FULL PAPER

Hydrogen Adsorption in Polyoxometalate Hybrid Compounds Based on Porous Metal-Organic Frameworks

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Two polyoxometalate hybrid compounds based on porous metal-organic frameworks (PMOFs/POMs) have been prepared by lithium ion exchange and their crystal structures, stabilities and gas adsorption properties have been characterized. Both compounds consist of neutral $Cu_3(BTC)_2$ (BTC = 1,3,5-benzentricarboxylate) metal-organic frameworks (MOFs) as hosts and Keggin polyoxometalates (POMs) anions and lithium ions as guests with the MOFs maintaining their permanent porosity. H_2 adsorption studies demonstrated that the guests play a key role in increasing the H_2 adsorption capacity of the frameworks. With the introduction of POMs and lithium ions, the compounds not only display strong hydrogen adsorption behavior, but also exhibit some differences in H_2 binding energy.

Introduction

Metal-organic frameworks (MOFs) represent a new class of crystalline materials consisting of multiple metal ions linked together by polyfunctional organic ligands, resulting in highly microporous networks.[1] The unique advantage of these emerging materials lies in the possibility of their highly specific functionalization for particular applications, such as catalysis,[2] magnetism,[3] separation,[4] and gas adsorption.[5] They not only offer higher surface areas and the potential for enhanced activity, but also provide shape/size selectivity, which is important for the incorporation of functional groups to increase the number of applications.[6] Recently, we developed an approach for the synthesis of promising crystalline materials that involves the encapsulation of polyoxometalates (POMs), which are the polyoxoanions of early-transition metals,[7] in the nanosized spaces of porous metal-organic frameworks (PMOFs). A series of polyoxometalate hybrid compounds based on porous metal-organic frameworks (PMOFs/POMs) have been prepared and studied for their use in catalysis.[8] In these compounds, Keggin polyanions were alternately arranged as noncoordinating guests in the cubo-octahedral cages of a Cu_3-$(BTC)_2$[9] (HKUST-1; BTC = 1,3,5-benzenetricarboxylate) MOF host matrix which maintained its permanent porosity.

On the other hand, owing to their exceptionally high surface areas and tailored pore dimensions, MOFs are ideal materials for H_2 storage based on physisorption. It is noteworthy that some MOFs have arguably reached or even surpassed the U.S. Department of Energy (DOE) 2010 H_2 storage target.[10] However, because of their typically weak interactions with H_2, these materials function best only at low temperature and high pressure. Clearly, significant innovations are necessary to build viable hydrogen-storage systems at near-ambient temperatures and the greatest challenge for physisorptive materials is increasing the strength of the H_2 binding interaction.

The H_2 adsorption enthalpy obtained from isotherms is an important measure of the H_2 binding energy within MOFs. More and more strategies are being employed to increase the H_2 adsorption enthalpy further to accomplish the target for H_2 storage. For instance, incorporating coordinatively unsaturated metal sites into the frameworks is particularly attractive because multiple metal–H_2 binding sites become available for producing higher H_2 affinity.[11,12] In addition, a recent development in the field of H_2 adsorption in MOFs is the use of Li.[13] This is considered to be an effective strategy for enhancing H_2 adsorption through guest ion-exchange, but only exposed Li^+ can increase the H_2 adsorption enthalpy. Nevertheless reports of H_2 adsorption capacity enhanced by anion guests are still rare. Herein, we present two new PMOFs/POMs, $Li_2[Cu_{12}(BTC)_8 \cdot 12H_2O][HPW_{12}O_{40}] \cdot 27H_2O$ (**NENU-29**) and $Li_2[Cu_{12}(BTC)_8 \cdot 12H_2O][H_2SiMo_{12}O_{40}] \cdot 25H_2O$ (**NENU-30**). In these two compounds, the POMs act as anion guests within the $Cu_3(BTC)_2$ hosts. In addition to thermal gravimetric analysis (TGA), infrared spectroscopy (IR), single-crystal X-ray diffraction and powder X-ray diffraction (PXRD), gas

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adsorption measurements have also been conducted to investigate the H_2 adsorption behavior of these two compounds.

Results and Discussion

Synthesis and Crystal Structures

Compounds **NENU-29** and **NENU-30** were prepared by immersing the crystals of as-synthesized **NENU-3** $\{(C_4H_{12}N)_2[Cu_{12}(BTC)_8\cdot12H_2O][HPW_{12}O_{40}]\cdot25H_2O\}$ and **NENU-4** $\{(C_4H_{12}N)_2[Cu_{12}(BTC)_8\cdot12H_2O][H_2SiMo_{12}O_{40}]\cdot28H_2O\}$,[8] respectively, in saturated solutions of $LiNO_3$ for a week, the $LiNO_3$ solution being refreshed everyday. In addition, if **NENU-3** and **NENU-4** were evacuated under a dynamic vacuum at 150 °C for 12 h, **NENU-3a** $\{H_2[Cu_{12}(BTC)_8][HPW_{12}O_{40}]\}$ and **NENU-4a** $\{H_2[Cu_{12}(BTC)_8][H_2SiMo_{12}O_{40}]\}$, respectively, were obtained, the $C_4H_{12}N^+$ guests having been eliminated. These compounds were then immersed in saturated solutions of $LiNO_3$ for 24 h to give **NENU-29** and **NENU-30**.

Single-crystal X-ray diffraction analysis revealed that the two PMOFs/POMs are isomorphic and consist of the $Cu_3(BTC)_2$ host framework and different Keggin-type POMs as guests. As shown in Figure 1, two kinds of pores contain the POM anions and Li^+. A view along the c axis of the cubic cell reveals two approx. 1-nm-sized channels (ca. 13 and 10 Å). The total accessible volumes in **NENU-29** and **NENU-30** after removal of the water molecules are 17.8 and 19.5%, as determined by using PLATON.[14] These values are smaller than those of **NENU-3** (29.8%) and **NENU-4** (25.2%).[8]
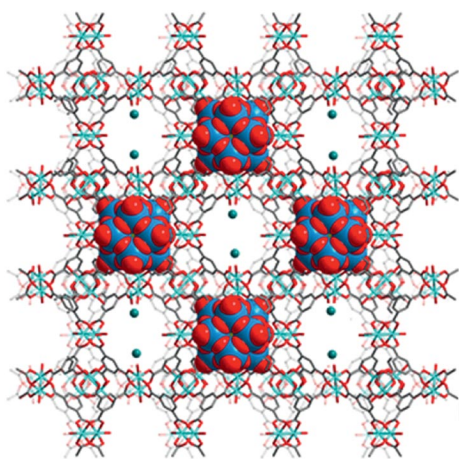

Figure 1. A view of the PMOFs/POMs along the c axis. All hydrogen and solvent water molecules have been omitted for clarity. Red, cyan, blue, grey and dark cyan represent O, Cu, W or Mo, C and Li, respectively.

Thermal Stabilities and Structural Integrities

Thermal gravimetric analysis (TGA; Figures S2 and S3) indicated weight loss of 11.82% (calcd. 11.67%) for **NENU-**

29 and 13.61% (calcd. 13.52%) for **NENU-30** at 150 °C, which corresponds to the loss of all the water molecules. The solids were thermally stable up to 300 °C. The PXRD patterns of the two compounds were coincident with the simulated patterns derived from the single-crystal X-ray data (Figures S4 and S5), which implies that the structures of the bulk samples are the same as those of the single crystals. The PXRD patterns also clearly confirm that the structures remained intact after Li^+ exchange. The elimination of $(CH_3)_4N^+$ from **NENU-3** and **NENU-4** was indicated by the disappearance of the C–H vibrating peak from the IR spectra (Figures S6 and S7). In addition, elemental analysis showed that nitrogen was not present in either **NENU-29** or **NENU-30**. All of these results reveal that complete ion exchange occurred without the loss of structural integrity.

Adsorption Studies

N_2 adsorption studies were conducted at 77 K to evaluate the permanent porosity of **NENU-29** and **NENU-30**. The samples were heated at 150 °C under vacuum for 12 h to give the desolvated $Li_2[Cu_{12}(BTC)_8][HPW_{12}O_{40}]$ (**NENU-29a**) and $Li_2[Cu_{12}(BTC)_8][H_2SiMo_{12}O_{40}]$ (**NENU-30a**). Both N_2 isotherms show typical Type-I adsorption behavior, which confirms the retention of microporous structures.[15] N_2 uptakes of 169 and 180 cm³ (STP) g⁻¹ (Figure 2) were observed, which correspond to 7.5 and 8.0 mmol g⁻¹. These values are higher than those for **NENU-3a** or **NENU-4a** [ca. 140 cm³ (STP) g⁻¹],[8] which indicates that the adsorption capacity increases by more than 20% on Li^+ exchange. The Brunauer–Emmett–Teller (BET) surface areas for **NENU-29a** and **NENU-30a** were estimated to be 466 and 487 m² g⁻¹ and the pore volumes were estimated to be 0.336 and 0.341 cm³ g⁻¹, respectively (Table 1).
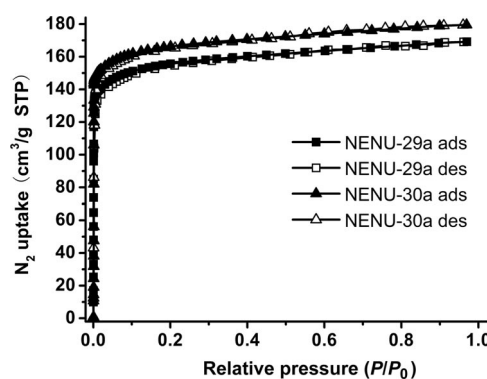

Figure 2. N_2 adsorption isotherms of **NENU-29a** and **NENU-30a** at 77 K.

H_2 adsorption measurements were also undertaken to evaluate H_2 storage performance. As shown in Figure 3, **NENU-29a** can store up to 1.75 wt.-% at 77 K and 1 atm. This value is comparable to those of reported porous MOFs with much larger surface areas and higher even than some famous MOFs. For instance, MOF-5 and MOF-177 display H_2 uptakes of 1.32 and 1.23 wt.-%, respectively, with BET

Table 1. N_2 and H_2 adsorption properties of **NENU-29a**, **NENU-30a**, and some other reported MOFs.

| | SA_{BET}[a] [$m^2 g^{-1}$] | Pore volume [$cm^3 g^{-1}$] | H_2 uptake [wt.-%] (77 K, 1 atm) | ρH_2[b] [$g cm^{-3}$] | H_2 uptake (298 K) | | ΔH_{ads}[c] [$kJ mol^{-1}$] | Ref. |
					P [bar]	Uptake [wt.-%]		
NENU-29a	466	0.336	1.75	0.052	20	0.31	7.42	this work
NENU-30a	487	0.341	1.83	0.054	20	0.40	7.94	this work
NENU-3a	405	0.314	1.59	0.050	–	–	7.28	this work,[8]
NENU-4a	422	0.319	1.67	0.051	–	–	7.79	this work,[8]
$Cu_3(BTC)_2$	1507	0.75	2.48	0.033	65	0.35	6.8	[17a,22]
MOF-5	3362	1.18	1.32	0.011	60	0.45	5.2	[16,17b]
MOF-177	4526	1.69	1.23	0.007	100	0.62	4.4	[10c,16]

[a] Obtained from the N_2 isotherms at 77 K. [b] Based on the pore volume and the H_2 uptake at 77 K and 1 atm. [c] Obtained from the H_2 isotherms at 77 and 87 K and 1 atm.

surface areas of 3362 and 4526 $m^2 g^{-1}$.[16] Although $Cu_3(BTC)_2$ exhibits a H_2 uptake of 2.48 wt.-%, its pore volume is 0.75 $cm^3 g^{-1}$,[17a] which is twice that of **NENU-29a**. **NENU-30a** has a higher H_2 uptake than **NENU-29a** with a value of 1.83 wt.-% (Figure 4). Notably, the densities for adsorbed H_2 in **NENU-29a** and **NENU-30a** are 0.052 and 0.054 $g cm^{-3}$, respectively. These values are clearly higher than that of $Cu_3(BTC)_2$ (0.033 $g cm^{-3}$) (Table 1) and high compared with the porous MOFs reported to date.[13a,18]
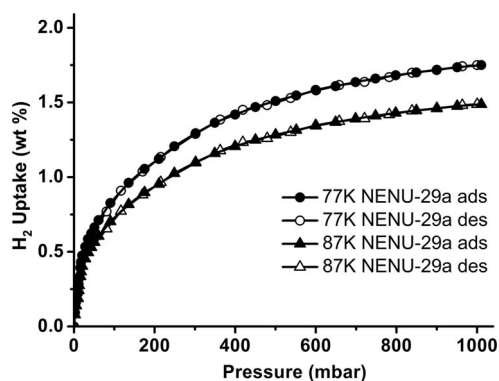

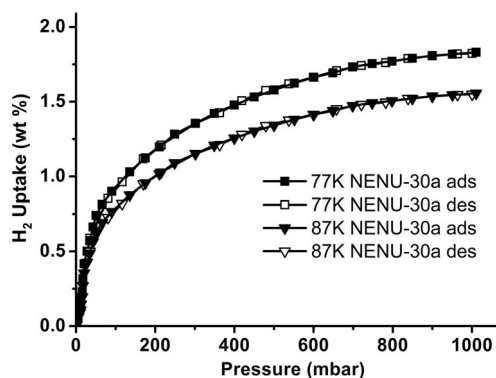Figure 3. H_2 adsorption isotherms of **NENU-29a** at 77 and 87 K and 1 atm.

Figure 4. H_2 adsorption isotherms of **NENU-30a** at 77 and 87 K and 1 atm.

A remarkable aspect of both **NENU-29** and **NENU-30** is that the POMs and Li^+ act as guests in the host framework. The enhancement of H_2 uptake that they exhibit is likely due to specific interactions between the H_2 molecules and

the guests. Compared with **NENU-3a** (1.59 wt.-%) and **NENU-4a** (1.67 wt.-%; Figures S8 and S9), which contain no Li^+, the H_2 adsorption capacity (77 K, 1 atm) of **NENU-29a** and **NENU-30a** is greater by around 10% upon Li^+ exchange. It is noteworthy that **NENU-29a** and **NENU-30a**, which contain Li^+ and have smaller volumes, adsorb a greater amount of H_2. This suggests that Li^+ could lead to an increase in the H_2 adsorption capacity. At the same time, a comparison of the data indicates that PMOFs/POMs adsorb a greater amount of H_2 per unit volume than the parent MOFs (Table 1). In other words, the presence of POMs is beneficial to the enhancement of H_2 uptake. In the limited space, the intimate contact between H_2 molecules and the O atoms of the POMs may also allow the increase of H_2 uptake. The strong interaction between O and H may enhance H_2 binding by the formation of H–O bonds. In addition, compounds containing different POM guests exhibit some differences in H_2 adsorption capacity. It is well known that $H_3PW_{12}O_{40}$ is the strongest Brønsted acid in the Keggin series and that the O atoms on its surface have weaker constraints on protons than $H_4SiMo_{12}O_{40}$.[19,20] Thus, **NENU-3a** and **NENU-29a**, in which $PW_{12}O_{40}^{3-}$ act as the guests, exhibit weaker binding interactions with H_2 than **NENU-4a** and **NENU-30a**, in which $SiMo_{12}O_{40}^{4-}$ are the anion guests, resulting in a lower enhancement of H_2 uptake.

To further investigate the influence of the guests on H_2 adsorption, we estimated the H_2 adsorption enthalpies. Thus, a second set of H_2 isotherms were measured at 87 K and the enthalpies of H_2 adsorption were calculated by using the modified Clausius–Clapeyron equation.[21] Moderate H_2 adsorption enthalpies of 7.42 and 7.94 $kJ mol^{-1}$ were estimated for **NENU-29a** and **NENU-30a**, respectively, at low coverage, which decreased with increasing H_2 loading (Figures S10 and S11). Although these values are lower than for some reported MOFs,[12a,13b,17a] they are both higher than those determined for $Cu_3(BTC)_2$ (6.8 $kJ mol^{-1}$),[17a] MOF-5 (5.2 $kJ mol^{-1}$),[17b] and MOF-177 (4.4 $kJ mol^{-1}$).[10c] By comparing the data for **NENU-3a** (7.28 $kJ mol^{-1}$) and **NENU-4a** (7.79 $kJ mol^{-1}$; Figures S12 and S13), we find that POMs play a more important role than Li^+ in the enhancement of the H_2 adsorption enthalpies. The H_2 adsorption enthalpies were found to be in the order: **NENU-30a** > **NENU-4a** > **NENU-29a** > **NENU-3a**. This is, in part, probably because Li^+ ions are surrounded

by other atoms and are inaccessible to H_2 molecules, whereas the terminal and bridging O atoms in the POMs can interact easily with H_2 molecules. These results led us to believe that the increased H_2 binding affinity can mainly be attributed to the presence of POMs. In addition, different POMs produce different degrees of enhancement owing to their different strengths of the interactions with H_2. We further corroborated this conclusion by measuring H_2 adsorption at 20 bar and 298 K (Figure 5). **NENU-29a** adsorbs 0.31 wt.-% of H_2 and **NENU-30a** adsorbs 0.40 wt.-% of H_2 at 298 K and 20 bar, which is more than that of $Cu_3(BTC)_2$ (0.35 wt.-%) at 298 K and 65 bar.[22] The results of H_2 adsorption at room temperature indicate that POMs as guests within MOF hosts can indeed enhance H_2 adsorption capacity and binding affinity.
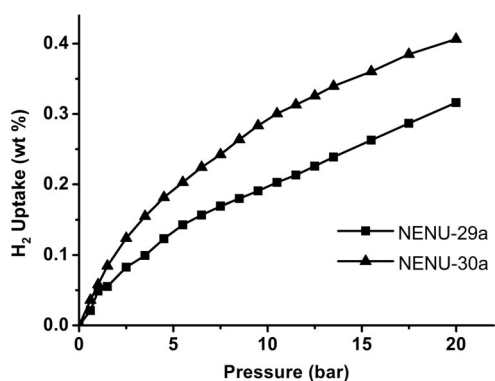

Figure 5. H_2 adsorption isotherms of **NENU-29a** and **NENU-30a** at 298 K and 20 bar.

Conclusions

We have presented herein two PMOFs/POMs that were obtained by Li^+ ion exchange. H_2 adsorption studies demonstrated that the guests play an important role in increasing the H_2 adsorption capacity of the MOFs. Despite their higher weight, POMs cannot be ignored for their contribution to the increase in the H_2 adsorption capacity and binding enthalpy of the MOFs, which is mainly a result of the oxygen-rich nature of the POMs. The mechanistic details of the interactions between H_2 molecules and the O atoms of the POMs are currently poorly understood. However, the results presented herein provide a feasible approach for increasing H_2 adsorption. Furthermore, these polyoxometalate hybrid compounds based on porous metal-organic frameworks display great potential as porous materials. On account of their particular nature, POM guests could provide an appropriate and controllable interaction with adsorbed molecules. By virtue of the porosity of the MOFs and the numerous properties of POMs, for example, as catalysts, this kind of material may find applications in other areas. Our future efforts will focus on the design and synthesis of stable MOFs with multifunctional guests for other applications, such as in vapor adsorption and gas-phase catalysis.

Experimental Section

Materials and Methods: All chemicals were obtained commercially and used without additional purification. Elemental analyses (C, H, and N) were performed with a Perkin–Elmer 2400 CHN elemental analyzer and analysis for Li was carried out with a PLASMA-SPEC(I) ICP atomic emission spectrometer. IR spectra were recorded in the range 400–4000 cm^{-1} with an Alpha Centaurt FT/IR spectrophotometer using KBr pellets. Thermal gravimetric analyses (TGA) were performed with a Perkin–Elmer TGA7 instrument in a flow of N_2 with a heating rate of 10 °C min^{-1}. Powder X-ray diffraction (PXRD) measurements were performed with a Rigaku D/MAX-3 instrument with Cu-K_α radiation in the 2θ range of 3–60° at 293 K.

Gas Adsorption: Gas adsorption measurements were performed with a Hiden Isochema Intelligent Gravimetric Analyser (IGA-100B). The sample (ca. 100 mg) was out-gassed to a constant weight at 423 K under a high vacuum (<10^{-6} mbar) prior to measurement of the isotherms. High purity gases (N_2, 99.999%; H_2, 99.9995%) were used for the gas adsorption measurements performed at 77, 87, and 298 K. The temperatures were maintained with liquid nitrogen, liquid argon, and a constant-temperature water bath, respectively. All data were rigorously corrected for the buoyancy of the system, samples and adsorbates.

Synthesis of the PMOFs/POMs

$Li_2[Cu_{12}(BTC)_8 \cdot 12H_2O][HPW_{12}O_{40}] \cdot 27H_2O$ (NENU-29)

Method 1: Crystals of as-synthesized **NENU-3** $\{(C_4H_{12}N)_2[Cu_{12}(BTC)_8 \cdot 12H_2O][HPW_{12}O_{40}] \cdot 25H_2O\}$[8] (2.0 g) were immersed in a saturated solution of $LiNO_3$ (100 mL) for a week with the $LiNO_3$ solution being refreshed everyday. The completely Li^+-exchanged crystals of **NENU-29** ($\approx$2.0 g) were obtained and washed with distilled water three times.

Method 2: As-synthesized crystals of **NENU-3** (2.0 g) were evacuated under a dynamic vacuum ($\approx$10^{-6} mbar) at 150 °C for 12 h, to give **NENU-3a** $\{H_2[Cu_{12}(BTC)_8][HPW_{12}O_{40}]\}$. These were immersed in a saturated solution of $LiNO_3$ (100 mL) for 24 h, during which time the $LiNO_3$ solution was refreshed once. The completely Li^+-exchanged crystals of **NENU-29** (ca. 2.0 g) were isolated and washed with distilled water three times. Both of the methods described above resulted in exactly the same product **NENU-29**. Yield 1.96 g (98%). IR (KBr): ṽ = 1888 (w), 1656 (vs), 1591 (w), 1456 (m), 1373 (vs), 1115 (w), 1078 (s), 976 (s), 903 (m), 821 (m), 799 (w), 762 (m), 728 (m), 599 (w), 495 (w) cm^{-1}. $C_{72}H_{128}Cu_{12}Li_2O_{127}PW_{12}$ (6039.20): calcd. C 14.32, H 2.12, N 0.00; found C 14.23, H 2.19, N 0.00.

$Li_2[Cu_{12}(BTC)_8 \cdot 12H_2O][H_2SiMo_{12}O_{40}] \cdot 25H_2O$ (NENU-30): Compound **NENU-30** was prepared following the procedure described for compound **NENU-29**, but **NENU-4** $\{(C_4H_{12}N)_2[Cu_{12}(BTC)_8 \cdot 12H_2O][H_2SiMo_{12}O_{40}] \cdot 28H_2O\}$ was used instead of **NENU-3**. Yield 1.92 g (96%). IR: ṽ = 1896 (w), 1653 (vs), 1593 (w), 1457 (m), 1373 (vs), 1114 (w), 1064 (s), 956 (s), 905 (m), 813 (m), 800 (w), 756 (m), 726 (m), 599 (w), 498 (w) cm^{-1}. $C_{72}H_{124}Cu_{12}Li_2Mo_{12}O_{125}Si$ (4945.48): calcd. C 17.48, H 2.52, N 0.00; found C 17.62, H 2.41, N 0.00.

We also tried to prepare **NENU-29** and **NENU-30** following the procedure used to synthesize **NENU-3** and **NENU-4** by changing $(CH_3)_4NOH$ to $LiOH$ under the same hydrothermal conditions. Unfortunately, the yields were so low that we failed to obtain suitable crystals for single-crystal X-ray diffraction.

X-Ray Crystallography: Single-crystal diffractometry was conducted on a Bruker Smart Apex CCD diffractometer with Mo-K_α

monochromated radiation (λ = 0.71073 Å) at room temperature. The linear absorption coefficients, scattering factors for the atoms, and anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography.[23] Empirical absorption corrections were applied. The structures were solved by using the direct method and refined by the full-matrix least-squares method on F^2 using SHELXS-97.[24] Anisotropic thermal parameters were used to refine all non-hydrogen atoms. The hydrogen atoms attached to carbon positions were placed in geometrically calculated positions. The crystallization water molecules were estimated by thermogravimetry, and only partial oxygen atoms of water molecules were analyzed in the X-ray structure determination. The most important crystallographic data are summarized in Table 2.

Table 2. Crystal data and structure refinement for **NENU-29** and **NENU-30**.

	NENU-29	NENU-30
Formula	$C_{144}H_{48}Cu_{24}Li_4O_{248}P_2W_{24}$	$C_{72}H_{24}O_{116}Cu_{12}Li_2SiMo_{12}$
Formula mass [gmol^{-1}]	11785.68	4700.90
Crystal system	cubic	cubic
Space group	$Fm\bar{3}m$	$Fm\bar{3}m$
a [Å]	26.3929(13)	26.3765(11)
V [Å^3]	18384.9(16)	18350.7(13)
Z	2	4
D_c [Mgm^{-3}]	2.129	1.702
μ [mm^{-1}]	8.935	2.247
$F(000)$	10832	9024
Reflns. collected	28109	22728
Indep. reflections	1197	877
GOF on F^2	1.101	1.118
R_{int}	0.0505	0.0535
R_1 [$I > 2\sigma(I)$][a]	0.0347	0.0437
wR_2 (all data)[b]	0.1108	0.1192

[a] $R_1 = \sum ||F_o| - |F_c||/\sum |F_o|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

CCDC-761127 (for **NENU-29**) and -761126 (for **NENU-30**) 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.

Supporting Information (see also the footnote on the first page of this article): IR spectra, TG curves, and PXRD data of the samples and details of the estimation of H$_2$ adsorption enthalpy.

Acknowledgments

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