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Communication

Sorting the Assemblies of Unsymmetrically Covalently Functionalized Mn-Anderson Polyoxometalate Clusters with Mass Spectrometry

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The unsymmetrical Mn-Anderson polyoxometalate cluster, $[N(C_4H_9)_4]_3[MnMo_6O_{18}(C_4H_6O_3NO_2)(C_4H_6O_3NH_2)]$ (**1**; $N(C_4H_9)_4^+$ = TBA$^+$), has been prepared and characterized by X-ray crystallography and electrospray ionization mass spectrometry (ESI-MS). Covalent functionalization of compound **1** leads to the controlled assemblies of unsymmetrical alkoxopolyoxometalate clusters of compounds **2**−**5**, which can be directly observed in solution as revealed by ESI-MS studies.

Polyoxometalates (POMs) are a class of discrete metal oxide clusters of V, Mo, W, Nb, etc., and they are attractive building blocks with an almost unmatched range of structural types and physical properties.[1] Importantly, POM-based building blocks can be regarded as transferable synthons for the assembly of large nanostructures, frameworks, and functional materials.[2,3] Although the assembly of large POM clusters is still challenging, POM-containing organic−inorganic hybrids combine the properties of the individual organic and inorganic parts and have shown potential for the construction of novel POM hybrids.[1] However, many "hybrids" reported so far have focused on supramolecular cation−anion interactions, and therefore it is difficult to control the systems at a molecular level. In contrast, the development of covalently modified POM architectures does promise more control but

requires the development of stable building blocks.[4] Therefore, POM hybrids based on covalently linked inorganic POMs and organic species require a strategy that allows the direct coupling of the organic part to the metal oxide cage of the POM, e.g., via replacement of the terminal oxo ligands on the POM framework with nitrido-, hydrazido-, imido-, and alkoxo-based systems.[4] In this respect, the direct covalent functionalization of the Lindqvist[4] $[Mo_6O_{19}]^{4-}$ and Anderson cluster[5] has been shown to hold a great deal of potential.

Herein, we present a route to the synthesis and isolation of a novel unsymmetrical Mn-Anderson hybrid, compound **1**, $[TBA]_3[MnMo_6O_{18}(C_4H_6O_3NO_2)(C_4H_6O_3NH_2)]$, which can be used as a foundation for the development of unsymmetrical hybrids of alkoxopolyoxometalate molecular assemblies. The strategy to construct compound **1** is shown in Scheme 1 (top), and the route to derivatize this hybrid further via a simple and convenient coupling reaction with aldehydes is also shown in Scheme 1 (bottom). In this work, tris(hydroxylmethyl)aminomethane ($C_4H_6O_3H_3NH_2$ = H$_3$L1) and tris(hydroxylmethyl)nitromethane ($C_4H_6O_3H_3$−NO$_2$ = H$_3$L2) were utilized as the sources for the capping of both sides of the Mn-Anderson cluster. The reaction of H$_3$L1 and H$_3$L2 with $[TBA]_4[Mo_8O_{26}]$ and $Mn(CH_3COO)_3$ in MeCN gives statistically controlled mixtures of $[MnMo_6O_{18}(L1)_2]^{3-}$, $[MnMo_6O_{18}(L1)(L2)]^{3-}$, and $[MnMo_6O_{18}(L2)_2]^{3-}$ with TBA as cations.
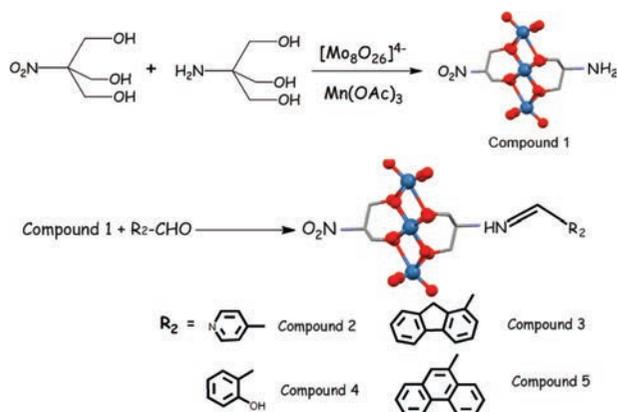
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Scheme 1. Synthetic Scheme of Compounds **1−5** via Capping of the Anderson (Top) and Reaction with an Aldehyde (Bottom)[a]

[a] The Mn-Anderson cluster is shown in ball-and-stick representation (O, red; Mo, blue). TBA cations are omitted for clarity.
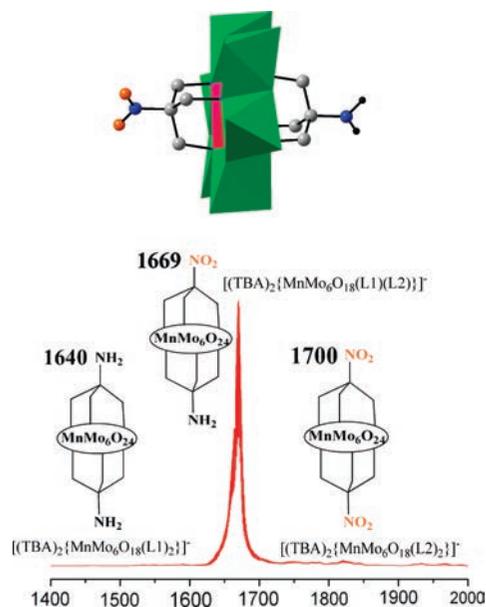

Figure 1. Top: One disorder part of the X-ray crystal structure of compound **1** in a polyhedral representation shows the nitro and amino groups capping both sides of the Mn-Anderson cluster (Mn, pink; Mo, green; C, gray; N, blue; O, orange; H, black). Below: ESI-MS spectrum of compound **1**. The molecular ion peaks of the corresponding symmetric products at m/z = 1640 and 1700 that do not appear are shown.

After the reaction for the synthesis of compound **1**, the system was set up for crystallization and the crystalline precipitates were isolated from the mother liquor by filtration every 6 h. Each batch of the crystalline samples was then analyzed using electrospray ionization mass spectrometry (ESI-MS) in order to determine the number of products present and their distribution, allowing the correct batch to be "sorted" from the bulk, statistically defined mixture. The batch corresponding to compound **1** (molecular ion with m/z = 1669) was collected (see the Supporting Information). This compound was recrystallized as yellow block crystals by the slow evaporation of an *N,N*-dimethylformamide solution, and the X-ray crystal structure of the unsymmetrical cluster is shown in Figure 1, in which the terminal amino ($-NH_2$) and the nitro ($-NO_2$) groups are disordered at both sides with 50% occupancy. The overall molecular structure of com-

pound **1** is very similar to those of the analogous symmetric Mn-Anderson compounds[6] except that terminal amino and nitro groups are present on opposite sides of the polyanion. All of the alkoxo ligands are bound to the Mn^{III} center, leading to a δ type of Anderson structure. Thus, because of the crystallographic disorder of the terminal nitro ($-NO_2$) and amino ($-NH_2$) groups, analysis by ESI-MS spectroscopy not only helps "sort" the reaction mixtures but also allows confirmation of the molecular structure, as shown in Figure 1. The peak at m/z = 1669 can be clearly assigned to the [(TBA)$_2$\{MnMo$_6$O$_{18}$(L1)(L2)\}]$^-$ anion. Additionally, the signal at m/z = 1669 is the only peak in the range of m/z = 1300−2000, with no peaks at m/z = 1700 or 1640, which would be expected from the presence/contamination of the other two possible symmetrical species of [(TBA)$_2$\{MnMo$_6$-O$_{18}$(L1)$_2$\}]$^-$ (m/z = 1640) and/or [(TBA)$_2$\{MnMo$_6$O$_{18}$-(L2)$_2$\}]$^-$ (m/z = 1700). Therefore, these experiments provide unambiguous proof that the unsymmetrical hybrid of compound **1** can be isolated as a pure compound (control experiments with all of the species mixed together intentionally show that the ion transmission intensity can be related to the concentration of the species in solution).[7]

It is important to note that L1, the C$_4$H$_6$O$_3$NH$_2$ group, in this unsymmetrical hybrid of compound **1** is nucleophilic, while L2, the C$_4$H$_6$O$_3$NO$_2$ group, is relatively inert from a reactivity perspective. As such, the unsymmetrical hybrid of compound **1**, with the free pendant amino group, provides a great opportunity to develop and construct new POM frameworks, and the controlled assemblies can be easily observed using ESI-MS measurements. To explore this idea, compound **1** is reacted with a number of aromatic aldehydes, for example, 4-pyridylcarboxylaldehyde, forming a series of new POM unsymmetrical hybrids whereby the amino group is transformed into an imine moiety. In the case of 4-pyridylcarboxylaldehyde, we were able to obtain compound **2** with the formula of (TBA)$_3$[MnMo$_6$O$_{18}$\{(OCH$_2$)$_3$CN=CH(C$_5$H$_4$N)\}(L2)], which has been fully characterized including mass spectrometry and single-crystal X-ray crystallography (see Figure 2). The crystal structure of compound **2** contains a pyridyl ring linked via a C=N bond to the Mn-Anderson cluster, and the alkoxo group on the other side of the Mn-Anderson cluster is terminated with a nitro group. The ESI-MS spectrum of compound **2** shows signals at m/z = 1758 and 1516 observed in the range of m/z = 1400−2000, which can be assigned as \{(TBA)$_2$[MnMo$_6$O$_{18}$\{(OCH$_2$)$_3$CN=CH(C$_5$H$_4$N)\}(L2)]\}$^-$ and \{H(TBA)[MnMo$_6$O$_{18}$\{(OCH$_2$)$_3$-CN=CH(C$_5$H$_4$N)\}(L2)]\}$^-$ anions, respectively, indicating that the pyridyl group has been grafted onto the Mn-Anderson cluster. These results provide definitive proof for the successful functionalization of compound **1** via the formation of the imine-based moiety.

The reactions of compound **1** with fluorene-2-carboxaldehyde, salicylaldehyde, and phenanthrene-9-carboxaldehyde

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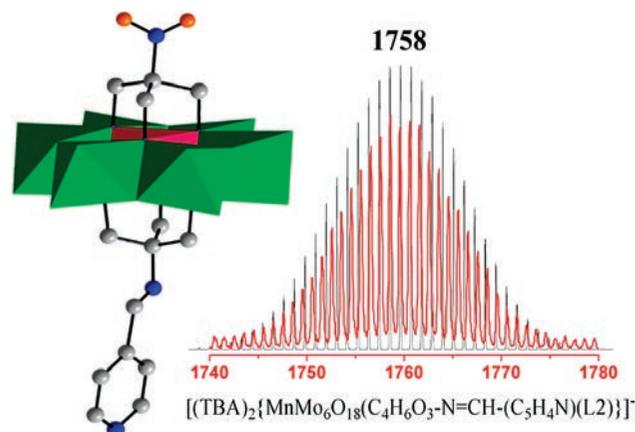
Figure 2. Left: X-ray crystal structure of compound **2** shown as a polyhedral representation showing that a pyridyl ring has been covalently tethered to the Mn-Anderson cluster (Mn, pink; Mo, green; N, blue; C, gray; O, orange). Right: ESI-MS spectrum of the molecular ion peak of compound **2** (actual spectrum in red; calculated spectrum in black).
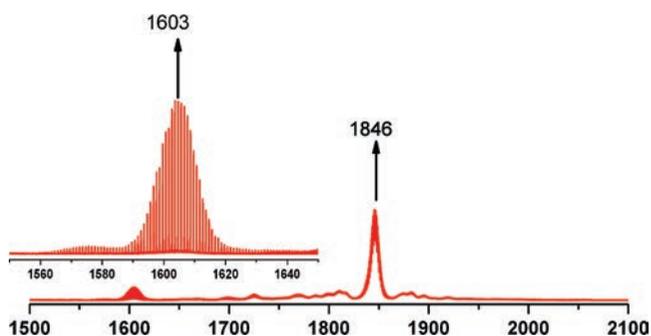

Figure 3. ESI-MS spectrum of compound **3** showing signals at $m/z =$ 1847 and 1603.

gave compounds **3**–**5**, respectively, whose compositions were established by mass spectrometry and chemical analysis. For compound **3** (see Figure 3), the signals at $m/z =$ 1846 and 1603 can be assigned to $\{(TBA)_2[MnMo_6O_{18}\{(OCH_2)_3CN{=}CHC_{13}H_9\}(L2)]\}^-$ and $\{H(TBA)[MnMo_6O_{18}\{(OCH_2)_3CN{=}CHC_{13}H_9\}(L2)]\}^-$, respectively, which are in accordance with the molecule with the aromatic "fluorene" ring grafted onto the Mn-Anderson cluster. In the case of compound **4**, the signal at $m/z =$ 1774 corresponds to $\{(TBA)_2[MnMo_6O_{18}\{(OCH_2)_3CN{=}CHC_6H_4OH\}(L2)]\}^-$ showing that the "phenol" ring has been attached to the Anderson cluster via the imine moiety.

For compound **5**, the signals at $m/z =$ 1858 and 1617 are unambiguously assigned to $\{(TBA)_2[MnMo_6O_{18}\{(OCH_2)_3CN{=}CHC_{14}H_9\}(L2)]\}^-$ and $\{H(TBA)[MnMo_6O_{18}\{(OCH_2)_3CN{=}CHC_{14}H_9\}(L2)]\}^-$, respectively, which demonstrate that the phenanthrene ring has been tethered onto the Mn-Anderson cluster. All of the observed ESI-MS peaks are summarized in Table 1, and these findings fully confirm our formula assignments of compounds **3**–**5** and provide important information

Table 1. Summary of the Observed ESI-MS (Negative Mode) Peaks (m/z) of Four New Unsymmetrical Hybrids

Compounds	Observed ESI-MS peaks (neg mode)	
compound 2	$\{(TBA)_2[MnMo_6O_{18}\{(OCH_2)_3C\text{-}N{=}CH\text{-}(C_5H_4N)\}(L2)]\}^{\cdot}$	1758
R2=	$\{H(TBA)[MnMo_6O_{18}\{(OCH_2)_3C\text{-}N{=}CH\text{-}(C_5H_4N)\}(L2)]\}^{\cdot}$	1516
compound 3	$\{(TBA)_2[MnMo_6O_{18}\{(OCH_2)_3C\text{-}N{=}CH\text{-}C_{13}H_9\}(L2)]\}^{\cdot}$	1846
R2=	$\{H(TBA)[MnMo_6O_{18}\{(OCH_2)_3C\text{-}N{=}CH\text{-}C_{13}H_9\}(L2)]\}^{\cdot}$	1603
compound 4	$\{(TBA)_2[MnMo_6O_{18}\{(OCH_2)_3C\text{-}N{=}CH\text{-}C_6H_4OH\}(L2)]\}^{\cdot}$	1774
R2=		
compound 5	$\{(TBA)_2[MnMo_6O_{18}\{(OCH_2)_3C\text{-}N{=}CH\text{-}C_{14}H_9\}(L2)]\}^{\cdot}$	1858
R2=	$\{H(TBA)[MnMo_6O_{18}\{(OCH_2)_3C\text{-}N{=}CH\text{-}C_{14}H_9\}(L2)]\}^{\cdot}$	1617

on the steps of controlled assembly of the POM cluster based on this unsymmetric hybrid of compound **1**.

The unambiguous assignment of the signals from ESI-MS measurements allows us to clarify the crystallographic study of compound **1** because of the presence of disorder of the $-NO_2$ and $-NH_2$ groups. At the same time, it also provides extremely useful information to determine compounds **2**–**5**. The observations demonstrate the potential of high-resolution and soft ionization mass spectrometry[7] or the isolation of the correct reactive species for further functionalization, and the characterization of the final products also provides vital supporting information, in conjunction with structural data, to correctly deduce the structure of the molecular hybrid organic—inorganic-based species.

In summary, the design and synthesis of the unsymmetrical Mn-Anderson hybrid of compound **1** presented herein not only allow us to functionalize the Mn-Anderson cluster in a controlled way but also provide the versatility to adjust the chemical and geometrical preferences of the resulting POM assemblies. Compared with symmetric Mn-Anderson clusters reported before,[5,6] the most important feature of this unsymmetrical hybrid of compound **1** is that this modular assembly approach brings both rational design and structural control into the synthesis of novel POM-based hybrids. In the future, we will explore the potential application of the above new assemblies and, at the same time, exploit further POM-containing functional materials based on this unsymmetrical POM hybrid to further extend and develop the controlled functionalization of POMs with novel organic components.

Supporting Information Available: X-ray crystallographic file in CIF format and synthetic details of compounds **1**–**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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