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Two Extended Organic-Inorganic Assemblies Based on Polyoxometalates and Copper Coordination Polymers with Mixed 4,4′-Bipyridine and 2,2′-Bipyridine Ligands

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Two new organic-inorganic hybrid compounds $\{Cu^{II}_4Cl(2,2'\text{-bipy})_4(4,4'\text{-bipy})_3(4,4'\text{-Hbipy})_2[PMo_{12}O_{40}]\}[PMo_{12}O_{40}]_2\cdot 2H_2O$ (**1**) and $[Cu^{I}_2(2,2'\text{-bipy})_2(4,4'\text{-bipy})][Cu^{I}_{1.5}(2,2'\text{-bipy})(4,4'\text{-bipy})]_2[H_3W_{12}O_{40}]$ (**2**) (2,2′-bipy = 2,2′-bipyridine, 4,4′-bipy = 4,4′-bipyridine) have been synthesised and subsequently characterised by elemental analysis, IR spectroscopy, thermal gravimetric analysis (TGA), electrochemical measurements and single-crystal X-ray diffraction. The most interesting feature of compound **1** is the Cu–Cl bond in the mixed ligand complex. Furthermore, **1** shows a 2D grid layered structure constructed from the $[PMo_{12}O_{40}]^{3-}$ polyoxoanion building units and 1D $[Cu_4(2,2'\text{-bipy})_4(4,4'\text{-bipy})_5Cl]_n^{n-}$ hybrid chains which are decorated by dangling polyoxoanion clusters that are disposed in a mutual *anti* orientation with respect to the layer plane. As fas as we know, compound **1** is the first characterised 2D structure with polyoxometalate clusters as pendants. Compound **2** represents the first 1D structure formed by ispolyoxotungstate building blocks $[H_2W_{12}O_{40}]^{6-}$ and transition metal complex fragments with mixed ligands.

Introduction

Organic-inorganic hybrid materials have been attracting considerable attention because of their structural diversity and fascinating properties with applications in catalysis, ion-exchange, sorption, magnetism, electrical conductivity and photochemistry.[1] To date, many organic-inorganic hybrid compounds have been reported.[2] The evolution of organic-inorganic hybrid materials is dependent upon the synthesis of new solids possessing unique structures and properties. One successful strategy is introduction of a transition-metal (called a secondary metal ion) which was traditionally usually used as an organic-inorganic linker because the metal can adopt various coordination geometries in different oxidation states. The influences of secondary metal ions as well as organic ligands linked to it have been extensively studied in view of their wide potential in a variety of applications.[3] Polyoxometalates (POMs), as a unique class of metal oxide clusters with varieties of structures and properties, are extremely versatile inorganic building blocks for constructing functional organic-inorganic hybrid materials.[4] Therefore, the functionality of organic-inorganic hybrid materials based on POMs can be multiplied by incorporation of coordination polymers into the POMs, resulting in numerous novel structures and properties due to the interplay and synergistic effects of organic and inorganic motifs.[5]

In recent years, the introduction of mixed organic ligands into a POM system has led to the successful syntheses of various unique structures[6] such as the unsymmetricalsurface-modified tungstosilicate $[\{Cu_2(O_2CMe)_2(5,5'\text{-dimethyl-}2,2'\text{-bipy})_2\}\{Cu(5,5'\text{-dimethyl-}2,2'\text{-bipy})_2\}SiW_{12}O_{40}]$,[6a] the polycatenated double-layered inorganic-organic hybrid material $[Zn_2\text{-}(tp)(4,4'\text{-bipy})V_2O_6]$ (tp = terephthalate) containing mixed organoamine and dicarboxylate ligands,[6b] the entangled compound $[Cu(4,4'\text{-bipy})(nic)(H_2O)]_2\text{-}Mo_8O_{26}$ (nic = nicotinic acid) [6c] with an interpenetrated multi-zigzag chain polymers, the 2D framework $[Co(en)_2]\text{-}[Co(2,2'\text{-bipy})_2]_2[PMo^{VI}_5Mo^{V}_3V^{IV}_8O_{44}]\cdot 4.5H_2O$ (en = ethylenediamine) [6d] in which the polyoxoanions are linked by two types of complex fragments, the 1D chainlike compound $[4,4'\text{-Hbipy}][\{Cu_2(2,2'\text{-bipy})_2(4,4'\text{-bipy})_{2.5}\}PW_{11}\text{-}CuO_{39}]\cdot 16H_2O$[6e] and, finally, the 3D host-guest compound $[Cu^{I}Cl(4,4'\text{-bipy})_4][Cu^{II}(1,10\text{-phen})_2Mo_8O_{26}]$ with a 1D organic-inorganic hybrid polyoxometalate chain as template including mixed 4,4′-bipy and 1,10-phen ligands.[6f]

Successful synthesis of hybrid materials with mixed ligands by our group and other groups further inspired our research efforts into constructing distinctive architectures. Very recently, we prepared a series of organic-inorganic hybrid compounds based on the POMs with mixed 2,2′-bipy

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and 4,4′-bipy ligands.[7] In the process of research, we found that introducing 2,2′-bipy and 4,4′-bipy ligands into a single structure has the following merits: (1) 4,4′-bipy has a doubly-connected rigid bridging feature with two terminal coordination sites which is favourable for constructing extended structures and (2) the chelating bidentate ligand 2,2′-bipy, as a metal-bridge or passivator, may induce new developments in structure and properties. As part of our continuing efforts along these lines, we herein report two novel compounds with different dimensions $\{Cu^{II}_4Cl(2,2'\text{-bipy})_4(4,4'\text{-bipy})_3(4,4'\text{-Hbipy})_2[PMo_{12}O_{40}]\}[PMo_{12}O_{40}]_2\cdot 2H_2O$ (**1**) and $[Cu^I_2(2,2'\text{-bipy})_2(4,4'\text{-bipy})][Cu^I_{1.5}(2,2'\text{-bipy})(4,4'\text{-bipy})]_2[H_3W_{12}O_{40}]$ (**2**). To the best of our knowledge, compound **1** represents the first 2D layered structure with polyoxometalate clusters as pendants and compound **2** represents the first example of a 1D structure built up from ispolyoxotungstate building blocks and transition metal complex fragments with mixed 2,2′-bipy and 4,4′-bipy ligands.

Results and Discussion

Synthesis

Compounds **1** and **2** were synthesised under hydrothermal conditions. Hydrothermal synthesis has recently been proved to be a particularly useful technique for the preparation of organic-inorganic hybrid materials.[8] It is well known that many factors can influence the outcome of a hydrothermal reaction, including the type of initial reactants, starting concentrations, pH, reaction time and temperature.[5]

Parallel experiments showed that the type of initial reactants and the pH of the reaction system are crucial for the formation of the title compounds. Compound **1** could only be obtained in the pH range 4–4.5. When the pH was greater then 4.5 or less than 4, no crystalline phase was formed and the product was a mixed powder. Meanwhile, if $(NH_4)_6Mo_7O_{24}\cdot 6H_2O$ and H_3PO_4 were replaced by $H_3PMo_{12}O_{40}\cdot 29H_2O$ at pH = 3.8, another compound $[Cu^I(4,4'\text{-bipy})]_3[PMo_{10}{}^{VI}Mo_2{}^{V}O_{40}\{Cu^{II}(2,2'\text{-bipy})\}]$,[7b] also reported by our group, could be synthesised.

Structure Description

The single-crystal X-ray diffraction analysis revealed that compound **1** exhibits a 2D layer formed by $[PMo_{12}O_{40}]^{3-}$ linking $\{(4,4'\text{-Hbipy})(2,2'\text{-bipy})_2(4,4'\text{-bipy})_{1.5}Cu^{II}_2Cl_{0.5}\}$ hybrid chains containing Cu–Cl bonds. Two crystallographically independent $[PMo_{12}O_{40}]^{3-}$ anions exist in this structure, hereafter labelled A-$[PMo_{12}O_{40}]^{3-}$ and B-$[PMo_{12}O_{40}]^{3-}$ in order to distinguish them. As shown in Figure 1, A-$[PMo_{12}O_{40}]^{3-}$ shows the typical structure of a disordered "α-Keggin" molecule. The central P atom is surrounded by a cube of eight oxygen atoms with each oxygen site half occupied. The central P–O distances vary from 1.486(19) to 1.57(2) Å with an average of 1.529(09) Å, the latter being within the range of reported values.[9] This structural feature often appears in $[XM_{12}O_{40}]^{n-}$ (X = P or Si, M = Mo or W) with the α-Keggin structure and this has been explained by several groups.[10] According to the coordination mode, there are three kinds of oxygen atom in the cluster: terminal oxygen atoms (Ot), edge-sharing bridging oxygen atoms (Oe), corner-sharing bridging oxygen atoms (Oc) and central oxygen atoms (Oa). Therefore, the Mo–O bond lengths fall into three classes: Mo–Ot 1.633(12)–1.683(13), Mo–$O_{e/c}$ 1.798(16)–2.001(14) and Mo–Oa 2.40(2)–2.52(2) Å. The mean values are 1.65, 1.83 and 2.48 Å, respectively. The B-$[PMo_{12}O_{40}]^{3-}$ anion is similar to that of the A-$[PMo_{12}O_{40}]^{3-}$ except that the central P atom is ordered.

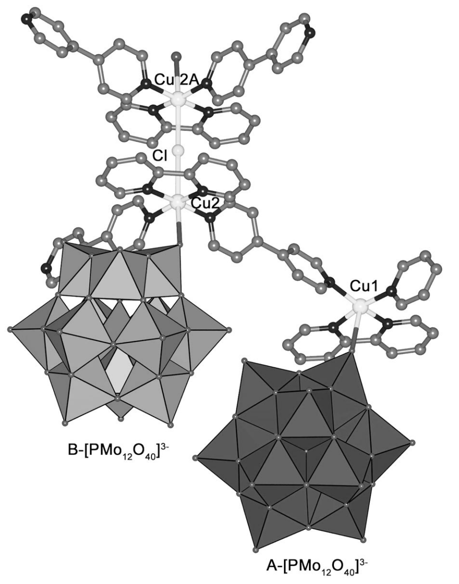

Figure 1. Polyhedral and ball-and-stick drawing of compound **1**. Hydrogen atoms and water molecules have been omitted for clarity.

As shown in Figure 2, two Cu(2) atoms are first connected together by sharing a Cl atom (Cu–Cl 2.577 Å) to form a dinuclear Cu unit and the dinuclear unit is then further linked with adjacent Cu(1) atoms through 4,4′-bipy ligands to generate a distinct mono- and a dinuclear mixed 1D wave-like chain. Notably, the three independent 4,4′-bipy ligands in this chain exhibit three different coordination environments: 4,4′-bipy^A bridges a dinuclear Cu(2) unit and a single Cu(1) atom in a bidentate coordination mode, 4,4′-bipy^B bridges two Cu(1) atoms in the same way, while 4,4′-bipy^C is a pendant ligand coordinated only to a Cu(2) atom in a monodentate mode and points in the direction opposite to that of the other pyridine group. Ligand 4,4′-bipy^C is monoprotonated, and this result agrees with the single-crystal X-ray diffraction analysis and the requirements of charge balance.

The most interesting aspect of **1** is the different roles played by A-$[PMo_{12}O_{40}]^{3-}$ and B-$[PMo_{12}O_{40}]^{3-}$ in the resultant structure. As illustrated in Figure 3 (a), the A-$[PMo_{12}O_{40}]^{3-}$ polyanions act as bidentate ligands bridging

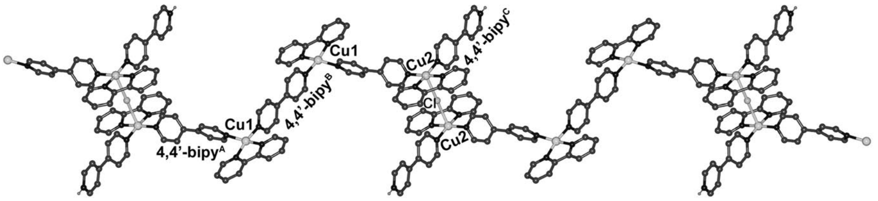

Figure 2. Ball-and-stick representation of the 1D hybrid wavelike chain in compound **1**.

adjacent 1D chains into a 2D square grid layer by means of weak Cu–O interactions (Cu1–O16 2.733 Å) while B-$[PMo_{12}O_{40}]^{3-}$ clusters act as dangling components which are weakly coordinated to the dinuclear copper units through Cu–O interactions (Cu2–O23 2.885 Å), the latter being disposed in a mutual *anti* orientation with respect to the layer plane. Therefore, compound **1** shows a unique 2D architecture with dangling polyoxoanion clusters (Figure 3, b). While it is quite common to find dangling organic ligands in coordination polymers,[11] we believe the presence of dangling POM clusters to be quite unusual. Such compounds may exhibit efficient photoinduced electron transfer from the polymer backbone to the POM cluster.[12] We are aware of three cases all of which exhibit 1D structures. The first was reported by Peng et.al. in 2005 [13] and in this material, hexamolybdate clusters are covalently attached, for the first time, to the side chains of conjugated polymers. The other two were reported by Peng[14] and our group.[7a] In these, saturated heteropolyoxoanion clusters hang from polymeric chains. Therefore, compound **1** represents the first example of a 2D structure with POM clusters as pendants.

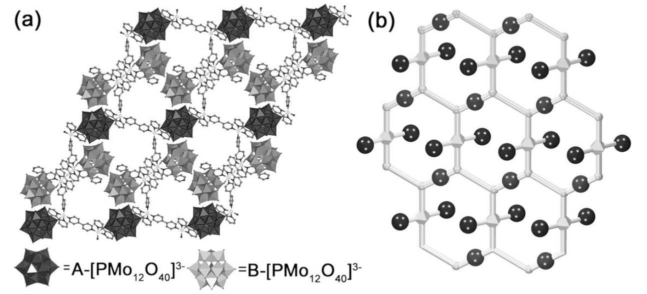

Figure 3. (a)View of the 2D layer structure of compound **1** constructed from 1D hybrid wavelike chains linked by A-$[PMo_{12}O_{40}]^{3-}$ polyanions by Cu–O interactions. (b) Schematic view of the layer structure in **1**.

As described above, the two crystallographically unique copper atoms [Cu(1) and Cu(2)] exhibit two different coordination geometries in compound **1**. Cu(1) is coordinated to four nitrogen atoms from a 2,2′-bipy and two 4,4′-bipy ligands and a terminal oxygen atom (O16) of an A-$[PMo_{12}O_{40}]^{3-}$ anion, thus the Cu(1) site can be described as having a "4+1"coordination geometry. For Cu(2), besides four nitrogen atoms of a 2,2′-bipy and two 4,4′-bipy ligands, a chlorine atom and a terminal oxygen atom of a B-$[PMo_{12}O_{40}]^{3-}$ unit are weakly bonded to it, thus the Cu(2) site can be described as having a "4+2" coordination geometry. Such coordination geometries are consistence with the fact that the Cu^{II} ion with a d^9 configuration tends to have a "4+1"or "4+2" coordination geometry because of a strong Jahn–Teller distortion effect.

To the best of our knowledge, only our group has ever reported a molybdenum phosphate compound containing copper together with 2,2′-bipy and 4,4′-bipy $[Cu^I(4,4'\text{-bipy})]_3[PMo_{10}{}^{VI}Mo_2{}^{V}O_{40}\{Cu^{II}(2,2'\text{-bipy})\}]$.[7b] Nevertheless, the coordination environments of the Cu centres are completely different in both compounds. In the above-mentioned compound, one type of Cu centre is linked by 4,4′-bipy to form a linear cationic chain while another type of Cu centre is coordinated to a 2,2′-bipy unit which caps the $[PMo_{12}O_{40}]^{5-}$ polyanion through four bridging oxo groups. As a result, the 2D structure is constructed from divalent copper $\{Cu^{II}(2,2\text{-bipy})\}^{2+}$ capped $[PMo_{12}O_{40}]^{5-}$ building blocks linked by $\{Cu(4,4'\text{-bipy})\}_n{}^{n+}$ linear cationic chains. In compound **1**, however, all the Cu centres are simultaneously coordinated to the mixed ligands and, more particularly, the dinuclear copper unit is formed by means of a Cu–Cl bond. This case is first observed in the POM system.

The structure of compound **2** is composed of the $\{[Cu^I{}_{1.5}(2,2'\text{-bipy})(4,4'\text{-bipy})]_2[H_3W_{12}O_{40}]\}^{2-}$ unit and $[Cu^I{}_2(2,2'\text{-bipy})_2(4,4'\text{-bipy})]^{2+}$ counterions (Figure 4). The $[H_2W_{12}O_{40}]^{6-}$ polyanion belongs to the α-metatungstate class of ions which has been reported previously [15] and exhibits an α-Keggin type structure. However it is different from the typically observed Keggin anions. The internal oxygen atom, common to three tungsten octahedra, is not bound to a central atom in a tetrahedral environment but the central cavity contains two protons.[16] It exhibits idealised T_d point symmetry and is constructed from four vertex-sharing W_3O_{13} trimers that result from the association of three edge-sharing WO_6 octahedra. In the $[H_2W_{12}O_{40}]^{6-}$ polyanion, the W–O bonds can be divided into three groups: (i) W–Ot, 1.562(14)–1.649(16) Å; (ii) W–Oe/c, 1.716(17)–1.89(2) Å; (iii) W–Oa, 2.23(3)–2.35(3) Å. These values reveal the strong interactions between the polyanions $[H_2W_{12}O_{40}]^{6-}$ and the copper-organonitrogen coordination complex.

Each $[H_2W_{12}O_{40}]^{6-}$ cluster is connected to two neighbouring clusters through (2,2′-bipy)Cu(4,4′-bipy)–Cu(4,4′-bipy)–Cu(2,2′-bipy) fragments into an infinite 1D chain running along the *a* axis with a Cu–O distance of 2.591 Å, as shown in Figure 5. It is noteworthy that the copper-organonitrogen groups in these chains are just like open arms protruding almost perpendicularly from both sides of the chains and all the open arms are stacked in parallel and arranged in a staggered fashion. Under this premise, these chains are first extended into a 2D supramolecular layer

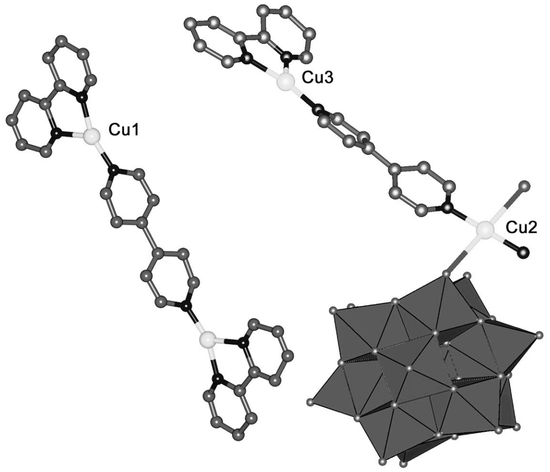

Figure 4. Polyhedral and ball-and-stick drawing of compound **2**.

parallel to the crystallographic *bc* plane by means strong of π-π stacking interactions (the face to face distance of 3.13 Å) from lateral arms of the bipy groups to give ligands (Figure 6). Neighbouring 2D layers are further extended into a 3D supramolecular network through strong π-π interactions with distances of 3.26 and 3.41 Å between $[Cu^{I}_2(2,2'\text{-bipy})_2(4,4'\text{-bipy})]^{2+}$ counterions and the open arms shown in Figure 7. It should be noted that polyoxoanions within currently known hybrid compounds containing mixed ligands are confined predominately to isopolyvanadium,[6b,17] isopolymolybdenum or heteropolyanions.[2b,6c,6f,18] In contrast, no previous structural examples of isopolytunstate as the inorganic component with mixed ligands have been observed. Therefore, compound **2** represents the first 1D structure formed by ispolyoxotungstate building blocks $[H_2W_{12}O_{40}]^{6-}$ and transition metal complex frameworks with mixed ligands.

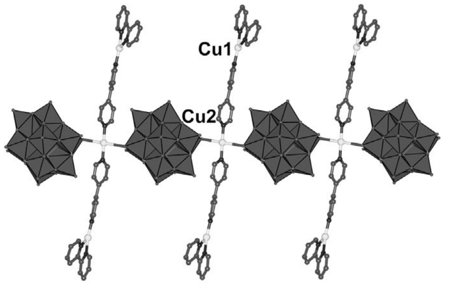

Figure 5. Polyhedral and ball-and-stick representation of the 1D chain structure of compound **2** formed by interconnection of $[H_2W_{12}O_{40}]^{6-}$ and (2,2′-bipy)–Cu(4,4′-bipy)–Cu(4,4′-bipy)–Cu(2,2′-bipy) along the *a* axis direction.

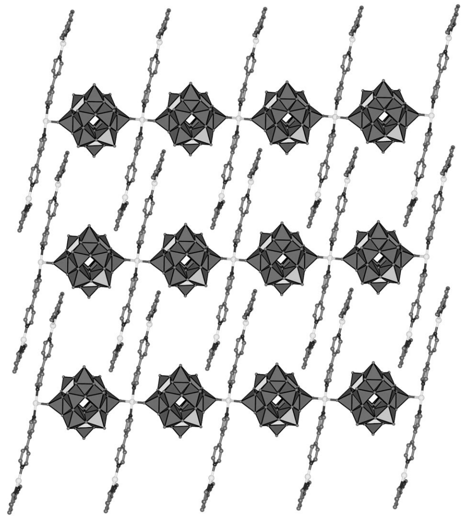

Figure 6. Polyhedral and ball-and-stick representation of the 2D layer structure of compound **2**.

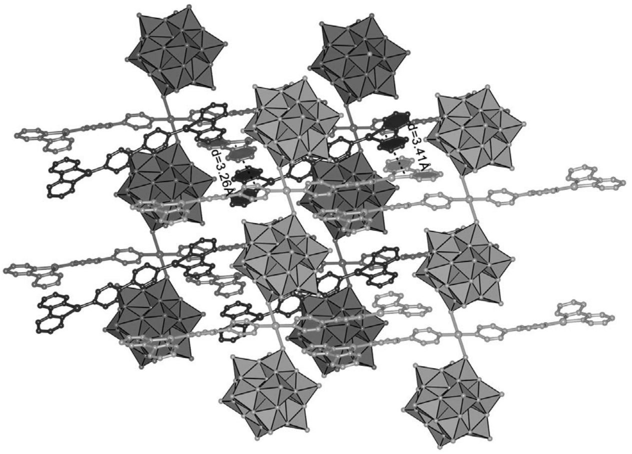

Figure 7. Polyhedral and ball-and-stick representation of the 3D supramolecular network of **2**.

In addition, the three crystallographically unique copper atoms exhibit two different coordination geometries: Cu(1) and Cu(3) display a trigonal $\{CuN_3\}$ geometry, defined by three nitrogen atoms from a 2,2′-bipy and a 4,4′-bipy ligand while Cu(2) shows a square $\{CuN_2O_2\}$ geometry, coordinated by two nitrogen atoms from a 4,4′-bipy ligand and two terminal oxygens from the adjacent POM clusters. Valence sum calculations on the Cu sites give values of 1.273, 1.072 and 1.190 for Cu(1), Cu(2) and Cu(3), respectively, confirmed by the particular coordination environments of Cu^{I}.

The experimental and simulated XRPD patterns of compound **1**–**2** are shown in Figures S1–S2. Their peak positions are in good agreement with each other, indicating the phase purity of the products. The differences in intensity may be due to the preferred orientation of the powder samples.

FTIR Spectroscopy

The IR spectrum of compound **1** (see Figure S3) exhibits four strong characteristic peaks at 1065, 962, 877 and 793 cm^{-1} which are due to the *ν*(P–Oa), *ν*(Mo–Ot), *ν*(Mo–Ob–Mo) and *ν*(Mo–Oc–Mo) vibrations, respectively. Compared with the IR spectroscopy of $\alpha\text{-}H_3PMo_{12}O_{40}\cdot nH_2O$,[19] the very similar shape and position of the peaks in the 700–1100 cm^{-1} range indicates that the skeleton of the polyanion

$[PMo_{12}O_{40}]^{3-}$ has not been influenced by the coordination of the Cu complex. This is in agreement with the results of single-crystal X-ray diffraction analysis. Additionally, the bands in the 1603–1169 cm^{-1} range are characteristic of the 4,4′-bipy and 2,2′-bipy ligands. For compound **2** (see Figure S4), the characteristic vibrations of the polyanions fall in the 992–824 cm^{-1} range and the characteristic peaks of the organic molecules are located at the 1215–1592 cm^{-1} range.

Thermal Stability Analysis

The TG curve of compound **1** (see Figure S5) shows three weight loss steps in the temperature range 45–800 °C. The process of the first step for the lattice water (calc. 0.5%) is clear, although there only exists weight loss of approximately 0.56% at 45–278 °C. A further weight loss of 19.94% containing two steps at 278–422 °C can be attributed to the decomposition of the organic ligands, 4,4′-bipy and 2,2′-bipy (calcd. 19.5%). For compound **2** (see Figure S6), the weight loss of approximately 26.2% (calculated 25.7%) in the temperature range 318–505 °C also exhibits two continuous processes which correspond to the decomposition of the organic components. No weight loss occurs above 505 °C. The loss of organic components in stages is perhaps evidence of the mixed ligands and their different coordination modes. These results further confirm the formulae of compounds **1**–**2**.

Electrochemical Properties

The redox properties of compounds **1**–**2** were studied in 1 M H_2SO_4 aqueous solution at a scan rate 50 mVs^{-1} and are shown in Figures 8 and 9. It can be clearly seen that in the potential range of –200 to 800 mV for **1** and –1000 to 600 mV for **2**, three pairs of redox peaks appear and the mean peak potentials $E_{1/2} = (E_{pa} + E_{pc})/2$ are 260 (*I*), 68 (II) and –69 (III) mV for compound **1** and –233 (*I*), –518 (II) and –830 (III) mV for compound **2**. The values of the peak-to-peak separations between the corresponding anodic and cathodic peaks (ΔE_p) are 38 (I–I′), 36 (II–II′) and 34 (III–III′) mV, which can be attributed to three two-electron process of molybdenum for compound **1**, and 24 (I–I′), 35 (II–II′) and 60 (III–III′) mV, which can be attributed to two two-electron and a one-electron processes of the tungstate for compound **2**.[20,21] The expected redox peaks of the copper ions have not been observed, although the scans were repeated under different conditions for compounds **1** and **2**.

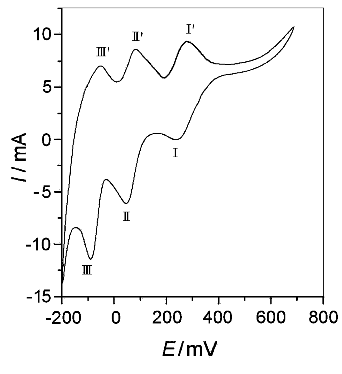

Figure 8. Cyclic voltammograms of the **1**-CPE in the 1 M H_2SO_4 aqueous solution at a scan rate 50 mV/s.

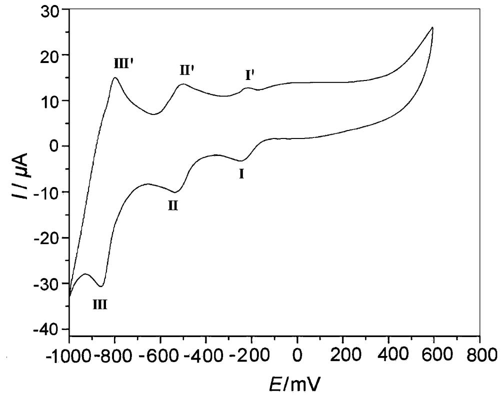

Figure 9. Cyclic voltammograms of the **2**-CPE in the 1 M H_2SO_4 aqueous solution at a scan rate 50 mV/s.

Conclusions

In summary, two novel complexes composed of polyoxoanion clusters and a copper complex with mixed 4,4′-bipy and 2,2′-bipy ligands have been obtained and characterised. The success in synthesising compounds **1** and **2** shows that the polyoxoanion clusters and copper coordination polymers are versatile building blocks and can be effectively combined by introducing linear and chelating ligands into to a single structure. Given the variations in the polyoxometal clusters and transition-metal complex linkers, the scope for the further synthesis of POM-based hybrid material with mixed ligands appears to be very inspiring.

Experimental Section

Materials and Measurement: All reagents were purchased commercially and used without further purification. Elemental analyses (C, H and N) were performed on a Perkin–Elmer 2400 CHN elemental analyser. Mo, W, P and Cu were determined using a Leaman inductively coupled plasma (ICP) spectrometer. The IR spectra were obtained on an Alpha Centaur FTIR spectrometer in the 400–4000 cm^{-1} region using KBr pellets. TGA were performed on a Perkin–Elmer TGA7 instrument under flowing N_2 with a heating rate of 10 °Cmin^{-1}. X-ray powder diffraction patterns were recorded on a Siemens D5005 diffractometer with Cu-K_α (λ = 1.5418 Å) radiation. All electrochemical measurements were carried out on a CHI 660 electrochemical workstation at room temperature (25–30 °C). Cyclic voltammograms were recorded on a 384B polarographic analyser. A typical three-electrode cell having a CPE working electrode, a platinum counter electrode and a silver/silver chloride reference electrode was used for the voltammetry experiments.

Synthesis of Compound 1: A mixture of $(NH_4)_6Mo_7O_{24}{\cdot}6H_2O$ (0.124 g, 0.1 mmol), H_3PO_4 (0.21 mL, 3 M), $CuCl_2{\cdot}2H_2O$ (0.052 g, 0.3 mmol), 4,4′-bipy (0.047 g, 0.3 mmol), 2,2′-bipy (0.028 g, 0.2 mmol) and H_2O (10 mL) was stirred for 0.5 h in air. The pH was then adjusted to 4.3 using dilute ethylenediamine solution and 4 M HCl. The mixture was transferred to a Teflon®-lined autoclave (23 mL) and kept at 165 °C for 4 d. After the sample had slowly cooled to room temperature, black crystals were filtered off, washed with distilled water and dried in a desiccator at room temperature to give a yield of 32.5% based on Mo. $C_{90}H_{80}ClCu_4Mo_{36}N_{18}O_{122}P_3$ (7202.07): calcd. C 15.01, H 1.14, N 3.50, Cu 3.53, P 1.29, Mo 47.96; found C 15.31, H 0.98, N 3.64, Cu 3.61, P 1.21, Mo 48.15.

Synthesis of Compound 2: A mixture of $Na_2WO_4\cdot 2H_2O$ (0.033 g, 0.1 mmol), $CuCl_2\cdot 2H_2O$ (0.052 g, 0.3 mmol), 4,4′-bipy (0.047 g, 0.3 mmol), 2,2′-bipy (0.028 g, 0.2 mmol) and H_2O (10 mL) was stirred for 0.5 h in air. The pH was then adjusted to 3.9 using dilute ethylenediamine solution and 4 M HCl. The mixture was transferred to a Teflon lined autoclave (23 mL) and kept at 165 °C for 4 d. After the sample had slowly cooled to room temperature, orange crystals were filtered off, washed with distilled water and dried in a desiccator at room temperature to give a yield of 38.2% based on W. $C_{70}H_{54}Cu_5N_{14}O_{40}W_{12}$ (4255.20): calcd. C 19.16, H 1.27, N 4.47, Cu 7.24, W 50.29; found C 19.45, H 1.24, N 4.39, Cu 7.14, W 50.18.

Preparation of Compound-1,2-Modified Carbon-Paste Electrode: The POM-modified carbon-paste electrode (CPE) was fabricated as follows: graphite powder (1.0 g) and POM **1** or **2** (40 mg) were mixed and ground together with an agate mortar and pestle to achieve an even, dry mixture. Nujol (0.66 mL) was then added to the mixture which was stirred with a glass rod. The homogenised mixture was used to pack 3 mm inner diameter glass tubes and the surface was wiped with weighing paper. Electrical contact was established with a copper rod through the back of the electrode.

X-ray Crystallographic Study: Single-crystals of compounds **1** and **2** were glued on a glass fibre. Data were collected on Rigaku RAXIS RAPID IP instrument with Mo-K_α monochromatic radiation (λ = 0.71073 Å) at 293 K and the structures were solved by direct methods and refined by full-matrix least-squares on F^2 by using the SHELXTL crystallographic software package.[22] Semi-empirical absorption corrections based on symmetry equivalent reflections were applied. A total of 31094 reflections for **1** were collected of which 14259 were unique [R(int) = 0.0683] (3.02° $< 2\theta <$ 25°). A total of 15256 reflections for **2** were collected of which 6731 reflections were unique [R(int) = 0.1046] (3.02° $< 2\theta <$ 25°). In the final difference map of **1**, the highest peak was 1.48 e Å^{-3} located 0.57 Å from Mo4 and the deepest hole was –1.32 e Å^{-3} located 0.82 Å from Mo18. In the final difference map of **2**, the highest largest peak was 3.92 e Å^{-3} located 0.85 Å from O11 and the deepest hole was –4.71 e Å^{-3} located 0.92 Å from O20. Anisotropic thermal parameters were used to refine all non-hydrogen atoms for **1** and **2**. No nonpositive-definite displacement parameters were observed in **1** but part of the central oxygen atoms (O5, O25, O27), the terminal (O15, O17), bridging oxygen (O11), W6 and N1 represent nonpositive-definite displacement parameters in **2**. All hydrogen atoms for water molecules were not located but were included in the structure factor calculations. Crystallographic data are given in Table 1 and selected bond lengths are listed in Tables S1 and S2.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallgraphic Data Centre, CCDC-689312 (for **1**) and -689313 (for **2**), respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystal data and structure refinements for compounds **1**–**2**.

	1	2
Empirical formula	$C_{90}H_{74}ClCu_4Mo_{36}N_{18}O_{122}P_3$	$C_{70}H_{54}Cu_5N_{14}O_{40}W_{12}$
Formula weight	7196.03	4255.17
T [K]	293(3)	293(5)
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a [Å]	11.819(2)	13.073(3)
b [Å]	18.924(4)	13.406(3)
c [Å]	20.027(4)	13.683(3)
α [°]	109.20(3)	86.84(3)
β [°]	100.94(3)	65.37(3)
γ [°]	93.72(3)	63.68(3)
V [Å^3]	4113.8(14)	1929.1(7)
Z	1	1
D_c [Mg m^{-3}]	2.905	3.663
μ [mm^{-1}]	3.307	19.258
F(000)	3406	1925
Data / restraints / parameters	14259 / 24 / 1250	6731 / 347 / 659
Goodness-of-fit on F^2	1.014	1.118
R_1[a] [$I > 2\sigma(I)$]	0.0660	0.0790
wR_2[b]	0.1669	0.1821

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

Supporting Information (see also the footnote on the first page of this article): The IR spectra, TG curves and the selected bond lengths of compounds **1** and **2**.

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