POM–Organic Frameworks

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Designed Synthesis of POM–Organic Frameworks from $\{Ni_6PW_9\}$ Building Blocks under Hydrothermal Conditions**

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Metal–organic frameworks (MOFs) have attracted considerable interest owing to their intriguing structures and wide potential applications in a variety of areas, including gas storage, separations, catalysis, magnetism, and nonlinear optical materials.[1] Over the past two decades, a large variety of MOFs based on linking metal ions with organic molecules have been reported. However, it is difficult to design or predict the structures and composition of the reaction products because the metal ions hold little directional information. In 2001, an attractive design strategy involving the use of rigid molecular blocks, formed in situ under well-defined conditions, as secondary building units (SBUs) to direct the assembly of MOFs was reviewed by Yaghi et al.[2] Since rigid SBUs have specific geometries and can maintain their structural integrity throughout the construction process, the design of the target frameworks may be realized starting from SBUs. Additionally, rigid SBUs not only can make robust frameworks but also impart their physical properties to the frameworks.[3] Owing to these attractive features, great efforts have been made to achieve the rational design of SBU-based MOFs in recent years.[4] For example, Yaghi et al. have created porous MOFs built by zinc carboxylate clusters for hydrogen storage.[4a] Similarly, Férey et al. have applied trimeric SBUs for making porous transition-metal carboxylates.[4b,c] In addition, Zheng et al. have elaborated supramolecular constructions using hexanuclear rhenium selenide clusters as SBUs.[4d,e] Using cadmium chalcogenide clusters as building blocks and further linking with organic ligands, Feng et al. have made a series of novel extended superstructures.[4f,g] Qiu et al. also obtained a novel 3D framework by utilizing nanosized undecanuclear $\{Cd_{11}\}$ clusters.[4h] More recently, the Eddaoudi group has extended the type of trimeric SBUs to p-block elements, resulting in two novel MOFs based on trinuclear indium carboxylate clusters.[4i]

Polyoxometalates (POMs) have been attracting extensive interest owing to their enormous structural variety and potential applications.[5] The POM clusters with different shapes, sizes, and composition provide a variety of SBUs for making novel and robust POM–organic frameworks (POMOFs), which belong to the cluster–organic frameworks (COFs). POM clusters are attractive inorganic building blocks owing to their nanometer size and tunable acid–base, redox, magnetic, catalytic, and photochemical properties. Therefore, the designed synthesis of COFs will open up a new avenue for the creation of a variety of novel functional materials. In particular, the combination of POM clusters and organic ligands is more interesting because of their inherently different natures and possible synergetic effects in making COF materials.

However, although many MOFs have been built with metal carboxylate SBUs,[4] only a few examples of POM-based MOFs have been reported.[6] So far, most of reported POM-based materials with extended structures are based on the linkages of POM clusters and metal complexes bridged by oxygen atoms.[7] The linking of POMs with rigid carboxylates into POMOFs has remained largely unexplored, mainly because POM clusters, usually having large negative charges and oxygen-rich compositions, preferentially bond metal cations rather than carboxylate anions. Therefore, the search for suitable POM clusters for making POMOFs is highly challenging.

We chose the Ni_6-substituted POM $[Ni_6(\mu_3\text{-}OH)_3(H_2O)_6L_3(B\text{-}\alpha\text{-}PW_9O_{34})]$ ($\{\mathbf{Ni_6PW_9}(H_2O)_6\}$, where $\mathbf{Ni_6} = [Ni_6(\mu_3\text{-}OH)_3L_n]^{9+}$, $\mathbf{PW_9} = B\text{-}\alpha\text{-}[PW_9O_{34}]^{9-}$ and B indicates the type of isomer of $\alpha\text{-}PW_9O_{34}$,[8] L = en or enMe; en = ethylenediamine, enMe = 1,2-diaminopropane) as SBU on the basis of the following considerations: 1) We have obtained well-defined reaction conditions for the in situ preparation of $\{\mathbf{Ni_6PW_9}(H_2O)_6\}$ SBUs.[8] 2) Each $\{\mathbf{Ni_6PW_9}(H_2O)_6\}$ SBU contains six terminal water ligands that offer the possibility for the design of POMOFs by replacing the water with rigid carboxylates. Notably, the POM-based SBUs can be isolated and are stable in the absence of the carboxylate ligands,[8] which differ from previously used metal carboxylate SBUs that are only stable in the presence of the carboxylate ligands.[4]

Accordingly, we successfully prepared a series of unprecedented POMOFs comprising $\{\mathbf{Ni_6PW_9}\}$ SBUs and rigid carboxylate linkers:

$$\{[Ni_6(OH)_3(H_2O)_2(enMe)_3(PW_9O_{34})](1,3\text{-bdc})\}[Ni(enMe)_2]\cdot 4\,H_2O \quad (\mathbf{1})$$

$$\{[Ni_6(OH)_3(H_2O)(en)_4(PW_9O_{34})](Htda)\}\cdot H_3O\cdot 4\,H_2O \quad (\mathbf{2})$$

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

$\{[Ni_6(OH)_3(H_2O)(en)_3(PW_9O_{34})][Ni_6(OH)_3(H_2O)_4(en)_3(PW_9O_{34})]\text{-}(1,4\text{-bdc})_{1.5}\}[Ni(en)(H_2O)_4]\cdot H_3O$ (**3**)

$\{[Ni_6(OH)_3(en)_3(PW_9O_{34})](1,3,5\text{-Hbtc})\}[Ni(en)(H_2O)_3]\cdot 2\,H_2O$ (**4**)

$\{[Ni_6(OH)_3(H_2O)_5(PW_9O_{34})](1,2,4\text{-Hbtc})\}\cdot H_2enMe\cdot 5\,H_2O$ (**5**)

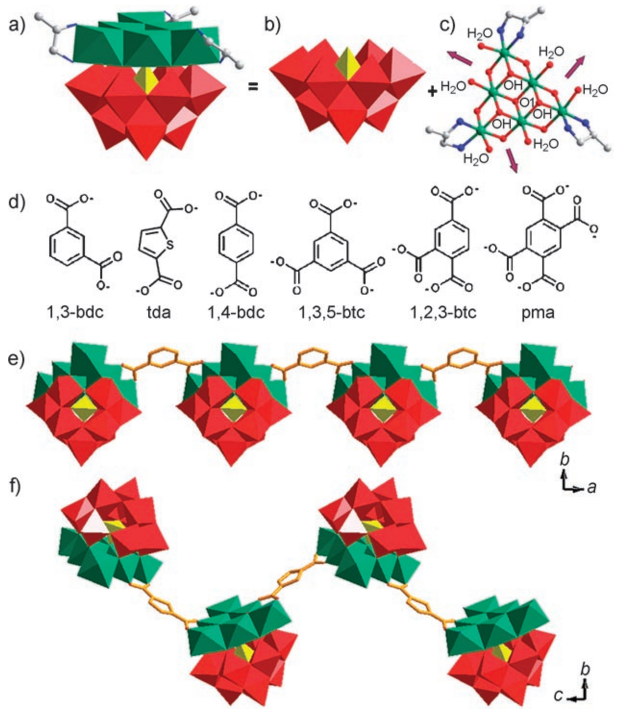


Figure 1. a) Structure of $\{\mathbf{Ni_6PW_9}(H_2O)_6\}$. b, c) Polyhedral (b) and ball-and-stick representations (c) of the $\{\mathbf{PW_9}\}$ and $\{\mathbf{Ni_6}\}$ units, respectively. d) Rigid carboxylate linkers. e, f) Views of 1D chain structures in **1** and **2**, respectively. WO_6: red; NiO_6/NiO_4N_2: green; PO_4: yellow; 1,3-bdc/tda: gold. The en and enMe ligands in (e) and (f) are omitted for clarity.

As shown in Figure 1 a–c, the structure of $\{\mathbf{Ni_6PW_9}(H_2O)_6\}$ can be described as a trilacunary Keggin B-α-$[PW_9O_{34}]^{9-}$ unit capped by a novel triangular $[Ni_6(\mu_3\text{-}OH)_3(H_2O)_6L_3]^{9+}$ core. The flat arrangement of the $\{\mathbf{Ni_6}\}$ core is built from three truncated $\{Ni_3O_4\}$ cubanes that share one edge with each other and all share a common vertex (μ_4-O1, Figure 1 c). On each side of the triangular $\{\mathbf{Ni_6}\}$ core, there are two terminal water ligands that can be substituted by a variety of rigid carboxylate ligands. Thus, the $\{\mathbf{Ni_6}\}$ core offers the opportunity to link $\{\mathbf{Ni_6PW_9}(H_2O)_n\}$ ($n<6$) units into POMOFs through rigid carboxylate bridges along three directions (Figure 1 c). Furthermore, owing to the ability of the $\{\mathbf{PW_9}\}$ unit (Figure 1 b) to share terminal oxo atoms with metal cations, the sizes of SBUs can be varied incrementally from discrete $\{\mathbf{Ni_6PW_9}(H_2O)_n\}$ units to aggregates and polymers through W=O−Ni linkages, which provide the potential for making tailor-made POMOFs. Thus, the combination of $\{\mathbf{Ni_6}\}$ and $\{\mathbf{PW_9}\}$ units makes $\{\mathbf{Ni_6PW_9}(H_2O)_6\}$ SBUs excellent candidates for constructing novel POMOFs. As expected, the addition of different rigid carboxylate ligands (Figure 1 d) to the well-defined $\{\mathbf{Ni_6PW_9}(H_2O)_6\}$ solutions[8] resulted in the formation of a series of novel POMOFs with 1D, 2D, and 3D frameworks comprising monomeric, dimeric, and infinite SBUs that are derived from the $\{\mathbf{Ni_6PW_9}(H_2O)_n\}$ units.

Use of the V-type dicarboxylate ligands 1,3-bdc and tda affords the 1D structures **1** and **2** based on $\{\mathbf{Ni_6PW_9}\}$ monomers as SBUs. The asymmetric unit of **1** consists of a $\{\mathbf{Ni_6PW_9}(H_2O)_2\}$ SBU, a 1,3-bdc bridging ligand, and an isolated $[Ni(enMe)_2]^{2+}$ cation, while that of **2** contains a $\{\mathbf{Ni_6PW_9}(H_2O)\}$ SBU and a tda bridging ligand (Figure S1 in the Supporting Information). The structure of the $\{\mathbf{Ni_6PW_9}(H_2O)\}$ unit in **2** is similar to that of the $\{\mathbf{Ni_6PW_9}(H_2O)_2\}$ unit in **1**, except that one terminal water ligand is unexpectedly substituted by a monodentate en ligand. X-ray analysis revealed that both **1** and **2** crystallize in space group $P2_12_12_1$ and are constructed from $\{\mathbf{Ni_6PW_9}\}$ SBUs linked by corresponding carboxylate ligands into 1D chains (Figure 1 e,f) through Ni–carboxylate interactions in which the carboxylate groups adopt the common η^1:η^1:μ_2 bonding mode (Ni−O 2.026(9)–2.130(13) Å). One remarkable difference between the structures is that the $\{\mathbf{Ni_6PW_9}(H_2O)_2\}$ SBUs in **1** are arranged in a shoulder-to-shoulder mode and are interlinked by 1,3-bdc ligands to generate straight chains along the a axis, while the $\{\mathbf{Ni_6PW_9}(H_2O)\}$ SBUs in **2** are arranged in a face-to-face mode and are interlinked by tda ligands to form zigzag chains along the c axis. It is notable that the vast majority of chiral coordination polymers are based on mononuclear metal centers.[9] POM-based solids with chiral structures are of particular interest.[10] Structures **1** and **2** exhibit the first two chiral 1D POMOFs.

Use of the linear dicarboxylate ligand 1,4-bdc affords the 2D structure **3**, which is based on $\{\mathbf{Ni_6PW_9}\}_2$ dimers as SBUs. The asymmetric unit of **3** contains the dimeric SBU $\{(\mathbf{Ni_6PW_9})_2(H_2O)_5\}$, 1.5 1,3-bdc units, and an isolated $[Ni(en)(H_2O)_4]^{2+}$ cation (Figure S2 a in the Supporting Information). As shown in Figure 2 a, the structure of the dimeric SBU consists of a $\{Ni_6(OH)_3(H_2O)(en)_3(PW_9O_{34})\}$ unit and a $\{Ni_6(OH)_3(H_2O)_4(en)_3(PW_9O_{34})\}$ unit linked together through one Ni−O=W linkage with the Ni-O-W angle of 161.6(1)°. By the inversion-center symmetry operation, the $\{Ni_6(OH)_3(H_2O)(en)_3(PW_9O_{34})\}$ unit in each SBU joins two 1,4-bdc ligands, which link adjacent SBUs through Ni–carboxylate interactions to form infinite $(\text{bdc-}\{(\mathbf{Ni_6PW_9})_2(H_2O)_5\})_\infty$ chains along the c axis, while the $\{Ni_6(OH)_3(H_2O)_4(en)_3(PW_9O_{34})\}$ unit in each SBU joins adjacent $(\text{bdc-}\{(\mathbf{Ni_6PW_9})_2(H_2O)_5\})_\infty$ chains along the $[1\bar{1}1]$ direction by another 1,4-bdc ligand to form a 2D layer (Figure 2 b). In each 2D layer, the coordination connectivity between the SBUs and 1,4-bdc ligands generates giant parallelogram-shaped rings with dimensions of $2.7\times 3.8\ nm^2$ (measured between opposite atoms) that lie in the plane parallel to (110). Each ring is circumscribed by six SBUs and six 1,4-bdc ligands. The 2D layers are stacked in parallel along the a axis (Figure S3 in the Supporting Information), and each layer is shifted by a with respect to the next one. Such stacking of the layers reduces the large tunnels along the [110] direction created by the parallelogram-shaped rings, but gives 1D channels along the a axis, in which the isolated $[Ni(en)(H_2O)_4]^{2+}$ complexes are located (Figure S4 in the Supporting Information).

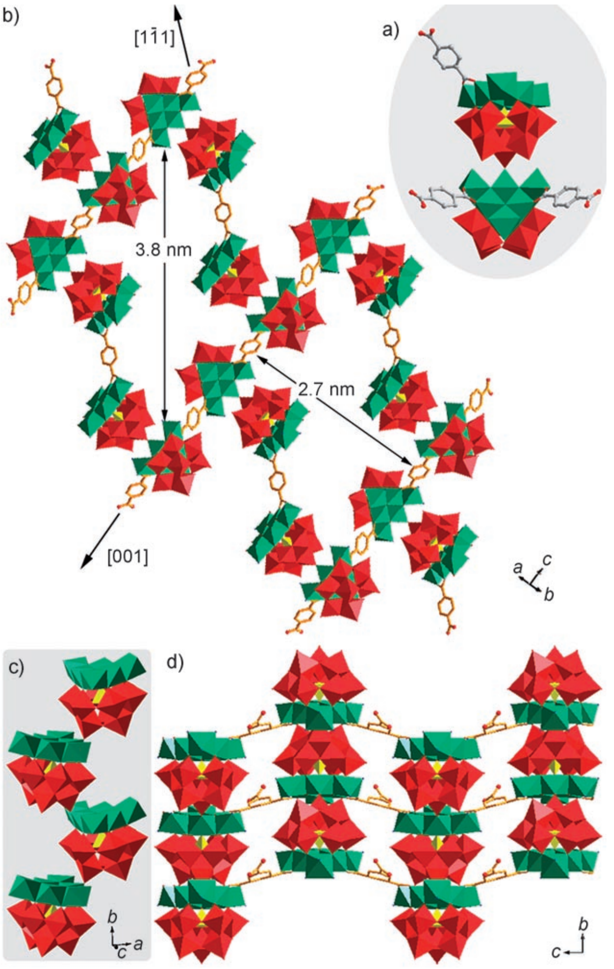


Figure 2. a, b) Views of $\{(\mathbf{Ni_6PW_9})_2(H_2O)_5\}$ dimer and 2D layer in **3**, respectively. c, d) Views of infinite $\{\mathbf{Ni_6PW_9}\}_\infty$ chain and 2D layer in **4**, respectively. The en ligands are omitted for clarity.

Comparison of structures **1**–**3** suggests that the 2D structure **3** may be derived from two straight/zigzag chains, (bdc-$\{\mathbf{Ni_6PW_9}(H_2O)\})_\infty$/(bdc-$\{\mathbf{Ni_6PW_9}(H_2O)_4\})_\infty$ (Figure S5 in the Supporting Information). These two kinds of chains are alternately connected together through Ni−O=W linkages to create a 2D layer. However, the connectivity between chains leads to significant distortion of the 1D zigzag (bdc-$\{\mathbf{Ni_6PW_9}(H_2O)_4\})_\infty$ chains and increases the spacing between $\{\mathbf{Ni_6PW_9}(H_2O)_4\}$ units. To harmonize the change, half of the 1,4-bdc ligands within the zigzag chains are broken away, resulting in the 2D structure **3**.

Finally, use of Y-type tricarboxylate ligands 1,3,5-btc and 1,2,4-btc affords a new 2D structure **4** and a 3D structure **5**, which are based on infinite $\{\mathbf{Ni_6PW_9}\}_\infty$ chains as SBUs. It is noteworthy that infinite SBUs have been recently recognized and used in the design and construction of MOFs.[4n] The asymmetric unit of **4** consists of one $\{\mathbf{Ni_6PW_9}\}$ unit, one 1,3,5-btc ligand, and one $[Ni(en)(H_2O)_3]^{2+}$ cation (Figure S2b in the Supporting Information). As shown in Figure 2c, each $\{\mathbf{Ni_6PW_9}\}$ unit links two adjacent ones through two Ni−O=W linkages to form infinite zigzag $\{\mathbf{Ni_6PW_9}\}_\infty$ SBUs along the *b* axis. Furthermore, the SBUs are bridged by 1,3,5-btc ligands through Ni–carboxylate interactions, thereby forming a new 2D POMOF (Figure 2d) which is different from that of **3**. The 2D layers are stacked along the *a* axis to give 1D rhombic channels filled by $[Ni(en)(H_2O)_3]^{2+}$ cations (Figure S6 in the Supporting Information). Interestingly, every 1,3,5-btc linker in **4** only affords two carboxyl groups to bridge adjacent SBUs in the common η^1:η^1:μ_2 mode, and the remaining carboxyl group points into the channel and functions as a monodentate ligand to the Ni center of a $[Ni(en)(H_2O)_3]^{2+}$ cation (Figure S2b in the Supporting Information), thus leaving an uncoordinated carboxyl O atom, which is protonated for charge balance. Notably, the 2D structure **4** also can be viewed as zigzag (btc-$\{\mathbf{Ni_6PW_9}\})_\infty$ chains linked to each other through Ni−O=W bonds (Figure S7 in the Supporting Information).

Compound **5** crystallizes in the space group $P4_1$ and thus represents the first chiral 3D POMOF. The asymmetric unit of **5** contains one $\{\mathbf{Ni_6PW_9}(H_2O)_5\}$ unit, one 1,2,4-btc ligand, and one isolated $[H_2enMe]^{2+}$ ion (Figure S8a in the Supporting Information). Interestingly, in contrast to other $\{\mathbf{Ni_6PW_9}(H_2O)_n\}$ units of **1**–**4**, no organic amine is found in the $\{\mathbf{Ni_6PW_9}(H_2O)_5\}$ unit of **5** because all the Ni coordination sites are occupied by H_2O ligands and O atoms from carboxylates and adjacent $\{\mathbf{PW_9}\}$ clusters. In **5**, each $\{\mathbf{Ni_6PW_9}(H_2O)_5\}$ unit is joined to two others through four W=O−Ni linkages (Figure 3a), generating a 1D $\{\mathbf{Ni_6PW_9}(H_2O)_5\}_\infty$ SBU which is arranged about a fourfold screw axis and forms a right-handed helical chain along the *c* axis (Figure 3c). All the right-handed helical SBUs are further linked together by 1,2,4-btc ligands along both the *a* and *b* axes to yield a 3D framework with 1D square channels (dimensions: 12.5×9.1 Å^2) along the *a* and *b* axes (Figure 3d) and 1D homochiral square channels (dimensions: 14.2×14.2 Å^2) along the *c* axis, inside which the $[H_2enMe]^{2+}$ ions and H_2O molecules are located (Figure 3f, and Figure S8c in the Supporting Information). The coordination mode of the 1,2,4-btc linkers is described as follows: the 1,2-carboxyl groups of 1,2,4-btc connect two $\{\mathbf{Ni_6PW_9}(H_2O)_5\}$ units of the same SBU in a η^1:η^1:μ_2 mode, while the 4-carboxyl group of 1,2,4-btc futher links one $\{\mathbf{Ni_6PW_9}(H_2O)_5\}$ unit of an adjacent SBU in a η^1:η^0:μ_1 mode, whereby the uncoordinated carboxyl O atom is protonated for charge balance (Figure 3b). To better understand the 3D framework, Figure 3e,f shows the simplified 3D structural diagrams viewed along the *b* and *c* axes, in which the green helical tubes and golden 3-connected nodes represent the $\{\mathbf{Ni_6PW_9}\}_\infty$ SBUs and 1,2,4-btc ligands, respectively.

We also attempted to prepare high-dimensional POMOFs by using 1,2,4,5-benzenetetracarboxylate (pma) as a starting linker. Unexpectedly, pma was converted into 1,3-bdc and 1,4-bdc through in situ decarboxylation reactions under the hydrothermal conditions (Scheme 1), thus resulting in a mixture of **1** and **3**. Although hydrothermal decarboxylation reactions have recently been shown to occur in the presence of metal ions,[11] the above hydrothermal decarboxylation of pma has, to our knowledge, not been documented so far.

In summary, a series of novel POMOFs with 1D, 2D, and 3D structures has been successfully synthesized by the use of a $\{\mathbf{Ni_6PW_9}\}$ cluster, formed in situ, as SBU and rigid carboxylate

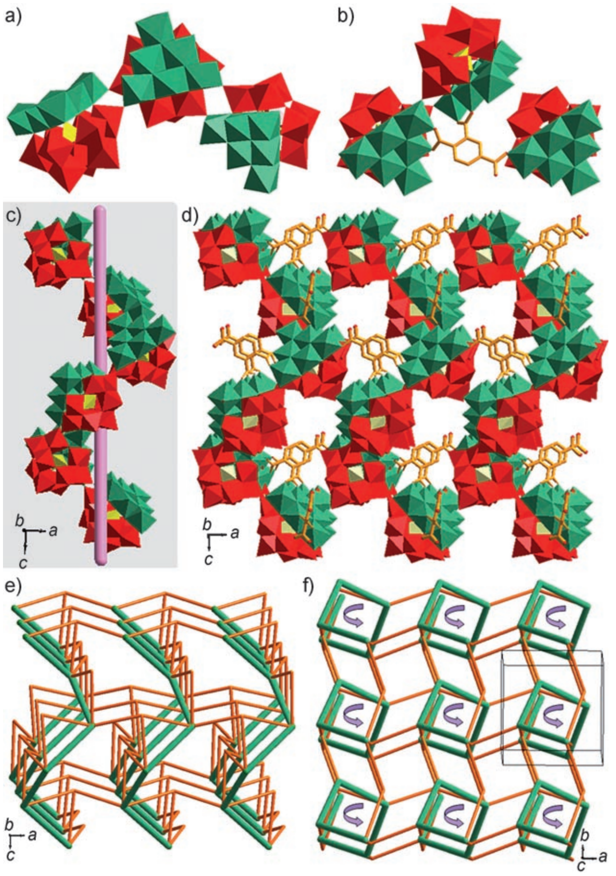
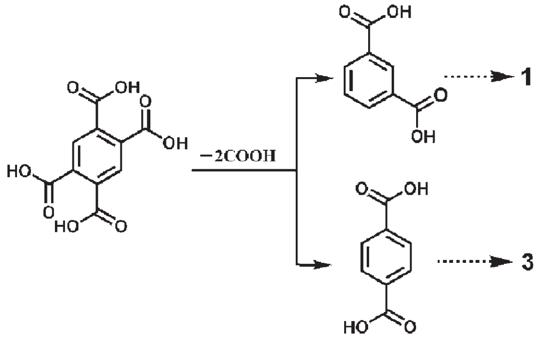


Figure 3. a, b) Views of connectivity modes between {**Ni$_6$PW$_9$**(H$_2$O)$_5$} units (a) and coordination mode of each 1,2,4-btc ligand in **5** (b). c, d) Views of 1D helical chain and 3D structure in **5**, respectively. e, f) Views of simplified diagrams of 3D framework **5** along the *b* and *c* axis, respectively. The arrows in (f) indicate right-helical channels.



Scheme 1. In situ hydrothermal decarboxylation reactions of pma.

ligands as linkers under hydrothermal conditions. The key points of the synthetic procedures have been well established, which indicates that this strategy offers an effective and feasible way for designing and making new POMOFs. Further work is in progress for making novel functional POMOFs by using larger rigid carboxylate linkers and various metal-substituted POM SBUs built from larger metal cluster aggregates and other types of multilacunary POM precursors (e.g. $[XW_{10}O_{36}]^{n-}$ (X = Si, Ge, P) $[P_2W_{12}O_{48}]^{14-}$, and $[X_2W_{15}O_{56}]^{n-}$ (X = P, As)), as well as mixed multilacunary POM precursors) under hydrotherml conditions. It is reasonable to believe that the present work will be important in expanding the study of POM-based COFs.

Experimental Section

Synthesis of **1**–**5**: Na$_9$[*A*-α-PW$_9$O$_{34}$]·*n*H$_2$O was prepared by a literature method.[12] A sample of Na$_9$[*A*-α-PW$_9$O$_{34}$]·*n*H$_2$O (0.30 g) and NiCl$_2$·6H$_2$O (0.80 g) was stirred in a 0.5 M sodium acetate buffer (pH 4.8, 10 mL) for 5 min, forming a green clear solution. Then, enMe (0.30 mL, for **1** and **5**) or en (0.30 mL, for **2**–**4**) was added dropwise with continuous stirring. To this solution 1,3-H$_2$bdc (0.20 g, for **1**), H$_2$tda (0.20 g, for **2**), 1,4-H$_2$bdc (0.20 g, for **3**), 1,3,5-H$_3$btc (0.20 g, for **4**), or 1,2,4-H$_3$btc (0.20 g, for **5**) was added and stirred for 120 min. The resulting solution was sealed in a 35-mL stainless steel reactor with a teflon liner and heated at 170 °C for 5 days, and then cooled to room temperature, upon which green prismatic crystals of **1**–**5** were obtained (note *B* type isomers were obtained from the *A* type starting material). Yields (based on NiCl$_2$·6H$_2$O): **1**: 17.5 % (281 mg); **2**: 14.5 % (258 mg); **3**: 16.6 % (266 mg); **4**: 14.6 % (227 mg); **5**: 11.0 % (192 mg). Details of elemental analysis, IR, XRD, TGA, electric conductivity, and magnetic measurements of **1**–**5** are given in the Supporting Information.

Crystal data: **1**: $M_r = 3334.47$, orthorhombic, space group $P2_12_12_1$, $a = 13.5242(1)$, $b = 14.3276(2)$, $c = 36.1740(1)$ Å, $V = 7009.4(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 3.160$ g cm^{-3}, $\mu = 16.654$ mm^{-1}, $F(000) = 6120$, GOF = 1.203, Flack parameter = 0.00. A total of 38487 reflections were collected, 13198 of which were unique ($R_{int} = 0.056$). $R_1/wR_2 = 0.0523/0.1027$ for 877 parameters and 12116 reflections ($I > 2\sigma(I)$). **2**: $M_r = 3153.57$, orthorhombic, space group $P2_12_12_1$, $a = 13.2810(2)$, $b = 19.3451(3)$, $c = 23.2401(4)$ Å, $V = 5971.1(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 3.508$ g cm^{-3}, $\mu = 19.269$ mm^{-1}, $F(000) = 5728$, GOF = 1.065, Flack parameter = 0.029(9). A total of 38995 reflections were collected, 13642 of which were unique ($R_{int} = 0.0578$). $R_1/wR_2 = 0.0404/0.0909$ for 784 parameters and 12908 reflections ($I > 2\sigma(I)$). **3**: $M_r = 6172.14$, triclinic, space group $P\bar{1}$, $a = 12.7821(8)$, $b = 19.7680(14)$, $c = 25.3812(18)$ Å, $\alpha = 86.9(1)$, $\beta = 89.9(2)$, $\gamma = 79.6(1)$°, $V = 6298(7)$ Å^3, $Z = 2$, $\rho_{calcd} = 3.255$ g cm^{-3}, $\mu = 18.373$ mm^{-1}, $F(000) = 5576$, GOF = 1.039. A total of 37119 reflections were collected, 23658 of which were unique ($R_{int} = 0.0676$). $R_1/wR_2 = 0.1048/0.2903$ for 1394 parameters and 15353 reflections ($I > 2\sigma(I)$). Although the final residuals (R_1/wR_2) are somewhat large owing to poor crystal quality, the POM backbone and organic ligands are well behaved, and there are no unusual temperature factors in the structure. **4**: $M_r = 3230.23$, tetragonal, space group $Pbcm$, $a = 16.6667(5)$, $c = 26.3429(8)$ Å, $V = 7307.1(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.936$ g cm^{-3}, $\mu = 15.970$ mm^{-1}, $F(000) = 5872$, GOF = 1.094. A total of 54890 reflections were collected, 8567 of which were unique ($R_{int} = 0.0428$). $R_1/wR_2 = 0.0402/0.1053$ for 504 parameters and 7953 reflections ($I > 2\sigma(I)$). **5**: $M_r = 3097.33$, tetragonal, space group $P4_1$, $a = 15.5419(4)$, $c = 26.4893$ (13) Å, $V = 6398.5(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 3.215$ g cm^{-3}, $\mu = 17.951$ mm^{-1}, $F(000) = 5592$, GOF = 1.098, Flack parameter = 0.002(7). A total of 49942 reflections were collected, 12662 of which were unique ($R_{int} = 0.0504$). $R_1/wR_2 = 0.0315/0.0779$ for 732 parameters and 12391 reflections ($I > 2\sigma(I)$).

Data were collected on a Mercury-CCD diffractometer with graphite-monochromated Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at room temperature. The program SADABS was used for the absorption correction. The structures **1**–**5** were solved by direct methods and refined on F^2 by full-matrix least-squares methods using the SHELX97 program package. CCDC-668398, 668399, 668400, 668401, and 668402 (**1**–**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from

The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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