Electronic supplementary Information

Dual-responsive ALS-type organogelators based on azobenzene-cholesteryl conjugates and their self-assemblies

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SEM measurements

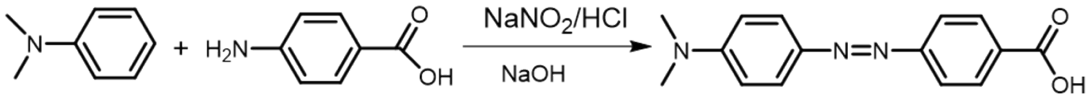
Gels prepared in sample tubes were frozen using liquid nitrogen, and then evaporated using a vacuum pump under reduced pressure for 1 day at room temperature. The obtained samples were sputter coated with platinum. The accelerating voltage of the electron microscope was 25 kV, and the beam current was 10 μA.

TEM measurements

A piece of the gel was placed on a carbon-coated copper grid. The sample was dried under vacuum 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 & characterization of precursors and target molecules

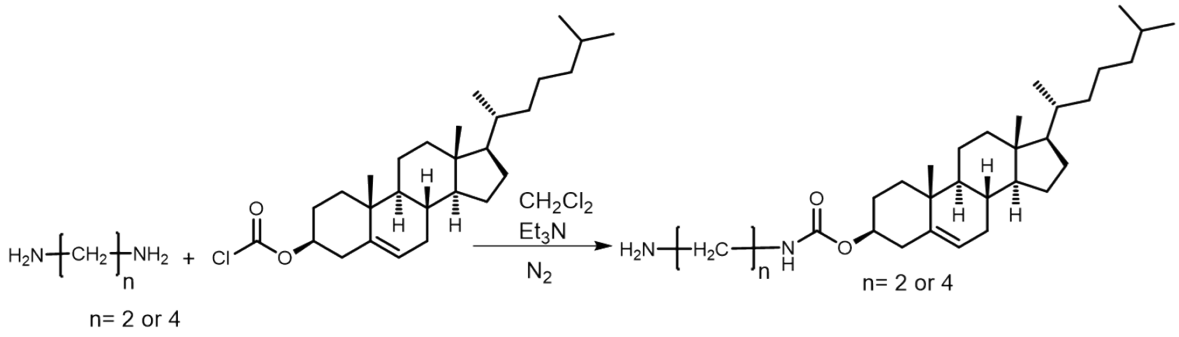
4-((4-(Dimethylamino)phenyl)diazenyl)benzoic acid (1)



A solution of 4-aminobenzoic benzoic acid (8.23 g, 60 mmol) in 37 wt% HCl (240 mmol) was placed in an ice-water bath. A cold aqueous solution of sodium nitrite (4.14 g, 60 mmol) was added dropwise to the above solution with vigorous stirring. To the $NaNO_2$ mixture, N,N-dimethylaniline (7.27 g, 60 mmol) in 300 ml of NaOH (9.6 g, 240 mmol) was added dropwise over 30 min with vigorous stirring in an ice-water bath and then stirred at room temperature for one hour. The aqueous solution was then acidified to pH=4 ~ 5 using dilute HCl, and the obtained precipitate was filtered off. The product was washed twice with water and dried. The crude product was recrystallized from ethanol to afford the target compound in 94% yield (15.13 g).

FT-IR (KBr, ν_{max} /cm^{-1})：3300-2500, 1682, 1415, 1301 (carboxylic acid), 2946 (CH), 1599, 1522 (benzene), 1365 (CH_3 bending), 1252 (tertiary amine), 1138 (C-OH), 820 (para-substituted aromatic ring). ^{1}H-NMR (acetone-d6, 500 MHz, δ in ppm)：3.14 (s, 6H, $(CH_3)_2N$), 6.87-6.89 (d, 2H, ArH), 7.88-7.89 (d, 2H, ArH), 7.90-7.91 (d, 2H, ArH), 8.16-8.18 (d, 2H, ArH).

Cholesteryl-oxycarbonyl-aminoalkylamine (2a and 2b)

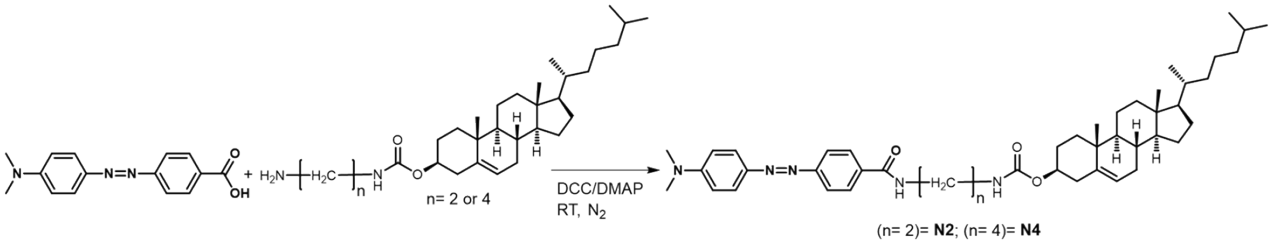


Cholesteryl-oxycarbonyl-aminoethylamine (2a) was synthesized as follows: in a double-neck round-bottom flask, 4.51 g (75 mmol) of ethylene diamine was dissolved in anhydrous dichloromethane and placed in an ice-water bath with stirring under a nitrogen atmosphere. To this solution, 0.7 ml (5 mmol) of trimethylamine was added dropwise over 30 min, followed by the addition of a solution of cholesteryl chloroformate (2.25 g, 5 mmol) in dichloromethane (50 ml) under vigorous stirring. The reaction temperature was maintained at 0 °C, and the reaction was continued for 24 hours. After the reaction, the content of the flask was washed with water 5 times, and the organic phases were collected. The combined organic phases were dried over anhydrous magnesium sulfate and then concentrated. The crude product was recrystallized from ethanol (with a small amount of THF) to afford 78% (1.84 g) of the target compound as a white solid. Similarly, cholesteryl-oxycarbonyl-aminobutylamine (2b) was synthesized via a similar procedure in which ethylene diamine was replaced with 1,4-butanediamine (6.62 g, 75 mmol), and 2b was isolated as a white solid in 72% yield (1.81 g).

Compound 2a: FT-IR (KBr, ν_{max} /cm^{-1})：3338 (NH), 2931, 2867 (C-H), 1699 (C=O), 1535, 1140 (CONH), 1462 (CH_2 bending), 1378 (CH_3 bending). ^{1}H-NMR ($CDCl_3$, δ in ppm)：0.69-2.50 (m, 45H, cholesteryl protons), 2.81 (t, 2H, NH_2CH_2), 3.22 (m, 2H, $NHCH_2$), 4.50 (m, 1H, oxycyclohexyl), 4.96 (t, 1H, chol-amide), 5.38 (s, 1H, alkenyl).

Compound 2b: FT-IR (KBr, ν_{max} /cm^{-1})：3352 (NH), 2932, 2868 (C-H), 1707 (C=O), 1562, 1144 (CONH), 1464 (CH_2 bending), 1377 (CH_3 bending). ^{1}H-NMR ($CDCl_3$, δ in ppm)：0.69-2.50 (m, 45H, cholesteryl protons), 3.17 (s, 2H, $NHCH_2$), 4.49 (m, 1H, oxycyclohexyl), 4.64 (t, 1H, chol-amide), 5.37 (s, 1H, alkenyl).

Cholesteryl 2-(4-(4-dimethylamino)-azobenzene-4'-amido)alkyl carbamate (N2 and N4)



Compound N2 was synthesized as follows: a solution of 4-dimethylaminopyridine (2.15 mmol) in 20 ml of dichloromethane was added to a solution of 4-((4- (dimethylamino)phenyl) diazenyl) benzoic acid (2.15 mmol) in 100 ml of dichloromethane. The solution was placed in a double-neck round-bottom flask and stirred for one hour. To this mixture, a solution of cholesteryl-oxycarbonyl-aminoethylamine (2.15 mmol) in 100 ml of dichloromethane was added followed by N,N'-dicyclohexylcarbodiimide (3.17 mmol) in 20 ml of dichloromethane. The content of the flask was allowed to react at room temperature under a nitrogen atmosphere for 48 hours. After completion of the reaction, the content of the flask was filtered. The filtrate was collected and washed three times with dilute hydrochloric acid. Then, the organic phase was collected, dried and concentrated using a rotary evaporator. The crude product was purified using column chromatography (silica gel, EA / hexane=2: 1), and after being recrystallized twice from ethanol, the target compound was yielded as an orange solid (0.99 g, 64% yield). Similar procedures were adopted for the synthesis of compound N4, in which cholesteryl-oxycarbonyl-aminoethylamine was used instead of cholesteryl-oxycarbonyl-aminoethylamine (0.89 g, yield 59%).

Cholesteryl 2-(4-(4-dimethylamino)-azobenzene-4'-amido)ethyl carbamate (N2)

FT-IR (KBr, ν_{max} /cm^{-1})：3291 (N-H), 2954, 2871 (C-H), 1687 (C=O), 1602, 1514 (C-C in Ar), 1363 (C-N). ^{1}H-NMR (acetone-d_6, δ in ppm)：0.69-2.50 (m, 45H, cholesteryl protons), 3.15 (s, 6H, $(CH_3)_2N$), 4.40 (m, 1H, oxycyclohexyl), 6.41 (s, 1H, alkenyl), 6.86-6.88 (d, 2H, ArH), 6.41 (t, 1H, chol-amide), 7.85-7.86 (d, 2H, ArH), 7.87-7.88 (d, 2H, ArH), 7.95 (t, 1H, azo-amide), 8.02-8.04 (d, 2H, ArH).

Cholesteryl 4-(4-(4-dimethylamino)-azobenzene-4'-amido)butyl carbamate (N4)

FT-IR (KBr, ν_{max}/cm^{-1})：3351 (N-H), 2943, 2863 (C-H), 1689 (C=O), 1602, 1523 (C-C in Ar), 1365 (C-N). ^{1}H-NMR (DMSO-d6, δ in ppm)：0.69-2.50 (m, 45H, cholesteryl protons), 3.08 (s, 6H, $(CH_3)_2N$), 4.26 (m, 1H, oxycyclohexyl), 5.29 (s, 1H, alkenyl), 6.84-6.86 (d, 2H, ArH), 7.07 (t, 1H, chol-amide), 7.80-7.81 (d, 2H, ArH), 7.81-7.83 (d, 2H, ArH), 7.96-7.98 (d, 2H, ArH), 8.53-8.55 (t, 1H, azo-amide).

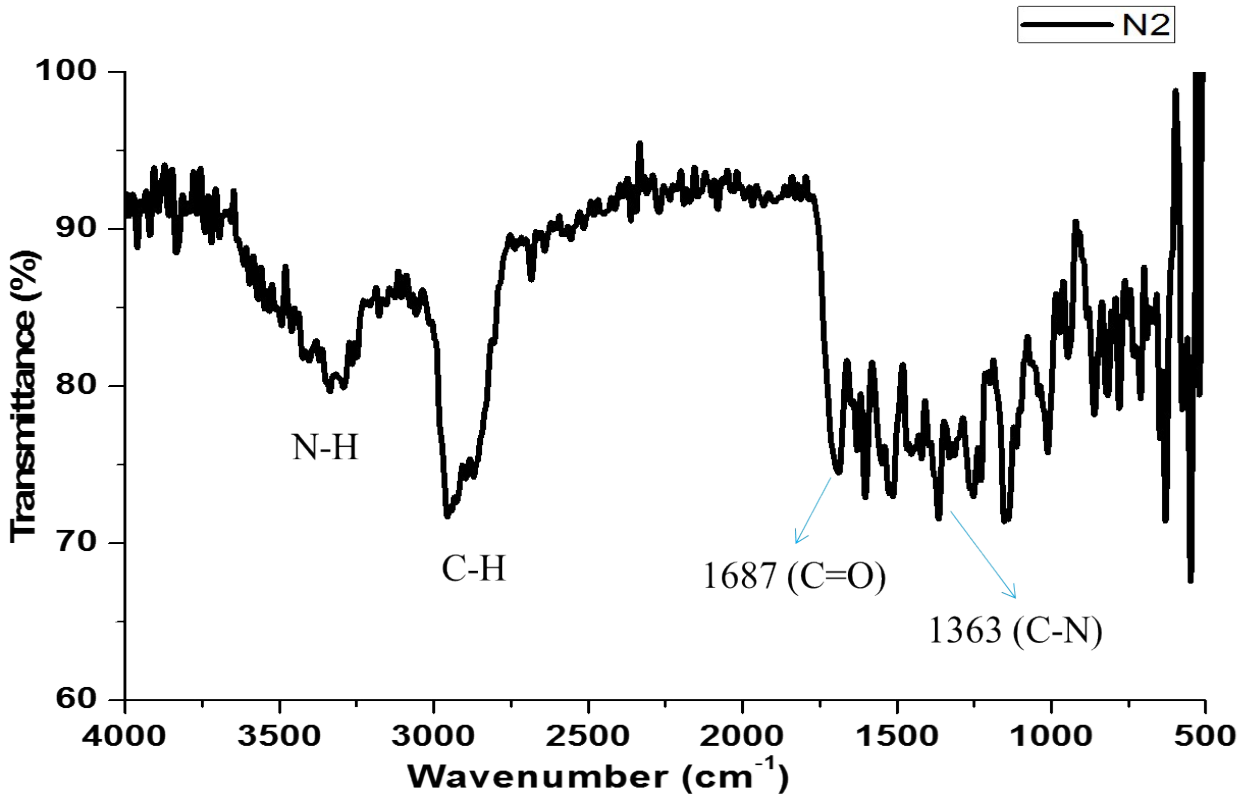


Fig. S1. FTIR spectrum of gelator N2

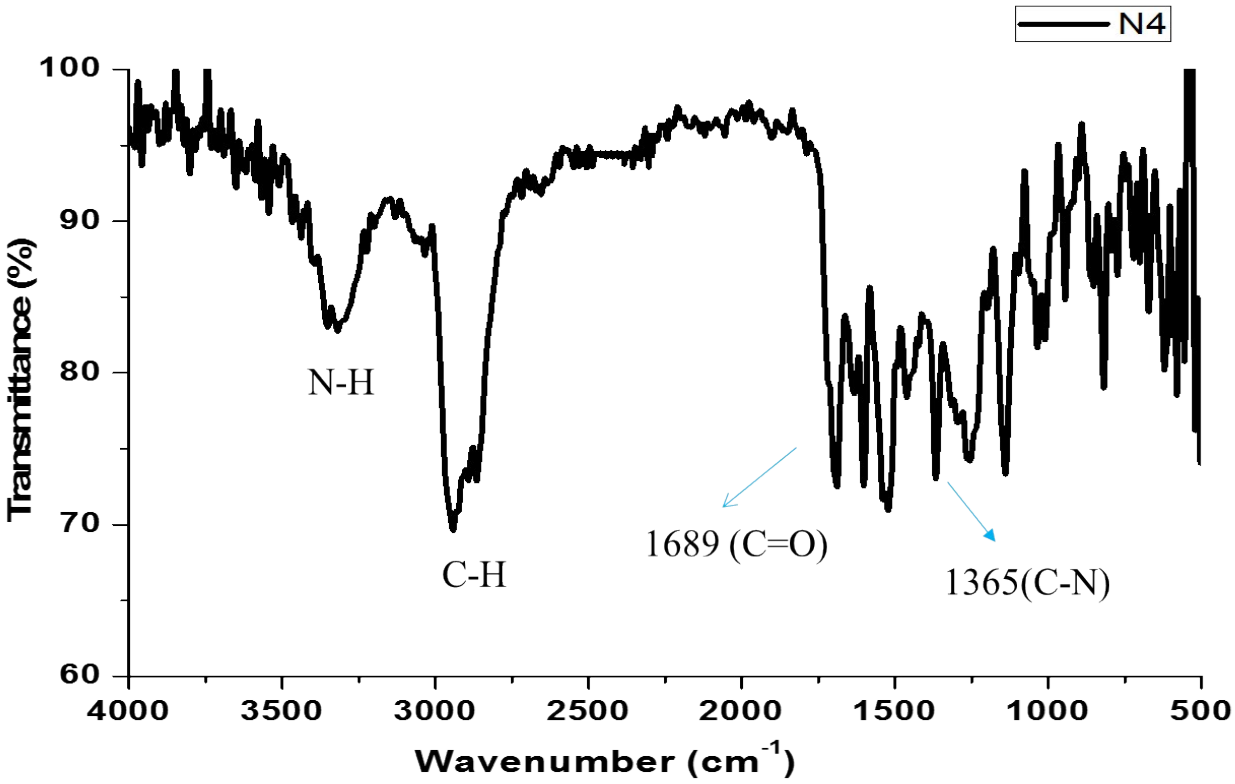


Fig. S2. FTIR spectrum of gelator N4

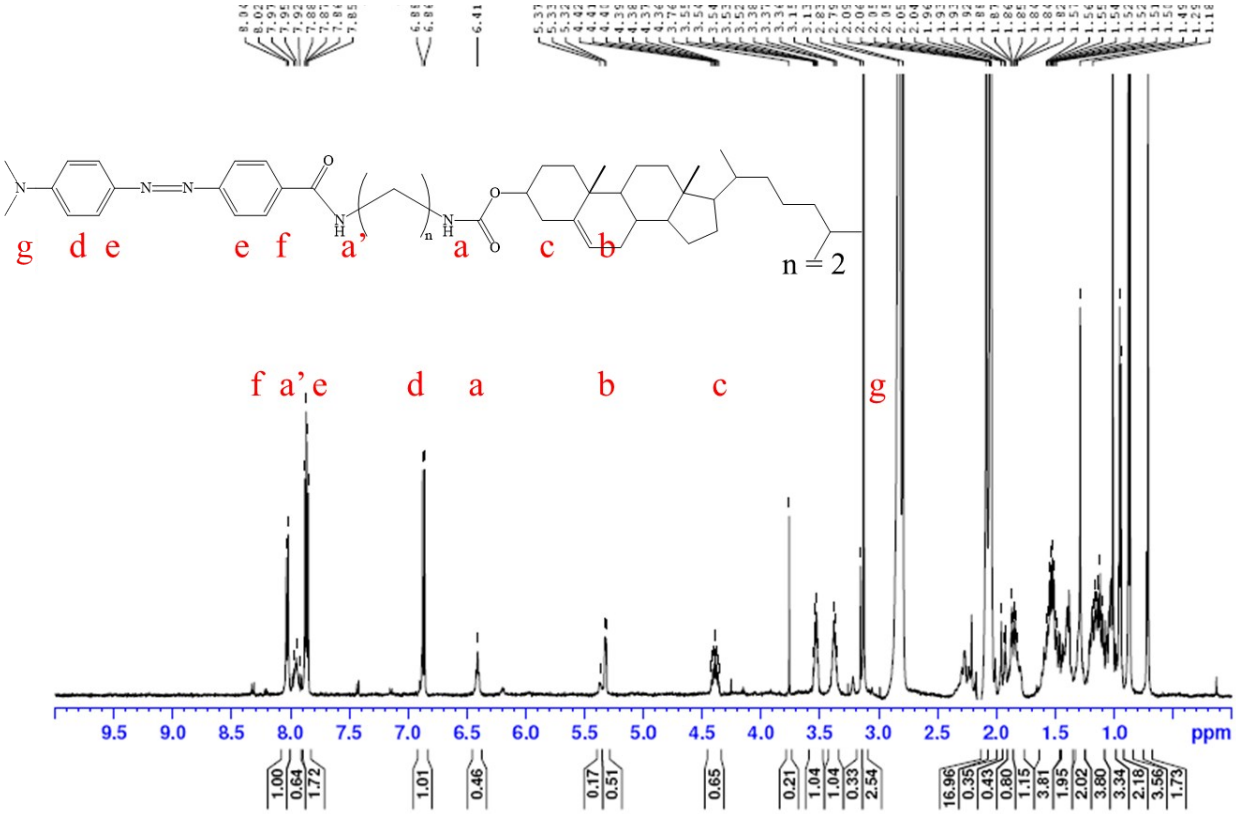


Fig. S3. [1]H-NMR spectrum of N2 in acetone-d6.

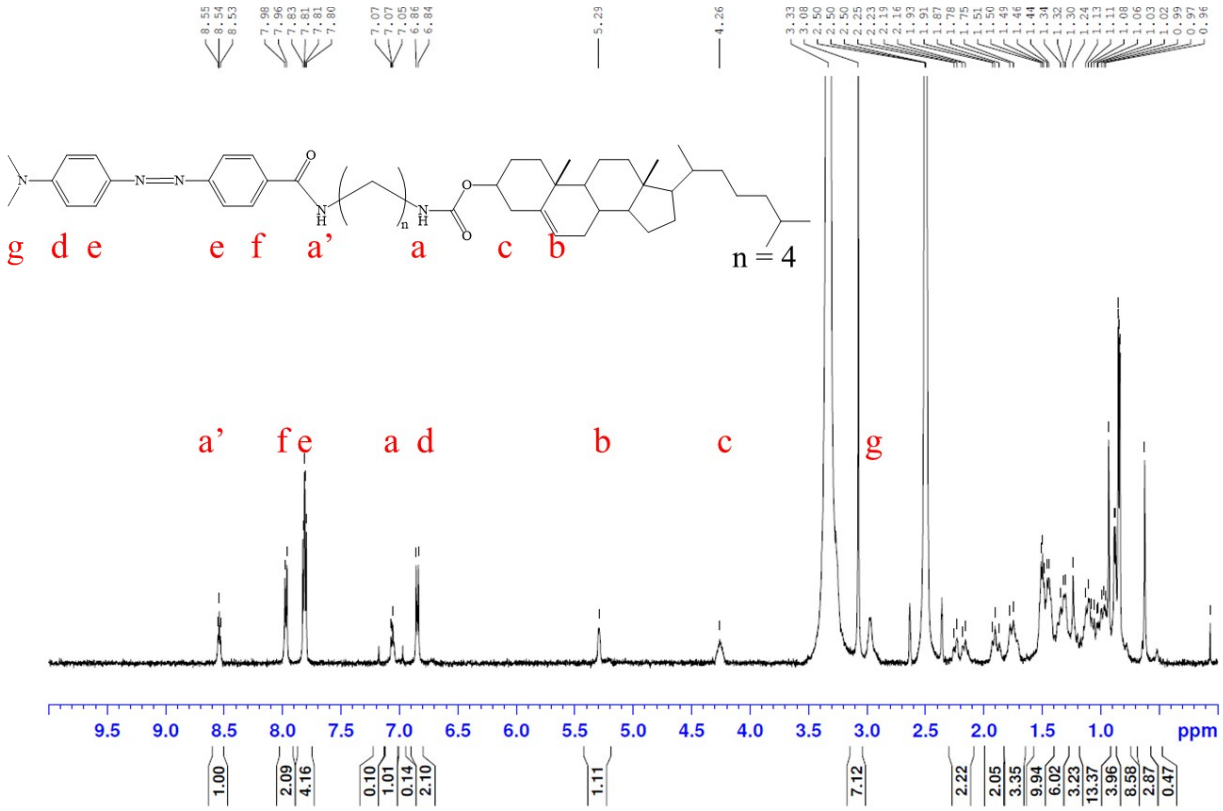


Fig. S4. [1]H-NMR spectrum of N4 in DMSO-d6.

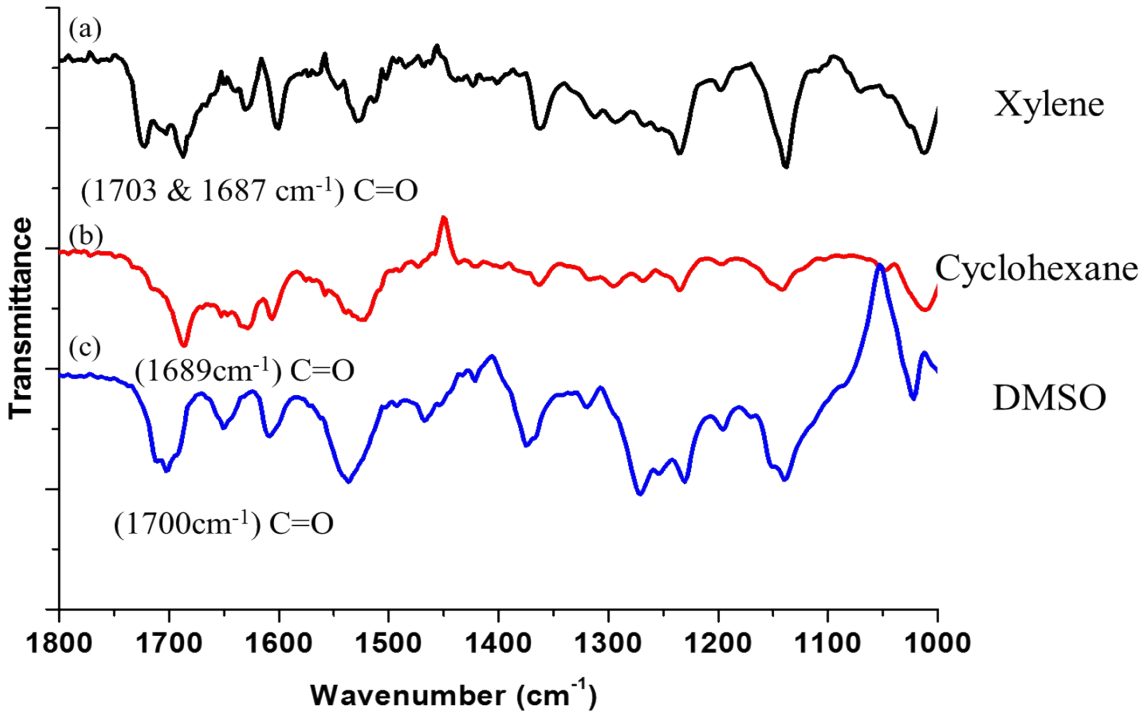


Fig. S5. ATR spectra of (a) N4-xylene gel, (b) N4-cyclohexane gel, and (c) N4-DMSO gel.

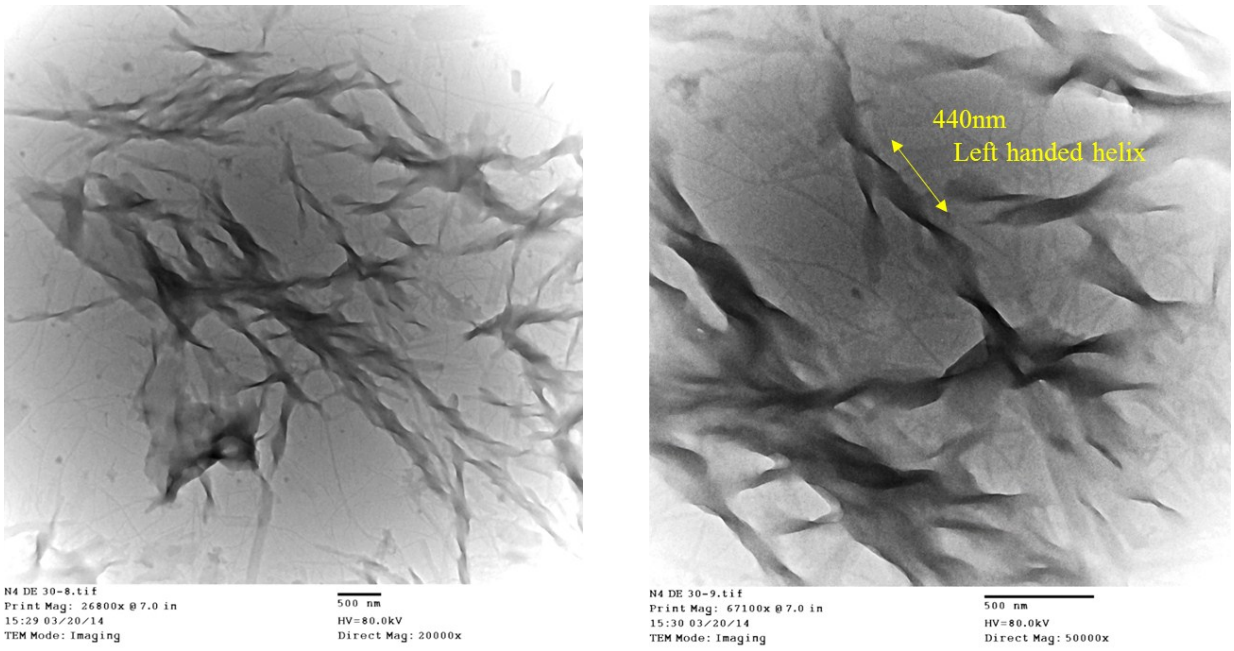


Fig. S6. TEM images of the self-assembled structures of N4 derived from diphenyl ether under different levels of magnification.

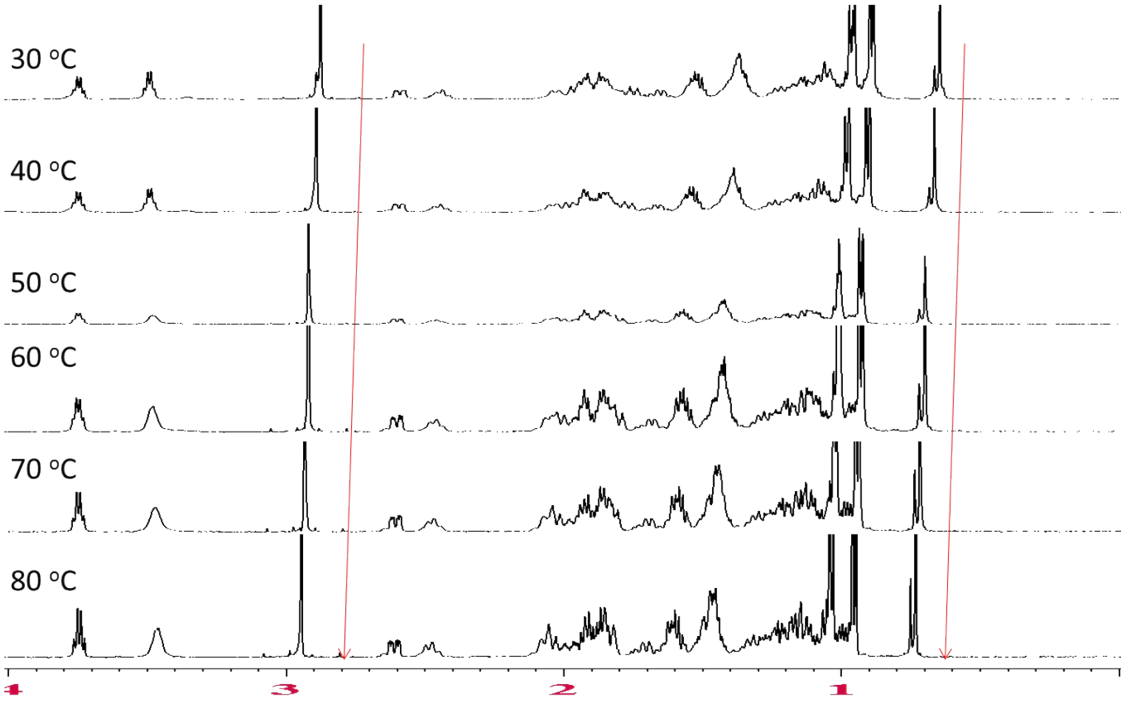


Fig. S7. Temperature-dependence proton NMR spectra of N4/pyridine gel over the temperature range of 30~ 80 °C from 0.0 ppm-4.0 ppm.

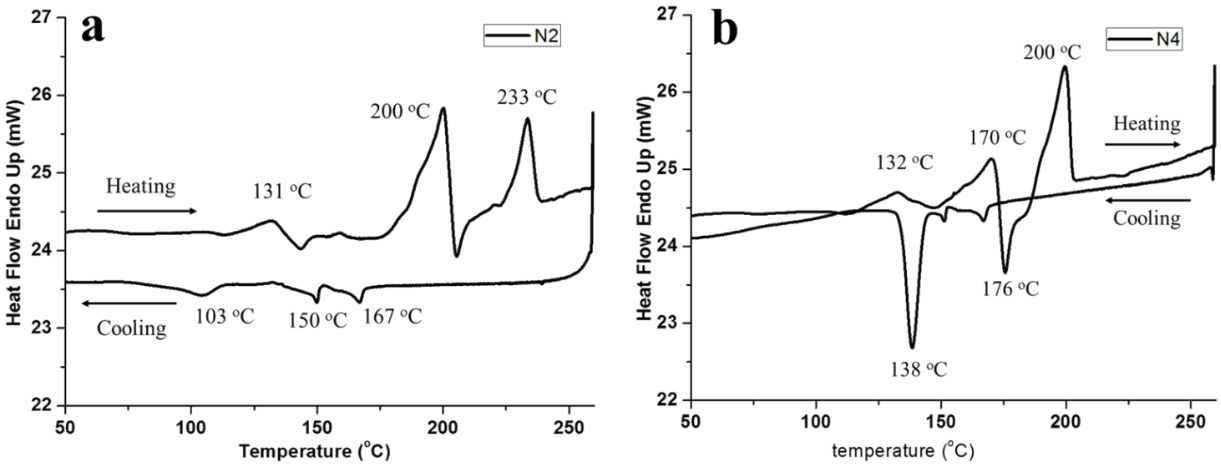


Fig. S8. DSC curves of the synthesized compounds (a) N2 and (b) N4.