Adsorption of a Catalytically Accessible Polyoxometalate in a Mesoporous Channel-type Metal–Organic Framework

Cassandra T. Buru,† Peng Li,† B. Layla Mehdi,‡ Alice Dohnalkova,§ Ana E. Platero-Prats,⊥ Nigel D. Browning,‡∥ Karena W. Chapman,⊥ Joseph T. Hupp,† and Omar K. Farha*†

†Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, United States
‡Physical and Computational Science Directorate, PNNL, Richland, Washington 99352, United States
§Environmental Molecular Sciences Laboratory, PNNL, Richland, Washington 99352, United States
∥Materials Science and Engineering, University of Washington, Seattle, Washington 98195, United States
⊥X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439-4858, United States
#Department of Chemistry, Faculty of Science, King Abdulaziz University, Jeddah, Saudi Arabia

*Supporting Information

ABSTRACT: A Keggin-type polyoxometalate (H₃PW₁₂O₄₀) was incorporated into a mesoporous Zr-based MOF (NU-1000) via an impregnation method in aqueous media, resulting in the hybrid material, PW₁₂@NU-1000. The POM@MOF composite was characterized by a suite of physical methods, indicating the retention of crystallinity and high porosity of the parent MOF. The hybrid material was also stable to leaching in aqueous media at varying pH. Finally, the material was tested as a heterogeneous catalyst for the oxidation of 2-chloroethyl ethyl sulfide using hydrogen peroxide as the oxidant. PW₁₂@NU-1000 was shown to have a higher catalytic activity than either of the individual constituents alone.

INTRODUCTION

Polyoxometalates (POMs) are anionic metal oxide clusters, mainly composed of high valent early transition-metal ions bridged by oxygen atoms.⁴−⁷ Their modular composition and size give rise to many examples of POMs.⁸−¹⁰ Owing to their acid–base and redox properties, POMs have found many applications in chemical catalysis, such as water oxidation, alkene epoxidation, and phosphoester hydrolysis.¹²,¹³ The recovery and reusability of POMs in these catalytic systems are hindered by their high solubility, low specific area, and poor stability under catalytic conditions.¹⁴,¹⁵ To overcome these drawbacks, supports such as mesoporous silica, polymers, covalent organic frameworks (COFs), and metal–organic frameworks (MOFs) have been used to anchor POMs to create hybrid heterogeneous materials.

MOFs are a class of materials consisting of metal nodes connected by multitopic organic linkers.²³,²⁴ The tunability and porosity of MOFs make them promising heterogeneous catalysts or excellent supports for anchored homogeneous catalysts.²⁵ Two techniques have been reportedly used to incorporate POMs in MOFs (also POM@MOF): impregnation and encapsulation.²⁶ The first instance of a POM@MOF was synthesized by Ferey and co-workers using the impregnation method with MIL-101, due to the large apertures and mesopores in its structure.²⁷ The impregnation method involves directly adding preformed POM to a MOF. This method necessitates large apertures in the MOF for POM diffusion. Though straightforward, the impregnation method has a number of limitations when used to obtain a potential catalytic material: low maximum loading (~0.2 POM/node), low homogeneity, occupation of large cavities limiting diffusion, and leaching.²⁷−³⁰ The encapsulation method, also known as the "bottle around the ship method," involves building the MOF in the presence of POM. Such a technique has been useful for HKUST-1 and other Cu-BTC frameworks (BTC = 1,3,5-benzene-tricarboxylate, these POM@MOFs are also known as the NENU series),³¹ MIL-100/101 (Fe, Cr, Al),³²,³³ and UiO-67³⁶ (see abbreviations). The cavities inside these MOFs are large enough to contain the desired POM, while the apertures are small enough to keep the POM from leaching out of the pores. This usually leads to reduced activity of the POM because the pores are blocked, such that the substrate cannot easily diffuse through the framework.³⁷,³⁹ Gascon and co-workers have demonstrated that one approach to avoid these problems is to use MIL-101 to encapsulate two POMs per medium cavity, leaving the larger cavities open.³⁰
This material relies on metal exchange of tungsten with the chromium framework, potentially limiting the scope of the POMs which can be encapsulated into this MOF.

To overcome some of these problems of POM and substrate diffusion, we propose to use a zirconium MOF with micro- and mesoporous channels, NU-1000, as a support for POMs. NU-1000, an eight-connected MOF, composed of \( \text{Zr}_6(\mu_3-\text{O})_4(\mu_2-\text{OH})_4(\text{H}_2\text{O})_4(\text{OH})_4 \) nodes connected by 1,3,6,8-tetrakis(p-benzoate)pyrene linkers (TBApy), fulfills these requirements because it has small triangular channels (12 Å) which will permit the incorporation of large POMs, while the larger (31 Å) hexagonal channels provide an auxiliary path for substrate diffusion (Figure 1). The use of this hierarchical MOF should ultimately circumvent the previously stated limitations imposed by other MOFs. Additionally, NU-1000 has been shown to be an excellent host material, supporting guests from the size of a single atom or small molecule to an enzyme. Intermediate-sized charged guests, like POMs, have yet to be studied in NU-1000. Previous studies have shown that NU-1000 readily adsorbs small oxyanions (selenites/selenates, sulfates) via displacement of hydroxide ions on the Zr₆ node for charge balancing. We hypothesized that guest molecules could be extended to larger oxyanions, namely POMs.

\( \text{H}_3\text{PW}_{12}\text{O}_{40} \) was selected as an archetypal POM based on size and demonstrated catalytic activity for the oxidation of organosulfides in the presence of peroxide. On the other hand, the nodes on NU-1000 have a structure analogous to zirconia, which can act as a counterion for \( \text{PW}_{12}\text{O}_{40} \) to prevent the Keggin unit from leaching once the nodes are protonated. Zirconia can also catalyze the oxidation of sulfides. Therefore, if the POMs and MOF nodes in the composite material are catalytically accessible. For the catalytic sulfide oxidation, \( \text{PW}_{12}@\text{NU}-1000 \) has higher activity than either component alone.

### RESULTS AND DISCUSSION

Due to the large channels in NU-1000, the direct impregnation method of installing \( \text{PW}_{12}\text{O}_{40} \) was considered. Since NU-1000 has anionic character at neutral pH and the POM is also anionic in water, the incorporation of the POM should rely upon the acidic nature of the POM precursor \( \text{H}_3\text{PW}_{12}\text{O}_{40} \). When the hydroxyl ligands on the MOF nodes are protonated at a highly acidic pH, then the MOF will no longer be anionic and POM uptake should be favorable. To synthesize \( \text{PW}_{12}@\text{NU}-1000 \), NU-1000 was added and suspended in an aqueous \( \text{H}_3\text{PW}_{12}\text{O}_{40} \) solution (pH 2.5). After 3 days at room temperature, the solid was washed and rigorously solvent-exchanged with acetone, resulting in \( \text{PW}_{12}@\text{NU}-1000 \). Detailed synthesis and activation of \( \text{PW}_{12}@\text{NU}-1000 \) are discussed in the Experimental Section.

**Characterization.** Inductively coupled plasma-optical emission spectroscopy (ICP-OES) data suggest that approximately 0.8 \( \text{PW}_{12}\text{O}_{40} \) per Zr₆ node is the maximum POM loading in NU-1000 after thorough washing. [NU-1000 crystallites have an apparently fully 12-connected secondary framework in the center of the crystallites which accounts for ~20% occupancy crystallographically. These defects have been quantified via acid–base titration (see refs 38 and 56).] This loading can be obtained from soaking the MOF in two or more equivalents of POM per node and is equivalent to 52 wt %. The loading of \( \text{PW}_{12}\text{O}_{40} \), however, can be modulated by soaking the MOF in lower concentrations of POM. Further characterization of \( \text{PW}_{12}@\text{NU}-1000 \) refers to the maximum 0.8 \( \text{PW}_{12}/\text{Zr}_6 \) loading.

Scanning electron microscopy (SEM) images show that the size and morphology of NU-1000 crystallites are maintained during POM installation (Figure 2, Figure S1). Energy dispersive X-ray spectroscopy (EDS) mapping suggests these POMs are located uniformly within, not just on the surface of, the MOF, except in the center where the crystal is known to have blocked pores (Figure 2).
The unit cell of PW$_{12}$@NU-1000, as seen by the Bragg peak positions on powder X-ray diffraction (PXRD, Figure S2), resembles that of NU-1000. However, locating the POM is not straightforward. Though the large mesopores in NU-1000 are large enough to accommodate the POM (Figure 3b), this possibility can be excluded by comparing the simulated and experimental PXRD of PW$_{12}$@NU-1000 (Figure S3). The diffraction pattern matches well with a predicted pattern where the POM is located between two nodes in the windows (Figure 3a) but does not definitively prove the location of these POMs.

Scanning transmission electron microscopy (STEM) images were taken of PW$_{12}$@NU-1000 in the attempt to locate the POMs. STEM images have previously been used to determine dispersion of POMs in carbon nanotubes.57 Figure S4 shows two Z-contrast images obtained from orthogonal directions where the node distribution in a representative area of the MOF is observed. The standard hexagonal distribution of nodes is clearly observed in the top half of Figure S4a. The orientation of the sample changes slightly across the image (bending), and the hexagonal pattern becomes distorted in the lower half of the image. This distortion could have been caused by sample preparation or the nature of the flexible organic linkers. The orthogonal direction shows a clear cubic arrangement of the nodes (Figure S4b). Importantly, no electron density within the hexagonal channels is consistent with a distribution like Figure 3a. However, further analysis is needed to pinpoint the exact location of the POM directly from the images.

To further elucidate the location of the POM, difference envelope density (DED) analysis was employed. This technique generates a surface envelope between regions of high and low electron density which can be extracted from low order, intense, independent reflections in a high resolution PXRD pattern. Using differential analysis with a parent framework can yield a coarse map of electron density attributed to the incorporation of guest molecules.58,59 DED analysis (Figure S5) of PW$_{12}$@NU-1000 localizes the electron density in the small channels in the plane of the nodes, akin to Figure 3c. This orientation maximizes the hydrogen bonding interaction between the oxo groups on the POM and the hydroxyl groups on the nodes.

The Brunauer–Emmett–Teller (BET) surface area calculated from the N$_2$ isotherm of PW$_{12}$@NU-1000 significantly decreases from 2100 to 850 m$^2$/g relative to bare NU-1000 (Figures S6 and S7), which is consistent with POM incorporation in NU-1000. Volumetrically, however, they achieve similar BET surface areas (1020 to 850 m$^2$/cm$^3$ for NU-1000 and PW$_{12}$@NU-1000, respectively, Figure 4). The N$_2$ isotherm of PW$_{12}$@NU-1000 shows a type IV feature, similar to that of NU-1000, which is associated with the mesoporous channel, and is also present in the pore size distribution (Figure 4). The calculated average pore width indicates a decrease in the length of the large hexagonal pores from 31 to 25 Å compared to NU-1000, but not as significant a decrease as if the POMs were located inside the hexagonal channels. This effect was also observed when smaller metal ions were deposited solvothermally in the windows between the channels of NU-1000.40 More strikingly, the large decrease in the differential pore volume of the micropores (3.8 to 1.0 cm$^3$/cm$^3$) further indicates that the POMs are located in the small channels.

Thermal gravimetric analysis (TGA) shows a mass loss of 50% for bare NU-1000 between 25 and 700 °C (Figure S8). The majority of this mass loss is due to the carbon decomposition at 500 °C. The TGA trace of the POM, H$_3$PW$_{12}$O$_{40}$, matches well with those reported in the literature, losing 13% of its initial mass due to water. The corresponding PW$_{12}$@NU-1000 loses 20% of its initial mass, consistent with a greater percentage of inorganic composition compared to NU-1000 which is not lost below 700 °C. The two features seen in the TGA profile indicate physisorbed water loss from the POM below 100 °C and carbon decomposition from NU-1000 around 500 °C (Figure S8). The composite material is highly hygroscopic, corroborated by TGA-mass spectrometry (MS). Water makes up approximately 10 wt % of the as-synthesized PW$_{12}$@NU-1000 mass prior to any catalytic studies.

Figure 3. Visual representations (top and side view) of the proposed structures for PW$_{12}$@NU-1000, where the POM is located inside the windows between the channels (a), in the hexagonal channels (b), or in the small triangular channels (c). DED mapping of PW$_{12}$@NU-1000 has led to the conclusion that c is most representative of the material.
Cyclic voltammetry (CV) shows that the redox activity of the POM in the MOF is retained (Figures S9 and S10). The slight positive shift in formal reduction potentials could indicate that the POM interacts with the support. Additionally, the solid state $^{31}$P magic angle spinning (MAS) NMR spectrum of H$_3$PW$_{12}$O$_{40}$ has two resonances (Figure S11), ascribed to a well-crystallized anhydrous phase (−13.9 ppm) and an amorphous phase (−15.3 ppm). A phosphoric acid impurity can be seen above 0 ppm. The $^{31}$P MAS NMR spectrum of the composite PW$_{12}$@NU-1000 shows a slight downfield chemical shift and much broader signal compared to the POM alone. On the basis of the shape, the observed signal is likely the sum of the POM interacting with the support. Additionally, the solid state NMR shows that both POM and MOF components are present in the composite material, as highlighted in the boxes in Figure 5. The features in the 750 to 1100 cm$^{-1}$ range correspond to W=O and P=O of the POM (983, 984, 1080 cm$^{-1}$), and the bands between 1300 and 1700 cm$^{-1}$ correspond to carboxylate stretches in NU-1000 (1420, 1520, 1610 cm$^{-1}$). The sharp O−H stretch at 3670 cm$^{-1}$ from the non-H bonded −OH and H$_2$O on the NU-1000 node is noticeably absent in the composite. The H-bonded H$_2$O and −OH peak at 2551 and 2745 cm$^{-1}$ are also absent. On the basis of these observations, it is tempting to conclude that the non-hydrogen bonded O−H stretches, carboxylate stretches, and P=O/W=O stretches are highlighted.

To test the stability toward leaching, PW$_{12}$@NU-1000 was exposed to aqueous solutions of HCl at pH ranging from 2 to 7 (Table S1). Zr-based MOFs are known for their chemical stability (pH 1−11). However, stability at higher pH was not investigated because of known decomposition of the POM in basic solutions. After 1 week under near neutral conditions (pH 6), the material lost only 13% of POMs by ICP-OES. At lower pH values, less POM was lost, demonstrating that the POMs are not easily displaced by competing chloride ions.

**Catalytic Studies.** POM@MOFs typically have reduced catalytic activity due to the blocking of pores and subsequent inhibition of substrate diffusion. In order to determine if PW$_{12}$@NU-1000 can overcome these limitations, the composite was tested for CEES oxidation (Scheme 1). Activity of H$_3$PW$_{12}$O$_{40}$ for the oxidation of sulfides in the presence of peroxide has been well documented. Zirconia, with composition analogous to the Zr$_6$ MOF nodes, also has the ability to oxidize sulfides in the presence of peroxides. To compare the catalysts, the loadings were normalized to the amount of active clusters, including both the POM and the Zr$_6$ nodes. In a typical run, the catalyst was suspended in 1 mL of acetonitrile (MeCN). CEES and hydrogen peroxide were added stepwise to the reaction vial, and the reaction was kept at 45 °C in a sand bath. Since NU-1000 has been reported to oxidize CEES in the presence of UV LED irradiation and O$_2$, the sand bath was necessary to block light and suppress any background reaction. Aliquots were taken at different time intervals and analyzed via gas chromatography-flame ionization detector (GC-FID) or solution NMR (see Experimental Section). The average reaction profile is shown in Figure 6. The initial turnover frequencies (TOF) from the graph are 3.1 min$^{-1}$ for NU-1000, 9.3 min$^{-1}$ for H$_3$PW$_{12}$O$_{40}$ and 10.4 min$^{-1}$ for PW$_{12}$@NU-1000 (Table 1 entries 4, 6, and 8). The reaction using H$_3$PW$_{12}$O$_{40}$ goes to full conversion after 90 min, while the reaction with PW$_{12}$@NU-1000 takes only 20 min under the same conditions. The Experimental Section has the TOF formula and a detailed procedure on calculating yield and conversion from NMR (Figure S12). Table 1 shows yield and selectivity under different catalytic conditions. All trials with reported error were performed in at
least triplicate. Background reactions without catalyst or peroxide, entries 1–3, showed minimal activity. The homogeneous H₃PW₁₂O₄₀ showed selective partial oxidation of the sulfide to CEESO (entry 4). Even in the presence of excess peroxide (entry 5), CEESO is the only observed product. Bare NU-1000 showed preference to the doubly oxidized CEESO₂ (entry 6). The MOF reaction was limited by the amount of peroxide, and in the presence of excess peroxide the reaction goes to completion with CEESO₂ as the only product (entry 7).

PW₁₂@NU-1000 showed faster initial rate and higher conversion than the POM or the MOF alone (entry 8). Since the amount of catalyst was normalized to the sum of the POM and Zr₆ nodes, the enhanced activity can be attributed to the cooperative effect of the POM and the MOF node. The sulfoxide selectivity suggests that both POM and MOF are active in the catalysis because CEESO and CEESO₂ are present in roughly equal amounts (entry 8).

To determine if the POMs are leaching out of the MOF during catalysis, the PW₁₂@NU-1000 reaction mixture was filtered at 2 min, and the reaction progress was further monitored (Figure S13). The conversion was approximately 10% after 1 h, which is only 5% above the background reaction. This indicates that minimal POMs are leaching under these conditions, if at all. Solution phase NMR spectroscopy of the filtered reactions shows no phosphorus signal, reaffirming that the material does not leak. Upon recycling, PW₁₂@NU-1000 was shown to be reusable. The retention of selectivity and reactivity upon recycling reaffirm that the material is stable under these catalytic conditions (Figure S14). Additionally, the PXRD, DRIFTS, and ³¹P MAS NMR spectroscopy results show that the integrity of the composite material remains unchanged (Figures S15, S16, and S17). Interestingly, the three broad overlapping peaks observed in the ³¹P MAS NMR spectrum prior to any catalysis become more distinct postcatalysis.

These catalytic studies indicate that active sites in the MOF are accessible after the installation of [PW₁₂O₄₀]³⁺. Importantly, the selectivity of the composite material suggests that the MOF nodes are also active, meaning that they are not completely blocked by the POM. Having access to all potential catalytic sites is important in the development of a robust catalyst. This study has demonstrated that with careful selection of MOF, we can incorporate POMs while maintaining accessibility and high surface area of the parent MOF. Future directions are aimed at improving composite selectivity by passivating the exposed Zr-node in NU-1000.

## CONCLUSIONS

We have synthesized and fully characterized a POM@MOF material, PW₁₂@NU-1000. This composite achieves the highest POM/node loading for a POM@MOF synthesized via impregnation, while still maintaining high porosity. PW₁₂@NU-1000 demonstrates enhanced catalytic activity for the oxidation of sulfide by hydrogen peroxide than either the POM or MOF under the same conditions. Future studies will explore other catalytically interesting POMs to be incorporated in NU-1000 and its family.

## EXPERIMENTAL SECTION

**Synthesis of PW₁₂@NU-1000.** In a centrifuge tube, H₃PW₁₂O₄₀ (303 mg, 0.09 mol) was dissolved in 20 mL of deionized water. The solution (pH about 2.5) was divided into two 10 mL quantities. To one solution, NU-1000 (50 mg, 0.023 mmol) was added and suspended by sonication for about 1 min. The suspension was shaken periodically. To monitor uptake of POM, the solutions with and without NU-1000 were analyzed by ICP-OES and compared to each other. After 3 days, the solid was washed with water three times. Then, the solid was washed with acetone. PW₁₂@NU-1000 was allowed to soak in acetone overnight before being washed two more times with acetone to ensure adequate removal of water. Samples were dried at 80 °C for 4 h under a vacuum prior to activation on the Smart VacPrep. The solid material was subject to ICP-OES to determine the final POM loading.

**Catalysis Procedure.** For 2-chloroethyl ethyl sulide (CEES) oxidation experiments, the catalyst (1.7 µmol of active site) was dispersed in 1 mL of acetonitrile in a 2 dram vial. For the POM and POM@MOF, the water weight was considered, so 1.7 µmol of active sites was equivalent to 3.7 mg of NU-1000, 5.7 mg of H₃PW₁₂O₄₀, and 4.7 mg of PW₁₂@NU-1000. CEES (10 µL, 85 µmol) and an internal standard (1-bromo-3,5-difluorobenzene, 5 µL) were added to the reaction vial. Then, hydrogen peroxide (30 wt % in water, 13 µL, 1.5

---

**Table 1. Summary of Catalytic Data**

<table>
<thead>
<tr>
<th>catalyst</th>
<th>loading (mol %)</th>
<th>temp. (°C)</th>
<th>time (min)</th>
<th>oxidant (eq)</th>
<th>initial TOF (min⁻¹)b</th>
<th>yield (%)</th>
<th>sulfoxide selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 none</td>
<td></td>
<td>45</td>
<td>180</td>
<td>1.5</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 H₃PW₁₂O₄₀</td>
<td>2</td>
<td>45</td>
<td>180</td>
<td>0</td>
<td>0.02c</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>3 NU-1000</td>
<td>2</td>
<td>45</td>
<td>180</td>
<td>0</td>
<td>0.01d</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>4 H₃PW₁₂O₄₀</td>
<td>2</td>
<td>45</td>
<td>90</td>
<td>1.5</td>
<td>9.3e</td>
<td>98 (2)</td>
<td>100 (0)</td>
</tr>
<tr>
<td>5 H₃PW₁₂O₄₀</td>
<td>2</td>
<td>45</td>
<td>60</td>
<td>5</td>
<td>1.6e</td>
<td>100 (0)</td>
<td>98 (2)</td>
</tr>
<tr>
<td>6 NU-1000</td>
<td>2</td>
<td>45</td>
<td>90</td>
<td>1.5</td>
<td>3.1e</td>
<td>77 (4)</td>
<td>23 (1)</td>
</tr>
<tr>
<td>7 NU-1000</td>
<td>2</td>
<td>45</td>
<td>60</td>
<td>5</td>
<td>1.3e</td>
<td>99 (1)</td>
<td>0 (0)</td>
</tr>
<tr>
<td>8 PW₁₂@NU-1000</td>
<td>1.1</td>
<td>45</td>
<td>20</td>
<td>1.5</td>
<td>10.4e</td>
<td>98 (2)</td>
<td>57 (1)</td>
</tr>
</tbody>
</table>

General: 1 mL MeCN, 10 µL CEES, 5 µL internal standard (1-bromo-3,5-difluorobenzene), H₂O₂ as the oxidant. TOF = moles product/(moles of total catalytic clusters x amount of time). ²Time = 180 min. ³Time = 30 min. ⁴Time = 2 min.

DOI: 10.1021/acs.chemmater.7b00750
equiv) was added. The vial was placed in a sand bath, which was preheated to 45 °C. Variations to this procedure are summarized in Table 1. Aliquots, approximately 50 µL, were withdrawn from the vials with a glass pipet at different time points, filtered, and diluted with dichloromethane for GC-FID or deuterated acetonitrile for NMR spectroscopy. GC-FID was used to monitor conversion, and NMR spectroscopy was used to determine selectivity. Figure S12 is a representative NMR spectrum of CEES, CEESO, and CEESO$_2$. Conversion was calculated by subtracting the peak at 3.71 ppm from the peaks at 3.93 ppm, and selectivity was calculated by subtracting the peak at 3.47 ppm from 3.93 ppm. In the event that the peak at 3.93 ppm was convoluted, the peak at 3.05 ppm was used instead. GC-MS at the final time point was used to confirm the identity of the products. For leaching studies, PW$_{12}$@NU-1000 was filtered out at 2 min, and any remaining reaction was monitored. To recycle the catalyst, the reaction mixture was centrifuged, and the solvent extracted. The solid material was washed three times with acetone and dried under a vacuum at 70 °C before reuse.

Turnover frequencies were calculated using the first time point for each run and the equation:

$$\text{TOF} = \frac{\text{moles of product}}{\text{moles of clusters} \times \text{amount of time}}$$

Moles of product are equal to the sum of CEESO and CEESO$_2$. The moles of catalytic clusters (POM or MOF node) were constant at 1.7 µmol.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.7b00750.

Materials, instrumentation, additional characterization (SEM, PXRD, STEM, DED, TGA, gravimetric isotherm, gravimetric pore size distribution, CV, $^{31}$P MAS NMR, leach study), and catalytic studies (NMR, conversion and selectivity graph, DRIFTS, PXRD, $^{33}$P MAS NMR) (PDF)

**AUTHOR INFORMATION**

Corresponding Author

*E-mail: o-farha@northwestern.edu.

ORCID

Cassandra T. Buru: 0000-0001-6142-8252

Peng Li: 0000-0002-4273-4577

Ana E. Platero-Prats: 0000-0002-2248-2739

Joseph T. Hupp: 0000-0003-3982-9812

Omar K. Farha: 0000-0002-9904-9845

Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

O.K.F. and J.T.H. gratefully acknowledge support by the Army Research Office (project no. W911NF-13-1-0229). C.T.B. acknowledges Martino Rimoldi for help with solid-state NMR and Nicolaas Vermeulen for helpful discussions. Visual structural representations were generated using CrystalMaker: a crystal and molecular modelling program for Mac and Windows, CrystalMaker Software Ltd, Oxford, UK (www.crystalmaker.com). Metal analysis was performed at the Northwestern University Quantitative Bioelement Imaging Center. This work made use of the J. B. Cohen X-ray Diffraction Facility supported by the MRSEC program of the National Science Foundation (DMR-1121262) at the Materials Research Center of Northwestern University. This work made use of the EPIC facility of Northwestern University’s NUANCE Center, which has received support from the Soft and Hybrid Nanotechnology Experimental (ShyNE) Resource (NSF NNCI-1542205); the MRSEC program (NSF DMR-1121262) at the Materials Research Center; the International Institute for Nanotechnology (IIN); the Keck Foundation; and the State of Illinois, through the IIN. This work made use of the IMSERC at Northwestern University, which has received support from the NSF (CHE-1048773 and DMR-0521267), Soft and Hybrid Nanotechnology Experimental (ShyNE) Resource (NSF NNCI-1542205), the State of Illinois, and International Institute for Nanotechnology (IIN). Work at Pacific Northwest National Laboratory (PNNL) was supported by the Chemical Imaging Initiative under the Laboratory Directed Research and Development Program. PNNL is a multiprogram national laboratory operated by Battelle for the U.S. Department of Energy (DOE) under Contract DE-AC05-76RL01830. A portion of the research was performed using the Environmental Molecular Sciences Laboratory (EMSL), a national scientific user facility sponsored by the DOE’s Office of Biological and Environmental Research at PNNL. Work done at Argonne was performed using the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

**ABBREVIATIONS**

POM, polyoxometalate; COFs, covalent organic frameworks; MOFs, metal–organic frameworks; HKUST, Hong-Kong University of Technology; BTC, 1,3,5-benzene-tricarboxylate; NENU, Northeast Normal University; MIL, Material Insititute Lavoisier; UiO, University in Oslo; NU, Northwestern University; TBAPy, 1,3,6,8-tetrakis(p-benzoate)pyrene; SALL, solvent assisted ligand incorporation; ICP-OES, inductively coupled plasma optical emission spectroscopy; SEM-EDS, scanning electron microscopy energy dispersive X-ray spectroscoopy; PXRD, powder X-ray diffraction; STEM, scanning transmission electron microscopy; HAADF, high angle annular dark field; DED, difference envelop density; TGA, thermal gravimetric analysis; MS, mass spectrometry; BET, Brunauer–Emmett–Teller; CV, cyclic voltammetry; MAS NMR, magic angle spinning nuclear magnetic resonance; DRIFTS, diffuse reflectance infrared Fourier transform spectroscopy; CEES, 2-chloroethyl ethyl sulﬁde; CEESO, 2-chloroethyl ethyl sulfoxide; CEESO$_2$, 2-chloroethyl ethyl sulfone; DCM, dichloromethane; MeCN, acetonitrile; GC, gas chromatography; FID, flame ionization detector

**REFERENCES**


