Supporting Information

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1. Materials

Fmoc-Rink Amide resin (MBHA, 0.64 mmol/g), Fmoc-*L*-Lys(Boc)-OH, Fmoc-*L*-Glu(tBu)-OH, Fmoc-*L*-Ser(tBu)-OH, Fmoc-*L*-Ala-OH, Fmoc-*L*-Leu-OH, Fmoc-*L*-Phe-OH, Fmoc-*L*-Trp(Me)-OH, and O-(6-Chloro-1-hydrocibenzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphat (HCTU, 99%) were purchased from GL Biochem (Shanghai) Ltd. N-Methylmorpholine (NMM, 98%), trifluoroacetic acid (TFA, 98%), acetic anhydride, nile red, anisole (98%) and triisopropylsilane (TIPS, 98%) were purchased from Tokyo Chemical Industry (TCI). Piperidine (99.9%) was purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai). Dimethyl formamide (DMF, 99.8%), sodium acetate and acetic anhydride were purchased from J&K Chemical Technology Company (Beijing), and acetonitrile (99.9%) was purchased from Spectrum Chemical Manufacturing Corp-China. Thioflavin T (ThT) was purchased from the Aladdin Industrial Corporation (Shanghai). The polyoxometalates (POMs) $K_6CoW_{12}O_{40}$ (CoW_{12}),[1] $K_6P_2W_{18}O_{62}$ (P_2W_{18}),[2] $K_9EuW_{10}O_{36}$ (EuW_{10}),[3] $K_{12.5}Na_{1.5}[NaP_5W_{30}O_{110}]$ (P_5W_{30}),[4] and $(NH_4)_{42}[Mo_{132}O_{372}(CH_3COO)_{30}\cdot(H_2O)_{72}]$ (Mo_{132})[5] were prepared according to the corresponding literatures. All the reagents and solvents used in the synthesis process of peptides and polyoxometalates in this article are commercially available and without further purification. Deionized water was obtained from a Reverse Osmosis Drinking water system at a resistivity of 18.25 MΩ·cm.

[1] a) L. W. Baker, T. P. Mccutcheon, *J. Am. Chem. Soc.* **1956**, *78*, 4503–4510; b) N. Casai-Pastor, P. Comez-Romero, G. B. Jameson, L. C. W. Baker, *J. Am. Chem. Soc*. **1991**, *113*, 5658–5663; c) C. C. Yuan, S. M. Wang, W. L. Chen, L. Liu, Z. M. Zhang, Y. Lu, Z. M. Su, S. W. Zhang, E. B. Wang, *Inorg. Chem. Commun.* **2014**, *46*, 89–93.

[2] R. Tayebee, M. M. Amini, H. Rostamiana, A. Aliakbarib, *Dalton Trans*. **2014**, *43*, 1550-1563.

[3] R. D. Peacock, T. J. R. Weakley, *J. Chem. Soc. A*. **1971**, 1836-1839.

[4] I. Creaser, M. C. Heckel, R. J. Neitz, M. T. Pope, *Inorg. Chem*. **1993**, *32*, 1573-1578.

[5] A. A. Ostroushko, M. O. Tonkushina, A. P. Safronov, S. Y. Menshikov, V. Y. Korotaev, *Russ. J. Inorg. Chem.* 2009, **54**, 172–179.

2. Synthesis of the peptides

All the peptides were prepared with a classical 9-fluorenylmethoxycarbonyl (Fmoc) solid-state synthesis method from C-terminal to N-terminal. The detailed synthetic procedure was as follows: the synthesis was initiated using 48 μmol of Fmoc-Rink Amide MBHA resin swelled fully by 3 mL of CH_2Cl_2, then 2 ml of dried piperidine/DMF solution (v/v = 20%) was added into it and stirred for 2 min to deprotect the resin twice for activating, and then DMF and CH_2Cl_2 were used to wash and filter successively at least three times. The chain extension was accomplished using an in situ neutralization/HCTU activation procedure, where 2-fold excess of Fmoc-amino acids (in relation to the resin) was pre-activated with 3 equivalents of HCTU (in relation to the resin) and 6 equivalents of NMM (in relation to the resin) in DMF (1 mL) for 2 min before it was added to the resin. After the coupling reaction, a dried piperidine/DMF solution (v/v = 20%, 2 mL) was added and stirred for 2 min to deprotect the resin twice. Then, the resin was rinsed using DMF and CH_2Cl_2 in turn. The cycle of Fmoc deprotection and coupling with N-terminal-protected amino acids was repeated until the designed peptide sequences were obtained. Each coupling step took 5 min, and each deprotection step took 2 min. After coupling all the amino acids, DMF solution containing acetic anhydride (30%) was added to protect the N-terminal of the peptide chain. The obtained peptide segments were cleaved from the resin manually by treatment with trifluoroacetic acid (TFA), anisole, water and triisopropyl silane ($V_{TFA}/V_{anisole}/V_{water}/V_{TIPS}$ = 88:5:5:2) for 5 h under constant agitation in a rotary shaker (25 ^{o}C, 480 rpm). The obtained mixing solution was dropped into ice diethyl ether (10 mL), then using a mixed solvent containing acetonitrile and water (v/v = 1:1) in the presence of 0.1% TFA to dissolve the obtained precipitate. The crude peptide solution was purified by reverse-phase High Performance Liquid Chromatography (HPLC) equipped with C18 reverse phase column (Vydac, USA) using the gradient agent with water and acetonitrile in the presence of 0.1% TFA and the column eluents were monitored by UV absorbance at 210 nm. The molecular weight of synthetic peptide is confirmed by **ESI-MS** (Agilent-6125B).

L1: (ESI -MS) m/z 1222.60 (1222.91 calcd for $[M+H]^+$), 612.00 (612.41 calcd for $[M+2H]^{2+}$).

L2: (ESI -MS) m/z 1140.45 (1140.75 calcd for $[M+H]^+$), 1162.45 (1163.04 calcd for $[M+Na]^+$).

L3: (ESI -MS) m/z 1222.70 (1222.50 calcd for $[M-H]^-$).

L4: (ESI -MS) m/z 949.40 (950.12 calcd for $[M+H]^+$), 475.40 (475.86 calcd for $[M+2H]^{2+}$).

L5: (ESI -MS) m/z 1105.55 (1105.18 calcd for $[M+H]^+$), 553.40 (553.91 calcd for $[M+2H]^{2+}$).

L6: (ESI -MS) m/z 1003.65 (1102.98 calcd for $[M+H^+]$), 1025.65 (1025.21 calcd for $[M+Na]^+$). 502.45 (502.76 calcd for $[M+2H]^{2+}$).

L7: (ESI -MS) m/z 877.45 (877.67 calcd for $[M+H]^+$), 439.30 (439.54 calcd for $[M+2H]^{2+}$).

3. Sample preparation (2D ordered nanosheets based on Peptides/POMs)

An aqueous solution of individual peptide (200 μM) or POM (200 μM) was firstly prepared, 200 μL of the POM aqueous solution was then added dropwise into the 200 μL of peptide solution with oscillation for 2 min, stable and uniformly dispersed assembly solution was finally obtained after standing for 3 h at room temperature. The final concentration of peptide in the assembly solution is kept at 100 μM and the molar ratio of peptide/POM was 2:1.

4. Measurements

ESI-MS. The ESI-MS data were obtained from HPLC system coupled to an Agilent (6125B) mass spectrometer with an Agilent ESI (electrospray ionization) source (N_2, 300 °C). The MS chamber parameters were set to a capillary voltage of 4.5 kV and a fragmentor voltage of 175 V. **MALDI-TOF-MS** was obtained from an Autoflex speed TOF/TOF (Brucker) operating in positive mode within a mass range from 700 to 2500 Da.

Transmission Electron Microscopy (TEM). The TEM images were performed on a JEOL-2010 electron microscope operating at 200 kV. The specimens were depositing onto a carbon coated copper grid and then dried completely in air. The individual peptide specimens were stained with fresh uranyl acetate aqueous solution (0.5 wt %, 3 μL) for 2-3 min, the excess amount of staining solution was removed by filter paper. However, the peptides/POMs specimens without staining agent were used directly for TEM measurements.

Cryogenic transmission electron microscopy (*Cryo*-TEM). *Cryo*-TEM was performed on a JEOL-JEM 2100 TEM instrument (about 90 K, 120 kV) equipped with a SC 1000 CCD camera (Gatan, Inc., USA). A liquid droplet of L1/P_2W_{18} (3 μL) was transferred to an ultrathin copper grid after hydrophilic treatment under the conditions of controlled temperature and humidity (97-99 %) to prevent sample solution from evaporating. Then, the superfluous liquid droplets were removed

using filter paper and the thin aqueous films were rapidly vitrified by plunging them into liquid ethane and cooled to approximately 90 K by liquid nitrogen. The excess amount of ethane was removed using blotting paper after the sample solution was frozen. Finally, the grid was inserted into a Gatan 626 cryo holder using a cryotransfer device for *cryo*-TEM measurements.

Atomic force microscopy (AFM). AFM measurements were performed on a Bruker Dimension 3100 instrument (Germany) via the tapping mode in air (25 ^{o}C). The AFM samples were prepared by casting the L1/P_2W_{18} solution on the surface of a mica wafer, and staying for 3 min. Subsequently, the unattached sample was taken away using filter paper, then the air-dried samples were used for AFM tests.

Laser scanning confocal microscopy (LSCM). LSCM measurements were recorded on a FV1000 confocal microscopy. Nile Red was used as an environment-sensitive hydrophobic probe, which exhibits an increase of emission when inserting into a hydrophobic domain. The Pep1/P_2W_{18} solution was incubated with Nile Red solution for at least 5 h, the resultant solution was casted on glass for LSCM measurements with an excitation wavelength of 488 nm.

Circular Dichroism (CD). Individual L1 and the L1/P_2W_{18} solutions were measured on a JASCO model J-810 spectropolarimeter (25 ^{o}C, Xe lamp) under a constant flow of nitrogen gas during operation to characterize the second structure. The samples were loaded into a rectangular quartz cell with a 0.1 cm path length, the wavelength range of CD spectra was captured from 260 to 190 nm with a step of 0.5 nm, a response time of 0.5 s, and a scan speed of 1 nm s^{-1}. The data were repeated three times and averaged. The JASCO software was used for background subtraction.

Fourier Transform Infrared (FT-IR). FT-IR spectra of all the lyophilized powder samples (L1, P_2W_{18}, and L1/P_2W_{18}) were analyzed by a Bruker Optics Vertex 80 V FT-IR spectrometer equipped with a DTGS detector (32 scans) with a resolution of 4 cm^{-1} using KBr pellets. The FT-IR spectra of solid samples were performed to confirm the structural stability of P_2W_{18} and investigate the secondary structure of Pep1, Pep1/P_2W_{18}.

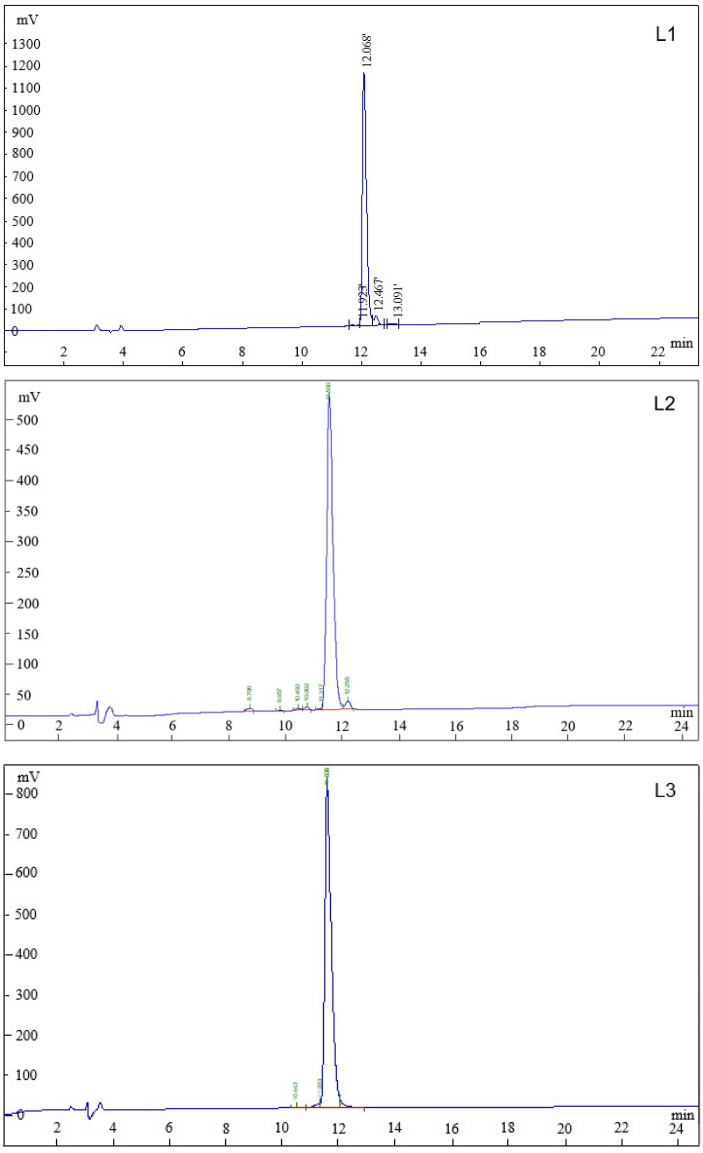
Thioflavin T (ThT) Binding Study. The binding study was carried out according to the following procedure. A ThT solution was added into the aqueous solution of L1/P_2W_{18}, and the final concentration of ThT was controlled at 5 μM. The resultant L1/P_2W_{18}/ThT solution (pH ~ 6.5) was incubated at room temperature for 5 h. The fluorescence spectra of individual ThT solution (5 μM) and the L1/P_2W_{18}/ThT sample were performed on a 5301PC spectrophotometer (Shimadzu, Toko,

Japan) with an excitation wavelength of 420 nm.

Dynamic Light Scattering (DLS). DLS experiments were performed at 25 °C on a Malvern Zetasizer Nano ZS (Malvern Instruments; UK) using a detection angle of 173° and a 3 mW He-Ne laser operating at λ = 633 nm. The temperature equilibration time was set to 120 s in all cases, and the measurements were repeated at least 3 times.

X-ray diffraction (XRD). XRD patterns of the powdered sample prepared by the lyophilization of the L1/P_2W_{18} assembly solution of 300 ml were taken over a range of 1.5 to 15º using a Rigaku SmartLab X-ray diffractometer with Cu $K\alpha_1$ radiation at wavelength of 1.542 Å.

5. Characterization



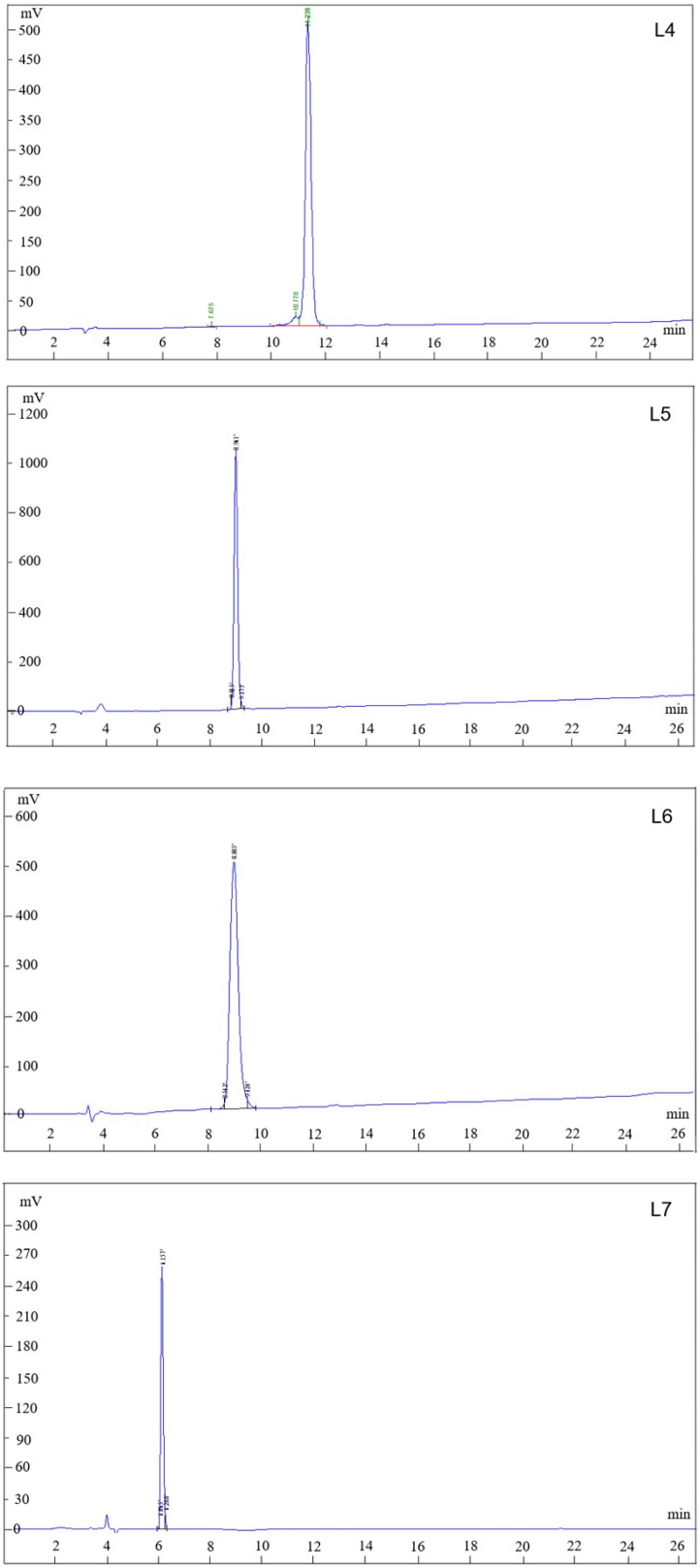
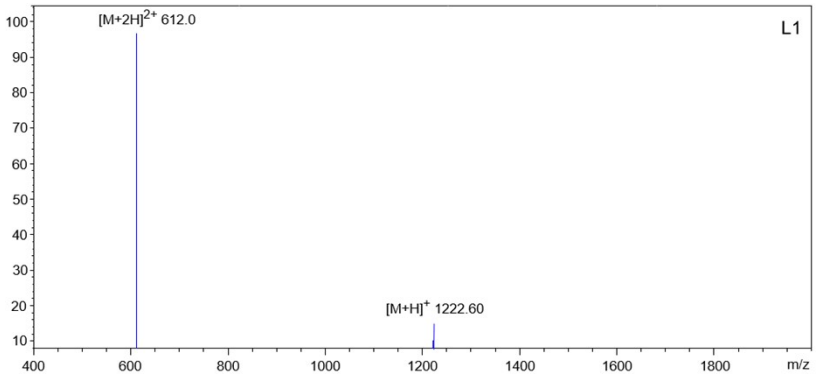
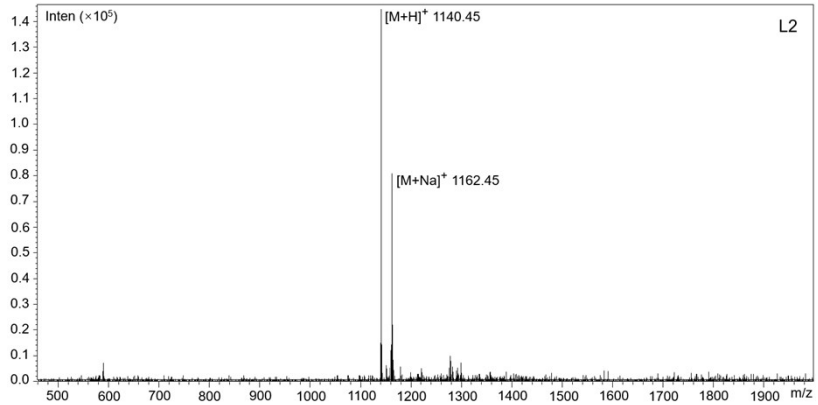
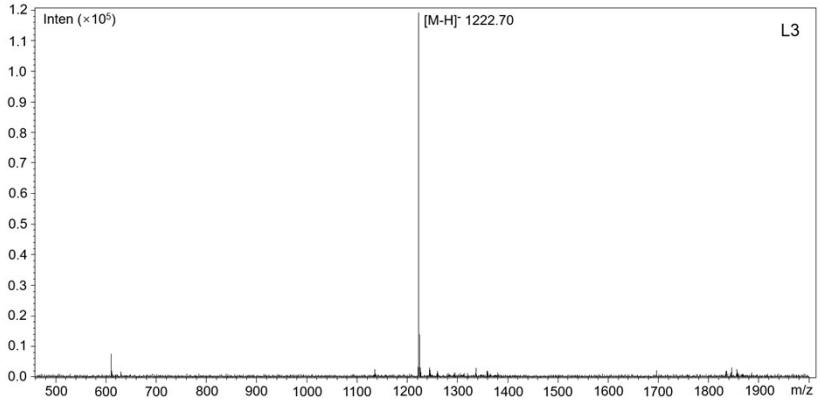
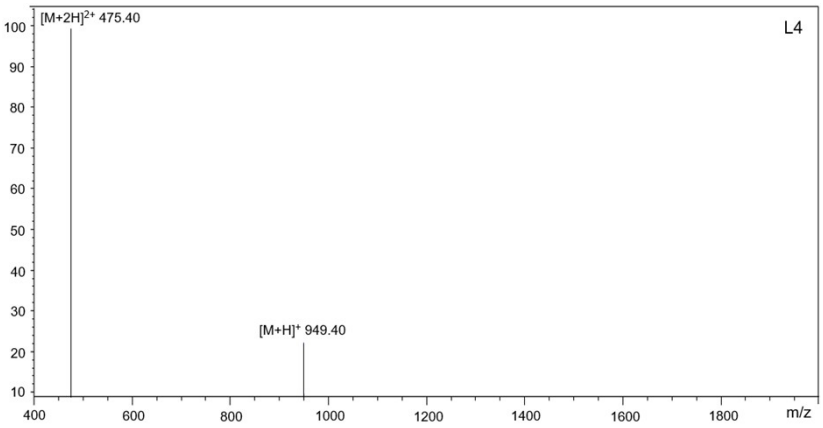


Fig. S1 HPLC profiles of the short peptides from L1 to L7.


L1
[M+2H]2+ 612.0
[M+H]+ 1222.60
m/z


L2
Inten (×10^5)
[M+H]+ 1140.45
[M+Na]+ 1162.45
m/z


L3
Inten (×10^5)
[M-H]- 1222.70
m/z


L4
[M+2H]2+ 475.40
[M+H]+ 949.40
m/z

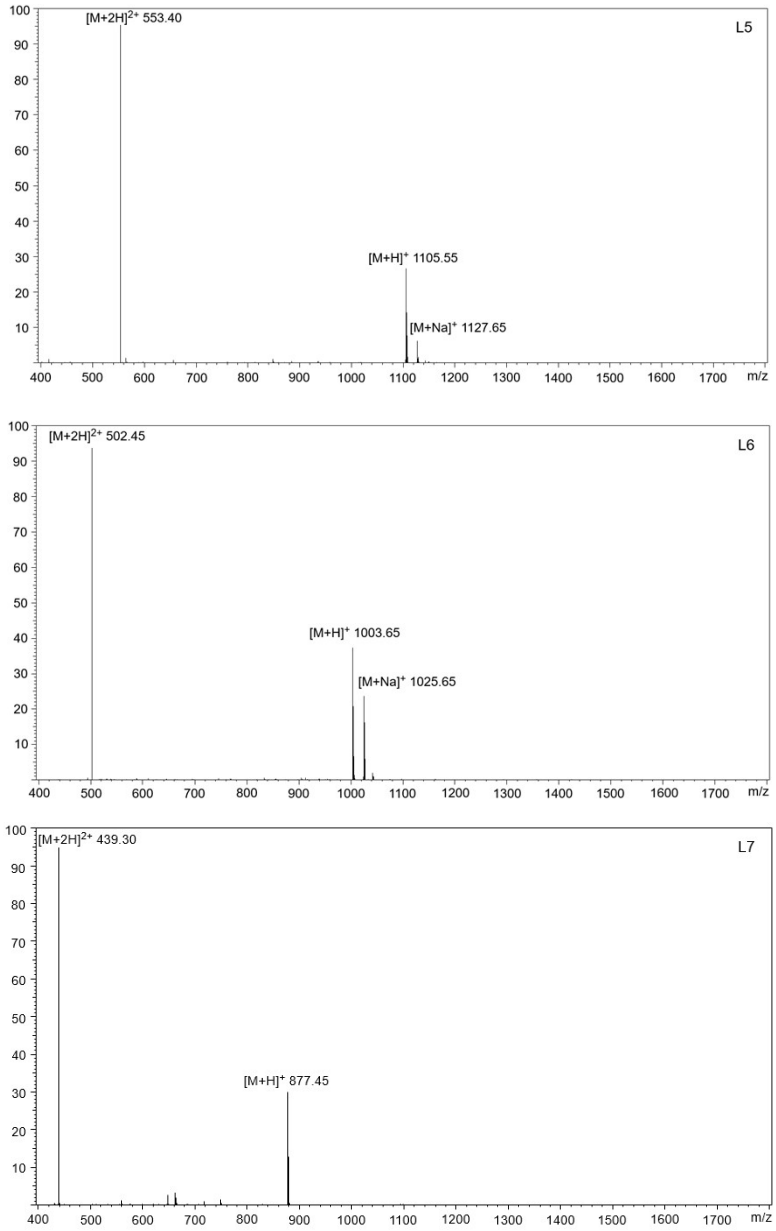


Fig. S2 ESI-MS data of the short peptides from L1 to L7.

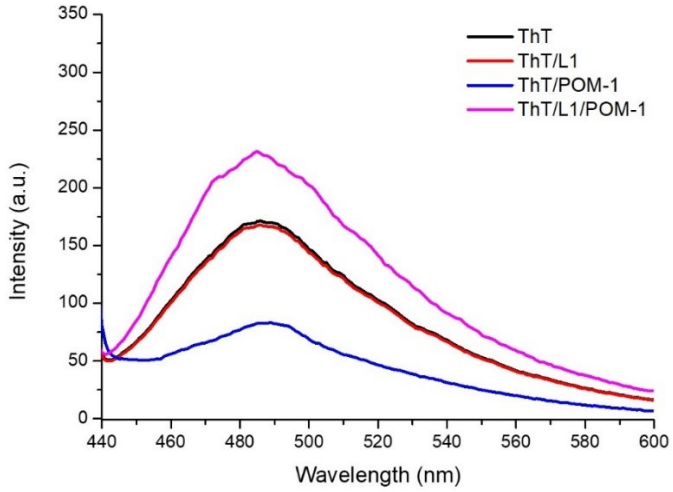


Fig. S3 Fluorescence spectra of thioflavin T (ThT) dissolved in water (blank), L1, POM-1 and L1/POM-1 aqueous solution (pH ~ 6.5). The final concentration of ThT in all samples was kept at 5 μM. (The enhancement of fluorescence intensity confirms the formation of β-sheet peptide in the L1/POM-1 aqueous solution).[6,7]

[6] P. Jana, M. Ehlers, E. Zellermann, K. Samanta, C. Schmuck, *Angew. Chem. Int. Ed*. 2016, **55**, 15287-15291.

[7] S. Samui, S. Biswas, K. Roy, I. Deb, J. Naskar, *ACS Chem. Neurosci.* 2019, **10**, 2915-2918.

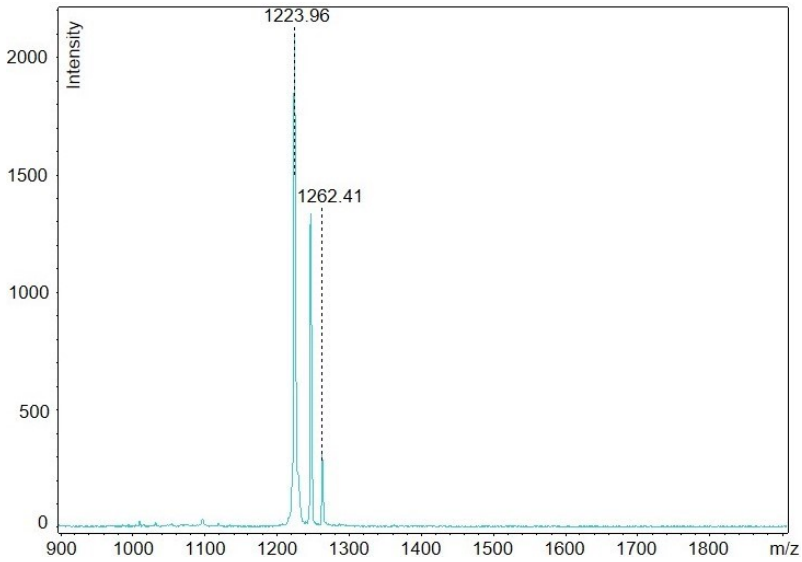


Fig. S4 MALDI-TOF-MS data of the L1 obtained from the aqueous solution of L1/POM-1.

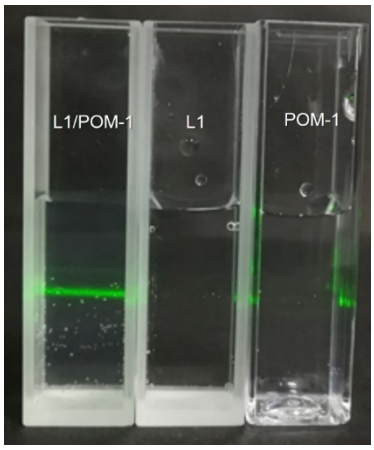


Fig. S5 Digital photographs of POM-1, L1 and L1/POM-1 aqueous solution.

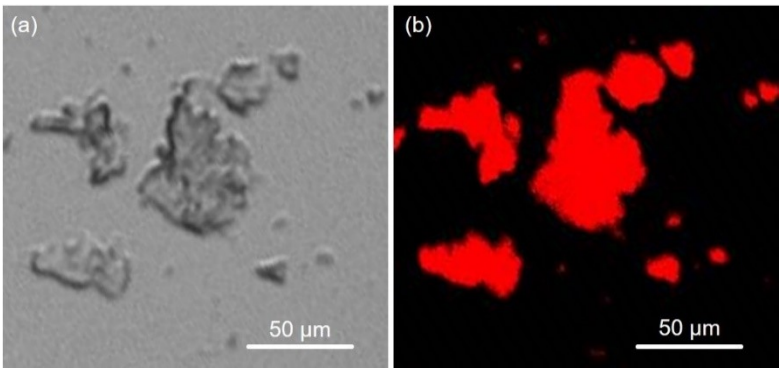


Fig. S6 LSCM images of L1/POM-1 solution sample (pH ~ 6.5) stained with Nile Red (5.0 μM): (a) bright field, and (b) dark field. (the concentration of L1 is 100 μM).

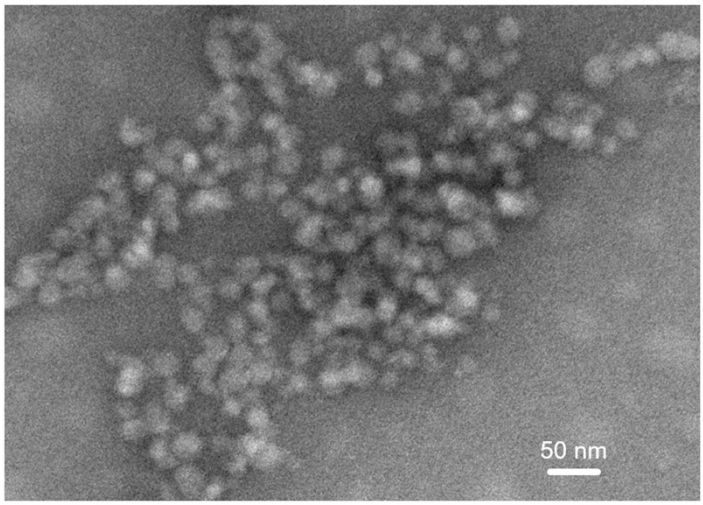


Fig. S7 TEM image of L1 alone.

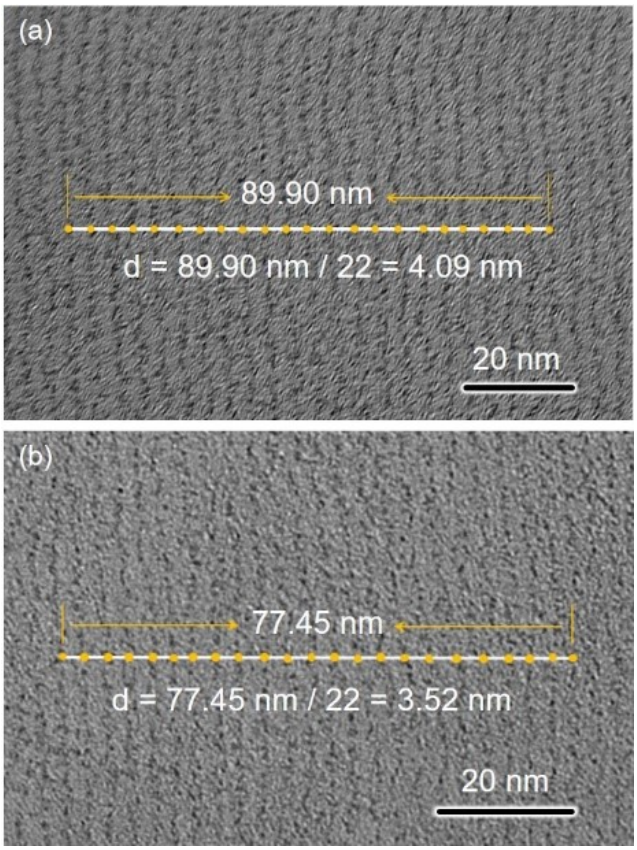


Fig. S8 HR-TEM images of (a) L1/POM-1 and (b) L4/POM-1. (the distance of the parallel srip was obtained by calculating 22 repeated strips and averaged).

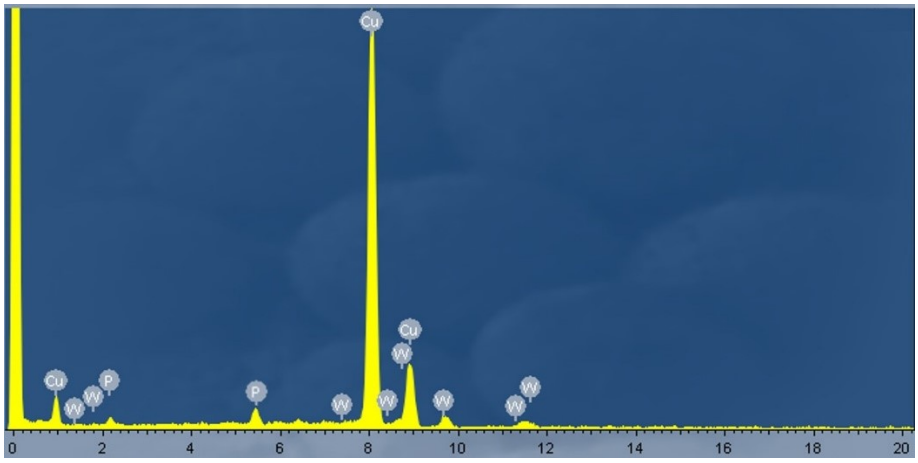


Fig. S9 Energy Dispersive X-ray **(**EDX**)** spectra of L1/POM-1 nanosheets. (The presence of W and P elements provides strong evidence that P_2W_{18} clusters are loaded in the nanosheets).

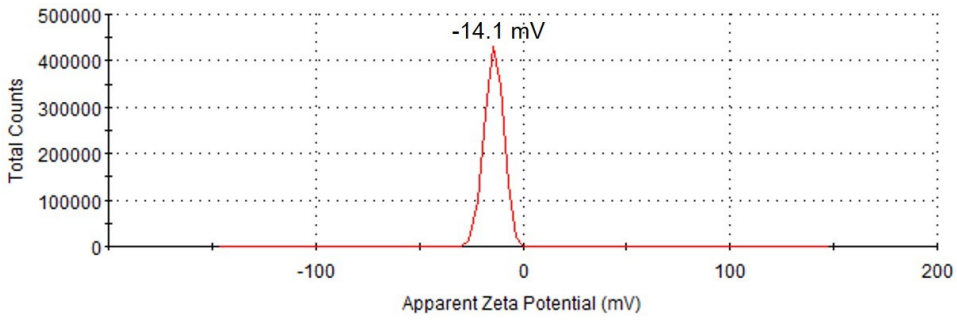


Fig. S10 Zeta potential of L1/POM-1 assembly. (the molar ratio of L1 to POM-1 is 2:1, and the concentration of L1 was kept at 100 μM).

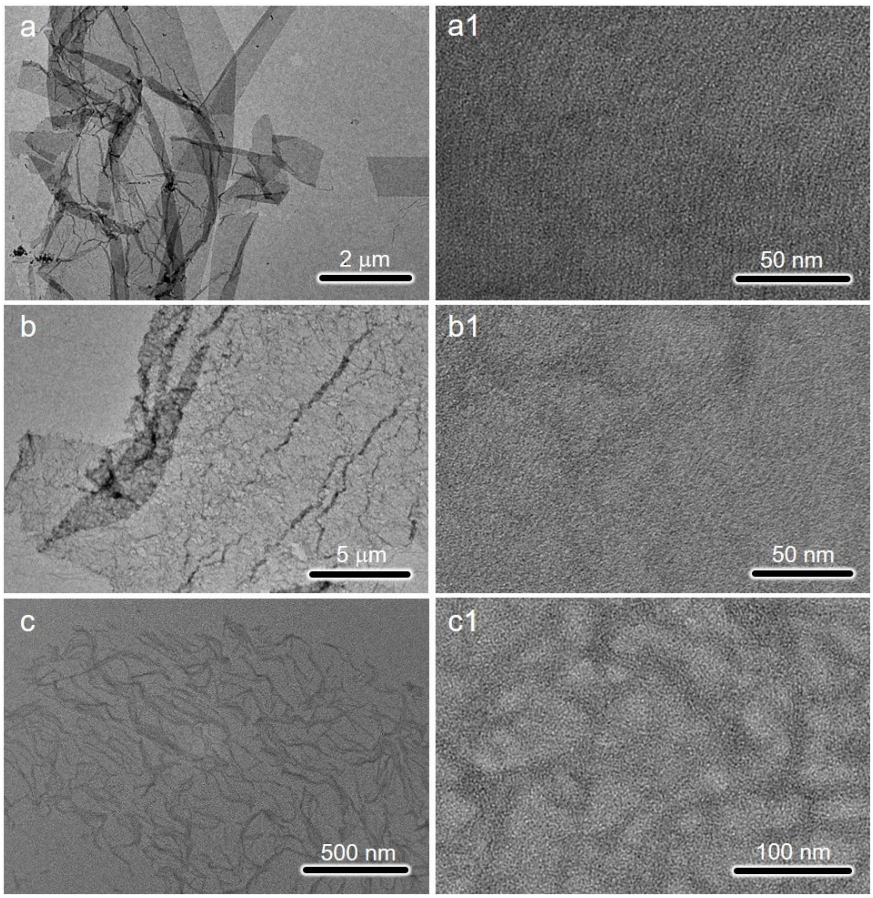


Fig. S11 TEM and the corresponding HR-TEM images of L5/POM-1 (a, a1), L6/POM-1 (b, b1) and L7/POM-1 (c, c1).

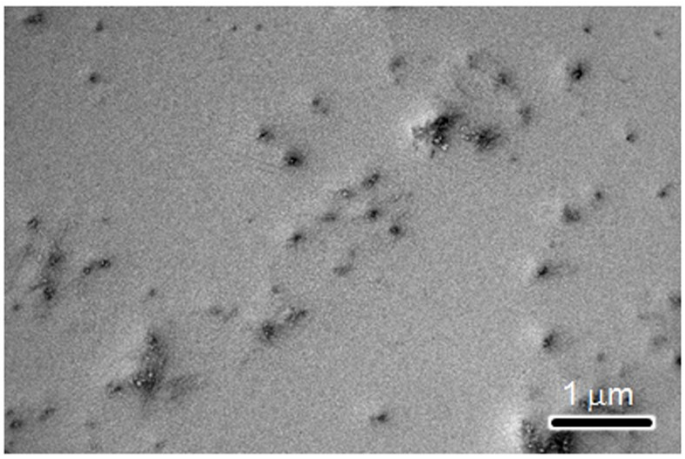


Fig. S12 TEM image prepared from the aqueous samples of L1/POM-5 complexes.

Table S1. The bulky volume of POMs from their CIF data

POMs	Size (a×b×c nm^3)	POMs	Size (a×b×c nm^3)
CoW_{12}	1.00×1.00×1.00	P_5W_{30}	1.49×1.49×1.00
EuW_{10}	1.43×0.80×0.80	Mo_{132}	2.90×2.90×2.90
P_2W_{18}	1.20×1.00×1.00		