

Supporting Information

For

Polyoxometalate Cluster-contained Hybrid Gelator and Hybrid Organogel: A New Concept of Softenization of Polyoxometalate Clusters

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1. General Materials and Methods.

1.1 Materials:

All reagents and solvent were purchased from major chemical suppliers and used without further purification unless otherwise noted.

1.2 Methods:

^1H NMR (400 MHz) spectra were recorded in $[\text{D}_1]$ chloroform and $[\text{D}_6]$ DMSO on a Varian Unity Plus-400 NMR spectrometer. ESI-MS data was acquired on a Quattro II triple quadrupole mass spectrometer in negative mode. Infrared spectra (IR) were recorded on a Bio-Rad FTS-135 FTIR spectrometer using the KBr pellet technique. Transmission electron microscopy (TEM) observations were performed using a FEI Tecnai F20 operated at 200 kV and a FEI Titan 80-300 operated at 300 kV. BF-TEM images were acquired at room temperature on the Tecnai F20, whereas electron diffraction and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were obtained on the Titan 80-300 operated at room temperature as well as at liquid nitrogen temperature. The samples were prepared by a slight touch of the gels onto copper grids. Then the grids were dried under vacuum. Atomic force microscopy (AFM) images were recorded on a multi-model atomic force microscope (Digital Instrumental Nanscope IV) using silica wafer as substrate of at room temperature. The samples were prepared by a slight touch of the gels onto a freshly cleaned silicon wafer surface. All

measurements were performed in tapping mode.

2. Experimental Procedure.

2.1 Synthesis of g_2 -PUA-COOH.

The synthesis was carried out following a route reported in previous work.¹ ^1H NMR (400 MHz CDCl_3): δ = 0.86 (t, 12H; CH_3), 1.24 (s, 104H; $(\text{CH}_2)_{13}$), 1.58 (m, 8H; $\text{CH}_2\text{CH}_2\text{OCO}$), 1.63–1.87 (m, 12H; $\text{CH}_2\text{CONHCH}_2\text{CH}_2\text{CH}_2\text{NCOCH}_2$), 2.54–2.74 (m, 12H; $\text{NCOCH}_2\text{CH}_2\text{CO}$), 3.03–3.45 (m, 24H; $\text{CONHCH}_2\text{CH}_2\text{CH}_2\text{NCO}$), 3.98–4.06 (m, 8H; $\text{CH}_2\text{CH}_2\text{OCO}$), 5.18–5.51 ppm (s, 6H; NHCO); ESI-MS: m/z : calcd for $[\text{MH}]$: 1729.41; found: 1729.11; elemental analysis calcd (%) for $\text{C}_{98}\text{H}_{187}\text{N}_9\text{O}_{15}$: C: 67.98, H: 10.89, N: 7.28; found: C: 67.98, H: 10.84, N: 7.20.

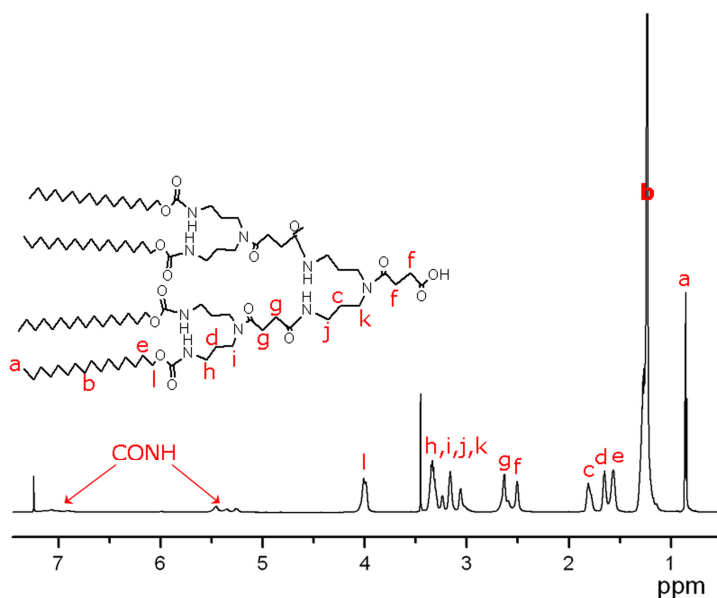


Fig. S1 ^1H NMR spectrum of g_2 -PUA-COOH.

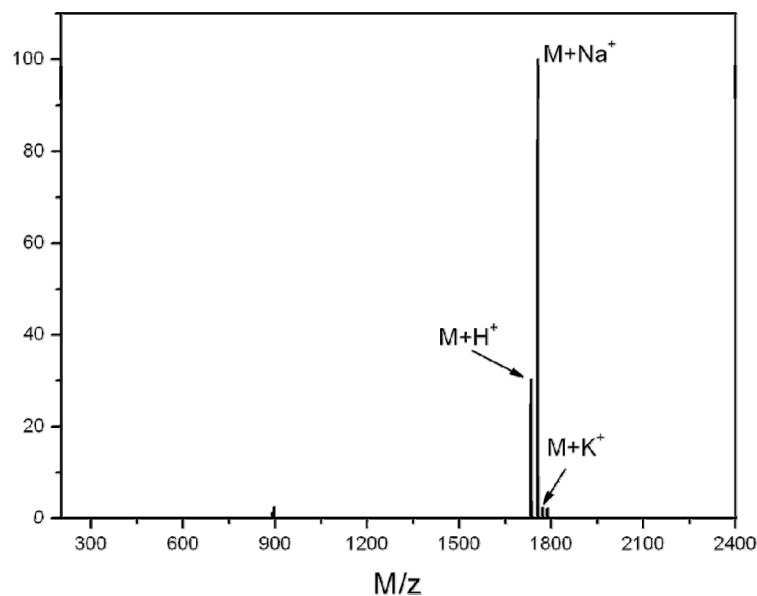


Fig. S2 ESI-MS spectrum of g_2 -PUA-COOH.

2.2 Synthesis of g_2 -PUA- H_3 POM- g_2 -PUA.

g_2 -PUA-COOH (94.5 mg, 54.6 μ mol), tris-POM-tris (50.0 mg, 26.4 μ mol), dried dichloromethane (10 mL), and *N,N*-dimethylformamide (2 mL) were added to a Schlenk tube flask (50 mL) at 30°C. After the mixture was dissolved, DCC (70.0 mg, 339.8 μ mol, 12 eq) was added into the system. The reaction was stirred at room temperature for two days under Ar atmosphere. TLC detection suggested that the reactants disappeared. The solvent was removed under reduced pressure, and the crude product was purified by silica gel column chromatography with dichloromethane/ethyl acetate/methanol (7:1:1.5) elution to yield a yellow-colored solid (85 mg, 63.4%)

2.3 Characterization of g_2 -PUA- H_3 POM- g_2 -PUA.

(1) FT-IR:

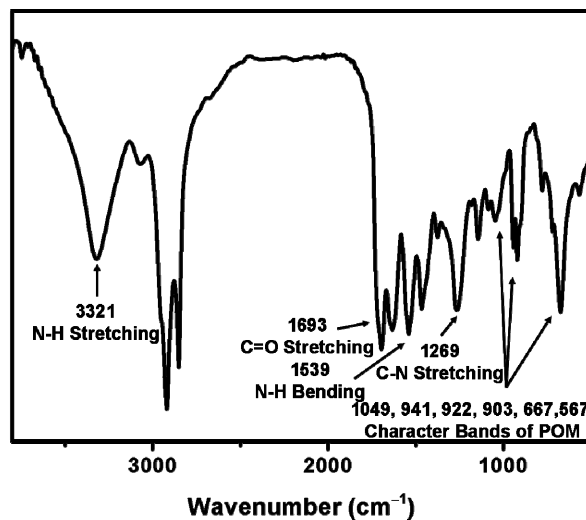


Fig. S3 FT-IR spectrum of g_2 -PUA- H_3 POM- g_2 -PUA. Bands at $\nu = 1693$ (C=O stretching), 1539 (N-H bending), 1269 (C-N stretching), and 3321 cm^{-1} (N-H stretching), indicating the formation of the amide bond. Moreover, the IR-frequencies occurred at 1049, 941, 922, 903, 667 and 567 cm^{-1} demonstrated that the Mn-Anderson POM remains intact and does not decompose upon encapsulation.

(2) ESI-MS:

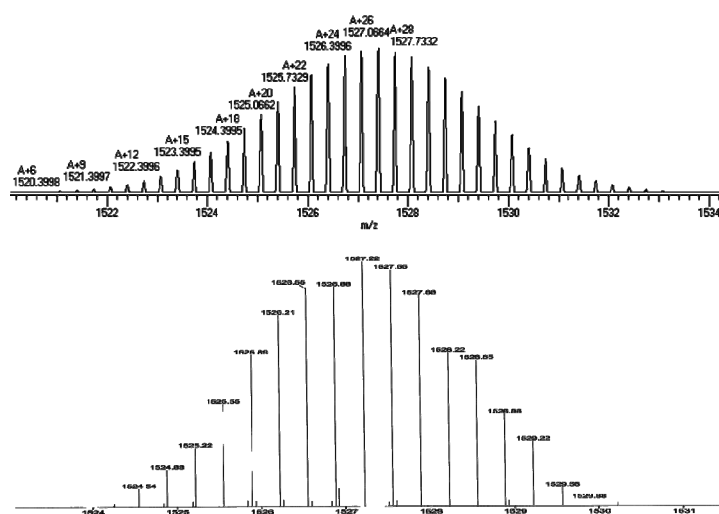


Fig. S4 ESI-MS spectrum of g_2 -PUA- H_3 POM- g_2 -PUA in DMF. The ‘top’ one is the simulated spectrum and ‘bottom’ one is the original one. ESI-MS (negative mode): 1527 g mol^{-1} ($[M-3H]^{3-}$).

(3) ^1H NMR (400 MHz, D_6 -DMSO: $\text{CDCl}_3 = 1:1$): $\delta = 0.83$ (t, 24H; CH_3), 1.21 (s, 208H; $(\text{CH}_2)_{13}$), 1.52 (m, 8H, $\text{CH}_2\text{CONHCH}_2\text{CH}_2\text{CH}_2\text{NCOCH}_2$), 1.56 (s, 16H; $\text{CH}_2\text{CH}_2\text{OCO}$), 1.69 (s, 16H; $\text{CONHCH}_2\text{CH}_2\text{CH}_2\text{NCO}$), 2.35–2.77 (m, 24H, $\text{NCOCH}_2\text{CH}_2\text{CONH}$), 2.90–3.01 (m, 48H, $\text{CONHCH}_2\text{CH}_2\text{CH}_2\text{NCO}$), 3.90 (tt, 16H, $\text{CH}_2\text{CH}_2\text{OCO}$), 4.61, 4.63 (s, 1H, NHCO), 5.79 (s, 2H, NHCO), 6.71 (s, 4H, NHCO), 6.94 (s, 4H, NHCO), 7.91, 7.99 (s, 1H, NHCO).

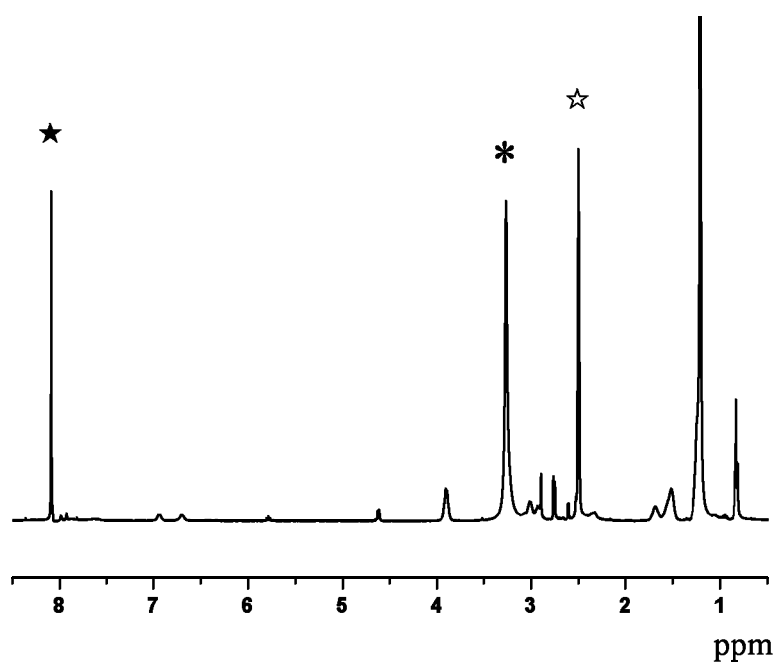


Fig. S5 ^1H NMR spectra of g_2 -PUA- H_3POM - g_2 -PUA in $[\text{D}_6]\text{DMSO}:\text{CDCl}_3 = 1:1$. (\star the peak of DMSO, \blackstar the peak of CDCl_3 , *the peak of H_2O).

3 Simulation of Molecular sizes.

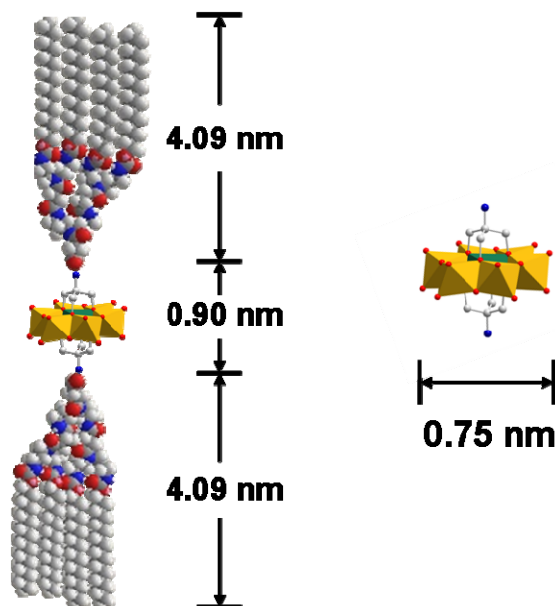


Fig. S6 The molecular sizes of dendrons are simulated by Chem3D Ultra 8.0 and the ones of Tris-POM-Tris are simulated according to the procedure reported in literature².

4 References.

- [1] (a) Kim, C.; Kim, K. T.; Chang, Y.; Song, H. H.; Cho, T.-Y.; Jeon, H.-J. *J. Am. Chem. Soc.* **2001**, *123*, 5586–5587. (b) Llinares, M.; Roy, R. *Chem. Commun.* **1997**, 2119–2120. (c) Rannard, S. P.; Davis, N. J. *Org. Lett.* **1999**, *1*, 933–936. (d) Rannard, S. P.; Davis, N. J. *Org. Lett.* **2000**, *2*, 2117–2120. (e) Chang, Y.; Park, C.; Kim, K. T.; Kim, C. *Langmuir* **2005**, *21*, 4334–4339.
- [2] Liu, C. M.; Huang, Y. H.; Zhang, D. Q.; Gao, S.; Jiang, F. C.; Zhang, J. Y.; Zhu, D. B. *Crystal Growth & Design*. **2005**, *5*, 1531–1538.