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## Ionothermal Synthesis of Five Keggin-Type Polyoxometalate-Based Metal–Organic Frameworks

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## Supporting Information

**ABSTRACT:** Five unique Keggin-type polyoxometalate (POM)-based metal-organic frameworks (POMFs), namely  $[CH_{2}L1]_{2}[(CuL1_{2})(PMo^{VI}_{9}Mo^{V}_{3}O_{40})]$  (1),  $[Zn_{0.5}(H_{2}O) (L1)][Zn(L1)_{1.5}Cl][H_2L1]_{0.5}[PMo_{12}O_{40}] \cdot 1.25H_2O$  (2),  $(TBA)[Cu(H_2O)_2L1_2][PMo_{12}O_{40}]$  (3),  $[Cu_2(H_2O)_2(L1)_3]$ - $[PM^{VI}_{11}Mo^{V}O_{40}]$  (4),  $(H_{2}L2)_{0.5}[(Cu^{I}L2)_{2}(PMo_{12}O_{40})]\cdot H_{2}O$ (5), L1 = 4,4'-bis((1H-1,2,4-triazol-1-yl)methyl)-biphenyl, L2 = 1,4-bis((1H-1,2,4-triazol-1-yl)methyl)-benzene, have been synthesized under ionothermal conditions. According to single-crystal data, 1 exhibits a novel mechanically interlocked molecular architecture (MIMA) constructed by two-dimensional (2D) interpenetrating polyrotaxane layers with unique cyclophanes (tetra-cationic viologen macrocycle cyclobis-



(paraguat-p-phenylene) (CBPOT<sup>4+</sup> system)), resulting in an H-bonded 3D supermolecule, and is the first synthesis of selfassembled cyclophane-PMOFs under ionothermal conditions. 2 shows a novel 2D three-fold interpenetrating polyrotaxane host and guest network. 1 and 2 are presented as the first MIMA polyrotaxane structures to have been synthesized under ionothermal conditions. Electrochemical impedance spectroscopy (EIS) reveals that 2, 4, and 5 show high proton conductivity owing to their unique structural properties. Solid-state diffuse reflection UV-vis-NIR measurements show the title compounds are potentially semiconductor materials. Photocatalytic investigations indicate that 1-5 possess high and stable photocatalytic H<sub>2</sub> evolution and rhodamine B (RhB) degradation under visible-light irradiation.

## INTRODUCTION

Because of the properties such as discrete, mobile ionic structure and tunable electronic band structure, polyoxometalates (POMs) have been regarded as attractive candidates for proton conduction and photocatalysis, both important for addressing the global energy shortage and environmental pollution.<sup>1-4</sup> However, the high solubility of POMs makes them difficult to be recycled as photocatalysts. Conversely, metal-organic frameworks (MOFs) are a kind of attractive hybrid material that can be easily recycled as heterogeneous catalysts, which have already been widely used in recent years.<sup>5</sup> Hence, polyoxometalate-based metal-organic frameworks (PMOFs) could offer a wonderful opportunity to combine the unique properties of their organic and inorganic substituents through the interaction of POMs and metalorganic components.<sup>6,7</sup> Inspired by the applications of POMs and MOFs to fuel cells and photocatalysis, the hybrids based on POMs and metal-organic phases as proton conductors and photocatalysts are model systems for high proton conductivity and photocataclytic activity.<sup>8-25</sup> Due to the distinct solubility of POMs and MOFs, it is extremely difficult to prepare PMOFs under traditional hydro/solvothermal conditions, resulting in one of the most pressing challenges in the field of synthetic chemistry. We introduce ionothermal synthesis to

overcome the challenge, as it is now regarded as a more effective and environmentally friendly synthetic method. We posit that introducing highly soluble ionic liquids (ILs) to the reaction system as the solvent can successfully promote the solubility of the POMs and metal-organic phases, resulting in an enhancement of the reactivity between organic and inorganic components.<sup>26–29</sup>

Modern room-temperature ionic liquids (RTILs) can be used as solvents or templates in preparing a wide variety of materials under ionothermal conditions. The two main reasons are as follows: (1) The RTILs used for ionothermal synthesis are often liquids below a certain temperature (often below 200  $^{\circ}$ C), as traditionally used in hydro/solvothermal synthesis. (2) RTILs often show a series of useful properties for preparing the hybrids, such as high solubility for most organic/inorganic reactants, tunable pH values, and lower vapor pressure, etc. Until now, lots of coordination polymers obtained under ionothermal conditions are two-/three-dimensional (2D/3D) structures, highlighting the promise of such a synthetic method for the preparation of PMOFs. It is very clear that changing the

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solvent from traditional water or organic solvents to RTILs leads to great successes in preparing the PMOFs.<sup>29</sup>

In previous work, organic-inorganic hybrids based on Wells-Dawson and isopolymolybdate have already been obtained under ionothermal conditions.<sup>30</sup> However, the hybrids based on Keggin in the same system have not been reported yet. Meanwhile, among the rapidly increasing number of PMOFs, mechanically interlocked molecular architecture (MIMA) polyrotaxane frameworks with characteristic "string" threading "loop" structures have seldom been observed.<sup>31-</sup> For the purpose of enriching the family of PMOFs with Keggin anions and MIMA polyrotaxane structures obtained under ionothermal conditions, we chose the IL 1-butyl-3-methylimidazolium bromide ([Bmim]Br) as the solvent and utilized two different kinds of semirigid/flexible N-donor organic ligands (4,4,-bis((1H-1,2,4-triazol-1-yl)methyl)biphenyl (short for BTMB) (L1); 1,4-bis((1H-1,2,4-triazol-1-yl)methyl)benzene (short for BBTZ) (L2)), Keggin-type POM H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>·nH<sub>2</sub>O as the second building blocks (SBU), and transition-metal (TM) cations to assemble POM-based hybrid networks. Five unique POMFs based on classic Keggintype anions  $[CH_2L1]_2[(CuL1_2)(PMo^{VI}_9Mo^V_3O_{40})]$  (1),  $[Zn_{0.5}(H_2O)(L1)][Zn(L1)_{1.5}C1][H_2L1]_{0.5}[PMo_{12}O_{40}]$ .  $[Cu_{0.5}(H_2O)(DI)][DI([U_1]_3O)(H_2O)(DI)][DI([U_1]_3O)(H_2O)($ sized. Their structures were determined by single-crystal X-ray diffraction. According to the final data, 1 exhibits a novel MIMA formed by 2D interpenetrating polyrotaxane layers with unique cyclophane and is the first synthesis of self-assembled cyclophane-PMOFs under ionothermal conditions. 2 exhibits a novel 2D three-fold interpenetrating polyrotaxane host and guest network. 1 and 2 are both presented as the first MIMA polyrotaxane structures to have been synthesized under ionothermal conditions. 3 is a 3D supramolecular host and guest framework constructed by (4,4) topological monolayers H-bonded from POMs anions and TBA<sup>+</sup> cations. 4 possesses a 3D supramolecular porous structure constructed by laddershaped topological monolayers, resulting in two kinds of channels, A and B, along the b-axis, where the cavities of channel B result in an open framework. 4 is shown to be porous, as confirmed by N2 adsorption measurements of the fully activated crystals and the result of the solvent accessible volume by SQUEEZE model of the PLATON. 5 represents a 3D supramolecular structure constructed by (6,3) honeycomb monolayers, resulting in channels along the b-axis filled with dissociative protonated organic ligands.

## MATERIALS AND METHODS

The organic and inorganic reagents and solvents were all purchased from the Aladdin and used without additional purification. The organic ligands L1, L2, and Keggin-type POM  $(H_3PMo_{12}O_{40}\cdot nH_2O)$ in this paper were all prepared based on previous literatures.<sup>42,43</sup> UV– vis absorption spectra and solid-state UV–vis-NIR diffuse reflectance spectra were both carried out on a cary 5000 UV–vis-NIR spectrophotometer. The N<sub>2</sub> adsorption measurement was carried on an ASAP 2020 HD88 BET surface analyzer. The single-crystal X-ray crystallography was collected on a BRUKER D8 Venture single-crystal diffractometer. EIS measurements were performed on a PARSTAT 2273 Advanced electrochemical impedance analyzer. A PerkinElmer 240C elemental analyzer was used to analyze the C, H, and N. A Leaman inductively coupled plasma (ICP) spectrometer was used to determine the Mo, Cu, and Zn. The produced H<sub>2</sub> was analyzed by a GC 7890T instrument. The X-ray photoelectron spectroscopy (XPS) of Mo and Cu was measured on Thermo ESCALAB 250. The thermal stability of the five compounds was measured on TA TGAQ500. The IR spectra were carried out on the ThermoFisher IS50. The powder X-ray diffraction (PXRD) was carried out on the Rigaku Smartlab.

 $[CH_2L1]_2[(CuL1_2)(PMO^{V_1}_{9}MO^{V_3}O_{40})]$  (1). [Bmim]Br (2.000 g, 4.600 mmol), H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> nH<sub>2</sub>O (0.400 g, about 0.200 mmol), CuCl<sub>2</sub>·2H<sub>2</sub>O (0.040 g, 0.200 mmol), BTMB (0.016 g, 0.050 mmol), one drop of dichloromethane (DCM, about 0.050 mL), and a little Vc were stirred for 0.5 h at room temperature. After that, the pH value of the mixture was adjusted to nearly 4.5 with HCl (conc.) and NaOH (solid) sealed in a 23 mL Teflon-lined stainless steel autoclave reactor at 170 °C for 5 d. After cooling to room temperature at a rate of 10 °C h<sup>-1</sup>, it was kept for 1 d. Brown block crystals of 1 were filtered off, washed with acetone, and dried in air (the crystals could be repeated easily and yield 65% based on Mo). Anal. calcd for 1 (%): C, 27.96; H, 2.16; N, 10.57; P, 0.97; Mo, 36.21; Cu, 2.00. Found: C, 27.06; H, 2.15; N, 10.01; P, 1.12; Mo, 36.01; Cu, 2.14. The IR spectrum of 1 is shown in Figure S20.

 $[Zn_{0.5}(H_2O)(L1)][Zn(L1)_{1.5}Cl][H_2L1]_{0.5}[PMo_{12}O_{40}] \cdot 1.25H_2O$  (2). Except for ZnCl<sub>2</sub>·3H<sub>2</sub>O (0.100 g, 0.450 mmol), without DCM and Vc, others were the same with 1 (the crystals could be repeated easily and yield about 58% based on Mo). Anal. calcd for 2 (%): C, 22.01; H, 1.83; N, 8.56; P, 1.05; Mo, 39.07; Zn, 3.33. Found: C, 22.38; H, 1.63; N, 8.90; P, 1.21; Mo, 39.24; Zn, 3.15. The IR spectrum of 2 is shown in Figure S20.

 $(TBA)[Cu(H_2O)_2L1_2][PMO_{12}O_{40}]$  (3). Except for BTMB (0.012 g, 0.040 mmol), a little TBAB, no DCM and Vc, and the pH value 4.0, others were the same with 1 (the crystals could be repeated easily and yield 60% based on Mo). Anal. calcd for 3 (%): C, 22.33; H, 2.60; N, 6.51; P, 1.11; Mo, 41.16; Cu, 2.27. Found: C, 22.05; H, 2.43; N, 6.44; P, 1.04; Mo, 41.66; Cu, 2.48. The IR spectrum of 3 is shown in Figure S20.

 $[Cu_2(H_2O)_2(L1)_3][PMo^{VI}_{11}Mo^VO_{40}]$  (4). Except for  $CuCl_2 \cdot 2H_2O$  (0.090 g, 0.450 mmol), no DCM, and the pH value 3.7, others were the same with 1 (the crystals could be repeated easily and yield 44% based on Mo). Anal. Calcd for 4 (%): C, 22.10; H, 1.79; N, 8.59; P, 1.06; Mo, 39.23; Cu, 4.33. Found: C, 22.29; H, 1.65; N, 8.65; P, 1.14; Mo, 39.88; Cu, 4.19. The IR spectrum of 4 is shown in ESI in Figure S20.

 $(H_2L2)_{0.5}[(Cu^{l}L2)_2(PMo_{12}O_{40})]$ ·H<sub>2</sub>O (5). Except for CuCl<sub>2</sub>·2H<sub>2</sub>O (0.095 g, 0.500 mmol), BBTZ (0.012 g, 0.050 mmol), no DCM and the pH value 4.0, others were the same with 1 (the crystals could be repeated easily and yield 61% based on Mo). Anal. calcd for 5 (%): C, 14.03; H, 1.30; N, 8.18; P, 1.21; Mo, 44.81; Cu, 4.95. Found: C, 14.35; H, 1.24; N, 8.06; P, 1.18; Mo, 44.77; Cu, 4.57. The IR spectrum of 5 is shown in Figure S20.

Single-crystals (1–5) were on the top of a 20 mm long glass fiber, and collected using a single-crystal diffractometer (BRUKER D8 Venture) with graphite monochromatic Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) and SMART CCD diffractometer at 293 (K). The structures of 1–5 were solved and refined using SHELXTL-2018 by direct method and full-matrix least-squares on  $F^2$  summarized in Table S1.<sup>44,45</sup> During the refinements, not all the non-hydrogen atoms in the compounds were refined with anisotropic thermal parameters. The details of the refinement process are attached in the CIF files; CCDC 1834889, 1040684, 1834890, 1040685, and 1040686 for 1–5 contain the crystal-lographic data. The CIF files can be obtained free of charge, by contacting CCDC, 12 Union Road, Cambridge CB2 1EZ, UK via fax (+44 1223 336033) or by e-mail (data\_request@ ccdc.cam.ac.uk).

## RESULTS AND DISCUSSION

**Structural Description.** Structural Description of 1. According to the single-crystal X-ray diffraction analysis, in the asymmetry unit, 1 is composed of one Keggin-type  $[PMo^{VI}_{9}Mo^{V}_{3}O_{40}]^{6-}$  anion, one  $[Cu^{II}L1_2]^{2+}$  metal-organic cation fragment, and one free  $[(CH_2L1)_2]^{4+}$  segment (Figure S1a). In 1, each Cu<sup>II</sup> center is in a hexa-coordinated environment, defined by four N atoms from four L1 organic

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Figure 1. (a) The representation of 1D interpenetration chain in 1 with the  $CBPQT^{4+}$  fragments (in yellow color). (b) The representation of the 2D topological layers in 1. The POMs short for red sticks, and the Cu centers short for blue nodes, and the organic ligands short for yellow and dark blue rings. (c) The topological view of the 3D supermolecule polyrotaxane network of 1.

ligands and two terminal O atoms from two different  $[PMo^{V_1}_{9}Mo^{V_3}O_{40}]^{6-}$  anions (with the bond distances of Cu1–N1 2.0041(77), Cu1–N4 1.9953(87), Cu1–O11 2.5517(91), Figure S1b). The organic ligands L1 coordinated with the Cu<sup>II</sup> centers are Z-type configurations (Figure S2b), resulting in 1D connected metal–organic ring chains (Figure 1a). Additionally, there are two kinds of rings, A and B (Figure S2a) in 1, which ring A chains interpenetrate through parallel ring B. Ring A is composed of Z-type organic ligands L1 and Cu<sup>II</sup> centers. However, ring B (tetrakis-imidazolium macrocycle), called cyclophane (34-membered cyclophane), is formed by two organic ligands (L1 in ring B is U-type configuration) linked by two  $-CH_2-$  groups through C–N bond with four positive charges. Scheme 1 shows the reaction

Scheme 1. Simple Process for the Reaction of the Organic Ligand with DCM Forming the CBPQT<sup>4+</sup>



process between the organic ligand L1 and dichloromethane (DCM) (step 1), including the reaction intermediate (step 2) and the final cyclophane structure (step 3).<sup>34–41</sup> This reaction represents the first demonstration of a self-assembled MIMA PMOF with cyclophane [tetra-cationic viologen macrocycle cyclobis(paraquat-*p*-phenylene) (CBPQT<sup>4+</sup> system)]. In previous works, MOFs with CBPQT<sup>4+</sup> systems were obtained by the method of stepwise synthesis in organic solvent.<sup>34–41</sup> We stress, however, that here the unique framework of 1 was obtained by a one-step process through self-assembly synthesis under ionothermal conditions from the original L1 organic ligand, Keggin-type anions, DCM, and TM. This novel

procedure illustrates a new, environmental friendly and relatively easy strategy to obtain MIMA MOFs with a CBPQT<sup>4+</sup> system. Ring A (continuous metal-organic ring) chains pass through the parallel arranged ring B (tetrakisimidazolium macrocycle, as shown in Figure 1a) and resulted 1D infinite interpenetrating polyrotaxane chains. The adjacent chains are connected by Cu<sup>II</sup> centers through [PMo<sup>VI</sup><sub>9</sub>Mo<sup>V</sup><sub>3</sub>O<sub>40</sub>]<sup>6-</sup> anions to form 2D infinite monolayers (Figure 1b). The 2D layers are a representation of 2D infinite interpenetration polyrotaxane structure. They will approximately be (4.4) connected layers where Cu<sup>II</sup> centers act as the 4-connection nodes, and organic ligands and the Keggin-type anions act as the linkers (Figure S3). The layers are packed along the *c*-axis in an eclipsed geometry, with a distance of 14.3 Å between the two adjacent sheets. These 2D sheets ultimately develop into a 3D supermolecule interpenetrated polyrotaxane framework by the interaction of H-bonds (Figures 1c and S4). The CBPQT<sup>4+</sup> rings are alternating throughout the 2D layers. We note that A and B are present in a 1:1 ratio in the crystal structure of 1.

Structural Description of 2. According to the single-crystal X-ray diffraction analysis, in the asymmetry unit, 2 is composed of one Keggin-type  $[PMo_{12}O_{40}]^{3-}$  anion, one  $[Zn_{0.5}(H_2O)$ - $L1]^+$  metal-organic cation fragment, one  $[Zn(L1)_{1.5}Cl]^+$ metal-organic cation fragment, half a dissociative protonated organic ligand  $[H_2L1]^{2+}$  segment, and one and a quarter dissociative water molecules (Figure S5a). The Zn<sup>II</sup> centers in the compound can be divided into two groups, Zn1 and Zn2. Each Zn1 center has a four-coordinated tetrahedral geometry defined by three N atoms from three organic ligands L1 and one Cl atom (with the distance of the bonds are Zn1-N3 1.9721(210), Zn1-N5 1.9290(105), Zn1-N9 2.0257(131), Zn1-Cl1 2.1924(48), as shown in Figure S5b); each Zn2 center has a six-coordinated octahedral geometry which is defined by four N atoms from organic ligands L1 and two O atoms from coordinated H2O molecules (with the bond distance of Zn2-N18 2.2002(230), Zn2-N8 2.0216(203), Zn2-O2W 2.2073(200), Figure S5b). The organic ligands, which coordinated with Zn<sup>II</sup> centers, are divided into two groups: one is Z-type, and the other is U-type (Figure S6e,f). The two U-type organic ligands are connected through Zn1 and Zn2 centers resulting in a two-connected metal-organic ring structure (A and B, in Figure 2a) by sharing one Zn2



Figure 2. (a) The representation of the 1D chain of the dimerization of rotaxanes in 2. (b) The topological view of the 1D chain of the dimerization of rotaxanes in 2. (c) The representation of the 3D supermolecule triple interpenetrated polyrotaxane network of 2. (d) Topological view of the 3D supermolecule triple interpenetrated polyrotaxane network of 2.

center. The adjacent two-ring fragments are connected by Zn1 centers through Z-type organic ligands resulting in 1D infinite polyrotaxanes chains (Figure 2a,b). The 1D chains, which could be considered as a two-ring polyrotaxanes, are constructed by three contiguous metal centers Zn1-Zn2-Zn1 connected with four U-type organic ligands (Figure 2a), and a metal center Zn2 through one Z-type organic ligand generates dimeric rotaxanes chains (Figure 2a). As shown in the Figure 2b, the two polyrataxanes that are in the 1D chain of the dimerization of polyrotaxanes are labeled A and B. The alkane parts of one rotaxane in the three adjacent dimerization rotaxanes thread A and B rings of the other two polyrotaxanes, resulting in three-fold interpenetrating polyrotaxanes layers (as shown in Figure 2c,d). The 2D interpenetrating network with cavities can hold nearly two Keggin-type [PMo<sub>12</sub>O<sub>40</sub>]<sup>3-</sup> anions in the holes (Figure 3a,b). These 2D structures ultimately develop into a 3D supermolecule triple interpenetrated polyrotaxane network by the interaction of H-bonds. The dissociative protonated organic ligand  $[H_2L1]^{2+}$  segments were located between the adjacent 2D layers.

Structural Description of **3**. According to the single-crystal X-ray diffraction analysis, in the asymmetry unit, **3** crystallizes in the tetragonal space group P4/n and is composed of a classical  $\alpha$ -Keggin-type anion  $[PMo_{12}O_{40}]^{3-}$ , one  $[Cu-(H_2O)_2L1_2]^{2+}$  metal-organic cation fragment and one dissociative TBA<sup>+</sup> cation as shown in Figure 4a. Each Cu<sup>II</sup> center is six-coordinated by four N atoms from the organic



Figure 4. (a) The representation of the unit call of 3. (b) The representation of the 2D metal-organic layers with the TBA<sup>+</sup> cations and the Keggin-type anions between them. (c) The space packing representation of adjacent metal-organic layers. (d) The representation of the metal-organic (4,4) topological layer. (e) Topological view of the adjacent (4,4) metal-organic layers.

ligands L1 and two O atoms from coordinated water molecules (with the bond distance of Cu1-N1 2.0173(65), Cu1-O1W 2.2374(123), and Cu1-O2W 2.3132(457), as shown in Figure 4a). And then the Cu<sup>II</sup> centers expand to 2D layers through the coordinated Z-type organic ligands L1, resulting in (4,4) topology layers with  $11.5 \times 11.5$  Å sized holes in it (Figure 4d). The packing period of the adjacent 2D (4,4)-layers is two in the 3D space in Figure 4e. In the two adjacent 2D layers, the linkers (organic ligands L1) from different layers show crossshaped structures along *c*-axis in Figure 4e. On each side of the two adjacent 2D layers, free Keggin-type  $[PMo_{12}O_{40}]^{3-}$  anions reside in the holes of the layers and the opposite side of the Cu<sup>II</sup> centers. However, the free TBA<sup>+</sup> cations are on the opposite side of the organic ligands L1, as shown in Figure 4b,c. On the other side of the two adjacent 2D layers, the space packing mode of the free Keggin-type [PMo<sub>12</sub>O<sub>40</sub>]<sup>3-</sup> anions and the TBA<sup>+</sup> cations is the same. The free Keggin-type anions and TBA<sup>+</sup> cations interacted with the 2D metal organic layers



Figure 3. (a) The 2D polyrotaxane-type network with the guests Keggin-type POMs in the holes of 2. (b) The topological representation of 2D polyrotaxane-type triple interpenetrated network with the guests Keggin-type POMs in the holes of 2.

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through the H-bonds and result in 3D supermoleculars, as shown in Figures 4b,c and S7.

Structural Description of 4. According to the single-crystal X-ray diffraction analysis, in the asymmetry unit, 4 is composed of one  $[PMo^{VI}_{11}Mo^{V}O_{40}]^{4-}$  anion and two  $[Cu(H_2O)-(L1)_{1.5}]^{2+}$  metal–organic cation fragments (Figure S8a). In 4, each Cu<sup>II</sup> center is in a distorted tetrahedral coordination environment, defined by three N atoms from three organic ligands L1 and one O atom from the coordinated water molecule (with the bond distance of Cu1–N1 2.1120(77), Cu1–N4 2.0108(102), Cu1–N8 2.0492(33), and Cu1–O1W 2.0007(37), as shown in Figure S8a). The organic ligands coordinated with Cu<sup>II</sup> centers show two different kinds of coordination configurations called Z- and U-type (Figure S8b). As shown in Figure 5a,b, the adjacent Cu<sup>II</sup> centers are



Figure 5. (a) The representation of the ladder-shape 1D chain in 4. (b) Topological ladder-shape structure in 4. (c) The representation of the adjacent ladder-shaped structures packing in the space existing two kinds of windows (A and B) along the *b*-axis. (d) Topological views of adjacent ladder-shaped structures of 4. (e) The representation of the 3D supermolecules with POM-encapsulated in the windows of A. (f) Topological views of the 3D supermolecules of 4.

connected through the U-type organic ligands generating 1D infinite chains, and the adjacent chains then extend to laddershaped structures with large holes in it by Z-type organic ligands L1 through the Cu<sup>II</sup> centers. These ladder-shaped 1D structures then pack to 2D ladder-shaped layers through Hbonds from the organic ligands L1 (Figure 5c). These adjacent layers then are further connected with H-bonds to form 3D porous supermolecules through Keggin-type anions. It can be observed that 4 is composed of two types of tubes (A and B) along the *b*-axis (Figure 5c,d). The channels (A) are filled by the Keggin-type [PMo<sup>VI</sup><sub>11</sub>Mo<sup>VO</sup><sub>40</sub>]<sup>4-</sup> anions (Figure 5e,f) interacted with the MOF via H-bond. Intriguingly, the tubes B are completely open cavities, and the size of the holes is about 8.5 × 7.5 Å (Figure S10). The SQUEEZE module of the PLATON analysis for the structure without the contribution of solvent shows that the effective free volumes in 4 are 22.1% of the whole crystal volume.<sup>46</sup> In order to confirm its porosity, N<sub>2</sub> adsorption measurements were subsequently implemented for the fully activated crystals (4) as shown in Figure S27.<sup>47–51</sup> As a result, it is a characteristic type II behavior for microporous materials with a slight hysteresis between the adsorption and desorption at 77 K. The phenomenon can be interpreted by the dynamic feature and cage effect of the framework. The Langmuir surface areas and Brunauer–Emmett–Teller (BET) were 714 m<sup>2</sup> g<sup>-1</sup> and 476 m<sup>2</sup> g<sup>-1</sup>, respectively. The maximum N<sub>2</sub> uptake reaches 204 cm<sup>3</sup> g<sup>-1</sup> (at standard temperature and pressure, STP) at 1 atm for 4.

Structural description of 5. According to the single-crystal X-ray diffraction analysis, in the asymmetry unit, 5 crystallizes in the triclinic space group P-1 and is composed of a classical  $\alpha$ -Keggin-type anion  $[PMo_{12}O_{40}]^{3-}$ , two metal–organic cation fragments  $(Cu^{I}L2)^{+}$ , one dissociative water molecule, and half of a dissociative protonated organic ligand  $(H_2L2)^{2+}$  (Figure S11a). In 5, there are two crystallographically independent Cu<sup>I</sup> centers (Cu1 and Cu2). Both Cu1 and Cu2 centers are threecoordinated by two N atoms from two organic ligands L2 and one terminal O atom from one  $[PMo_{12}O_{40}]^{3-}$  anion in a slightly distorted T-type coordination configuration (with the bond distance of Cu1-N3 1.8711(110), Cu1-N4 1.8822(128), Cu1-O15 2.6857(116), Cu2-N9 1.8583(111), Cu2-N15 1.8709(122), and Cu2-O24 2.8232(98), Figure S11b). The metal Cu1 and Cu2 centers are linked by Z-type organic ligands L2, resulting in 1D infinite helix chains (Figure 6a,b). These helix chains (left:right = 1:1) formed a racemic compound without chiral in 3D space (Figure 7b,c), because the adjacent two chains connected to Keggin-type anions are inversion symmetry (Figure 7a) in the space. The 2D (6,3) honeycomb monolayers are constructed through Cu1-Cu1-Cu1-Cu2-Cu2-Cu2 connecting alternately by the Keggintype anions and organic ligands L2 (Figure 6c,d). The size of the honeycomb is about  $16 \times 17$  Å, which could nearly hold two Keggin-type anions. The adjacent layers are further linked into a 3D supermolecule framework with channels along the *b*axis, and the channels are filled by dissociative protonated organic ligands L2 (Figure S12a).

Synthesis Discussion. Under ionothermal conditions, RTILs can act as solvents, potential templates, or structural directing agents to aid the assembly of solids, because of their weak coordination, good solubility, low competition between solvents and frameworks, and tunable acidity.<sup>29</sup> 1-5 were all based on the system of Keggin-type POMs anions/TM (Cu and Zn)/BTMB or BBTZ organic ligands. According to the structural properties of the five compounds discussed above, they could be divided into two groups: One is the polyrotaxane MIMAs, and the other is 3D supramolecular layer structures without rotaxane (Scheme 2). In the first group, 1 and 2 both possess MIMAs constructed by the 2D interpenetrating polyrotaxane layer structures. The organic ligands BTMB in both 1 and 2 adopt the U- and Z-type coordination modes (the U-type BTMB organic ligands in 1 were used to form the CBPQT<sup>4+</sup> system) inclined to a formation of rotaxane structures because of their long chain structure and flexibility. In addition, the six-coordinated TM centers promote the formation of 1 and 2 as well (there are two kinds of coordination numbers (4 and 6) in 2). As a result, the high coordination number of the TM centers and the flexibility

Article



**Figure 6.** (a) The representation of 1D helix chain in 5. (b) The topological view of the 1D chain. (c) 2D (6,3) honeycomb monolayers in 5. (d) The topological view of the (6,3) honeycomb monolayer (the POMs and the organic ligands short for blue sticks and the Cu centers short for blue nodes).



**Figure 7.** (a) The representation of the inversion symmetry of the two adjacent helical chains in **5**. (b) The representation of the racemic left- and right-handed single-helical chains.

Scheme 2. Keggin-Based PMOFs with Polyrotaxane or 2D Layer Supermolecule Structures Were Obtained Under ILs Conditions



(two configurations of U and Z-type) of the long organic ligands result in the polyrotaxane 2D layer structures 1 and 2. In the other group, 3-5 all emerge 3D supramolecular layer structures without rotaxane constructed by (4,4) topological monolayers, 1D infinite ladder-shaped structures, and (6,3) honeycomb monolayers, respectively. Even though the configurations of the BTMB in 4 are also shown in U- and Z-type, the coordination number of the Cu<sup>II</sup> centers is low to 4. More importantly, one of the coordination atoms is O from the coordinated water molecule, so that the coordinated

configurations of the Cu<sup>II</sup> centers are T-type in fact. Hence, the two configurations of the organic ligands and T-type coordinated Cu<sup>II</sup> centers create 1D infinite ladder-shape structures instead of polyrotaxane MIMAs. Compared to 4, the configuration of the organic ligands in 3 is simply Z-type resulting in (4,4) topological monolayers. However, compared to 3 and 4, the shorter organic ligand BBTZ was applied in 5 instead of BTMB, which only exhibits Z-type configuration. The single configuration of the organic ligands BBTZ (Z-type) results in the (6,3) honeycomb monolayer for 5. According to the discussion above, the long and flexible organic ligands, more configurations of the organic ligands and the high TM coordination number are the main factors forming the polyrotaxane MIMAs.

As we all know, several factors can influence the structures under ionothermal conditions. In this paper, 1 and 2 were absolutely obtained under the same pH value (about 4.5) and reaction temperature (170 °C). With the same mole ratio and temperature to 2, changing the pH value to 3.7 and adding a small quantity of Vc, 4 (without polyrotaxane MIMAs) was obtained. As the same mole ratio and temperature as 1, 3 (without polyrotaxane MIMAs) was synthesized by decreasing the pH value to about 4.0. With the same pH value and the temperature as 3, 5 was obtained by changing the mole ratio and adding a small quantity of Vc. The different oxidation states of Mo and Cu cations in 1, 4, and 5 were due to the addition of the small amount of Vc as the reducing agent. In addition, the charge of valence states of Mo and Cu cations in 1, 4, and 5 was measured by XPS as shown in Figures S28-S30. According to the discussion above, it is shown that the pH value of the reaction system is the main factor to obtain the polyrotaxane MIMAs.

**Proton Conductivity.** It is clearly shown that 2, 4, and 5 all possess 2D layered structures with dissociative Keggin-type anions or protonated organic molecule ligands interacting with neighboring metal—organic layers or channels. According to the structural properties, they are potentially proton conductors. Hence, we measured the water-assisted proton conduction of 2, 4, and 5 under the conditions of 65 °C and different RH.

From Figures 8–10, the electro-conductibility of 2, 4, and 5 increases with the increasing temperature under the conditions of 45% RH, 70% RH, and 95% RH, respectively. According to other reports, the increasing RH can increase the up-take of the water molecules into the hydrophilic channels or layers as well as facilitating higher proton transportation.<sup>52</sup> Compared with the three different RHs, the conductivity under the



Figure 8. Nyquist plot of proton conduction for 2 at 65 °C. (a) 45% RH, (b) 70% RH, (c) 95% RH. (d) Arrhenius plots of proton conductivities for 2 at different RH.



Figure 9. Nyquist plot of proton conduction for 4 at 65 °C. (a) 45% RH, (b) 70% RH, (c) 95% RH. (d) Arrhenius plots of proton conductivities for 4 at different RH.

condition of 95% RH is the highest for **2**, **4**, and **5**. The high conductivity for **2**  $(2.2 \times 10^{-4} \text{ S cm}^{-1} \text{ under the conditions of 65 °C and 95% RH, Figure 8) was carried out by EIS$ 

measurements. According to Arrhenius equation, the activation energy is 0.39, 0.41, and 0.44 eV for 95% RH, 70% RH, and 45% RH in **2**, respectively. In addition, the proton conductivity



Figure 10. Nyquist plot of proton conduction for 5 at 65 °C. (a) 45% RH, (b) 70% RH, (c) 95% RH. (d) Arrhenius plots of proton conductivities for 5 at different RH.

of 2 (65 °C and 95% RH) is much higher than that of classic MIL-53-based MOFs (ca.  $10^{-6}$  to ca.  $10^{-9}$  S cm<sup>-1</sup> under the condition of 25 °C and 95% RH by Kitagawa et al.), and it is nearly the same with the graphene oxide (GO) nanosheets (ca. 10<sup>-4</sup> S cm<sup>-1</sup> under the condition of 25 °C and 60% RH by Matsumoto et al.).<sup>53</sup> The same measurements show that the activation energy of 4 is 0.40, 0.42, and 0.45 eV (95% RH, 70% RH, 45% RH) and 0.43, 0.45, and 0.48 eV (95% RH, 70% RH, 45% RH) for 5. Meanwhile, the high conductivity is  $2.8 \times 10^{-4}$ S cm<sup>-1</sup> (65 °C and 95% RH) for 4, in Figure 9 and  $1.9 \times 10^{-4}$ S cm<sup>-1</sup> (65 °C and 95% RH) for **5**, in Figure 10. According to the results above, it can be concluded that the three compounds exhibit little differences in their proton conductivity and activation energy. This is likely observed because the similar structures of the three compounds are all 3D supermolecules constructed by 2D infinite layers interacting through H-bonds from the POMs anions and organic fragments.

The vehicular mechanism is consistent with the results of proton conduction under the condition of different RH and the architectural features of **2**, **4**, and **5**. In the channels or layers, there are a limited number of water molecules and organic ligands acting as vehicles for proton conductivity.<sup>54</sup> The additional protons can be incorporated by the water molecules lost H-bond from the networks and directly diffuse in the channels and layers under higher RH.<sup>55</sup>

## PHOTOCATALYTIC ACTIVITY

**Photocatalytic RhB Degradation.** Due to the similar light absorption and electrochemical band-edge positions to  $TiO_2$ , POMs show prominent photocatalytic activity (especially the organic small molecule dye photodegradation) under

visible-light irradiation.<sup>6,7,16–23</sup> Introducing the POMs into MOFs, the PMOFs inherit advantages such as high thermal stability, easy recyclability, definite structures and chemical components, porosity, large surface area, high metal content, and flexible active sites. The advantages discussed above and structural properties make the organic–inorganic hybrid materials ideal representations to organize light-harvesting and catalytic sites achieving solar energy conversion.<sup>23</sup>

As the photocatalyst, the optical band gap  $(E_g)$  is a main influence for the decomposition efficiency of the small molecular organic dyes.<sup>13,14</sup> First, the low-energy adsorption bands of 1-5 are similar over about 460 nm (2.71 eV) as shown in Figure S13. Then, solid-state diffuse reflectivity measurements were carried out to obtain the  $E_g$  to investigate the semiconductor properties of 1-5 with dry crystalline state powder at room temperature (Figure S14). The  $E_g$  values are 2.20, 2.30, 2.18, 2.71, and 2.35 eV for 1-5, respectively. Due to the results of the UV-vis-NIR, it is shown that 1-5 are potentially semiconductor materials for visible-light photocatalysts. Because of the layer-structure properties and narrow optical gaps  $E_{\rm g}$  of 1–5, they were chosen to be photocatalysts to investigate the RhB photodegradation under visible-light irradiation. Due to the five undissolved compounds (1-5), they can only be used as heterogeneous catalysts. Figures 11 and S15 clearly show that the absorption peak of RhB dramatically decreases with increasing reaction time under visible-light irradiation, which means RhB rapidly degraded. In the presence of 1, the RhB degrades from 100% to 7.69% during the first 120 min with a degradation rate of 46.16% per hour. This result demonstrates that 1 shows a great photocatalytic activity for the photodegradation of RhB. For 2-5, the RhB degrades from 100% to 26.67% during 180 min



Figure 11. Conversion of the RhB with reaction time for 1-5 and the blank experiment (without catalyst).

with a degradation rate of 24.44% per hour, from 100% to 40% during 180 min with a degradation rate of about 20.00% per hour, from 100% to 18.75% during 210 min with a degradation rate of about 23.21% per hour, and from 100% to 28.57% during 180 min with a degradation rate of about 23.81% per hour, respectively. To compare with 1-5, the RhB photodegradation experiments with H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> as catalysts and without any catalysts were both analyzed as shown in Figures 11, S15, and S16, respectively (the photodegradation of RhB with  $H_3[PMo_{12}O_{40}]$  or without any catalyst was examined with the conversion rates 69% and <10% in 6 h). As a photodegradation catalyst, 1 is among the best PMOFs with high photocatalytic activity under visible-light irradiation.<sup>23</sup>

The PMOFs, as heterogeneous photocatalysts, have the benefit of simultaneously adsorbing the reactants (organic substrates and dioxygen) on the catalyst surface and suitable light energy.<sup>56,57</sup> Meanwhile, the modifications in 1-5 to Keggin-type  $[PMo_{12}O_{40}]^{3-}$  anions by the metal-organic fragments possibly enhance the organic molecules photodegradation activity under visible-light irradiation, because Cu/ Zn-BTMB/BBTZ metal-organic subunits as linkers, hosts, and layers could promote the POM to POM electron transfer or prevent the POMs deactivation and conglomeration.<sup>23</sup> Moreover, before the visible-light RhB photodegradation, the thermal stability of the five compounds was confirmed by TGA curves in Figure S23. It is shown that the five compounds could be stable below 200 °C. After the RhB photodegradation experiment, the PXRD and IR spectra of the five compounds as catalysts under visible-light irradiation were compared with the data before the experiment and the simulated ones as shown in Figures S18-S21. From the result of long-term stability, it can be concluded that the five compounds are stable and reusable for the visible-light RhB photodegradation at least after three cycles.

Hydrogen Evolution. The RhB photodegradation as a catalytic test is not enough for the research of photocatalytic activity for 1-5. Hence, the photocatalytic activity of  $H_2$ evolution under visible-light irradiation for 1-5 has also been investigated and compared to the previous literatures.<sup>58-64</sup> In Figure 12,  $H_2$  is continuously produced under visible-light radiation in this catalytic system. The total amount of H<sub>2</sub> was 12.2  $\mu$ mol (at a rate of 29.6  $\mu$ mol g<sup>-1</sup> h<sup>-1</sup>) in 6 h for 1. It almost possesses the same activity as that of well-known



Article



14

Figure 12. Representation of the time course of photocatalytic H<sub>2</sub> evolution from 100 mg 1-5, respectively, loaded with 1.2% Pt, in 100 mL (80 mL water and 20 mL methanol) solution under visible-light irradiation and the blank experiment (without catalyst).

catalysts, such as phosphoniobate-based/amino-functionalized Ti<sup>IV</sup>/dye-sensitized Pt@UiO-66(Zr) frameworks, post-synthesis modification of MOF-253-Pt, as well as some high active POMs based PMOFs.<sup>18-23</sup> Compared with 1, the blank experiment (without catalyst) was also performed with the total amount of  $H_2$  producing <0.1  $\mu$ mol in 6 h. The photocatalytic H<sub>2</sub> evolution activity of 1 was also studied in methanol (100%) and water (100%), respectively. The total amount of the H<sub>2</sub> in methanol was similar with that in 100 mL 20% methanol solution and much higher than that in water (100%), as shown in Figure S25. Additionally, the same experiments were also taken to investigate the photocatalytic  $H_2$  evolution activities of 2-5 and were shown to be a little less active than 1 (Figure 12). From the result of photocatalytic  $H_2$  evolution, it is suggested that 1-5 is highly active for photocatalytic H<sub>2</sub> evolution under visible-light irradiation. The little difference of the H<sub>2</sub> evolution rate can be caused by the different  $E_{g}$  values and different structures among the five compounds. In addition, long-tern stability for H<sub>2</sub> evolution of 1-5 as the catalysts under visible-light irradiation was studied as well. In Figure S24, it is shown that 1-5 are very stable and reusable for at least three times. After the three cycles of  $H_2$ evolution, the PXRD of the five compounds matched well with the ones before and simulated from the structural data, as shown in Figures S18 and S26.

## CONCLUSIONS

Five remarkable classic Keggin-type PMOFs have been successfully synthesized under ionothermal conditions. It is the first report of self-assembled cyclophane structures with tetra-cationic viologen macrocycle cyclobis(paraquat-p-phenylene) CBPQT<sup>4+</sup> system via ionothermal synthesis. It is also the first report of Keggin-type PMOFs with MIMAs (polyrotaxane structures) (1 and 2) synthesized under ionothermal conditions. According to the structural properties, the EIS measurements of 2, 4, and 5, show a high conductivity (2.2  $\times$  $10^{-4}$  S cm<sup>-1</sup>, 2.8 ×  $10^{-4}$  S cm<sup>-1</sup> and  $1.9 \times 10^{-4}$  S cm<sup>-1</sup> under the condition of 65 °C and 95% RH), with an activation energy of 0.44, 0.45, and 0.48 eV for proton conduction, respectively. Proton conduction for the three compounds is

proved to be through a vehicular mechanism. Photocatalytic investigations indicate that the five compounds are active and stable for photocatalytic  $H_2$  evolution and RhB degradation under visible-light irradiation. As a result, this work presents a new strategy from which to synthesize PMOFs with entangled, cyclophane, polyrotaxane, and 2D layered structures with high proton conductivity and photocatalytic activity by an ionothermal method.

## ASSOCIATED CONTENT

## **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b02277.

The single-crystal data and the structure refinements for 1-5, the additional figures for 1-5, and the experimental section details (the synthesis of the Keggin, L1, L2, and the ILs used in the paper, the experimental details of the proton conduction, photocatalytic RhB degradation, and H<sub>2</sub> evolution). The solid-state emission spectra, UV-vis-NIR diffuse reflectance spectra, long-term stability experiment of 1-5 for the RhB photocatalytic degradation and H<sub>2</sub> evolution under visible-light irradiation, the TGA curve of the five compounds, the PXRD and the IR spectra of the five compounds before and after the photocatalysis, the XPS of the Mo and Cu in 1, 4, and 5, and the N<sub>2</sub> sorption of 4. The mechanism of the proton conduction, photocatalytic RhB degradation, and H<sub>2</sub> evolution analysis (PDF)

## Accession Codes

CCDC 1040684–1040686, 1834889, and 1834890 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/ data\_request/cif, or by emailing data\_request@ccdc.cam.ac. uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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