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An Unprecedented 3D POM-MOF based on (7, 8)-Connected Twin Wells-Dawson Clusters: Synthesis, Structure, Electrocatalytic and Photocatalytic Properties†

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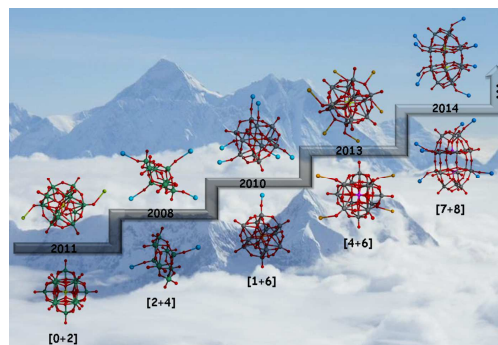
The first (7, 8)-connected polyoxometalate-based metal-organic framework (POM-MOF) has been constructed by seven- and
10 **eight-connected twin Wells-Dawson clusters, representing the highest connection number of polyoxometalates to any mixed-connected POM-MOF to date and a unique structural motif that contains both an organic-inorganic and an all-inorganic network.**

15 Metal-organic frameworks (MOFs, also known as porous coordination polymers) are an emerging class of porous materials constructed from metal-containing nodes and organic linkers.[1] The rational design and assembly of MOFs have received remarkable attention in order to develop new functional materials
20 with various potential applications and intriguing topological structures.[2] From a structural point of view, MOFs with both high- and mixed-connected topologies are very interesting since there exists a correlation between structural complexity and multifunctionality in coordination networks. Nevertheless, only a
25 limited number of MOFs with both high- and mixed-connected topologies have been constructed until now[3] because of limitations by the number of available coordination sites at single-metal ion centres.

Recently, the utilization of metal clusters as nodes in place of
30 single-metal ions has provided a promising strategy toward the construction of highly connected MOFs.[4] Polyoxometalates (POMs), as a large family of metal-oxygen clusters, cover an enormous range in size and structure and thereby provide access to a huge library of readily available and controllable secondary
35 building units (SBUs).[5] In addition to their structural appeal, POMs often show many potential applications, especially in heterogeneous and homogeneous catalysis.[6] In this context, a new class of hybrid materials has emerged by introducing POMs into MOF systems, so-called POM-MOFs.[7] The POM-MOFs can
40 combine the advantages of both POMs and MOFs, and open up new possibilities in the pursuit of multifunctional materials with designed functional properties and aesthetic topological structures. Thanks to the work of POM chemists, a large number of POM-MOFs have been reported.[8] The POM-MOFs

45 constructed by mixed-connected POM clusters are interesting for their structural complexity. However, after carefully searching the CSD database and previous literature, we observe that POM-MOFs constructed by mixed-connected POM clusters have been extremely rarely reported.[9] Only four POM-MOFs based on
50 mixed-connected POM clusters have been reported hitherto (see Table S1 and Scheme 1). In these cases, the POM clusters exhibit [0+2],[9a] [2+4],[9b] [1+6],[9c] and [4+6][9d] coordination numbers, respectively, and unfortunately the highest connection number of POMs is no more than six. Therefore, the exploration of POM-
55 MOFs based on both high- and mixed-connected POM clusters is important because high-connected MOFs are more stable.[4f]

Furthermore, after carefully analyzing the structures of the four reported POM-MOFs based on mixed-connected POM clusters,[9] we found that all of these POM-MOFs are constructed by either
60 octamolybdate or Keggin POMs (see Table S1 and Scheme 1). Nevertheless, in contrast to the octamolybdate or Keggin POMs, the Wells-Dawson POMs possess more surface oxygen atoms and higher negative charges in their clusters, which makes them favourable for the formation of complicated and interesting
65 structures.[10] In addition, the multidentate bis(triazole) ligand 1,4-bis(1,2,4-triazol-1-yl)butane (btb) possesses various coordination modes and flexible conformations, and thus exhibits a strong capacity to interconnect transition metal centres (such as copper ions) to afford diverse structures, which is a suitable linker for the
70 synthesis of highly-connected POM-MOFs.[11] Therefore, we chose to use the combination of these linkers in pursuit of highly-connected POM-MOFs. Herein, we communicate the preparation and structure of a 3D POM-MOF based on (7, 8)-connected twin Wells-Dawson clusters, namely,
75 $H_2[Cu_{11}(btb)_{19}(H_2O)_6(P_2W_{16}^{VI}W_2^VO_{62})_3]\cdot12H_2O$ (**1**). To the best

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Scheme 1. View of the known POM-MOFs based on mixed-connected POM clusters.
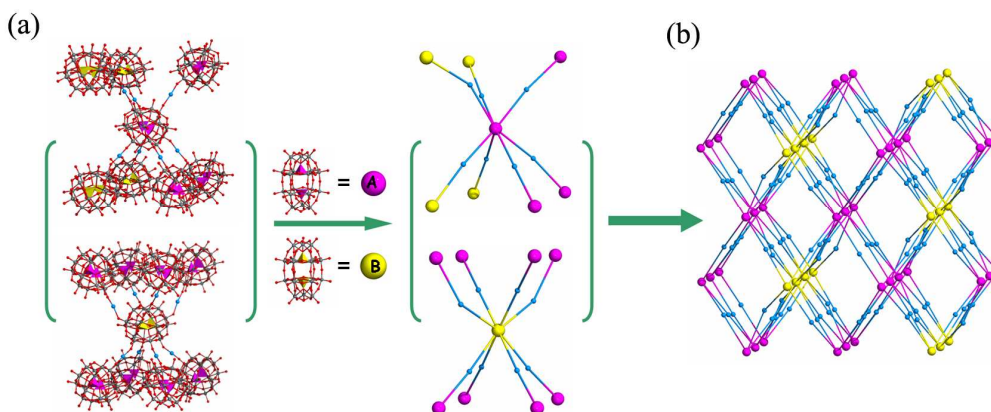
Fig. 1 The unique (7, 8)-connected 3D all-inorganic framework constructed by (a) two types of POM-Cu connections and (b) resulting framework.

of our knowledge, compound **1** not only represents the first example of a (7, 8)-connected 3D POM-MOF, but also shows improved photocatalytic properties and possesses the highest connection number of POMs for mixed-connected POM-MOFs
80 to date.

Compound **1** was hydrothermally synthesized in a mixture of α-$K_6P_2W_{18}O_{62} \cdot 15H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, btb and triethylamine in water at 170 °C for 5 days (ESI†). Single-crystal X-ray diffraction (ESI†) reveals that **1** crystallizes in the monoclinic
85 space group *C2/c* (No. 15) and consists of eleven Cu ions, nineteen btb ligands, six coordinated water molecules and three reduced Wells-Dawson $[P_2W_{16}^{VI}W_2^{V}O_{62}]^{8-}$ (P_2W_{18}) clusters (Fig. S1, ESI†).

There are six crystallographically-independent Cu ions that exist
90 in three different distorted octahedral geometry coordination environments in **1** (Fig. S2, ESI†). All six Cu ions are coordinated by two different POMs in the *trans* position. Cu1 is coordinated by one oxygen from each of the two P_2W_{18} anions, one water molecule, and three nitrogen atoms from three btb ligands. Cu2 is coordinated
95 by one oxygen from each of the two P_2W_{18} anions, two water molecules, and two nitrogen atoms from two btb ligands. The coordination environment of Cu3, Cu4, Cu5 and Cu6 are chemically equivalent, achieved by one oxygen from each of the two the P_2W_{18} anions, and four nitrogen atoms from four btb
100 ligands. The bond lengths and angles around the Cu ions are in the range of 1.95(2)−2.04(2) Å (Cu−N), 1.98(3)−2.42(2) Å (Cu−O), 86.5 (10)−180.0(13)° (N−Cu−N) and 86.0(9)−175.9(13)° (N−Cu−O). All of these bond lengths and angles are within the normal ranges observed in other Cu(II)-containing complexes.[12]

105 The most important structural feature of **1** is the unprecedented 3D POM-MOF based on (7, 8)-connected twin Wells-Dawson clusters, which consists of two crystallographically-distinct motifs: an organic-inorganic framework and an all-inorganic framework. In the organic-inorganic framework, there are ten
110 crystallographically-independent btb ligands and they show two types of conformation modes: "Z"-type and "U"-type btb (Fig. S3, ESI†). Notably, in **1**, all of the btb ligands are μ^2 bridging ligands and coordinate with two Cu ions. Due to the versatility of the btb ligand, three kinds of macrocycles are formed: (i) a heart-
115 shaped 44-membered macrocycle is generated by the btb5, btb6,

btb7 and btb8 ligands which link to Cu3, Cu4, Cu5 and Cu6 ions; (ii) a dumbbell-shaped 44-membered macrocycle is generated by the btb9 and btb10 ligands which link to Cu5 and Cu6 ions; (iii) a rare six-nuclear Cu loop (66-membered macrocycle) with the size
120 of window *ca.* 12.77 × 24.63 Å which is generated by the btb5, btb6 and btb9 ligands that link to Cu3, Cu5 and Cu6 ions (Fig. S4, ESI†). Finally, these three kinds of macrocycles are fused together by sharing Cu ions to form an intricate 3D organic-inorganic framework (Fig. S5a, ESI†). From the topological
125 view, if each Cu1 ion is considered as a 3-connected node, Cu2 ion acts as a 2-connected node, Cu3, Cu4, Cu5 and Cu6 ions act as 4-connected nodes, the organic-inorganic framework can be simplified as a (3, 4, 4, 4, 4)-connected network with a $(6^1 \cdot 14^1 \cdot 18^1)(4^1 \, 6^2 \cdot 8^2 \cdot 12^1)(4^2 \cdot 6^2 \cdot 8^2)_3$ topology (Fig. S5b, ESI†).
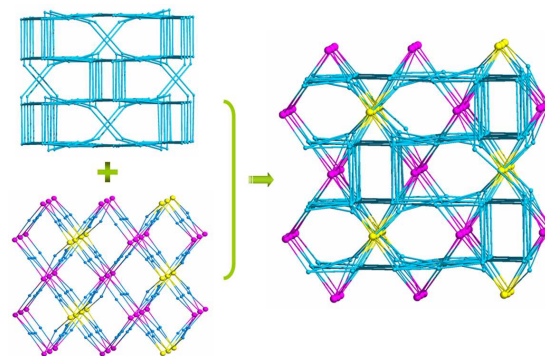

Fig. 2 The combination of the organic-inorganic and all-inorganic frameworks in **1**.

130 In the all-inorganic framework, there are two crystallographically-distinct P_2W_{18} clusters (P_2W_{18}-A and P_2W_{18}-B) with completely different connection modes (Fig. S6, ESI†). The P_2W_{18}-A cluster acts as a μ^7 bridging inorganic ligand by offering seven terminal oxygen atoms to coordinate with seven Cu ions
135 (Cu1, Cu2, Cu3, Cu4, Cu4#1, Cu5 and Cu6). In contrast, the P_2W_{18}-B cluster is a μ^8 bridging inorganic ligand by offering eight terminal oxygen atoms to coordinate with eight Cu ions (Cu1, Cu1#3, Cu2, Cu2#2, Cu5, Cu5#3, Cu6 and Cu6#2). Moreover, each P_2W_{18}-A cluster links seven adjacent P_2W_{18} clusters (four P_2W_{18}-B
140 and three P_2W_{18}-A clusters), while each P_2W_{18}-B cluster links eight

neighboring P_2W_{18}-A clusters. Consequently, a (7, 8)-connected inorganic framework with a novel $(8^{13}\cdot12^8)(8^{18}\cdot12^{10})$ topology is formed by these unprecedented connections (Fig. 1a and 1b). Finally, the organic-inorganic framework and all-inorganic
145 framework are fused into one intricate network in such a way that identical metal center nodes align (Fig. 2 and Fig. S7, ESI†), displaying the highest connection number of polyoxometalates to any mixed-connected POM-MOFs to date.[9]

It is well known that POMs possess photocatalytic activities in
150 the degradations of organic dyes under UV irradiation.[13] Thus, the photocatalytic performance of **1** in the photodegradation of methylene blue (MB) has been investigated (see experimental section in ESI†). The results of the photocatalytic experiments show that after irradiation of compound **1** for 150 min, the
155 photocatalytic decomposition rate (defined as $1-C/C_0$) is 81.5% for **1** (Fig. 3). In contrast, the photocatalytic decomposition rate using insoluble $(NBu_4)_6[P_2W_{18}O_{62}]$ as the catalyst and a blank MB solution without any catalyst are 33.7% and 7.5%, respectively. These results illustrate that the creation of a POM-MOF could
160 improve the photocatalytic performance of $(NBu_4)_6[P_2W_{18}O_{62}]$, or other POM systems. The enhanced photocatalytic performance may arise from two reasons: one is that the Cu-btb MOF of **1** may act as photosensitizer under UV light, namely, promoting the transfer of electrons onto POMs;[14a] Another reason is that the
165 reduced-polyanion $[P_2W^V_2W^{VI}_{16}O_{62}]^{8-}$, which possesses a higher charge density and exerts considerable influence on the pseudo-liquid phase behaviour of POMs.[14b] The photocatalytic mechanism can be deduced as follows (equations of photocatalytic mechanisms in the ESI†): during the photocatalytic reaction,
170 $[*P_2W^V_2W^{VI}_{16}O_{62}]^{8-}$ (*POM) abstracts electrons from water molecules and holds the electrons (Eq. (1) and (2)). The reduced POM (POM⁻) is quite stable, but is rapidly re-oxidized in the presence of O_2 through Eq. (3). The main function of O_2 in the

POM reactions seems to be the re-oxidation (regeneration) of the
175 catalyst. The re-oxidation step accompanies the generation of superoxides. These cycles occur continuously while the system is exposed to UV light. Furthermore, the MB dye is also excited by UV light to generate *MB molecules, as shown in Eq. (4). After several photo-oxidation cycles, degradation of the MB dye by
180 hydroxyl radicals and superoxides occurs (Eq. (5)).[15] Additionally, after three runs of photocatalytic tests on one sample of **1**, the photoactivity of compound **1** did not show significant loss when MB was added to the system again (Fig. S11, ESI†). In order to determine the stability of compound **1** after the photocatlytic
185 process, the XRD patterns of the title compound were tested (Fig. S12, ESI†). The results reveal that **1** maintained itsstructure after the third run of photocatalytic experiments. Thus, compound **1** may be a potential stable photocatalyst with improved photocatalytic activities in the reduction of organic dyes.

190 In summary, we have prepared and characterized the first (7, 8)-connected POM-MOF constructed by μ^7 and μ^8 bridging twin Wells-Dawson clusters, representing the highest connection number of polyoxometalates to any mixed-connected POM-MOFs until now. The successful isolation of this species not only
195 provides an intriguing example of a POM-MOF with an unprecedented topology, but also shows that the Wells-Dawson clusters, thanks to their many surface oxygen atoms and high negative charge, present a very useful ability to act as multi-dentate ligands towards metal ions and can incorporate flexible
200 ligands for the formation of complicated structures.

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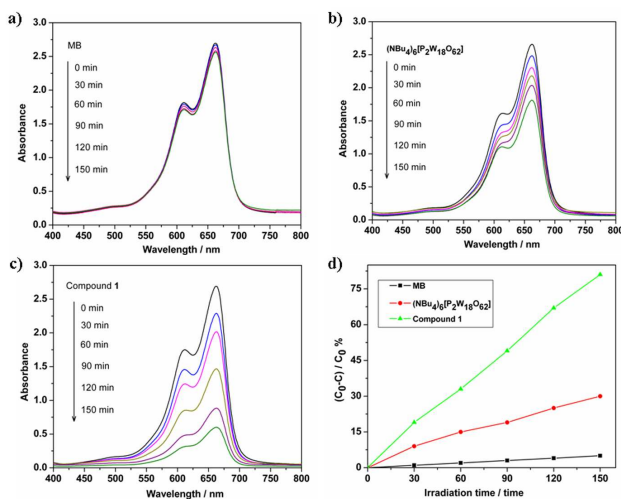

Fig. 3 Absorption spectra of the MB aqueous solution during the photodegradation under 250 W Hg-lamp irradiation with (a) no catalyst, (b) $(NBu_4)_6[P_2W_{18}O_{62}]$, (c) compound **1**, and (d) conversion rate of MB with the reaction time.

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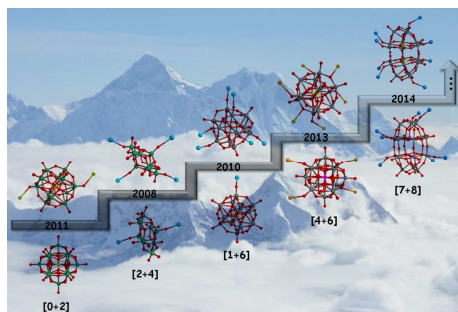
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