A highly stable polyoxometalate-based metal–organic framework with an ABW zeolite-like structure†

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A novel polyoxometalate-based metal–organic framework (POMOF) with an ABW network, NENU-601, was synthesized in situ. To the best of our knowledge, this is the first POMOF with a zeolite-like structure, which was designed by regulating the length and angle of mixed ligands and rationally choosing suitable Polyoxometalates (POMs) as nodes.

Zeolites are a significant class of inorganic crystalline materials with wide applications like in petroleum refining, catalysis, ion-exchanging and so on due to their remarkable chemical and thermal stability, which are necessarily built from MO₄ tetrahedra (M = Si, Al or P, etc.) and connected to four adjacent tetrahedra by vertex O atoms leading to 3D four-connected frameworks. The only fly in the ointment is that zeolites can only adjust the ratio of Si:Al for functionalisation. To break the bottleneck, researchers tried to utilize crystallographic theory to tuneably synthesize more zeolite-like structures. Metal–organic frameworks (MOFs), a class of materials constructed with metal ions or clusters as nodes and multi-functional organic ligands as linkers, have received much attention because of their high surface areas and tunable structures. As for this point, nodes and linkers can be well-designed to get the expected structures, pore volumes, functions and properties. One representative sub-family of MOFs is the group of zeolite-like MOFs (ZMOFs) that use tetrahedral-connected nodes and ligands corresponding to Si/Al–O tetrahedra and O atoms, respectively, combining the advantages of MOFs and the high stability of zeolites. In particular, a series of frameworks have been synthesised in recent decades by assembling Zn²⁺ or Co²⁺ ions and imidazolates, namely zeolitic imidazolate frameworks (ZIFs), which have drawn extensive attention and research due to their zeolite-like structures (Scheme 1).

Compared to the synthesis of novel structures, the derived material applications are more concerning. Recently, a large number of MOFs have been applied as electrode materials for batteries to solve energy issues due to their porosity and large surface areas. However, the problem with using MOFs directly for electrode materials is that the poor redox ability of normal MOFs affects their reversible capacity, which greatly restricts their energy storage applications. POMs are a subset of inorganic clusters that contain various metal ions which reveal superior performances in redox reactions and favourable Lewis and Brønsted acidity, resulting in their application in various fields. Therefore, more attention has been focused on introducing POM units to MOFs to construct POMOFs. POMOFs can almost be divided into two types: one has loaded POMs as templates in the network of known MOFs and the other has fixed POMs in the framework of MOFs as nodes connected to ligands. To date, POMOFs have been synthesized and applied

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Scheme 1 Schematic representation of the design strategies for the construction of a zeolite, ZIF and ZPOMOF.
to some fields like heterogeneous electro/photocatalysis, electroanalytical domains, proton conductivity and chemical separations. This kind of framework has shown excellent development prospects because of its stable skeleton and high redox ability. But there is no report on the structure of zeolite-like POMOF (ZPOMOF) materials. Design strategies for the construction of ZPOMOFs are still under exploration and here are some feasible methods and difficulties:

(i) POMs are utilized as templates and synthesized inside the cages of ZMOFs. But the big volume of the POMs causes them to be hardly implanted in pores of the known ZMOFs;

(ii) POMs are used to replace metal ions or clusters as nodes in the network of the available MOFs. But there are few kinds of POM that possess suitable 4-connected nodes. Moreover, the size of the POMs is approximately five times larger than metal ions so it is not easy to choose suitable ligands to match POMs and form 3D frameworks.

The strategy of designing the structure in this work can be divided into three modules. The 4-connected POM node we chose is the $\text{e}^+\{\text{Zn}_2\text{PMo}_{12}\text{O}_{40}\}$ cluster. The imidazololate or triazole ligands provide a metal–Im–metal angle that has a similar value to the Si–O–Si angle in zeolites. Furthermore, the moderate length of the linker is also a critical parameter to choose when building ZPOMOFs. Based on the points above, through our topological calculation and design, we finally chose Hbzt as the ligand to provide the 145° metal–Im–metal angle and 1,4H2bdc as the secondary bridging ligand (Fig. S1, ESI†). As expected, we successfully synthesized the first POMOF with an ABW zeolite-like topological structure (NENU-601). It shows high chemical and thermal stability which means that it can keep its crystalline integrity in aqueous solution in a range of pH values from 1 to 12 and keep its skeleton intact at 370°C (Fig. S4, ESI†). We directly utilized NENU-601 as an anode material for lithium-ion batteries (LiBs). This rigid structure showed its superior chemical and structural stability during the electrochemical process, and the $\text{e}^+\{\text{Zn}_2\text{PMo}_{12}\text{O}_{40}\}$ cluster units as SBUs showed favourable and reversible performances.

X-ray crystallography revealed that NENU-601 crystallized in the orthorhombic space group $Ibam$ with eight formula units (Z = 8) per unit cell (Table S1, ESI†). The asymmetric unit consists of the inorganic building unit of $\text{e}^+\{\text{Zn}_2\text{PMo}_{12}\text{O}_{40}\}$ and organic ligands including three deprotonated bzt− units and one bdc2− unit. The $\text{e}^+\{\text{Zn}_2\text{PMo}_{12}\text{O}_{40}\}$ cluster is a member of compounds based on the $\text{e}^+\text{Keggin}$ $\{\text{PMo}_{12}\text{O}_{40}\}$ anion which has four capping Zn(II) ions. This inorganic building block has a tetrahedral configuration and Zn(II) ions in the vertex, providing the possibility of forming a 3D network. Each Zn(II) ion has a distorted tetrahedral geometry and the Zn(II)-bzt/Zn(II) angles vary from 133° to 137°, which is near to the 145° that we expected. The coordination modes of the Zn(II) ions can be divided into two distinct types. Three of them (Zn2, Zn3 and Zn4) are coordinated to three nitrogen atoms (N2, N1#1 and N4) belonging to the bzt− ligands and the remaining one (Zn1) is coordinated to an oxygen atom (O1) from the carboxylate group of the bdc2− ligands (Fig. 1a). The average Zn–N and Zn–O distances are 1.983 Å and 1.927 Å, respectively. In the topology analysis,

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The phase purity of rhombus crystalline NENU-601 was determined by comparing experimental and simulated powder X-ray diffraction (PXRD) patterns (Fig. 3). NENU-601 can be stable in air for more than 300 days, furthermore, the patterns obviously reveal that the crystalline integrity of NENU-601 means that it can be kept in aqueous solution in different pH values (pH = 1, 3, 5, 9, 11 and 12, adjusted by HCl or NaOH) for 24 hours and in electrolyte for 12 hours, which indicates that NENU-601 has excellent chemical stability. The stability in electrolyte shows the possibility of utilizing NENU-601 as an electrode material and guarantees the cyclic stability of LIBs.

The highly stable structure lays the foundation for its application in LIBs. As we predicted, NENU-601 revealed excellent electrochemical performance, indicated by electrochemical measurements such as cyclic voltammetry (CV), as well as excellent charge–discharge voltage, cycling performance and rate performance. Fig. 4a shows the CV curves in the voltage range from 0.01 to 3.0 V (scan rate = 0.2 mV s\(^{-1}\)). The cathodic peak at 0.6 V in the first discharge was ascribed to the formation of a solid–electrolyte interphase (SEI) film. In the next two cycles, the reversibility of 1.1 V for the reductive peak and 1.5 V for the oxidative peak indicates an electrochemical process, which may be a consequence of the redox reaction of Zn and Mo. 30,31 It also demonstrates the good cycle stability for the superposition of the following curves in Fig. 4c. The cycling performance of NENU-601 is shown in Fig. 4b with a current density of 100 mA g\(^{-1}\). NENU-601 obtains a discharge specific capacity at 1389.1 mA h g\(^{-1}\) in the 1st cycle and its first charge specific capacity can deliver 626.6 mA h g\(^{-1}\), which results in an initial coulombic efficiency (CE) of over 45%. The initial irreversible capacity loss is principally because of the formation of the SEI film after the electrolyte decomposes. Along with the charge–discharge process, the pore activation of NENU-601 causes the reversible capacity to be 780 mA h g\(^{-1}\) after 200 cycles as a result of its stable framework, 32,33 which is superior to that for previously reported porous materials (Table S4, ESI\(^{†}\)). At the same time, we chose Z-POMOF1 (Fig. S5, ESI\(^{†}\)) for the comparison. Z-POMOF1 achieves a capacity of 545 mA h g\(^{-1}\) under the same testing conditions after 100 cycles. In addition, pure Hbztt and H\(_2\)bdc ligands are also tested and achieve capacities of 216 mA h g\(^{-1}\) and 148 mA h g\(^{-1}\), respectively. NENU-601 has better lithium ion storage properties than Z-POMOF1 because it benefits from lower impedance (Fig. 6b, ESI\(^{†}\)) and the contribution of N-containing ligands.
NENU-601 also has a good rate performance at various current densities from 50 to 500 mA g\(^{-1}\) [Fig. 4d]. When changing the current density from 50 mA g\(^{-1}\) to 100 mA g\(^{-1}\), 200 mA g\(^{-1}\), 300 mA g\(^{-1}\) and 500 mA g\(^{-1}\), the discharge capacities progressively decrease from 910 mA h g\(^{-1}\) to 753 mA h g\(^{-1}\), 532 mA h g\(^{-1}\), 364 mA h g\(^{-1}\) and 260 mA h g\(^{-1}\), respectively. After the current density comes back to 200 mA g\(^{-1}\), 100 mA g\(^{-1}\) and 50 mA g\(^{-1}\), the average discharge capacities quickly resume, indicating an excellent cycling performance. Furthermore, we did a stability test of NENU-601 at a current density of 500 mA g\(^{-1}\). NENU-601 exhibits a high reversible capacity (Fig. 4e) of 470 mA h g\(^{-1}\). As we expected, the discharge capacities progressively decrease from 351 mA h g\(^{-1}\) to 214 mA h g\(^{-1}\), 78 mA h g\(^{-1}\) and 35 mA h g\(^{-1}\), respectively. An excellent rate performance at various current densities from 50 to 1000 mA g\(^{-1}\), the discharge capacities progressively decrease from 532 mA h g\(^{-1}\) to 214 mA h g\(^{-1}\), 78 mA h g\(^{-1}\) and 35 mA h g\(^{-1}\), respectively. After the current density comes back to 200 mA g\(^{-1}\), 100 mA g\(^{-1}\) and 50 mA g\(^{-1}\), the average discharge capacities quickly resume, indicating an excellent cycling performance. Furthermore, we did a stability test of NENU-601. NENU-601 exhibits a high reversible capacity (Fig. 4e) of 470 mA h g\(^{-1}\). As we expected, the discharge capacities progressively decrease from 351 mA h g\(^{-1}\) to 214 mA h g\(^{-1}\), 78 mA h g\(^{-1}\) and 35 mA h g\(^{-1}\), respectively. After the current density comes back to 200 mA g\(^{-1}\), 100 mA g\(^{-1}\) and 50 mA g\(^{-1}\), the average discharge capacities quickly resume, indicating an excellent cycling performance.