Supporting Information

Redox-Responsive Organogel Based on Selenium-Containing Low Molecular Mass Gelator

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Number of scheme: 1

Number of figure: 5

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1 Experimental Section

1.1 NMR Experiments

All 400MHz 1H NMR studies were carried out on a AVANCE III HD 400 MHz spectrometer at 298.15 K.

1.2 Mass Spectrometry

Mass spectra were recorded on a LCZ/2690 XE/996 mass spectrometer.

1.3 Field Emission Scanning Electron Microscopy (FE-SEM)

Morphologies of the organogel were investigated by FE-SEM. For the SEM study, the gel has been dried by lyophilization and coated with gold. Then the micrographs were taken in a SEM apparatus (JEOL microscope S-4800).

1.4 X-ray Diffraction Study

X-ray powder diffraction data were collected on a Bruker D8 Advance diffractometer using Cu Kα radiation with a wavelength of 1.54 Å at 2θ values between 2 - 60 °. The machine was run at a voltage of 40 kV and current of 40 mA. The diffraction patterns were recorded using a scintillation scan detector.

1.5 The Measurement of Gel Transition Temperature

The transition temperature of gel was measured by differential scanning calorimetry (DSC822e), using sample weights between 2 and 15 mg. The heating started from 25 ^{o}C at a heating rate of 10 ^{o}C/min in a nitrogen atmosohere at 1 atm. All the DSC traces were normalized and redrawn according to temperature and heatflow rate.

1.6 Polarizing Optical Light Microscope (POM)

POM was performed on a Carl Zeiss Axio Imager A2POL. For the POM study, a

small quantity of organogel was put on a microscope slide and covered with a glass coverslip, which was sealed immediately at the edges with glue to prevent the evaporation of solvent.

1.7 Molecular Modeling

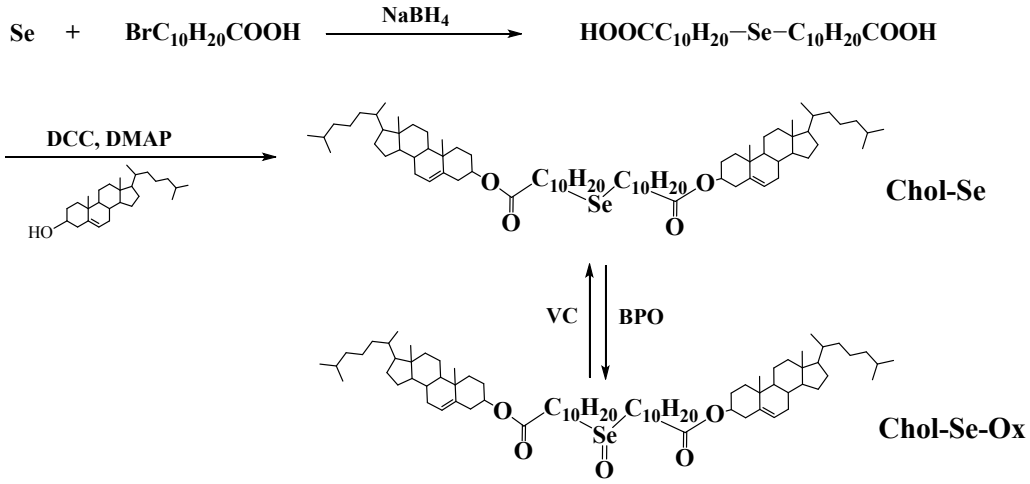
Calculations were performed with Gauaaian'09 using the B3LYP/sto-3g hybrid density functional theory and the Se, C, H, and O atoms are processed using the def2-tzvp basis set.

1.8 Redox-stimulus responsive property

An equal amount (in moles) of dibenzoyl peroxide (BPO) (solid) was added into the organogel. The system was cooled to room temperature after BPO was dissolved under slightly heating.

An equivalent amount (in moles) of ascorbic acid (VC) (solid) was added into the oxidized system. The system was cooled to room temperature after VC was dissolved under slightly heating.

2 Synthesis procedures



Scheme S1. Synthesis of Chol-Se

2.1 Synthesis of Double-11-alkyl carboxylic acid sodium selenide (Se-COOH)

A solution of sodium borohydride (1.5806 g) in deionized water (10 mL) was added into a suspension of Se power solution (Se, 1.5 g; deionized water, 15 mL) under N_2. The mixture was continuous stirred for 20 min at 55 ºC. Then a solution of 11-bromoundecanoic acid (10.0761 g) in DMF (75 mL) was added dropwise into the reaction mixture and then stirred for 18 h. After coolling to room temperature, the reaction mixture was diluted with CH_2Cl_2 and extracted with deionized water for 3 times. The organic extract was separated and dried over $MgSO_4$, and the solvent was removed under reduced pressure to afford the crude product (Yield 87%).

2.2 Synthesis of bis-(undecanoic acid cholesteryl ester)-selenide (Chol-Se)

A solution of crude Se-COOH in CH_2Cl_2 (200 mL) was added to flask where cholesterol (3.2167 g), dicyclohexylcarbodiimide (2 g) and 4-dimethylaminopyridine (0.1627 g) were existed. The reaction mixture was stirred for 10 h at 0 °C, and then stirred for another 24 h at room temperature. The produced precipitates were removed by filtration and the filtrate was wished with 0.1 M hydrochloric acid, 0.5 M sodium carbonate solution and deionized water for 3 times successively. The organic extract was separated and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude material was purified by silica gel column chromatography using petroleum ether to give a light yellow solid (Yield 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.38-5.37 (t, 2H, C64-1H, C34-1H), 4.65-4.57 (m, 2H, C58-1H, C30-1H), 2.32-2.24 (m, 8H, C11-2H, C21-2H, C31-2H, C57-2H), 2.02-1.84 (m, 10H, C35-2H, C63-2H, C10-2H, C20-2H, C45-1H, C74-1H), 1.74-1.68 (m, 4H, C2-2H, C12-2H), 1.66-1.43 (m, 20H, C42-2H, C43-2H, C41-2H, C40-2H,

C44-1H, C70-2H, C71-2H, C66-2H, C65-2H, C69-1H, C49-1H, C78-1H), 1.35-1.26 (m, 36H, C3-2H, C13-2H, C4-2H, C14-2H, C5-2H, C15-2H, C6-2H, C16-2H, C9-2H, C19-2H, C29-2H, C28-2H, C7-2H, C8-2H, C59-2H, C60-2H, C17-2H, C18-2H), 1.21-1.06 (m, 14H, C46-2H, C47-2H, C48-2H, C37-1H, C75-2H, C76-2H, C77-2H, C61-2H), 1.02 (s, 10H, C73-3H, C62-1H, C68-1H, C52-3H, C36-1H, C38-1H), 0.92-0.91 (d, 6H, C54-3H, C81-3H), 0.87-0.86 (m, 12H, C50-3H, C51-3H, C79-3H, C80-3H), 0.68 (s, 6H, C53-3H, C72-3H).

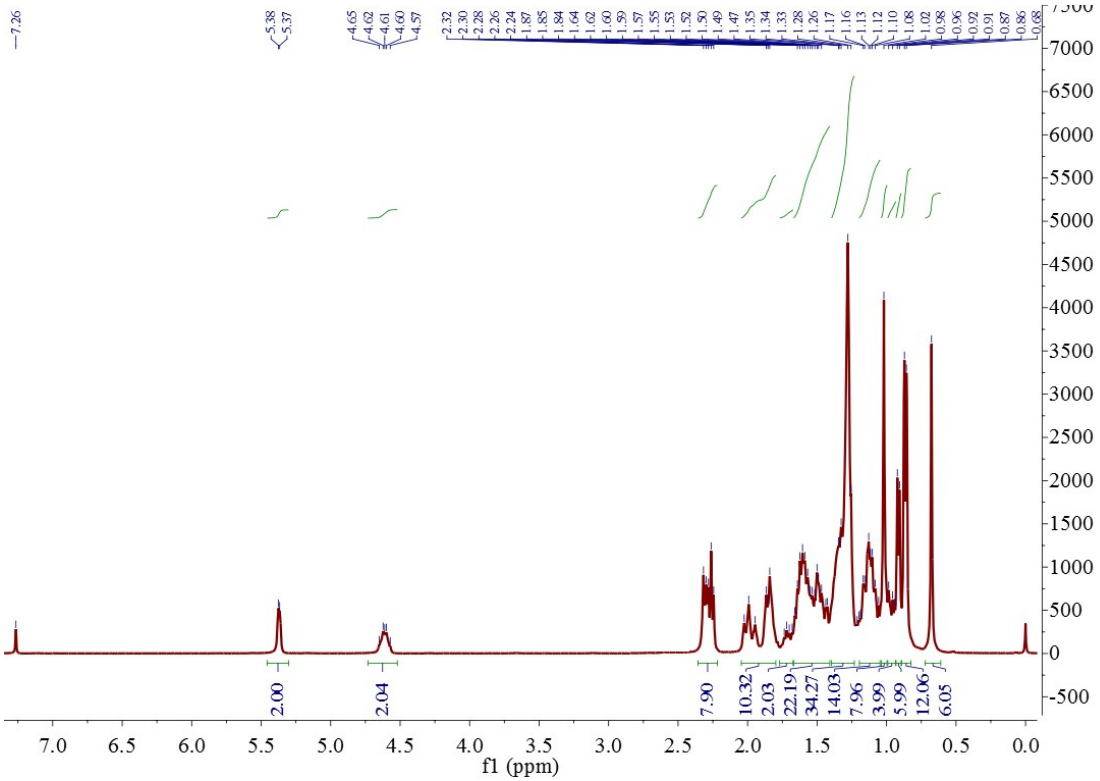


Figure S1. ^{1}H NMR spectrum of Chol-Se

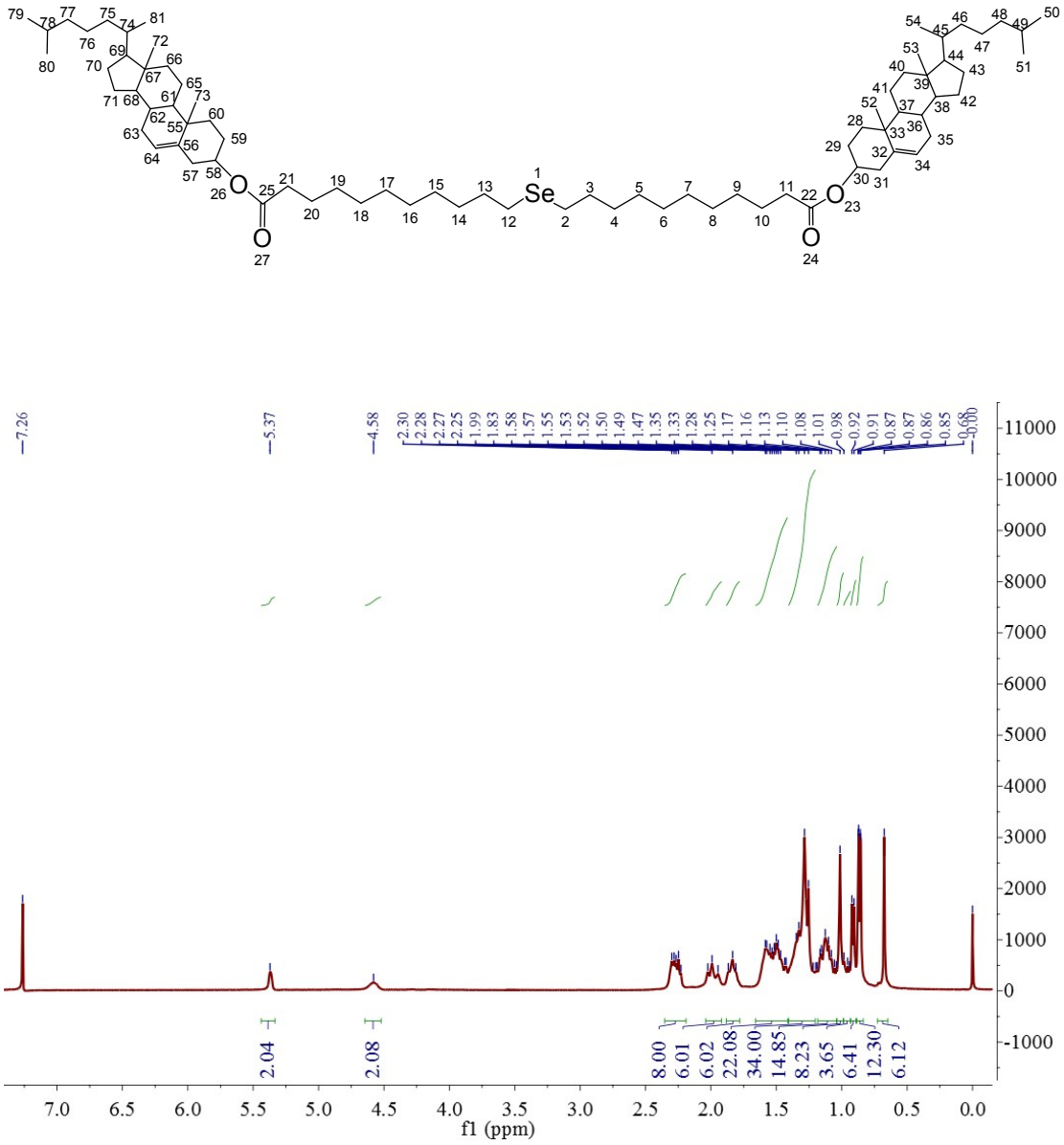
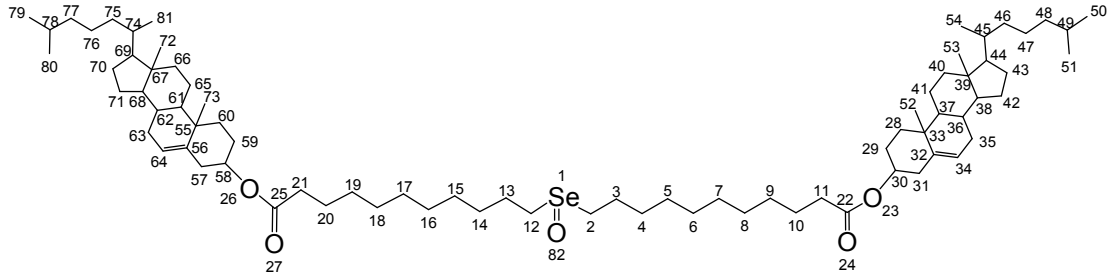


Figure S2. ^{1}H NMR spectrum of Chol-Se-Ox



^{1}H NMR (400 MHz, $CDCl_3$) δ5.37 (t, 2H, C64-1H, C34-1H), 4.58 (m, 2H, C58-1H, C30-1H), 2.30-2.23 (m, 8H, C11-2H, C21-2H, C31-2H, C57-2H), 2.02-1.84 (m, 14H, C35-2H, C63-2H, C10-2H, C20-2H, C45-1H, C74-1H, C2-2H, C12-2H), 1.58-1.42 (m, 22H, C42-2H, C43-2H, C41-2H, C40-2H, C44-1H, C70-2H, C71-2H, C66-2H, C65-2H, C69-1H, C49-1H, C78-1H, C3-2H, C13-2H), 1.35-1.25

(m, 32H, C4-2H, C14-2H, C5-2H, C15-2H, C6-2H, C16-2H, C9-2H, C19-2H, C29-2H, C28-2H, C7-2H, C8-2H, C59-2H, C60-2H, C17-2H, C18-2H), 1.24-1.04 (m, 14H, C46-2H, C47-2H, C48-2H, C37-1H, C75-2H, C76-2H, C77-2H, C61-2H), 1.02 (s, 10H, C73-3H, C62-1H, C68-1H, C52-3H, C36-1H, C38-1H), 0.92-0.91 (d, 6H, C54-3H, C81-3H), 0.87-0.85 (m, 12H, C50-3H, C51-3H, C79-3H, C80-3H), 0.68 (s, 6H, C53-3H, C72-3H)

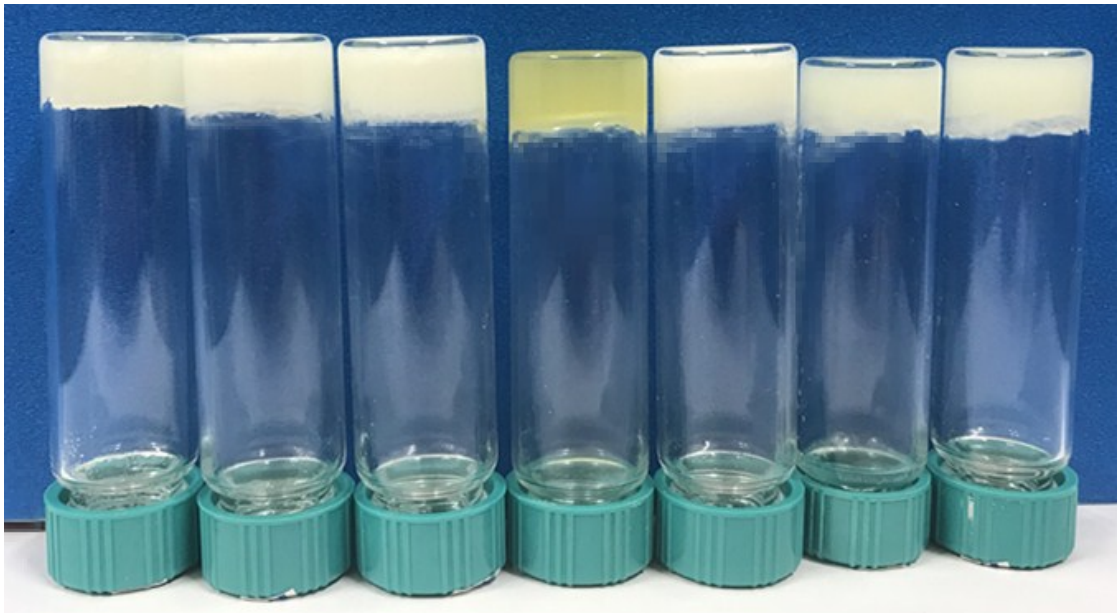


Figure S3. The appearance of gel formed by Chol-Se in different organic solvents. (a) ethyl acetate; (b) pentanol; (c) hexanol; (d) benzyl alcohol; (e) octanol; (f) n-decane; (g) dodecane

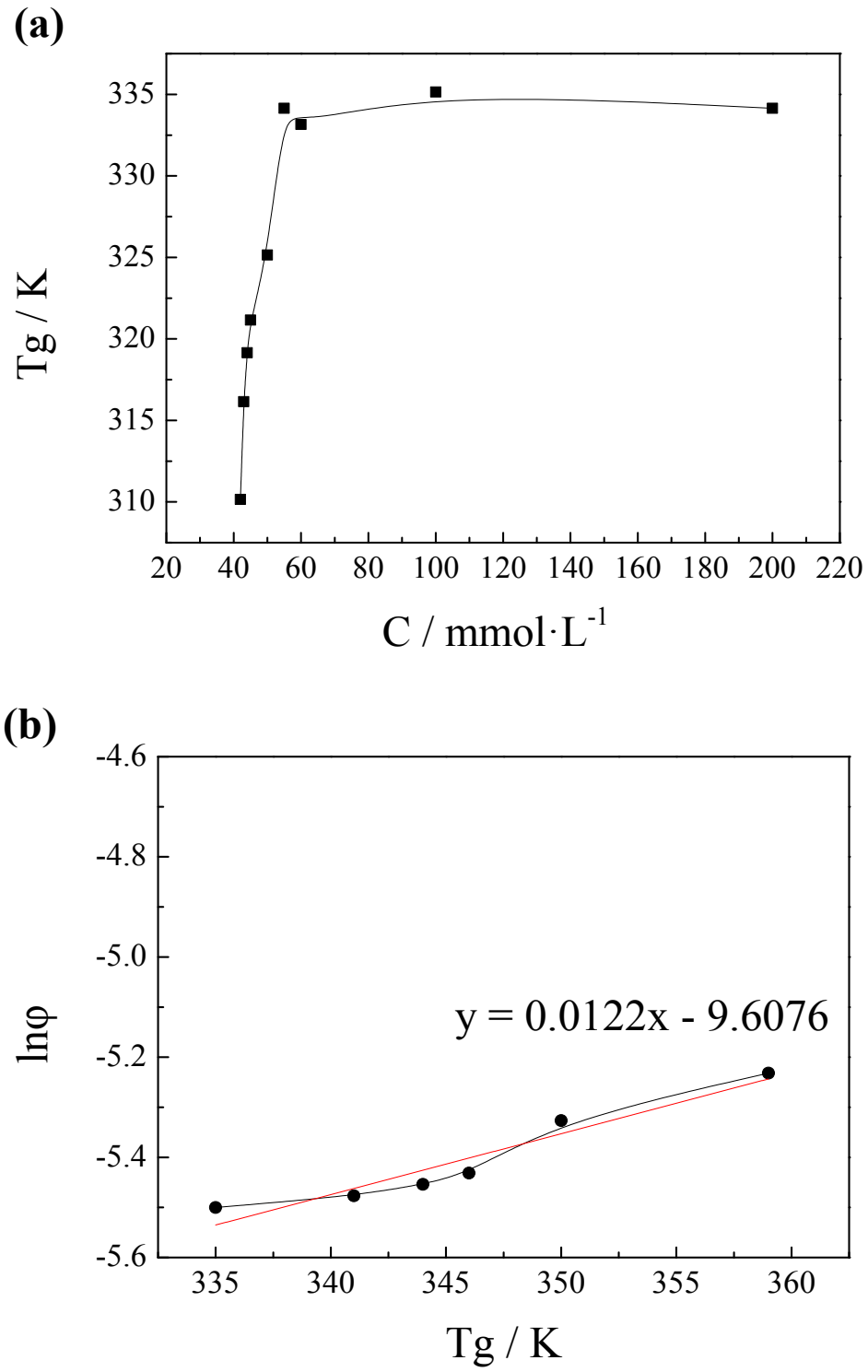


Figure S4. (a) Phase transformation temperature (T_g) versus the concentration of the gelator molecular in ethyl acetate; (b) Plot of lnφ versus Tg in ethyl acetate.

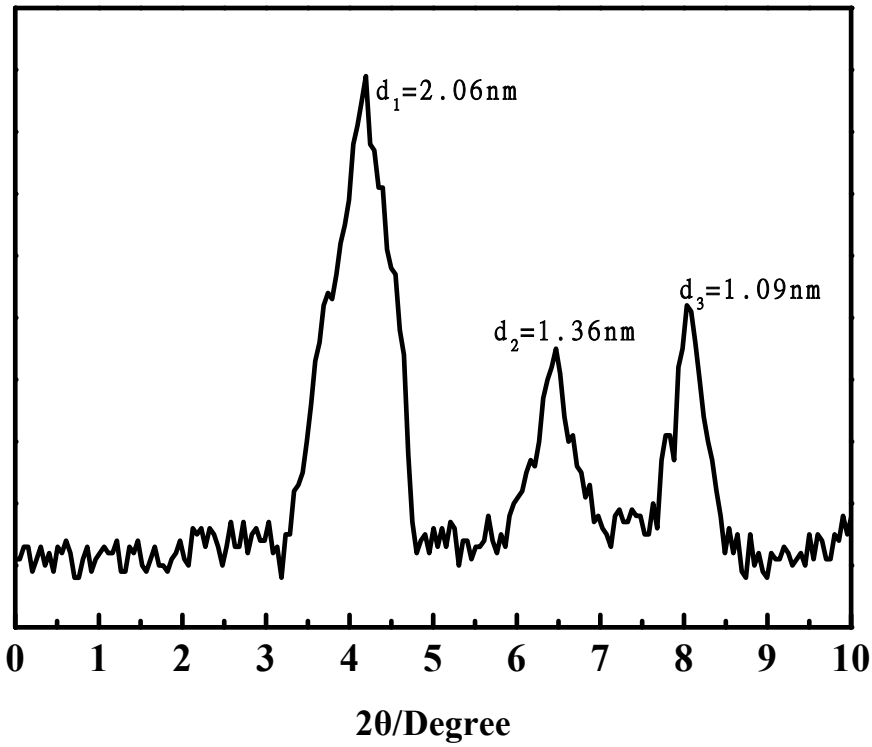


Figure S5. The XRD spectrum of gel formed in ethyl acetate (60 mM).