

Supporting Information

An ultrastable, flexible POM-based coordination polymer with redox properties

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Experimental section

General information. All reagents and solvents were purchased from commercial sources and used without further purification. Powder X-ray diffraction (PXRD) patterns were collected on a Rigaku D_{\max} 2000 X-ray diffractometer with graphite monochromatized Cu $K\alpha$ radiation ($\lambda = 0.154$ nm). The FT-IR spectrum was measured in KBr pellets in the range 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. Elemental analysis (EA) for C, H and N was performed on a Perkin-Elmer 2400 Elemental Analyzer. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer Thermal Analyzer under nitrogen atmosphere at a heating rate of 10 $^{\circ}\text{C min}^{-1}$. Cyclic voltammograms were obtained by a CHI 660 electrochemical workstation at room temperature. Platinum gauze was used as counter electrode, and an Ag/AgCl electrode as the reference electrode.

X-Ray crystallography. Crystallographic diffraction data for **1** was recorded on a Bruker Apex CCD diffractometer with graphite monochromatized Mo- $K\alpha$ radiation ($\lambda = 0.71073$ Å) at 293k. The structure was solved by Direct Method of SHELXS-97 and refined by full-matrix least-squares techniques using the SHELXL-97 program.¹ All non-hydrogen atoms were refined with anisotropic temperature parameters. All hydrogen atoms on organic ligands were placed in geometrically idealized position as a riding mode. The water hydrogen atoms were located from difference Fourier maps. The solvent water molecules in the crystal are highly disordered and are removed by using the SQUEEZE routine of PLATON.² The crystallographic data for **1** is summarized in Table 1, and the selected bond lengths and angles are listed in Table S3.

Table S1. Crystal data and structure refinements for **1**.

Compounds	1
Formula	$\text{C}_{36}\text{H}_{49}\text{CuN}_{12}\text{O}_{48}\text{PW}_{12}$
Fw	3718.42
Temp (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$C2/c$
a (Å)	37.962(9)
b (Å)	21.391(4)
c (Å)	24.996(4)
α (deg)	90
β (deg)	119.840(4)
γ (deg)	90

V (Å ³)	17607(6)
Z	8
Reflns coll./unique	44611/15510
R_{int}	0.0772
GOF	1.028
$R1, wR2$ [$I > 2\sigma(I)$] ^a	0.0763, 0.2168
$R1, wR2$ (all data) ^a	0.1202, 0.2394

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}; wR_2 = \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]}^{1/2}.$$

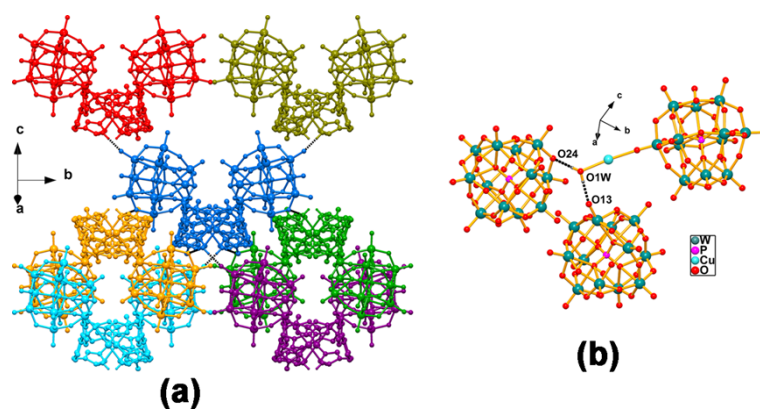


Fig. S1 (a) The chains are connected by hydrogen-bonds to generate a 3D supramolecular architecture. (b) Representation of O1W \cdots O24 and O1W \cdots O13 hydrogen-bonding interactions.

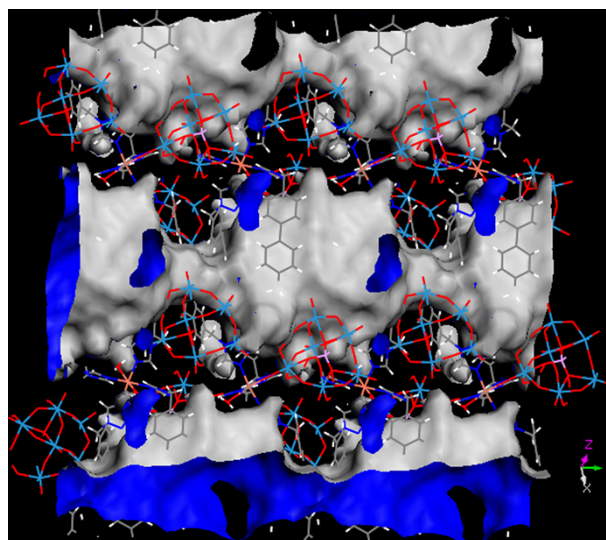


Fig. S2 View of the 1D channels. Connolly surface (blue internal and gray external) is created with a spherical probe with 1.6 Å radius. The PCP framework is represented as wires and sticks.

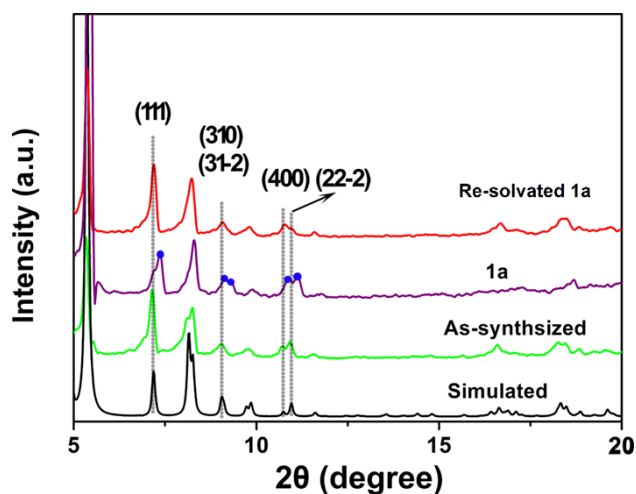


Fig. S3 PXR D experiments show that part of diffraction peaks of **1a** shift to the higher angle and these peaks of re-solvated **1a** can turn back after immersed in water for 10 hours.

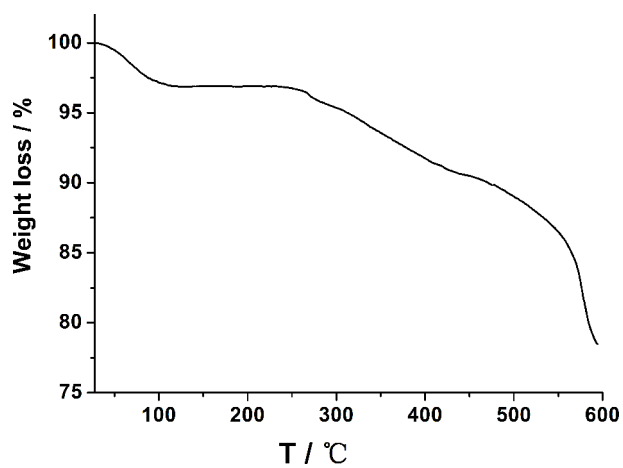


Fig. S4 The TGA curve of **1**.

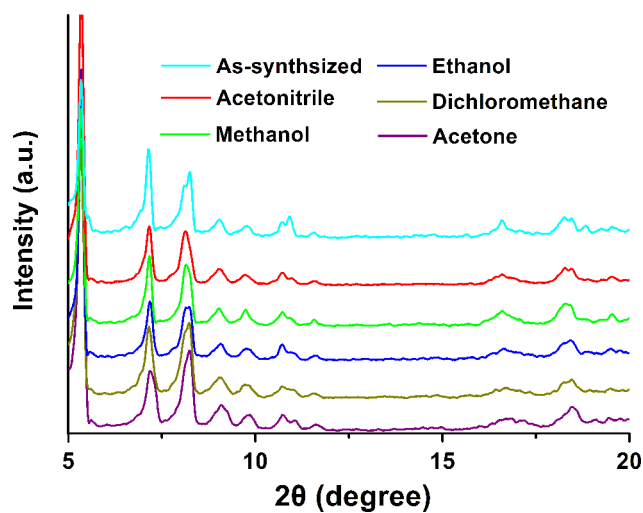


Fig. S5 PXR D patterns for as-synthesized **1** and crystals of **1** after soaking in different organic solvents for 24 hours.

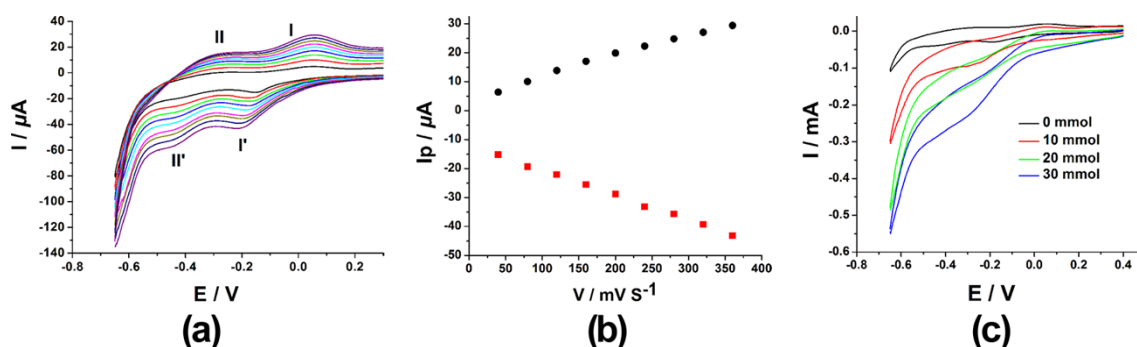


Fig. S6 (a) Cyclic voltammograms of **1**-CPE in 1 mol L⁻¹ H₂SO₄ solution at different scan rates (from inner to outer: 40, 80, 120, 160, 200, 240, 280, 320 and 360 mV s⁻¹). (b) The cathodic peak (I) and anodic peak (I') currents of **1**-CPE were proportional to the scan rate. (c) Cyclic voltammograms of **1**-CPE in 1 mol L⁻¹ H₂SO₄ solution containing 0.0-30.0 mmol L⁻¹ NaNO₂. Scan rate: 200 mV s⁻¹.

Table S2. Hydrogen-bonding geometry parameters for compound **1**.

D-H...A	Symmetry code	d(D-H) (Å)	d(H...A) (Å)	d(D...A) (Å)	<(DHA) (°)
O1W-H1WA...O24	0.5-x, 0.5+y, 0.5-z	0.85	2.10	2.95(2)	179
O1W-H1WB...O13	x, -y, 0.5+z	0.85	1.96	2.81(3)	179
C3-H3A...O6	0.5-x, 0.5-y, -z	0.97	2.39	3.24(4)	146
C15-H15...O29	0.5-x, 0.5+y, 0.5-z	0.93	2.42	3.33(5)	164
C16-H16B...O16	0.5+x, 0.5+y, 1+z	0.97	2.32	3.27(4)	168

Table S3. Selected bond lengths (Å) and angles (°) of **1**.^a

Cu(1)-N(10)#1	2.05(3)	Cu(1)-N(4)	2.08(3)
Cu(1)-N(7) #1	2.06(2)	Cu(1)-O(40)	2.410(15)
Cu(1)-N(1)	2.07(3)	Cu(1)-O(1W)	2.416(18)
N(10) #1-Cu(1)-N(7) #1	88.0(10)	N(4)-Cu(1)-O(1W)	96.6(10)
N(10) #1-Cu(1)-N(1)	93.0(10)	O(40)-Cu(1)-O(1W)	172.0(6)
N(7) #1-Cu(1)-N(1)	171.9(11)	N(7) #1-Cu(1)-O(40)	85.4(8)
N(10) #1-Cu(1)-N(4)	176.0(12)	N(1)-Cu(1)-O(40)	86.6(9)
N(7) #1-Cu(1)-N(4)	91.3(10)	N(4)-Cu(1)-O(40)	87.5(10)
N(1)-Cu(1)-N(4)	87.1(11)	N(10) #1-Cu(1)-O(1W)	87.3(9)
N(10) #1-Cu(1)-O(40)	88.4(10)	N(7) #1-Cu(1)-O(1W)	87.7(8)
N(1)-Cu(1)-O(1W)	100.3(9)		

^a Symmetry codes: #1, -0.5+x, 0.5-y, -0.5+z.

References:

- 1 (a) G. M. Sheldrick, *SHELXS-97: Programs for X-ray Crystal Structure Solution*, University of Göttingen: Göttingen, Germany, 1997; (b) G. M. Sheldrick, *SHELXL-97: Programs for X-ray Crystal Structure Refinement*, University of Göttingen: Göttingen, Germany, 1997.

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