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A Novel Copper(I) Halide Framework Templated by Organic–Inorganic Hybrid Polyoxometalate Chains Formed In Situ: A New Route for the Design and Synthesis of Porous Frameworks

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A 1D organic–inorganic hybrid polyoxometalate chain has been used as a non-coordinating anionic template for the construction of a novel 3D copper halide 4,4′-bipy framework, namely $[Cu_3^{I}Cl(4,4'\text{-bipy})_4][Cu^{II}(1,10\text{-phen})_2Mo_8O_{26}]$. X-ray diffraction experiments revealed that the title compound consists of chloride-bridged trinuclear Cu^{I} units linked by neutral organic 4,4′-bipy groups into a 3D framework with hexagon-like channels in which 1D organic–inorganic hybrid polyoxometalate chains reside. This is the first example of a 1D organic–inorganic hybrid polyoxometalate chain functioning as a novel anionic template for the construction of a 3D framework.

Introduction

Porous materials have attracted much attention because of interest in the creation of nanometer-sized spaces and their potential applications in gas storage, separation, ion exchange, or heterogeneous catalysis.[1] A promising approach toward the synthesis of these porous materials is the design of metal-organic frameworks built up from transition-metal ions and bridging organic ligands.[2] In this field, copper halides bridged by organic species have been subjected to a vast number of studies owing to the fact that the architectures of copper halides can be tuned at the molecular level so as to design and control, at least partly, the molecular structures of the final products,[3] especially since the so-called secondary building block (SBU) concept was proposed and extended by Yaghi and co-workers.[4] However, it is still important to synthesize robust 3D frameworks with high porosity.[5]

Anions are capable of directing the formation of some porous entities through either cation–anion interactions or hydrogen-bonding interactions between an organic host and an anionic guest.[6] Compared to simple anionic templates, POMs are bigger, have more diverse topologies, a higher charge, and are more suitable as guest units in the metal-organic host as they lead to larger pores, channels, and cavities. In this field, several interesting host–guest complex with various dimensional structures have been prepared.[7] Zubieta and co-workers, for example, have reported $[Fe(tpypor)_3Fe][Mo_6O_{19}]\cdot xH_2O$[7a] (tpypor = tetrapyridylporphyrin), which possesses a 3D $[Fe(tpypor)_3Fe]^{2+}$ host framework with a $[Mo_6O_{19}]^{2-}$ molecule encapsulated, and Zheng et al. have recently reported the novel decavanadate-anion-templated copper framework $[Cu_3(2\text{-pzc})_4(H_2O)_2(V_{10}O_{28}H_4)]\cdot 6.5H_2O$ (2-pzc = 2-pyrazinecarboxylate).[7b] In 2002, the Keller group first prepared the novel compound $[Cu_3(4,4'\text{-bipy})_5(MeCN)_2]PW_{12}O_{40}\cdot 2C_6H_5CN$[7c] constructed from a 3D Cu-4,4′-bipy coordination polymer with a large pore as host and Keggin-type heteropolyoxoanions as template. More recently, the 2D layer-like compound $Na_3[4,4'\text{-Hbipy}]\{Cu_4(4,4'\text{-bipy})_8(H_2O)_8\}[PW_{11}CuO_{39}(H_2O)][PW_{10}Cu_2O_{38}(H_2O)_2]\cdot 38H_2O$[7d] with Keggin-type POMs as guests has been characterized by the Dolbecq group. As part of our continuing efforts in the construction of functional porous coordination polymers,[8] we have exploited the Lindquist-type POM $[Mo_6O_{19}]^{2-}$ to synthesize several novel polyoxometalate-templated, supramolecular networks based on lanthanide dimers.[9] To the best of our knowledge, no metal-organic frameworks using an organic–inorganic hybrid polyoxometalate chain as template has been reported thus far.

In the hope that the combination of copper halides with POMs not only shows value-added properties and possible synergistic effects but also allows the creation of new networks with unique physical properties, we report here the unprecedented compound $[Cu_3^{I}Cl(4,4'\text{-bipy})_4][Cu^{II}(1,10\text{-phen})_2Mo_8O_{26}]$ (**1**), which exhibits a novel 3D copper halide 4,4′-bipy framework templated by a 1D organic–inorganic hybrid polyoxometalate chain. Additionally, we have also

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prepared another compound by changing the reaction conditions, namely $(H_3O)[Cu^I(4,4'\text{-bipy})]_3[Mo_8O_{26}]$, which exhibits a new 2D supramolecular network consisting of β-$[Mo_8O_{26}]^{4-}$ clusters and copper-organonitrogen coordination polymer chains via weak long-range Cu–O interactions.

Results and Discussion

Syntheses

The successful isolation of compounds **1** and **2** depends on the use of hydrothermal techniques. Hydrothermal synthesis has recently been proved to be a particularly useful technique for the preparation of organic–inorganic hybrid materials.[10] The exploitation of hydrothermal conditions requires a paradigm shift from the thermodynamic to the kinetic such that equilibrium phases are replaced by structurally more complex metastable phases.[11] In the hydrothermal environment, the reduced viscosity of the solvent results in enhanced rates of solvent extraction of solids and crystal growth from solution. Furthermore, since different solubility problems can be minimized, a variety of organic and inorganic precursors can be introduced. However, hydrothermal synthesis is still a relatively complex process because many factors can influence the outcome of reaction, such as the type of initial reactants, starting concentrations, pH values, reaction time, and temperature.[12]

Parallel experiments showed that the pH value of the reaction system is crucial for the crystallization of compound **1**: dark-green crystals of compound **1** could only be obtained in the pH range 3.9–4.5. In addition, the nature of the divalent transition metal is crucial for the formation of compound **1**. We tried to replace $CuCl_2{\cdot}2H_2O$ with $NiCl_2{\cdot}6H_2O$, $CoCl_2{\cdot}6H_2O$, $MnCl_2{\cdot}4H_2O$, or $FeCl_2{\cdot}4H_2O$ in the synthesis of compound **1**, but no isostructural compounds were obtained. When $CuCl_2{\cdot}2H_2O$ was replaced with $NiCl_2{\cdot}6H_2O$ or $CoCl_2{\cdot}6H_2O$ $[\{Ni(1,10\text{-phen})_2\}_2(\xi\text{-}Mo_8O_{26})]{\cdot}H_2O$[13] or $\{Co(1,10\text{-phen})_3\}_2[Mo_6O_{19}][Mo_8O_{26}]{\cdot}2H_2O$[14] could be synthesized. However, when $CuCl_2{\cdot}2H_2O$ was replaced with $MnCl_2{\cdot}4H_2O$ or $FeCl_3{\cdot}6H_2O$ no crystalline phase was formed. $[Cu(1,10\text{-phen})]_2[\{Cu(1,10\text{-phen})\}_2\text{-}Mo_8O_{26}]{\cdot}2H_2O$[15] could be synthesized without 4,4′-bipy, and compound **2** could be synthesized without 1,10-phen.

Structure Description

The single X-ray structural analysis revealed that the structure of **1** is constructed from a coordination complex $\{[Cu_3^ICl(4,4'\text{-bipy})_4]\}_n^{2n+}$ scaffolding and encapsulating organic–inorganic hybrid $\{Cu^{II}(1,10\text{-phen})_2Mo_8O_{26}\}_n^{2n-}$ polyoxometalate chains.

The metal-organic framework is composed of hexagon-grid layers pillared by 4,4′-bipy ligands in which there are two distinct copper centers: one resides in the corner of the hexagon lattice in each layer and is additionally coordinated to three nitrogen atoms of 4,4′-bipy and one chlorine atom, while the second copper center is coordinated to two pyridyl nitrogen donors and one chlorine atom, thus two Cu(3) and one Cu(2) are connected into a trinuclear copper cluster through the chlorine atom. The hexagon-grid layer lies parallel to the *ab* plane (Figure 1). Each layer consists of hexagonal lattices, in which the Cu atoms are located at the corners, while the 4,4′-bipy ligands and Cl atoms are located at the edges. As shown in Figure 2, there is no interpenetration between the layers, thus this type of arrangement leads to hexagonal channels of about 5.3 × 11.1 × 11.1 Å^3, in which organic–inorganic hybrid $\{Cu^{II}(1,10\text{-phen})_2Mo_8O_{26}\}_n^{2n-}$ polyoxometalate chains are located. The octamolybdate $[Mo_8O_{26}]^{4-}$ cluster, which is built up from eight distorted $\{MoO_6\}$ edge-shared octahedra, is a typical β-octamolybdate. The valence sum calculations[16] show that all molybdenum atoms are in the +6 oxidation state; the average value is +5.952. The oxygen atoms can be divided into four categories: 1.694(2)–1.706(3) Å for Mo–O(t), 1.908(2)–2.305(2) Å for Mo–O(μ2), 1.943(8)–2.331(2) Å for Mo–O(μ3), and 2.184(2)–2.462(2) Å for Mo–O(μ5); the mean values are 1.700(1), 1.999(7), 2.146(9), and 2.314(4) Å, respectively. All these bond lengths are within the normal ranges and in close agreement with those described in the literature.[17] It is noteworthy that the polyoxoanion acts as a ligand covalently bonded to two $[Cu^{II}(1,10\text{-phen})_2]^{2+}$ units to form a 1D chain (see Figure 3) through terminal oxygen atoms, with Cu–O distances of 2.663(7) Å.[18] In the $[Cu^{II}(1,10\text{-phen})_2]^{2+}$ unit, Cu is coordinated by four N atoms of two 1,10-phen ligands and one terminal oxygen atom of the β-octamolybdate anion to form a distorted octahedron with Cu–N distances in the range 1.974(3)–2.014(4) Å. Thus, the three crystallographically unique copper atoms have three different coordination geometries: Cu(1) exhibits a octahedral geometry in the

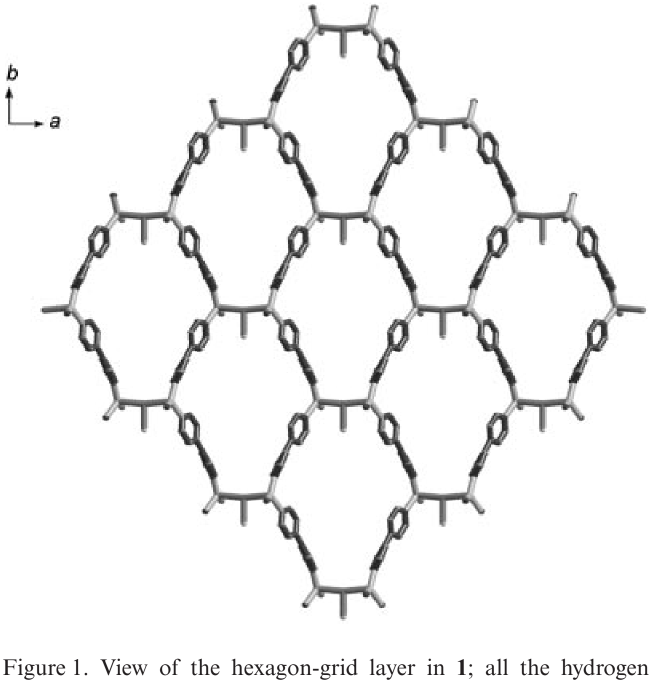

Figure 1. View of the hexagon-grid layer in **1**; all the hydrogen atoms have been omitted for clarity.

form of $\{CuN_4O_2\}$, Cu(2) displays a distorted $\{CuN_3Cl\}$ tetrahedral geometry, while Cu(3) shows trigonal $\{CuN_2Cl\}$ geometry. Valence sum calculations on the Cu sites give values of 1.848, 1.127, and 1.239 for Cu(1), Cu(2), and Cu(3), respectively. Having studied the literature, we noticed that the exploitation of discrete POMs as guests in the construction of 3D frameworks has been reported;[7a,7c] however, there are no examples of organic–inorganic POM chain-templated frameworks to date (see Figure 4a).

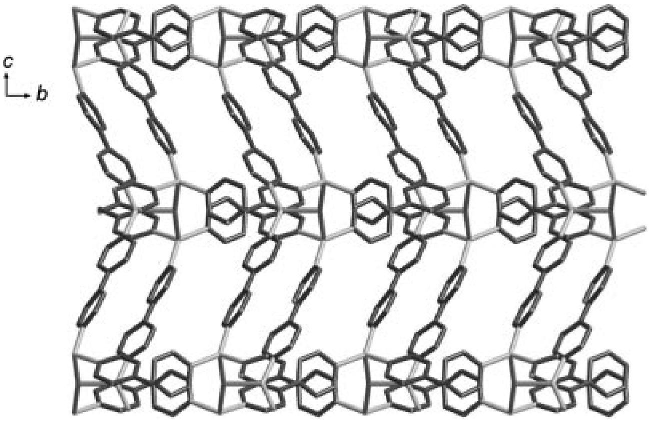

Figure 2. View of the $\{[Cu_3^{I}Cl(4,4'\text{-bipy})_4]\}_n^{2n+}$ coordination complex scaffolding composed of hexagon-grid layers pillared by 4,4′-bipy ligands in **1**; all the hydrogen atoms have been omitted for clarity.

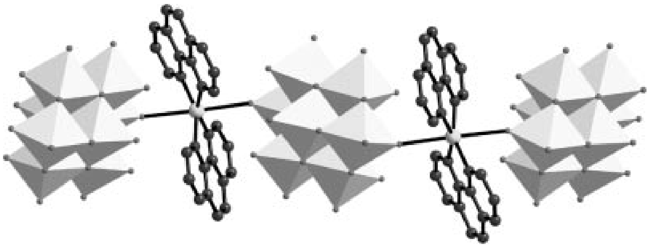

Figure 3. Polyhedral representation of the organic–inorganic hybrid polyoxometalate chain in **1**; all the hydrogen atoms have been omitted for clarity.

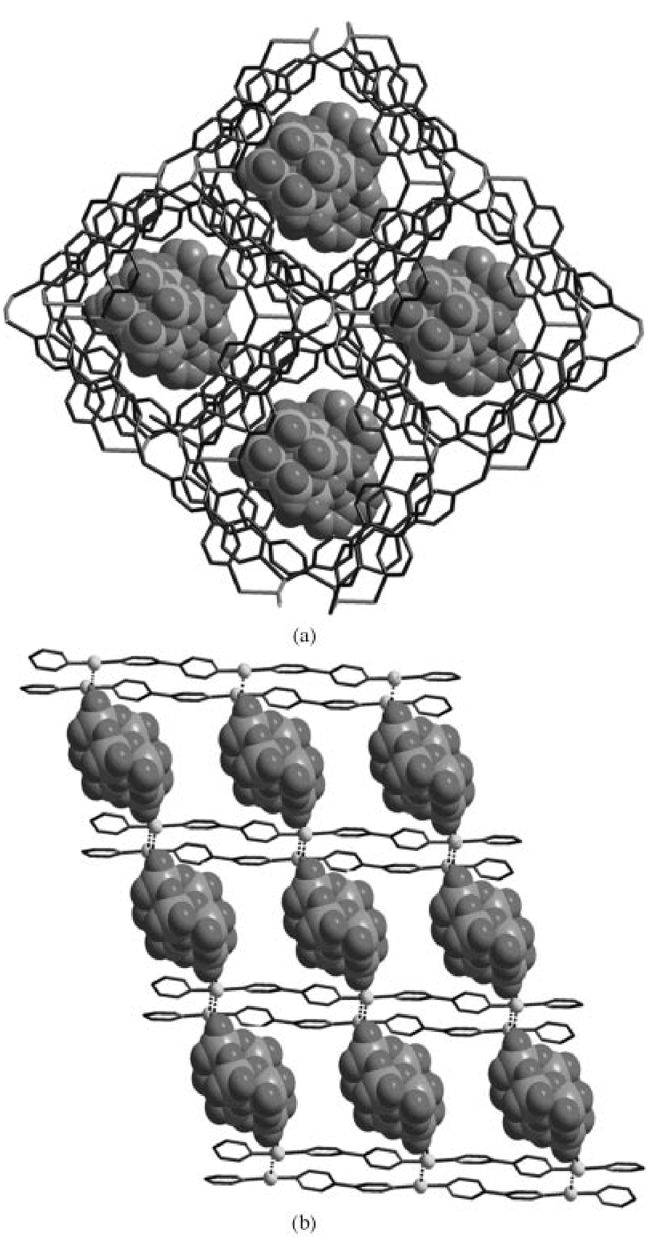

Figure 4. (a) Projection of the 3D framework of **1**; all the hydrogen atoms have been omitted for clarity. (b) View of the 2D supramolecular structure of **2**; all the hydrogen atoms and the water molecules have been omitted for clarity.

The single X-ray structural analysis revealed that the structure of **2** is composed of β-$[Mo_8O_{26}]^{4-}$, $\{Cu(4,4'\text{-bipy})\}_n^{n+}$ chains, and lattice water molecules. The structure of $[Mo_8O_{26}]^{4-}$ is a typical β-$[Mo_8O_{26}]^{4-}$ anion, similar to that of compound **1**. The Mo–O bonds can be divided into four groups, i.e. Mo–O_t, Mo–O(μ2), Mo–O(μ3), and Mo–O(μ5) bonds, with bond lengths in the ranges 1.685(2)–1.702(6), 1.746(9)–2.259(8), 2.149(8)–2.394(2), and 2.149(8)–2.450(8) Å, respectively; the mean values are 1.696(9), 1.944(7), 2.104(3), and 2.334(6) Å. All the mean values of the Mo–O distances are shorter than those of compound **1**. These results may be due to the influence of the outer coordination environment in compound **1**.

As shown in Figure 4b, the β-$[Mo_8O_{26}]^{4-}$ clusters link the $\{Cu(4,4'\text{-bipy})\}_n^{n+}$ chains into a 2D supramolecular structure with a weak, long-range Cu–O interaction of 2.501(66)–2.563(27) Å.

EPR Spectroscopy

The EPR spectrum of **1** at room temperature shows a Cu^{2+} signal with $g_{[par\,]} = 2.2281$ and $g_{\perp} = 2.0506$ (Figure 5), in good accordance with the valence sum calculation.

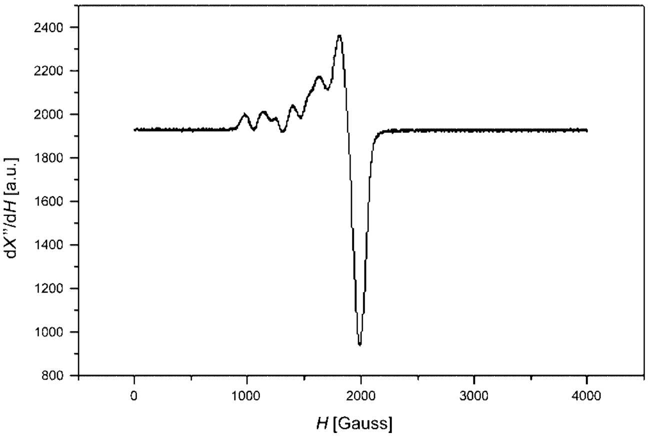

Figure 5. The EPR spectrum of **1**.

Electrochemistry

The POM-modified carbon paste electrode (CPE) was fabricated as follows: 1.0 g of graphite powder and 40 mg of POM **1** or **2** were mixed and ground together with an agate mortar and pestle to achieve an even, dry mixture. Nujol (0.66 mL) was then added to the mixture and stirred with a glass rod. The homogenized mixture was used to pack 3-mm inner diameter glass tubes, and the surface was wiped with weighing paper. Electrical contact was established with a copper rod through the back of the electrode. Platinum gauze was used as counter electrode and an SCE was used as reference electrode.

Figure S1 shows the voltammetric behavior of the working electrodes made from **1** and **2** in 30 mL of aqueous 1 M H_2SO_4 solution at a scan rate of 100 mV s^{-1}. It can be seen that one reversible redox peak appears in the potential range –800 to +1000 mV. In compounds **1** and **2**, the mean peak potential $E_{1/2} = (E_{pa} + E_{pc})/2$ is 11.6 and –58.5 mV, respectively. The redox peaks might be ascribed to the Mo^{VI}/Mo^{V} couple.[19]

FT-IR Spectroscopy

In the IR spectrum of compound **1** (Figure S2), the characteristic bands at 943, 915, 842, 730, 704, and 655 cm^{-1} can be attributed to the Mo=O and Mo–O–Mo vibrations. On comparing the IR spectrum of compound **1** with that of β-$[Mo_8O_{26}]^{4-}$,[20] it can be seen that the shape of the peaks in the range 600–1000 cm^{-1} is nearly identical to that of β-$[Mo_8O_{26}]^{4-}$ except for slight shifts of some peaks due to the effect of coordination, which indicates that the polyoxoanion in compound **1** still retains the basic β-$[Mo_8O_{26}]^{4-}$ structure. This is in agreement with the result of the single-crystal X-ray diffraction analysis. In addition, bands in the 1601–1408 cm^{-1} region can be assigned to characteristic peaks of the ligands 4,4′-bipy and 1,10-phen.

Conclusions

In summary, compound **1** provides an unprecedented 3D host–guest structure with an organic–inorganic hybrid polyoxometalate chain-like template and confirms the utility of hydrothermal methods for the synthesis of new compounds with novel structures. Furthermore, compound **1** demonstrates that both the vast class of polyoxoanion clusters and organic–inorganic polyoxometalate chains may act as templates in the design of higher organic–inorganic hybrid porous materials. Given the variations in the organic–inorganic polyoxometalate chains and metal-organic frameworks, the scope for the further synthesis of POM-based porous materials appears to be very promising.

Experimental Section

Materials: All chemicals purchased were of reagent grade and were used without further purification.

Physical Methods: Elemental analyses (C, H, and N) were performed on a Perkin–Elmer 2400 CHN elemental analyzer. Mo and Cu were determined with a Leaman inductively coupled plasma (ICP) spectrometer. The FTIR spectra were recorded in the range 400–4000 cm^{-1} on an Alpha Centaurt FT/IR spectrophotometer as pressed KBr pellets. TG analyses were performed on a Perkin–Elmer TGA7 instrument in flowing N_2 at a heating rate of 10 °C min^{-1}. The EPR spectrum was recorded with a Bruker ER 200D spectrometer at room temperature. All electrochemical measurements were carried out on a CHI 660 electrochemical workstation at room temperature (25–30 °C).

Synthesis of Compound 1: A mixture of $(NH_4)_6Mo_7O_{24}\cdot 6H_2O$ (0.1 mmol), $CuCl_2\cdot 2H_2O$ (0.3 mmol), 4,4′-bipy (0.3 mmol), 1,10-phen (0.2 mmol), and H_2O (10 mL) was stirred for half an hour in air. The pH was then adjusted to 4.0 with 4 M HCl, and the mixture transferred to a Teflon-lined, 23-mL autoclave and kept at 165 °C for 4 d. After slowly cooling to room temperature, dark-green crystals were filtered off, washed with distilled water, and dried in a desiccator at room temperature. Yield: 0.153 g (54.8% based on Mo). $C_{64}H_{44}ClCu_4Mo_8N_{12}O_{26}$ (2454.2): calcd. C 31.24, H 1.96, Cu 10.34, Mo 31.22, N 6.84; found C 31.54, H 2.13, Cu 10.67, Mo 30.86, N 7.07.

Synthesis of Compound 2: A mixture of $(NH_4)_6Mo_7O_{24}\cdot 6H_2O$ (0.1 mmol), $CuCl_2\cdot 2H_2O$ (0.3 mmol), 4,4′-bipy (0.3 mmol), and H_2O (10 mL) was stirred for half an hour in air. The pH was then adjusted to 4.8 with 4 M HCl and the mixture transferred to a Teflon-lined, 23-mL autoclave and kept at 165 °C for 4 d. After slowly cooling to room temperature, orange crystals were filtered off, washed with distilled water, and dried in a desiccator at room temperature. Yield: 0.079 g (37.5% based on Mo). $C_{30}H_{27}Cu_3Mo_8N_6O_{27}$ (1861.7): calcd. C 19.35, H 1.46, Cu 10.24, Mo 41.23, N 4.52; found C 19.49, H 1.53, Cu 10.09, Mo 41.08, N 4.68.

X-ray Crystallography: Crystallographic data for **1** and **2** were collected at 298 K with a Rigaku R-axis Rapid IP diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.710373 Å) and the IP technique. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL-97 crystallographic software package.[21] Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Carbon-bound hydrogen atoms were placed in geometrically calculated positions; oxygen-bound hydrogen atoms were located in the difference Fourier maps. Further details of the X-ray structural analysis are given in Table 1. Selected bond lengths and angles for compounds **1** and **2** are listed in Tables S1 and S2 in the Supporting Information.

CCDC-600762 (**1**) and -600763 (**2**) 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.

Table 1. Crystal data and structure refinement for **1** and **2**.

	1	**2**
Chemical formula	$C_{64}H_{44}ClCu_4Mo_8N_{12}O_{26}$	$C_{30}H_{27}Cu_3Mo_8N_6O_{27}$
Formula weight	2454.24	1861.74
Crystal system	monoclinic	triclinic
Space group	*C*2/c	$P\bar{1}$
a [Å]	19.748(4)	10.837(2)
b [Å]	17.494(4)	11.274(2)
c [Å]	22.160(4)	11.321(2)
α [°]	90	68.49(3)
β [°]	109.83(3)	83.08(3)
γ [°]	90	64.04(3)
V [Å^3]	7202(2)	1155.7(4)
Z	4	1
D [mg m^{-3}]	2.264	2.701
T [K]	293(2)	293(2)
Reflns. collected	34103	9534
Reflns. unique	8222	4270
R(int)	0.0283	0.0322
Goodness of fit on F^2	0.895	0.747
R_1[a]	0.0286	0.0256
wR_2[b]	0.1038	0.0622

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

Supporting Information (see footnote on the first page of this article): Cyclic voltammograms, IR spectra, and selected bond lengths and angles for compounds **1** and **2**.

Acknowledgments

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