Electronic Supporting Information

Metal(II)-directed self-assembly of amino acid functionalized polyoxometalates

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Fig. S1 Schematic representation of the $4^4$ topology of 1.
Fig. S2 View of the 3D superamolecular framework in 1, showing the hydrogen bonds between the neighboring layers.

Fig. S3 Schematic representation of (3,6)-connected net with Schlāfli symbol $(3\cdot6^2)_2(3^4\cdot4^2\cdot6^2\cdot7^4\cdot8^3)$ in 4.
Fig. S4 IR spectra for 1–6.
**Analysis:** The UV-vis spectra of compounds 1–6 are shown in Figure S5, ranging from 190 to 500 nm. The plots display two intense absorption bands for O→Mo charge transfer, which is characteristic of polyoxomolybdates. The strong bands at 209 nm for 1, 210 nm for 2, 210 nm for 3, 209 nm for 4, 210 nm for 5, and 211 nm for 6 are attributed to Ot→Mo charge transfer transition; the weak bands at 231 nm for 1, 232 nm for 2, 232 nm for 3, 232 nm for 4, 233 nm for 5, and 233 nm for 6 are assigned to the Ob,c→Mo charge transfer.
Fig. S6 TG curves for 1–6.
(c) Compound 3

Calculated pattern

Experimental pattern

2 Theta/degree

(d) Compound 4

Calculated pattern

Experimental pattern

2 Theta/degree
Fig. S7 The calculated and experimental PXRD patterns for 1–6.
**Fig. S8** The CVs of 1, 4 and 5 (0.5 mM) in a pH = 4 buffer solution (0.4M CH₃COONa + CH₃COOH), 200 mVs⁻¹ scan rate. The CV curves were detected every 24 hours, and totally detected five times. These CV curves remain almost unchanged.

**Fig. S9** CV of 0.5 mM 5 in the potential range +0.600 to -0.700 V, pH 4.0 sodium acetate buffer, scan rate 200 mV s⁻¹, at ambient temperature.