Electronic supplementary Information

Structure-property relationships of symmetrical and asymmetrical azobenzene derivatives as gelators and their self assemblies

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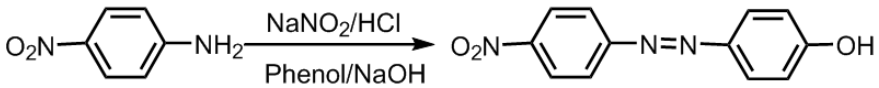
SEM measurements

Gel that was prepared in a sample tube was frozen by liquid nitrogen. Next, the sample was evaporated using a vacuum pump under reduced pressure for 1 day at room temperature. The obtained sample was coated with platinum using sputter coating. The accelerating voltage of the electron microscope was 25 kV, and the beam current was 10 μA.

TEM measurements

A piece of the gel was placed in a carbon-coated copper grid. The sample was dried using a vacuum pump under reduced pressure for 1 day at room temperature. The accelerating voltage of the transmission electron microscope was 120 kV, and the beam current was 65 A.

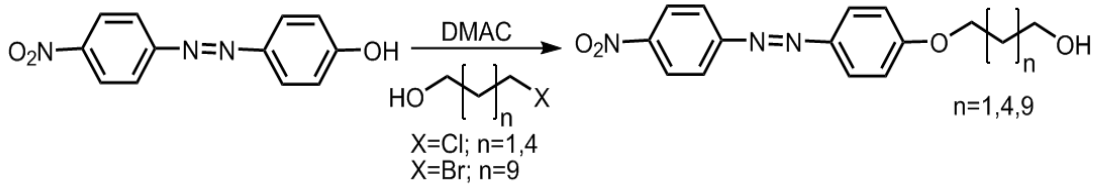
Synthesis of 4-hydroxy-4'-nitroazobenzene (1)[1a]



4-Nitroaniline (5 g, 36.32 mmol) was placed in a conical flask and dissolved in a mixture of 6 ml of 12N HCl solution and 120 ml of water with stirring in an ice bath. Next, an ice-cold solution of sodium nitrite (3.53 g, 51.16 mmol) was added dropwise with constant stirring. The temperature of the solution was not allowed to rise above 2°C. In another flask, phenol (5 g, 53.19 mmol) was dissolved in NaOH solution (4.4 g, 110 mmol in 100 ml water) and stirred for 30 min in an ice bath at 0 ℃. The diazotized solution was slowly added to this alkaline phenolic solution with vigorous stirring at 0 ℃. Next, the reaction mixture was allowed to stand in the ice bath for 30 min before neutralizing with HCl to precipitate the product. The resulting precipitate was filtered, washed with water and dried *in vacuo*. The crude product was recrystallised from ethanol to yield a red-brown solid (yield 63%).

FT-IR (KBr, ν_{max}/cm^{-1})：3457 (-OH), 1515, 1585 (C-C in Ar), 1342 (NO_2). ^{1}H-NMR ($CDCl_3$, 500MHz, δ in ppm)：7.0 (d, 2H, Ar-H), 7.9-8.0 (m, 4H, Ar-H), 8.4 (d, 2H, Ar-H).

Synthesis of 3-hydroxypropyloxy-4-phenylazo-4'-nitrobenzene (2a)[1b]



Compound **2a** was synthesized as follows: Compound **1** (4 g, 0.0165 mol) was dissolved in N,N-dimethylacetamide (DMAC) and K_2CO_3 (1.1 g, 0.0198 mol) before adding a catalytic amount of KI (10%). The mixture was heated to reflux at 80°C, and 3-chloro-propanol (0.280 mol, 30 ml) was added dropwise to the reaction mixture, and the heating was continued for 48 h. Next, the reaction mixture was allowed to cool to room temperature before pouring into 200 ml of water and acidifying with a dilute HCl solution. The resulting precipitate was filtered, washed with water and dried *in vacuo*. Next, the crude product was recrystallized from ethanol (52%).

FT-IR (KBr, ν_{max}/cm^{-1}) : 3440 (-OH), 2860, 2935 (CH_2),1510, 1596 (C-C in Ar), 1345 (NO_2), 1266 (COC). ^{1}H-NMR ($CDCl_3$, 500MHz, δ in ppm) : 3.9 (d, 2H, CH_2), 4.2-4.3 (d, 2H, CH_2), 7.0-7.1 (d, 2H, Ar-H), 7.9-8.1 (m, 4H, Ar-H), 8.4 (d, 2H, Ar-H).

A similar procedure was adopted for the synthesis of precursors **2b** and **2c** by using 6-chloro-hexanol and 11-bromo-undecanol instead of 3-chloro-propanol in the above procedure.

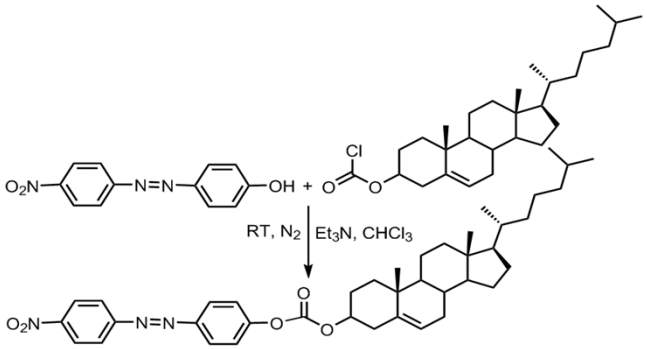
Synthesis of 6-hydroxyhexyloxy-4-phenylazo-4'-nitrobenzene (2b)

Yield (59%); FT-IR (KBr, ν_{max}/cm^{-1}) : 3552 (-OH), 2864, 2941 (CH_2),1506, 1598 (C-C in Ar), 1345 (NO_2), 1258 (COC). ^{1}H-NMR ($CDCl_3$, 500MHz, δ in ppm) : 3.7 (d, 2H, CH_2), 4.1 (d, 2H, CH_2), 7.0-7.1 (d, 2H, Ar-H), 8.0 (m, 4H, Ar-H), 8.4 (d, 2H, Ar-H).

Synthesis of 11-hydroxyundecyloxy-4-phenylazo-4'-nitrobenzene (2c)

Yield (74%); FT-IR (KBr, ν_{max}/cm^{-1}) : 2858, 2920 (CH_2),1500, 1593 (C-C in Ar), 1340 (NO_2), 1252 (COC). ^{1}H-NMR ($CDCl_3$, 500MHz, δ in ppm) : 3.6-3.7 (d, 2H, CH_2), 4.0-4.1 (d, 2H, CH_2), 7.0-7.1 (d, 2H, Ar-H), 8.0 (m, 4H, Ar-H), 8.3-8.4 (d, 2H, Ar-H).

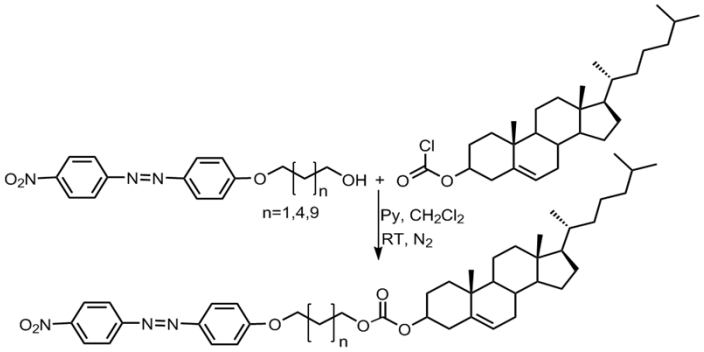
Cholesteryl (4-nitro-azobenzene-4′-oxy) carbonate (AAC0**)**



Compound **1** (2.432 g, 10 mmol) and triethylamine (3.036 g, 30 mmol) were placed in double neck round bottom flasks with nitrogen inlets and dissolved in dry chloroform. Next, a small amount of 4-(dimethylamino)pyridine (DMAP) dissolved in chloroform was slowly added to these solutions with constant stirring under a nitrogen atmosphere. Then, cholesteryl chloroformate (4.491 g, 10 mmol) that was dissolved in chloroform was added dropwise to the solutions through a funnel. After this addition, the reaction mixture was stirred at room temperature for 48 h. Next, the contents of the flasks were extracted with excess chloroform and washed with aqueous sodium bicarbonate, a brine solution and water. This procedure was used to obtain the organic phase, which was dried over anhydrous magnesium sulfate and then concentrated. The resulting crude product was recrystallized from ethanol to obtain a pure final compound (yield 82%).

FT-IR (KBr, ν_{max}/cm^{-1}) : 2875, 2950 (CH_2), 1764 (C=O), 1494, 1587 (C-C in Ar), 1346 (NO_2), 1251 (COC). ^{1}H-NMR ($CDCl_3$, 500MHz, δ in ppm) : 0.6-0.7 (s, 3H, CH_3 in chol.), 2.5 (d, 2H, CH_2CH in chol.), 4.6 (m, 1H, OCH in chol.), 5.4-5.5 (t, 1H, $CHCH_2$ in chol.), 7.4 (d, 2H, Ar-H), 8.0-8.1 (m, 4H, Ar-H), 8.4 (d, 2H, Ar-H).

Cholesteryl-n-(4-nitro-azobenzene-4′-oxy) alkyl carbonate (AAC3, AAC6 and AAC11**)** [1c]



Compound **2a** (2.477 g, 8.22 mmol) was placed in a double neck round bottom flask and dissolved in dry dichloromethane under a nitrogen atmosphere. Pyridine (1.63 g, 20.61 mmol) was added to this solution before stirring at room temperature for 30 min. Next, cholesteryl chloroformate (7.38 g, 16.44 mmol) dissolved in dichloromethane was added dropwise to this mixture through a dropping funnel, and the mixture was stirred for 48 h. Finally, the reaction mixture was washed with water, and the organic phase was dried over anhydrous magnesium sulfate and then concentrated. The resulting crude product was purified using column chromatography (CH_2Cl_2/*n*-hexane, 1:1 v/v) to yield the pure final compound (yield 68%). A similar procedure was adopted for the synthesis of the AAC6 and AAC11 compounds by using the respective starting materials of 2b and 2c..

FT-IR (KBr, ν_{max}/cm^{-1}) : 2888, 2944 (CH_2), 1743 (C=O), 1521, 1583 (C-C in Ar), 1342 (NO_2), 1249 (COC). ^{1}H-NMR ($CDCl_3$, 500MHz, δ in ppm) : 0.7 (s, 3H, CH_3 in chol.), 2.4 (d, 2H, CH_2CH in chol.), 4.1-4.4 (t, 4H, OCH_2), 4.5 (m, 1H, OCH in chol.), 5.4 (t, 1H, $CHCH_2$ in chol.), 7.0-7.1 (d, 2H, Ar-H), 7.9-8.0 (m, 4H, Ar-H), 8.3-8.4 (d, 2H, Ar-H).

Cholesteryl-6-(4-nitro-azobenzene-4′-oxy) hexyl carbonate (AAC6)

Yield 71%; FT-IR (KBr, ν_{max}/cm^{-1}) : 2867, 2940 (CH_2), 1745 (C=O), 1519, 1602 (C-C in Ar), 1344 (NO_2), 1255 (COC). ^{1}H-NMR ($CDCl_3$, 500MHz, δ in ppm) : 0.7 (s, 3H, CH_3 in chol.), 2.5-2.6 (d, 2H, CH_2CH in chol.), 3.6-4.1 (t, 4H, OCH_2), 4.2 (m, 1H, OCH in chol.), 5.3-5.5 (t, 1H, $CHCH_2$ in chol.), 7.0-7.1 (d, 2H, Ar-H), 7.9-8.1 (m, 4H, Ar-H), 8.4 (d, 2H, Ar-H).

Cholesteryl-11-(4-nitro-azobenzene-4′-oxy) undecyl carbonate (AAC11)

Yield 69%; FT-IR (KBr, ν_{max}/cm^{-1}) : 2850, 2938 (CH_2), 1733 (C=O), 1525, 1600 (C-C in Ar), 1342 (NO_2), 1253 (COC). ^{1}H-NMR ($CDCl_3$, 500MHz, δ in ppm) : 0.6-0.7 (s, 3H, CH_3 in chol.), 2.3-2.4 (d, 2H, CH_2CH in chol.), 4.0-4.2 (t, 4H, OCH_2), 4.4-4.5 (m, 1H, OCH in chol.), 5.4 (t, 1H, $CHCH_2$ in chol.), 7.0 (d, 2H, Ar-H), 7.9-8.0 (m, 4H, Ar-H), 8.3-8.4 (d, 2H, Ar-H).

Synthesis of 4,4'-(diazene-1,2-diyl)dibenzoic acid (3)

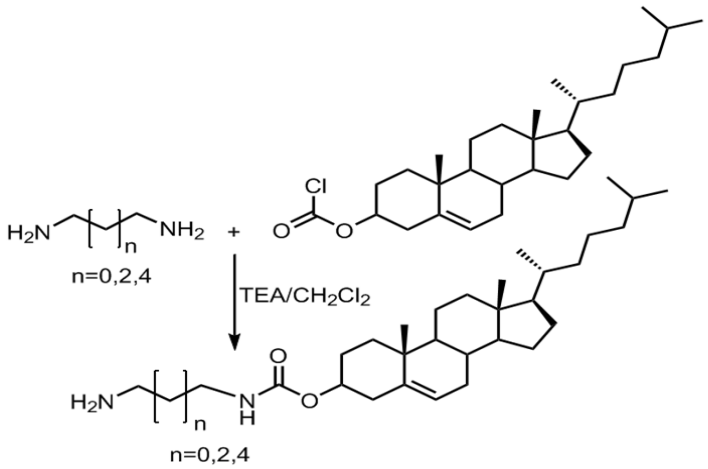
This compound was synthesized according to previously reported procedures as follows: A solution of glucose (60 g, 330 mol) in water (100 mL) was slowly added at 70^{o}C to a solution of *p*-nitrobenzoic acid (7.0 g, 42 mmol) and sodium hydroxide (12.0 g, 330 mmol) in water (100 mL). Next, a stream of air was passed through the mixture overnight. The resulting precipitate was filtered, washed with cold water and acidified with acetic acid. The resulting precipitate was

filtered, washed with water and dried. The resulting crude product was purified by dissolution in 1.0 M ammonium hydroxide, followed by acidification with acetic acid to yield the pure desired product.

FTIR (KBr) (cm^{-1}): 2900 (-OH), 1680 (C=O), 1580 (N=N).

^{1}H NMR (DMSO-d_6, 500MHz, δ in ppm): 8.19 (d, 4H), 8.04 (d, 4H).

Preparation of precursors 4a-5c



All of the compounds were synthesized according to previously reported procedures[1d]. A solution of cholesteryl chloroformate (4.00 g, 8.91 mmol, 1 eq.) in dry dichloromethane (75 mL) was added dropwise to a solution of ethane-1,2-diamine (7.22 mL, 133.59 mmol, 15 eq.) and dry triethylamine (1.24 mL, 8.91 mmol, 1 eq.) in dry dichloromethane (75 mL) at 0°C. This mixture was stirred at ambient temperature under a nitrogen atmosphere for 18 h. The resulting precipitate was filtrated, and the filtrate was washed four times with a brine solution. Next, the organic layer was dried over Na_2SO_4 and evaporated to obtain the desired white solid (76% yield, 3.2 g). The other compounds of the same series (**4b** and **4c**) were prepared using a similar procedure, but 1,4-butanediamine and 1,6-hexanediamine were used rather than ethylenediamine. The adamantyl derivatives (**5a-5c)** were synthesized using a procedure similar to that used for the cholesteryl derivatives except that 1-adamantanecarbonyl chloride was used rather than cholesteryl chloroformate.

FT-IR (KBr, ν_{max}/cm^{-1}) : 3335 (NH stretching), 1714 (C=O), 1253 (COC). ^{1}H-NMR ($CDCl_3$, 500MHz, δ in ppm) : 5.37 (s, 1H, C=CH in cholesteryl), 4.96 (s, 1H, -N<u>H</u> –C(=O)O-Chol), 4.50

(t, 1H, Cholesteryl C<u>H</u>-O-C=O), 3.22 (2H, t, C<u>H</u>$_2$-NH-C=O), 2.82 (2H, t, NH$_2$-C<u>H</u>$_2$-), 1.01 (s, 3H, CH$_3$ in Cholestryl), 0.92 (d, 3H, CH$_3$ in Cholestryl), 0.87 (s, 3H, CH$_3$ in Cholestryl), 0.68 (s, 3H, CH$_3$ in Cholestryl), 1.33 (t, 2H, CH$_2$ in Cholesteryl), 1.53 (t, 2H, CH$_2$ in Cholesteryl). ^{13}C NMR (125.7 MHz, $CDCl_3$, δ in ppm): δ= 156.41 (C=O), 139.87, 122.46, 74.34, 56.72, 56.18, 50.06, 43.74 (CH$_2$ in ethylenediamine), 42.33, 41.83 (CH$_2$ in ethylenediamine), 39.77, 39.53, 38.59, 37.02, 36.58, 36.20, 35.79, 31.90, 31.90, 28.22, 28.19, 28.00, 23.84, 21.05, 18.71, 14.29, 12.01.

4b: Yield 76%; FT-IR (KBr, ν_{max}/cm^{-1}) : 3330 (NH stretching), 1717 (C=O), 1250 (COC). ^{1}H-NMR ($CDCl_3$, 500MHz, δ in ppm) : 5.39 (s, 1H, C=CH in cholesteryl), 4.94 (s, 1H, -N<u>H</u> – C(=O)O-Chol), 4.51 (t, 1H, Cholesteryl C<u>H</u>-O-C=O), 3.24 (2H, t, C<u>H</u>$_2$-NH-C=O), 2.80 (2H, t, NH$_2$-C<u>H</u>$_2$-), 1.50-0.66 (m, all protons in cholesteryl group are similar as in compound **4a**). ^{13}C NMR (125.7 MHz, $CDCl_3$, δ in ppm): δ= 156.21 (C=O), 139.83, 122.65, 75.26, 56.70, 56.16, 50.03, 43.32 (CH$_2$ in ethylenediamine), 42.33, 40.83 (CH$_2$ in ethylenediamine), 39.75, 39.51, 38.57, 37.00, 36.58, 36.19, 35.79, 31.89, 31.90, 28.21, 28.19, 28.00, 24.28, 19.31, 14.31, 11.80.

4c: Yield 49%; FT-IR (KBr, ν_{max}/cm^{-1}) : 3338 (NH stretching), 1715 (C=O), 1256 (COC). ^{1}H-NMR ($CDCl_3$, 500MHz, δ in ppm) : 5.38 (s, 1H, C=CH in cholesteryl), 4.93 (s, 1H, -N<u>H</u> – C(=O)O-Chol), 4.50 (t, 1H, Cholesteryl C<u>H</u>-O-C=O), 3.22 (2H, t, C<u>H</u>$_2$-NH-C=O), 2.83 (2H, t, NH$_2$-C<u>H</u>$_2$-), 1.53-0.71 (m, all protons in cholesteryl group are similar as in compound **4a** and **4b**). ^{13}C NMR (125.7 MHz, $CDCl_3$, δ in ppm): δ= 156.17 (C=O), 139.80, 122.76, 75.22, 56.71, 56.19, 50.11, 43.23 and 40.83 (CH$_2$ in ethylenediamine), 42.31, 39.73, 39.51, 38.56, 37.06, 36.53, 36.17, 35.76, 31.83, 31.87, 28.19, 28.17, 28.13, 24.18, 19.33, 14.30, 11.83.

5a: Yield 78%; FT-IR (KBr, ν_{max}/cm^{-1}) : 3330 (NH stretching), 2850, 2938 (CH$_2$), 1716 (C=O). ^{1}H-NMR ($CDCl_3$, 500MHz, δ in ppm) : 6.4 (s, 1H, NH), 3.3-3.4 (t, 2H, C<u>H</u>$_2$NH), 2.1 (s, 2H, NH$_2$), 1.90-2.0 (t, 2H, C<u>H</u>$_2$NH$_2$), 1.5-1.8 (m, 15H, adamantyl group). ^{13}C NMR (125.76 MHz, $CDCl_3$, δ in ppm): δ= 178.07 (C=O), 40.48 (<u>C</u>H$_2$-NH-C=O), 39.23 (<u>C</u>H$_2$-NH$_2$), 39.03 (<u>C</u>H$_2$-C-C=O), 38.57 (adamantly <u>C</u>-C=O), 26.95 (<u>C</u>H-CH$_2$ in adamantyl).

5b: Yield 53%; FT-IR (KBr, ν_{max}/cm^{-1}) : 3336 (NH stretching), 2855, 2940 (CH$_2$), 1715 (C=O). ^{1}H-NMR ($CDCl_3$, 500MHz, δ in ppm) : 5.9 (s, 1H, NH), 3.2-3.3 (t, 2H, C<u>H</u>$_2$NH), 2.1 (s, 2H, NH$_2$), 1.90 (t, 2H, C<u>H</u>$_2$NH$_2$), 1.3-1.8 (m, C<u>H</u>$_2$ and C<u>H</u> in spacer and adamantyl group). ^{13}C NMR

(125.76 MHz, $CDCl_3$, δ in ppm): δ= 177.91 (C=O), 40.46 ($\underline{C}H_2$-NH-C=O), 39.20 ($\underline{C}H_2$-NH_2), 39.13 ($\underline{C}H_2$-C-C=O), 38.45 (adamantly $\underline{C}$-C=O), 27.46 ($\underline{C}$H-CH_2 in adamantyl).

5c : Yield 39%; FT-IR (KBr, ν_{max}/cm^{-1}) : 3338 (NH stretching), 2852, 2942 (CH_2), 1715 (C=O),. ^{1}H-NMR ($CDCl_3$, 500MHz, δ in ppm) : 5.9 (s, 1H, NH), 3.2-3.3 (t, 2H, C$\underline{H}_2$NH), 2.7-2.8 (t, 2H, C$\underline{H}_2$$NH_2$), 2.1 (s, 2H, NH_2), 1.3-1.9 (m, CH_2 and CH in spacer and adamantyl group). ^{13}C NMR (125.76 MHz, $CDCl_3$): δ= 178.01 (C=O), 40.44 ($\underline{C}H_2$-NH-C=O), 39.17 ($\underline{C}H_2$-NH_2), 38.93 ($\underline{C}H_2$-C-C=O), 38.53 (adamantly $\underline{C}$-C=O), 27.35 ($\underline{C}$H-CH_2 in adamantyl).

Synthesis of SAC2

All of the compounds (SAC2-SAA6) were synthesized according to the reported procedure[1e-j]. For example, SAC2 was synthesized as follows. First, compound 3 (0.135 g, 0.5 mmol) was added to a solution of **4a** (0.472 g, 1 mmol), 4-(dimethylamino)pyridine (0.061 g, 0.5 mmol) and N,N′-dicyclohexylcarbodiimide (0.21 g, 1 mmol) in dry dichloromethane. This solution was stirred for 48 h at room temperature. Next, the contents of the flask were washed with water followed by a brine solution. Then, the organic layer was collected, dried over magnesium sulfate and concentrated under reduced pressure. The resulting crude product was purified using column chromatography (*n*-hexane:EtOAc 1:2.5) to obtain the pure compound as a yellow solid (yield 63%). The remaining compounds of the same series and the adamantyl series (SAA series) were synthesized by using the above procedure, but with the respective amine compounds rather than 4a.

FT-IR (KBr, ν_{max}/cm^{-1}) : 3334 (NH stretching), 1719 (C=O), 1525, 1600 (C-C in Ar), 1253 (COC). ^{1}H-NMR (DMSO-d_6, 500MHz, δ in ppm) :8.4 (s, 2H, Ar-C(=O)-N$\underline{H}$) 8.1 (4H, d, ArH), 7.8 (4H, d, ArH), 6.8 (2H, N$\underline{H}$-C(=O)-O-), 5.32 (s, 2H, C=CH in cholesteryl), 4.48 (t, 2H, Cholesteryl C$\underline{H}$-O-C=O), 3.22 (4H, t, C$\underline{H}_2$-NH-C=O), 1.03 (m, 6H, CH_3 in Cholestryl), 0.93 (d, 6H, CH_3 in Cholestryl), 0.84 (m, 6H, CH_3 in Cholestryl), 0.67 (m, 6H, CH_3 in Cholestryl), 1.30 (t, 4H, CH_2 in Cholesteryl), 1.52 (t, 4H, CH_2 in Cholesteryl). ^{13}C NMR (125.7 MHz, $CDCl_3$, δ in ppm): δ= 167, 156.21, 140.44, 139.80, 130.61, 122.85, 122.45, 76.75, 40.49, 39.75, 56.72, 56.18, 50.06, 42.33, 39.77, 38.59, 37.02, 36.58, 36.20, 35.79, 31.89, 28.21, 28.17, 27.80, 23.84, 21.15, 18.43, 14.31, 12.00.

SAC4: Yield 48%; FT-IR (KBr, ν_{max}/cm^{-1}) : 3336 (NH stretching),1714 (C=O), 1528, 1610 (C-C in Ar), 1256 (COC). ^{1}H-NMR (DMSO-d_6, 500MHz, δ in ppm) :8.3 (s, 2H, Ar-C(=O)-N<u>H</u>) 8.1 (4H, d, ArH), 7.9 (4H, d, ArH), 6.8 (2H, N<u>H</u>-C(=O)-O-), 5.30 (s, 2H, C=CH in cholesteryl), 4.50 (t, 2H, Cholesteryl C<u>H</u>-O-C=O), 3.21 (4H, t, C<u>H</u>$_2$-NH-C=O), 1.14 (m, 6H, CH_3 in Cholestryl), 0.97 (d, 6H, CH_3 in Cholestryl), 0.86 (m, 6H, CH_3 in Cholestryl), 0.66 (m, 6H, CH_3 in Cholestryl), 1.32 (t, 4H, CH_2 in Cholesteryl), 1.49 (t, 4H, CH_2 in Cholesteryl). ^{13}C NMR (125.7 MHz, DMSO-d_6, δ in ppm): δ= 167.4, 156.41, 140.47, 139.79, 130.61, 122.83, 122.42, 76.69, 40.47, 39.73, 56.71, 56.21, 50.09, 42.33, 39.75, 38.60, 37.11, 36.61, 36.21, 35.77, 31.88, 28.23, 28.15, 27.83, 23.86, 21.27, 18.39, 14.29, 11.80.

SAC6: Yield 21%; FT-IR (KBr, ν_{max}/cm^{-1}): 3330 (NH stretching), 1725 (C=O), 1525, 1605 (C-C in Ar), 1250 (COC). ^{1}H-NMR (DMSO-d_6, 500MHz, δ in ppm) :8.4 (s, 2H, Ar-C(=O)-N<u>H</u>), 8.2 (4H, d, ArH), 7.8 (4H, d, ArH), 6.7 (2H, N<u>H</u>-C(=O)-O-), 5.28 (s, 2H, C=CH in cholesteryl), 4.51 (t, 2H, Cholesteryl C<u>H</u>-O-C=O), 3.24 (4H, t, C<u>H</u>$_2$-NH-C=O), 0.99 (m, 6H, CH_3 in Cholestryl), 0.91 (d, 6H, CH_3 in Cholestryl), 0.81 (m, 6H, CH_3 in Cholestryl), 0.70 (m, 6H, CH_3 in Cholestryl), 1.20 (t, 4H, CH_2 in Cholesteryl), 1.49 (t, 4H, CH_2 in Cholesteryl). ^{13}C NMR (125.7 MHz, DMSO-d_6, δ in ppm): δ= 166.91, 156.22, 140.63, 139.83, 130.60, 122.84, 122.49, 76.70, 40.52, 39.73, 56.70, 56.16, 50.03, 42.30, 39.75, 38.59, 37.31, 36.54, 36.17, 35.75, 31.86, 28.23, 28.15, 27.74, 23.80, 21.16, 18.43, 14.29, 11.93.

SAA2: Yield 53%; FT-IR (KBr, ν_{max}/cm^{-1}) : 3339 (NH stretching), 2850, 2938 (CH_2), 1720 (C=O), 1525, 1600 (C-C in Ar),. ^{1}H-NMR ($CDCl_3$, 500MHz, δ in ppm) : 8.3 (s, 2H, Ar-C(=O)-N<u>H</u>), 8.2 (4H, d, ArH), 7.8 (4H, d, ArH), 6.45 (s, 2H, N<u>H</u>-C(=O)-O-), 3.3-3.4 (t, 2H, C<u>H</u>$_2$NH), 0.9-1.8 (m, 15H, adamantyl group). ^{13}C NMR (125.76 MHz, $CDCl_3$, δ in ppm): δ= 176.07 (Adamantyl-C=O), 168.02 (Ar-<u>C</u>=O), 139.80 (Ar<u>C</u>-C=O), 130.61 (Ar<u>C</u>), 122.85 (Ar<u>C</u> azo terminal) 40.12 (<u>C</u>H$_2$-NH-C=O), 39.36 (<u>C</u>H$_2$-NH$_2$), 38.93 (<u>C</u>H$_2$-C-C=O), 38.43 (adamantly <u>C</u>-C=O), 26.95 (<u>C</u>H-CH$_2$ in adamantyl).

SAA4: Yield 63%; FT-IR (KBr, ν_{max}/cm^{-1}) : 3336 (NH stretching), 2854, 2944 (CH_2), 1730 (C=O), 1520, 1610 (C-C in Ar). ^{1}H-NMR ($CDCl_3$, 500MHz, δ in ppm) : 8.4 (s, 2H, Ar-C(=O)-N<u>H</u>), 8.2 (4H, d, ArH), 7.9 (4H, d, ArH), 6.4 (s, 2H, N<u>H</u>-C(=O)-O-), 3.4 (t, 2H, C<u>H</u>$_2$NH), 0.8-1.7

(m, 15H, adamantyl group). ^{13}C NMR (125.76 MHz, $CDCl_3$, δ in ppm): δ= 176.21, 168.13, 140.06, 130.43, 122.91, 40.11, 39.46, 38.99, 38.40, 27.02.

SAA6: Yield 59%; FT-IR (KBr, ν_{max}/cm^{-1}) : 3338 (NH stretching), 2855, 2939 (CH_2), 1728 (C=O), 1530, 1617 (C-C in Ar). ^{1}H-NMR ($CDCl_3$, 500MHz, δ in ppm) : 8.4 (s, 2H, Ar-C(=O)-N<u>H</u>), 8.2 (4H, d, ArH), 7.8 (4H, d, ArH), 6.38 (s, 2H, N<u>H</u>-C(=O)-O-), 3.46 (t, 2H, C<u>H</u>$_2$NH), 0.9-1.7 (m, 15H, adamantyl group). ^{13}C NMR (125.76 MHz, $CDCl_3$, δ in ppm): δ= 176.33, 168.36, 140.01, 130.35, 122.98, 40.17, 39.40, 39.06, 38.44, 27.12.

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Table S1 Gelation properties of all the synthesized compounds in various solvent systems [G=gel; PG=partial gel; P=precipitate; S=soluble; I= insoluble; CGC values (gL^{-1}) were given brackets]

Solvents/Compound	**AAC0**	**AAC3**	**AAC6**	**AAC11**	**SAC2**	**SAC4**	**SAC6**	**SAA2**	**SAA4**	**SAA6**
n-Hexane	G (0.7)	P	G (2)	P	S	S	S	I	I	I
Cyclohexane	G (2)	S	G (6)	P	G (6)	G (7)	PG (8)	I	I	I
Cyclopentanone	P	S	S	S	G (5)	G (7)	PG (7)	I	I	I
Cyclohexanone	G(9)	S	S	P	G (7)	G	G	I	I	I
Methyl ethyl ketone	G (5)	S	P	P	I	I	I	I	I	I
Ethanol	I	I	I	I	I	P	P	I	I	I
Methanol	I	I	I	I	I	I	P	P	I	P
1-Propanol	G (0.7)	G (5)	G (4)	P	G (4)	G (4)	G (5)	S	S	S
2-Propanol	I	P	G (9)	P	G (6)	PG (6)	PG (7)	S	S	S
1-Butanol	G (0.6)	G (7)	G (5)	P	PG (6)	G (6)	S	S	P	S
2-Butanol	G (0.6)	G (7)	G (3)	P	G (6)	G (5)	PG (6)	P	S	S
1-Hexanol	G (0.8)	G (6)	G (3)	P	G (5)	G (8)	PG (8)	S	S	S
1-Octanol	G (0.8)	G (6)	G (3)	P	G (8)	G (7)	S	S	S	S
1,4-Butanediol	I	I	S	S	I	I	I	I	I	I
m-Cresol	G (10)	S	S	S	P	P	S	S	P	S
Benzene	S	S	S	S	S	S	P	I	I	S
Toluene	S	S	S	S	G (9)	P	P	S	S	S
Xylene	S	S	S	S	PG (6)	G (7)	S	S	S	S
1,4-Dioxane	G(10)	S	S	S	S	P	S	S	I	P
THF	S	S	S	S	S	S	S	S	S	S
DMF	P	P	G (10)	P	P	P	S	P	S	S
DMSO	I	P	P	P	PG (6)	PG (6)	P	I	S	S
Water	I	I	I	I	I	I	I	I	I	I
Acetone	I	P	P	S	I	P	P	I	I	I
Pyridine	G (8)	S	S	S	S	S	S	S	S	S
Anisole	S	S	S	S	S	S	S	I	S	S
Chloroform	S	S	S	S	S	S	S	S	S	S
Dichloromethane	S	S	S	S	S	S	S	S	S	S
Diphenyl ether	G (9)	S	S	S	S	S	S	I	P	S

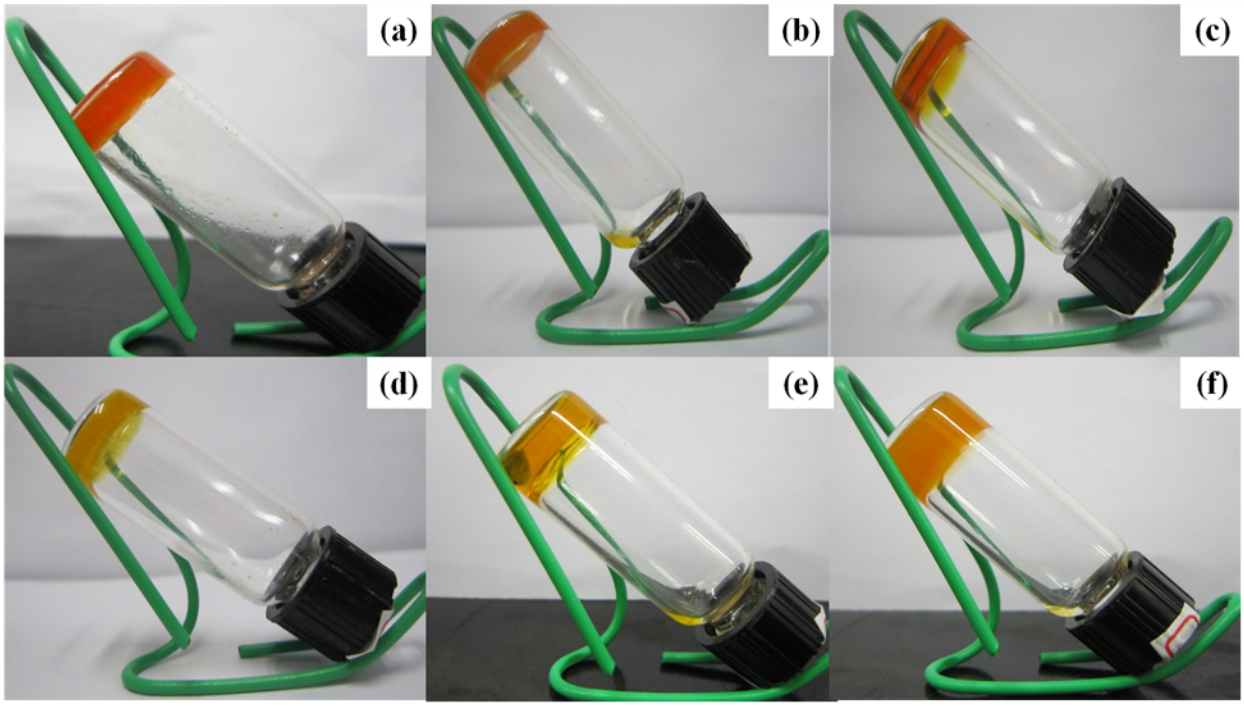

Fig. S1 Selected photographic images of the gel systems (a) AAC0 in pyridine, (b) AAC3 in butanol, (c) AAC6 in *n*-Hexane, (d) SAC2 in 1-propanol, (e) SAC4 in cyclohexane and (f) SAA2 in cyclohexanone.

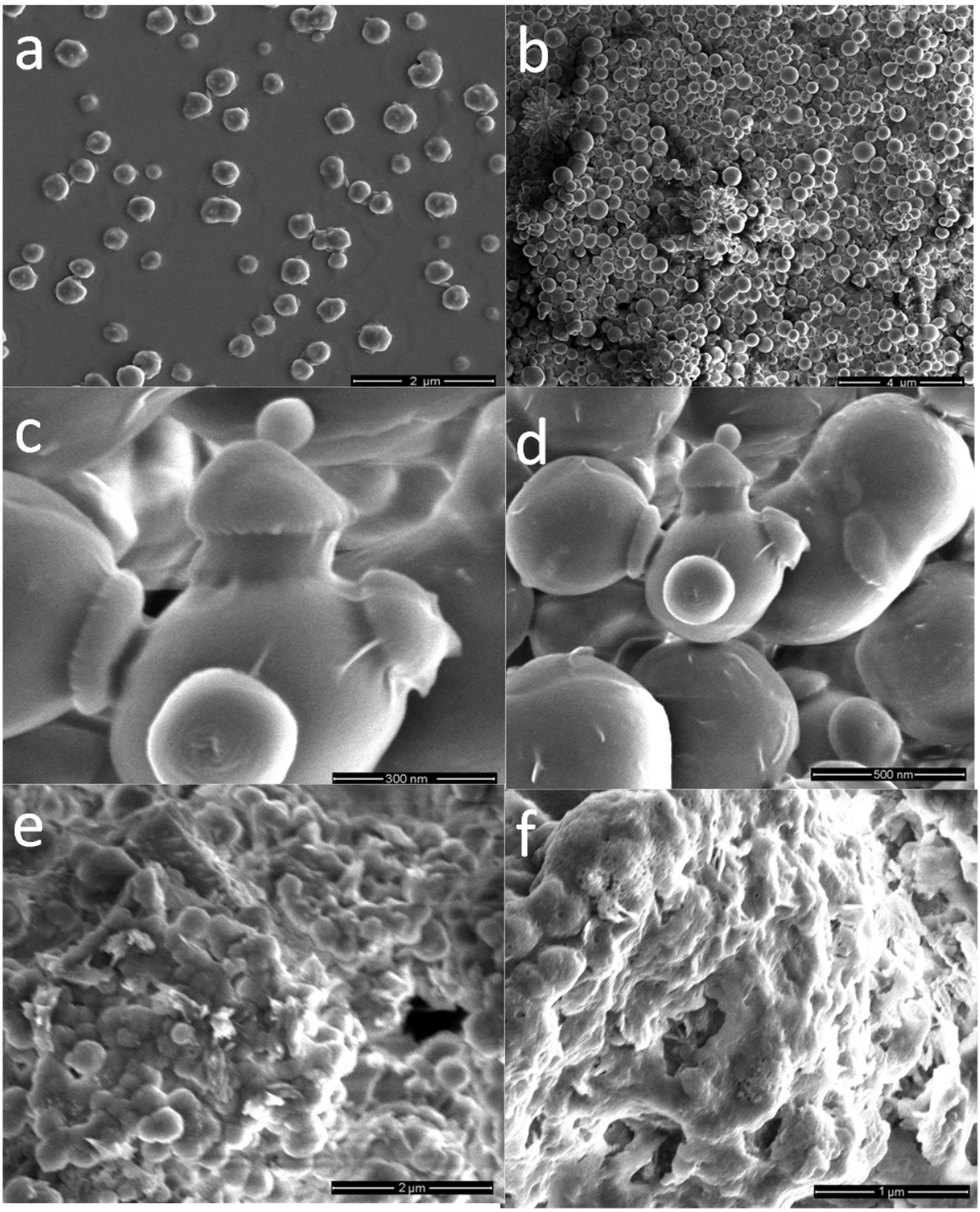

Fig. S2. Representative SEM images of (a-f) increasing SAC2 concentrations in 1-butanol (**c** and **d** show how the interconnection of nanospheres forms the entangled network of **e** and **f**).

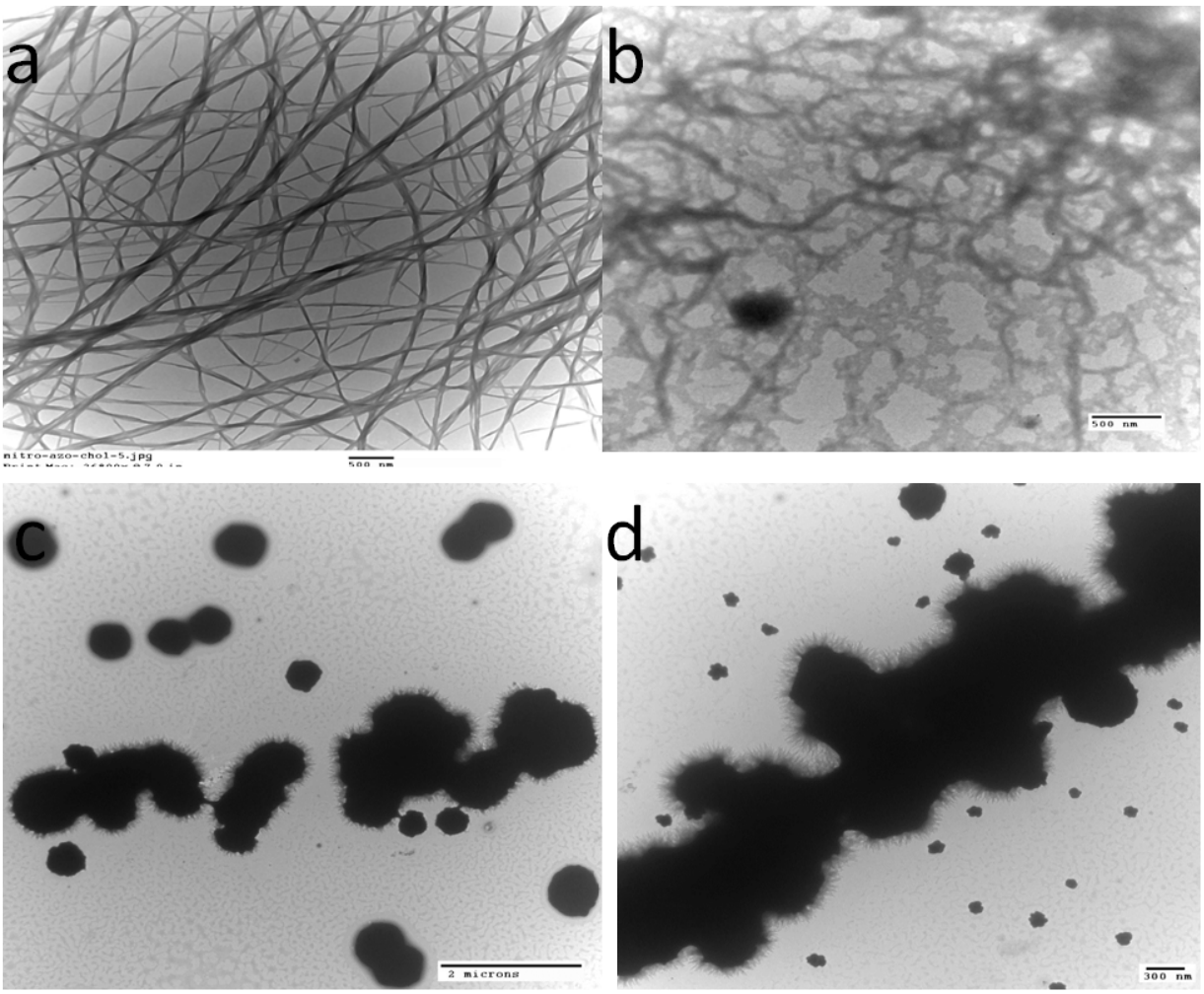

Fig. S3 Representative TEM images of (a) AAC0 in 2-butanol, (b) SAC2 in 1-propanol, (c) SAC2 in 1-butanol and (d) a higher concentration of SAC2 in 1-butanol (>10gL^{-1}).

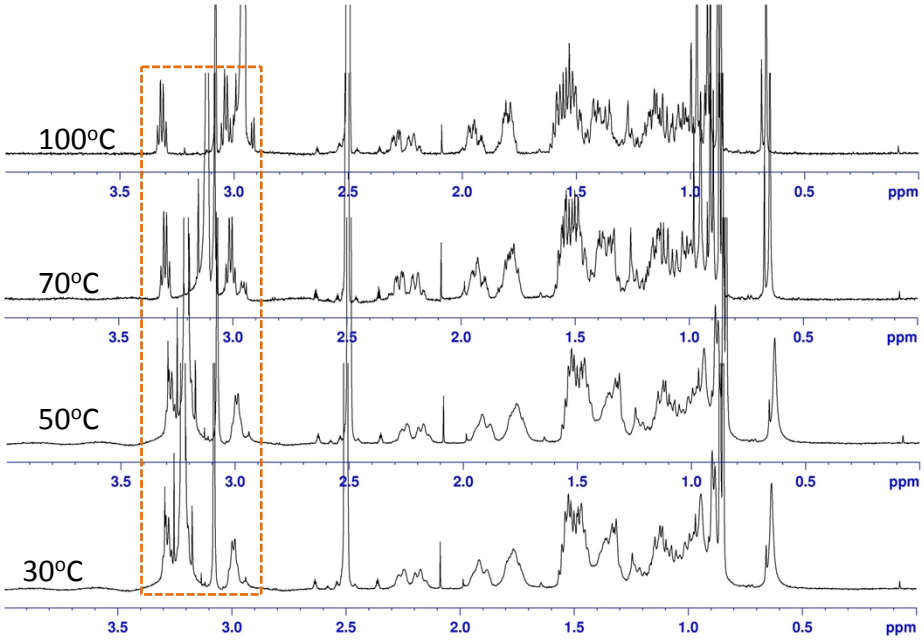

Fig. S4 Temperature dependent ^{1}H-NMR spectra of SAC2/DMSO-d_6 gel at 0-4 ppm.

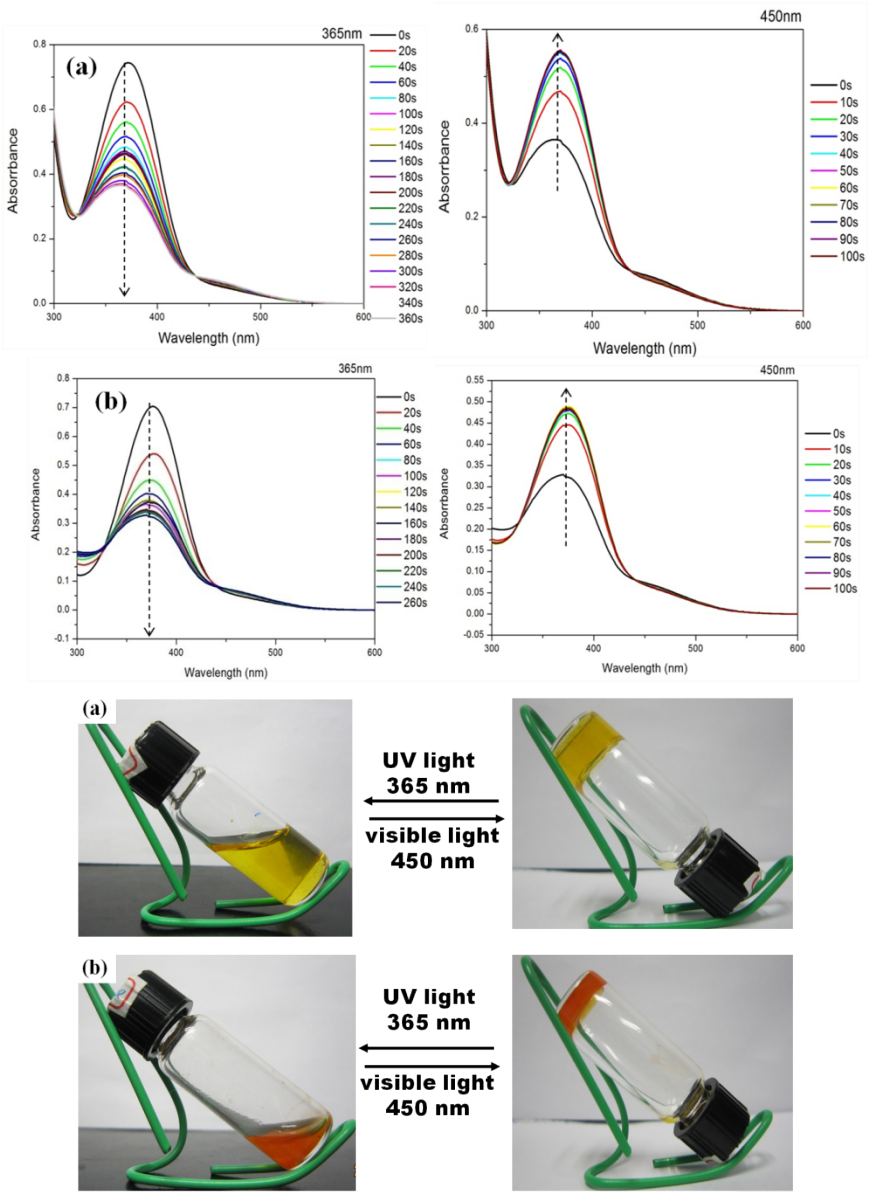

Fig. S5 Changes in the UV and vis spectra (above) and real images of phase transition (below) of SAC2 (a) and AAC6 (b) in cyclohexane with irradiation wavelength of 365 and 450 nm.

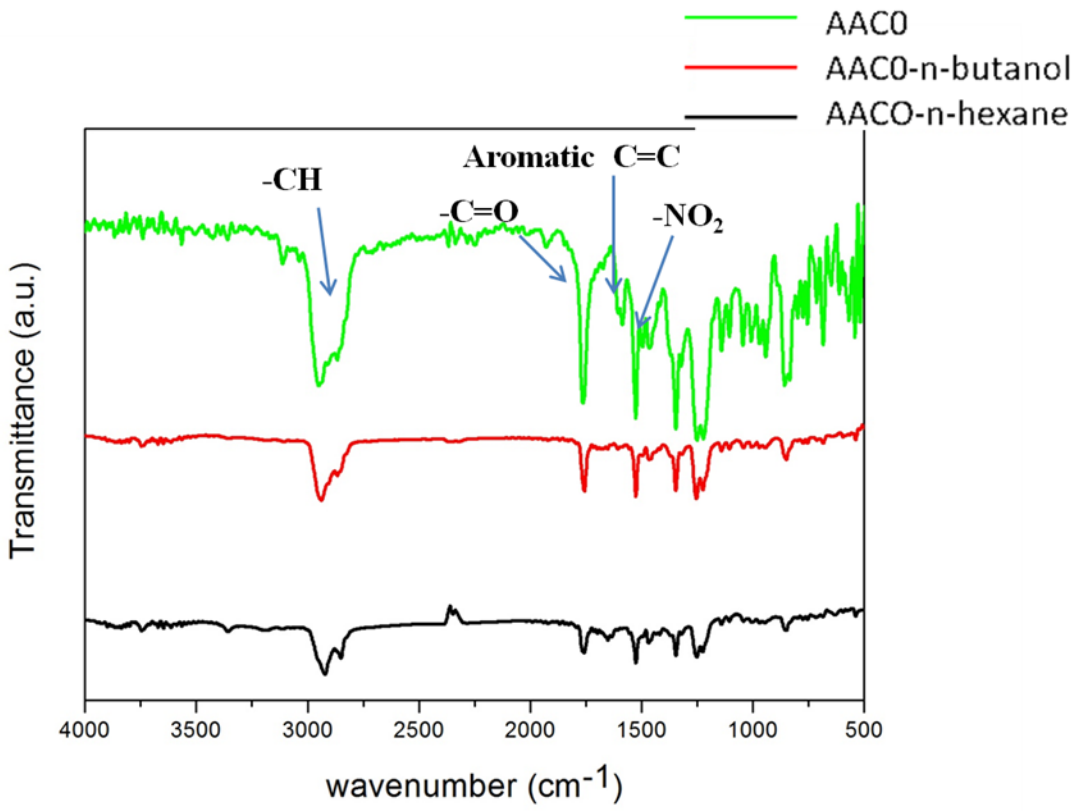

Fig. S6 FTIR spectra of the AAC0 prepared from various solvents.

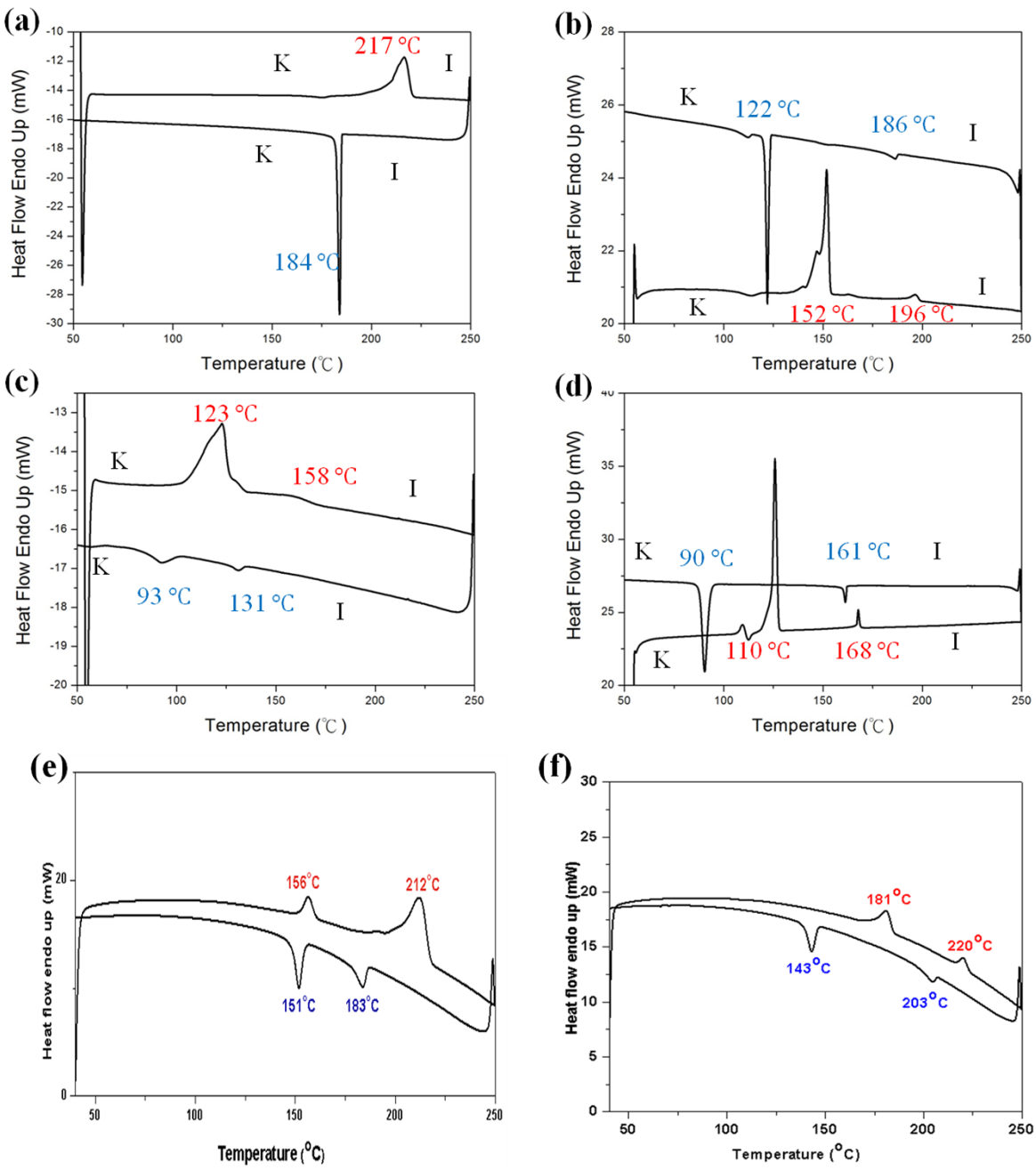

Fig. S7 Representative DSC curves of the azobenzene-cholesterol derivatives, (a) AAC0, (b) AAC3, (c) AAC6, (d) AAC11, (e) SAC4 and (f) SAC2.

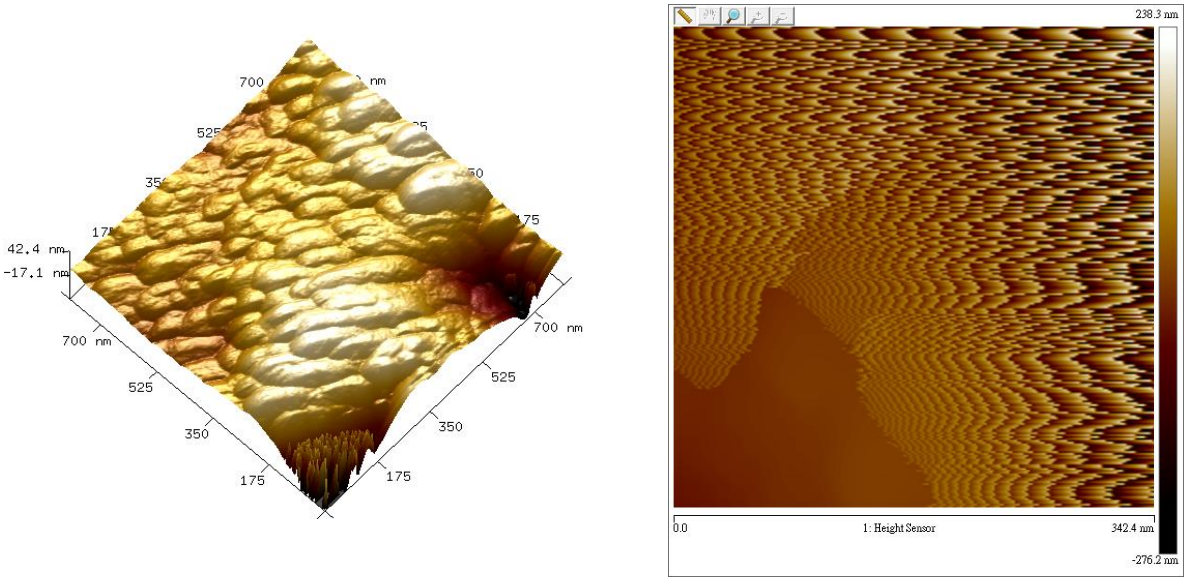

Fig. S8 Representative AFM images of xerogel of SAC6 (1-propanol).