

Supplementary information

Thermal-induced dynamic self-assembly of adenine grafted polyoxometalate complexes

Zhenfeng He, Yi Yan, Bao Li, Hui Ai, Huanbing Wang, Haolong Li,* and Lixin Wu

*State Key Laboratory of Supramolecular Structure and Materials, College of
Chemistry, Jilin University, Changchun 130012, China*

*To whom correspondence should be addressed. E-mail: hl_li@jlu.edu.cn

Synthetic procedures:

Synthesis of ethyl (9-adeninyl) acetate (1): Under a N₂ atmosphere, adenine (2.0 g, 14.8 mmol), sodium hydride (0.65 g, 20 mmol) was dissolved in dry DMF and stirred for 2 h at room temperature. And then, ethyl bromoacetate was added into the mixture slowly. The mixture was further stirred for 72 h. After removing the salt by filtration and evaporating most of the solvent under reduced pressure, the sample was poured into ice water and filtered. The formed white precipitate was collected as the crude product, which was further purified by silica gel chromatography with chloroform: methanol (20:1 v/v) as eluent. Finally, the pure product was obtained as a white solid. The yield was 1.8 g (50%). ¹H NMR (500 MHz, DMSO-*d*₆, TMS, ppm): δ = 1.21 (3H, triplet, *J* = 7.5 Hz), 4.14 (2H, quartet), 5.05 (2H, singlet), 7.248 (2H, singlet), 8.106(1H, singlet), 8.12 (1H, singlet).

Synthesis of N-tris (hydroxymethyl) methy (9-adeninyl) acetamide: A mixture of 1 (1.18 g, 5.0 mmol), potassium carbonate (0.60 g, 5.0 mmol), and dry DMSO (20 mL) was stirred at room temperature in a N₂ atmosphere for 24 h. After the removal of salt by filtration, the crude product was obtained after evaporating DMSO under reduced pressure. Then, the sample was washed with a lot of ethanol and the pure product was obtained as a white solid. The yield was 1.25 g (79 %). ¹H NMR (500 MHz, DMSO-*d*₆, TMS, ppm): δ = 3.55 (6H, doublet), 4.63 (2H, triplet), 4.87 (3H, singlet), 7.20 (2H, singlet), 7.66(1H, singlet), 8.03 (1H, singlet), 8.11 (1H, singlet).

Experimental conditions of single crystal structure:

Single crystal X-ray diffraction experiments were performed with a Rigaku/MSM mercury diffractometer with graphite monochromated Mo K α radiation ($\lambda=0.71073 \text{ \AA}$) at 293 K. Empirical absorption corrections based on equivalent reflections were applied. The complex was solved by direct method and refined by full matrix least squares fitting on F2 using the SHELXTL-97 software.

Additional characterizations:

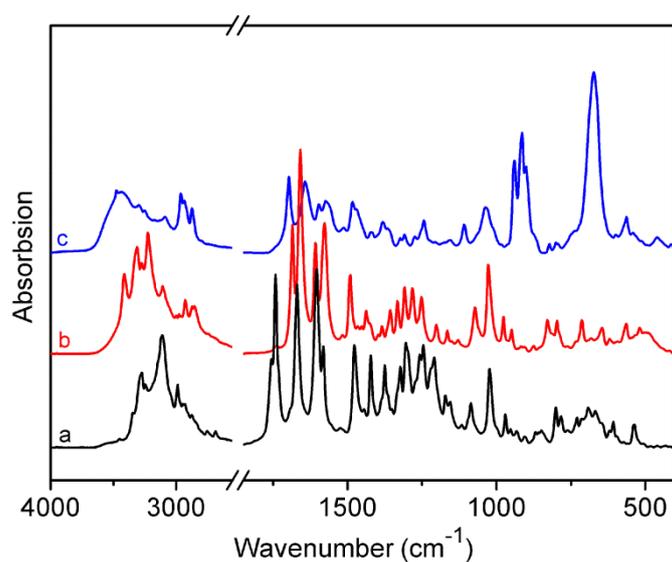


Fig. S1 FT-IR spectra of (a) Ethyl (9-adeninyl) acetate, (b) N-tris (hydroxymethyl) methyl (9-adeninyl) acetamide, and (c) SEOP-1 in KBr pellets.

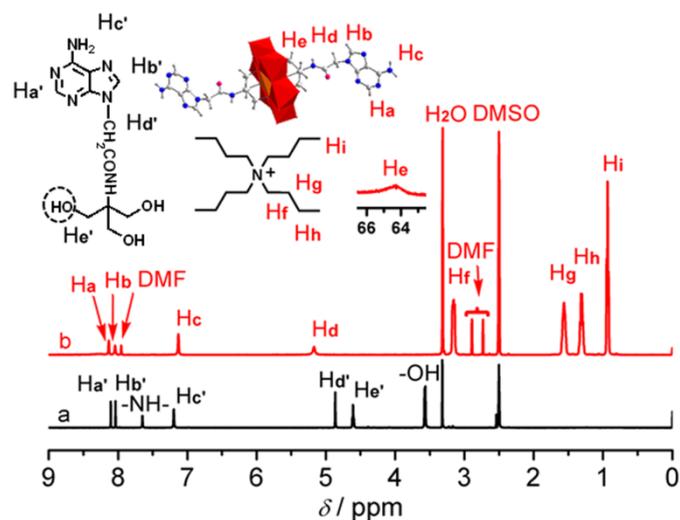


Fig. S2 ¹H NMR spectra of (a) N-tris (hydroxymethyl) methy (9-adeninyl) acetamide, (b) SEOP-1 in DMSO-*d*₆.

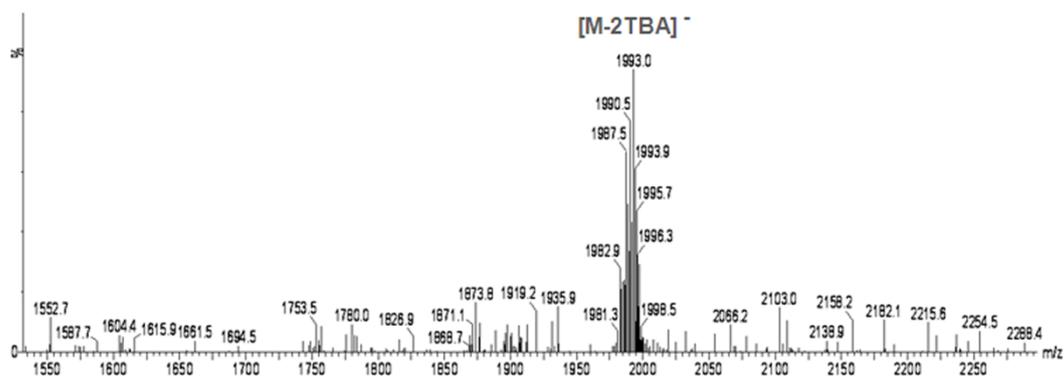


Fig. S3 ESI-MS spectrum of SEOP-1 in DMF.

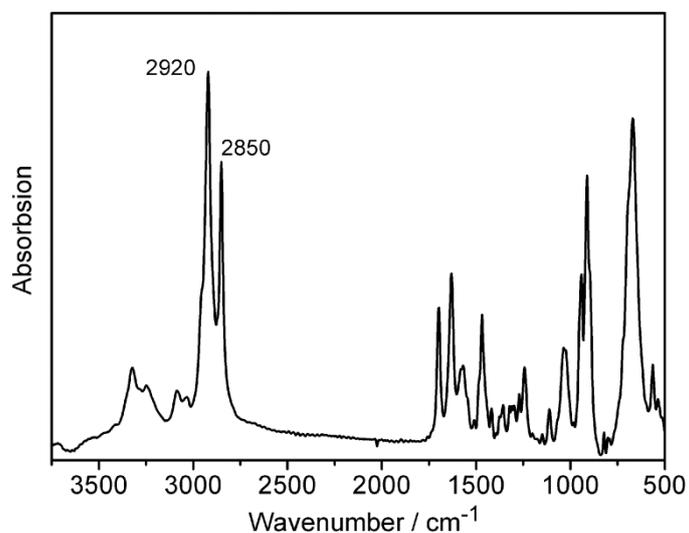


Fig. S4 FT-IR spectrum of SEOP-2 in KBr pellet.

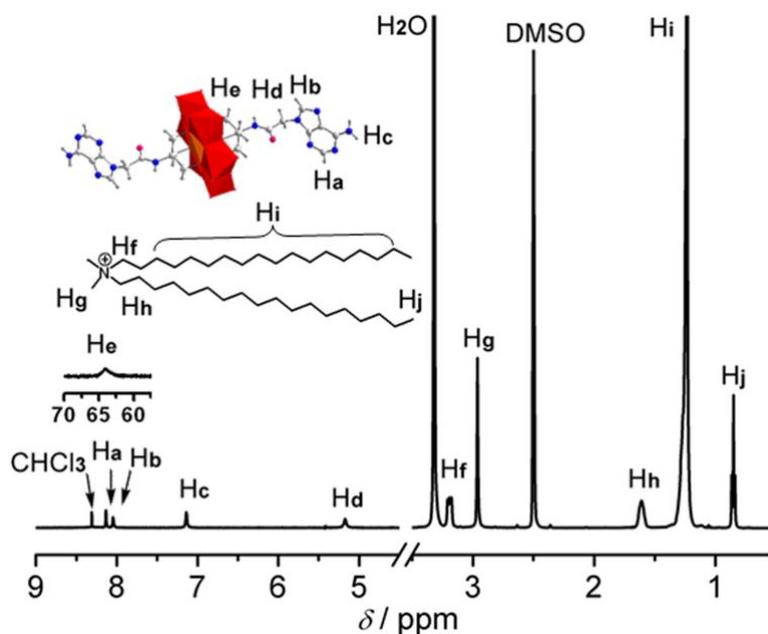


Fig. S5 ^1H NMR spectrum of SEOP-2 in $\text{DMSO-}d_6$.

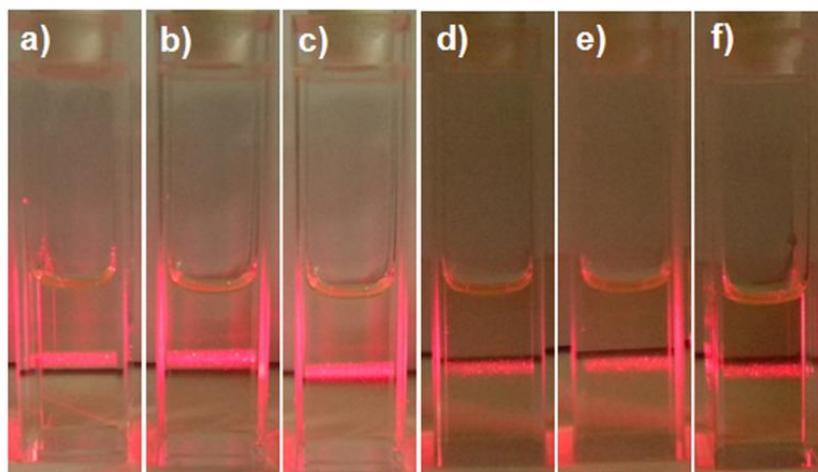


Fig. S6 Tyndall effect of the SEOPs solutions at different temperatures: a-c) corresponds to the acetonitrile solutions of SEOP-1 at 5, 15, and 45 °C, respectively; d-f) corresponds to the DMF solutions of SEOP-2 at 25, 45, and 65 °C, respectively.

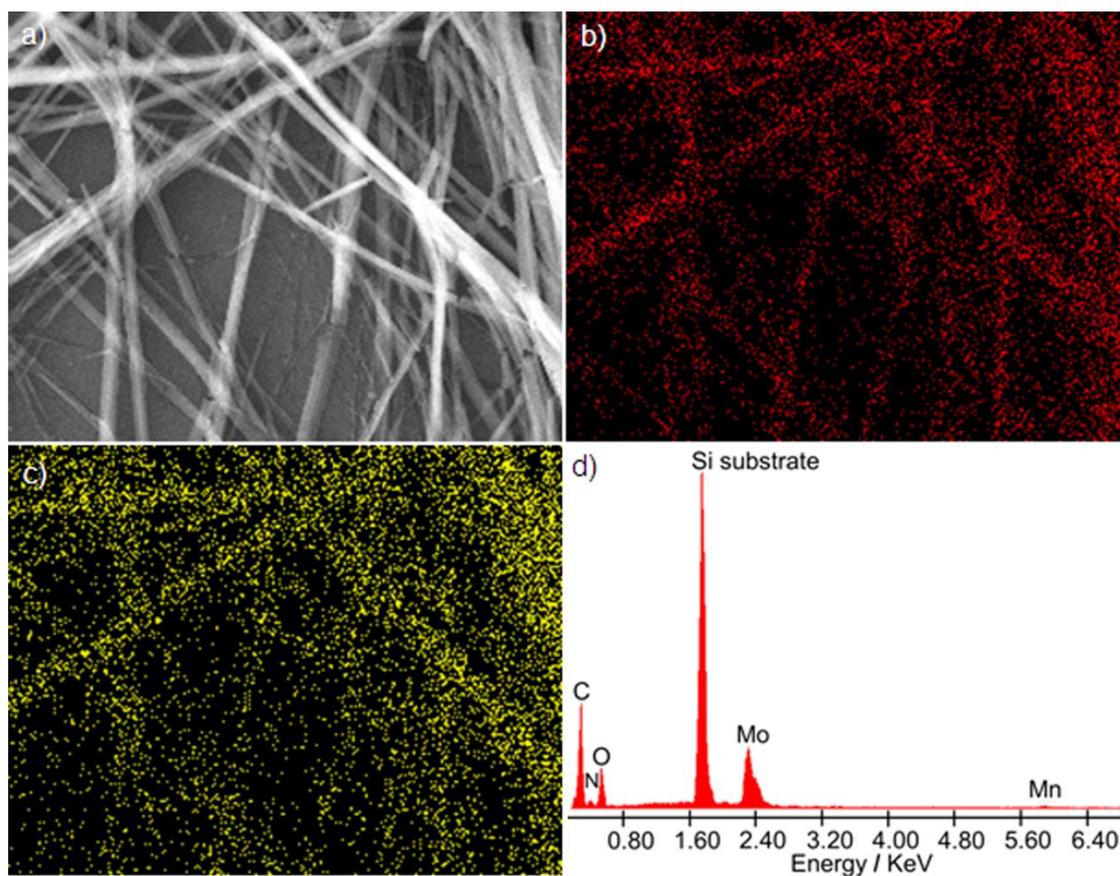


Fig. S7 X-ray energy-dispersive spectroscopy (EDX) analysis of the fibrous assemblies of SEOP-1 on silica substrate: a) the SEM image of the fibrous assemblies; (b) the EDX-mapping image of C element distribution as red dots; (c) the region EDX-mapping image of Mo element distribution as yellow dots; (d) the binding energy spectrum of the region of image (a).

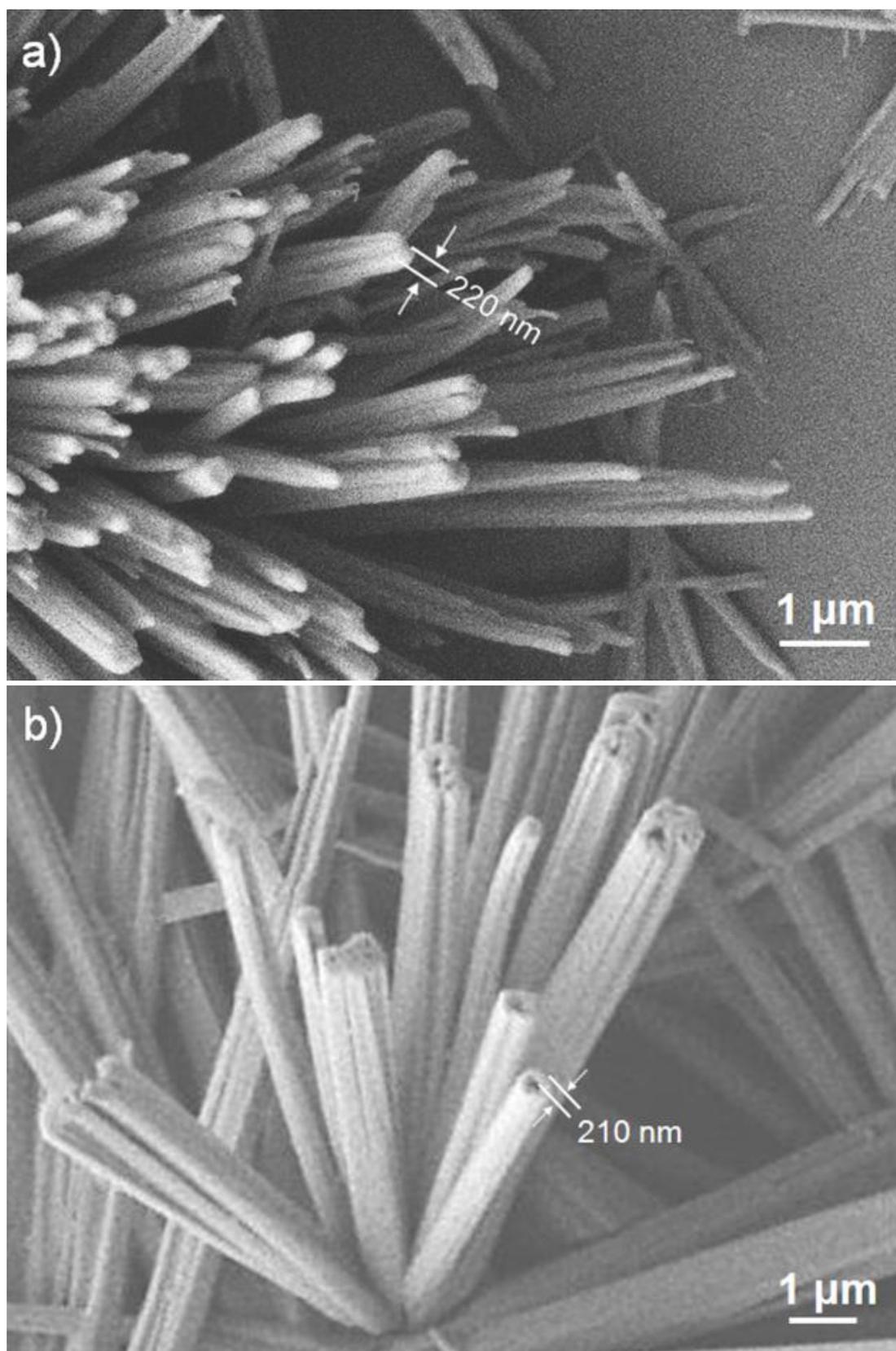


Fig. S8 Magnified SEM images of SEOP-1 assemblies: a) rods; b) tubes.

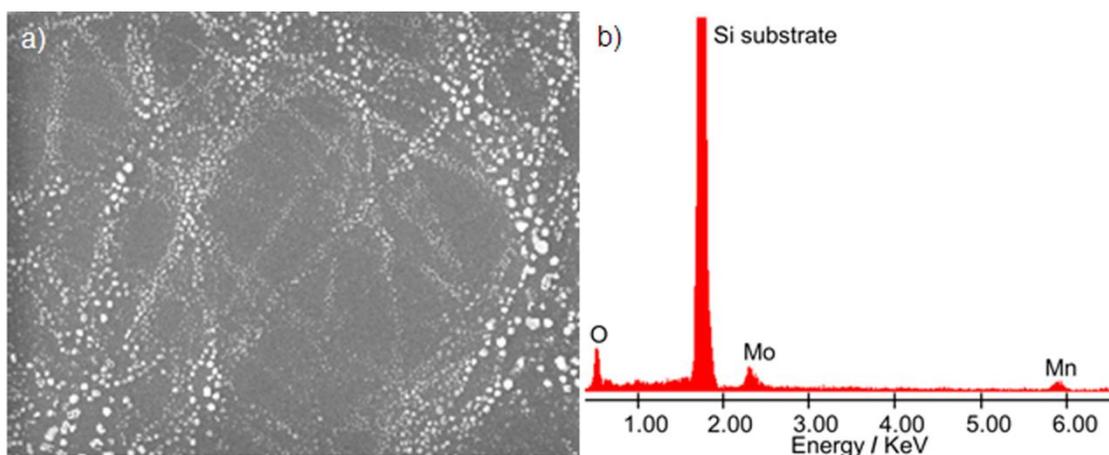


Fig. S9 X-ray energy-dispersive spectroscopy (EDX) analysis of the fibrous assemblies of SEOP-1 on silica substrate after calcination at 650 °C in air for 1 h: a) the SEM image of the retained fibrous assemblies; (b) the binding energy spectrum of the region of image (a), which shows the complete decomposition of the carbon-containing organic part of the fibrous structure.

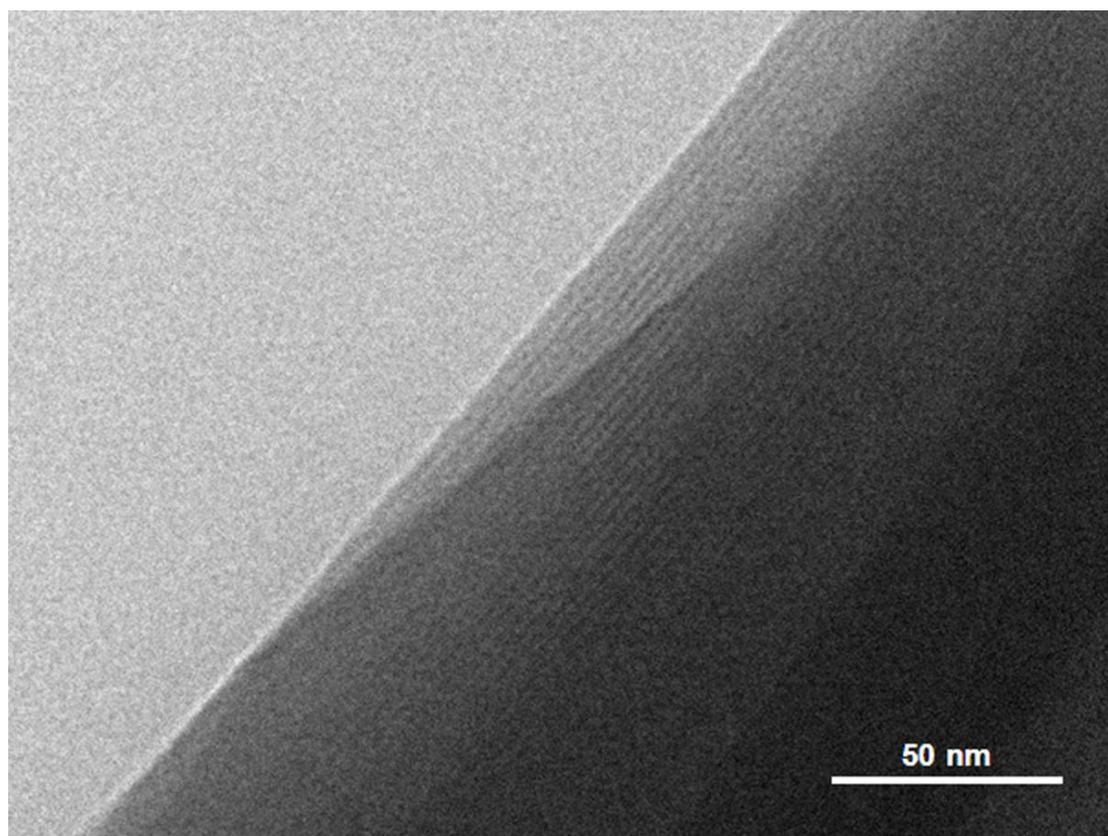


Fig. S10 A magnified TEM image of fibrous SEOP-2 assemblies formed at 25 °C.

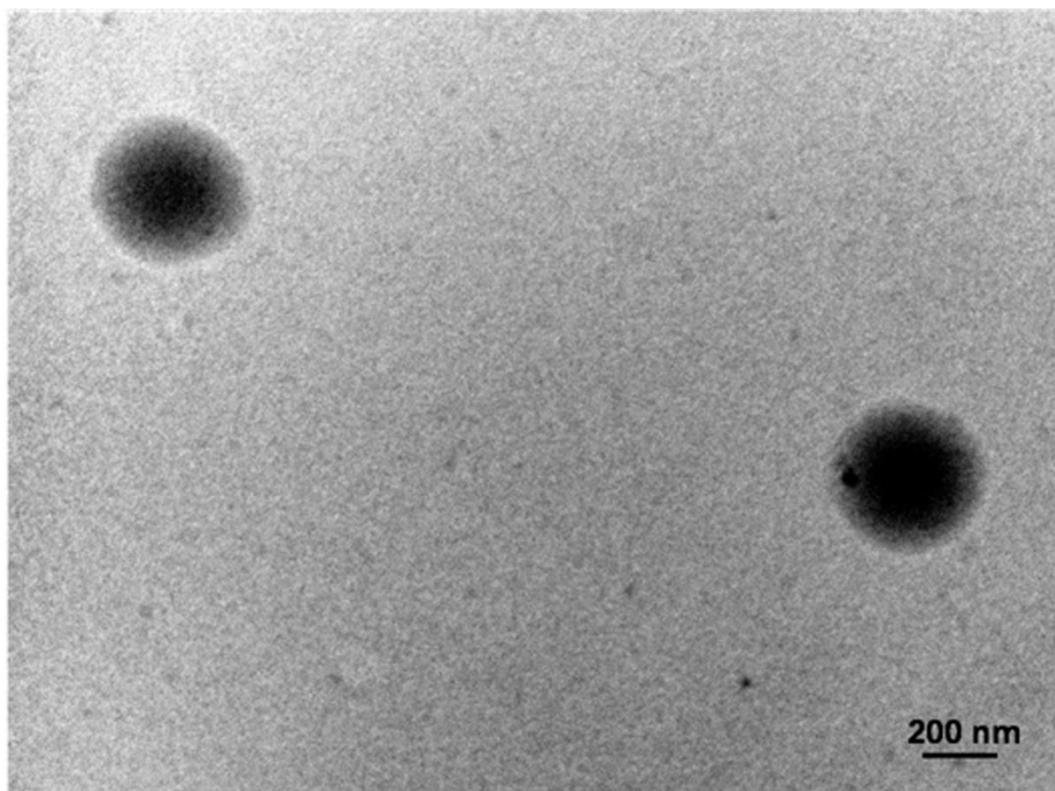


Fig. S11 TEM image of spherical SEOP-2 assemblies formed at 65 °C.

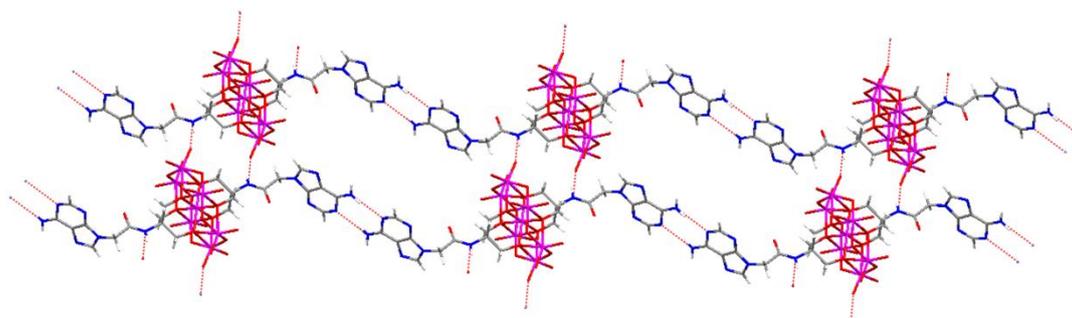


Fig. S12 Extended crystal structure of SEOP-1 connected by two types of hydrogen bonds: the axial hydrogen bonds between the terminal oxygen of MnMo₆ cluster and the hydrogen of amide group, and the lateral hydrogen bonds between the nitrogen of adenine cycle and the hydrogen of amino group, in which the TBA part is hidden.

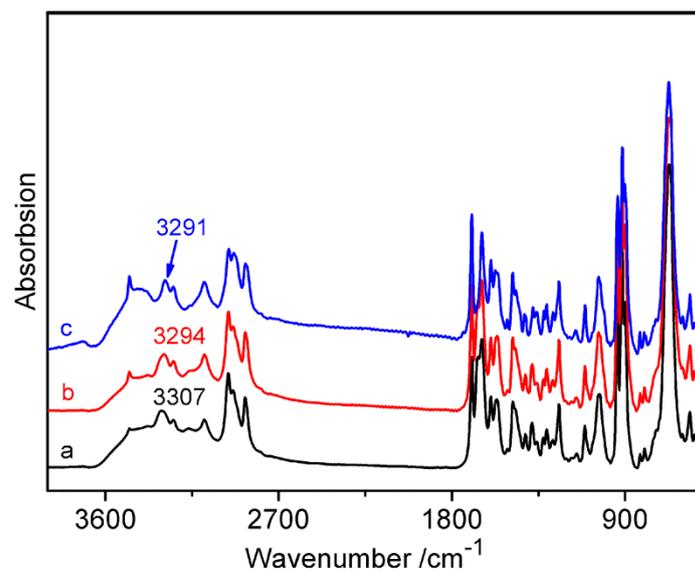


Fig. S13 IR spectra of the SEOP-1 assemblies with different morphologies: (a) fiber, (b) rod, and (c) tube.

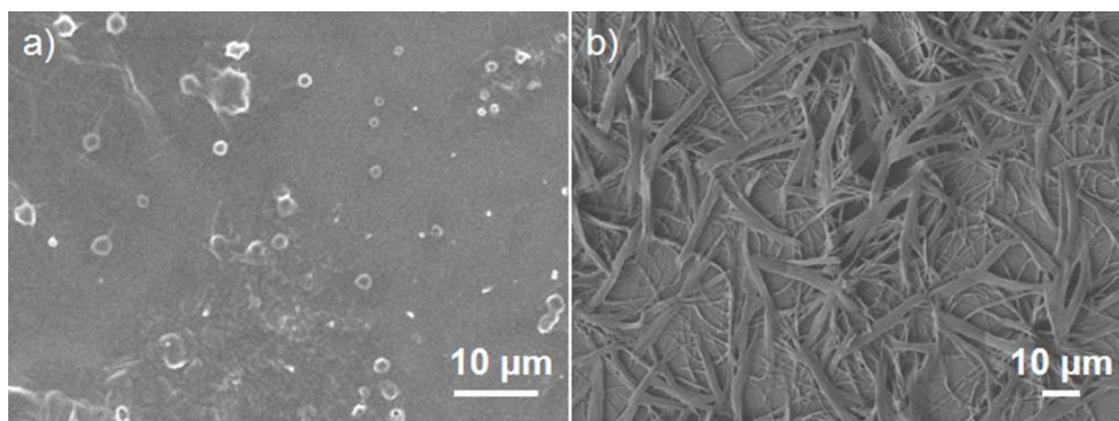


Fig. S14 SEM images of SEOP-2 assemblies formed in DMF solution upon cooling: a) 65, and b) 25 °C.

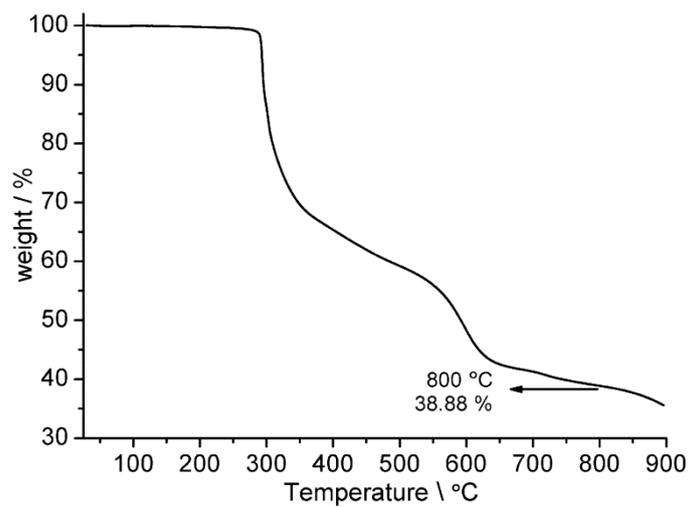


Fig. S15 TGA diagram of SEOP-1.

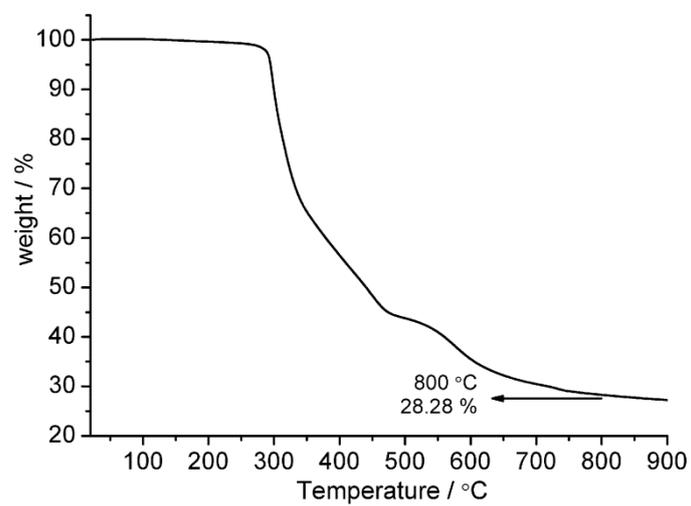


Fig. S16 TGA diagram of SEOP-2.