Organoimido-Derivatized Hexamolybdates with a Remote Carboxyl Group: Syntheses and Structural Characterizations

Guohui Sima,[†,||] Qiang Li,[‡,||] Yi Zhu,[§,||] Chunlin Lv,[†] Rao Naumaan Nasim Khan,[†] Jian Hao,[†] Jin Zhang,*[,†] and Yongge Wei*[,†]

[†]Department of Chemistry, Tsinghua University, Beijing 100084, PR China
[‡]Department of Chemistry, College of Science of Beijing Forestry University, Beijing 100083, PR China
[§]Department of Chemistry, Jinan University, Guangzhou 510632, PR China

Ⓢ Supporting Information

ABSTRACT: Four novel organoimido derivatives of hexamolybdate containing a remote carboxyl group have been synthesized: $[Bu_4N]_2[Mo_6O_{18}(N-C_6H_4-3-COOH)]$ (**1**), $[Bu_4N]_2[Mo_6O_{18}(N-C_6H_4-2-CH_3-4-COOH)]$ (**2**), $[Bu_4N]_2[Mo_6O_{18}(N-C_6H_4-2-CH_3-5-COOH)]$ (**3**), and $[Bu_4N]_2[Mo_6O_{18}(N-C_6H_4-2-CH_3-3-COOH)]$ (**4**) with 3-aminobenzoic acid, 4-amino-3-methylbenzoic acid, 3-amino-4-methylbenzoic acid, and 3-amino-2-methylbenzoic acid as the imido-releasing agents, respectively. Their structures have been characterized by IR, UV−vis, ^{1}H NMR, ESI−MS, and single-crystal X-ray diffraction techniques. Hydrogen bonding interactions play an important role in the supramolecular assemblies of these compounds in the solid state. Although the incorporated organic ligands are similar to each other, their supramolecular assembly behaviors are quite different. For compound **1**, the dimer structure is formed via hydrogen bonding between the carboxyl group and the POM cluster of two neighboring cluster anions. For compound **2**, the 1D chain structure is formed via hydrogen bonding between the carboxyl groups and the POM clusters of the cluster anions. For compound **3**, the 2D plane structure is formed via two types of hydrogen bonding between the aromatic rings and the POM clusters of the cluster anions. For compound **4**, the 1D plus 2D structures are formed via three types of hydrogen bonding between the aromatic rings and the POM clusters of the two types of cluster anions with different orientations.
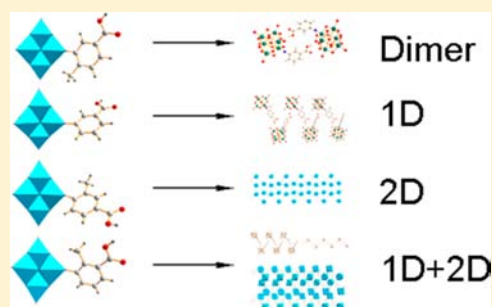
INTRODUCTION

Polyoxometalates (POMs) are a unique class of metal−oxygen cluster compounds consisting of early transition-metal ions in the highest oxidization states that are linked by oxygen anions as ligands. They present remarkable structural diversity, chemical reactivity, and self-assembly behaviors as well as excellent magnetic, photonic, and electronic properties that have potential applications in diverse fields such as materials, catalysis, and medicinal sciences.[1−10] The realizability of the processing and modifying of POMs is very important for their subsequent research and application. An effective method to achieve this goal is through the organic modification of POMs to obtain organic−inorganic hybrids.

Since the pioneering work of Klemperer,[11] Harlow[12], and Pope,[13] organically functionalized POMs with covalently grafted organic ligands have been studied extensively. As expected, the resulting organic−inorganic hybrid materials not only have both the advantages of the organic ligands, such as fine electronic properties and easy processing, and the advantages of the inorganic POM components, such as good structural stability and electron acceptability, but also have fascinating synergistic effects that originate from the interaction between the organic ligands and the inorganic clusters.[14] Therefore, such hybrid materials have drawn a great amount of

attention because of their novel structures and properties. However, there are some difficulties in the synthesis chemistry that is used to obtain such POM-based hybrid materials.

Among the different kinds of organically functionalized POMs, the organoimido derivatives with metal−nitrogen multiple bonds, which largely modify the electronic structures and redox properties of the parent POMs, have obtained great attention in recent decades, and a large number of organoimido derivatives of the Lindqvist-type hexamolybdates have been synthesized and studied successfully. From the time that Kang and Zubieta first described an organoimido derivative,[15] the imidoylization of POMs has been synthetically investigated and was initially reported by Maatta,[16] Proust,[17] and Errington.[18] Thus, three kinds of reactions for the synthesis of the organoimido derivatives of hexamolybdates have been developed, including reactions with phosphinimines, isocyanates, and aromatic amines. Subsequently, Peng and Wei discovered the N,N′-dicyclohexylcarbodiimide (DCC) protocol in which the reaction of hexamolybdates and amines was remarkably promoted by DCC to obtain the organoimido derivatives of POMs.[19] Next, Wei discovered that the reaction

of α-octamolybdates and amine hydrochlorides in the presence of DCC, in which both the proton and the DCC produce effects, could afford the organoimido derivatives of hexamolybdates in higher yields.[20] Since then, a large number of organoimido derivatives of hexamolybdates containing different kinds of remote groups, such as amino,[21] nitro,[22] hydroxyl,[23] ester,[24] and halo,[25,26] have been synthesized and investigated by using this DCC protocol.

The organoimido derivatives of hexamolybdates with remote groups can also serve as building blocks in further functionalization or fabrication to obtain more complicated and fascinating POM-based organic−inorganic hybrid materials via postmodification or self-assembly procedures. In recent years, several inorganic and organic reactions, including coordination,[27] esterification,[28] Sonogashira coupling,[29] the Heck reaction,[30] and addition polymerization,[31] of organo-imido-substituted hexamolybdates have been investigated. In addition, the alkylimido derivatives of hexamolybdates have been discovered to undergo a C−C coupling reaction to form a C=C double bond via the doubly dehydrogenative coupling (DDHC) reaction of the two saturated sp^3 C−H bonds closest to the nitrogen of the imido groups that are activated by POMs,[32] providing a novel method for C=C double bond formation besides traditional coupling reactions.

Although a large number of organoimido derivatives of hexamolybdate containing different kinds of remote groups have been obtained, reports of organically functionalized hexamolybdates containing remote carboxyl groups have been surprisingly rare until now.[33,34] The organoimido derivatives of hexamolybdate containing a remote carboxyl group, as an active group for further coordination and for some organic reactions, can undergo postmodification to afford either novel POM-based organic−inorganic hybrid materials or supramolecular self-assemblies in addition to the organic−inorganic hybrids formed via the noncovalent interaction between POMs and organic ligands.[35,36] Mialane reported the hybrid compounds formed by the rare earth POMs and carboxylate ligands through coordination,[37] which ranged from macromolecular complexes to open framework systems. The Lindqvist-type POM-based coordination network with terbium and carbox-ylate was reported by Hill[38] and had good catalytic properties in the O_2-based oxidations. Furthermore, Su and Liu reported the synthesis of a solid, porous MOF by the reaction of a Keggin-type POM, copper salt, and a carboxylate ligand[39] that displayed fine nerve gas adsorption. This work indicates that the POM-based hybrids that are formed via the modification of the carboxyl group show special structural and application characteristics. Therefore, in this work we synthesized four novel organoimido derivatives of hexamolybdates containing a remote carboxyl group on different relative positions of the imido nitrogen and methyl groups on a benzene ring. Then we characterized and investigated the title compounds, especially the hydrogen bonding interaction in the formation of the supramolecular assemblies, and we hope to give some information on the reaction chemistry of such POM derivatives and the further preparation of novel POM-based organic−inorganic hybrid materials via reactions with carboxyl groups.

■ EXPERIMENTAL SECTION

General Methods and Materials. All of the syntheses and the manipulations were carried out under dry N_2 gas. The $(Bu_4N)_4[Mo_8O_{26}]$ was conveniently synthesized according to an improved literature method[40] by the addition of an Bu_4NBr aqueous

solution to an $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ aqueous solution, from which the product immediately precipitated and was dried before use. The hydrochlorides of 3-aminobenzoic acid, 4-amino-3-methylbenzoic acid, 3-amino-4-methylbenzoic acid, and 3-amino-2-methylbenzoic acid were prepared by adding concentrated HCl to the corresponding compounds and were also dried before use. The acetonitrile was dried by refluxing in the presence of CaH_2 and was distilled prior to use. DCC, acetone, diethyl ether, and ethanol were directly used without further purification. Elemental analysis was measured with a ThermoQuest FLASH-1112 instrument. IR spectra were obtained using KBr pellets with a PerkinElmer FT-IR spectrometer. UV−vis spectra were measured in an acetonitrile solution with a Shimadzu UV-2100S spectrophotometer. ^1H NMR spectra were measured using d_6-DMSO as the solvent with a Bruker ARX400 NMR spectrometer. ESI−MS spectra were measured in an acetonitrile solution with a ThermoFisher LTQ spectrometer. The negative mode was used for the experiments.

Synthesis of $[Bu_4N]_2[Mo_6O_{18}(N-C_6H_4-3-COOH)]$ (1). A mixture of $(Bu_4N)_4[Mo_8O_{26}]$ (2.15 g, 1.0 mmol), 3-aminobenzoic acid hydrochloride (0.231 g, 1.33 mmol), and DCC (0.454 g, 2.2 mmol) was dissolved in 10 mL of anhydrous acetonitrile and heated to reflux at 110 °C for 3 h. After cooling to room temperature, the reaction solution was filtered to remove white precipitate 1,3-dicyclohexylurea (DCU), and the filtrate was poured into 100 mL of ether to remove some of the unreacted organic compounds, resulting in precipitation. This precipitate was dissolved in acetone and filtered to remove the unreacted octamolybdate. After the filtrate had evaporated in the open air, the remaining solid was washed with ethanol to further remove more of the unreacted organic compounds. The remaining crude product was then redissolved in acetonitrile, and the red single crystals for X-ray diffraction were obtained by the diffusion of ether into the acetonitrile solution. The yield for the crystalline product after crystallization (based on Mo) was 12%. Anal. Calcd for $C_{42}H_{83.5}O_{20.5}N_{3.5}Mo_6$ (1541.26): C, 32.73; H, 5.46; N, 3.18. Found: C, 31.36; H, 5.12; N, 2.94. IR (KBr pellet, cm^{-1}): 2962, 2874, 1724, 1482, 1382, 977, 953, 889, 794. UV−vis (CH_3CN, nm): λ_{max} = 343. ^1H NMR (d_6-DMSO, 400 MHz): δ 0.93 (t, 24H, −CH_3, $[Bu_4N]^+$), 1.31 (m, 16H, −CH_2−, $[Bu_4N]^+$), 1.56 (m, 16H, −CH_2−, $[Bu_4N]^+$), 3.16 (t, 16H, N−CH_2−, $[Bu_4N]^+$), 7.42 (d, 1H, ArH), 7.57 (t, 1H, ArH), 7.67 (t, 1H, ArH), 7.74 (d, 1H, ArH), 13.34 (s, 1H, −COOH). ESI−MS (CH_3CN, m/z): 499.77 (100%, $[Mo_6O_{18}(N-C_6H_4-3-COOH)]^{2-}$), 1242.75 (35%, $[Bu_4N][Mo_6O_{18}(N-C_6H_4-3-COOH)]^-$).

Synthesis of $[Bu_4N]_2[Mo_6O_{18}(N-C_6H_4-2-CH_3-4-COOH)]$ (2). The synthesis method was similar to that of compound **1** except that 4-amino-3-methylbenzoic acid hydrochloride was used instead of 3-aminobenzoic acid hydrochloride, and the reaction time was 9 h. The red single crystals for X-ray diffraction were obtained by the diffusion of ether into the acetonitrile solution. The yield for the crystalline product after crystallization (based on Mo) was 20%. Anal. Calcd for $C_{40}H_{79}O_{20}N_3Mo_6$ (1497.70): C, 32.08; H, 5.32; N, 2.81. Found: C, 32.32; H, 5.44; N, 2.94. IR (KBr pellet, cm^{-1}): 2961, 2873, 1715, 1480, 1379, 977, 955, 883, 794. UV−vis (CH_3CN, nm): λ_{max} = 358. ^1H NMR (d_6-DMSO, 400 MHz): δ 0.93 (t, 24H, −CH_3, $[Bu_4N]^+$), 1.31 (m, 16H, −CH_2−, $[Bu_4N]^+$), 1.57 (m, 16H, −CH_2−, $[Bu_4N]^+$), 2.57 (s, 3H, Ar−CH_3), 3.16 (t, 16H, N−CH_2-, $[Bu_4N]^+$), 7.25 (d, 1H, ArH), 7.79 (d, 1H, ArH), 7.84 (s, 1H, ArH), 13.03 (s, 1H, −COOH). ESI−MS (CH_3CN, m/z): 507.72 (100%, $[Mo_6O_{18}(N-C_6H_4-2-CH_3-4-COOH)]^{2-}$), 1255.92 (30%, $[Bu_4N][Mo_6O_{18}(N-C_6H_4-2-CH_3-4-COOH)]^-$).

Synthesis of $[Bu_4N]_2[Mo_6O_{18}(N-C_6H_4-2-CH_3-5-COOH)]$ (3). The synthesis method was similar to that of compound **1** except that 3-amino-4-methylbenzoic acid hydrochloride was used instead of 3-aminobenzoic acid hydrochloride, and the reaction time was 10 h. After cooling to room temperature, the reaction solution was filtered to remove white precipitate DCU. The filtrate was evaporated slowly in the open air to remove the octamolybdate and hexamolybdate by filtration because they crystallized first, resulting in a crude oily product. This crude product was redissolved in acetonitrile, and the red single crystals for X-ray diffraction were obtained by the diffusion of ether into the acetonitrile solution. The yield for the crystalline

Table 1. Crystallographic Data for Compounds 1−4

	compound **1**	compound **2**	compound **3**	compound **4**
empirical formula	$C_{42}H_{83.5}O_{20.5}N_{3.5}Mo_6$	$C_{40}H_{79}O_{20}N_3Mo_6$	$C_{40}H_{79}O_{20}N_3Mo_6$	$C_{40}H_{79}O_{20}N_3Mo_6$
formula weight	1541.26	1497.70	1497.70	1497.70
temperature, K	102	100	103	104
wavelength, Å	0.71073	0.71073	0.71073	0.71073
space group	$Pcca$ (no. 54)	$C2/c$ (no. 15)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)
a, Å	19.9827(6)	41.278(3)	12.6439(3)	37.0279(7)
b, Å	24.1195(10)	12.2444(8)	20.7751(4)	12.3515(3)
c, Å	23.8593(7)	24.4842(14)	20.4235(4)	24.2391(5)
α, degrees	90	90	90	90
β, degrees	90	115.901(7)	94.375(2)	92.2844(19)
γ, degrees	90	90	90	90
V, Å^3	11499.5(7)	11131.8(12)	5349.2(2)	11077.0(4)
Z	8	8	4	8
D_{calcd} [g cm^{-3}]	1.780	1.787	1.860	1.796
μ [mm^{-1}]	1.341	1.381	1.437	1.388
R_1 $[I > 2\sigma(I)]^a$	0.0481	0.0530	0.0434	0.0538
wR_2 $[I > 2\sigma(I)]^b$	0.1380	0.1537	0.0832	0.1746

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

product after crystallization (based on Mo) was 10%. Anal. Calcd for $C_{40}H_{79}O_{20}N_3Mo_6$ (1497.70): C, 32.08; H, 5.32; N, 2.81. Found: C, 32.38; H, 5.48; N, 3.13. IR (KBr pellet, cm^{-1}): 2964, 2874, 1718, 1481, 1379, 977, 952, 881, 793. UV−vis (CH$_3$CN, nm): λ_{max} = 346. ^{1}H NMR (d_6-DMSO, 400 MHz): δ 0.93 (t, 24H, −CH$_3$, [Bu$_4$N]$^+$), 1.31 (m, 16H, −CH$_2$−, [Bu$_4$N]$^+$), 1.57 (m, 16H, −CH$_2$−, [Bu$_4$N]$^+$), 2.59 (s, 3H, Ar−CH$_3$), 3.16 (t, 16H, N−CH$_2$−, [Bu$_4$N]$^+$), 7.42 (d, 1H, ArH), 7.61 (s, 1H, ArH), 7.64 (d, 1H, ArH), 13.18 (s, 1H, −COOH). ESI−MS (CH$_3$CN, m/z): 506.20 (100%, [Mo$_6$O$_{18}$(N-C$_6$H$_4$-2-CH$_3$-5-COOH)]$^{2-}$), 1013.40 (45%, [HMo$_6$O$_{18}$(N-C$_6$H$_4$-2-CH$_3$-5-COOH)]$^-$).

Synthesis of [Bu$_4$N]$_2$[Mo$_6$O$_{18}$(N-C$_6$H$_4$-2-CH$_3$-3-COOH)] (4). The synthesis method was similar to that of compound **1** except that 3-amino-2-methylbenzoic acid hydrochloride was used instead of 3-aminobenzoic acid hydrochloride, and the reaction time was 6 h. The red single crystals for X-ray diffraction were obtained by the diffusion of ether into the acetonitrile solution. The yield for the crystalline product after crystallization (based on Mo) was 14%. Anal. Calcd for $C_{40}H_{79}O_{20}N_3Mo_6$ (1497.70): C, 32.08; H, 5.32; N, 2.81. Found: C, 32.06; H, 5.42; N, 2.94. IR (KBr pellet, cm^{-1}): 2963, 2874, 1736, 1470, 1380, 975, 954, 882, 796. UV−vis (CH$_3$CN, nm): λ_{max} = 345. ^{1}H NMR (d_6-DMSO, 400 MHz): δ 0.93 (t, 24H, −CH$_3$, [Bu$_4$N]$^+$), 1.31 (m, 16H, −CH$_2$−, [Bu$_4$N]$^+$), 1.56 (m, 16H, −CH$_2$−, [Bu$_4$N]$^+$), 2.74 (s, 3H, Ar−CH$_3$), 3.16 (t, 16H, N−CH$_2$−, [Bu$_4$N]$^+$), 7.34 (t, 1H, ArH), 7.38 (d, 1H, ArH), 7.56 (d, 1H, ArH), 13.13 (s, 1H, −COOH). ESI−MS (CH$_3$CN, m/z): 505.78 (100%, [Mo$_6$O$_{18}$(N-C$_6$H$_4$-2-CH$_3$-3-COOH)]$^{2-}$), 1254.70 (80%, [Bu$_4$N][Mo$_6$O$_{18}$(N-C$_6$H$_4$-2-CH$_3$-3-COOH)]$^-$).

Single-Crystal Structure Determinations. Suitable single crystals were mounted on a glass fiber and transferred directly to an Agilent Gemini CCD diffractometer at room temperature. The data collections were performed at 102 K for compound **1**, 100 K for compound **2**, 103 K for compound **3**, and 104 K for compound **4** by graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The data reduction, cell refinement, and absorption correction were processed with CrysAlisPro software (Agilent, 2011, version 1.171.35.11). The structures were solved by direct methods and refined by full-matrix least squares. All the nonhydrogen atoms were refined anisotropically, and the hydrogen atoms were generated geometrically. All of the computations were performed with the program package SHELXTL, version 6.14.[41,42]

■ RESULTS AND DISCUSSION

Preparation of the Compounds. Two methods have been developed to synthesize the monosubstituted organo-imido derivatives of hexamolybdates: the reaction of (Bu$_4$N)$_2$[Mo$_6$O$_{19}$] with amines and the reaction of (Bu$_4$N)$_4$[Mo$_8$O$_{26}$] with amine hydrochlorides. Both of these reactions were carried out in the presence of DCC as a dehydrating agent. Thus, both methods were carried out in this article to synthesize the four target derivatives.

When (Bu$_4$N)$_2$[Mo$_6$O$_{19}$], an aromatic carboxylic acid with an amino group, and DCC were used in the reaction, the solution turned brown or green after some time, which meant that the hexamolybdate oxidized the organic compound and was itself reduced, resulting in a brown- or green-colored appearance. The absence of a red-colored appearance indicated that the electron exchange occurred between the POM cluster and the organic group before the formation of the organoimido product. Additionally, the oxidation state of the organic group might form a radical on the nitrogen atom that could undergo further reaction, including the polymerization of the organic reactant. The experimental parameters were then changed, including the reactant ratio, reaction temperature, and reaction time, but they still could not give rise to the organoimido products. However, when (Bu$_4$N)$_4$[Mo$_8$O$_{26}$], a hydrochloride of the aromatic carboxylic acid with an amino group, and DCC were used in the reaction, the organoimido products were obtained for every corresponding organic compound by controlling the different reaction conditions. The single crystals were obtained by using different processing approaches for the different compounds. In the imidoylization of the POMs and the amines with different kinds of groups other than the carboxyl group, both the hexamolybdate method and the octamolybdate method can, for the most part, afford the organoimido products. The difference between the two methods is that the latter one can afford the organoimido products faster, in higher yield, and under milder conditions. In the imidoylization of the POMs and the organic compounds with a carboxyl group, according to the experimental investigation, the organoimido products cannot be obtained with the hexamolybdate method. They can be obtained with the octamolybdate method, although the yield is not high. The carboxyl group must have played some role in the formation of the organoimido product because of its acidity and oxidizability, which can also react with the amino group to produce an amide

Table 2. Selected Bond Lengths (Angstroms) and Angles (Degrees) for Compounds 1−4

	Mo1−N1	N1−C1	Mo1−N1−C1	Mo1−O1	Mo6−O1
compound **1**	1.732(5)	1.390(7)	171.1(4)	2.197(4)	2.359(4)
compound **2**	1.739(5)	1.384(7)	169.3(5)	2.205(4)	2.362(4)
compound **3**	1.734(4)	1.391(6)	169.1(4)	2.223(3)	2.359(3)
compound **4**	1.736(5)	1.377(8)	166.9(5)	2.209(4)	2.361(4)

Table 3. Summary of Hydrogen Bonding (Angstroms and Degrees) for Compounds 1−4

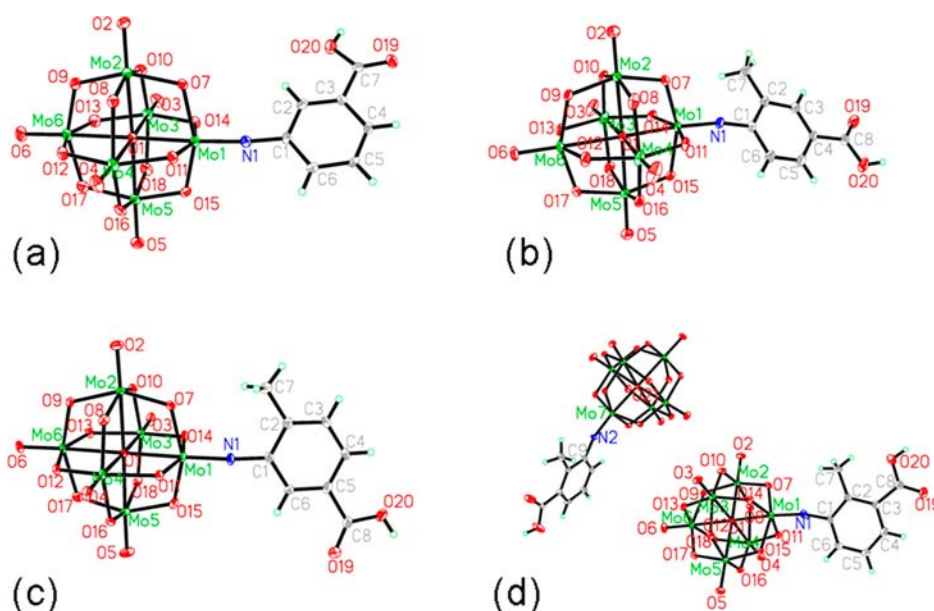|	D−H···A	symmetry transformation	d(D-H)	d(H···A)	d(D···A)	∠(DHA)
compound **1**	O20−H20···O7	$-x + 3/2, -y, z$	0.82	1.90	2.712(6)	170.8
compound **2**	O20−H20···O11	$-x + 3/2, y - 1/2, -z + 1/2$	0.82	1.85	2.646(6)	164.2
compound **3**	O20−H20···O16	$-x + 1/2, y + 1/2, -z + 1/2$	0.82	1.93	2.706(5)	158.5
	C3−H3···O10	$-x + 1, -y + 1, -z$	0.93	2.45	3.292(6)	150.5
compound **4**	O20−H20···O7	$-x, y + 1/2, -z + 1/2$	0.82	1.97	2.745(7)	156.9
	C5−H5···O11	$-x, -y + 2, -z + 1$	0.93	2.48	3.402(8)	172.0
	O40−H40···O22	$x, -y + 1/2, z + 1/2$	0.82	2.03	2.786(7)	153.6

Figure 1. ORTEP drawings of the cluster anions for compound **1** (a), compound **2** (b), compound **3** (c), and compound **4** (d) (30% probability ellipsoids).
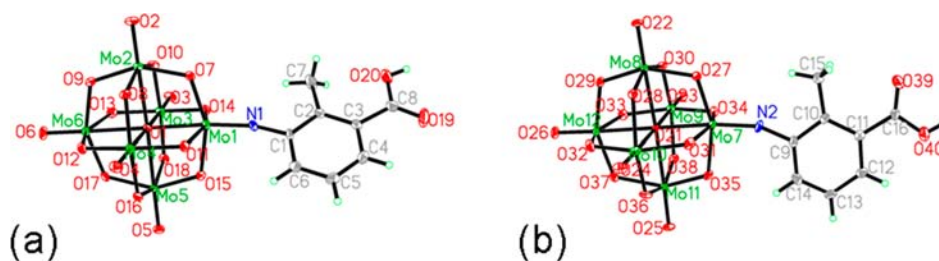

Figure 2. ORTEP drawings of the Mo1 cluster (a) and the Mo7 cluster (b) in compound **4** (30% probability ellipsoids).

under the reaction conditions. Besides this, the presence of water in the system also affects the yield to some extent, according to the experimental results. By contrast, the carboxyl group has more of an effect on the reaction. It completely ruins the intermediate state in the reaction of $(Bu_4N)_2[Mo_6O_{19}]$ and the aromatic carboxylic acid with an amino group, making the formation of the organoimido product impossible. The reaction of $(Bu_4N)_4[Mo_8O_{26}]$ and hydrochlorides of the aromatic carboxylic acid with an amino group can finally afford the

title compounds because the carboxyl group can only partially counteract the formation of the organoimido product.

Structure Description. A summary of the crystallographic data and the structural determinations for compounds **1−4** are presented in Table 1. The selected bond lengths and angles for compounds **1−4** are summarized in Table 2. The summary of the hydrogen bonding lengths and angles for compounds **1−4** are presented in Table 3.

Crystal Structures of Compounds 1−4. In the structures of compounds **1−4**, there is an asymmetric unit that contains one crystallographically independent POM cluster anion, two counter tetrabutylammonium cations, half of an acetonitrile molecule, and half of an ether molecule for compound **1**; one crystallographically independent POM cluster anion and two counter tetrabutylammonium cations for compounds **2** and **3**; and two crystallographically independent POM cluster anions and four counter tetrabutylammonium cations for compound **4**. The ORTEP drawings of the cluster anions for the four compounds are presented in Figures 1 and 2. They display the typical structure of monosubstituted organoimido derivatives of hexamolybdate with one terminal oxygen atom (O_t) of the hexamolybdate cluster replaced by the organoimido ligand. The relatively short Mo−N bond length and the nearly linear Mo−N−C bond angle (Table 2) show that the organic ligand and the hexamolybdate are linked together covalently via sp hybridization to obtain the organic−inorganic hybrid. The inorganic part of the cluster anion retains the parent Lindqvist-type hexamolybdate framework well. However, the central oxygen atom (O_c) in the cluster is closer to the imido-bearing Mo atom (Mo1−O1 bond lengths of 2.197, 2.205, 2.223, and 2.209 (2.197 for Mo7−O21) Å for compounds **1−4**) and is farther from the opposite Mo atom (Mo6−O1 bond lengths of 2.359, 2.362, 2.359, and 2.361 (2.364 for Mo12−O21) Å for compounds **1−4**) because of the different negativity between the imido ligand and the oxo ligand. It is worth mentioning that in the structure of compound **4** the orientation of the two cluster anions is quite different. Facing neither the same direction nor the opposite direction, they form a certain angle with a trans mode. Another characteristic of compound **4** is that in the asymmetric unit the two cluster anions, the Mo1 cluster (Figure 2a) and the Mo7 cluster (Figure 2b), are conformational isomers. In the Mo1 cluster, the hydroxyl is close to the methyl group, and the carbonyl oxygen is farther from the methyl group, whereas in the Mo7 cluster, the carbonyl oxygen is close to the methyl group, and the hydroxyl is farther from the methyl group.

Supramolecular Assemblies of Compounds 1−4. In addition to the cluster anion structures, the intermolecular hydrogen-bonding interaction also plays an important part in the supramolecular assemblies of the four compounds in the solid state. For compound **1**, the hydroxyl oxygen atom in the carboxyl group of one cluster anion acts as a hydrogen bond donor, and one bridging oxygen atom (O_b) in the neighboring cluster anion acts as a hydrogen bond acceptor to form a hydrogen bond (O20−H20···O7, 2.712 Å, 170.8°). Likewise, another of the same kind of hydrogen bond is formed between one bridging oxygen atom (O_b) in the cluster anion and the hydroxyl oxygen atom in the carboxyl group of the neighboring cluster anion, with the donor and acceptor exchanged. Such interactions form an 18-membered ring between the two neighboring cluster anions consisting of 18 atoms with two hydrogen bond donors and two acceptors (Figure 3), which is represented by the symbol $R_2^2(18)$. The dimer-structure aggregates are obtained by connecting the neighboring cluster anions via $R_2^2(18)$ hydrogen bonding.

This hydrogen-bonding interaction also exists in compound **2**, which is different from that of compound **1**. A hydrogen bond (O20−H20···O11, 2.646 Å, 164.2°) is formed between the hydroxyl oxygen atom in the carboxyl group of the cluster anion as a donor and one bridging oxygen atom (O_b) in the
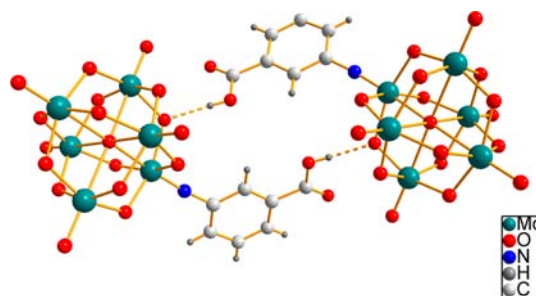

Figure 3. Dimer structure of the cluster anions in compound **1**.

neighboring cluster anion as an acceptor. The same kind of hydrogen bond is formed between the hydroxyl oxygen atom in the carboxyl group of the neighboring cluster anion as a donor and one bridge oxygen atom (O_b) in the next neighboring cluster anion as an acceptor. Thus, the hydrogen-bonding interactions connect the cluster anions into a 1D zigzagging infinite chain (Figure 4).
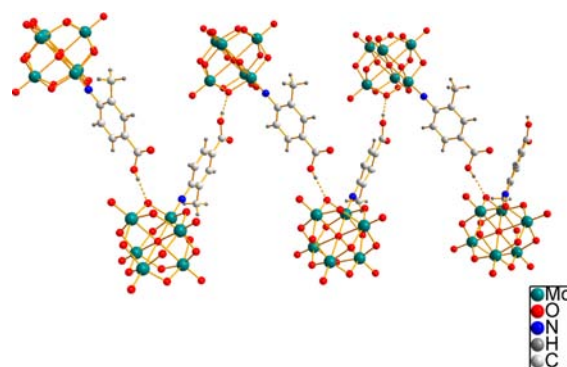

Figure 4. One-dimensional zigzagging chain of the cluster anions in compound **2**.

There are some hydrogen-bonding interactions in compound **3** as well, which are different from those in compounds **1** and **2**. The hydrogen bond (O20−H20···O16, 2.706 Å, 158.5°) is formed between the hydroxyl oxygen atom in the carboxyl group of the cluster anion as a donor and one bridge oxygen atom (O_b) in the neighboring cluster anion as an acceptor, connecting the cluster anions into a 1D zigzagging infinite chain (Figure 5a). Furthermore, the existence of relatively weak hydrogen bond (C3−H3···O10, 3.292 Å, 150.5°) between one carbon atom on the aromatic ring of the cluster anion in the 1D zigzagging infinite chain and one bridge oxygen atom (O_b) of the cluster anion in the neighboring 1D-zigzagging infinite chain assembles the cluster anions into a 2D planar supramolecular structure (Figure 5b).

The intermolecular hydrogen-bonding interactions also play some part in compound **4**, although they are different from those of compounds **1−3**. The hydrogen bond (O20−H20···O7, 2.745 Å, 156.9°) is formed between the hydroxyl oxygen atom in the carboxyl group of one cluster anion (the Mo1 cluster, Figures 1d and 2a) in the asymmetric unit as a donor and one bridging oxygen atom (O_b) in the same kind of cluster anion in the neighboring asymmetric unit as an acceptor, connecting the Mo1 cluster anions into a 1D zigzagging infinite chain (Figure 6a). Another hydrogen bond (O40−H40···O22, 2.786 Å, 153.6°) exists between the hydroxyl oxygen atom in the carboxyl group of the other
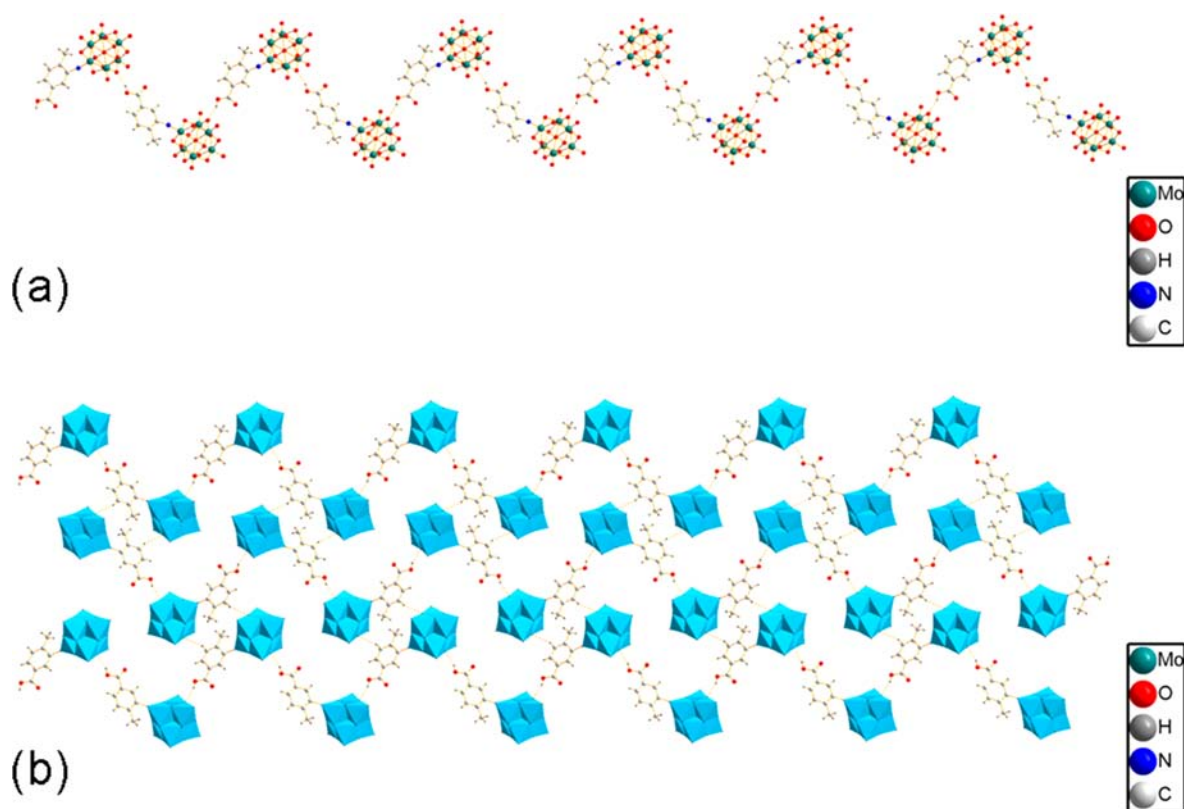
Figure 5. One-dimensional zigzagging chain (a) and 2D plane (b) of the cluster anions in compound **3**.

cluster anion (the Mo7 cluster, Figures 1d and 2b) in the asymmetric unit as a donor and one terminal oxygen atom (O_t) in the same kind of cluster anion in the neighboring asymmetric unit as an acceptor, making the Mo7 cluster anions into another 1D zigzagging infinite chain (Figure 6b). Furthermore, the existence of relatively weak hydrogen bond (C5−H5···O11, 3.402 Å, 172.0°) between one carbon atom on the aromatic ring of the Mo1 cluster anion in the 1D zigzagging infinite chain and one bridge oxygen atom (O_b) in the same kind of cluster anion in the neighboring 1D zigzagging infinite chain makes the Mo1 cluster anions into a 2D planar supramolecular structure (Figure 6c). The different orientations of the Mo1 cluster anion and the Mo7 cluster anion in the asymmetric unit result in different intermolecular interactions for each cluster. The Mo1 cluster anions exhibit two types of hydrogen bonding to form a 2D planar structure, whereas the Mo7 cluster anions exhibit one type of hydrogen bonding to form the 1D zigzagging infinite chain. There are no hydrogen-bonding interactions between the Mo1 cluster anions and the Mo7 cluster anions. Thus, the 1D chain formed by the Mo7 cluster anions and the 2D plane formed by the Mo1 cluster anions exist together to afford the entire structure of anions in compound **4**.

Spectroscopic Characterization. The IR spectra of compounds **1−4** are similar. All of them show two very strong absorption peaks near 950 and 790 cm^{-1} that are assigned to the vibration of Mo−O_t and Mo−O_b−Mo of the Lindqvist structure, respectively. The visible shoulder peak near 975 cm^{-1} is the characteristic absorption peak of a monosubstituted organoimido derivative of a hexamolybdate and is 977 cm^{-1} for compounds **1−3** and 975 cm^{-1} for compound **4**. The spectra also show relatively strong absorption peaks near 1700 cm^{-1} because of the existence of carboxyl groups in the compounds:

1724 cm^{-1} for compound **1**, 1715 cm^{-1} for compound **2**, 1718 cm^{-1} for compound **3**, and 1736 cm^{-1} for compound **4** (Figures S1−S4). Compared to the corresponding organic ligand, each compound displays a shift to the higher wavenumber for the carboxyl group. This reflects the electron-withdrawing nature of the hexamolybdate cluster, increasing the force constant of the C=O bond and resulting in the shift of the absorption peak. This can also be proven by the shortening of the C=O bond length in the compounds as compared to that in the pure organic ligand. In addition, the absorption peaks at around 2900 cm^{-1} are assigned to the stretching vibrations of the methyl and methylene groups in the tetrabutylammonium cations and the methyl group on the aromatic ring.

The UV−vis spectra of compounds **1−4** show the absorption characters of the monosubstituted organoimido derivatives of hexamolybdate. The maximum absorption wavelength of the parent hexamolybdate is 325 nm, which is derived from the charge-transfer transition from the oxygen π-type HOMO to the molybdenum d-type LUMO. In the organoimido products, the maximum-absorption wavelength red shifts to 343 nm for compound **1**, 358 nm for compound **2**, 346 nm for compound **3**, and 345 nm for compound **4** (Figure S5), resulting from the formation of the Mo−N bond and the delocalization system as a result of the strong d−π interaction between the organic ligand and the inorganic hexamolybdate cluster. Besides the bathochromic shift, the difference among the organic ligands makes some difference in the absorption spectra of the organoimido products. Compound **2** shows the largest bathochromic shift, resulting from having the best delocalization system with a carboxyl group at the para position relative to the Mo−N moiety.
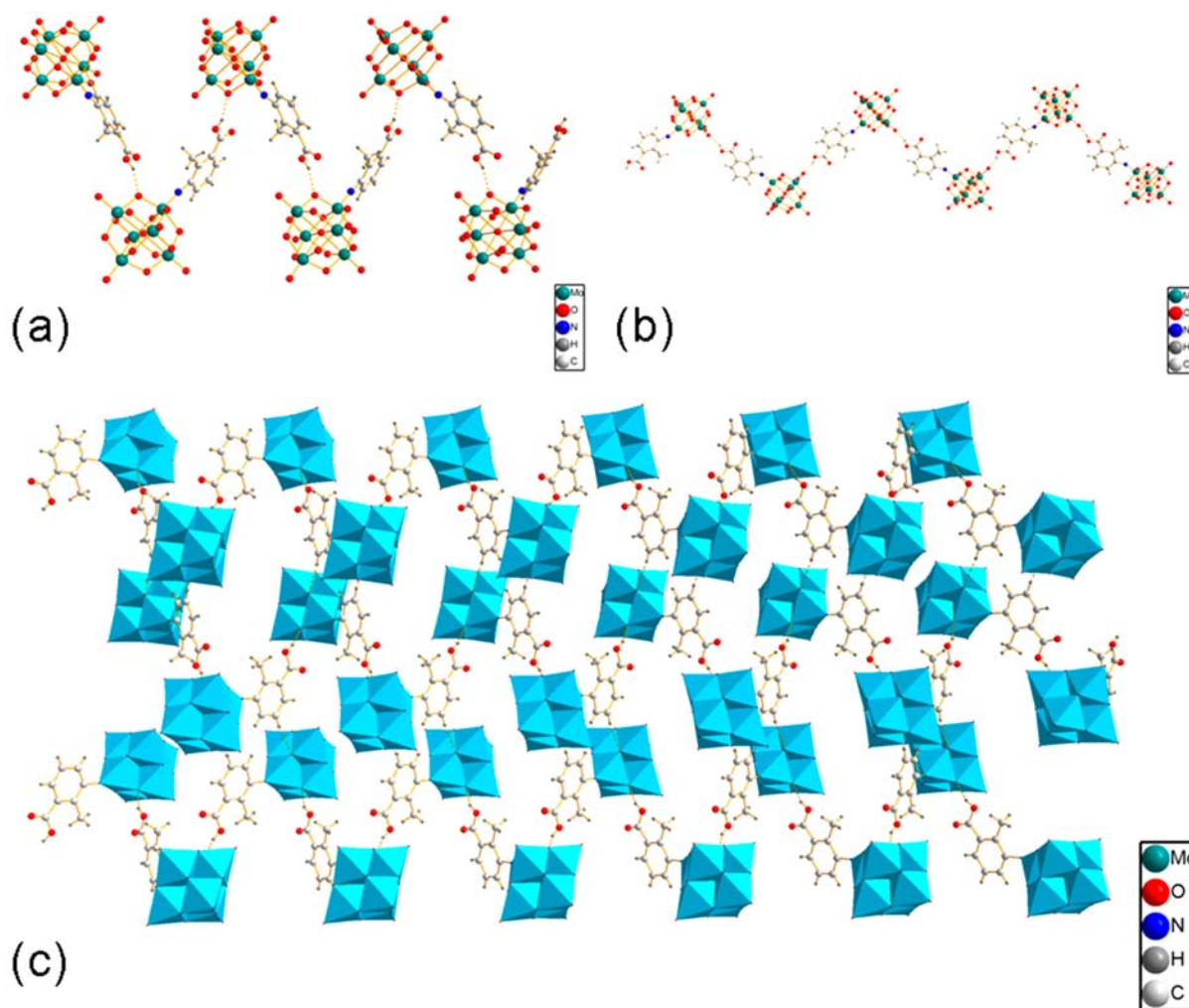
Figure 6. One-dimensional zigzagging chain for the Mo1 cluster (a), 1D zigzagging chain for the Mo7 cluster (b), and 2D plane for the Mo1 cluster (c) of the cluster anions in compound **4**.

The ^1H NMR spectra of compounds **1**−**4** show clear signals that can be assigned easily for the hydrogen atoms in the different environments (Figures S6−S9). The integration of the peaks is in accord with the structures of the title compounds. Compared to the corresponding organic ligands, the chemical shifts of all of the hydrogen atoms exhibit some downfield change, indicating that the shielding effect of the POM cluster is weaker than that of the amino group. This also reflects the electron-withdrawing nature of the hexamolybdate cluster. In addition, the relative positions of the carboxyl and methyl groups relative to the Mo−N moiety also change the aromatic hydrogen chemical shift to some extent.

The ESI−MS spectra of compounds **1**−**4** confirm the formation of these organoimido products (Figure S10). For compound **1**, the isotopic peaks centered at m/z 499.77 (100%) can be assigned to the cluster anion $[Mo_6O_{18}(N-C_6H_4-3-COOH)]^{2-}$ (calcd m/z: 499.37), and the isotopic peaks centered at m/z 1242.75 (35%) can be assigned to the aggregate of the cluster anion and one $[Bu_4N]^+$ cation $[Bu_4N][Mo_6O_{18}(N-C_6H_4-3-COOH)]^-$ (calcd m/z: 1241.21). For compound **2**, the peaks around m/z 507.72 (100%) and 1255.92 (30%) can be assigned to the cluster anion $[Mo_6O_{18}(N-C_6H_4-2-CH_3-4-COOH)]^{2-}$ (calcd m/z 506.39) and to the aggregate of the cluster anion and one $[Bu_4N]^+$ cation $[Bu_4N][Mo_6O_{18}(N-C_6H_4-2-CH_3-4-COOH)]^-$ (calcd

m/z: 1255.24), respectively. For compound **3**, the peaks around m/z 506.20 (100%, $[Mo_6O_{18}(N-C_6H_4-2-CH_3-5-COOH)]^{2-}$ (calcd m/z: 506.39)) and 1013.40 (45%, $[HMo_6O_{18}(N-C_6H_4-2-CH_3-5-COOH)]^-$ (calcd m/z: 1013.78)) can be assigned. For compound **4**, the peaks around m/z 505.78 (100%, $[Mo_6O_{18}(N-C_6H_4-2-CH_3-3-COOH)]^{2-}$ (calcd m/z: 506.39)) and 1254.70 (80%, $[Bu_4N][Mo_6O_{18}(N-C_6H_4-2-CH_3-3-COOH)]^-$ (calcd m/z: 1255.24)) can also be assigned.

■ CONCLUSIONS

In summary, four novel organoimido derivatives of hexamolybdate containing remote carboxyl groups with 3-aminobenzoic acid, 4-amino-3-methylbenzoic acid, 3-amino-4-methylbenzoic acid, and 3-amino-2-methylbenzoic acid as the imido-releasing agents, denoted as $[Bu_4N]_2[Mo_6O_{18}(N-C_6H_4-3-COOH)]$ (**1**), $[Bu_4N]_2[Mo_6O_{18}(N-C_6H_4-2-CH_3-4-COOH)]$ (**2**), $[Bu_4N]_2[Mo_6O_{18}(N-C_6H_4-2-CH_3-5-COOH)]$ (**3**), and $[Bu_4N]_2[Mo_6O_{18}(N-C_6H_4-2-CH_3-3-COOH)]$ (**4**), respectively, have been synthesized using the DCC protocol. Their structures have been characterized by IR, UV−vis, ^1H NMR, ESI-MS, and single-crystal X-ray diffraction techniques. The hydrogen-bonding interactions play an important role in the supramolecular assemblies of these compounds in the solid state. Similar organic moieties in the organoimido products

result in different supramolecular assembly behaviors. The dimer structure is formed via one type of hydrogen bonding for compound **1**. The 1D zigzagging chain structure is formed via one type of hydrogen bonding for compound **2**. The 2D planar structure is formed via two types of hydrogen bonding for compound **3**. The 1D plus 2D structures are formed via three types of hydrogen bonding for compound **4** resulting from different orientations of the cluster anions. In addition, the chemical reactivity of the carboxyl groups makes these compounds potentially applicable in the design and synthesis of higher-level POM-based organic−inorganic hybrid materials, which is underway in our laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
The IR, UV−vis, ^{1}H NMR, and ESI−MS spectra of the compounds. Crystallographic data for the compounds in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: jinjin_eva@163.com (J.Z.), yonggewei@mail.tsinghua. edu.cn (Y.W.).

Author Contributions
‖These authors contributed equally.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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