A new molybdenum-oxide-based organic–inorganic hybrid framework templated by double-Keggin anions†

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A new double-Keggin-ion-templated, molybdenum-oxide-based organic–inorganic hybrid compound has been hydrothermally synthesized and its electrocatalytic properties investigated.

New porous materials such as zeolites and zeolite-like compounds have attracted intense interest owing to their extensive applications in gas storage, ion exchange, selective catalysis and molecular sieves.[1–5] A current important synthetic strategy in this field is the use of templates.[3–6] Organic amine cations are one of popular templates to prepare novel porous compounds,[3–5] which can condense various inorganic anion building blocks around themselves so as to construct open frameworks. In contrast, large inorganic anions can also be employed as templates to build novel porous frameworks[6] whereas the host segments should be changed into metal ions, organic linkers and/or cationic metal–organic complexes during the assembly. In this aspect, polyoxometalates (POMs) are one of the suitable inorganic templates owing to their versatile structural topologies and abundant chemical combinations that endow them with controllable shape, size and high negative charges.[7] In fact, POMs have been extensively used as anionic templates to build cationic coordination polymer hosts.[6c,8,9] Furthermore, Müller *et al.* have reported huge inorganic cage hosts templated by various POMs.[10] In all known POM-templated compounds, the host frameworks generally include metal ions and organic linkers or pure inorganic metal oxides. In addition, metal-oxide-based organic–inorganic hybrid materials, as a rapidly developing multifunctional system in recent years,[6a,11,12] could be another type of potential building blocks for the construction of porous hosts, although no such examples have been observed so far. Since most hybrid metal oxides exhibit anionic (or neutral) and rigid scaffoldings,[6a,11c] it is difficult to effectively aggregate these host units around polyanion clusters due to the charge mismatching and/or size- and shape-selection demands. Therefore, it is still a current challenge to synthesize POM-templated organic–inorganic hybrid metal oxide frameworks. Nevertheless, numerous known hybrid materials suggest that the introduction of binary metal centers and neutral N-donor organic ligands usually leads to the formation of cationic metal–organic complex segments and linear or layered metal oxide units,[6a,11,12] which might satisfy the afore-mentioned requirements for POM-templated assembly. Hence, the use of binary metal ions and neutral pyridine or bipyridine ligands was fully considered in our synthetic efforts for new POM-templated organic–inorganic hybrid metal oxide compounds. Herein, we report a new compound, $[\{Mn(bpy)(py)(H_2O)_2\}\{Mo_{12}O_{34}(bpy)_{12}\}][PMo_{12}O_{40}]_2\cdot 2H_2O$ (bpy = 2,2′-bipyridine, py = pyridine) **1**, which represents the first molybdenum-oxide-based organic–inorganic hybrid framework templated by double Keggin anions.

Compound **1**‡ was hydrothermally synthesized with a mixture of $H_3PMo_{12}O_{40}$, MoO_3, $MnSO_4\cdot H_2O$, bpy and py in water at 160 °C (5 days). Single-crystal X-ray diffraction analysis§ reveals that **1** consists of a cationic organic–inorganic hybrid molybdenum oxide host, Keggin anion templates and lattice water molecules (see Fig. 1 and Fig. S1, ESI†).

The $[PMo_{12}O_{40}]^{3-}$ anions possess the well-known α-Keggin-type structure. The cationic molybdenum-oxide-based hybrid unit exhibits an infinite chainlike structure decorated with $\{Mn(bpy)(py)(H_2O)_2\}$ moieties. All Mo and Mn centers exhibit the hexa-coordination environment. Three adjacent $\{MoO_4N_2\}$ octahedra are linked into a linear trimer, while another three $\{MoO_4N_2\}$ into a triangle unit *via* two different corner-sharing modes. Such two different trimers alternately join together to form the infinite wavelike chain. The bpy ligands are coordinated directly to the molybdenum oxide skeleton. In addition, the $\{Mn(bpy)(py)(H_2O)_2\}$ unit[13] is grafted on each $\{Mo_{12}O_{34}(bpy)_{12}\}$ moiety *via* the bridging O atom (O51) between Mo16 and Mn1. The bond length of Mn1–O51 is 2.255(9) Å (see Fig. S1, ESI†). On the *ab* plane, the adjacent hybrid chains are linked together based on the H-bonds (O1W···O51 3.387(2) Å) (see Fig. S2, ESI†) to

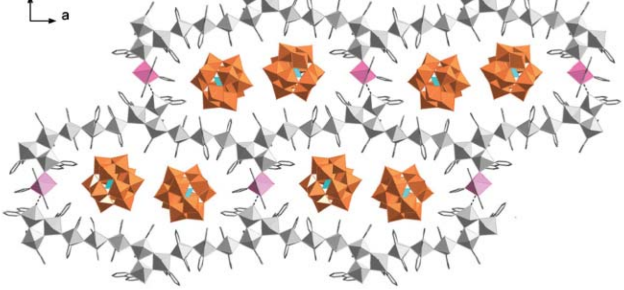

Fig. 1 Polyhedral representation of **1**: $\{MoO_4N_2\}$ octahedra, grey; $\{MnO_3N_3\}$ octahedra, pink; Keggin polyanions, orange; bpy and by, grey.

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† Electronic supplementary information (ESI) available: The unit cell and packing arrangement of **1**, crystal data, TG, XPS and IR spectra of **1**. See DOI: 10.1039/b700511c

form an interesting 2-D supramolecular network with very large pores (*ca.* 28.3 × 11.7 Å, see Fig. S3, ESI†). Strikingly, the pore is large enough to accommodate two Keggin ions (*ca.* 10.4 × 10.4 Å) in a "shoulder by shoulder" mode (see Fig. 1). It is supposed that these double Keggin ions may serve as templates during the assembly so that hybrid cationic building blocks are aggregated around them (see Fig. S3, ESI†), leading to the large-porous supramolecular network. Such a host templated by double Keggin anions has never been observed so far.[14]

Furthermore, the neighbouring 2-D networks are parallel to each other and stacked along the *c* axis to form a 3-D supramolecular framework (Fig. S4 and S5, ESI†). These 2-D layers are stabilized *via* extensive H-bonds between bpy ligands and terminal oxygen atoms from adjacent molybdenum oxide layers (see Fig. S4, ESI†). However, the rectangular pores in two neighboring layers are not well-overlapped but half staggered to each other (see Fig. 2) so that the predicted 3-D supramolecular framework with very large tunnels (section size *ca.* 28.3 × 11.7 Å) does not exist along the *c* axis. Actually, a 3-D supramolecular metal-oxide-based composite scaffolding with a half size of the "predicted" tunnels is observed (see Fig. 3 and Fig. S5, ESI†). The section size of the tunnel is *ca.* 14.1 × 11.7 Å (based on the size of Keggin anions).

In the tunnel, the $[PMo_{12}O_{40}]^{3-}$ templates are arranged in a staggered manner in an ABAB… mode along the *c* axis (see Fig. 4). Further, there exist extensive H-bonding interactions between Keggin ions and bpy groups from the host framework (see Fig. S3c, ESI†), which stabilize the whole crystal structure. The lattice water molecules also reside in the tunnels, H-bonding with bpy ligands on the inorganic skeleton.

In compound **1**, all Mo and Mn centers exhibit the +6 and +2 oxidation states, respectively, based on charge balance consideration and bond valence sum calculations.[15] The oxidation states of Mo and Mn are further confirmed by XPS measurements, which were carried out in the energy region of Mn $2p_{1/2}$, Mn $2p_{3/2}$, Mo $3d_{5/2}$ and Mo $3d_{3/2}$, respectively. The XPS spectra give two peaks at *ca.* 654.8 and 643.1 eV, attributable to Mn^{2+} ions,[16a] and two peaks at 236.1 and 232.1 eV, attributable to Mo^{6+} ions (see Fig. S6, ESI†).[16b] In the IR spectrum of **1** (see Fig. S7, ESI†), strong peaks at 1060, 956, 875 and 798 cm^{-1} are due to the $v_{as}(P–O_a)$, $v_{as}(Mo=O_d)$, $v_{as}(Mo–O_b–Mo)$ and $v_{as}(Mo–O_c–Mo)$ vibrations, respectively.[7a] The bands at 1597, 1471, 1442 and 1315 cm^{-1} are assigned to bpy ligands. The TG curve of **1** (see Fig. S8, ESI†) exhibits three weight-loss steps after 250 °C attributed to the loss of lattice and coordinated water molecules, decomposition and loss of pyridine and bipyridine, and the loss of P_2O_5. The total weight loss is about 31.2%, in consistence with the calculated value of 30.7%.

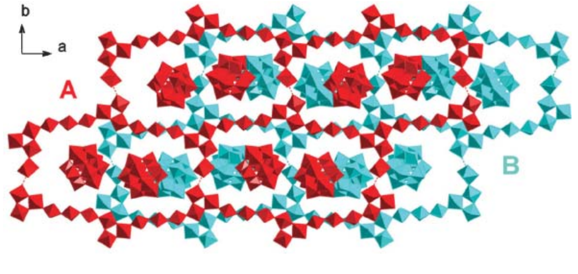

Fig. 2 View of the stacking mode between two adjacent layers of **1** along the *c* axis. Layer A (red, upper), layer B (blue, below).

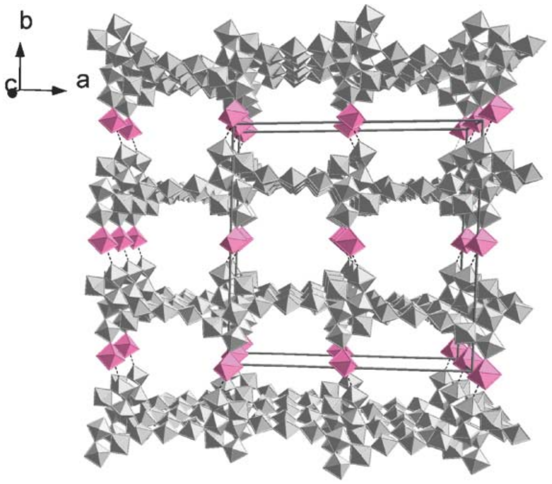

Fig. 3 Polyhedral representation of the 3-D supramolecular metal-oxide-based composite host with 1-D tunnels along *c* axis in **1**. Keggin anion templates are omitted for clarity.

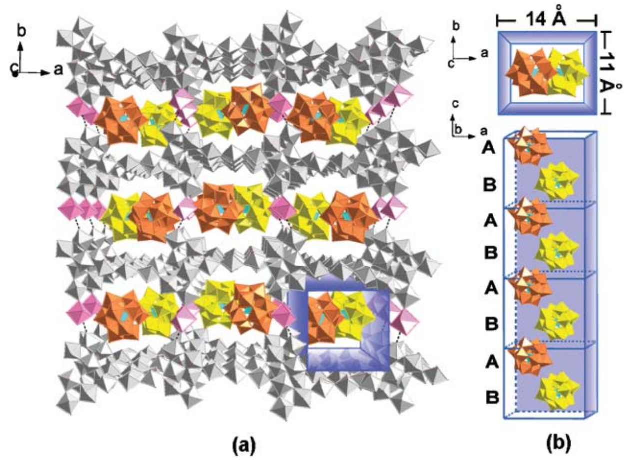

Fig. 4 (a) View of the 3-D hybrid molybdenum oxide "host" encapsulating the Keggin ions of **1**. (b) View of the arrangement of Keggin ions in the tunnels. The polyanions in layer A, orange; in layer B, yellow.

Its high thermal stability before 250 °C and extremely low solubility in various solvents as well as the POM-enriched character[17] suggest that **1** could be an ideal hybrid material for electrocatalysis.

The electrochemical behavior of a **1**-modified carbon paste electrode (**1**-CPE) and its electrocatalytic reduction of nitrite were investigated. The cyclic voltammetric behavior for **1**-CPE in 1 M H_2SO_4 aqueous solution at different scan rates was recorded (see Fig. S9a, ESI†), exhibiting three reversible redox peaks in the potential range of +700 to −100 mV, attributable to the $[PMo_{12}O_{40}]^{3-}$ polyanions.[17,18] At scan rates lower than 150 mV s^{-1}, the peak currents were proportional to the scan rate (see Fig. S9b, ESI†), indicating that the redox process of **1**-CPE is surface-controlled. It is noteworthy that **1**-CPE possesses a high stability. When the potential range is maintained between +700 and −100 mV, the peak currents remain almost unchanged over 300 cycles at a scan rate of 100 mV s^{-1}. After **1**-CPE was stored at room temperature for one month, the peak current decreased only 5% and could be renewed by squeezing a little carbon paste out of the tube. The high stability of **1**-modified CPE could be ascribed to the host–guest structural feature of **1** that stabilizes the Keggin-ions in the compound. Further, compound **1** is insoluble in the acidic aqueous medium of this experiment, avoiding the loss of the modifier during measurements. Thus, **1**-CPE could be an ideal electrode material to investigate electrocatalytic properties. Actually, **1**-CPE displays good electrocatalytic activity to reduce nitrite (Fig. S10, ESI†).

At the **1**-CPE, with the addition of nitrite, all three reduction peak currents increased while the corresponding oxidation peak currents dramatically decreased, suggesting that nitrite was reduced by all three reduced polyanion species.[19] Furthermore, the catalytic activities were enhanced with increasing extent of the Keggin ion reduction. In contrast, the reduction of nitrite at a bare electrode generally requires a large overpotential and no obvious response was observed at a bare CPE.

In summary, compound **1** represents the first example of molybdenum-oxide-based organic–inorganic hybrid frameworks templated by double Keggin-ions. With hindsight, we can imagine that more new metal-oxide-based hybrid materials could be prepared by replacement of organic–manganese complex segments and/or by selection of different Keggin-ion or other polyanion templates. Further, if Keggin-ion templates could be successfully removed or substituted by small anions without collapse of the host framework, an actual porous material will be obtained. These efforts are currently going on in our group.

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Notes and references

‡ *Preparation* of compound **1**: The initial compound $H_3PMo_{12}O_{40}\cdot xH_2O$ (x ~20) was synthesized according to the literature.[20] The mixture of $H_3PMo_{12}O_{40}\cdot xH_2O$ (1.09 g, 0.5 mmol), MoO_3 (0.432 g, 3 mmol), $MnSO_4\cdot H_2O$ (0.084 g, 0.5 mmol), 2,2′-bipyridine (0.468 g, 3 mmol) and pyridine (0.08 mL, 1 mmol) was dissolved in 8 mL H_2O, sealed in a 18-mL Teflon-lined reactor and kept at 160 °C for 5 days. Green plate-like crystals were obtained in a yield of 50% (based on Mo) with unknown amorphous solids. Calc. for $C_{135}H_{117}N_{27}O_{118}P_2MnMo_{36}$: C 21.40, H 1.56, N 4.99, Mn, 0.73, Mo 45.59. Found: C 21.45, H 1.49, N 4.91, Mn 0.65, Mo 45.67%.

§ *Crystal data* for **1**: $C_{135}H_{117}N_{27}O_{118}P_2MnMo_{36}$, M = 7576.28, orthorhombic, space group *Aba*2, a = 34.826(7), b = 35.777(7), c = 16.575(3) Å, U = 20652(7) Å^3, T = 293 K, Z = 4, μ(Mo-Kα) = 2.282 mm^{-1}, 73762 reflections measured, 18161 unique (R_{int} = 0.1164) which were used in all calculations; R_1 = 0.0465 and wR_2 = 0.0943 for $I > 2\sigma(I)$. CCDC 295098. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b700511c

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