Supporting Information For:

A novel poly(polyoxometalate) built by \{Cu_9\}/\{Cu_5\} clusters and
\{PW_9\}/\{PW_{10}\}/\{PW_{11}\} lacunary fragments

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Experimental Section:

**Materials and physical measurements**: Na$_9$[$A$-$\alpha$-PW$_9$O$_{34}$]$\cdot$7H$_2$O is synthesized according to the literature. The other chemicals were commercially purchased and used without further purification. The elemental analyses for C, H, N were performed on a Vario EL III elemental analyzer. The FT-IR spectra (KBr pellets) were recorded by using an ABB Bomen MB 102 spectrometer over a range 400-4000 cm$^{-1}$. Thermogravimetric analyses were performed on a Mettler TGA/SDTA 851$^e$ analyzer with a heating rate of 10 °C/min from 30 to 1000 °C under air atmosphere. Powder X-ray diffraction (PXRD) data were collected on a Rigaku Mini Flex II diffractometer using Cu K$_\alpha$ radiation (\(\lambda = 1.54056\) Å) under ambient conditions. ICP analyses of P, Cu and W were conducted on an Ultima2 spectrometer. The UV diffuse reflection data were recorded at room temperature using a powder sample with BaSO$_4$ as a standard (100% reflectance) on a PerkinElmer Lamda-950 UV spectrophotometer and scanned at 200-800 nm. The band gap (E$_g$) was determined as the intersection point between the energy axis and the line extrapolated from the linear portion of the absorption edge in a plot of Kubelka-Munk function against energy E. Kubelka-Munk function,$^2$ $\alpha/S = (1–R)^2/2R$, was converted from the recorded diffuse reflectance data, where $\alpha$ is the absorption coefficient, S is the scattering coefficient, R is the reflectance of an infinitely thick layer at a given wavelength. Magnetic measurements were performed on a MPMS XL magnetometer in the temperature range from 2 to 300 K at an applied magnetic field of 2 kOe.

**Synthesis of [{Cu$_6$(μ$_3$-OH)$_3$(en)$_3$(H$_2$O)$_3$}(B-$\alpha$-PW$_9$O$_{34}$)]$\cdot$7H$_2$O**

Na$_9$[$A$-$\alpha$-PW$_9$O$_{34}$]$\cdot$7H$_2$O (PW$_9$)$_1$ (0.256 g, 0.1 mmol), CuCl$_2$·2 H$_2$O (0.170 g, 1.0 mmol), en (0.05 mL, 0.75 mmol), and acetate (0.10 mL, 1.75 mmol) were successively added into distilled water (5 mL, 278 mmol). Being stirred at room temperature for 30 min (pH 3.9), the mixture was sealed in a 30 mL Teflon-lined stainless steel autoclave, heated under autogeneous pressure at 80 °C for 5 days, and then cooled to room temperature naturally in air (pH 3.8). Green strips of crystals were collected by filtration, washed with distilled water, and dried in air. Yield: 13% (based on PW$_9$).

**X-ray crystallography**: A suitable single crystal of compound I was mounted on a glass fiber for indexing and intensity data were collected at 293 K on Rigaku SATURN70 CCD diffractometer with a graphite-monochromatized Mo K$_\alpha$ (\(\lambda = 0.71073\) Å). All absorption corrections were performed by using the SADABS program. Direct methods were used to solve the structures and to locate the heavy atoms using the SHELXTL-97 program package.$^3$ The remaining atoms were found from successive full-matrix least-squares refinements on $F^2$. All non-H atoms were refined anisotropically except for free water molecules and some carbon atoms. The Cu9 and W31 atoms were disordered with the occupation factors of 0.75 and 0.25, respectively. Residual electron density located in these voids was unable to be assigned unambiguously and so was treated with SQUEEZE. CCDC-807965 contain the supplementary crystallographic data for this paper for compound I. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Supporting Figures and Table:

**Fig. S1.** The photographs of the crystalline sample in 2009 and at present.

**Table S1** The comparison of cell parameters of the crystalline sample in 2009 and at present

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<tr>
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<th>2009</th>
<th>at present</th>
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<td>Crystal system</td>
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<td>Triclinic</td>
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<td>( P\bar{T} )</td>
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<tr>
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<td>( c/A )</td>
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<td>Temperature/K</td>
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</table>

**Fig. S2.** IR spectrum of compound 1.

As shown in Fig. S2, the big absorb band from 4000-1500 cm\(^{-1}\) generally attribute to the organic functional groups, and the characteristic vibrations in the region 1100-700 cm\(^{-1}\) are derived from the inorganic Keggin POTs. The stretching bands of the -OH, –NH\(_2\), and –CH\(_3\) groups are observed at 3550-3400, 3350-3150, and 2980-2930 cm\(^{-1}\), respectively. The vibrations at about 1600 to 1400 cm\(^{-1}\) are corresponding to the asymmetric and stretching vibrations of the carboxyl group, respectively. In addition, the bands at around 1110 and 1050 cm\(^{-1}\) can be assigned to the \( \nu(P-O) \) stretching vibration. The \( \nu(W-O) \) stretching vibration bands resulting from the Keggin-type POT framework, namely, \( \nu(W-O_a) \), \( \nu(W-O_b) \) and \( \nu(W-O_c) \) appear at 954, 880, 800-695 cm\(^{-1}\), respectively.
**Fig. S3.** The experimental PXRD pattern of compound 1 and the simulated PXRD pattern derived from the single crystal X-ray diffraction data.

**Fig. S4.** The molecular structure of compound 1 and the zoom view of the doubly protonated en. Color code: WO$_6$ red, PO$_4$ yellow, CuO$_x$N$_y$ green, Cu green, C black, N blue, O red, H yellow.

**Fig. S5.** The scheme representation of the assembly of the \{Cu\}_6 cluster. The $\mu_3$-OH bridges are emphasised in ball view.
**Fig. S6.** Polyhedral view of \( \{ \text{Cu}_3\text{PW}_{10} \} \) and coordination environment of Cu8.

**Fig. S7.** Schematic illustration of the assembly of the sandwich Cu-substituted dimer. Red polyhedra WO\(_6\), yellow polyhedra PO\(_4\), green polyhedra CuO\(_x\)N\(_y\).

**Fig. S8.** View of the hexamers on bc plan (left) and stacking mode along the c-axis (right). Red polyhedra WO\(_6\), yellow polyhedra PO\(_4\), green polyhedra CuO\(_x\)N\(_y\).
As shown Fig. S9, the TG thermal behaviour of compound 1 was investigated on crystalline samples under an air atmosphere from 30 to 1000 °C. The TG curve indicates compound 1 undergo three steps of weight loss. The first step weight loss from 30-135°C (3.88%) corresponds to the release of water molecules and acetate (calcd. 3.78%). The following weight loss from 135-325°C is 2.36% (calcd. 2.31%), involving the removal of hydroxyl groups and seven 

en ligands. The third weight loss of 4.07% from 325-500°C approximately assigned to the decomposition of the left twelve en ligands (calcd. 3.85%). Assuming that the residue corresponds to CuO, P$_2$O$_5$ and WO$_3$, the observed weight (89.69%) is in good agreement with the calculated value (90.06%).

Fig. S10. Plots of Kunelka-Munk function versus energy $E_g$ (eV) for compound 1.

Fig. S11. Temperature dependence of $\chi_M^{-1}$ for 1. The solid line is the best-fit according to the Curie-Weiss law.