

Photoreversible Dendritic Organogel

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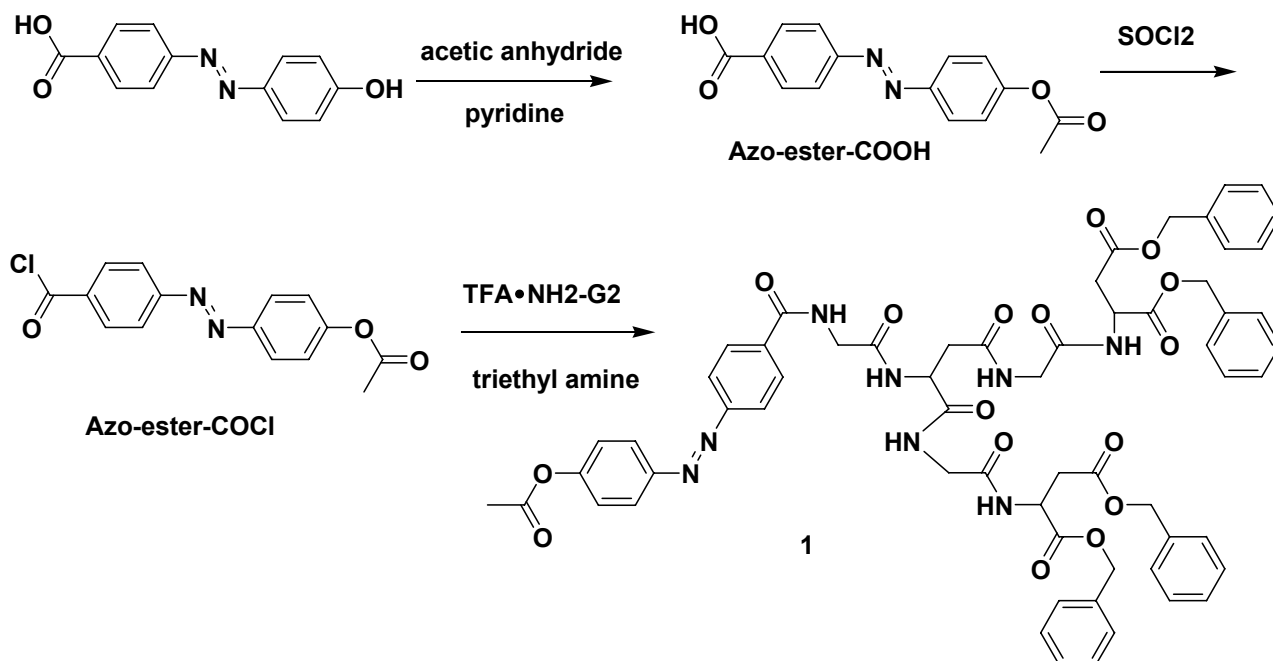
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General

Unless stated otherwise, all reagents and common solvents were obtained from commercial sources and used as received. ¹H NMR and ¹³C NMR spectra were recorded on Bruker 400 MHz spectrometer. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass-spectra were acquired on a BIFLE XIII time-of-flight MALDI mass spectrometer with α -cyano-4-hydroxycinnamic acid (CCA) as the matrix. FT-IR spectra were obtained using a Bruker VECTOR22 IR spectrometer. Tapping-mode Atomic Force Microscopy (AFM) measurement was performed using a SPA-400 Multimode AFM and SPI3800N Probe Station. For the preparation of AFM samples, the loose gel was dropped on a freshly cleaved mica surface and air-dried at room temperature before imaging. Powder wide-angle X-ray diffraction (WAXD) patterns of xerogels were obtained using a Bruker D8 Discover diffractometer with GADDS as a 2D detector. Air scattering was subtracted from the sample patterns. Diffraction patterns were recorded in a transmission mode at room temperature employing Cu K α radiation. Gel was naturally dried for two days at room temperature before WAXD experiment. DSC measurements were carried out on a Thermal Analysis Q 100 DSC system.

Synthesis

TFA·NH₂-G₂ was synthesized according to ref 1. 4-(*p*-Hydroxyphenylazo)benzoic acid was obtained according to ref 2.



4-(*p*-Hydroxyphenylazo) benzoic acid (0.12 g, 0.5 mmol), acetic anhydride (1.02 g, 8 mmol) and pyridine (0.78 g, 10 mmol) were refluxed for 3 hours. The reaction mixture was poured into ice water and acidified by 10% HCl to pH = 6. The precipitate was recrystallized with methanol. The obtained ester was refluxed in SOCl₂ for 3 hours and the solvent was evaporated to dryness under reduced pressure. 25 mL CH₂Cl₂ was added and evaporated again. To a CHCl₃ (2 mL) solution Azo-ester-ClO (0.04 g, 1.34 mmol) was added dropwise a CHCl₃ solution of TFA·NH₂-G₂ (0.2 g, 0.19 mmol) and triethylamine (0.5 mL). After the reaction mixture was stirred for 24 hours under an atmosphere of N₂, the solvents were evaporated. The residue was dissolved in a small amount of 1:9 CH₃OH:CHCl₃, precipitated in cold diethyl ether, filtered, and dried. The crude product was precipitated by diethyl ether and subjected to column chromatography (SiO₂:CH₂Cl₂/MeOH 10:1). Yield: 30%; ¹H NMR (400 MHz, d₆-DMSO, RT, TMS): δ = 8.87-8.27 (m, 6H, NHCO), 8.09-7.88 (m, N₂C₆H₄CO), 7.38-7.32 (m, 20H, Ar-H), 7.10-6.89 (m, N₂C₆H₄CO), 5.09-5.05 (m, 8H, COCH₂C₆H₅), 4.79 - 4.72 (m, 2H, NHCHCO), 4.64-4.62 (m, 1H, NHCHCO), 3.98-3.3.95 (m, 2H, NHCH₂CO), 3.77-3.73 (m, 4H, NHCH₂CO), 2.93-2.56 (m, 6H, CHCH₂CO), 2.32-2.21(d, 3H, COCH₃) ppm. ¹³C NMR (400 MHz, RT, d₆-DMSO) δ = 170.67-168.38 (CH₂CO), 165.71 (N₂ArCO), 161.52(C₆H₄OH) 153.21-152.84 (N₂C₆H₄CO), 149.37 (N₂C₆H₄OH), 135.94 - 135.38 (CH₂C₆H₅), 128.27-127.25 (Ar-C), 123.56 (C₆H₄OCO), 122.47 (C₆H₄OCO), 121.90 (C₆H₄OCO),

65.99-65.54 (OCH₂C₆H₅), 49.84-48.44 (NHCH₂CO), 42.72-41.70 (NHCH₂CO), 37.13 (CHCH₂CO), 35.60 (CHCH₂CO), 20.46(COCH₃) ppm. MALDI-TOF C₆₁H₆₀N₈O₁₆ *m/z* Cal. 1160, found [M + Na] 1183, [M + K] 1199.

FT-IR spectra:

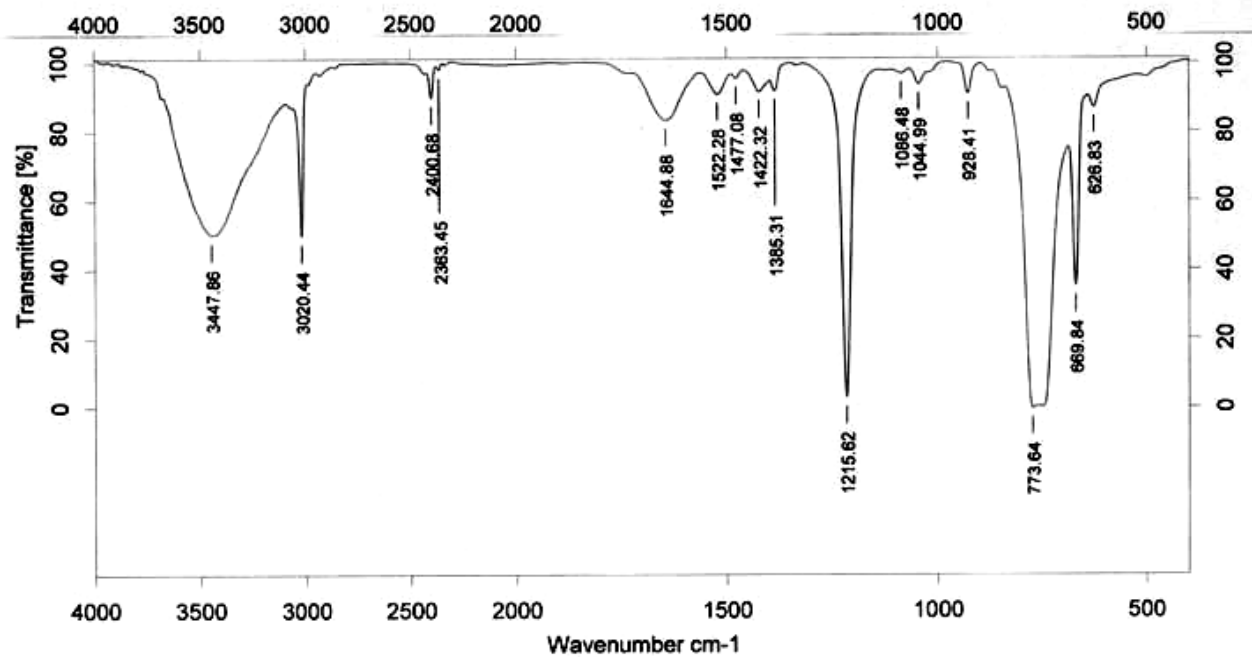


Figure S-1. IR spectrum of 1 in CHCl₃ solution

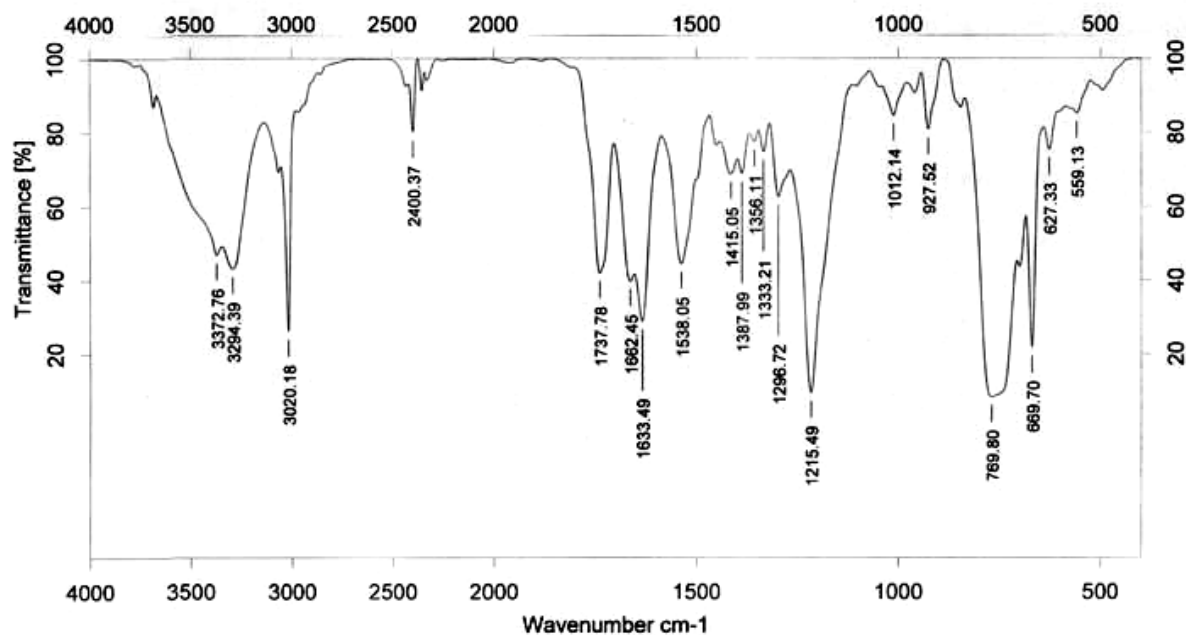


Figure S-2. IR spectrum of 1 in CHCl₃ gel

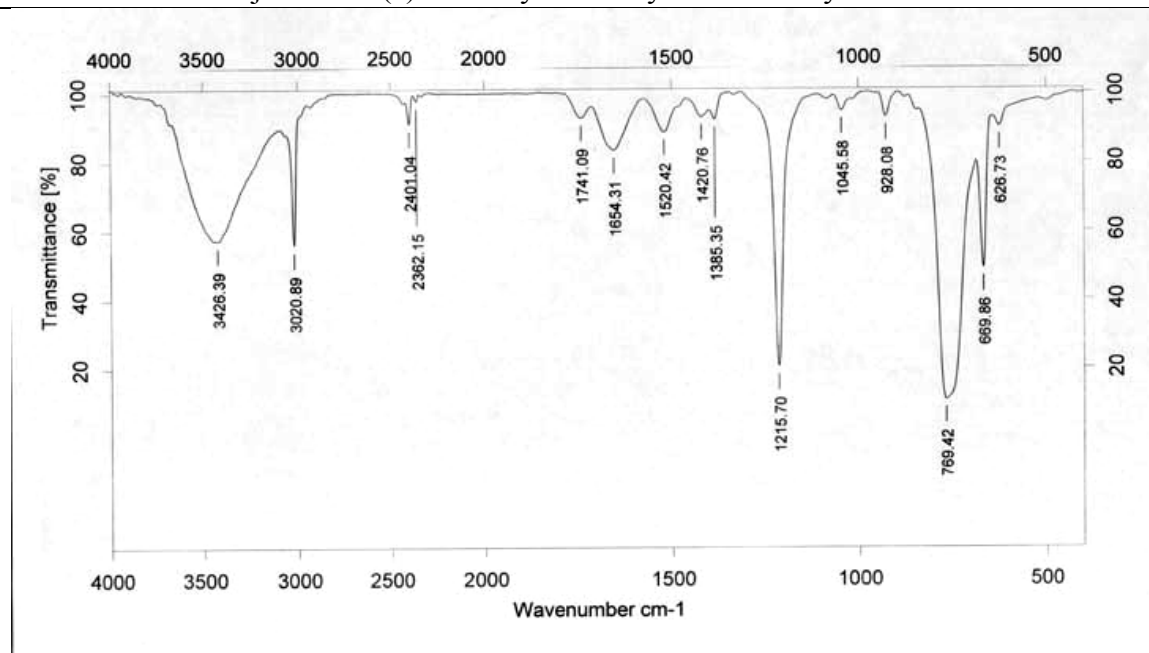


Figure S-3. IR spectrum of **1** in CHCl₃ solution obtained from gel irradiated by UV

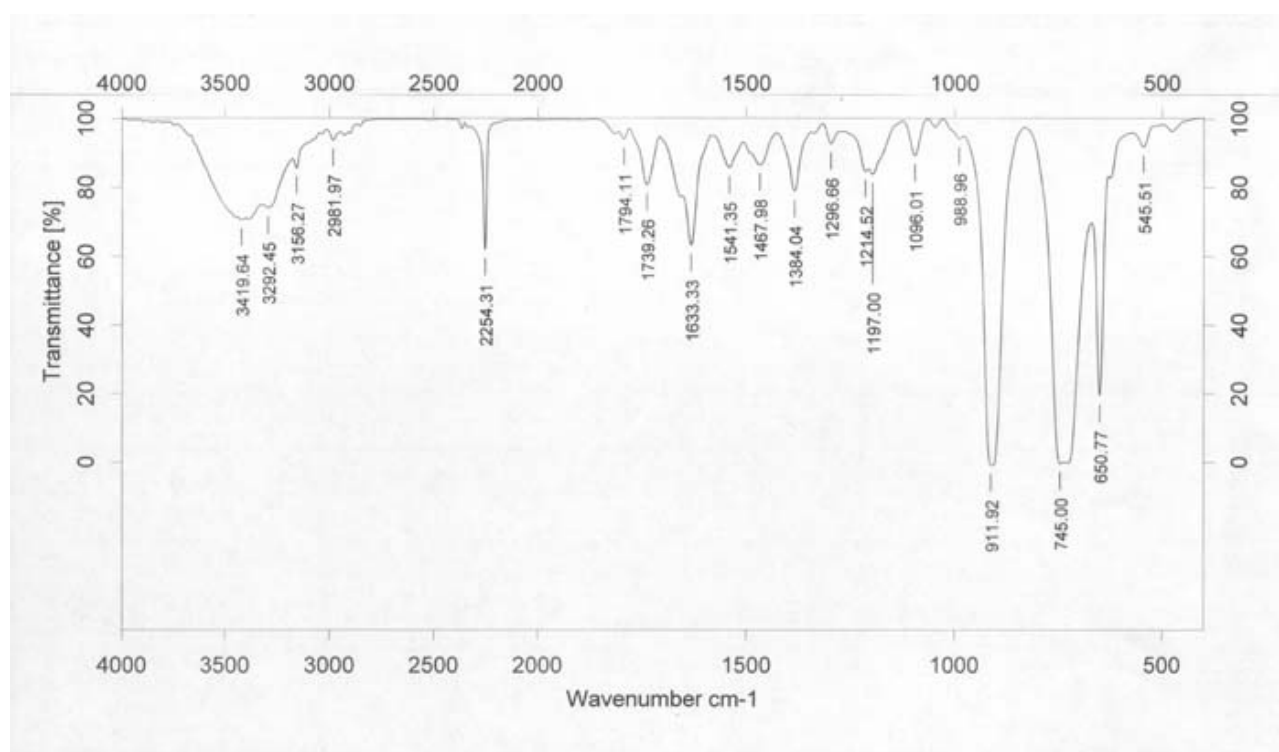


Figure S-4. IR spectrum of **1** in reformed CHCl₃ gel

UV spectra of 1 (in solution of ethyl acetate and gel phase):

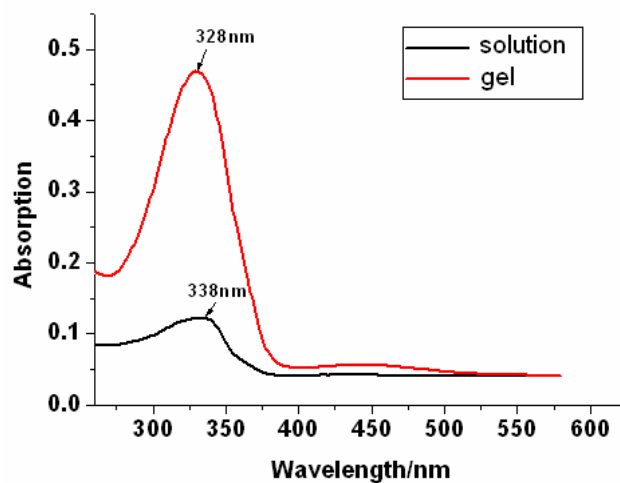


Figure S-5 UV-vis spectra of **1** acetate solution and gel (Solution concentration: 1.5×10^{-5} M, gel concentration: 1.1×10^{-3} M)

NMR spectra:

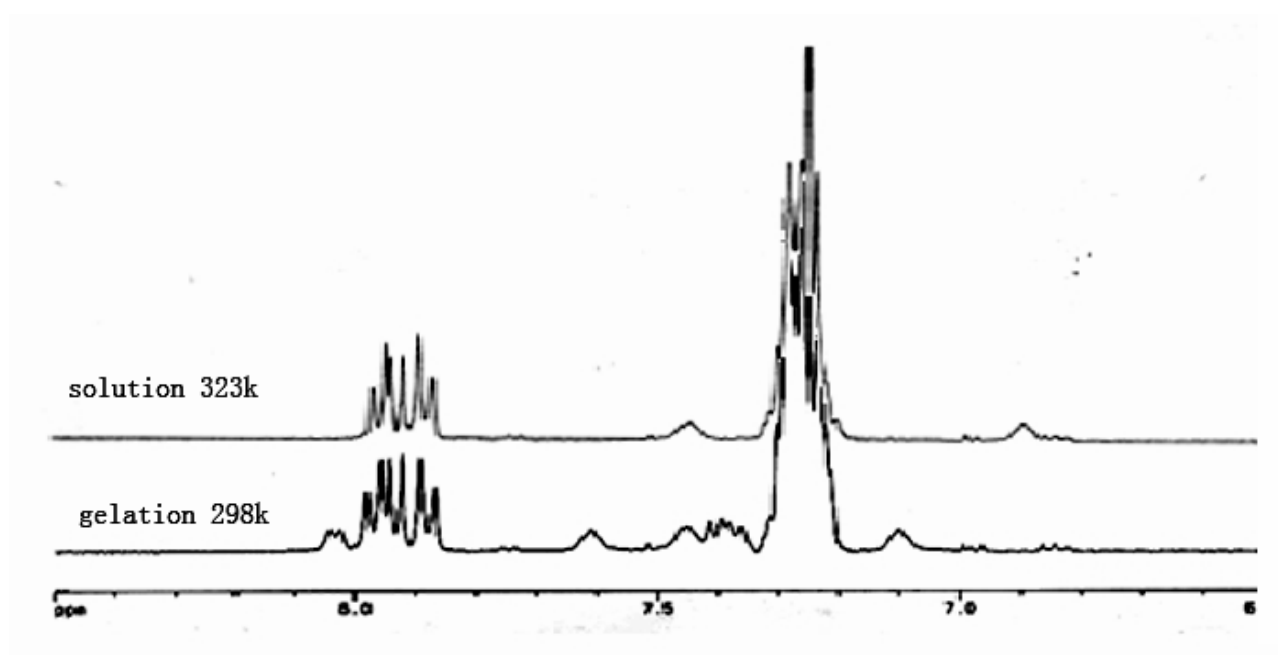


Figure S-6 H-NMR spectra of **1** (10.8 mg/ml in CDCl₃) in gel state (RT) and in solution (50 °C)

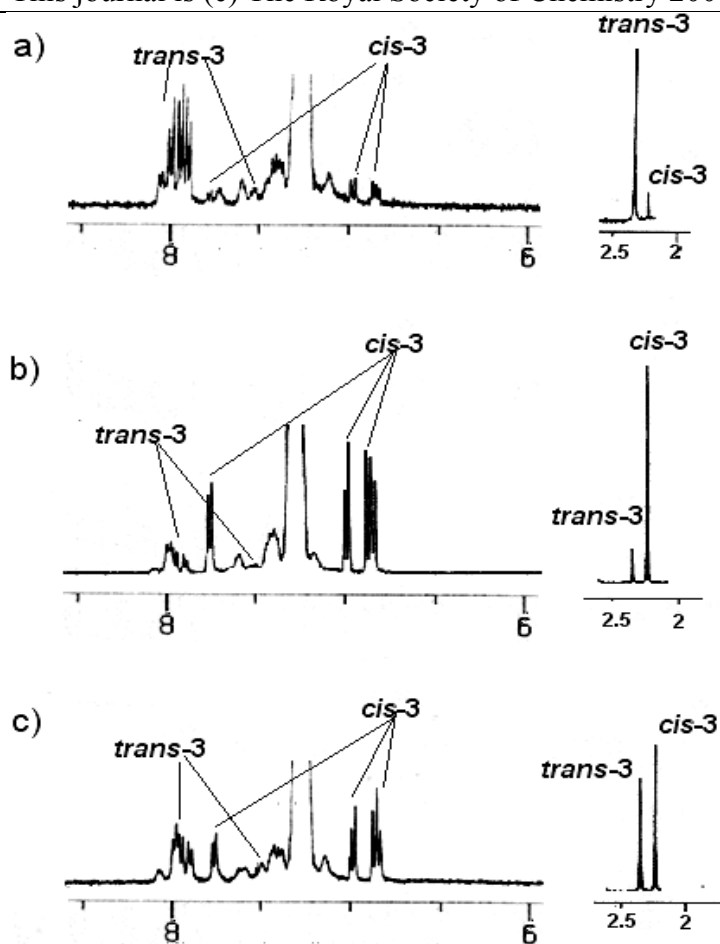


Figure S-7. ^1H NMR spectra of **1** in the CDCl_3 gel (a), the *cis*-rich solution (b), and the reformed gel (c). The concentration of **1** is 20 mg/mL.

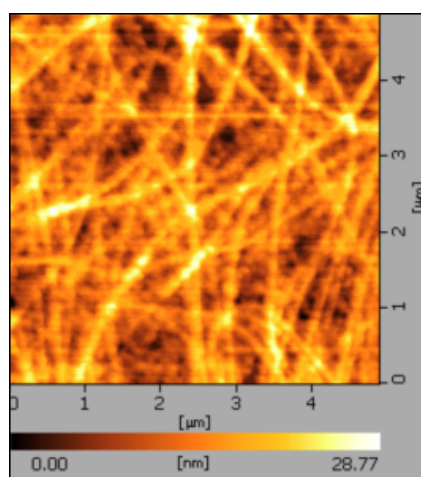


Figure S-8. AFM height image of xerogel of **1** after drying from ethyl acetate gel ($[\mathbf{1}] = 0.1\text{wt}\%$)

Wide-angle X-ray diffraction of reformed xerogel 1:

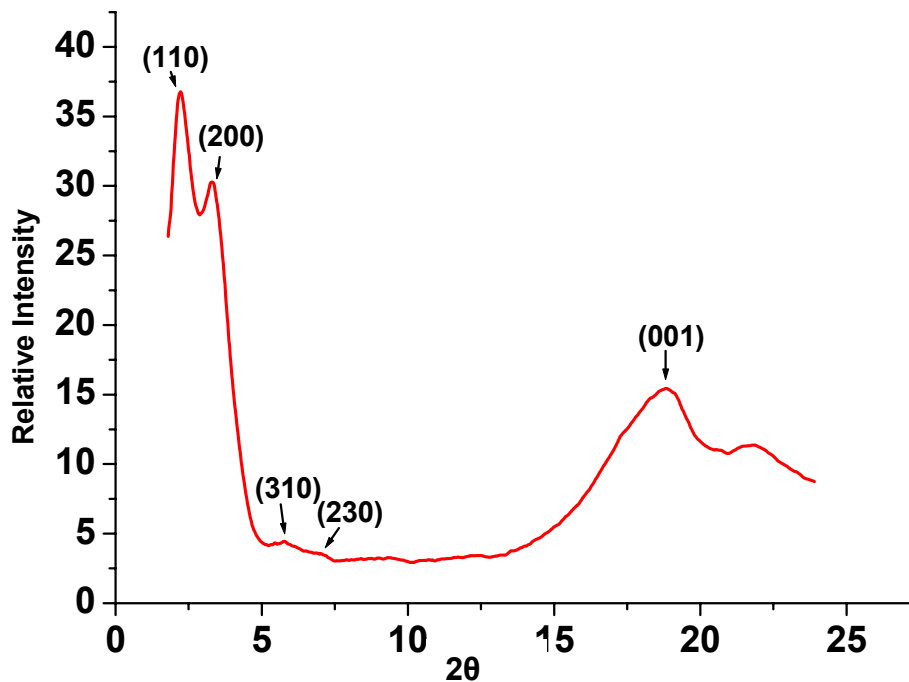


Figure S-9. WAXD patterns of the dried reformed **1** gel at 70°C

DSC of xerogel:

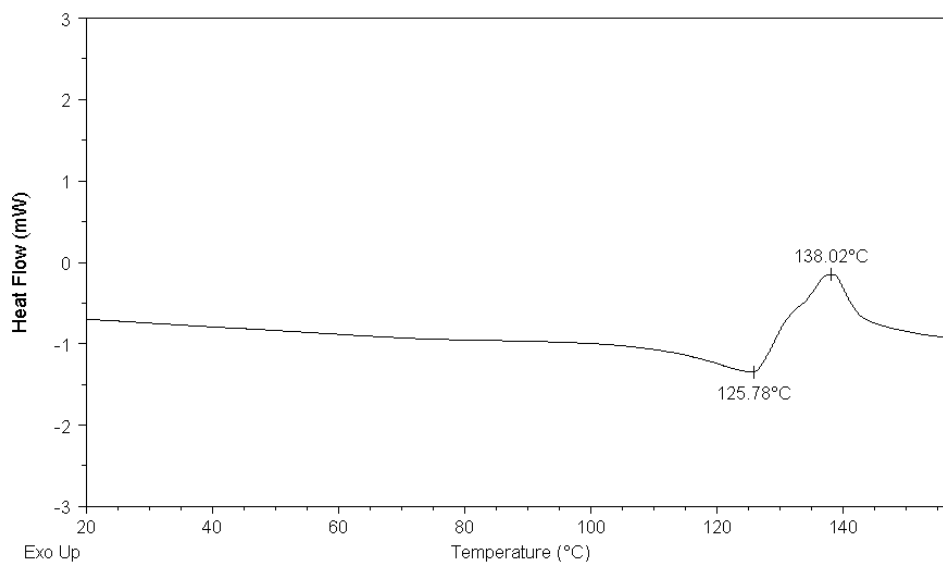


Figure S-10. DSC of the **1** xerogel (heating rate: 10°C/min)

Reference

1. Y. Ji, Y. F. Luo, X. R. Jia, E. Q. Chen, Y. Huang, C. Ye, B. B. Wang, Q. F. Zhou, Y. Wei, *Angew. Chem. Int. Ed. Engl.* **2005**, *44*, 6025-6029.
2. L. Corvazier, Y. Zhao, *Macromolecules* **1999**, *32*, 3195-3200.