spacers to gelation and mesogen formation in the presence of alkali metal ions

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Table of contents:

a) Physical Measurements and Instrumentation.

Gelation Studies. The gelation test of each of these compounds was performed in various organic solvents. A weighed amount of a particular compound was added into a sealed glass vial and heated to get a clear solution. The solution was then cooled to room temperature and left for 0.5 h to check the stability of the gel using inverse flow method and each experiment was performed in duplicate. If a gel was formed, it was evaluated quantitatively by determining the minimum gelator concentration (MGC) defined as the minimum amount of gelator required to immobilize 1 mL of a particular solvent. When the compound did not dissolve completely, it was labelled as "insoluble" whereas "precipitation" indicated that precipitation occurred with cooling from its solution.

UV-Vis and Circular Dichroism Spectroscopy. The UV-Vis and circular dichroism spectra were recorded on a Shimadzu model 2100 spectrophotometer and JASCO J-815 spectrometer respectively, equipped with appropriate temperature controller baths.

Scanning Electron Microscopy (SEM). The gels were carefully scooped onto the brass stubs and were allowed to freeze-dry overnight. The samples were then coated with gold vapour and analyzed on a Quanta 200 SEM operated at 15 kV.

Atomic Force Microscopy (AFM). Samples were drop caste on freshly cleaved mica sheets and air-dried at room temperature. Each of the samples was analyzed using Bruker Dimension ICON with ScanAsyst instrument in the tapping mode.

Solid Phase Differential Scanning Calorimetry (DSC). Solid phase DSC experiment of each of these compounds in the solid state was performed using a Differential Scanning Calorimeter (DSC; Perkin-Elmer, Model Pyris 1D) with heating and cooling rate fixed at 5 ºC min^{-1} for all the measurements. This technique was used to detect the thermal transitions and to monitor the rate of heat flow from the sample during phase changes in the temperature range of 30-200 ºC.

Polarized Optical Microscopy (POM). The changes in the birefringent textures of each of these compounds during thermal phase transition were followed under a polarized optical microscope (Olympus BX51) equipped with a heating stage (Mettler FP82HT) and a central processor (Mettler FP90). Before experiment, 2-3 mg sample was placed on glass slide and covered with a cover slip. A sample was heated until it reached the isotropic state and then it

was cooled slowly to 30 ºC with a cooling rate of 5 ºC min^{-1}. Repeated heating and cooling cycles were performed to confirm the reproducibility of the phases appeared under POM.

Wide-angle X-ray diffraction (WAXD). WAXD measurements were recorded on a Philips-X'Pert (PANanalytical XRD instrument). The X-ray beam generated with rotating Cu anode at the wavelength of Kα beam at 1.5418Å.

b) Materials and Instruments. All chemicals, solvents and silica gel for TLC and column chromatography were obtained from well-known commercial sources and were used without further purification, as appropriate. Solvents were distilled and dried by standard procedure before use. FT-IR studies were performed on a Perkin-Elmer FT-IR Spectrometer BX model by incorporating the samples in KBr disk and were reported in wave numbers (cm^{-1}). ^{1}H-NMR and ^{13}C-NMR spectra were recorded in Bruker-400 Avance NMR spectrometer. Chemical shifts were reported in ppm downfield from the internal standard tetramethylsilane (TMS).

d) Synthetic procedure and characterization data.

Synthesis. Compounds **1**-**6** were synthesized according to the reaction scheme 1 and were characterized by ^{1}H-NMR, ^{13}C-NMR, FT-IR and ESI-MS. Compounds **2**, **3** and **4** were synthesized according to the previous reports.[1]

General procedure for the synthesis of phthalimide derivatives (5a-5c). The respective alcohol (0.2 mmol) was dissolved in dry DMF (6 mL). Phthalimide (0.147 gm, 1 mmol), triphenylphosphine (0.262 gm, 1 mmol) and diisopropyl azodicarboxylate (0.176 mL, 1 mmol) were added to the reaction mixture and stirred at room temperature for 6 h. The reaction was quenched by addition of water (4 mL) and the separated aqueous layer was extracted with $CHCl_3$ (10 mL). Finally, the organic layer was washed with water (5 mL), brine (5 mL), dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by column chromatography over silica gel using mixture of petroleum ether and ethyl acetate.

Cholest-5-en-3β-oxypent-3-oxan-5-phthalimide (5a). Yield: 95%; FT-IR (neat): 2936, 2903, 1714, 1608, 1593, 1470 cm^{-1}; ESI-MS: m/z 626.4185 $[M+Na]^+$; ^{1}H-NMR (400 MHz, $CDCl_3$, rt, TMS): δ (ppm) 0.67 (s, 3H), 0.85-2.34 (m, 40H), 3.12-3.21 (m, 1H), 3.60-3.93 (m, 8H), 5.31 (d, 1H, *J* = 4.0 Hz), 7.70-7.72 (m, 2H), 7.83-7.86 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, rt, TMS): δ (ppm) 11.72, 18.52, 19.22, 21.57, 22.42, 22.67, 23.69, 24.12, 27.87, 28.15, 31.75, 31.8, 35.65, 36.06, 36.7, 37.1, 38.85, 39.38, 39.66, 42.19, 50.09, 56.07, 56.65, 67.13, 67.71, 69.95, 79.21, 121.34, 123.42, 131.97, 134.12, 140.94, 168.08.

Cholest-5-en-3β-oxy-oct-3,6-oxan-8-phthalimide (5b). Yield: 96%; FT-IR (neat): 2937, 1714, 1613, 1514, 1468 cm^{-1}; ESI-MS: m/z 670.445 $[M+Na]^+$; ^{1}H-NMR (400 MHz, $CDCl_3$, rt, TMS): δ (ppm) 0.67 (s, 3H), 0.85-2.36 (m, 40H), 3.13-3.21 (m, 1H), 3.57-3.93 (m, 12H), 5.34 (d, 1H, *J* = 4.0 Hz), 7.70-7.75 (m, 2H), 7.83-7.86 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, rt, TMS): δ (ppm) 11.63, 18.57, 19.23, 21.57, 22.41, 22.67, 23.68, 24.15, 27.87, 28.19, 31.76, 31.81, 35.64, 36.05, 36.72, 37.12, 39.89, 39.38, 39.65, 42.18, 50.05, 56.02, 56.65, 66.99, 67.83, 69.98, 70.39, 70.76, 79.4, 121.37, 123.09, 131.99, 133.75, 140.87, 168.07.

Cholest-5-en-3β-oxy-undeca-3,6,9-oxan-11-phthalimide (5c). Yield: 97%; FT-IR (neat): 2929, 2853, 1747, 1638, 1593, 1456 cm^{-1}; ESI- MS: m/z 714.48 $[M+Na]^+$; ^{1}H-NMR (400 MHz, $CDCl_3$, rt, TMS): δ (ppm) 0.67 (s, 3H), 0.85-2.44 (m, 40H), 3.13-3.21 (m, 1H), 3.60-

3.93 (m, 16H), 5.33 (d, 1H, J = 4.0 Hz), 7.71-7.75 (m, 2H), 7.82-7.86 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, rt, TMS): δ (ppm) 11.71, 18.57, 19.24, 21.57, 22.42, 22.67, 23.68, 24.14, 27.88, 28.21, 31.75, 31.81, 35.64, 36.05, 36.73, 37.13, 38.88, 39.43, 39.69, 42.18, 50.02, 56.02, 56.64, 67.11, 67.78, 69.9, 69.96, 70.4, 70.47, 70.7, 79.31, 121.37, 123.38, 131.74, 134.07, 140.93, 168.22.

General procedure for the synthesis of amine derivatives (6a-6c). Each respective phthalimide derivative (0.15 mmol) was dissolved in pyridine (5 mL). Hydrazine monohydrate (36 μL, 0.75 mmol) was added to each solution, and the mixture was stirred for 24 h at room temperature. Water (5 mL) was added to the resulting mixture and the aqueous layer was extracted with chloroform (2 × 10 mL). The organic layer was separated, washed with water (5 mL), brine (5 mL) and concentrated under reduced pressure to get a yellowish white gummy solid. The crude product was purified by column chromatography over silica gel using mixture of petroleum ether and ethyl acetate.

Cholest-5-en-3β-oxypent-3-oxan-5-amine (6a). Yield: 82%; FT-IR (neat): 3366, 2934, 2868, 1645, 1467 cm^{-1}; ESI-MS: m/z 496.413 $[M+Na]^+$; ^{1}H-NMR (400 MHz, $CDCl_3$, rt, TMS): δ (ppm) 0.67 (s, 3H), 0.85-2.39 (m, 42H), 2.97 (t, 2H, J = 4.4 Hz), 3.16-3.23 (m, 1H), 3.48-3.63 (m, 6H), 5.35 (d, 1H, J = 4.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$, rt, TMS): δ (ppm) 11.88, 18.74, 19.39, 21.09, 22.57, 22.83, 23.84, 24.31, 28.02, 28.25, 31.86, 31.96, 35.8, 36.21, 36.89, 37.19, 37.24, 39.13, 39.53, 39.79, 42.34, 50.14, 56.21, 56.79, 66.55, 69.23, 70.5, 79.76, 121.49, 140.81.

Cholest-5-en-3β-oxy-oct-3,6-oxan-8-amine (6b). Yield: 83%; FT-IR (neat): 3363, 2934, 2869, 1658, 1467 cm^{-1}; ESI-MS: m/z 518.45 $[M+H]^+$; ^{1}H-NMR (400 MHz, $CDCl_3$, rt, TMS): δ (ppm) 0.67 (s, 3H), 0.85-2.38 (m, 42H), 2.97 (t, 2H, J = 4.4 Hz), 3.16-3.23 (m, 1H), 3.48-3.63 (m, 10H), 5.35 (d, 1H, J = 4.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$, rt, TMS): δ (ppm) 11.95, 18.57, 19.4, 21.44, 22.63, 22.72, 23.36, 24.15, 27.15, 28.03, 31.24, 31.59, 35.77, 36.18, 36.73, 37.45, 37.83, 39.02, 39.52, 40.2, 41.47, 51.23, 56.28, 57.83, 67.36, 69.73, 70.27, 70.79, 70.97, 79.35, 121.13, 140.95.

Cholest-5-en-3β-oxy-undeca-3,6,9-oxan-11-amine (6c). Yield: 85%; FT-IR (neat): 3365, 2934, 2868, 1727, 1667, 1467 cm^{-1}; ESI-MS: m/z 562.483 $[M+H]^+$; ^{1}H-NMR (400 MHz, $CDCl_3$, rt, TMS): δ (ppm) 0.67 (s, 3H), 0.85-2.39 (m, 42H), 2.94 (t, 2H, J = 4.4 Hz), 3.16-3.20 (m, 1H), 3.58-3.66 (m, 14H), 5.34 (d, 1H, J = 4.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$, rt,

TMS): δ (ppm) 11.62, 18.58, 19.24, 21.80, 22.42, 22.67, 23.68, 24.15, 27.87, 28.09, 31.76, 31.81, 35.64, 36.05, 36.73, 37.09, 38.85, 38.92, 39.38, 39.65, 42.15, 50.05, 56.02, 56.64, 67.09, 69.95, 70.23, 70.38, 70.44, 70.48, 70.74, 79.6, 121.13, 140.93.

General procedure for the synthesis of pyrimidine derivatives (1a-1c). Compound **2** (0.77 mmol) was dissolved in dry CH_2Cl_2 at room temperature and treated with a solution of corresponding amines (1.93 mmol) in CH_2Cl_2 followed by addition of N,N-diisopropylethylamine (2.3 mmol). The reaction mixture was stirred for 6 h at room temperature. The reaction mixture was diluted with CH_2Cl_2 and the organic layer was washed with H_2O. After drying over anhydrous Na_2SO_4, solvent was evaporated under reduced pressure and the resultant residue was purified by column chromatography over silica gel using a mixture of chloroform and methanol.

4-chloro-2,6-bis(cholest-5-en-3β-oxypent-3-oxan-5-amino)-pyrimidine-5-carbaldehyde (1a). Yield: 81%; FT-IR (neat): 3261, 2934, 2867, 1727, 1645, 1585, 1555, 1437, 1466, 1416 cm^{-1}; ESI -MS: m/z 1107.79 $[M+Na]^+$; ^{1}H-NMR (400 MHz, $CDCl_3$, rt, TMS): δ (ppm) 0.67 (s, 6H), 0.85-2.35 (m, 80H), 3.15-3.20 (m, 2H), 3.62-3.73 (m, 16H), 5.34 (s, 2H), 6.026 (s, 1H), 9.44 (s, 1H), 10.03 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$, rt, TMS): δ (ppm) 11.85, 18.71, 19.36, 21.06, 22.55, 22.8, 23.83, 24.28, 27.99, 28.22, 31.89, 31.94, 35.76, 36.19, 36.85, 37.23, 39.04, 39.51, 39.79, 42.32, 50.18, 56.17, 56.78, 67.38, 69.34, 70.8, 79.56, 101.96, 121.54, 140.88, 160.81, 162.4, 165.81, 188.31.

4-chloro-2,6-bis(cholest-5-en-3β-oxy-oct-3,6-oxan-8-amino)-pyrimidine-5-carbaldehyde (1b). Yield: 83%; FT-IR (neat): 3283, 2935, 2869, 1725, 1676, 1654, 1638, 1588, 1560, 1466, 1419 cm^{-1}; ESI-MS: m/z 1195.851 $[M+Na]^+$; ^{1}H-NMR (400 MHz, $CDCl_3$, rt, TMS): δ (ppm) 0.67 (s, 6H), 0.85-2.39 (m, 80H), 3.14-3.20 (m, 2H), 3.65-3.72 (m, 24H), 5.32 (s, 2H), 6.12 (s, 1H), 9.44 (s, 1H), 10.02 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$, rt, TMS): δ (ppm) 11.83, 18.70, 19.35, 21.05, 22.54, 22.79, 23.82, 24.27, 27.98, 28.21, 31.88, 31.92, 35.76, 36.18, 36.85, 37.22, 39.04, 39.5, 39.77, 42.3, 50.17, 56.16, 56.76, 67.26, 69.3, 70.5, 70.64, 70.98, 79.52, 101.93, 121.53, 140.97, 160.79, 162.36, 165.77, 188.28.

4-chloro-2,6-bis(cholest-5-en-3β-oxy-undeca-3,6,9-oxan-11-amino)-pyrimidine-5-carbaldehyde (1c). Yield: 85%; FT-IR (neat): 3282, 2934, 2868, 1725, 1641, 1587, 1554, 1467, 1415 cm^{-1}; ESI-MS: m/z 1283.9 $[M+Na]^+$; ^{1}H-NMR (400 MHz, $CDCl_3$, rt, TMS): δ (ppm) 0.67 (s, 6H), 0.85-2.39 (m, 80H), 3.16-3.18 (m, 2H), 3.64-3.71 (m, 32H), 5.32 (s, 2H),

6.22 (s, 1H), 9.44 (s, 1H), 10.02 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$, rt, TMS): δ (ppm) 11.83, 18.70, 19.35, 21.04, 22.53, 22.78, 23.81, 24.27, 27.98, 28.2, 31.88, 31.93, 35.76, 36.18, 36.85, 37.23, 39.04, 39.5, 39.78, 42.3, 50.18, 56.16, 56.76, 67.25, 69.31, 70.32, 70.59, 70.67, 70.85, 70.87, 79.46, 101.91, 121.50, 140.96, 160.80, 162.36, 165.76, 188.27.

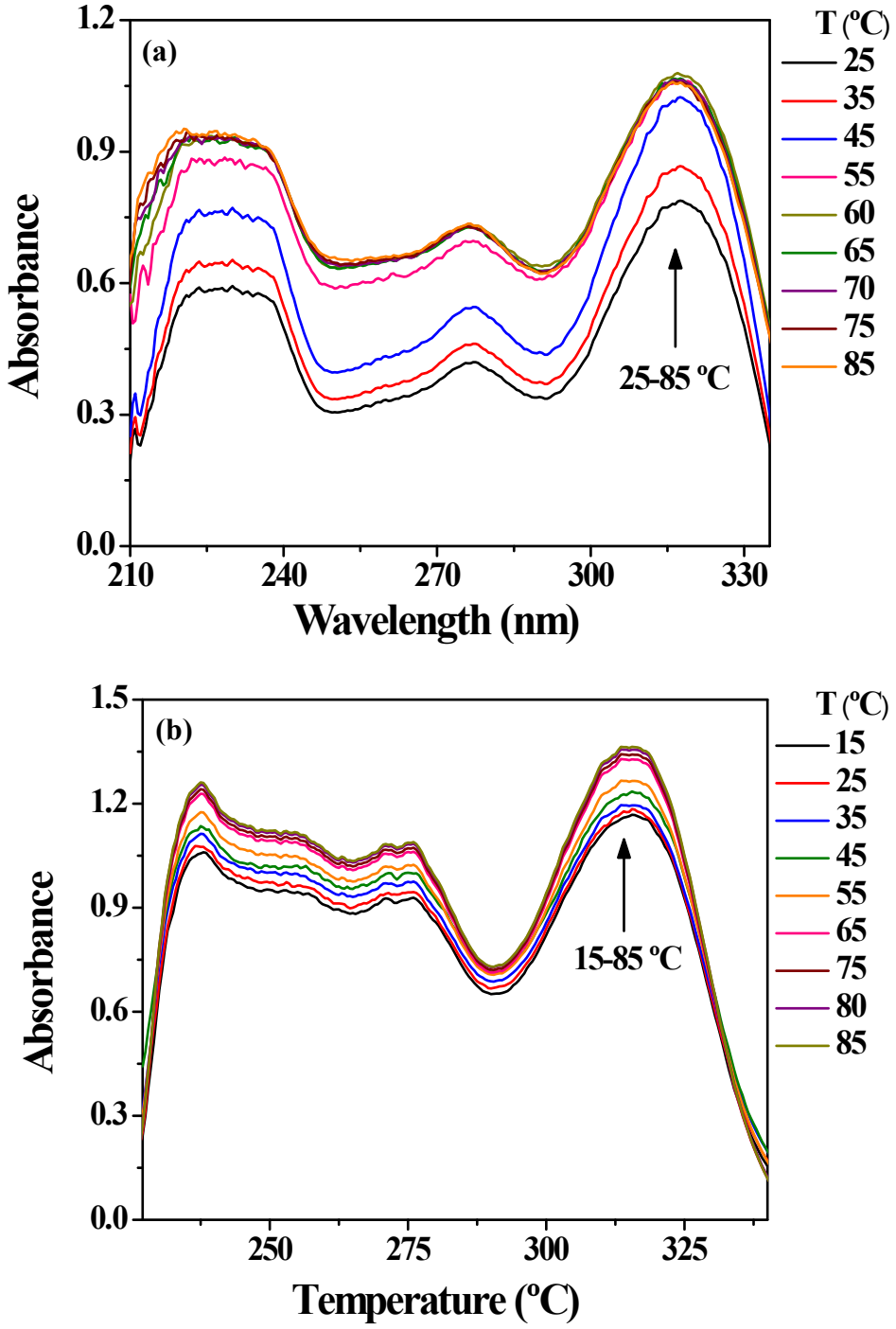

Figure S1. Temperature-dependent changes in the UV-Vis spectra of **1a** in (a) *n*-butanol and (b) *n*-dodecane at the concentration of 0.046 mM.

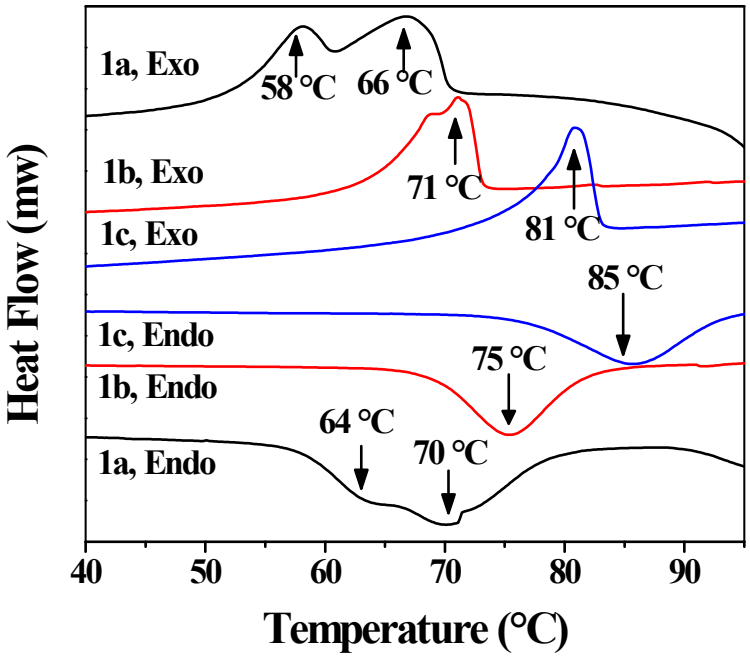

Figure S2. DSC thermograms of (a) **1a** (b) **1b** and (c) **1c**.

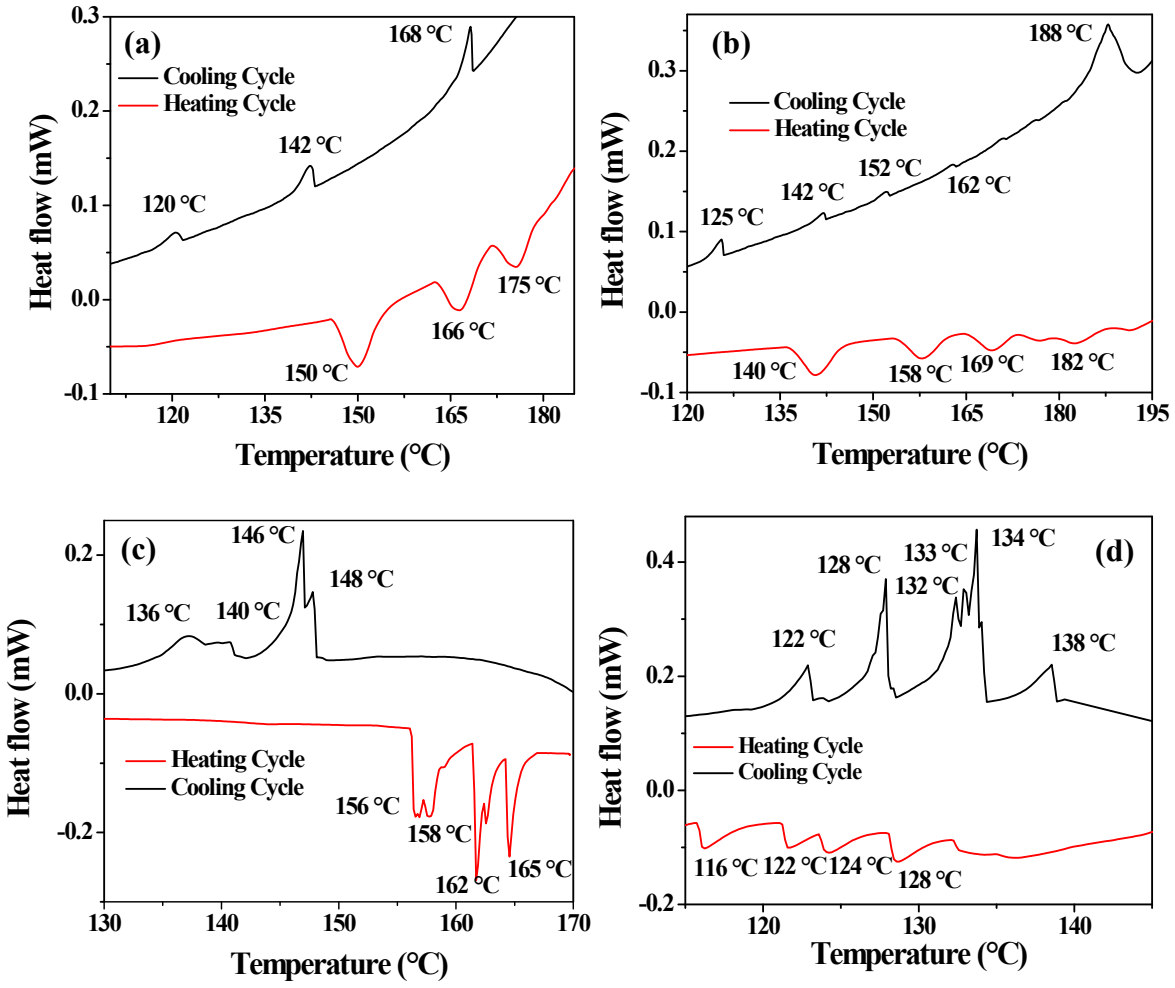

Figure S3. DSC thermograms of (a) **1b**-Li^+ (1 equiv.), (b) **1c**-Li^+ (1 equiv.), (c) **1b**-Na^+ (1 equiv.) and (d) **1c**-Na^+ (1 equiv.).

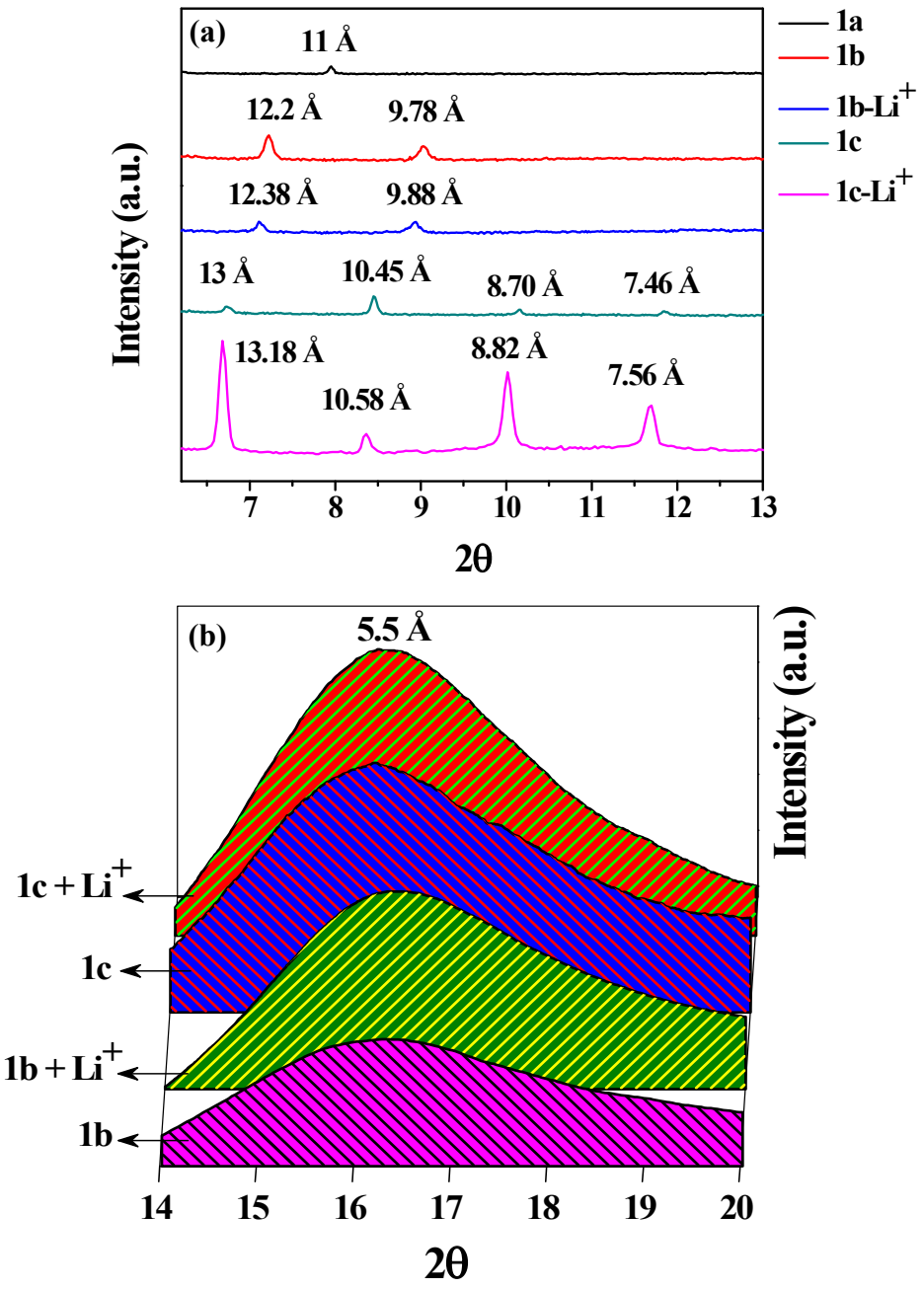

Figure S4. WAXD plots of **1a-c** and **1b-Li**$^+$ (1 equiv.) and **1c-Li**$^+$ (1 equiv.) in solid state.

Table S1. Gelation ability of compounds **1a-c** in different solvents.[a]

Solvent	1a (*n* = 2)	1b (*n* = 3)	1c (*n* = 4)
Benzene	S	S	S
Toluene	S	S	S
n-Hexane	P	P	P
n-Dodecane	OG (4.60)	P	P
$CHCl_3$	S	S	S
CH_2Cl_2	S	S	S
THF	S	S	S
tert-Butanol	P	P	P
n-Butanol	OG (3.68)	S	S

[a]OG = opaque gel, P = precipitate and S = soluble. Parentheses contain the mgc in mM of the individual gelator molecule.

Table S2. Wide-angle X-ray diffraction (WAXD) data of the xerogels of **1a** obtained from *n*-butanol and *n*-dodecane.

Solvent	Phase	d_{obs} [Å]	*hkl*	Lattice constants [Å]
n-butanol	Col_h	24	100	a = 27.7
		15	110	
		12	200	
n-dodecane	Col_h	19	100	a = 21.9
		12	110	
		9	200	

Table S3. Wide-angle X-ray diffraction (WAXD) data of the compounds **1a-c** and their associated Li^+-complexes.

Compound	**Phase**	d_{obs} **[Å]**	***hkl***	**Lattice constants [Å]**	**~ n[a]**
1a	Col_h	22 14 11	100 110 200	a = 25.4	2
1b	Col_h	24.5 16 12.2 9.7	100 110 200 210	a = 28.3	2
1b-Li^+	Col_h	24.9 16.5 12.4 9.8	100 110 200 210	a = 28.8	2
1c	Col_h	24.7 16.8 13 10.4 8.7 7.4	100 110 200 210 300 220	a = 28.5	2
1c-Li^+	Col_h	27 18 13.3 10.5 8.8 7.5	100 110 200 210 300 220	a = 31.2	2

[a] Number of molecules arranged side-by-side in a single column slice.

Table S4. Wide-angle X-ray diffraction (WAXD) data of the Na^+ complexes of **1a-c**.

Compound	**Phase**	d_{obs} **[Å]**	***hkl***	**Lattice constants [Å]**	**~ n[a]**
1b-Na$^+$	Col_h	24.7 16.4 12.4	100 110 200	a = 28.5	2
1c-Na$^+$	Col_h	25.9 17.3 13	100 110 200	a = 29.9	2

[a] Number of molecules arranged side-by-side in a single column slice.

References.

1. a) A. Bajaj, P. Kondiah and S. Bhattacharya, *J. Med. Chem.* **2007**, *50*, 2432-2442; b) S. Bhattacharya and Y. Krishnan-Ghosh, *Langmuir* **2001**, *17*, 2067-2075; c) M. A. Müller, M. Gaplovsky, J. Wirz and W.-D. Woggon, *Helv. Chim. Acta* **2006**, *89*, 2987-3001.