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# Introduction

Isopolymolybdates are important members of the polyoxometalate (POM) family, and they have been the focus of materials scientists in recent decades to build multifunctional complexes because of their tailored structures and broad range of applications in medicine, chiral materials, lithium-ion batteries, electro-catalysts, photo-catalysts, supercapacitors, and so on.<sup>1</sup> Isopolymolybdates can be divided into two types of building units in reported POM materials: huge Mo and small Mo clusters, for example, { $Mo_{132}$ } type Keplerate clusters are first reported by Müller *et al.*, using medium ratios of [ $Mo^V$ ]/ [ $Mo^{VI}$ ] atoms present in ammonium molybdate;<sup>2</sup> T. Yamase carried out the photoreductive self-assembly of [ $Mo_7O_{24}$ ]<sup>6–</sup> to

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# Four new dual-functional electro-catalysts formed from small molybdenum clusters and Cu-pyridyl complexes†

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By changing N-heterocyclic ligands in the same Mo<sub>7</sub>/Cu/N-ligand reaction systems, four new organicinorganic hybrids based on isopolymolybdates,  $[Cu_2(tpy)_2(\beta-Mo_8O_{26})_{0.5}(\gamma-Mo_8O_{26})_{0.5}] \cdot 0.25H_2O$  (1),  $[Cu_2(tpy)_2(H_2O)_2(\beta-Mo_8O_{26})]$  (2),  $[Cu(bpy)(Mo_3O_{10})] \cdot H_2O$  (3), and  $[Cu(bpy)(H_2O)(\beta-Mo_8O_{26})_{0.5}]_{0.5}$  (4) (tpy = 2,2':6',2"-terpyridine and bpy = 2,6-bis(pyrazol-1-yl) pyridine), were prepared using hydrothermal methods at different pH values. X-ray structural analysis shows that compound 1 has a 1D {- $\beta$ -[Mo\_8O\_{26}]-Cu<sub>2</sub>- $\gamma$ -[Mo\_8O\_{26}]\_n straight chain structure with mixed  $\beta$ -[Mo\_8O\_{26}] and  $\gamma$ -[Mo\_8O\_{26}] polyoxoanions; compound 2 possesses a 3D supramolecular structure based on  $[Cu(tpy)]^{2+}$  motifs and  $\beta$ -[Mo\_8O\_{26}] clusters; and compound 3 has a 1D chain structure built from  $[Cu(bpy)]^{2+}$  and  $[Mo_3O_{10}]^{2-}$  units. In compound 4, [ $\beta$ -Mo\_8O\_{26}] clusters are linked by  $[Cu(bpy)]^{2+}$  motifs to give rise to a 2D sheet structure including {( $\beta$ -Mo\_8O\_{26})\_4Cu\_4} 8-membered rings. Cyclic voltammograms of compounds 1-4 display discrepant dual-functional electro-catalytic activities toward the reduction of nitrite and the oxidation of ascorbic acid in acidic solution. Electrocatalytic tests indicate that the  $[Mo_3O_{10}]^{2-}$ -based organic-inorganic hybrid exhibits better electro-catalytic performances than  $[Mo_8O_{26}]^{4-}$ -type hybrids towards oxidation and reduction.

> obtain a carboxylate-coordinated {Mo142} Mo-blue nanoring in the presence of carboxylic acids,<sup>3</sup> and so on. Small Mo clusters include octamolybdates ( $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ,  $\varepsilon$ ,  $\zeta$ ,  $\eta$  and  $\theta$ -type  $[Mo_8O_{26}]^{4-1}$ clusters), Mo<sub>6</sub> clusters,<sup>4</sup> and the like. Cu is also an important d<sup>10</sup> transition metal owing to its widespread application in catalysis for organic synthesis. For instance, S. L. Buchwald et al. prepared a Cu-based catalyst for the X-arylation (X = O, N) of aminophenols;<sup>5</sup> Shi et al. reported the cuprous catalyzed diamination of conjugated dienes;<sup>6</sup> A. Leyva-Pérez et al. reported C-X (X = N, C, O, S, P) bond-forming reactions through Cu clusters within a polymeric film;<sup>7</sup> Zhang et al. reported asymmetric nitrone synthesis by using ligand-enabled copper-catalyzed hydroamination of cyclopropene,<sup>8</sup> and so on. A feasible strategy to prepare organic-inorganic hybrids is to utilize small Mo clusters/mixed Mo clusters and transition metals linked by flexible N-donor ligands as building units, through a one-pot method,<sup>9</sup> as these kinds of hybrids show concerted catalysis including fragments of isopolymolybdates and Cu-organic complexes. In this work, we select (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O, hydrated copper nitrate, and tpy/bpy as starting materials to generate small Mo clusterbased organic-inorganic hybrid compounds. Four new compounds,  $[Cu_2(tpy)_2(\beta-Mo_8O_{26})_{0.5}(\gamma-Mo_8O_{26})_{0.5}] \cdot 0.25H_2O$  (1),  $[Cu_2(tpy)_2(H_2O)_2(\beta MO_8O_{26})]$  (2),  $[Cu(bpy)(MO_3O_{10})] \cdot H_2O$  (3),



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<sup>†</sup>Electronic supplementary information (ESI) available. Crystal data and struc-

ture refinement for compounds 1–4. Selected bond lengths and angles, IR spectra, TG curves, PXRD patterns, CVs and CAT% data obtained for compounds 1–4. CCDC 1950999–1951002. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/C9DT03560E

and  $[Cu(bpy)(H_2O)(\beta-Mo_8O_{26})_{0.5}]_{0.5}$  (4), were obtained by the hydrothermal method. The electrochemistry and electro-catalytic properties of compounds 1–4 have also been studied by cyclic voltammetry.

## Experimental

All the reagents purchased were of reagent grade and used without further purification. Elemental analyses of C, H and N were performed on a Perkin-Elmer 2400 CHN elemental analyzer. Elemental analyses of Cu and Mo were performed on a Leeman inductively coupled plasma (ICP) spectrometer. IR spectra were recorded on a Nicolet 6700 FTIR spectrometer with KBr pellets in the range of 4000-400 cm<sup>-1</sup>. Thermogravimetric (TG) analyses were carried out in a N2 environment on a Diamond TG analyzer from 50 °C to 1000 °C at a rate of 10 °C min<sup>-1</sup>. Powder X-Ray Diffraction (PXRD) was performed on a Bruker D2 Phaser diffractometer equipped with a monochromatic Cu-K $\alpha$  ( $\lambda$  = 1.5418 Å) radiation source in the range of  $5 \le 2\theta \le 50$ , at a scanning rate of  $4^{\circ}$  s<sup>-1</sup>. Fieldemission scanning electron microscopy (FE-SEM) was performed to investigate the crystal surface by using a Hitachi SU-8010 FE-SEM. Cyclic voltammograms were obtained with a CHI-660E electro-chemical workstation at ambient temperature, with a platinum wire as the counter electrode, an Ag/AgCl electrode as the reference electrode, and the carbon paste electrode (CPE) modified with compounds 1-4 as working electrodes. The electrochemical and electro-catalytic properties of 1-4-CPEs were studied in a 1 M  $H_2SO_4$  +  $Na_2SO_4$  supporting electrolyte (pH = 1) through CV measurements in the potential range from +300 to -1000 mV at a scan rate of 0.1 V s<sup>-1</sup>.

The *n*-CPEs (n = 1-4) were processed as follows: 0.01 g of compounds 1–4 and 0.10 g of carbon dust were mixed and ground together to form a homogeneous mixture, into which two drops of paraffin oil was added with stirring. The such-obtained paste was packed into a glass tube with 2.0 mm inner diameter, and the surface was wiped with smooth paper. Electrical contact was established with a thin copper rod through the back of the electrode.

Selected good single crystals were fixed onto thin glass fibers by epoxy glue for data collection. Diffraction data were collected on a Bruker D8 Quest Eco CCD with Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The structures of the crystals were solved through the direct method and refined by full-matrix least-squares on  $F^2$ . All calculations were performed using the SHELX-2014/7 program package.<sup>10</sup> All the Mo, Cu, O, C and N atoms were anisotropically refined except for H atoms. Further details of the X-ray structural analysis of compounds 1–4 are given in Table S1<sup>†</sup> and the selected bond lengths and angles are listed in Tables S2–S5.<sup>†</sup>

#### $[Cu_{2}(tpy)_{2}(\beta - Mo_{8}O_{26})_{0.5}(\gamma - Mo_{8}O_{26})_{0.5}] \cdot 0.25H_{2}O(1)$

A mixture of  $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$  (0.1500 g),  $Cu(NO_3)_2\cdot 6H_2O$  (0.1200 g) and tpy (0.0430 g) was dissolved in 7 mL of distilled water and stirred for 1 h. The pH was adjusted to 4.30 with

HCl (2 M), and the resulting suspension was sealed in a 25 ml reaction still and heated at 433 K for 5 days. Blue crystals were obtained (0.0230 g, yield 4.65% based on Mo). Elemental analysis for  $C_{30}H_{22.50}N_6O_{26.25}Cu_2Mo_8$ : found (calcd) (%): Mo 42.80 (43.08), Cu 7.00 (7.13), C 20.00 (20.21), H 1.35 (1.26), N 4.50 (4.72). IR (cm<sup>-1</sup>): 3450 (s), 3123 (w) 1586 (s), 1509 (s), 1315 (s), 1252 (s), 1134 (m), 1078 (s), 940 (s), 890 (s), 850 (s), 703 (s) 640 (s) 703 (w).

#### $[Cu_2(tpy)_2(H_2O)_2(\beta-Mo_8O_{26})](2)$

Compound 2 was prepared by a method similar to that of compound 1, except that pH was adjusted to 4.10. Blue crystals were harvested (0.0200 g, yield 7.95% based on Mo). Elemental analysis for  $C_{30}H_{26}N_6O_{28}Cu_2Mo_8$ : found (calcd) (%): Mo 41.70 (42.33), Cu 6.50 (7.00), C 20.00 (19.85), H 1.30 (1.43), N 4.50 (4.63). IR (cm<sup>-1</sup>): 3560 (s), 1605 (s), 1475 (s), 1328 (s), 1088 (m), 943 (s), 882 (s), 720 (s), 550 (m).

#### [Cu(bpy)(Mo<sub>3</sub>O<sub>10</sub>)]·H<sub>2</sub>O (3)

A mixture of  $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$  (0.1480 g),  $Cu(NO_3)_2 \cdot 6H_2O$ (0.1300 g) and bpy (0.0450 g) was dissolved in 7 mL of distilled water and stirred for 1 h. The pH of the solution was adjusted to 4.50 with HCl (2 M), and the resulting suspension was sealed in a 25 ml-reaction still and heated at 433 K for 5 days. Green crystals were harvested (0.0020 g, yield 5.22% based on Mo). Elemental analysis for  $C_{11}H_{11}N_5O_{11}CuMO_3$ : found (calcd) (%): Mo 37.60 (38.86), Cu 9.00 (8.57), C 18.00 (17.82), H 1.40 (1.49), N 9.50 (9.45). IR (cm<sup>-1</sup>): 3490 (s), 3122 (m), 1610 (s), 1571 (s), 1490 (s), 1405 (s), 1349 (s), 1216 (m), 1167 (m), 1050 (s), 978 (s), 917 (s), 882 (s), 790 (s), 650 (s), 527 (s).

#### $[Cu(bpy)(H_2O)(\beta-Mo_8O_{26})_{0.5}]_{0.5}$ (4)

The same synthetic method as for 3 was used except for pH = 4.70. Blue crystals were obtained (0.0220 g, yield 9.02% based on Mo). Elemental analysis for  $C_{11}H_9N_5O_{14}CuMo_4$ : found (calcd) (%): Mo 44.00 (43.48), Cu 7.00 (7.20), C 15.00 (14.96), H 0.95 (1.02), N 8.00 (7.93). IR (cm<sup>-1</sup>): 3428 (m), 1620 (s), 1460 (m), 1397 (s), 1342 (s), 1167 (s), 1050 (s), 507 (s), 458 (m).

### Results and discussion

Fig. 1 shows the SEM images of compounds 1–4, in which block-like crystals represent the title compounds. Single-crystal X-ray diffraction analyses indicate that compound 1 consists of mixed Mo<sub>8</sub> clusters (γ-Mo<sub>8</sub>O<sub>26</sub> and β-Mo<sub>8</sub>O<sub>26</sub>) and two  $[Cu(tpy)]^{2+}$  motifs with a 1D straight chain and crystallizes in the triclinic space group  $P\overline{1}$ . As shown in Fig. 2, the asymmetric unit of compound 1 contains two copper ions, two tpy ligands, γ-Mo<sub>8</sub>O<sub>26</sub>, β-Mo<sub>8</sub>O<sub>26</sub> clusters and one dissociative water molecule. The γ-[Mo<sub>8</sub>O<sub>26</sub>]<sup>4-</sup> cluster consists of six distorted {MoO<sub>6</sub>} octahedra and two distorted {MoO<sub>5</sub>} pentahedra including four kinds of O atoms: two  $\mu_4$ -O, four  $\mu_3$ -O, six  $\mu_2$ -O and fourteen O<sub>t</sub> atoms.<sup>11</sup> The β-[Mo<sub>8</sub>O<sub>26</sub>]<sup>4-</sup> anion included two centro-symmetric [Mo<sub>4</sub>O<sub>13</sub>]<sup>2-</sup> interleaving units linked *via* a bridging oxygen atom. Each [Mo<sub>4</sub>O<sub>13</sub>]<sup>2-</sup> unit was made up of



Fig. 1 SEM images of compounds 1-4.



**Fig. 2** Ball/stick view of the asymmetric unit of compound **1**. The hydrogen atoms and crystallization water molecules are omitted for clarity. Symmetry operation: #1 - x, 1-y, 1-z; #2 - 1-x, -y, 2-z.

four {MoO<sub>6</sub>} edge-sharing octahedra. The oxygen atoms of the  $\beta$ - $[Mo_8O_{26}]^{4-}$  anion could be divided into four groups according to their bonding features, namely, Ot atoms with Mo-O distances of 1.685–1.973 Å,  $\mu_2$ -O atoms with Mo–O distances of 1.751-2.290 Å, µ<sub>3</sub>-O atoms with Mo-O distances of 2.006–2.275 Å, and a  $\mu_5$ -O atom (O12) with a Mo–O distance of 2.290 Å. The average Mo-O distance of these four groups was 1.722, 2.057, 2.010 and 2.290 Å, respectively. The result showed that these  $\{MoO_6\}$  polyhedra were distorted octahedra. In the asymmetric unit, there are two crystallographically independent copper atoms (Cu1 and Cu2), which exhibit the same coordination geometries. The two Cu atoms are five-coordinated in a square pyramidal geometry by three N atoms from a tpy ligand and two oxygen atoms from  $\gamma$ -Mo<sub>8</sub>O<sub>26</sub> and  $\beta\text{-}Mo_8O_{26}$  clusters, completed by N1, N2, N3, O1, and O2 atoms for the Cu1 atom and N3, N4, N5, O3, and O4 atoms for the Cu2 atom. The bond distances and angles around Cu1 are 1.85(3)-1.91(3) Å (Cu1-N), 2.561 Å (Cu1-O1), 174.21(4)° (N-Cu1-N), and 90.36-95.33° (N-Cu1-O1) and the bond distances and angles around Cu2 are 1.82(3)-1.89(3) Å (Cu2-N), 2.785 Å (Cu2-O2), 178.63° (N-Cu2-N), and 86.61-92.43° (N-Cu2-O1).



**Fig. 3** The1D straight chain of  $\{-\gamma-Cu_2Mo_8O_{26}-Cu-\beta-Mo_8O_{26}-\}_n$  in compound **1** along the *c*-axis.

The 1D straight chain of compound **1** is featured by two moieties: {γ-Cu<sub>2</sub>Mo<sub>8</sub>O<sub>26</sub>} clusters and the β-octamolybdate anion  $[Mo_8O_{26}]^{4-}$  (Fig. 3). Firstly,  $[Cu1(tpy)]^{2+}$  and its crystallographic partners are linked by γ-Mo<sub>8</sub>O<sub>26</sub> through Cu1–O1–Mo5 and Cu1–O2–Mo6 bridges to form {γ-Cu<sub>2</sub>Mo<sub>8</sub>O<sub>26</sub>} clusters. Secondly, {γ-Cu<sub>2</sub>Mo<sub>8</sub>O<sub>26</sub>} clusters and β-Mo<sub>8</sub>O<sub>26</sub> are linked by  $[Cu2(tpy)]^{2+}$  alternately by using Cu2–O3–Mo1 and Cu2–O4–Mo4 bonds leading to a 1D straight chain of {-γ-Cu<sub>2</sub>Mo<sub>8</sub>O<sub>26</sub>-n.

As shown in Fig. 4, the asymmetric unit of compound 2 consists of one Cu ion, a  $[\beta-Mo_8O_{26}]^{4-}$  anion, a tpy ligand and one crystallization water molecule. Cu1 is five-coordinated in a square pyramidal geometry by three N atoms (N1, N2, and N3) from one tpy ligand and two oxygen atoms (O1 and O1 W) from  $\beta-Mo_8O_{26}$  clusters and the water molecule. The distances/Å for Cu1 are: Cu1–N1 = 2.021(8), Cu1–N2 = 1.932(8), Cu1–N3 = 2.015(8), Cu1–O1 W = 1.969(7), and Cu1–O1 = 2.227(6) and the angles/° for Cu1 are: N1–Cu1–N2 = 80.3(3), N2–Cu1–N3 = 80.2(4), and N3–Cu1–O1 W = 97.1(3).

The 3D supramolecular structure of compound **2** stems from two building units:  $[Cu1(tpy)]^{2+}$  and  $\beta$ - $[Mo_8O_{26}]^{4-}$  anions (Fig. 5). Firstly,  $[Cu1(tpy)]^{2+}$  and its crystallographic partners are linked by  $\beta$ -Mo<sub>8</sub>O<sub>26</sub> through Cu1–O1–Mo2 bonds to form a { $\beta$ -Mo<sub>8</sub>O<sub>26</sub>Cu<sub>2</sub>} unit. Secondly, the adjacent { $\beta$ -Mo<sub>8</sub>O<sub>26</sub>Cu<sub>2</sub>} units are linked *via* O–H···O interactions to form a 3D supramolecular structure.

As shown in Fig. 6, the asymmetric unit of compound 3 consists of one Cu ion, a  $[Mo_3O_{10}]^{2-}$  unit, a bpy ligand and one water molecule. Cu1 is five-coordinated in a square pyramidal geometry by three N atoms (N1, N2, and N3) from one



Fig. 4 Ball/stick view of the asymmetric unit of compound 2. The hydrogen atoms and crystallization water molecules are omitted for clarity. Symmetry operation: #12-x, -y, 1-z.



Fig. 5 View of the 3D supramolecular structure of compound 2.



Fig. 6 Ball/stick view of the asymmetric unit of compound 3. The hydrogen atoms and crystallization water molecules are omitted for clarity. Symmetry operation: #1 - 1 - x, 1 - y, 1 - z.

bpy ligand and two oxygen atoms (O1 and O2) from Mo1O<sub>6</sub> and Mo2O<sub>6</sub> clusters. The distances/Å for Cu1 are: Cu1–N1 = 2.013(3), Cu1–N2 = 1.987(3), Cu1–N3 = 1.948(3), Cu1–O1 = 1.893(3), and Cu1–O2 = 2.347(3) and the angles/° for Cu1 are: O1–Cu1–N2 = 97.20(13), N2–Cu1–N3 = 79.06(14), and N1–Cu1–O1 = 101.99(13). The  $[Mo_3O_{10}]^{2-}$  cluster consists of three distorted {MoO<sub>6</sub>} octahedra including two kinds of O atoms: four  $\mu_3$ -O (O3, O6, O7 and O8) and six O<sub>t</sub> (O1, O2, O4, O5, O9, and O10). The bond lengths of Mo–O (1.701–2.280 Å) are in a reasonable range.

As shown in Fig. S1,<sup>†</sup> two Mo atoms (Mo1 and Mo2) and their crystallographic partners are linked by Mo3 through four  $\mu_3$ -O (O3, O6, O7, and O8) to build a Mo<sub>5</sub> cluster; the adjacent Mo<sub>5</sub> clusters are linked by Mo3's partners to form an infinite molybdenum oxide chain along the *a*-axis, and Cu1(bpy) and its crystallographic partners are added to reinforce it through Mo2–O1–Cu1 and Mo1–O2–Cu1 bonds (Fig. 7).

As shown in Fig. 8, the asymmetric unit of compound 4 contains one Cu ion, a  $[\beta - Mo_8O_{26}]^{4-}$  anion, the bpy ligand and water molecules. The Cu1 ion is six-coordinated in a distorted octahedron geometry defined by three N atoms (N1, N2, and N3) from one bpy ligand, three O atoms (O1 and O2) from  $\beta$ -Mo<sub>8</sub>O<sub>26</sub> and one from the water molecule (O1 W). The dis-



Fig. 7 The infinite molybdenum oxide chain in compound 3.



**Fig. 8** Ball/stick view of the asymmetric unit of compound 4. The hydrogen atoms and crystallization water molecules are omitted for clarity. Symmetry operation: #1 x, 1.5 - y, 0.5 + z; #2 1 - x, 1 - y, 2 - z; #3 1 - x, -0.5 + y, 1.5 - z.

tances/Å for Cu1 are: Cu1–N1 = 1.951(16), Cu1–N2 = 2.019(19), Cu1–N3 = 1.99(2), Cu1–O1 W = 1.949(15), Cu1–O1 = 2.341(16), and Cu1–O2 = 2.532 and the angles/° for Cu1 are: O1 W–Cu1– N1 = 169.0(7), O1 W–Cu1–N3 = 104.8(7), N1–Cu1–N3 = 78.9(8), and N1–Cu1–N2 = 79.3(7). Bond valence sum calculations<sup>12</sup> for compounds 1–4 indicate that all the Mo atoms are in the +vi oxidation state and copper atoms in the +ii oxidation state.

The 2D sheet structure of compound **4** is featured by two subunits:  $[Cu1(bpy)]^{2^+}$  units and  $\beta$ -Mo<sub>8</sub>O<sub>26</sub> clusters. One bpy ligand is connected by Cu1 atoms coordinated to three N atoms (N1, N2, and N3) to generate a  $[Cu1(bpy)]^{2^+}$  group. The  $\beta$ -Mo<sub>8</sub>O<sub>26</sub> anion acts as a four-connected inorganic ligand to coordinate with Cu1 to form Mo–O–Cu1 bridges, leading to a 2D sheet structure with {( $\beta$ -Mo<sub>8</sub>O<sub>26</sub>)<sub>4</sub>Cu<sub>4</sub>} 8-membered rings (Fig. 9).

Generally, hydrothermal reaction systems are regarded as a riddle, in which many conditions can affect reaction mechanisms and conformations of final products. As shown in Fig. 10, in this work, compounds 1–4 were obtained under the same reaction conditions, except for organic ligands and pH: tpy for compounds 1 and 2 and bpy for compounds 3 and 4. Parallel experiments showed that pH and organic ligands are crucial for the formation of the title compounds 1–4. Compounds 1 and 2 with two different structures were

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Fig. 9 The 2D sheet structure of compound 4.



Fig. 10 Illustration of the structural features of compounds 1–4 generated at different pH values and using different organic ligands.

obtained in the same Cu/POM/tpy reaction process except for different pH values. Compound 1 was obtained at a higher pH value (4.30). When the pH value was decreased, a mixture of compounds 1 and 2 was obtained. By further decreasing the pH to 4.10, only compound 1 was isolated. The ligand tpy and copper ions exhibit the same coordination modes in compounds 1 and 2: two types of mixed Mo<sub>8</sub> clusters ( $\gamma$ -Mo<sub>8</sub>O<sub>26</sub> and  $\beta$ -Mo<sub>8</sub>O<sub>26</sub>) in 1 and only the  $\beta$ -Mo<sub>8</sub>O<sub>26</sub> anion in 2; tpy acts as a tridentate ligand coordinated to Cu<sup>2+</sup> ions that are coordinated to three N atoms in 1 and 2, and although the copper ions in compounds 1 and 2 are all five-coordinated, the coordinated atoms are different. Similar to 1 and 2, compound 4 was obtained at a higher pH value (4.70). When the pH value was decreased to 4.50, compound 3 was obtained. Cu1 exhibits different coordination modes, five-coordinated for 3 and sixcoordinated for 4. The connection mode of molybdenum atoms in these two compounds is different, an infinite molybdenum oxide chain in 3 and  $\beta$ -Mo<sub>8</sub>O<sub>26</sub> clusters in 4. It can be concluded that different pH values not only influence the formation of compounds 1-4, but also affect the types of small molybdenum clusters as well as their final structures. Among the organic N-donor ligands, tpy and bpy as rigid ligands usually exhibit  $\mu_3$  coordination modes to link transition metals to give transition metal-organic complexes through three neighbouring N-donors. The difference is that the alkalinity of bpy is higher than tpy owing to diverse molecular groups, three pyridine rings in tpy and one pyridine ring and two imidazole rings in bpy. We find that higher pH allows for obtaining a higher dimensional structure, a 0D discrete structure for compound 2, 1D chain structures for compounds 1 and 3; and a 2D sheet structure for compound 4.

The IR spectra of compounds 1–4 are shown in Fig. S2.† In the spectra, the characteristic bands at 645, 842, and 945 cm<sup>-1</sup> for 1, 640, 855, and 922 cm<sup>-1</sup> for 2, 655, 877, and 921 cm<sup>-1</sup> for 3 and 665, 789, and 950 cm<sup>-1</sup> for 4 are ascribed to  $\nu$ (Mo=O<sub>t</sub>) and  $\nu$ (Mo–O–Mo) of the [Mo<sub>8</sub>O<sub>26</sub>]<sup>4–</sup>/[Mo<sub>3</sub>O<sub>10</sub>]<sup>2–</sup> anion, respectively. The bands in the regions of 1076–1623 cm<sup>-1</sup> for 1, 1025–1602 cm<sup>-1</sup> for 2, 1060–1614 cm<sup>-1</sup> for 3 and 1177–1629 cm<sup>-1</sup> for 4 can be assigned to the N-heterocyclic ligand. The bands at around 3400 cm<sup>-1</sup> are due to the water molecules.

The TG curves of **1–4** show roughly two steps of weight loss. A total weight loss of *ca.* 28.0% in the range of 50–800 °C corresponds to the loss of the water molecules and organic ligands, in detail, 27.8% (calculated 27.0%) for compound **1**, 24.6% (calculated 26.5%) for compound **2**, 30.5% (calculated 30.9%) for compound **3**, and 26.0% (calculated 24.8%) for compound **4** (Fig. S3).†

To indicate the phase purities of compounds **1–4**, PXRD experiments were carried out. As shown in Fig. S4,<sup>†</sup> the experimental and simulated patterns of XRD for compounds **1–4** are consistent, which shows that the phase purities of compounds **1–4** are good.

The energy dispersive spectra of compounds **1–4** are shown in Fig. 11. EDX data were collected for the four compounds, which indicated the presence of Mo, Cu, C, N and O at the levels expected.

The cheap 1–4-CPEs were assembled to investigate their electrochemical properties owing to the insolubility of the four compounds in water and most organic solvents. The cyclic voltammograms are shown in Fig. S5.† The midpoint potentials  $(E_{\rm m})$  of the redox couples I–I', II–II', III–III' and IV–IV', estimated by using the two tangent method, are 0.13, -0.38, and -0.62 V for 1-CPE; 0.12, -0.33, and -0.55 V for 2-CPE; 0.12, 0.01, -0.32, and -0.53 V for 3-CPE; and 0.10, -0.45, and-0.65 V for 4-CPE. The couple I–I' can be attributed to the redox processes of Cu(II)/Cu, and the couples II–II', III–III' and IV–IV' can be derived from the redox processes of Mo<sup>VI</sup>/Mo<sup>V</sup> centers.

Electrocatalysis is an important application of POMs because they store multiple protons/electrons during redox processes. Nitrite ( $NO_2^-$ ) and ascorbic acid (AA) are often selected as probes of electrocatalytic redox reactions in the electrocatalytic field.<sup>13</sup> The electrocatalytic properties of compounds **1–4** are measured by using CV measurements with *n*-CPEs (*n* = **1–4**) in the presence of nitrite and AA in a 1 M



Fig. 11 Energy dispersive spectrum from compounds 1-4.



**Fig. 12** Cyclic voltammograms showing the electrocatalytic reduction of  $NO_2^-$  by (a) **1**-CPE, (b) **2**-CPE, (c) **3**-CPE and (d) **4**-CPE in 1 M H<sub>2</sub>SO<sub>4</sub> + Na<sub>2</sub>SO<sub>4</sub> solutions (pH = 1) with increase of concentration of  $NO_2^-$ , from top to bottom: 0, 2, 4, 6, 8 mM. Scan rate: 0.1 V s<sup>-1</sup>.

 $H_2SO_4 + Na_2SO_4$  supporting electrolyte (pH = 1), respectively (Fig. 12 and 13).

It can be easily found from Fig. 12 that a distinct change in the reduction peak currents (II', III' and IV') following the addition of nitrite is observed and the corresponding oxidation peak currents remained unchanged basically, showing that II', III' and IV' cathodic peaks of *n*-CPEs (n = 1-4) indicate good electrocatalytic activity for the reaction of nitrite reduction. It is well known that NO<sub>2</sub><sup>-</sup> disproportionates into NO and NO<sub>3</sub><sup>-</sup> in acidic solutions.<sup>14</sup> We infer that the reduction mechanism involves the reduction of NO<sub>2</sub><sup>-</sup> and NO by the heteropoly blue species (eqn (1) and (2) in the ESI<sup>†</sup>).

Proposed mechanisms for the electrocatalytic reduction of nitrite by compounds **1–4** are as follows:

In Fig. 13, an obvious increase of the oxidation peak currents of  $Cu^{II}/Mo^{VI}$  in compounds 1–4 along with the addition

of AA concentration is observed. The oxidation reactions of AA are electro-catalyzed clearly by means of the redox couples  $Cu^{II}/Cu$  and  $Mo^{VI}/Mo^{V}$ . In Fig. 13c, it is interesting to note that an unexpected change in the oxidation peak currents (II for 3-CPE) is observed along with the increase of AA concentration at a potential of 100 mV, indicating electro-catalytic activity towards the oxidation of AA ascribed to the  $Mo^{VI}$ -centre. Electrocatalytic oxidation of AA ascribed to both  $Mo^{VI}$  and  $Cu^{II}$ -centres is firstly found.

The proposed oxidation mechanism is provided in eqn (3). We deduce the oxidation mechanism as follows because ascorbic acid undergoes a two-proton dehydrogenation process:

$$Cu^{II}/Mo^{VI} + C_6H_8O_6 \rightarrow Cu/Mo^V + C_6H_6O_6$$
(3)

According to the method proposed by Keita, the electrocatalytic efficiencies (CAT) of *n*-CPEs (n = 1-4) are calculated by the following formula:<sup>15</sup>

$$CAT = 100\% \times [I_p(C, POM + substrate) - I_p(POM)]/I_p(POM)$$

where  $I_p$  (C, POM + substrate) is the current intensity of a catalytic wave for an electro-catalyst in the presence of NO<sub>2</sub><sup>-</sup> or AA



**Fig. 13** Cyclic voltammograms showing the electrocatalytic oxidation of AA by (a) 1-CPE, (b) 2-CPE, (c) 3-CPE and (d) 4-CPE in 1M  $H_2SO_4$  +  $Na_2SO_4$  solutions (pH = 1) with increase of concentration of AA, from bottom to top: 0, 2, 4, 6, 8 mM. Scan rate: 0.1 V s<sup>-1</sup>.



Fig. 14 Charts of CAT% vs. concentration of  $NO_2^-$  (a) and concentration of AA (b) for 1–4-CPEs.

and  $I_p$  (POM) is the current intensity of the catalyst without  $NO_2^-$  and AA. In this work, the CAT% is defined according to the current intensities of the cathodic wave of IV' in the presence of  $NO_2^-$  and the current intensities of the anodic wave of  $Cu^{II}/Mo^{VI}$  (I for  $Cu^{II}$  and II for  $Mo^{VI}$ ) in the presence of AA. Histograms of CAT% for 1–4-CPEs along with concentrations of  $NO_2^-$  and AA are shown in Fig. 14 for an intuitional comparison of their electro-catalytic properties.

As shown in Tables S6 and S7,† the CAT% of 2-CPE towards 2.0, 4.0, 6.0, and 8.0 mM  $NO_2^-$  was calculated to be 359%, 400%, 616% and 1721%, and that of 3-CPE was calculated to be 392%, 547%, 1012% and 1093%; and the CAT% of 3-CPE-Mo<sup>II</sup> towards 2.0, 4.0, 6.0, and 8.0 mM AA was calculated to be 29%, 58%, 90% and 123%, and that of 3-CPE-Cu<sup>II</sup> was calculated to be 26%, 61%, 87% and 96%, respectively. The electrocatalytic efficiencies of n-CPEs are in the order of 3-CPE > 2-CPE > 4-CPE > 1-CPE for low concentration of lean NO<sub>2</sub><sup>-</sup> (2 mM) and 2-CPE > 4-CPE >3-CPE > 1-CPE for high concentration of  $NO_2^-$  (8 mM). The electrocatalytic efficiencies of *n*-CPE are in the order of 1-CPE >2-CPE > 3-CPE-Mo<sup>II</sup> >3- $CPE-Cu^{II} > 4-CPE$  for low concentration of lean AA (2 mM) and 3-CPE-Mo<sup>II</sup> >3-CPE-Cu<sup>II</sup> > 2-CPE > 1-CPE > 4-CPE for high concentration of AA oxidation. The results indicate that the [Mo<sub>3</sub>O<sub>10</sub>]<sup>2-</sup>-type organic-inorganic hybrid exhibits better performance than  $[Mo_8O_{26}]^{4-}\text{-type} \ (\gamma\text{-}Mo_8O_{26} \ \text{and} \ \beta\text{-}Mo_8O_{26} \ \text{for} \ 1$ and  $\beta$ -Mo<sub>8</sub>O<sub>26</sub> for 2 and 4) hybrids towards the electrocatalytic reduction of NO<sub>2</sub><sup>-</sup> (2 mM) and the  $\beta$ -Mo<sub>8</sub>O<sub>26</sub><sup>-</sup>-type hybrids show better properties than the  $[Mo_3O_{10}]^{2-}$  unit and mixed Mo<sub>8</sub>O<sub>26</sub>-type hybrids during the process of electrocatalytic reduction of  $NO_2^{-}$  (8 mM); in a similar way, the  $[MO_3O_{10}]^{2-}$ type hybrid exhibits better activities towards the electrocatalytic oxidation of AA than [Mo<sub>8</sub>O<sub>26</sub>]<sup>4-</sup>-type hybrids. It's worth mentioning that 3-CPE-Mo<sup>VI</sup> is superior to 3-CPE-Mo<sup>VI</sup> for the oxidation of AA. In a word, the  $[Mo_3O_{10}]^{2-}$ -based organic-inorganic hybrid exhibits better performances than  $[Mo_8O_{26}]^{4-}$ -type hybrids towards not only the electro-catalytic reduction of NO<sub>2</sub><sup>-</sup> but also the electro-catalytic oxidation of AA. The discrepancy in electro-catalytic performances among different small molybdenum cluster-based hybrids should be ascribed to the differences in their structures and electrochemical properties. In summary, 1-4-CPEs possess dual functional electrocatalytic activities towards the reduction of NO<sub>2</sub><sup>-</sup> ascribed to the Mo<sup>VI</sup>-center and the oxidation of AA ascribed

to the Cu<sup>II</sup>/Mo<sup>VI</sup>-centre. We have done three parallel experiments to check the stability of the electrocatalysts for the electrocatalytic reduction of  $NO_2^-$  (2 mM) by 2-CPE under identical conditions. Fig. S6<sup>†</sup> demonstrates that the electrocatalytic activity for reduction of  $NO_2^-$  is unchanged basically during the reduplicate catalytic experiments.

## Conclusions

We have prepared four new organic-inorganic hybrid compounds based on small Mo clusters and Cu-pyridyl segments by adjusting pH. Compound 1 shows a 1D  $\{-\beta - [Mo_8O_{26}]\}$  $Cu_2-\gamma$ - $[Mo_8O_{26}]_n$  straight chain structure including mixed  $\beta$ -[Mo<sub>8</sub>O<sub>26</sub>] and  $\gamma$ -[Mo<sub>8</sub>O<sub>26</sub>] clusters; compound 2 possesses a 3D supramolecular structure stemming from  $\beta$ -[Mo<sub>8</sub>O<sub>26</sub>] units and [Cu(tpy)]<sup>2+</sup> motifs; and compound 3 has a 1D chain structure built from  $[Mo_3O_{10}]^{2-}$  anions and  $[Cu(bpy)]^{2+}$  units. The  $[\beta-MO_8O_{26}]$  clusters are bridged by  $[Cu(bpy)]^{2+}$  motifs leading to a 2D sheet structure in compound 4. Furthermore, the electrochemical and electro-catalytic properties of compounds 1-4 were investigated in 1 M H<sub>2</sub>SO<sub>4</sub> + Na<sub>2</sub>SO<sub>4</sub> electrolyte solution through CV measurements. The results show that n-CPEs (n = 1-4) have different dual electro-catalytic activities for not only the reduction of NO2<sup>-</sup> but also the oxidation reaction of AA. We will extend our research to isopolyvanadates to prepare POV/M/L hybrid compounds with novel structures and multifunctional properties.

# Conflicts of interest

There are no conflicts to declare.

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