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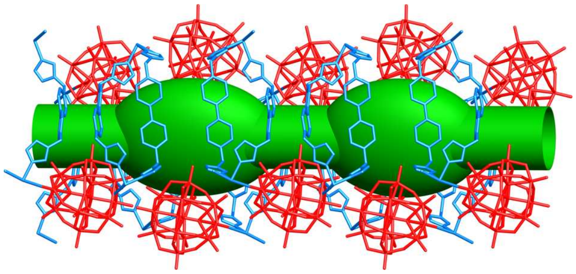
Graphical abstract

A new porous coordination polymer (**1**) has been prepared under hydrothermally condition. The flexible framework of **1** shows dynamic behavior accompanied with removal/adsorption of guest water molecules. Remarkably, crystals of **1** can remain intact even in 8 mol L^{-1} hydrochloric acid, dilute NaOH solution (pH = 12) and boiling water.



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ARTICLE TYPE

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

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A new flexible coordination polymer based on Keggin-type $H_3PW_{12}O_{40}{\cdot}xH_2O$, $[Cu(L)_2(H_2O)H(PW_{12}O_{40})]{\cdot}7H_2O$ (1), has been prepared. The framework of 1 shows dynamic behavior accompanied with removal/adsorption of guest water molecules. Compound 1 can remain intact even in 8 mol L^{-1} hydrochloric acid, dilute NaOH solution (pH = 12) and boiling water.

Porous coordination polymers (PCPs), constructed by joining metal-containing units with organic linkers, are attracting more and more research interests for their virtually tunable structures and potential applications, especially in gas storage, fluorescence, catalysis and separation.[1] Flexible and dynamic properties of PCPs have been considered as one of most important discoveries in this field. Such frameworks with dynamic behavior are able to form multi-stable phases and thus can be utilized for preparing special materials, such as highly selective sensors and magnetic materials.[2] On the basis of the previous reports, scores of dynamic PCPs have been prepared by using purposeful strategies, such as the employment of flexible ligands and metal ions with flexible coordination models.[2d, 3] The framework flexibility also can be derived from H-bonds, *π*-electron stacking, rotation or wobbling of free linkers and van der Waals interactions.[4] On the other hand, high chemical stabilities have been generally considered as an important indicator to practical applications of PCPs.[5] However, seldom flexible PCPs were reported to be chemically resistant in acidic and basic solution. Consequently, it is worthwhile to discover new flexible PCPs that are stable undergo the treatment with acidic and basic media and other extreme conditions.

Polyoxometalates (POMs), a large family of early transition metal oxide clusters, have been wildly concerned for their nano-sized structure and interesting redox and molecular properties.[6] An interesting aspect of POM chemistry is that these cluster anions can be served as desirable building blocks for the controlled construction of novel structures with functionality.[7] POMs also can act as good candidates for the designed assembly of tailored dynamic PCPs with special properties. Firstly, POMs which contain large number of surface oxygen atoms can display multiple coordination modes to connect metal ions or metal-organic moieties to generate many kinds of structures. Secondly, the surface oxygen atoms of POMs can also form hydrogen bonding interactions. These weak interactions may play a positive role in dynamic framework transformation. Thirdly, the high steric hindrance arising from bulk clusters can help maintain the crystallinity of the structure after removing guest molecules, which provides a favorable opportunity for reversible transformations. Based on above considerations, we try to utilize flexible ligand 4,4'-bis((1H-1,2,4-triazol-1-yl)methyl)biphenyl (L) and Keggin-type $H_3PW_{12}O_{40}{\cdot}xH_2O$ (H_3PW_{12}) to construct flexible and dynamic PCPs. Herein, we report a one-dimensional (1D) PCP, $[Cu(L)_2(H_2O)H(PW_{12}O_{40})]{\cdot}7H_2O$ (**1**), which shows dynamic behavior accompanied with removal/adsorption of guest water molecules. Furthermore, the flexible framework exhibits ultrahigh stability, which can retain its structure even in 8 mol L^{-1} hydrochloric acid, boiling water and dilute NaOH solution (pH = 12). The electrochemical properties of **1** have also been studied.

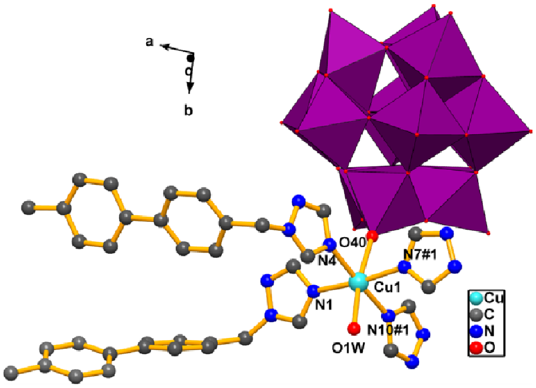

Fig. 1 The coordination environment of Cu(II) ion in **1**. Symmetry codes: #1, −0.5+*x*, 0.5−*y*, −0.5+*z*.

The reaction of $CuCl_2{\cdot}2H_2O$, L, H_3PW_{12} and water under hydrothermally condition generates green block crystals of **1**.‡ A single crystal X-ray diffraction study shows that the crystal of **1** crystallize in the monoclinic space group *C*2/*c*.[8] The asymmetric unit of **1** contains one Cu(II) ion, two L ligands, one $\{PW_{12}\}^{3-}$ anion, and one coordination water molecule. The solvent water molecules in the crystal are highly disordered and cannot be assigned. The formula of **1** was supported by elemental analysis (EA) and thermogravimetric analysis (TGA). To balance the charges of **1**, one proton should also be added to the formula. The proton is assumed to be delocalized over the entire structures and cannot be located by X-ray analysis.[9] As shown in Fig. 1, each Cu(II) ion is six-coordinated in a distorted octahedral coordination geometry, defined by four nitrogen atoms from four L molecules, one oxygen atom from one $\{PW_{12}\}^{3-}$ anion and one

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oxygen atom from one coordination water molecule (Cu–N 2.05(3)-2.08(3) Å, Cu–O 2.410(15)-2.416(18) Å). Cu(II) ions are linked into a 1D inter-connected 2-fold *meso*-helical chain with coordination water molecules and $\{PW_{12}\}^{3-}$ anions projecting on it (Fig. 2). Thanks to these coordination water molecules and polyanions, the chains are connected by hydrogen-bonding interactions to generate a 3D supramolecular architecture (Fig. S1). View along the *b* axis, the framework of **1** contains 1D channels, which are occupied by highly disordered water molecules (Fig. 3 and Fig. S2). The total potential solvent-accessible volume of **1** is calculated to be 32.8% (5780.9 $Å^3$ out of 17607.0 $Å^3$ per unit cell volume) by using the PLATON program[10]

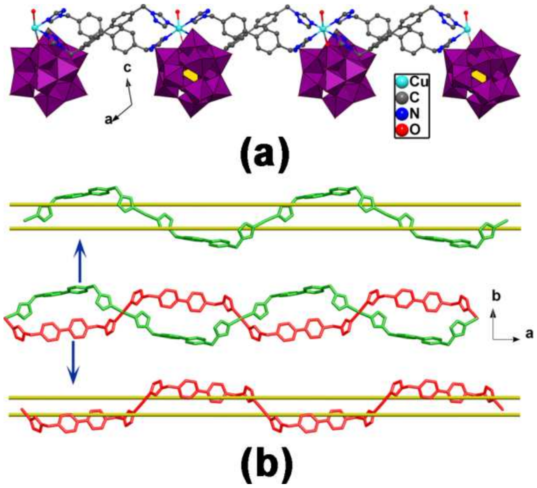

Fig. 2 (a) View of 1D chain constructed by L ligands connecting Cu(II) ions. (b) Illustration of the 1D inter-connected 2-fold *meso*-helical chains.

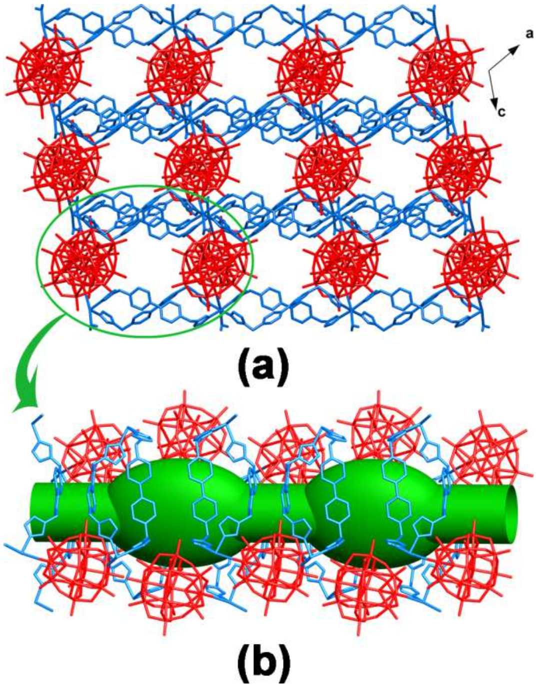

Fig. 3 (a) View of 3D supramolecular structure of **1**. (b) A schematic view of the 1D channel in the framework of **1**.

The powder X-ray diffraction (PXRD) pattern of the as-synthesized compound matched well with the simulated pattern, indicating its crystalline phase purity (Fig. S3). The TGA curve shows a weight loss of about 3.3% from room temperature to 110 °C, which is related to the loss of solvent water molecules (Fig. S4). The further weight loss at 260 °C may be attributed to the decomposing of the framework of **1**. Variable temperature powder X-ray diffraction (VTPXRD) experiments have also been carried out to examine the thermal stability of the framework of **1**. As shown in Fig. 4, as temperature increased over 120 °C, the main peaks of VTPXRD patterns of **1** remain, but part of them shift to the higher angle. These may be attributed to the shrinking of the channels of the framework after removing the guest water molecules.[4a, 11] We then heated the crystals of **1** at 110 °C under vacuum for 24 hours to give **1a**. It is worth noting that **1a** can turn back to **1** by immersed in water for 10 hours (Fig. S3). These results indicate that compound **1** shows a dynamic structural transformability upon reversible removing/adsorbing of guest water molecules. The VTPXRD patterns also show that the framework of **1** retains up to 240 °C. Afterward, the framework undergoes irreversible phase transformation into an amorphous state. The result of VTPXRD experiments is well consistent with the TGA date.

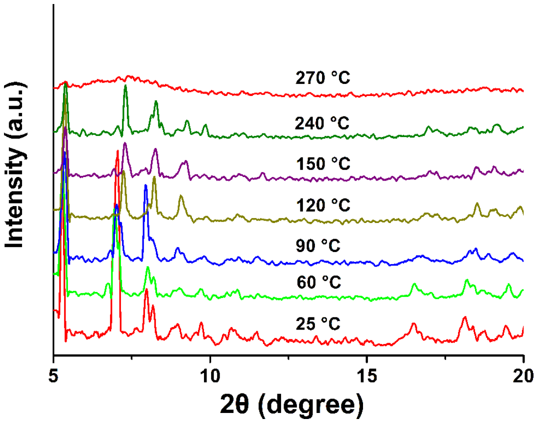

Fig. 4 VTPXRD patterns of **1**.

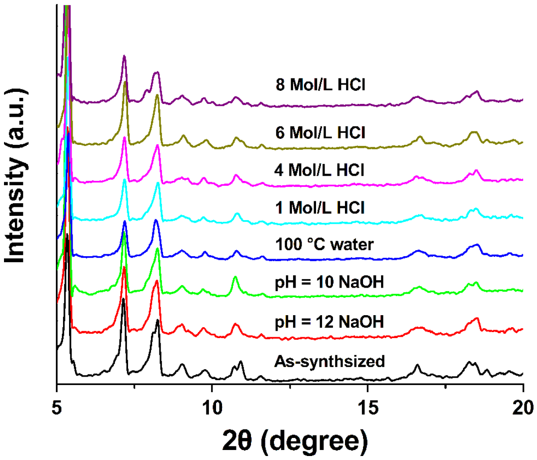

Fig. 5 PXRD patterns for as-synthesized **1** and crystals of **1** after soaking in different concentrations of HCl, boiling water, or base solution for 24 hours.

Surprisingly, the flexible framework of **1** exhibits very high chemical stability (Fig. 5). Fresh prepared crystals of **1** were soaked in aqueous solutions with different pH value for 24 hours.

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Then the crystals were filtered and dried under ambient condition. PXRD analyses show that these crystals remain intact even in 8 mol L^{-1} hydrochloric acid, boiling water and dilute NaOH solution (pH = 12). Otherwise, the crystals of **1** can also stable in methanol, ethanol, acetonitrile, acetone and dichloromethane over 24 hours (Fig. S5). Although some of PCPs were reported stable in highly acidic and basic conditions, the flexible PCP with such good chemical stability was first reported.[5]

The redox properties of compound **1** were studied by using the compound bulk-modified carbon paste electrode (CPE) as the working electrode, which was fabricated according to the literatures (15 mg of compound **1** and 130 mg of graphite powder were used in this work).[12] The cyclic voltammograms (CVs) of compounds **1** in 1 mol L^{-1} H_2SO_4 aqueous solution at different scan rates were recorded in the potential range from –650 to 300 mV. The CVs of **1**-CPE show two pairs of reversible redox peaks (Fig. S6a). The mean peak potentials $E_{1/2} = (E_{pa} + E_{pc})/2$ are approximately −76 and −370 mV for **1** (Scan rate: 200 mV s^{-1}), which correspond to one-electron processes of the W centres of $\{PW_{12}\}^{3-}$.[13] These results indicate that $\{PW_{12}\}^{3-}$ is the active centre for electrochemical redox activity in CPE. As shown in Fig. S6a, with increasing of the scan rates, the cathodic peak potentials shift to the negative direction and the corresponding anodic peak potentials shift to the positive direction. The peak currents are proportional to the scan rate, suggesting that the redox process of **1**-CPE is surface-controlled (Fig. S6b).[14]

In addition, **1**-CPE displays good electrocatalytic activities to reduce nitrite (Fig. S6c). It is clear that with the addition of nitrite, the two reduction peak currents of **1**-CPE increase gradually while the corresponding oxidation peak currents decrease, which indicates that both of the reduced species of the $\{PW_{12}\}^{3-}$ in **1** show good electrocatalytic activities toward the reduction of nitrite. In contrast, direct electroreduction of nitrite generally requires a large overpotential at most electrode surfaces, and no obvious response could be observed at a bare CPE.[15]

In conclusion, a new POM-based PCP, $[Cu(L)_2(H_2O)H(PW_{12}O_{40})]\cdot 7H_2O$ (**1**), has been successfully prepared by hydrothermal method. Structural stabilities analyses reveal that the 3D supramolecular structure of **1** shows dynamic behavior accompanied with removal/adsorption of guest water molecules. Remarkably, the flexible framework of **1** can retain its structure even in 8 mol L^{-1} hydrochloric, dilute NaOH solution (pH = 12) and boiling water. The successful synthesis of **1** provides useful information on the construction of new flexible PCPs that are stable under extreme chemical conditions.

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Notes and references

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† Electronic supplementary information (ESI) available: X-ray crystallographic data in CIF format, structure diagrams for compound **1**, PXRD patterns, TGA curves, tables of hydrogen bonds and selected bond lengths and angles. CCDC reference number: 988702 (**1**). For ESI and crystallographic data in CIF or other electronic format see DOI: xxxx.

‡ Synthesis of **1**: A mixture of $CuCl_2\cdot 2H_2O$ (0.1 mmol, 17.0 mg), H_3PW_{12} (0.025 mmol, 70 mg), L (0.05 mmol, 15 mg) and H_2O (10 mL) was stirred at room temperature for about 4 hours. And the pH of the mixture was adjusted to about 3.0 by adding two drops of hydrochloric acid (1 mol/L). Then the mixture was transferred into a 23 mL Teflon-lined stainless steel autoclave reactor and heated at 170 °C for 96 hours. After cooling to room temperature at a rate of 10 °C h^{-1}, dark green block crystals suitable for X-ray structural analysis were isolated by ultrasonically cleaning the sample, washing with water several times and dring in air. Yield: *ca.* 45 % (based on H_3PW_{12}). Anal. calcd for $C_{36}H_{49}CuN_{12}O_{48}PW_{12}$ (%): C, 11.63; H, 1.33; N, 4.52. Found: C, 11.61; H, 1.27; N, 4.49. IR (KBr, cm^{-1}): ν = 3461 (w), 3130 (w), 1612 (m), 1525 (m), 1434 (m), 1282 (m), 1124 (s), 1075 (s), 972 (s), 892 (s), 775 (s), 669 (s), 503 (m).

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8 Crystal data for **1**: $C_{36}H_{49}CuN_{12}O_{48}PW_{12}$, Fw = 3718.42 g/mol, Monoclinic, $C2/c$, a = 37.962(9) Å, b = 21.391(4) Å, c = 24.996(4) Å, β= 119.840(4) deg, V = 17607(6) Å^3, Z = 8, T = 293(2) K, R(int) = 0.0772, 44611 reflections collected, D_{cal} = 2.710 g/cm^3, GOF = 1.028 for 15510 reflections with $I > 2\sigma(I)$, $R1$ = 0.0763, $wR2$ = 0.2168 ($I > 2\sigma(I)$).

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