

Supplementary Information

Heat-Set Gels and Egg-Like Vesicles Using Two-Component Gel System Based on Chiral Calix[4]arenes

Jin-Lan Zhou, Xian-Jie Chen and Yan-Song Zheng*

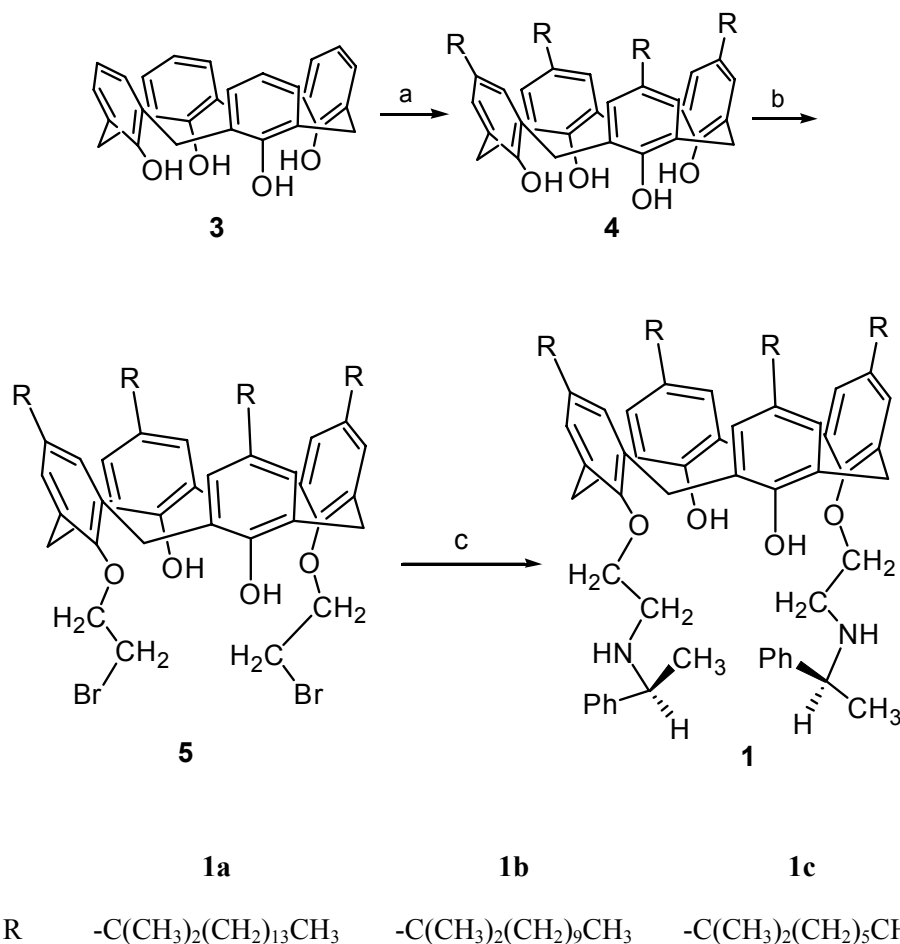
Department of Chemistry and Hubei Key Laboratory of Materials Chemistry and Service Failure, Huazhong University of Science and Technology, Wuhan 430074, P. R. China

Materials and Methods

Materials. All reagents and solvents were chemical pure (CP) grade or analytical reagent (AR) grade and were used as received. Even chloroform used as gelled solvent did not need to remove the added ethyl alcohol as protecting reagent. *D*-(+)-dibenzoyltartaric acid (99%), *L*-(+)-dibenzoyltartaric acid (99%), (*R*)- α -methylbenzylamine (98%) and (*S*)- α -methylbenzylamine (98%) bought both from Aldrich Chemical Co. Ltd and from chemical companies in China gave same results. *p*-*tert*-Butylcalix[4]arene and calix[4]arene starting materials were prepared according to supporting reference (*S1*) and (*S2*) respectively. Long alkyl tertiary alcohols were prepared by the reaction of acetone with Grignard reagent of corresponding long *n*-alkyl bromide.

Measurements. ¹H NMR spectra were measured on a Bruker AV 400 spectrometer at 400 MHz at 298 K. Circular dichroism (CD) spectra were recorded on a JASCO J-810 spectrometer. Field emission scanning electron microscopy (FE-SEM) images were taken on a FEI Sirion200 electron microscope operating at 5 kV or 10 kV. Transmission electron micrographs (TEM) were recorded on a FEI Technai G2 20 electron microscope at 200 kV. Atomic Force Microscopy (AFM) images were got on a VEECO Nano Scope IV instrument using tapping mode, and the showed AFM images are phase amplitude. Dynamic light scattering (DLC) was measured on a Horiba LB-550 Particle Size Analyzer. HRMS spectra were recorded on a Bruker BioApex FTMS instrument.

Synthesis of chiral calix[4]arene **1** bearing long tertiary alkyl groups at upper rim



(a) $\text{CH}_3(\text{CH}_2)_n(\text{CH}_3)_2\text{COH}$ ($n = 5, 9, \text{ or } 13$), concentrated H_2SO_4 , CHCl_3 ; (b) $\text{BrCH}_2\text{CH}_2\text{Br}$, K_2CO_3 , CH_3CN , refluxing; (c) *S*-1-phenylethylamine, K_2CO_3 , CHCl_3 , refluxing.

Scheme S1 Synthetic route for the chiral calix[4]arenes **1**

General procedure for synthesis of calix[4]arene **4**.

Concentrated sulfuric acid (1.1 mL, 20 mmol) was dropped into the solution of calix[4]arene **3** (0.42 g, 1 mmol) and alkyl tertiary alcohol (8 mmol) in CHCl_3 (10 mL) at 0°C under stirring. After finished dropping, the mixture was stirred at room temperature for 16 – 24 h. Then ice was added and the mixture was abstracted with chloroform three times. The combined organic phase was dried over anhydrous sodium sulfate and evaporated to dryness.

The residue was purified by flash chromatography (CHCl₃ : petroleum ether 1 : 5) to give calix[4]arene **4**.

General procedure for synthesis of calix[4]arene **5**.

To the solution of calix[4]arene **4** (0.30 mmol) and 1, 2-dibromoethane (2 mL, 23 mmol) in acetonitrile (3 mL) was added anhydrous K₂CO₃ (91 mg, 0.66 mmol). The mixture was refluxed for 1.5–3 h until the calix[4]arene **4** disappeared. After evaporated solvent and retained 1, 2-dibromoethane the chloroform was added into the residue. Upon washed with water and dried over anhydrous Na₂SO₄, most of solvent was evaporated. Then methanol was added to give precipitates. Crude product was collected by filtration, which was directly used in next synthesis.

General procedure for synthesis of calix[4]arene **1**.

To the solution of calix[4]arene **5** (0.15 mmol) and (*S*)- α -methylbenzylamine (0.18 g, 1.5 mmol) in CHCl₃ (5 mL) was added anhydrous K₂CO₃ (46 mg, 0.34 mmol). The mixture was refluxed for 24–48 h. Then the mixture was washed with water and dried over anhydrous Na₂SO₄. Upon evaporated to dryness, the residue was purified by flash chromatography (ethyl acetate : petroleum ether 1 : 5) to afford **1**.

Calix[4]arene **1a**: 0.225 g, yield 89.8%; [α]_D²⁵ = +1.59 (*c* = 1.0, CHCl₃); ¹H NMR (400MHz, CDCl₃) δ : 7.43(d, *J* = 8.0Hz, 4H, Ar*H*), 7.33 (t, *J* = 7.2Hz, 4H, Ar*H*), 7.24 (s, 2H, Ar*OH*), 7.22 (t, 2H, Ar*H*), 7.0 (s, 4H, Ar*H*), 6.7 (s, 4H, Ar*H*), 4.36, 4.28 (2d, *J* = 13Hz, 4H, ArCH₂Ar), 4.17~4.09 (m, 2H, NH*CH*), 4.05~3.95 (m, 4H, OCH₂), 3.33, 3.28 (2d, *J* = 13.2Hz, 4H, ArCH₂Ar), 3.07~2.99 (m, 2H, -NHCH₂), 2.93~2.84 (m, 2H, -NHCH₂), 1.46 (d, *J* = 6.7Hz, 6H, -NHCHCH₃), 1.27~1.19 (m, 104H, -(CH₂)₁₃CH₃), 0.87 (t, *J* = 6.7Hz, 12H, -CH₂CH₃), 0.82 (s, 24H, -C(CH₃)₂); IR (KBr) ν : 3324, 3025, 2925, 1465, 1367 cm⁻¹. ESI⁺ HRMS *m/z* for C₁₁₆H₁₈₇N₂O₄ 1672.4491 [M + H⁺]; found 1672.4482 [M + H⁺].

Calix[4]arene **1b**: 0.38g, yield 65.7%; [α]_D²⁵ = +0.91 (*c* = 1.0, CHCl₃); ¹H NMR (400MHz, CDCl₃) δ : 7.42 (d, *J* = 8.0Hz, 4H, Ar*H*), 7.33 (t, *J* = 7.2Hz, 4H, Ar*H*), 7.22 (t, 2H, Ar*H*), 7.0 (s, 4H, Ar*H*), 6.7 (s, 4H, Ar*H*), 4.38, 4.29 (2d, *J* = 13Hz, 4H, ArCH₂Ar), 4.15~4.07 (m, 2H, NH*CH*), 4.03~3.95 (m, 4H, OCH₂), 3.33, 3.29 (2d, *J* = 13.2Hz, 4H, ArCH₂Ar), 3.06~3.00 (m, 2H, -NHCH₂), 2.90~2.85 (m, 2H, -NHCH₂),

1.45 (d, $J=6.7\text{Hz}$, 6H, $-\text{NHCHCH}_3$), 1.27~1.20 (m, 72H, $-\text{C}(\text{CH}_2)_9$), 0.87 (t, $J=6.7\text{Hz}$, 12H, $-\text{CH}_2\text{CH}_3$), 0.82 (s, 24H, $-\text{C}(\text{CH}_3)_2$); IR (KBr) ν : 3324, 3025, 2926, 1475, 1364 cm^{-1} . ESI⁺ HRMS m/z for $\text{C}_{100}\text{H}_{155}\text{N}_2\text{O}_4$ 1448.1987 $[\text{M} + \text{H}^+]$; found 1448.1983 $[\text{M} + \text{H}^+]$.

Calix[4]arene **1c**: 0.14 g, yield 31.2%; $[\alpha]_{\text{D}}^{25} = +1.26$ ($c = 1.0$, CHCl_3); ^1H NMR (400MHz, CDCl_3) δ : 7.34 (d, $J=8.0\text{Hz}$, 4H, ArH), 7.22 (t, $J=7.2\text{Hz}$, 4H, ArH), 7.13 (t, 2H, ArH), 6.94 (s, 4H, ArH), 6.71~6.51 (m, 4H, ArH), 4.31, 4.21 (2d, $J=13\text{Hz}$, 4H, ArCH₂Ar), 4.03~4.0 (m, 2H, NHCH), 3.96~3.92 (m, 4H, OCH₂), 3.26, 3.23 (2d, $J=13.2\text{Hz}$, 4H, ArCH₂Ar), 2.96~2.95 (m, 2H, $-\text{NHCH}_2$), 2.82 (m, 2H, $-\text{NHCH}_2$), 1.37 (d, $J=6.7\text{Hz}$, 6H, $-\text{NHCHCH}_3$), 1.18~1.12 (m, 64H, $-\text{C}(\text{CH}_3)_2(\text{CH}_2)_5$), 0.78 (t, $J=6.7\text{Hz}$, 12H, $-\text{CH}_2\text{CH}_3$); IR (KBr) ν : 3323, 3025, 2926, 1469, 1367 cm^{-1} . ESI⁺ HRMS m/z for $\text{C}_{84}\text{H}_{123}\text{N}_2\text{O}_4$ 1223.9483 $[\text{M} + \text{H}^+]$; found 1223.9467 $[\text{M} + \text{H}^+]$.

Supporting References

S1. C. D. Gutsche, M. Iqbal, D. Stewart, *J. Org. Chem.* **51**, 742 (1986).

S2. C. D. Gutsche, L. G. Lin, *Tetrahedron* **42**, 1633 (1986).

Supporting Figures

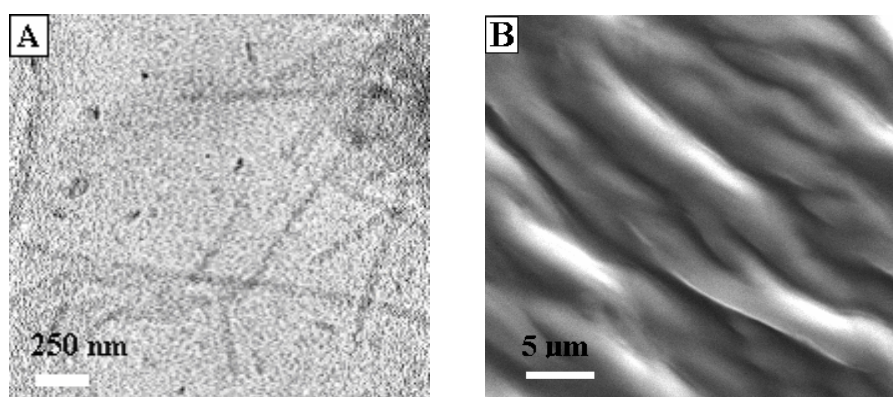


Fig. S1. Morphology of self-assembled objects by interaction of **1a** (5 mM) and **L-2** (10 mM) in cyclohexane at 20 °C. (A) TEM images. (B) FE-SEM images.

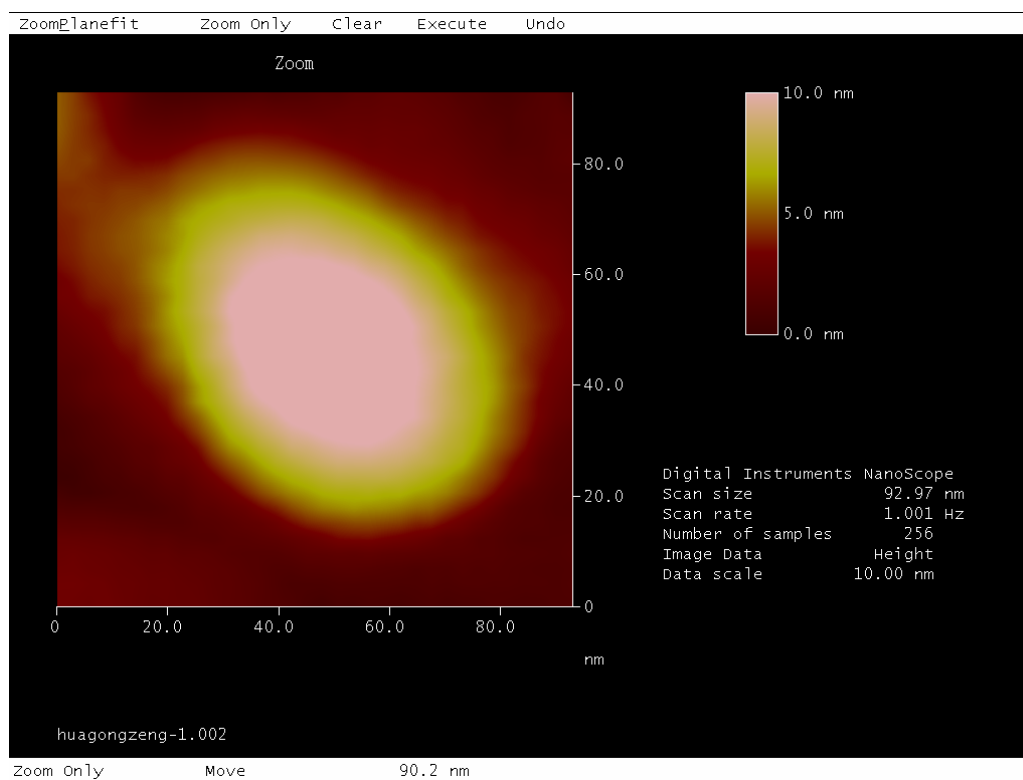


Fig. S2. AFM image of solution of **1a** (5 mM) and **D-2** (10 mM) in cyclohexane at 20 °C. The solution was diluted five times with cyclohexane, dropped on freshly broken mica and air dried.

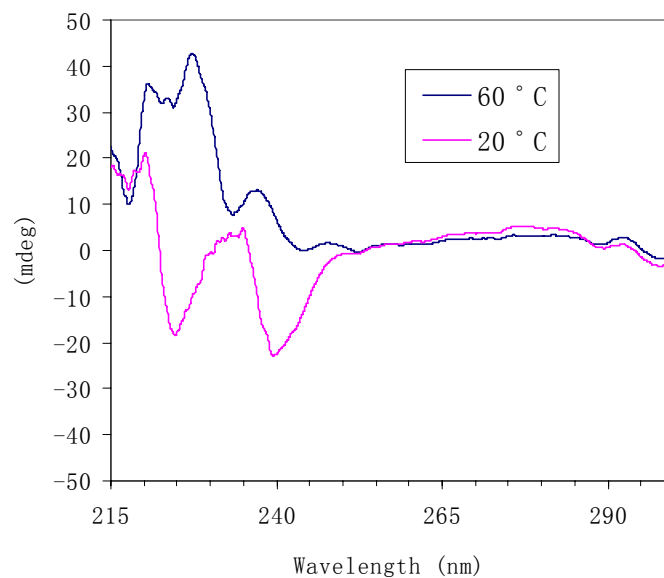


Fig. S3. Circular dichroism (CD) spectra of solution of **1a** (5 mM) and **D-2** (10 mM) in cyclohexane diluted 5 times with cyclohexane. Black line was measured at 60 °C; Red line was done at 20 °C.

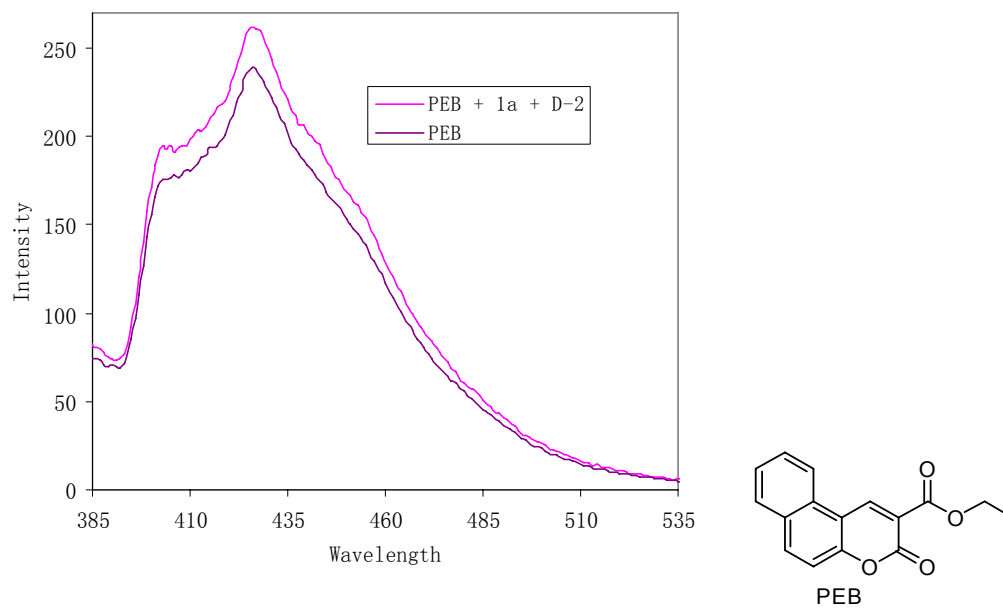


Fig. S4. Fluorescent emission spectra of PEB (0.1 mM) in solution of **1a** (5 mM) and **D-2** (10 mM) in cyclohexane (red line) and PEB solution (0.1 mM) in cyclohexane (black line). Exciting wavelength: 377 nm. Same result was obtained in three parallel experiments.

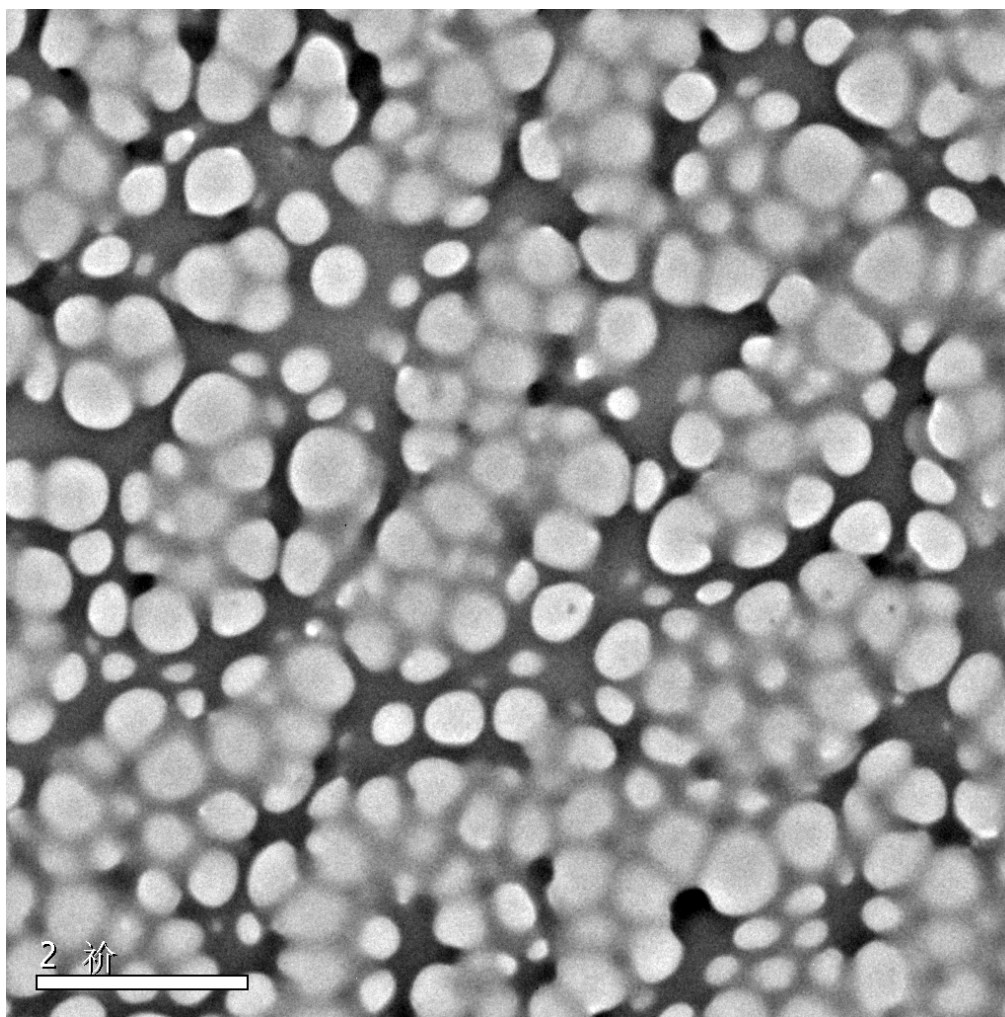


Fig. S5. TEM image of gel obtained by interaction of **1a** (5 M) and *D-2* (10 M) in cyclohexane at 20 °C. The gel was diluted 5 times with cyclohexane, and dropped onto a copper grid on filter paper and air dried. Bar is 2 μm.

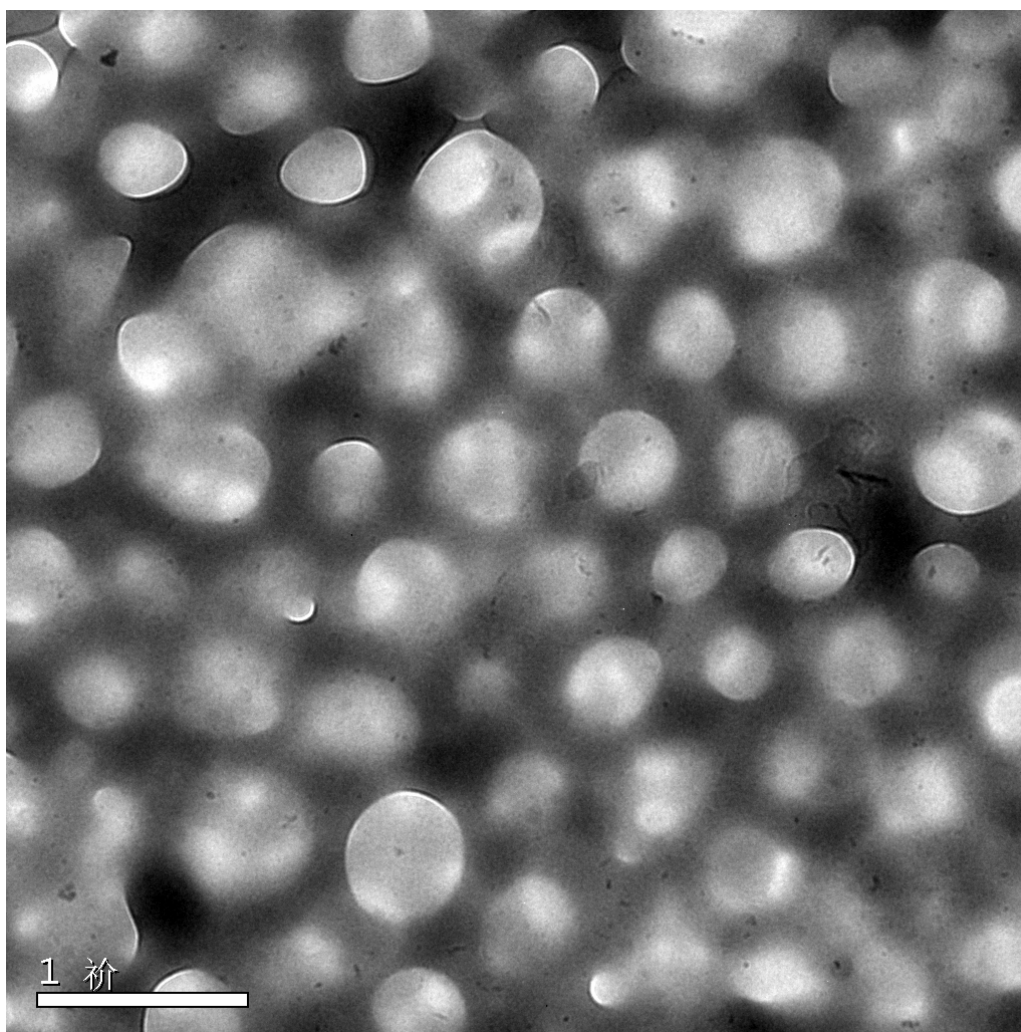


Fig. S6. TEM image of gel obtained by interaction of **1a** (5 M) and *D-2* (10 M) in cyclohexane at 20 °C. The gel was diluted 5 times with cyclohexane, and dropped onto a copper grid on filter paper and air dried. Bar is 1 μm.

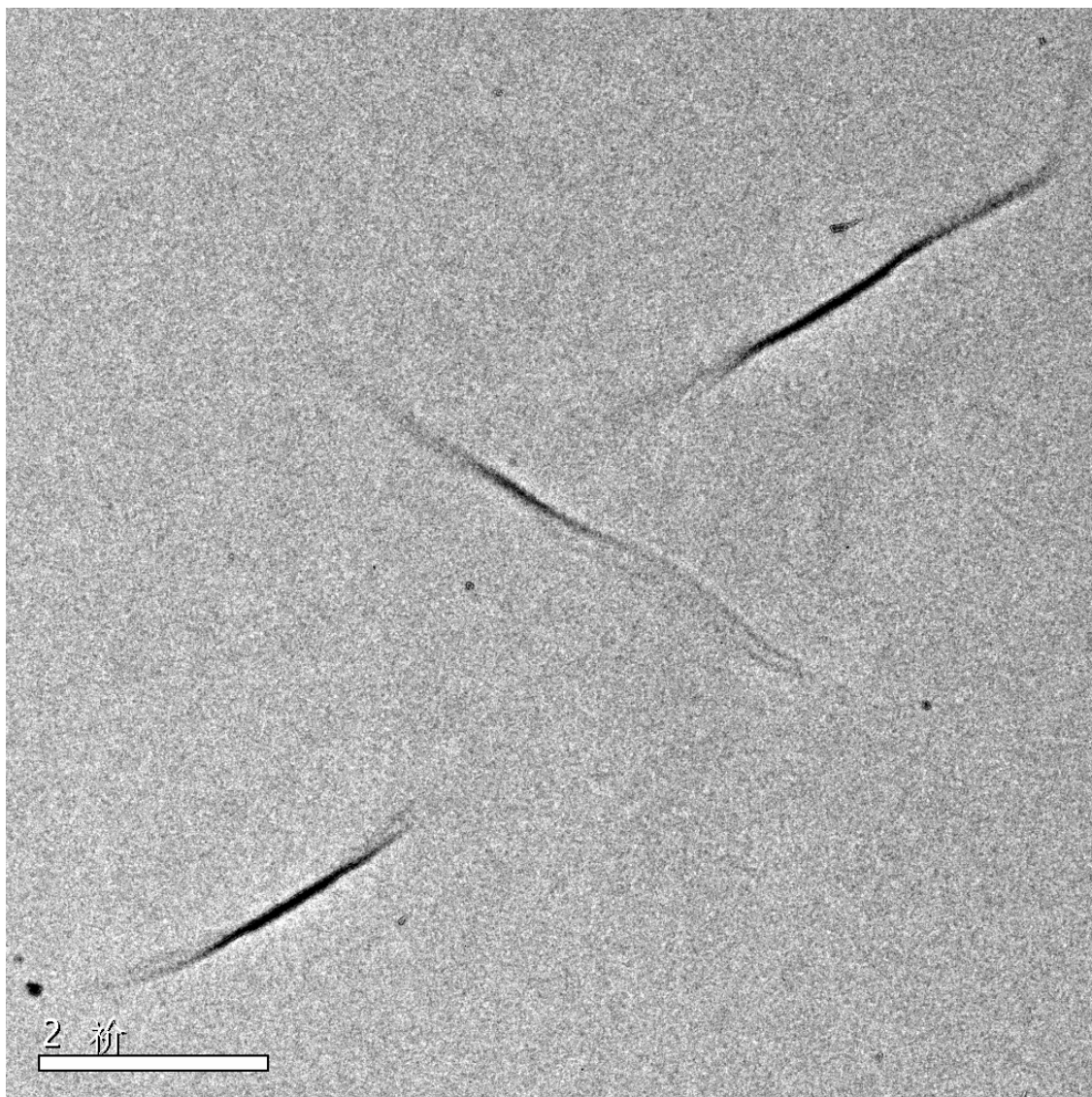


Fig. S7. TEM image of gel obtained by interaction of **1a** (5 M) and *D-2* (10 M) in cyclohexane at 60 °C. The gel was diluted 5 times with cyclohexane, and dropped onto a copper grid on filter paper and air dried. Bar is 2 μm .

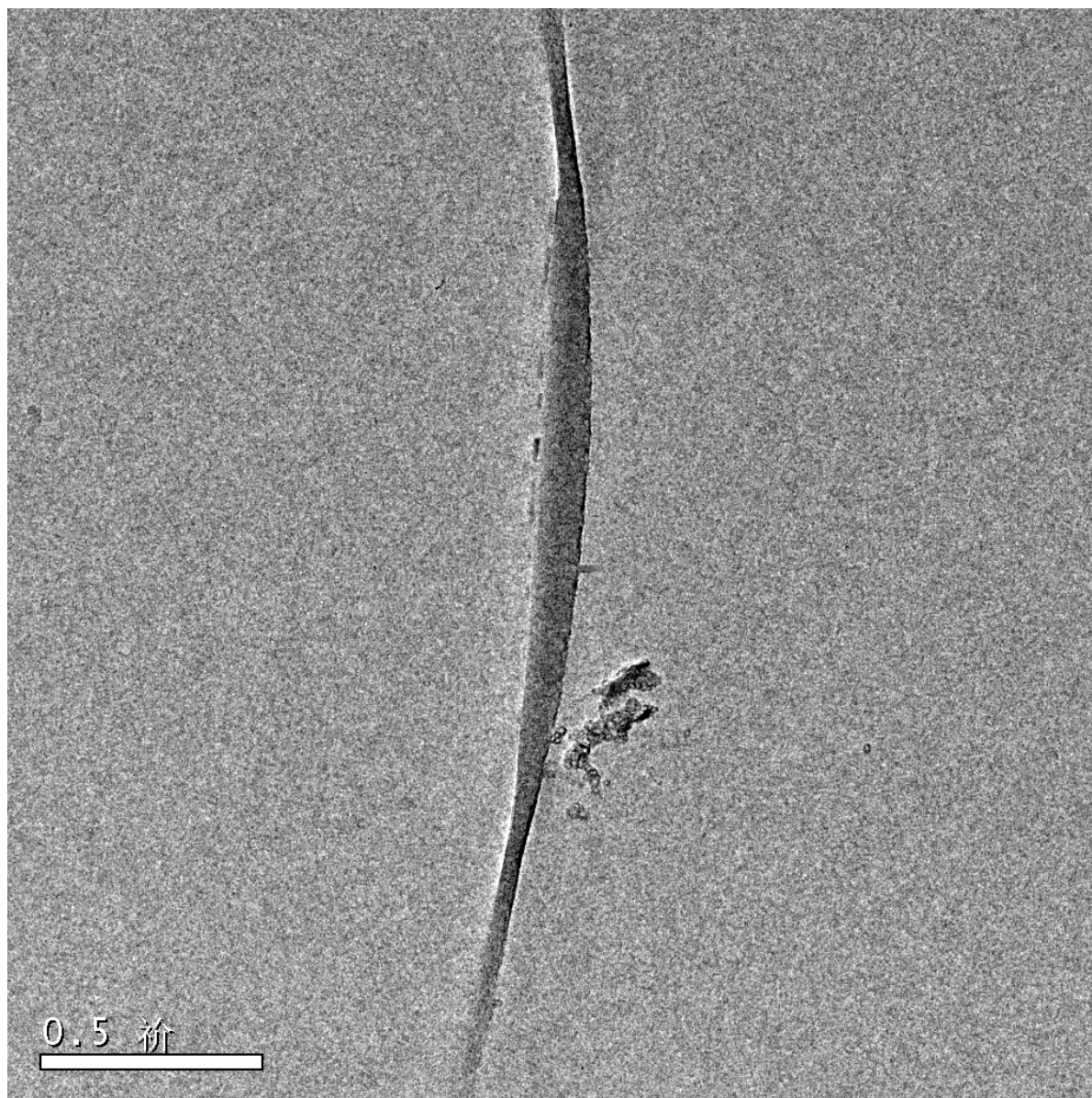


Fig. S8. TEM image of gel obtained by interaction of **1a** (5 M) and *D-2* (10 M) in cyclohexane at 60 °C. The gel was diluted 5 times with cyclohexane, and dropped onto a copper grid on filter paper and air dried. Bar is 500 nm.

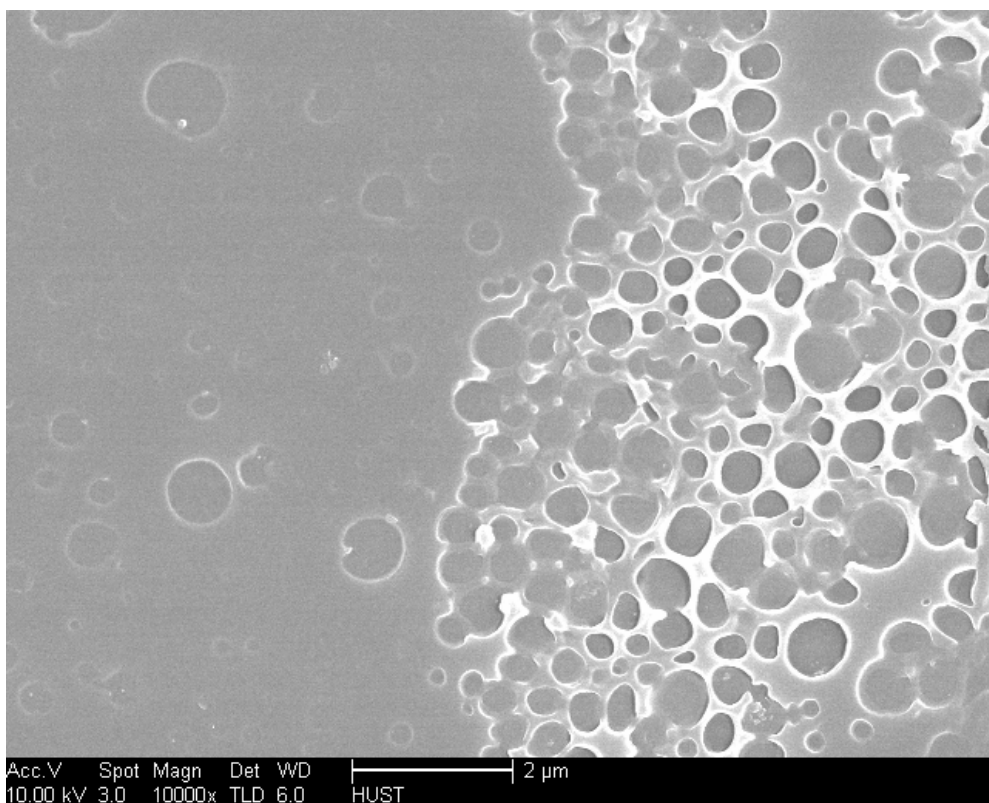


Fig. S9. FE-SEM images of gel obtained by interaction of **1b** (5 M) and *D-2* (10 M) in cyclohexane at 20 °C. The sample was prepared by casting the gel diluted five times with cyclohexane onto a glass slide and let it air dry.

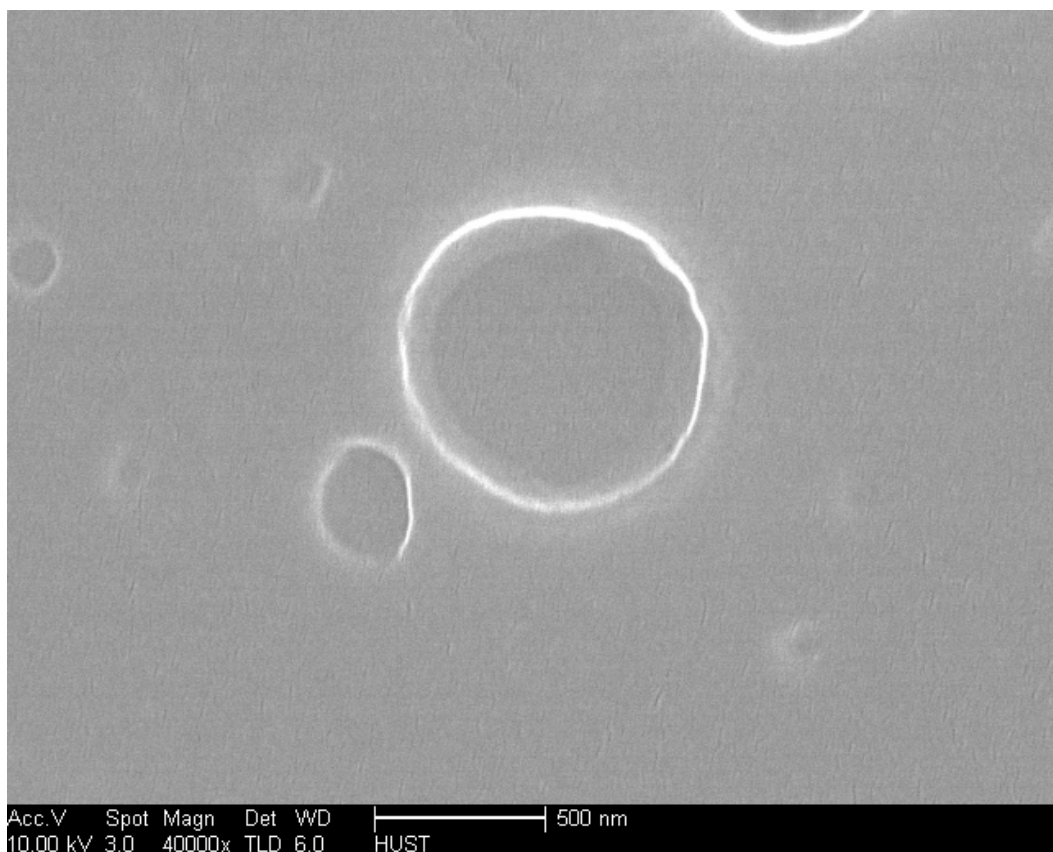


Fig. S10. FE-SEM images of gel obtained by interaction of **1b** (5 M) and *D-2* (10 M) in cyclohexane at 20 °C. The sample was prepared by casting the gel diluted five times with cyclohexane onto a glass slide and let it air dry.

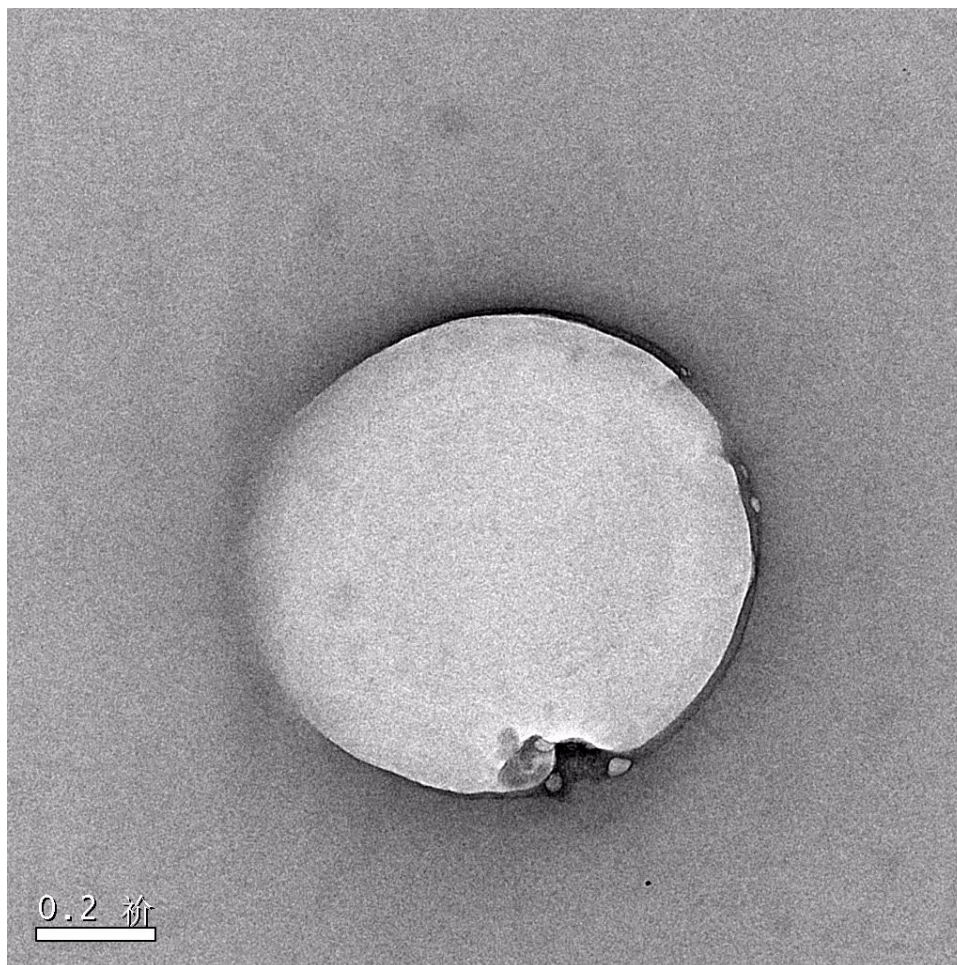


Fig. S11. TEM image of gel obtained by interaction of **1c** (5 M) and *D-2* (10 M) in cyclohexane at 20 °C. The gel was diluted 5 times with cyclohexane, and dropped onto a copper grid on filter paper and air dried. Bar is 200 nm.

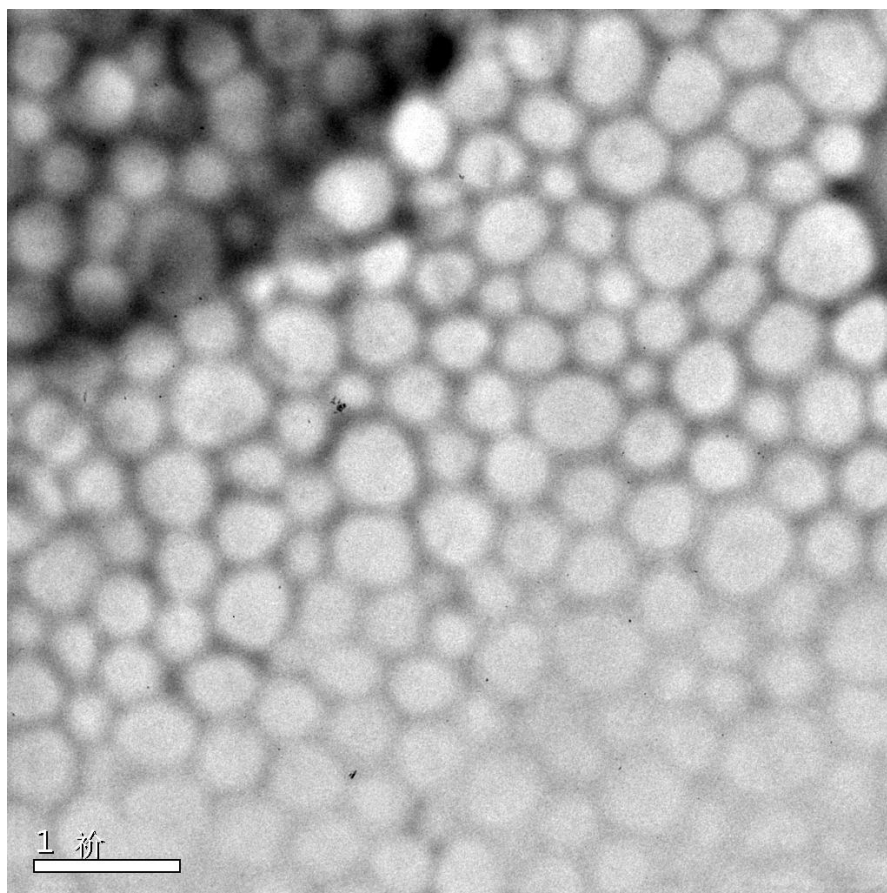


Fig. S12. TEM image of gel obtained by interaction of **1b** (5 M) and *L-2* (10 M) in cyclohexane at 20 °C. The gel was diluted 5 times with cyclohexane, and dropped onto a copper grid on filter paper and air dried. Bar is 1 μm.

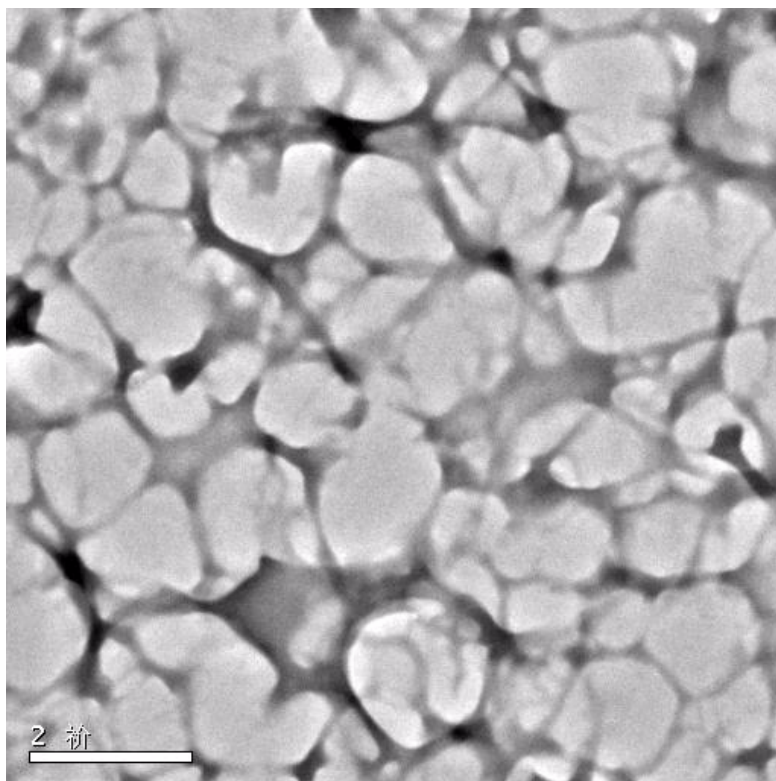


Fig. S13. TEM image of gel obtained by interaction of **1c** (5 M) and *L-2* (10 M) in cyclohexane at 20 °C. The gel was diluted 5 times with cyclohexane, and dropped onto a copper grid on filter paper and air dried. Bar is 2 μm .