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Assembly of three organic–inorganic hybrid supramolecular materials based on reduced molybdenum(V) phosphates



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ABSTRACT

Three supramolecular materials based on {P₄Mo₆} polyoxoanions, (Hbbi)₂(H₂bbi)[Cu₃Mo¹₂O₂₄(OH)₆ (H₂O)₆(HPO₄)₄(H₂PO₄)₂(PO₄)₂] · 3H₂O (**1**), (Hbbi)₂(H₂bbi)[Ni₃Mo¹₂O₂₄(OH)₆(H₂O)₂(HPO₄)₄(H₂PO₄)₂(PO₄)₂] · 9H₂O (**2**), (Hbpy)(bpy)₃[Ni₂(H₂O)₁₀Na(PCA)₂][NiMO¹₂O₂₄(OH)₆(H₂PO₄)₆(PO₄)₂] · 6H₂O (**3**) (bbi = 1,1'-(1,4-butanediyl)bis(imidazole), bpy = 4,4'-bipyridine, PCA=pyridine-4-carboxylic acid), have been hydrothermally synthesized and structurally characterized by the elemental analysis, TG, IR, UV-vis, PXRD and the singlecrystal X-ray diffraction. Compounds **1** and **2** exhibit covalent 1-D chains constructed from *M*[P₄Mo₆]₂ dimeric cluster and {*M*(H₂O)_{*n*}} (*M*=Cu, *n*=3 for **1** and *M*=Ni, *n*=**1** for **2**) linker. Compound **3** possesses an unusual POMMOF supramolecular layers based on [Ni(P₄Mo₆)]₂ dimeric units and 1-D metal–organic strings [Ni(H₂O)₅Na(PCA)]_{*n*}, in which an in situ ligand of PCA from 1,3-bis(4-pyridyl)propane (bpp) precursor was observed. Furthermore, the electrochemical behavior of **1–3**-CPE and magnetic properties of **1–3** have been investigated in detail.

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1. Introduction

Polyoxometalate (POM) organic–inorganic hybrid materials have recently attracted great interests in creating nanoscale structures and supramolecular assemblies due to not only their fascinating structural topologies, but also their potential applications in catalysis [1], adsorption [2–4], photochemistry [5,6], biomedicine [7], and various electromagnetic functional materials [8–11]. During the construction of hybrid supramolecular assemblies, POMs are one of active inorganic clusters with high-enriched oxygen surfaces, which tend to coordinate with various metal linkers. In this subfamily, the {P₄Mo₆X₃₁} (X=O or OH) units (abbr. {P₄Mo₆}) represent one of the ideal building blocks to construct the supramolecular assemblies: First, the reduced Mo^V centers lead to the high negative charges of the whole clusters, which can induce more cationic linking units into the crystal structures and lead to plenty of structural topologies. Second, the four extrude {PO₄}

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fragments provide versatile coordination modes to various linking units [12–35]. Third, the { P_4Mo_6 } units are one of easy available clusters that can be in situ synthesized with simple starting materials in the hydrothermal environment or by routine synthesis.

On the other hand, the introduction of various linking units is another important element to construct the POM-based supramolecular assemblies. The transitional metal ions have been widely used as the linking units to construct the {P₄Mo₆}-based complexes due to their relatively strong coordination abilities. A large amount of {P₄Mo₆}-based compounds have been reported [12–35]. However, most of them are {P₄Mo₆} clusters including manganese [12–15], iron [16–20], cobalt [21–25], and zinc [26–30] etc transitional metal. Up to now, the POM-based compounds are modified by nickel and copper are still less common [31–35]. In particular, the examples of copper as linkers to assemble {P₄Mo₆} unit are relatively rare and only two compounds have been reported [34–35]. Thus, it would be a challenging but attractive area to synthesize this kind of compound.

As is well-known, an important feature of supramolecular assemblies is the extension of low-dimensional building blocks to high-dimensional networks through weak intermolecular interactions. The N-donor ligands such as organic amine, and pyridineor imidazole-containing ligands are excellent structure-directing agents, which play important roles in the construction of $\{P_4Mo_6\}$ -

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based assemblies. On the one hand, they can always act as reducing agents to reduce Mo^{VI} into Mo^{V} centers. On the other hand, they can induce the {P₄Mo₆}-based inorganic fragments to form different dimensions or various packing arrangements in the final hybrid materials via hydrogen bonding, π - π stacking and weak Van der Waals force. Sometimes, the breaking and oxidation cracking reaction for C–C bond of some flexible ligand was observed, that is, organic ligands was transformed into new ligand via certain in situ reaction. It provides an opportunity to generate organic ligands that are difficult to be synthesized in a conventional method. Thus, it could make a significant contribution to design and synthesize various novel POM-based hybrid assemblies.

Based on aforementioned considerations, we introduce nickel (II) and copper(II) cation as linkers into the {P₄Mo₆} system under hydrothermal conditions via changing the ligand to synthesize three new supramolecular assemblies based on {P₄Mo₆} cluster, namely, (Hbbi)₂(H₂bbi)[Cu₃Mo¹₂O₂₄(OH)₆(H₂O)₆(HPO₄)₄(H₂PO₄)₂ (PO₄)₂] \cdot 3H₂O (**1**), (Hbbi)₂(H₂bbi)[Ni₃Mo¹₂O₂₄(OH)₆(H₂O)₁₀Na(PCA)₂] [NiMo¹₂O₂₄(OH)₆(H₂O)₁₀Na(PCA)₂] [NiMo¹₂O₂₄(OH)₆(H₂O)₂] · 6H₂O (**3**). Our result further suggests that organonitrogen ligands is an excellent template reagent and linker unit to induce new {P₄Mo₆}-based supramolecular assemblies.

2. Experimental

2.1. Materials and general procedures

All chemicals purchased were of reagent grade and used without further purification. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. Mo, P, Cu, Na, and Ni were determined with a Leaman inductively coupled plasma (ICP) spectrometer. IR spectra were recorded in the range $400-4000 \text{ cm}^{-1}$ on a Alpha Centaurt FT/IR spectrophotometer with the pressed KBr pellets. Diffuse reflectance UV-vis spectra (BaSO₄ pellets) were obtained with a Varian Cary 500 UV-vis NIR spectrometer. XRD patterns were collected on a Rigaku Dmax 2000 X-ray diffractometer with graphite monochromatized CuK α radiation ($\lambda = 0.154$ nm) and 2θ ranging from 5 to 50°. TG analyses were performed on a Perkin-Elmer TGA7 instrument in flowing N₂ with a heating rate of 10 $^{\circ}$ C min⁻¹. The electrochemical measurement was carried out on a CHI 660 electrochemical workstation at room temperature (25-30 °C). A conventional three- electrode system was used. The working electrode was a carbon paste electrode (CPE), a Pt wire as the counter electrode and Ag/AgCl (3 M KCl) electrode was used as a reference electrode. Magnetic susceptibility data were collected over the temperature range of 2-300 K in a magnetic field of 10 kOe on a Quantum Design MPMS-5 SQUID magnetometer.

2.2. Synthesis

2.2.1. Preparation of $(Hbbi)_2(H_2bbi)$

 $[Cu_{3}Mo_{12}^{V}O_{24}(OH)_{6}(H_{2}O)_{6}(HPO_{4})_{4}(H_{2}PO_{4})_{2}(PO_{4})_{2}] \cdot 3H_{2}O(\mathbf{1})$

The mixture of $Na_2MoO_4 \cdot 2H_2O$ (1.252 g, 5.17 mmol), Cu $(NO_3)_2 \cdot 3H_2O$ (0.516 g, 2.14 mmol), $H_3PO_4 \cdot (2 \text{ mL}, 30 \text{ mmol})$, bbi (0.382 g, 2.36 mmol), and H_2O (18 mL, 1.0 mol) was stirred for half an hour and adjusted with 1 M NaOH solution to pH=3.5. Then, the above mixture was sealed in a 25-mL Teflon reactor and heated at 165 °C for 5 days. Dark red block crystals of **1** were isolated. The crystalline products were collected by filtration, washed with distilled water, and air-dried to give a yield of 46% (based on Mo). Elemental anal. Calculated values (%) for C₃₀H₅₇Cu₃Mo₁₂O₇₁P₈ (3311.57): C, 10.88; H, 1.74; N, 5.08; P, 7.48; Mo, 34.77; Cu, 5.76. Experimental: C, 10.83; H, 1.70; N, 5.12; P, 7.53; Mo, 34.72; Cu, 5.82.

2.2.2. Preparation of (Hbbi)₂(H₂bbi)

$[Ni_{3}Mo_{12}^{V}O_{24}(OH)_{6}(H_{2}O)_{2}(HPO_{4})_{4}(H_{2}PO_{4})_{2} \cdot (PO_{4})_{2}] \cdot 9H_{2}O(\mathbf{2})$

Compound **2** was prepared similar to the method of compound **1**, except that the initial chemicals $Cu(NO_3)_2 \cdot 3H_2O$ were substituted by $Ni(NO_3)_2 \cdot 4H_2O$ (0.564 g, 2.21 mmol). Dark red block crystals of **2** were isolated. The crystalline products were collected by filtration, washed with distilled water, and air-dried to give a yield of 47% (based on Mo). Elemental anal. Calculated values (%) for $C_{30}H_{61}Mo_{12}N_{12}Ni_3O_{73}P_8$ (Mr=3333.02) (%): C, 10.81; H, 1.84; N, 5.04; P, 7.43; Mo, 34.54; Ni, 5.28; Experimental (%): C, 10.85; H, 1.80; N, 5.09; P, 7.39; Mo, 34.51, Ni, 5.31

2.2.3. Preparation of $(Hbpy)(bpy)_3[Ni_2(H_2O)_{10}Na(PCA)_2]$ $[NiMo_{12}^{V}O_{24}(OH)_6 \cdot (H_2PO_4)_6(PO_4)_2] \cdot 6H_2O$ (**3**)

Compound **3** was prepared similar to the method of compound **2**, except that the initial chemicals bbi were substituted by bpp (0.512 g, 2.58 mmol) and 4,4'-bipyridine, (0.425 g, 2.72 mmol). Dark red block crystals of **3** were isolated. The crystalline products were collected by filtration, washed with distilled water, and air-dried to give a yield of 43% (based on Mo). Elemental anal. Calculated values (%) for C_{52} H₇₂Mo₁₂ N₁₀Na Ni₃O₈₂P₈ (Mr=3747.30) (%): C, 16.67; H, 1.94; N, 3.74; P, 6.61; Mo, 30.72, Na, 0.62, Ni, 4.70; Experimental (%): C, 16.71; H, 1.90; N, 3.78; P, 6.56; Mo, 30.76; Na, 0.69, Ni, 4.64.

2.3. Preparation of 1-, 2-, and 3-CPEs

Complexes **1**, **2**, and **3** modified carbon paste electrodes (**1**-, **2**-, and **3**-CPEs) were prepared as follows: 300 mg of graphite powder and 30 mg of complex were mixed and ground together by agate mortar and pestle to achieve a uniform mixture. To the mixture, three drops of nujol were added with stirring. The homogenized mixture was used to pack into a glass tube with 3 mm inner diameter, and the surface was pressed tightly onto weighing paper with a copper rod through the back. Electrical contact was established with a copper rod through the back of the electrode.

2.4. X-ray crystallography

The crystal data of **1**, **2**, and **3** were collected on a Bruker SMART CCD diffractometer with MoK α radiation (λ =0.71073 Å) at 293 K. The structures were solved by the direct methods and refined by the full-matrix least-squares method on F^2 with the SHELXTL 97 crystallographic software package [36,37]. Anisotropic thermal parameters were used to refine non-hydrogen atoms. Hydrogen atoms on C and N atoms of the organic ligands were included in their calculated positions. Hydrogen atoms attached to lattice water molecules were found from the difference Fourier maps. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center (CCDC no. 980058 for compound **1**, 980059 for compound **2**, and 980060 for compound **3**). A summary of crystal data and structure refinement for compounds **1**, **2**, and **3** is provided in Table 1. Selected bond lengths and angles **1**, **2**, and **3** are listed in Table S1.

3. Results and discussion

3.1. Synthesis

During our exploration on the new $[P_4Mo_6]$ -based supramolecular assembly, we are interested in employing transition metal Ni²⁺ and Cu²⁺ cation as the possible linkage unit to induce different $[P_4Mo_6]$ -based materials. Complexes **1–3** were achieved by changing organic ligands and metal cations under the similar reaction temperature and time. The self-assembly reactions of Na₂MoO₄· 2H₂O, H₃PO₄, TM(NO₃)₂ (TM=Cu and Ni), H₂O, and bbi

Table 1

Crystal data and structure refinement parameters for compounds 1, 2 and 3.

Compound	1	2	3
Formula	C ₃₀ H ₅₇ Cu ₃ Mo ₁₂ N ₁₂ O ₇₁ P ₈	C ₃₀ H ₆₁ Mo ₁₂ N ₁₂ Ni ₃ O ₇₃ P ₈	C ₅₂ H ₇₂ Mo ₁₂ N ₁₀ Na Ni ₃ O ₈₂ P ₈
Mr	3311.57	3333.02	3747.30
Crystal. size (mm ³)	$0.26 \times 0.24 \times 0.20$	$0.24 \times 0.22 \times 0.20$	$0.26 \times 0.22 \times 0.20$
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	P 21	P - 1	C 2
a (Å)	17.972(3)	13.676(3)	21.0239(17)
b (Å)	23.869(4)	14.029(3)	23.5020(18)
<i>c</i> (Å)	20.487(3)	23.714(5)	15.592(2)
α (deg)	90.00	69.1420(10)	90.00
β (deg)	95.886(3)	96.118(3)	131.1020(10)
γ (deg)	90.00	88.1080(10)	90.00
$V(Å^3)$	8742(2)	4506.6(17)	3403.1(3)
Ζ	4	4	2
D_{calcd} (kg m ⁻³)	2.516	2.456	2.122
$\mu(MoK\alpha) (mm^{-1})$	2.642	2.484	1.947
F(000) (e)	6423	3270	3642
θ Range (deg/°)	1.31-25.00	0.86-25.00	1.57-25.00
Reflections collected/unique/Rint	40499/15296/0.0337	22527/15868/0.0166	14412/5237/0.0456
Data/restraints/parameters	15296/68/1228	15718/58/1247	5237/735/373
$R_1/wR_2 \ [I \ge 2\sigma(I)]^a$	0.0517/0.1130	0.0401/0.0804	0.0415/0.0912
$R(F)/wR(F^2)^a$ (all refl.)	0.0994/0.1635	0.0650/0.1040	0.0750/0.1025
GoF $(F^2)^a$	1.052	1.012	1.073
$\Delta \rho fin (max/min) (eÅ^{-3})$	1.791–1.399	2.311/-1.900	1.836/-2.055

 $aR_1 = \sum ||F_0| - |F_C|| / \sum |F_0|; \ wR_2 = \sum [w(F_0^2 - F_C^2)^2] / \sum [w(F_0^2)^2]^{1/2}.$



Scheme 1. The mechanism for in situ generation of PCA from bpp.

ligands under pH value of 3.5 gave rise to complex 1 and 2 with 1-D chains based on [P₄Mo₆] polyoxoanions and Cu or Ni linker. When another flexible ligands of bpp instead of bbi in the preparations of 1 and 2, no compounds were obtained. In order to generate novel structure, two kinds of ligands bbi and bpy were introduced into 2. Another unusual supramolecular POMMOF layers (compound **3**) based on [Ni(P₄Mo₆)]₂ dimeric units and 1-D metal-organic strings $[Ni(H_2O)_5Na(PCA)]_n$ were obtained under the same pH value. It is worth mentioning that an in situ ligand of PCA was generated from bpp through an unusual POMs-mediated in situ reaction. The reaction activity of bpp often appears in some in situ synthesis, which has been explained by several groups [38,39]. In the process of in situ synthesis, an oxidation cracking reaction of C–C bond was observed, that is, bpp was transformed into PCA. The reaction mechanism is not clear, but as is wellknown, polyoxometalates (POMs) have catalytic-oxidation activity. and under presence of POM, the bpp might be oxidized by the oxidative materials, such as NO_3^- , and O_2 in the acid system under hydrothermal conditions (Scheme 1). If the reactant bbi was replaced by 4,4'-bpy and bpp in 1, no compounds were obtained, which further indicated that Ni²⁺ plays an important role in the formation of PCA ligand. Moreover, at above lower pH value (3.5), the longer N-ligand group bbi of compound 1 and 2 tend to be protonated and fail to bond to the metal ions. The formations of c 1–3 are shown in Scheme 2.

3.2. Crystal structure

X-ray diffraction analysis reveals that the structures of compounds **1–3** are based on the sandwich-type $TM{P_4Mo_6X_{31}}_2^{n-1}$ (TM=Cu and Ni; X=O, OH) cluster. As usually observed, the basic building unit $[P_4Mo_6O_{31}]^{12-1}$ is made up of six { MoO_6 } octahedra and four { PO_4 }

tetrahedra. The six oxygen-bridged molybdenum centers [Mo-O: 1.643(11)–2.346(7) Å] lie approximately in the same plane, which exhibits a ring of six edge-sharing [MoO₆] octahedra with alternating Mo–Mo single bonds (av. 2.59 Å) and nonbonding Mo…Mo contacts (av. 3.56 Å). Four $\{PO_4\}$ tetrahedra are linked to the ring by sharing corners with three {PO₄} groups around the periphery of the ring and the other one group located on its center. The P-O bond distances are in the range of 1.43(2)–1.601(9) Å and the angles of O–P–O are from 102.0(6) to 115.6(5)°. The central transitional metal ion connects two {P₄Mo₆} units via three bridging-oxygen atoms between Mo and Mo single bonds to form the sandwich-type moiety TM[P₄Mo₆]₂ with a local symmetry of Ci. It is worth mentioning that the central phosphate groups and the Mo-Mo bonds on the two rings are staggered to each other. In addition, Cu1 atoms in Compound 1, Ni1 and Ni2 atoms in Compound 2, and Ni1 atoms in compound 3 lie on their inversion centres.

Bond-valence sum (BVS) calculations [40,41] show the values 5.12– 5.33 for all molybdenum atoms and 4.92–5.14 for all phosphate atoms in compounds **1–3**, indicating that all Mo and P are in the +5 oxidation state. In addition, BVS calculations present the values from 1.14 to 1.36 for the protons of the phosphato groups and *u*-O atoms (only bridge two adjacent nonbonding Mo centers). The terminal water ligands linked to the Cu or Ni centers (0.28–0.36) are also determined by the BVS calculations. The Cu in **1**, and Ni in **2** and **3** are all in the +2 oxidation states. Na in **3** is +1 oxidation states. Moreover, one or two extra protons should be added to the organic structural-directing agents in compounds **1–3** for the charge balance.

3.2.1. Structure description of 1

Compound **1** crystallizes in the monoclinic space group *P*21 and is composed of one sandwich-type unit $Cu[P_4Mo_6]_2$, two $Cu(H_2O)_3$



Fig. 1. Polyhedral and ball-and-stick representation of the 1-D chain of 1.

linker, three protonated bbi ligands, and three lattice water molecules (Fig. S1). There are three crystallographically independent copper atoms (Cu1, Cu2, and Cu3), which are six-coordinate exhibiting different coordination environments. Cu1 displays an octahedral CuO₆ coordination geometry and connects two {P₄Mo₆} units via three bridging-oxygen atoms to form dimeric cluster Cu [P₄Mo₆]₂. The Cu1–O bond distances vary from 2.118(7) Å to 2.209 (7) Å. Cu2 and Cu3 atoms are in the center of a distorted octahedron, which is defined by three coordinated water molecules and three phosphate O atoms from two Cu[Mo₆P₄]₂ clusters. The Cu-O distances are in the range of 2.038(8)-2.239(8) Å. In Compound 1, each dimeric unit Cu[P₄Mo₆]₂ acts as a hexa-dentate ligand coordinating to four {Cu(H₂O)₃} fragments to form a 1-D inorganic chain (Fig. 1). In the packing arrangement, the adjacent 1-D chains are parallel with each other and are linked up together to form a 2D supramolecular layer in ABAB mode via strong supramolecular interactions among terminal phosphate O atoms of polyoxoanions (Fig. 2). The typical supramolecular interactions are 052...058 2.672 Å and 054...055 2.579 Å. Moreover, bbi ligand also acts as another linker to connect with phosphate O atoms of adjacent 1-D chains via supramolecular interactions (O65...N6 2.871 Å). The adjacent layers are further linked together by strong hydrogen-bonding interaction between O atoms of water molecules and surface O atoms of polyoxoanions to form 3-D supramolecular framework (Fig. S2). The typical hydrogen bonds are 014...02W 3.020(17) Å, 02W...046 2.638(17) Å, 034... 026 2.933(5) Å, 034...028 2.969(6) Å.

3.2.2. Structure description of 2

Compound **2** crystallizes in the triclinic space group P-1 and consists of sandwich-type Ni[P₄Mo₆]₂ unit, Ni(H₂O) linker,

protonated bbi ligands, and lattice water molecules (Fig. S3). There are four crystallographically independent nickel atoms (Ni1, Ni 2, Ni 3, and Ni 4). Ni(1) and Ni(2) bridge two $[Mo_6P_4]_2$ units via six O atoms which link the metal bonded Mo atoms together to produce the sandwich-like $Ni(1)[Mo_6P_4]_2$ and $Ni(2)[Mo_6P_4]_2$ clusters. Ni (3) and Ni(4) atoms have four-coordinated tetrahedron geometry which is defined by two peripheral phosphate O atoms from two Ni(1)[Mo₆P₄]₂, one central phosphate O atoms, and one water molecule with the distance of Ni-O 1.898(4)-2.212(4) Å. It is noteworthy that two kinds of Ni[P₄Mo₆]₂ clusters are not crystallographically identical, indicated as Ni(1)[P₄Mo₆]₂ and Ni(2) [P₄Mo₆]₂ respectively. The main difference between the two clusters is their arrangement in the crystal lattice along two different directions. In the structure, two kinds of sandwich cluster ${Ni[P_4Mo_6]_2}$ are linked by ${Ni(3)(H_2O)}$ or ${Ni(4)(H_2O)}$ linker to form infinite 1-D inorganic chain (Fig. 3). In the packing arrangement, the adjacent inorganic 1-D chains are bonded together to form a 2D supramolecular layer in ABAB mode via supramolecular interaction between terminal O atoms of phosphate and C atoms of protonated bbi (Fig. 4). The typical supramolecular interactions are C20...O44 3.144 Å, C32...O42 3.039, C14...O57 3.040, C4...O23 3.031, and O51...O65 2.453 Å. Furthermore, hydrogen bond and supermolecular interactions between oxygen atoms of water molecule and terminal oxygen atoms of polyanions are also found to stabilize the 3-D supramolecular framework (Fig. S4). The typical interactions are 045...05W 2.800(6) Å, 05W...029 3.422 (6), and O5W...O15 2.806 Å.

3.2.3. Structure description of 3

The single-crystal X-ray analysis reveals that compound **3** is composed of one discrete $Ni[P_4Mo_6]_2$ anions, mixed metal complexes



Fig. 2. The 2D supramolecular sheet of 1.



Fig. 3. Polyhedral and ball-and-stick representation of the 1-D chain of 2.



Fig. 4. The 2D supramolecular sheet of 2.



Fig. 5. (a) The 1-D metal–organic chains $[Ni(H_2O)_5Na(PCA)]n$ formed by Na⁺, Ni²⁺, and isonicotinic acid units (PCA); (b) the $[Ni(P_4Mo_6)]_2$ dimeric units are grafted on the double rails formed by four $[Ni(H_2O)_5Na(PCA)]n$ metal–organic chains via hydrogen bonds interactions.

chain {Ni₂(H₂O)₁₀Na(PCA)₂}, four 4,4'-bpy ligands, and six lattice water molecules (Fig. S5). In the mixed metal complexes chain $\{Ni_2(H_2O)_{10}Na(PCA)_2\}$, Ni2 atoms are in the center of a distorted octahedron, which is defined by five coordinated water molecules and one N atoms from PCA ligand with the average distance Ni-O 1.984 Å and Ni2-N3 1.987 Å. Na(1) atom has unusual fourcoordinated rectangle geometry which is defined by four oxygen atoms from two PCA organic ligands with the distance of Na1-O23, 2.22(5) Å. The O-Na-O angles are in the range 56.1(15)-123.4(2) Å. The PCA ligand acts as tri-dentate ligand coordinating with one Ni and one Na atom via coordination sites N and O. In this linkage mode, Na(1) links two symmetrical Ni(PCA)(H₂O)₅ fragments to generate dimeric chain {Ni₂(H₂O)₁₀Na(PCA)₂} unit. The adjacent dimeric chain unit are aggregated together via strong supramolecular interactions between two symmetrical O atoms of Ni(PCA)(H₂O)₅ fragments to form infinit 1D polymeric chains (Fig. 5a). Each Ni[P₄Mo₆]₂ anions as a pendent ligand is bonded to four parallel polymeric chains via hydrogen bond with 016...021 2.83(3) and 09...022 2.77(4) Å (Fig. 5b and Fig. S6). Meanwhile, each Ni[P₄Mo₆]₂ polyoxoanion connects to adjacent four dimeric cluster via supramolecular interactions (O17...O18 2.597 Å) to lead a 2D supramolecular layer along a axis (shown in Fig. 6a). In this mode, parallel polymeric chains are joined together by Ni[P₄Mo₆]₂ spheres to build up a rail-liked chain, in which the $Ni[P_4Mo_6]_2$ acts as the middle train. Thus, compound 3 exhibits a novel 2-D supramolecular sheet structure constructed by Ni [P₄Mo₆]₂ polyoxoanions and 1-D polymeric chains (Fig. 6b). Furthermore, these adjacent layers are further linked together by weak interaction between surface O atoms of polyoxoanions to form 3-D supramolecular framework (Fig. S7). Typical supramolecular interaction is 012...023 2.821 Å.

3.3. Spectroscopic and thermal analyses

The IR spectra of compounds **1–3** exhibit the similar characteristic peaks (Fig. S8a–c). The peaks at 615, 733, 964, and 1036 cm⁻¹ for **1**, 682, 744, 962, and 1051 cm⁻¹ for **2**, 625, 747, 967, and 1016 cm⁻¹ for **3** are attributed to ν (Mo–Oc–Mo), ν (Mo–Ob–Mo), ν (Mo=Od), and ν (P–O) respectively of the P₄Mo₆ polyanions. The peaks at 1152, 1440, 1637 for **1**, 1120, 1508, and 1632 cm⁻¹ for **2** correspond to ν (C=N) vibrations of protonated bbi ligands. The peaks at 1646 and 1509 of **3** correspond to ν_{as} (COO) and ν_{s} (COO) of PCA, respectively. The peaks at 1125 cm⁻¹ in **3** are associated with ν (C=N) vibrations of PCA and bpy ligands. Furthermore, the broad peaks between 3430–3264 cm⁻¹ can be assigned to ν (N–H) and/or ν (O–H) of the protonated ligands and isolated solvent water molecules.

The simulated PXRD patterns of the three compounds were obtained by rietveld refinement on the basis of the crystallographic files. The simulated and experimental PXRD patterns of them in the angular region $5-50^{\circ}$ are shown in Fig. S9. We see that the diffraction peaks of both simulated and experimental patterns of **1–3** match in the key positions, respectively, indicating the phase purities of the four compounds. The differences in intensity may be due to the preferred orientation of the powder samples.

In the UV spectra of **1–3** (Fig. S10), the two strong bands in the range of 220–240 nm and 270–290 nm are attributed to (LMCT) $p\pi$ (O_{terminal}) $\rightarrow d\pi^*$ (Mo) electronic transitions in the Mo=O bonds and $d\pi$ – $p\pi$ – $d\pi$ electronic transitions between the energetic levels of the Mo–O–Mo bonds, respectively. The broad bands near 520–550 nm are assigned to the intervalence charge transfer (IVCT) in reduced polyoxoanions [42]. The bond displacement comparing literature may relate to the effect of polyanions and their different chemical environments of hybrid framework.

Thermogravimetric analyses of compound 1-3 were investigated under N₂ atmosphere from 50 °C to 900 °C, and the TG curves are shown in Fig. S11a-c. In the TG curve of compound 1. the first weight loss of 8.32% in the temperature of 180–245 °C are attributed to three lattice water molecules, six coordinated water molecules and six composition water molecules in compound 1 (calculated value 8.15% for 15H₂O). The second weight loss of 17.17% between 285 and 580 °C arises from the loss of bbi organic ligands. The value is close to the calculated value of 17.21% (for 3 bbi). The overall weight loss of 25.49% is accordant with the calculated value of 25.36%. For 2, the first weight losses of 9.26% (calculated value 9.18%) at 180–290 °C correspond to the loss of all lattice, coordinated and composition water molecules (17H₂O). The second step in the range of 308–560 °C is attributed to the decomposition of bbi organic ligands. (calc. weight loss: 17.10%; found: 16.89%). For 3, the first losses of 10.63% (calculated value 10.56%) at 180-280 °C correspond to the loss of all lattice, coordinated and composition water molecules (22H₂O). The second and third weight loss of 23.76% at 320-525 °C is related to the loss of all 4,4'-bpy and PCA ligands (calculated value 23.89%). All the weight losses from the TG curves are accordant with the molecular formula of compound 1-3.

3.4. Electrochemical and electrocatalysis properties

The electrochemical behaviors of compounds **1–3** were investigated with a **1**, **2**, and **3**-modified carbon paste electrodes (**1**, **2**, and **3**-CPE) due to the insolubility of compounds **1–3** in water and common organic solvents. The cyclic voltammetric (CV) behaviors for **1**, **2**, and **3**-CPE in 1.0 M H₂SO₄ aqueous solution at different scan rates were recorded (Fig. S12). There exist three or four reversible redox peaks with the half-wave potentials $E_{1/2} = (Epa + Epc)/2$ at -0.42(I-I'), 0.03(II-II'), and 0.38(III-III') V for **1**, -0.38(I-I'), 0.06(II-II'), and 0.46(III-III') V for **2**, and -0.64(I-I'), -0.37(II-II'), -0.08(III-III') and 0.44(IV-IV') for **3**, respectively (the scan rate of 40 mV/s), which attributes to the redox processes of Mo [43,44]. Note that there should exist a redox peak



Fig. 6. (a) The 2D supramolecular layer of $[Ni(P_4Mo_6)]_2$ dimeric anion. (b) The POMMOF supramolecular layer based on $[Ni(P_4Mo_6)]_2$ dimeric units and 1-D metal–organic chains $[Ni(H_2O)_5Na(PCA)]_1$ via supermolecular and hydrogen bonds interactions.

in 100-200 mV attributed to Cu(II) or Ni(II) for the compounds, which was not observed, may be due to the overlap of Mo redox peak. The CV peak positions of compound **3** are different from those in compounds 1 and 2, which may be due to the different extending structural topologies. Moreover, the cathodic peak potentials of all three compounds 1-3 shift toward the negative direction and the corresponding anodic peak potentials shift to the positive direction with increasing scan rates, as shown in Fig. S12. The peak potentials change gradually following the scan rate from 20 to 500 mV s^{-1} . Furthermore, the peak-to-peak separations between the corresponding anodic and cathodic peaks increased, but the average peak potentials do not change on the whole. The plots of anodic peak current(II) vs. scan rates (see inset plots in Fig. S12) indicate that the redox process of 1- and 2-CPE are surface-controlled, while 3-CPE is surface-controlled below the scan rate of 150 mV s^{-1} , while at scan rates higher than 150 mV s⁻¹, the peak currents were proportional to the square root of the scan rate, suggesting that redox processes are diffusioncontrolled [45,46]. It is also noteworthy that **1–3**-CPE possesses the high stability. When the potential range is maintained between -1.0 and 1.0 V, the peak currents remains almost unchanged over 300 cycles at a scan rate of 100 mV s^{-1} .

Furthermore, **1–3**-CPE displays good electrocatalytic activity on reduction of hydrogen nitrite (Fig. 7). At the **1–3**-CPE, with the addition of NaNO₂, all reduction peak currents increased while the corresponding oxidation peak currents dramatically decreased, suggesting that NaNO₂ was reduced by all four reduced polyoxoanion species [47]. It has been noted that the catalytic activities were enhanced with the increasing extent of the anion reduction.

3.5. Magnetic properties

The variable temperature magnetic susceptibility of **1–3** were measured from 300 to 2 K at 1000 Oe and plotted as $\chi_m T$ and χ_m versus *T*, as shown in Fig. 8. The $\chi_m T$ vs *T* curves of compound **1** show value of 0.35 cm³ K mol⁻¹ at 300 K and continuously

decrease with cooling of the temperature, as shown in Fig. 8a. The effective number of Bohr magnetons (determined from equation $\mu_{\text{eff}}=2.828(\chi_m T)^{1/2})$ per formula unit at 300 K ($\mu_{\text{eff}}=1.67 \mu_B$), is much lower than the expected value ($\mu_{\text{eff}}=3 \mu_B$) for **3** uncoupled Cu^{II} ions (S=1/2, g=2.00), but close to the expected value ($\mu_{eff}=1.73 \mu_B$) for **1** uncoupled Cu^{II} ions (S=1/2, g=2.00). This result suggests that there exist antiferromagnetic interactions in compound **1**. The $1/\chi_{\rm M}$ vs *T* curves of **1** are consistent with the Curie–Weiss law $[\chi_m = C/(T\theta)]$ with the C=0.43 cm³ K mol⁻¹, $\theta = -71.25$ K (Fig. S13a). The negative Weiss constants also indicate antiferromagnetic interactions in compound **1**. The magnetic behaviors of compound **2** and **3** are shown in Fig. 8b and c. The $\chi_m T$ products of 2.78 cm³ K mol⁻¹ and 2.68 cm³ K mol⁻¹ at 300 K, respectively (μ_{eff} =4.72 μ_B for **2** and μ_{eff} =4.63 μ_B for **3**), are a little smaller than the expected value $(\mu_{\text{eff}}=4.90 \,\mu_{\text{B}})$ for 3 uncoupled Ni^{II} ions (S=1, g=2.00). On cooling, the $\chi_m T$ value of **2** and **3** decreases continuously indicating antiferromagnetic interaction in 2 and 3. Between 100 K and 300 K, the magnetic behaviors obey the Curie-Weiss law with $C = 2.83 \text{ cm}^3 \text{ K mol}^{-1}$, $\theta = -7.60 \text{ K for } 2$ and $C = 2.78 \text{ cm}^3 \text{ K mol}^{-1}$, $\theta = -11.82$ K for **3** suggesting the presence of weak antiferromagnetic interactions in the whole compounds (Fig. S13b and c). Although valence states of Mo atoms are +5 in compounds of 1-3, owing to formation of Mo-Mo metal bonds they have no contribution to magnetism of compound **1–3** [48].

4. Conclusions

In this paper, we report three organic–inorganic hybrid supramolecular materials. In compounds **1** and **2**, as new linking unit, $Cu(H_2O)_3$ and $Ni(H_2O)$ cations are introduced into the {TM $(P_4Mo_6)_2$ } reaction systems, leading to the assembly of two novel covalent 1-D chains, which are further extended into 3-D supramolecular materials via hydrogen bond and supermolecular



Fig. 7. Cyclic voltammograms of 1-, 2-, and 3-CPE in 1 M H₂SO₄ solution containing nitrite at different concentrations (Potentials vs. SCE. Scan rate: 60 mV s⁻¹).



Fig. 8. Plot of χ_m and $\chi_m T$ versus *T* for for **1** (a), **2** (b), and **3** (c).

interactions among bbi ligand, polyanion clusters, and water molecules. Compound **3** exhibits a novel 2-D supramolecular sheet structure constructed by $Ni[P_4Mo_6]_2$ polyoxoanions and 1-D polymeric chains $[Ni(H_2O)_5Na(PCA)]_n$. Furthermore, Electrochemical analysis shows that **1–3-**CPE displays unique redox properties

and good electrocatalytic activity to reduce nitrite. Magnetic investigations reveal that compounds 1-3 exhibit antiferromagnetic interactions between the metal centers. This works enrich {P₄Mo₆}-based inorganic–organic hybrid materials and provide useful prototype for design and synthesis of hybrids.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jssc.2014.05.010.

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