Electronic Supplementary Information

Controllable Gelation of Coordination Nanocages from the Physical Interactions among Surface Grafted Cholesteryl Groups

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This PDF file includes six sections:

1. Materials and Solvents

Materials: Cholesteryl chloroformate (97 %, Aladdin), copper (II) acetate monohydrate (99.0 %, Aladdin), sodium carbonate anhydrous (≥ 99.8 %, General-reagent), sodium chloride (99.5 %, Aladdin), 2-bromoethanol (98%+, Adamas), potassium carbonate (K_2CO_3) (98%, Aladdin), potassium iodide (KI) (≥ 99.0%, Macklin), 4-dimethylaminopyridine (DMAP) (99%, Aladdin), triethylamine (TEA) (99%, Adamas), trifluoroacetic acid (TFA) (99%, Aladdin), propargyl alcohol (99%, Aike Reagent), copper(I) bromide (CuBr) (99%, Adamas), N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA) (99%, Aladdin), 1,12-dibromododecane (97%, Aladdin), NaN_3 (≥99.5%, Sigma-Aldrich).

Solvents: *N, N*-Dimethylacetamide (99.0 %, Aladdin), acetone (Guangzhou Chemical Reagent), methanol (99.5 %, Aladdin), toluene (≥ 99.5 %, General-reagent), tetrahydrofuran (≥ 99.8 %, General-reagent), dichloromethane (≥ 99.5 %, General-reagent), petroleum ether (≥ 99.5 %, General-reagent), ethylacetate (≥ 99.5 %, General-reagent), hexane (≥ 99.5 %, General-reagent), all organic solvents or monomers were used without further purification. Deionized water was obtained from the Ultra-pure water system (Water Purifier, WP-RO-10B).

2. Methods

2.1 Nuclear Magnetic Resonance (NMR) Spectroscopy

All the samples were dissolved in deuterium solvents with tetramethylsilane (TMS) as reference. ^{1}H NMR and ^{13}C NMR have recorded on Bruker AVANCE II 500 spectrometer at 298 K.

2.2 UV-Vis Spectroscopy

UV-vis data was collected on a Shimadzu UV-1800 spectrophotometer. The sample was dissolved in anhydrous solvents (THF) with a concentration of 0.5 mg mL^{-1} and a 10 mm quartz cuvette was used as a container during the test.

2.3 Gel Permeation Chromatography (GPC)

GPC analysis of the polymer samples is carried out on Japan Analytical Industry model, equipped with an LC-100 column oven (40 °C), a refractive index detector (JAI RI

Detector RI-7), and two polystyrene gel columns in series (Shodex KF-803 and KF-805). THF (HPLC grade) is used as eluent with a flow rate of 1 mL min^{-1}. The number-average (M_n) and weight-average (M_w) molecular weights of samples are determined with monodispersed polystyrene standards (Shodex, Standard Polystyrene SM - 105). The polymer dispersity indexes (PDI) of the molecular weights are evaluated to be 1.03, 1.02 and 1.05 for Chol-CNC-3, Chol-CNC-7, and Chol-CNC-16, respectively.

2.4 Electrospray ionization mass spectrometry (ESI-MS)

The synthetic compounds (Chol-IPAs) were dissolved in THF with a concentration of 1 mg mL^{-1}, and then subjected to Bruker Daltonics Apex IV spectrometer to collect the mass information.

2.5 Small Angle X-ray Scattering (SAXS)

The Chol-CNCs gels were sealed in a custom-made hollow U-shaped sample container with two layers of 3M tape. The Chol-CNC bulk was sealed by two layers of 3M tape. The SAXS data were recorded on the beamline (BL-16B) of the Shanghai Synchrotron Radiation Facility (SSRF) with a Pilatus 2M detector. The wavelength of the incident X-ray beam is 1.23984 Å and the exposure time was set to 10 s to collect the structural information. Silver behenate (AgBh) was used as the standard sample for calibration. For all the samples, the background was the two layers of 3M tape. Fit2D software is used to convert two-dimensional scattering data into a one-dimensional scattering curve, while the contribution of background scattering is subtracted, and the real one-dimensional scattering data is finally obtained.

2.6 Rheology

A controlled-stress rotational rheometer (Anton Paar MCR-302) with parallel plate geometry was used to investigate the rheological properties of supramolecular gels. As a way to prevent the rapid evaporation of the solvents, cylinder-shaped glass bottles were used to hold the as-prepared organogels with a thickness of 4 ~ 5 mm and a diameter of 25 mm. Then, the bottle was fixed on the base plate of the rheometer. Amplitude sweeps with constant frequency (ω = 5 rad s^{-1}) at 25 ^{o}C were performed to determine the linear viscoelastic region. Bearing this in mind, small amplitude oscillatory shear (SAOS) experiments were subsequently carried out to quantitatively

evaluate the viscoelastic performances of different Chol-CNC gels within the frequency window ranging from 0.1 ~ 100 rad s^{-1} at 25 °C. To ensure the credibility of our data, the rheology experiments for each sample were repeated at least 2 times. The storage modulus (G') and loss modulus (G'') were obtained from the above-mentioned dynamic rheology experiments.

2.7 Scanning Electron Microscope (SEM)

JEOL JSM-7900F SEM was exploited to characterize the microstructures of the supramolecular gels. The afforded gels were fixed on the SEM sample table and then frozen in a liquid nitrogen chamber during vacuolization, then transferred to the sample chamber. After sublimating for 15 minutes to remove the solvents, the gels were sprayed with gold (5 mA, 45 s) to improve the conductivity. After that, these samples are used for further cryo-SEM experiments at 5 kV.

The Chol-CNCs supramolecular gels were freeze-dried and spread on a sample stand with conductive tape. The samples were sprayed with gold (30 mA, 45 s) before imaging to improve the conductivity for the further SEM experiments at 5 kV and energy dispersive X-ray analysis (EDX) at 15 kV.

2.8 Transmission Electron Microscopy (TEM)

The Chol-CNCs supramolecular gels were freeze-dried and dispersed in ethanol at a concentration of 2.0 mg mL^{-1}. Then a small amount of the suspension liquids dropped onto a holey carbon film placed on a copper grid was dried and used to take images with a digital CCD camera in a JEOL-1230 microscope with an accelerating voltage of 120 keV.

2.9 Small angle neutron scattering (SANS)

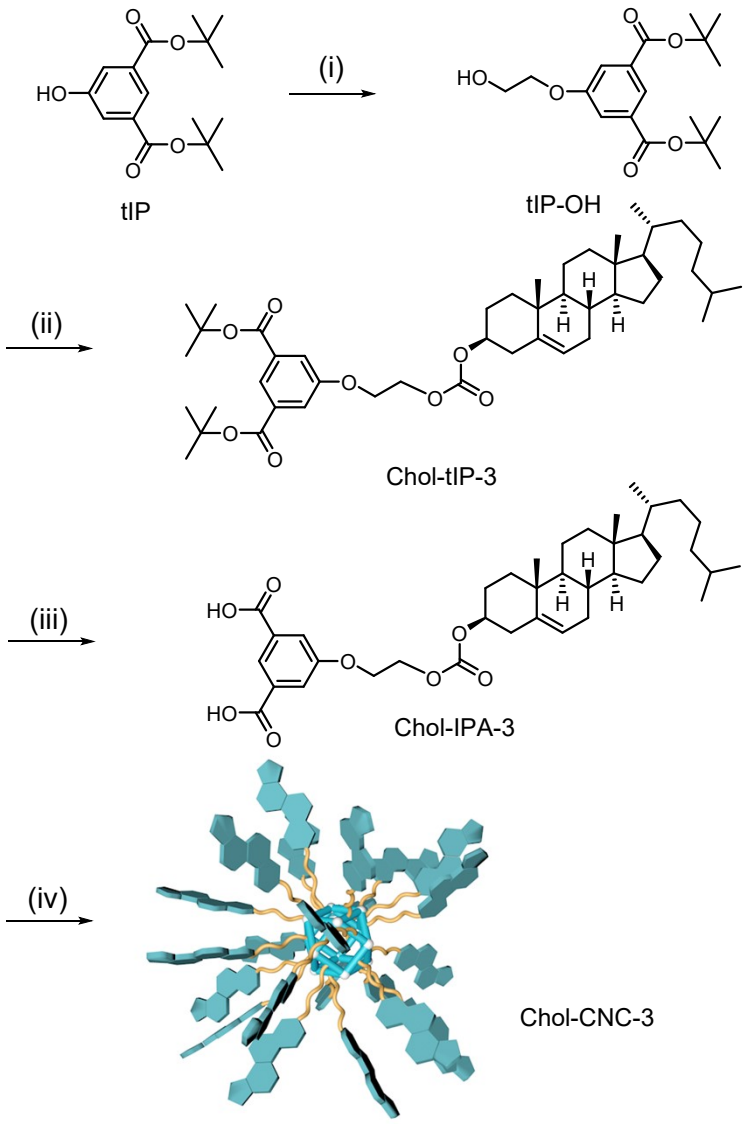
SANS data were collected at China Spallation Neutron Source (CSNS)[1]. Chol-CNC was dispersed in deuterium THF (THF-d_8) to improve the contrast and the volume ratio was around 2%. The wavelength of the incident neutron was 1.2 ~ 9.5 Å and the exposure time for each sample was 2 h to acquire the form factor of Chol-CNC. For the Chol-CNC gels, the gels were formed in situ within THF-d_8 and toluene-d_8 mixed solvents in a quartz container with a thickness of 2 mm. The supramolecular gels were exposed to the neutron beams and the scattered neutrons were detected by the area

detector. The obtained two-dimensional data were then converted to one-dimensional data. The solvent background was subtracted to afford the final scattering curve.

2.10 Molecular dynamics (MD) simulations

All-atom molecular dynamics simulations were conducted using the LAMMPS software package, and COMPASS force fields parameters are applied to describe the inter- and intra-atomic interactions of Chol-CNC-7 systems with THF/toluene solvent systems is applied for systems. The simulations were carried out at a volume ratio of toluene/THF in 2/1 conditions with an implicit solvent. The time step was 1 fs and the cutoff distance was 9.5 Å for our calculations. In order to ensure the Chol-CNC-7 system reached equilibrium at the chosen temperatures, the sample was treated for 2 ns with an NPT ensemble (p = 1 bar, T = 300 K). In this process, the system was initiated from random configurations and evolved toward more organized states of Chol-CNC-7 self-assembly.

3. Synthetic Procedures



Scheme S1. Reaction conditions: (i) 2-bromoethanol, K_2CO_3, KI, acetone, 80 °C; (ii) Chol-Cl, DMAP, TEA, CH_2Cl_2, RT; (iii) TFA, CH_2Cl_2, RT; (iv) Cu $(CH_3CO_2)_2 \cdot H_2O$, DMF, THF, RT.

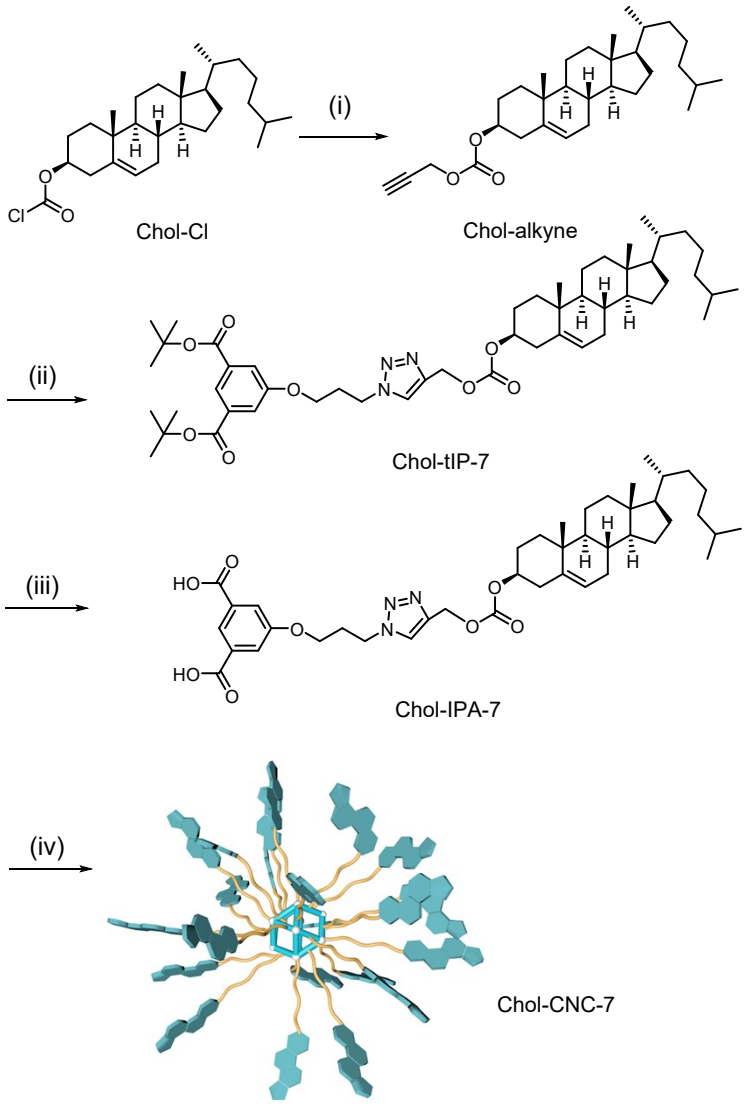
Synthesis of tIP-OH: tIP was synthesized by referencing to the previous literature[2]. tIP (1.47 g, 5.0 mmol), 2-bromoethanol (1.25 g, 10 mmol), K_2CO_3 (1.38 g, 10 mmol), and KI (166 mg, 1.0 mmol) were added to a 150 mL flask. 70 mL acetone was added to dissolve the reagents. The reaction mixture was heated to 80 °C under N_2 atmosphere and stirring was kept for another 12 h. After cooling to room temperature, the precipitate was filtered and solvent was evaporated under reduced pressure. The residual was then subjected to flash column chromatography with CH_2Cl_2: PE (4:1, v/v) as eluents to afford the product as white solid (1.15 g, 68%). ^{1}H NMR (500 MHz,

$CDCl_3$) δ: 8.18 (d, 1H), 7.69 (d, 2H), 4.16 (t, 2H), 3.99 (t, 2H), 1.59 (s, 19H).

Synthesis of Chol-tIP-3: Chol-Cl was obtained from commercial source and used without further purification. Chol-Cl (1.35 g, 3.0 mmol), tIP-OH (0.68 g, 2.0 mmol), DMAP (37 mg, 0.3 mmol), and TEA (0.3 g, 3.0 mmol) were dissolved in 30 mL anhydrous CH_2Cl_2. Reaction was performed under room temperature for 14 h. The solvent was evaporated under reduced pressure and the crude product was collected. Then, it was subjected to flash column chromatography with CH_2Cl_2: PE (1:1, v/v) as eluents to afford the product as white solid (1.05 g, 70%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.19 (s, 1H), 7.68 (s, 2H), 5.39 (d, 1H), 4.59 - 4.40 (m, 3H), 4.37 - 4.18 (t, 2H), 2.49 - 2.27 (m, 2H), 2.04 - 1.73 (m, 5H), 1.59 (s, 24H), 1.52 - 0.54 (m, 38H).

Synthesis of Chol-IPA-3: Chol-tIP-3 (0.75 g, 1.0 mmol) and TFA (11.4 g, 100 mmol) were dissolved in 46 mL anhydrous CH_2Cl_2. Reaction was performed under room temperature for 10 h. After that, the solvent was evaporated under reduced pressure. The crude product was washed with saturated NaCl aqueous solution for three times to remove the excess TFA. The organic layer was collected, evaporated and then dried under vacuum condition to afford the final product as white solid (0.51 g, 80%). ^{1}H NMR (500 MHz, THF-d_8) δ: 8.27 (d, 1H), 7.75 (s, 2H), 5.39 (d, 1H), 4.49 - 4.39 (m, 3H), 4.29 (t, 2H), 2.44 - 2.26 (m, 2H), 2.13 - 1.78 (m, 6H), 1.69 - 0.63 (m, 47H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.82, 158.77, 154.37, 141.66, 132.64, 123.35, 122.42, 119.37, 78.68, 66.64, 66.81, 56.84, 56.28, 50.20, 42.28, 39.82, 39.51, 36.21, 35.87, 31.89, 28.03, 24.70, 24.54, 24.38, 24.22, 24.06, 23.81, 21.97, 18.23, 11.31. MS (ESI-MS, m/z): Calc. for $C_{38}H_{44}O_8$: 637.3741. Found: 637.3771[M-H]$^{1-}$.

Synthesis of Chol-CNC-3: THF solution (10 mL) of Chol-IPA-3 ligands (0.51 g) is added to a DMF solution (2 mL) of Cu $(CH_3CO_2)_2$•H_2O (1.2 eq.) with vigorous stirring. After 24 h reaction, the product is precipitated three times in methanol, and collected as a blue solid by filtration and dried under vacuum. SEC (THF, UV detector): M_n = 10130 g/mol, M_w = 10443 g/mol, PDI = 1.03.



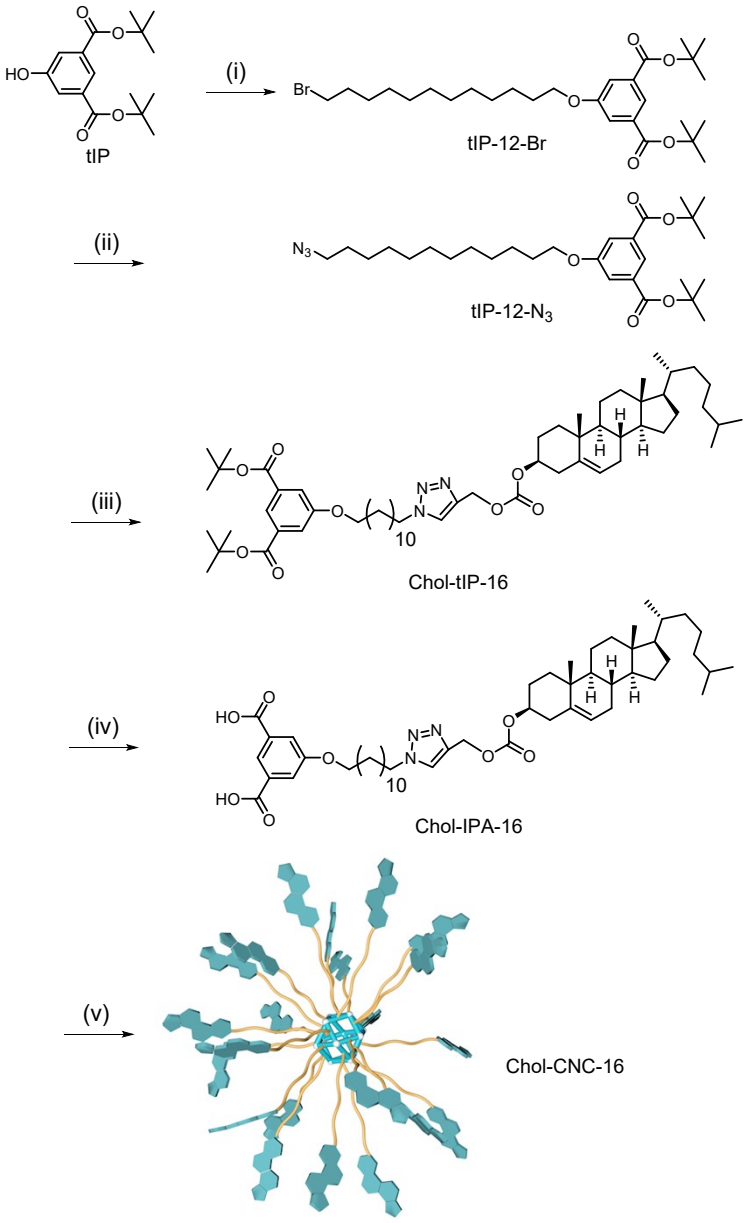
Scheme S2. Reaction conditions: (i) propargyl alcohol, DMAP, TEA, CH_2Cl_2, RT; (ii) tIP-N_3, CuBr, PMDETA, toluene, RT; (iii) TFA, CH_2Cl_2, RT; (iv) Cu $(CH_3CO_2)_2 \cdot H_2O$, DMF, THF, RT.

Synthesis of Chol-alkyne: Chol-Cl (0.90 g, 2.0 mmol), propargyl alcohol (0.22 g, 4.0 mmol), DMAP (49 mg, 0.4 mmol), and TEA (0.4 g, 4.0 mmol) were added to a 100 mL flask. 30 mL anhydrous CH_2Cl_2 was subsequently introduced as solvent. The reaction was performed at room temperature for 10 h. After that, the solvent was removed under reduced pressure and residual was subjected to flash column chromatography with CH_2Cl_2: PE (1:1, v/v) as eluents to afford the product as shining plate-like crystal (0.69 g, 73%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.38 (dd, 1H), 4.71 (d, 2H), 4.59 - 4.41 (m, 1H), 2.51 (t, 1H), 2.47 - 2.29 (m, 2H), 2.10 - 1.72 (m, 5H), 1.73 - 0.60 (m, 39H).

Synthesis of Chol-tIP-7: tIP-N_3 was synthesized by referencing to the previous literature[3]. Chol-alkyne (0.70 g, 1.5 mmol), tIP-N_3 (0.68 g, 1.8 mmol), CuBr (6.0 mg, 0.042 mmol), and PMDETA (21 mg, 0.12 mmol) were added to a 20 mL vial. Then, the vial was transferred to glove box. 15 mL anhydrous toluene was introduced as solvent and reaction was performed under room temperature for 12 h. The reaction mixture was subjected to flash column chromatography with CH_2Cl_2: EA (10:1, v/v) as eluents to afford the product as white solid (1.05 g, 83%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.16 (t, 1H), 7.66 (s, 1H), 7.64 (d, 2H), 5.38 (d, 1H), 5.25 (s, 2H), 4.59 (t, 2H), 4.52 - 4.40 (m, 1H), 4.06 (t, 2H), 2.55 - 2.27 (m, 4H), 2.08 - 1.74 (m, 5H), 1.73 - 1.55 (m, 23H), 1.55 - 0.55 (m, 36H).

Synthesis of Chol-IPA-7: Chol-IPA-7 was synthesized by following the similar procedure of Chol-IPA-3 as mentioned above. ^{1}H NMR (500 MHz, THF-d_8) δ: 8.26 (t, 1H), 7.92 (s, 1H), 7.74 (d, 2H), 5.36 (dd, 1H), 5.15 (s, 2H), 4.57 (dt, J = 2H), 4.45 - 4.31 (m, 1H), 4.11 (t, 2H), 2.44 - 2.26 (m, 4H), 2.09 - 1.79 (m, 5H), 1.66 - 0.64 (m, 38H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.93, 158.66, 156.43, 156.03, 154.51, 141.90, 140.30, 138.66, 132.67, 124.06, 123.30, 121.62, 119.32, 78.69, 66.82, 66.12, 56.80, 56.29, 42.28, 39.82, 39.50, 36.68, 35.86, 31.87, 29.91, 28.02, 24.70, 24.54, 24.05, 22.20, 21.97, 20.97, 18.56, 18.23, 11.29. MS (ESI-MS, m/z): Calc. for $C_{42}H_{58}N_3O_8$: 732.4224. Found: 732.4278[M-H]$^{1-}$.

Synthesis of Chol-CNC-7: Chol-CNC-7 was synthesized by following the similar procedure of Chol-CNC-3 as mentioned above. SEC (THF, UV detector): M_n = 8796 g/mol, M_w = 9145 g/mol, PDI = 1.02.



Scheme S3. Reaction conditions: (i) 1,12-dibromododecane, K_2CO_3, KI, acetone, 80 °C; (ii) NaN_3, DMF, 80 °C; (iii) CuBr, PMDETA, toluene, RT; (iv) TFA, CH_2Cl_2, RT; (v) Cu $(CH_3CO_2)_2 \cdot H_2O$, DMF, THF, RT.

Synthesis of tIP-12-Br: tIP (0.89 g, 3.0 mmol), 1,12-dibromododecane (1.97 g, 6.0 mmol), K_2CO_3 (0.83 g, 6.0 mmol), and KI (0.10 g, 0.6 mmol) were added to a 150 mL flask. 60 mL acetone was added to dissolve the reagents. The reaction mixture was heated to 80 °C under N_2 atmosphere and stirring was kept for 14 h. After cooling to room temperature, the precipitate was filtered and solvent was evaporated under reduced pressure. The crude product was then subjected to flash column chromatography with CH_2Cl_2: PE (1.5:1, v/v) as eluents to afford the product as white

solid (0.85 g, 52%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.15 (t, 1H), 7.65 (d, 2H), 4.02 (t, 2H), 3.40 (t, 2H), 1.89 - 1.73 (m, 4H), 1.59 (s, 21H), 1.50 - 1.08 (m, 22H).

Synthesis of tIP-12-N_3: tIP-12-Br (1.08 g, 2.0 mmol) and NaN_3 (190 mg, 2.9 mmol) were dissolved in 40 mL DMF under N_2 atmosphere. The reaction was performed at 80 ^{o}C for 20 h. Then, the reaction mixture was poured to 100 mL deionized water accompanied with stirring. CH_2Cl_2 was used to extract the reaction product. Then, it was washed with saturated NaCl aqueous solution for three times. The organic layer was collected, evaporated, and dried under reduced pressure to afford the product (0.91 g, 90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.15 (t, 1H), 7.66 (d, 2H), 4.02 (t, 2H), 3.25 (t, 2H), 1.85 - 1.74 (m, 2H), 1.63 - 1.54 (m, 22H), 1.50 - 1.08 (m, 20H).

Synthesis of Chol-tIP-16: Chol-alkyne (0.56 g, 1.2 mmol), tIP-12-N_3 (0.5 g, 1.0 mmol), CuBr (6.0 mg, 0.042 mmol), and PMDETA (21 mg, 0.12 mmol) were added to a 20 mL vial. Then, the vial was transferred to glove box. 14 mL anhydrous toluene was introduced as solvent and reaction was performed under room temperature for 12 h. The reaction mixture was subjected to flash column chromatography with CH_2Cl_2: EA (10:1, v/v) as eluents to afford the product as white solid (0.78 g, 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.15 (t, 1H), 7.65 (d, 2H), 7.62 (s, 1H), 5.38 (d, 1H), 5.26 (s, 2H), 4.54 - 4.41 (m, 1H), 4.34 (t, 2H), 4.02 (t, 2H), 2.43 - 2.29 (m, 2H), 2.05 - 1.70 (m, 11H), 1.59 (s, 22H), 1.53 - 0.61 (m, 57H).

Synthesis of Chol-IPA-16: Chol-IPA-16 was synthesized by following the similar procedure of Chol-IP-3 as mentioned above. ^{1}H NMR (500 MHz, THF-d_8) δ: 8.24 (t, 1H), 7.83 (s, 1H), 7.72 (d, 2H), 5.38 (d, 1H), 5.14 (s, 2H), 4.44 - 4.35 (m, 1H), 4.33 (t, 2H), 4.06 (t, 2H), 2.40 - 2.25 (m, 2H), 2.09 - 1.76 (m, 10H), 1.66 - 0.63 (m, 56H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.09, 159.27, 154.41, 141.65, 139.65, 138.83, 132.62, 123.58, 123.56, 122.93, 122.44, 120.50, 119.27, 78.70, 77.40, 66.67, 66.13, 60.54, 56.95, 56.17, 49.50, 42.27, 39.81, 39.50, 37.49, 36.68, 35.86, 31.88, 29.55, 28.00, 24.71, 24.55, 24.03, 22.21, 21.98, 20.96, 18.24, 11.30. MS (ESI-MS, m/z): Calc. for $C_{51}H_{76}N_3O_8$: 858.5632. Found: 858.5678[M-H]$^{1-}$.

Synthesis of Chol-CNC-16: Chol-CNC-16 was synthesized by following the similar procedure of Chol-CNC-3 as mentioned above. M_n = 12835 g/mol, M_w = 13095 g/mol,

PDI = 1.05.

4. Supplementary Figures and Tables

4.1 Supplementary figures

Fig. S24 Photographs of Chol-CNC-16 in THF/hexane (20 mg Chol-CNC-16, hexane (0.20 mL)/THF (0.10 mL)).

Fig. S25 Photographs of Chol-CNCs in THF/toluene.

Fig. S26 Photographs of control experiments.

Fig. S27 SEM and EDX images of the freeze-dried Chol-CNC-3 supramolecular gel.

Fig. S28 SEM images of the freeze-dried Chol-CNC-7 supramolecular gel.

Fig. S29 SEM images of the freeze-dried Chol-CNC-16 supramolecular gel.

Fig. S30 Slice images of Chol-CNC-7 gels (THF/toluene) samples during the self-assembly process.

Fig. S31 Amplitude sweep and frequency sweep of Chol-CNC-7 supramolecular gels in THF/toluene and THF/hexane mixed solvent.

Fig. S32 SAXS patterns of bulk Chol-CNC-7 and theoretical curve of Chol-CNC-7.

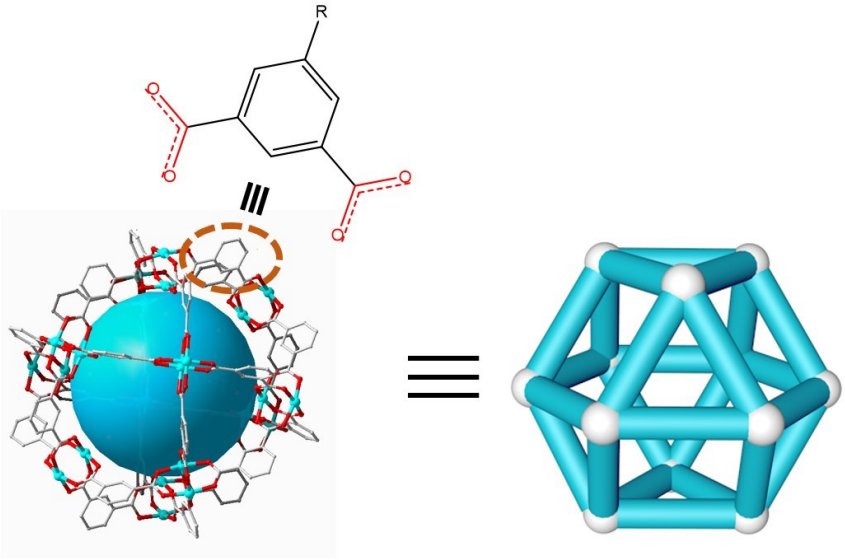


Fig. S1 Structure of a cuboctahedron copper coordination nanocages.

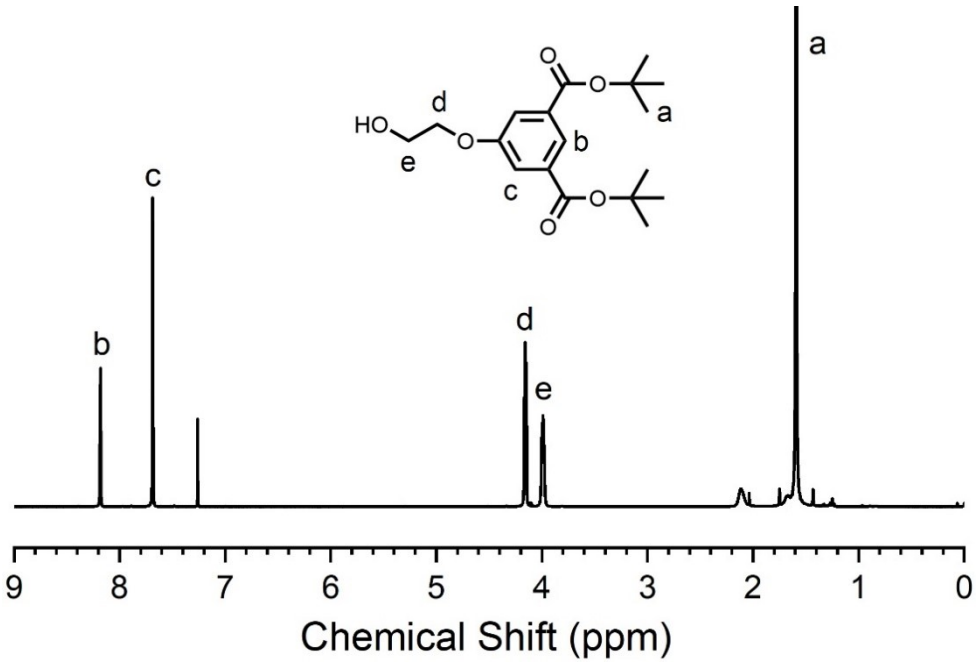


Fig. S2 ^{1}H NMR spectrum of tIP-OH in $CDCl_3$ at 298 k.

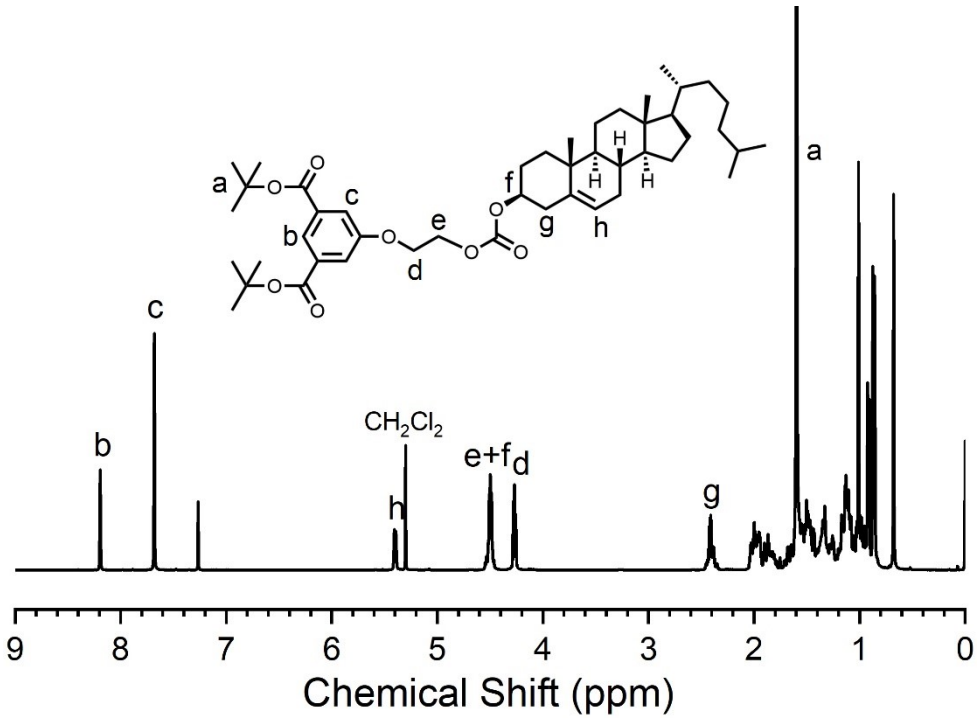


Fig. S3 ^{1}H NMR spectrum of Chol-tIP-3 in $CDCl_3$ at 298 k.

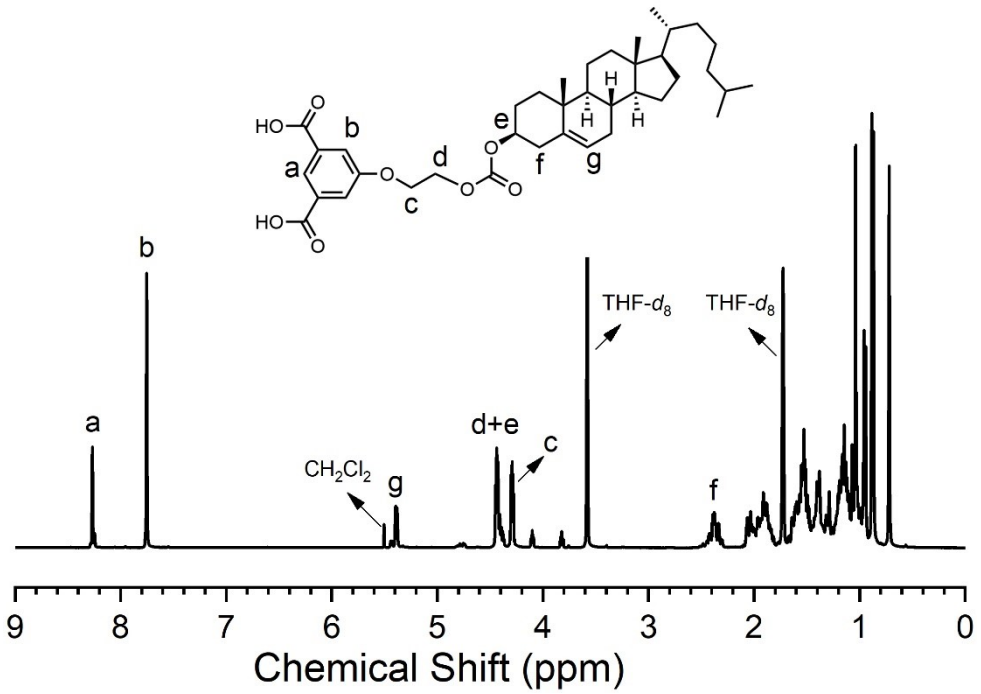


Fig. S4 ^{1}H NMR spectrum of Chol-IPA-3 in THF-d_8 at 298 k.

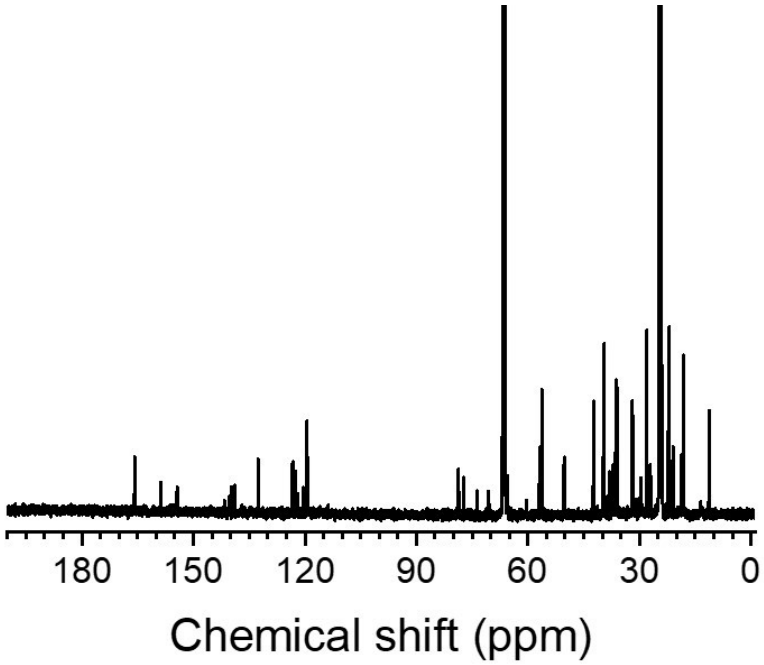


Fig. S5 ^{13}C NMR spectrum of Chol-IPA-3 in THF-d_8 at 298 k.

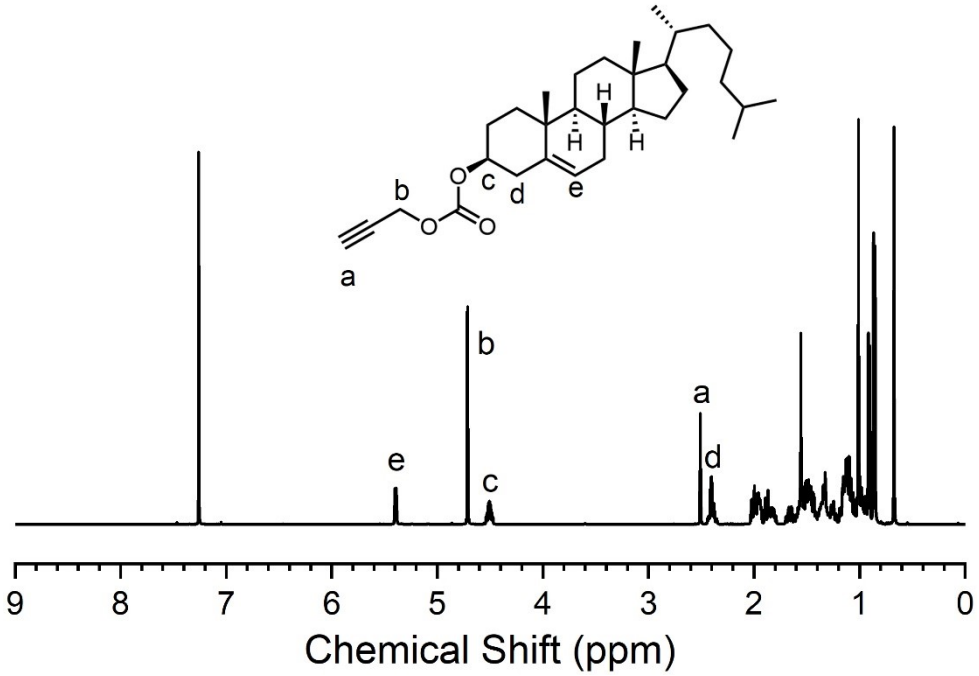


Fig. S6 ^{1}H NMR spectrum of Chol-alkyne in $CDCl_3$ at 298 k.

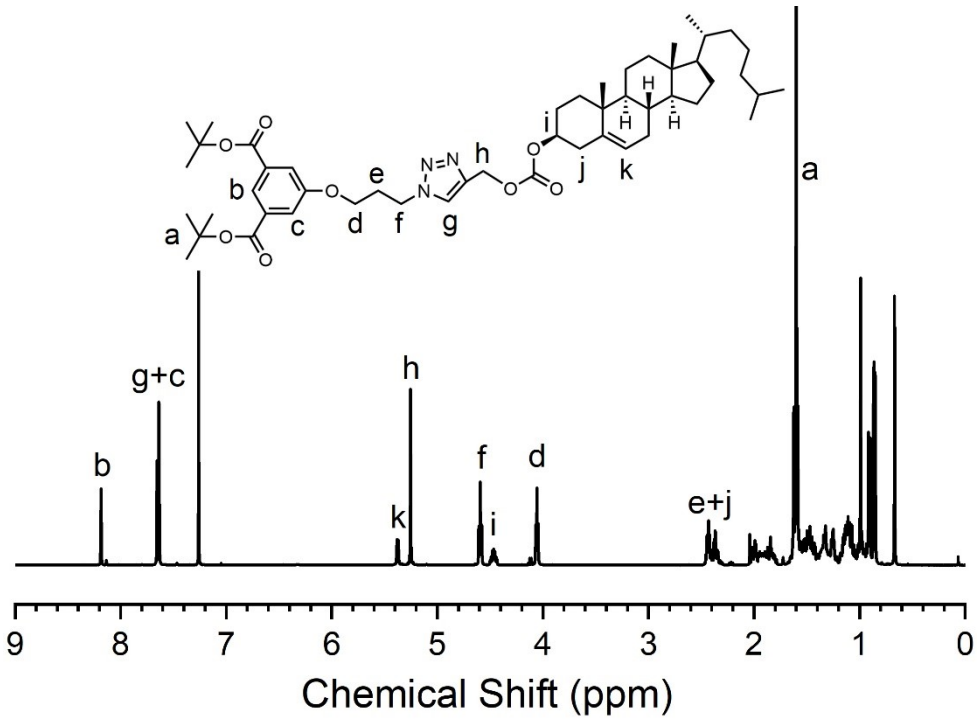


Fig. S7 ^{1}H NMR spectrum of Chol-tIP-7 in $CDCl_3$ at 298 k.

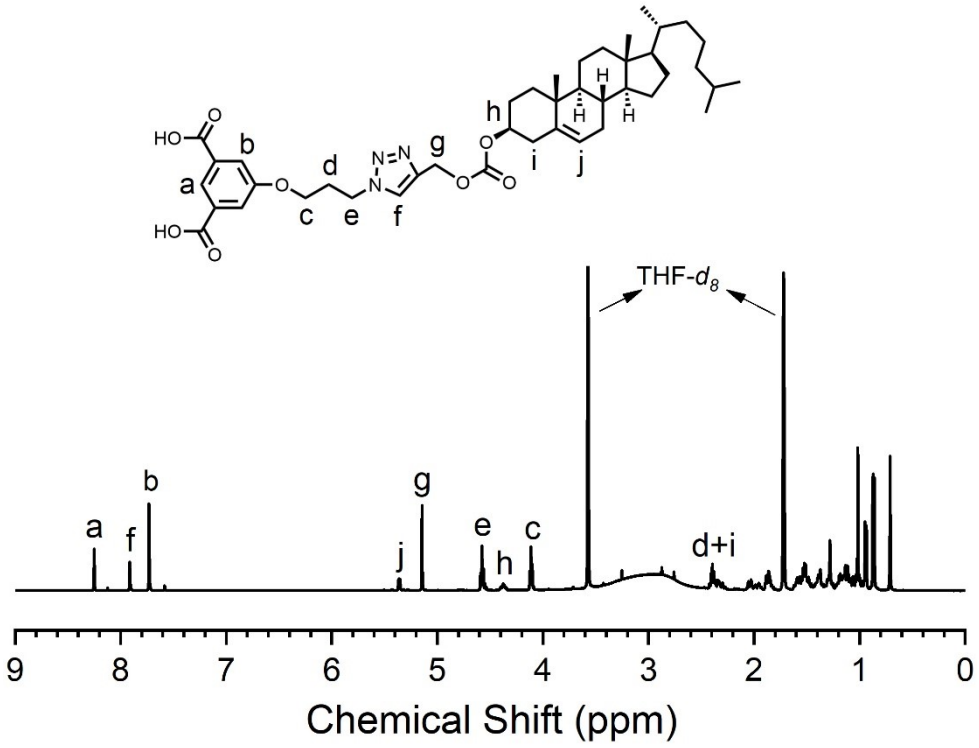


Fig. S8 ^{1}H NMR spectrum of Chol-IPA-7 in THF-d_8 at 298 k.

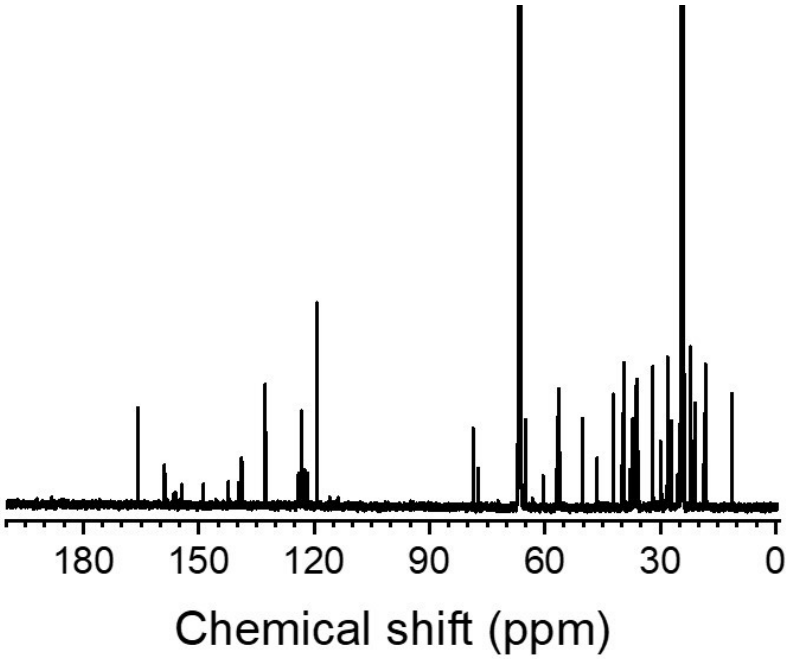


Fig. S9 ^{13}C NMR spectrum of Chol-IPA-7 in THF-d_8 at 298 k.

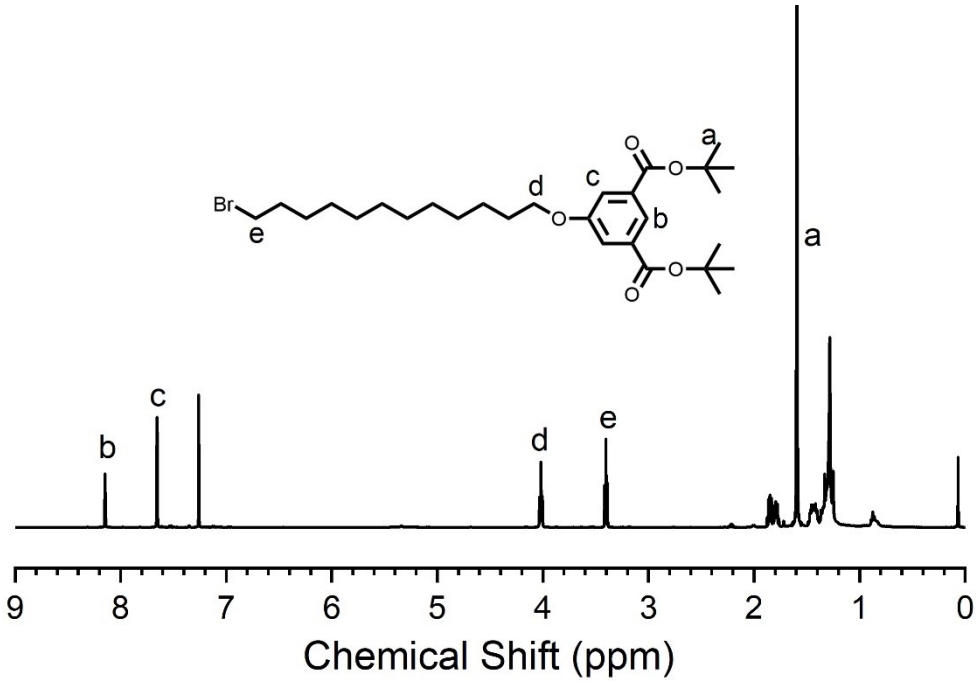


Fig. S10 ^{1}H NMR spectrum of tIP-12-Br in $CDCl_3$ at 298 k.

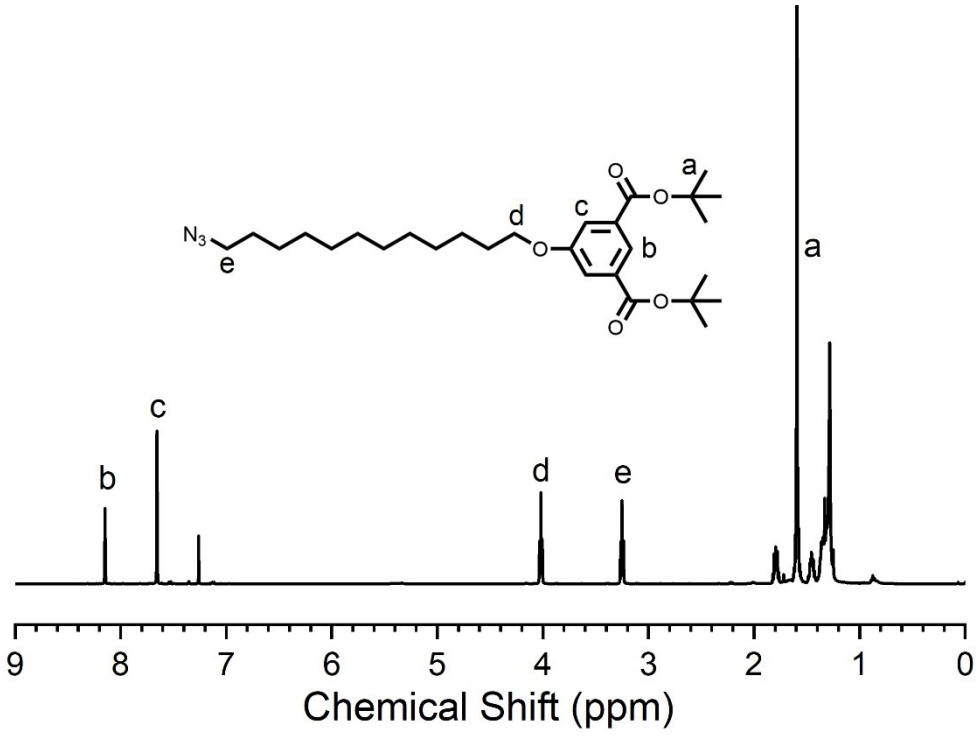


Fig. S11 ^{1}H NMR spectrum of tIP-12-N_3 in $CDCl_3$ at 298 k.

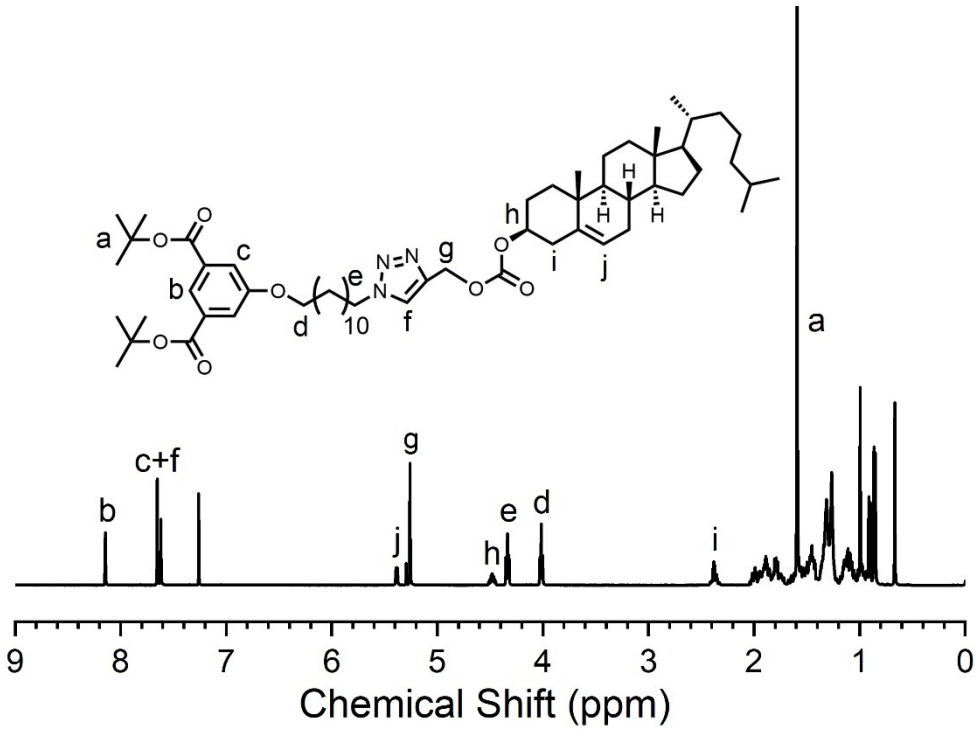


Fig. S12 ^{1}H NMR spectrum of Chol-tIP-16 in $CDCl_3$ at 298 k.

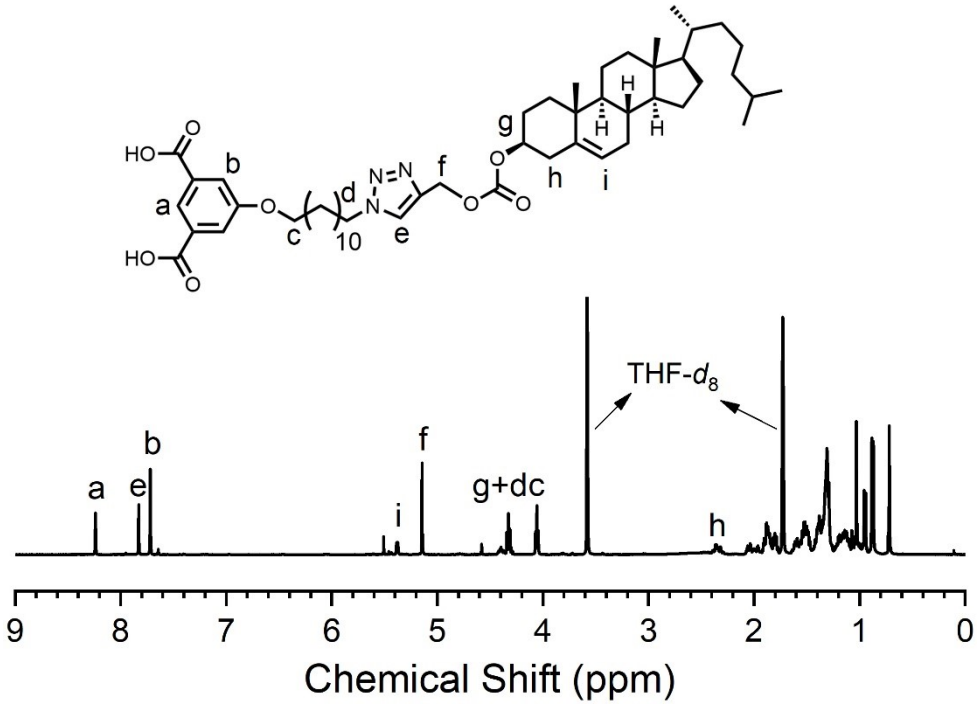


Fig. S13 ^{1}H NMR spectrum of Chol-IPA-16 in THF-d_8 at 298 k.

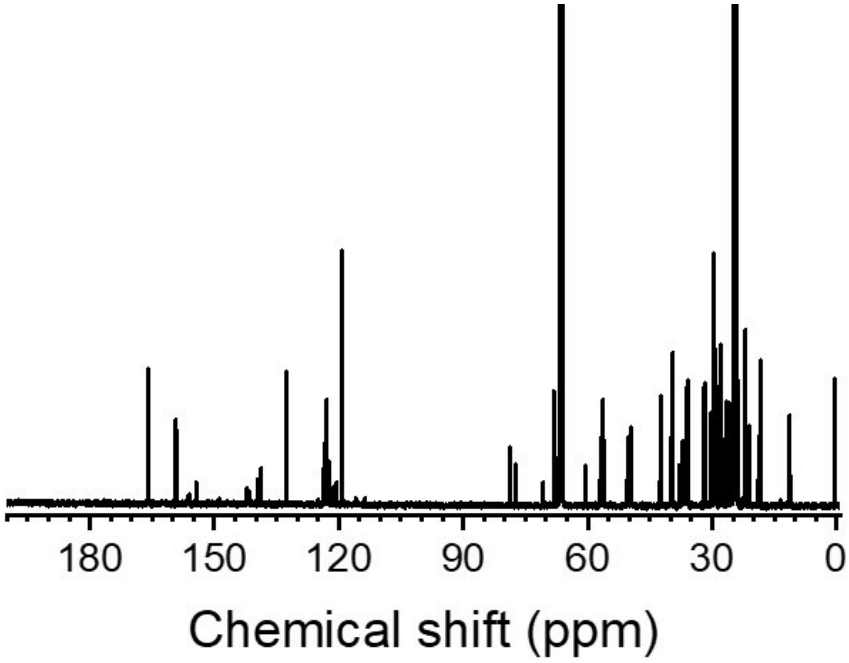


Fig. S14 ^{13}C NMR spectrum of Chol-IPA-16 in THF-d_8 at 298 k.

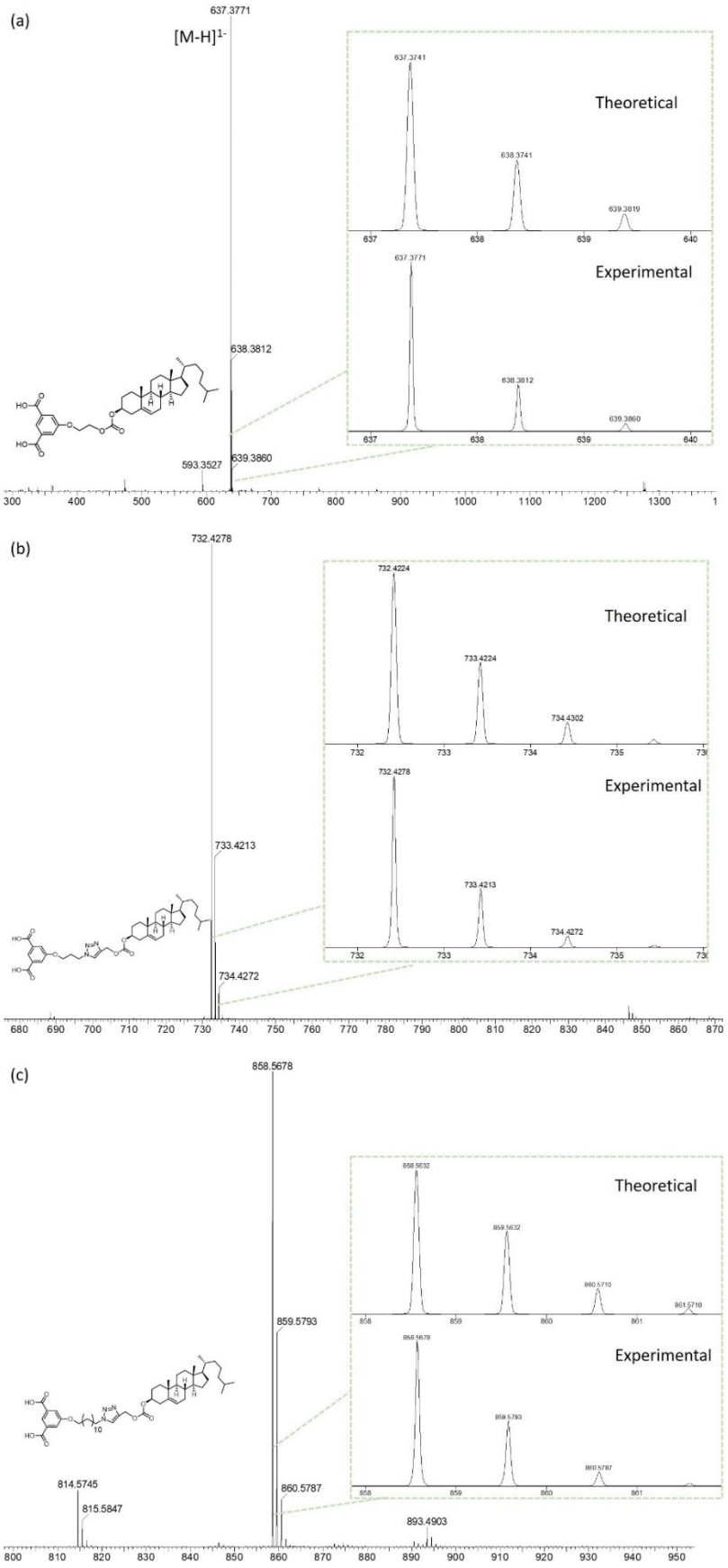


Fig. S15 ESI-MS of Chol-IPAs in THF-d_8 at 298 k. (a) Chol-IPA-3. (b) Chol-IPA-7. (c) Chol-IPA-16.

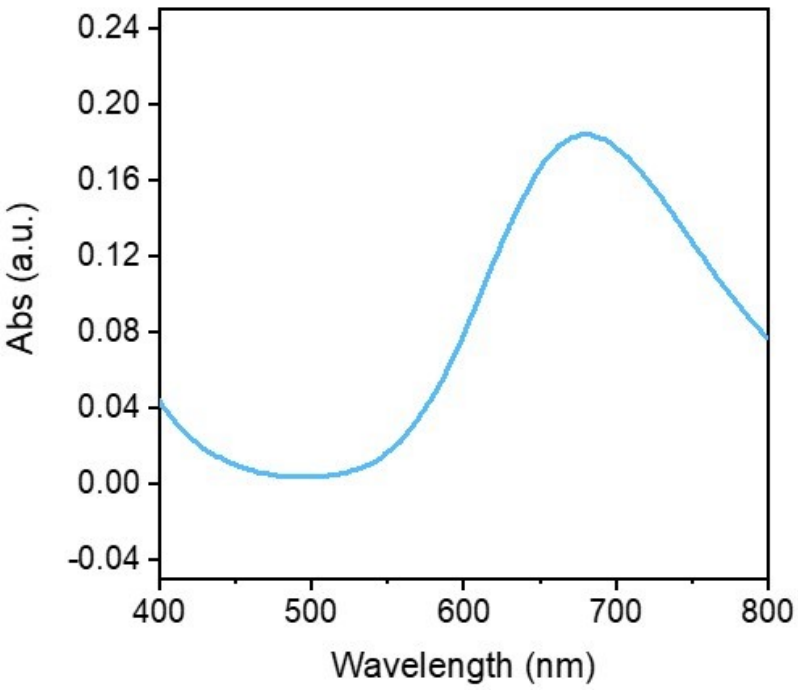


Fig. S16 UV-Vis spectrum of Chol-CNC-3 in THF.

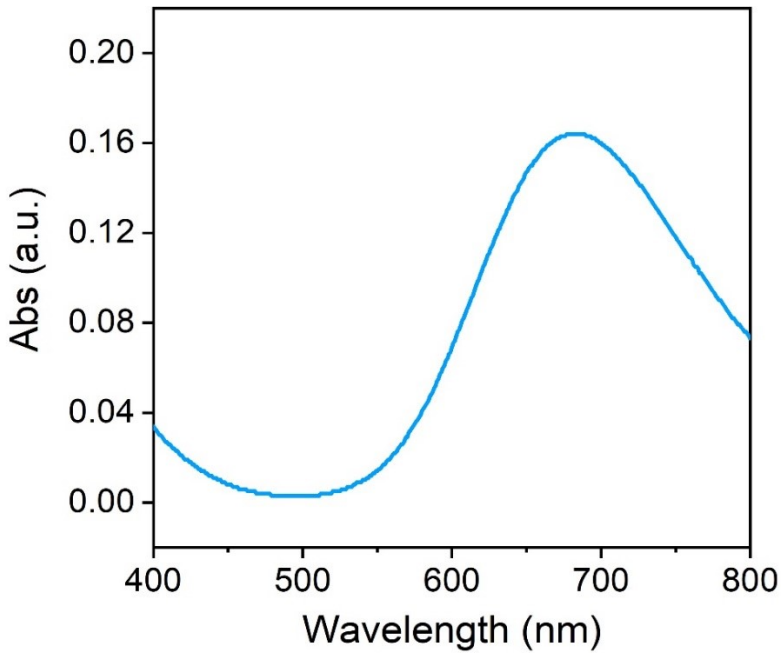


Fig. S17 UV-Vis spectrum of Chol-CNC-7 in THF.

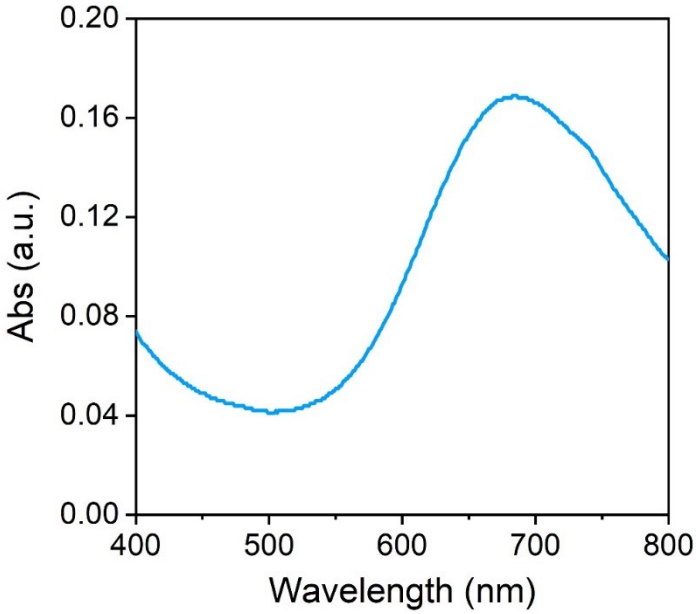


Fig. S18 UV-Vis spectrum of Chol-CNC-16 in THF.

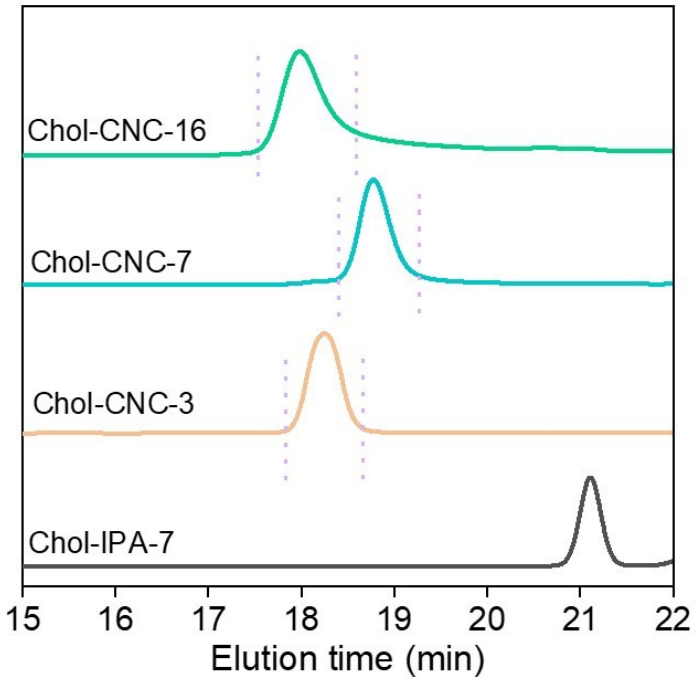


Fig. S19 GPC traces of the Chol-IPA-7 and Chol-CNCs, the polymer dispersity indexes (PDI) of the molecular weights are evaluated to be 1.03, 1.02 and 1.05 for Chol-CNC-3, Chol-CNC-7, and Chol-CNC-16, respectively.

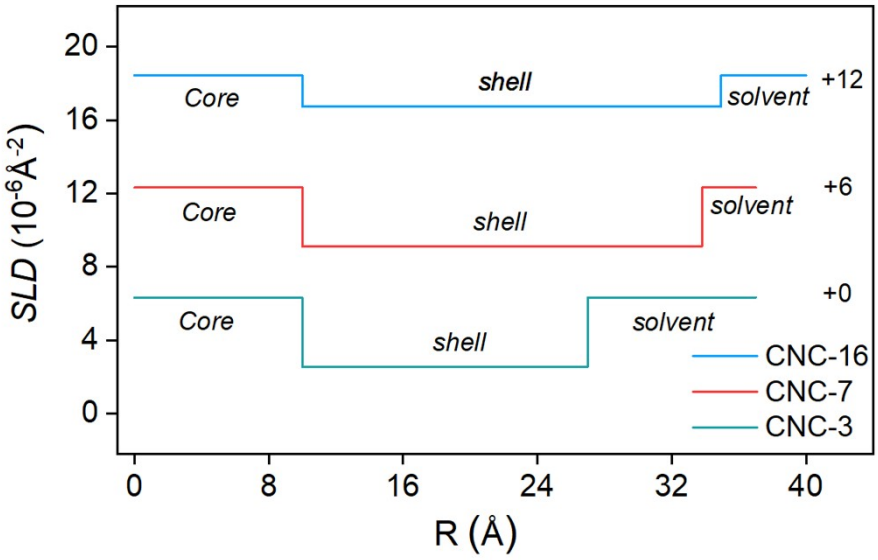


Fig. S20 The fitted scattering length density (SLD) profile of Chol-CNCs arising from the SANS data on the basis of core-shell model, which reflects the contrast of inner core and outer shell character.

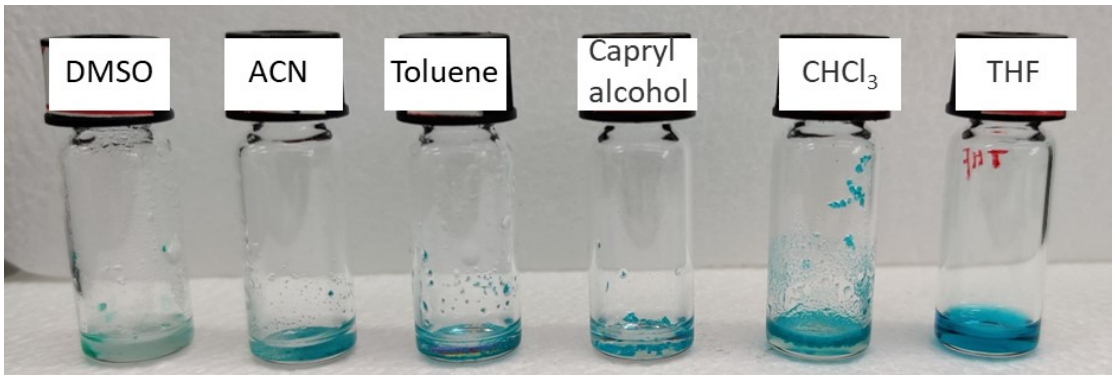


Fig. S21 Solubility of Chol-CNC-7 in different kinds of solvents.

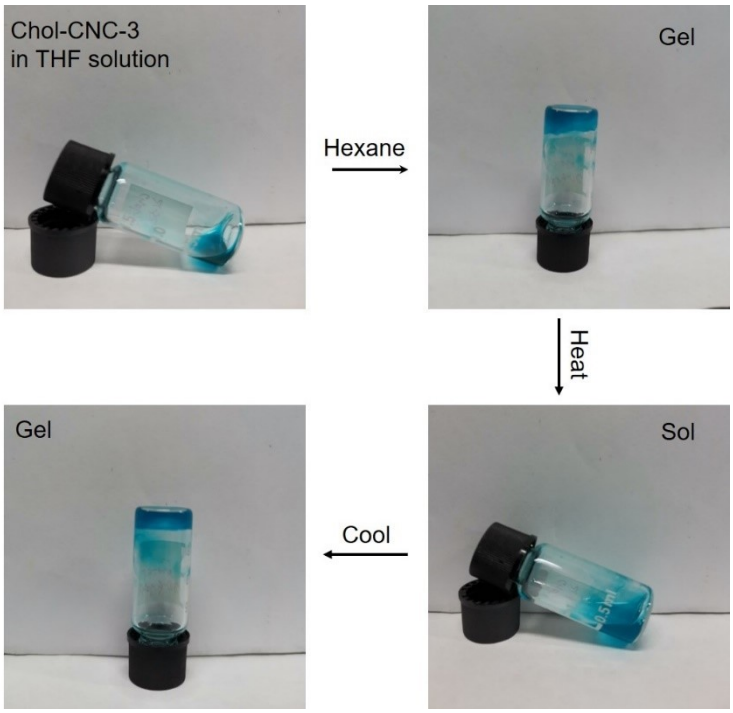


Fig. S22 Photographs of Chol-CNC-3 in THF/hexane (20 mg Chol-CNC-3, hexane (0.14 mL)/THF (0.04 mL)).

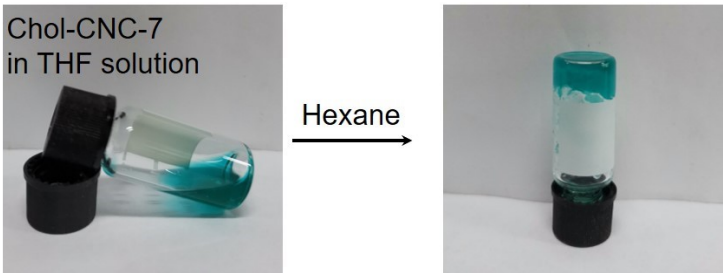


Fig. S23 Photographs of supramolecular gel of Chol-CNC-7 in THF/hexane (20.0 mg Chol-CNC-7, hexane (0.2 mL)/THF (0.2 mL)).

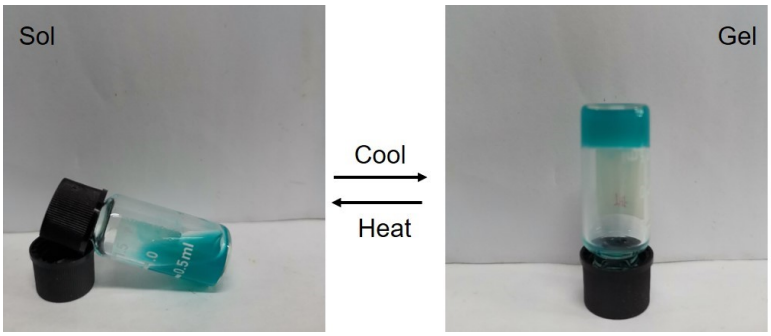


Fig. S24 Photographs of Chol-CNC-16 in THF/hexane (20 mg Chol-CNC-16, hexane (0.20 mL)/THF (0.10 mL)).

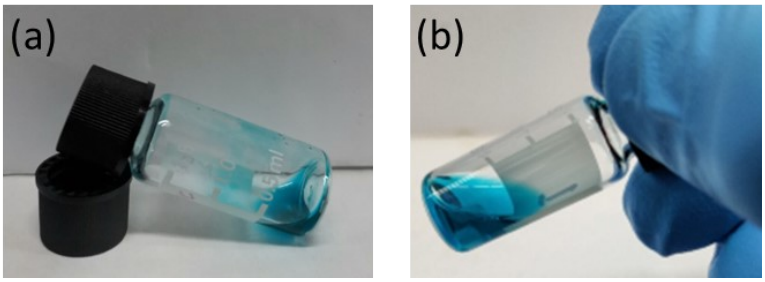


Fig. S25 Photographs of Chol-CNCs in THF/toluene. (a) 20 mg Chol-CNC-3, toluene (0.02 mL)/ THF (0.02 mL). (b) 20 mg Chol-CNC-16, toluene (0.15 mL)/ THF (0.10 mL).

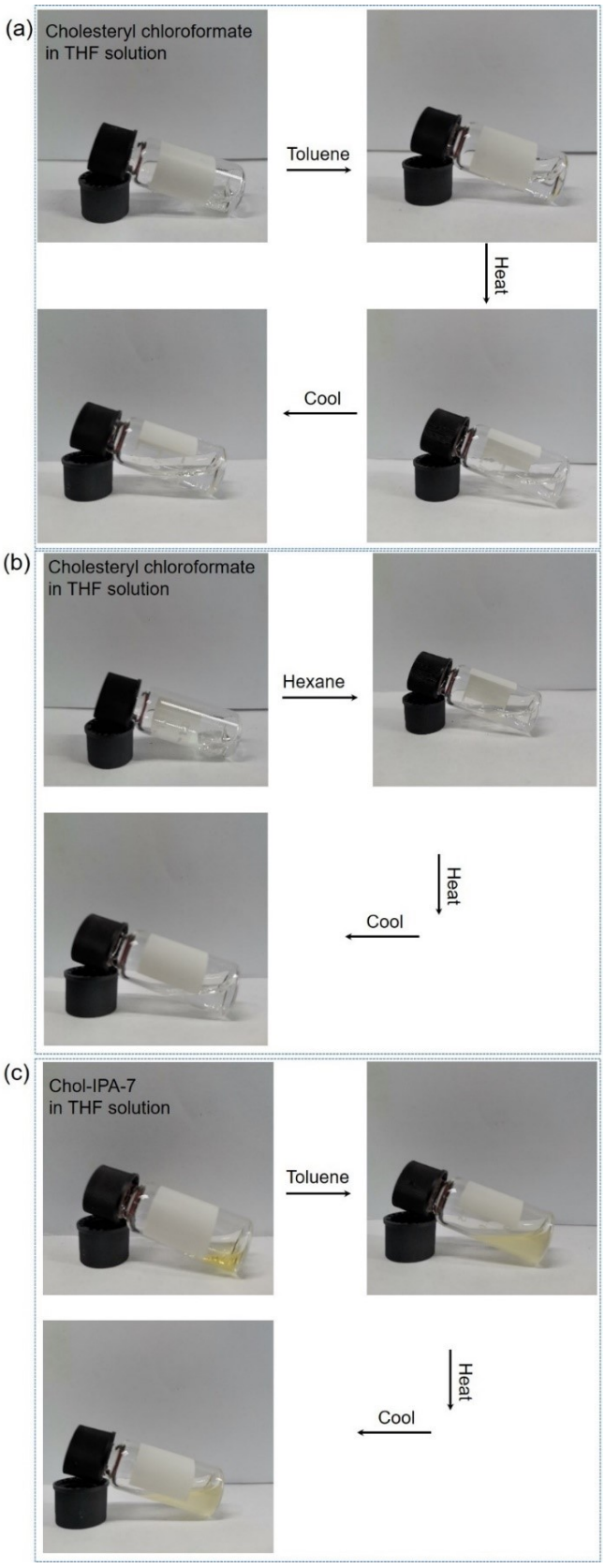


Fig. S26 Photographs of control experiments. (a) 20 mg Cholesteryl chloroformate, toluene (0.20 mL)/THF (0.10 mL). (b) 20 mg Cholesteryl chloroformate, hexane (0.20 mL)/THF (0.10 mL). (c) 20 mg Chol-IPA-7, toluene (0.20 mL)/THF (0.10 mL).

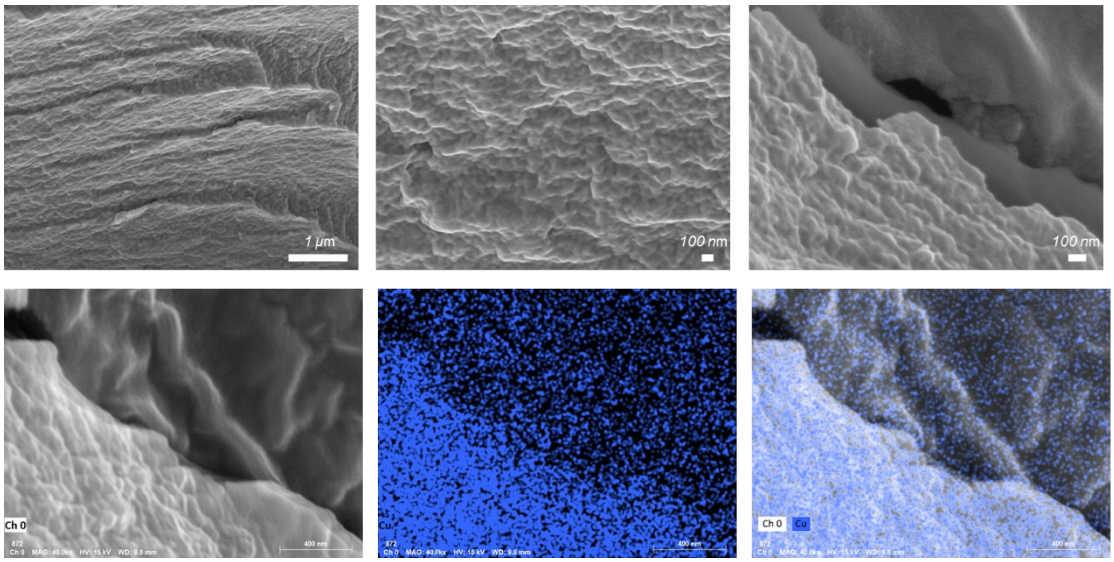


Fig. S27 SEM and EDX images of the freeze-dried Chol-CNC-3 supramolecular gel (20.0 mg Chol-CNC-3, hexane (0.14 mL)/THF (0.04 mL)) (blue, Cu atom).

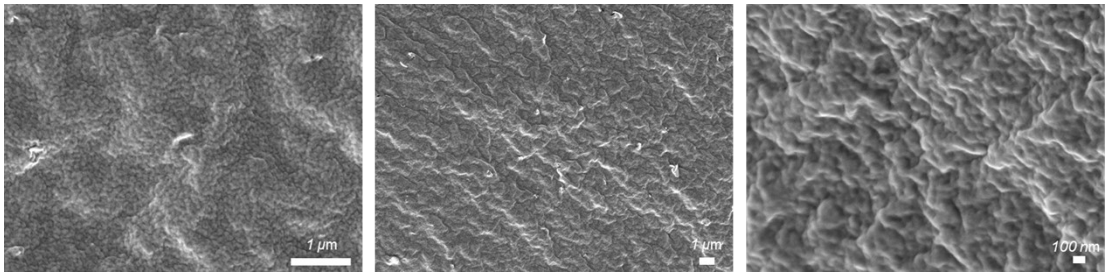


Fig. S28 SEM images of the freeze-dried Chol-CNC-7 supramolecular gel (160.0 mg Chol-CNC-7, hexane (0.7 mL)/THF (0.8 mL)).

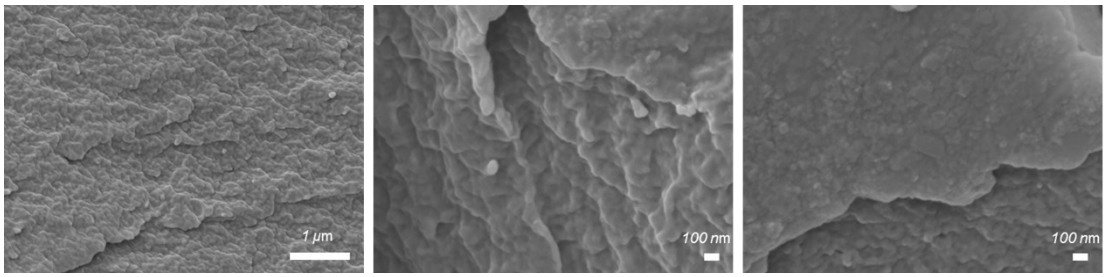


Fig. S29 SEM images of the freeze-dried Chol-CNC-16 supramolecular gel (20.0 mg Chol-CNC-16, hexane (0.14 mL)/THF (0.08 mL)).

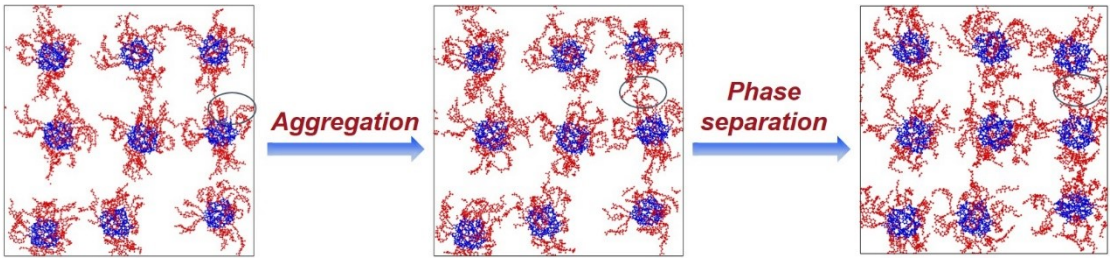


Fig. S30 Slice images of Chol-CNC-7 gels (THF/toluene) samples during the self-assembly process.

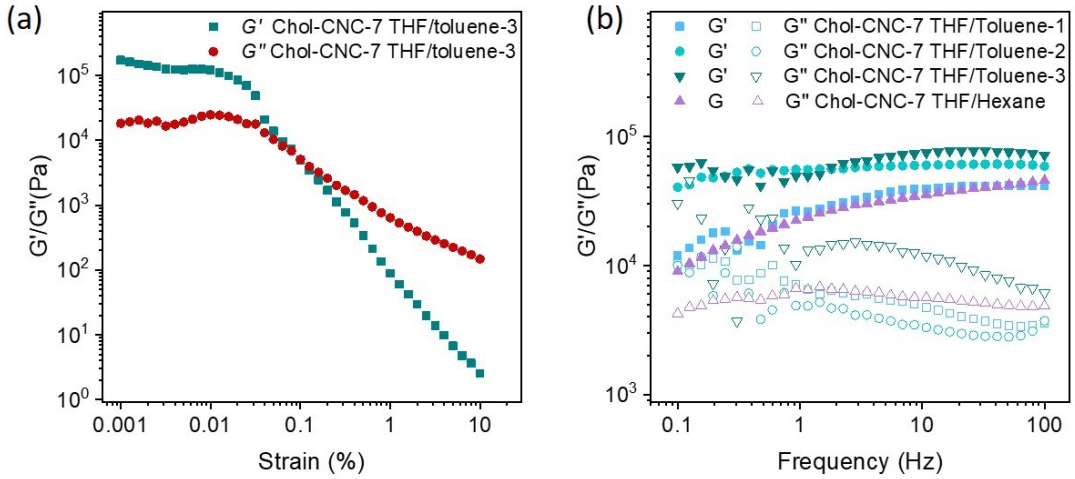


Fig. S31 (a) Amplitude sweep of Chol-CNC-7 supramolecular gels (130.0 mg Chol-CNC-7, toluene (1.0 mL)/ THF (0.7 mL), 25 °C, ω = 5 rad s^{-1}). (b) Frequency sweep of Chol-CNC-7 supramolecular gels (THF/Toluene-1: 130.0 mg Chol-CNC-7, toluene (1.5 mL)/ THF (0.5 mL); THF/Toluene-2: 140.0 mg Chol-CNC-7, toluene (1.5 mL)/ THF (0.5 mL); THF/Toluene-3: 130.0 mg Chol-CNC-7, toluene (1.0 mL)/ THF (0.7 mL); THF/Hexane: 160.0 mg Chol-CNC-7, hexane (0.7 mL)/ THF (0.8 mL), 25 °C, γ = 0.005%).

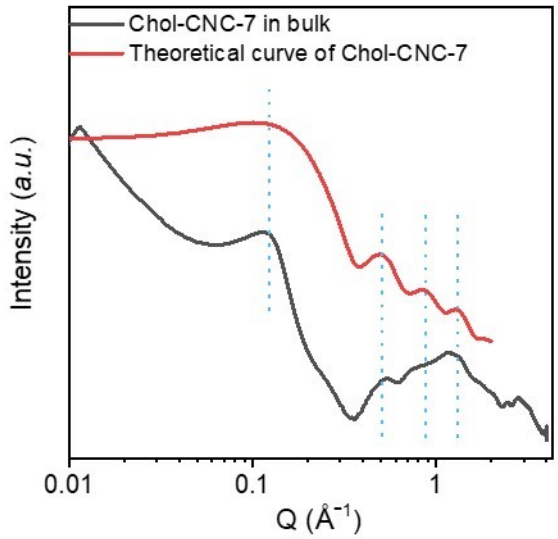


Fig. S32 SAXS patterns of bulk Chol-CNC-7 and theoretical curve of Chol-CNC-7.

4.2 Supplementary tables

Table S1. Gelation properties of Chol-CNC-3 at RT (THF/Hexane)

Table S2. Gelation properties of Chol-CNC-7 at RT (THF/Hexane)

Table S3. Gelation properties of Chol-CNC-16 at RT (THF/Hexane)

Table S4. Gelation properties of Chol-CNC-3 at RT (THF/Toluene)

Table S5. Gelation properties of Chol-CNC-7 at RT (THF/Toluene)

Table S6. Gelation properties of Chol-CNC-16 at RT (THF/Toluene)

Table S1. Gelation properties of Chol-CNC-3 at RT (THF/Hexane)

Materials	Concentration in THF (mg mL^{-1})	Solvent	Volume ratio	State
Chol-CNC-3	500	THF/Hexane	2 : 1	S
Chol-CNC-3	500	THF/Hexane	1 : 1	S
Chol-CNC-3	500	THF/Hexane	2 : 3	S

Chol-CNC-3	500	THF/Hexane	1 : 2	S
Chol-CNC-3	500	THF/Hexane	2 : 5	S
Chol-CNC-3	500	THF/Hexane	1 : 3	S
Chol-CNC-3	500	THF/Hexane	2 : 7	G
Chol-CNC-3	500	THF/Hexane	1 : 5	G
Chol-CNC-3	333	THF/Hexane	2 : 1	S
Chol-CNC-3	333	THF/Hexane	1 : 1	S
Chol-CNC-3	333	THF/Hexane	2 : 3	S
Chol-CNC-3	333	THF/Hexane	1 : 2	S
Chol-CNC-3	333	THF/Hexane	2 : 5	S
Chol-CNC-3	333	THF/Hexane	1 : 6	S

S: solution, G: gel.

Table S2. Gelation properties of Chol-CNC-7 at RT (THF/Hexane)

Materials	Concentration in THF (mg mL^{-1})	Solvent	Volume ratio	State
Chol-CNC-7	280	THF/Hexane	5 : 3	PG
Chol-CNC-7	225	THF/Hexane	3 : 1	PG
Chol-CNC-7	200	THF/Hexane	5 : 1	S

Chol-CNC-7	200	THF/Hexane	5 : 2	S
Chol-CNC-7	200	THF/Hexane	5 : 3	S
Chol-CNC-7	200	THF/Hexane	5 : 4	S
Chol-CNC-7	200	THF/Hexane	1 : 1	PG
Chol-CNC-7	150	THF/Hexane	1 : 1	PG
Chol-CNC-7	140	THF/Hexane	7 : 6	G
Chol-CNC-7	100	THF/Hexane	10 : 1	S
Chol-CNC-7	100	THF/Hexane	5 : 1	S
Chol-CNC-7	100	THF/Hexane	10 : 3	S
Chol-CNC-7	100	THF/Hexane	5 : 2	S
Chol-CNC-7	100	THF/Hexane	2 : 1	S
Chol-CNC-7	100	THF/Hexane	5 : 3	S
Chol-CNC-7	100	THF/Hexane	10 : 7	S
Chol-CNC-7	100	THF/Hexane	5 : 4	G
Chol-CNC-7	100	THF/Hexane	1 : 1	PG

S: solution, PG: partial gel, G: gel.

Table S3. Gelation properties of Chol-CNC-16 at RT (THF/Hexane)

Materials	Concentration in	Solvent	Volume	State

	THF (mg mL^{-1})		ratio	
Chol-CNC-16	250	THF/Hexane	4 : 1	S
Chol-CNC-16	250	THF/Hexane	2 : 1	S
Chol-CNC-16	250	THF/Hexane	4 : 3	S
Chol-CNC-16	250	THF/Hexane	1 : 1	S
Chol-CNC-16	250	THF/Hexane	4 : 5	G
Chol-CNC-16	250	THF/Hexane	2 : 3	G
Chol-CNC-16	250	THF/Hexane	4 : 7	PG
Chol-CNC-16	250	THF/Hexane	6 : 5	G
Chol-CNC-16	200	THF/Hexane	1 : 1	S
Chol-CNC-16	200	THF/Hexane	1 : 2	G
Chol-CNC-16	100	THF/Hexane	1 : 1	S

S: solution, PG: partial gel, G: gel.

Table S4. Gelation properties of Chol-CNC-3 at RT (THF/Toluene)

Materials	Concentration in Toluene (mg mL^{-1})	Solvent	Volume ratio	State
Chol-CNC-3	500	THF/Toluene	2 : 3	S
Chol-CNC-3	500	THF/Toluene	1 : 2	S

Chol-CNC-3	500	THF/Toluene	2 : 5	S
Chol-CNC-3	500	THF/Toluene	1 : 3	S
Chol-CNC-3	500	THF/Toluene	2 : 7	S
Chol-CNC-3	500	THF/Toluene	1 : 4	S
Chol-CNC-3	500	THF/Toluene	1 : 1	S
Chol-CNC-3	200	THF/Toluene	1 : 1	S
Chol-CNC-3	200	THF/Toluene	2 : 3	S
Chol-CNC-3	200	THF/Toluene	2 : 5	S
Chol-CNC-3	100	THF-Toluene	1 : 2	S

S: solution.

Table S5. Gelation properties of Chol-CNC-7 at RT (THF/Toluene)

Materials	Concentration in THF (mg mL^{-1})	Solvent	Volume ratio	State
Chol-CNC-7	320	THF/Toluene	1 : 1	G
Chol-CNC-7	200	THF/Toluene	1 : 1	S
Chol-CNC-7	200	THF/Toluene	1 : 2	G
Chol-CNC-7	200	THF/Toluene	1 : 3	G
Chol-CNC-7	200	THF/Toluene	1 : 4	S
Chol-CNC-7	130	THF/Toluene	1 : 1	S

Chol-CNC-7	130	THF/Toluene	1 : 2	G
Chol-CNC-7	130	THF/Toluene	1 : 3	G
Chol-CNC-7	130	THF/Toluene	7 : 10	G
Chol-CNC-7	93	THF/Toluene	1 : 1	S

S: solution, G: gel.

Table S6. Gelation properties of Chol-CNC-16 at RT (THF/Toluene)

Materials	Concentration in Toluene (mg mL^{-1})	Solvent	Volume ratio	State
Chol-CNC-16	500	THF/Toluene	2 : 3	S
Chol-CNC-16	500	THF/Toluene	1 : 2	S
Chol-CNC-16	500	THF/Toluene	2 : 5	S
Chol-CNC-16	500	THF/Toluene	1 : 3	S
Chol-CNC-16	500	THF/Toluene	2 : 7	S
Chol-CNC-16	500	THF/Toluene	1 : 4	S
Chol-CNC-16	200	THF/Toluene	1 : 1	S
Chol-CNC-16	200	THF/Toluene	2 : 3	S
Chol-CNC-16	200	THF/Toluene	2 : 5	S
Chol-CNC-16	100	THF-Toluene	1 : 1	S
Chol-CNC-16	100	THF-Toluene	1 : 2	S

S: solution.

5. Details for Supplementary Movie

Movie S1: The overall view of Chol-CNC-7 in THF/toluene mixed solvent (MP4)

All-atom non-equilibrium molecular dynamics simulations are performed on Chol-CNC-7 systems, and THF/toluene solvent systems is applied for the systems.

6. Reference

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S2. Y. Lai, M. Li, M. Zhang, X. Li, J. Yuan, W. Wang, Q. Zhou, M. Huang and P. Yin, *Macromolecules*, 2020, **53**, 7178-7186.

S3. J.-F. Yin, Z. Zheng, J. Yang, Y. Liu, L. Cai, Q.-Y. Guo, M. Li, X. Li, T. L. Sun, G. X. Liu, C. Huang, S. Z. D. Cheng, T. P. Russell and P. Yin, *Angew. Chem. Int. Ed.*, 2021, **60**, 4894-4900.