Organic–Inorganic Hybrids

DOI: 10.1002/anie.200704546

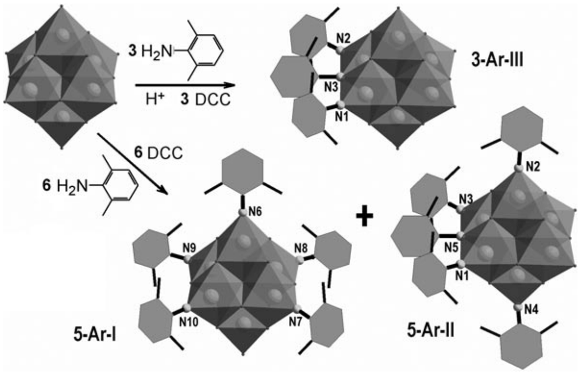
Unprecedented Replacement of Bridging Oxygen Atoms in Polyoxometalates with Organic Imido Ligands**

Jian Hao, Yun Xia, Longsheng Wang, Laurent Ruhlmann, Yulin Zhu, Qiang Li, Panchao Yin, Yongge Wei,* and Hongyou Guo*

Polyoxometalates (POMs)[1] are a rich and diverse family of metal–oxygen clusters made up of early transitional metals with unique photonic, electronic, and magnetic properties and chemical reactivity that has promised dramatic applications in quite diverse disciplines, including catalysis, medicine, and materials sciences.[2] Nowadays, from traditional Lindqvist and Keggin POMs to A. Müller and co-workers' nanotires and nanoballs,[3] a wide structural variety of POMs has been obtained by chemists.[4] Especially, among the reported nanoscale POMs,[3,5] some POMs have been discovered to show remarkable self-assembly in solution[6] or on surfaces,[7] and even to function as artificial cells to model the transport of cations under physiological conditions.[8,9]

Over the past quarter century, functionalization of POMs with organic species,[10] especially the organoimido functionality,[10b,c] has drawn tremendous attention since the pioneering work was published by the groups of Klemperer,[11] Pope[12] and Knoth.[13] Such a POM–organic ligand connection possess particular merits in fabricating POM-based hybrid materials with finely tunable properties, easy processability, and novel synergistic effects between the POM and the organic components.

Owing to the long-term endeavors of the groups of Maatta,[14] Errington,[15] and Proust,[16] terminally substituted mono- and even multifunctionalized organoimido derivatives of POMs can now be conveniently prepared with various imido-releasing reagents, including phosphinimines, isocyanates, and aromatic amines.[14–18] In principle, the bridging oxygen atoms in POMs can also be replaced by organoimido ligands; however, such a bridging organoimido-substituted POM has not been obtained to date. This result is surprising, as bridging organoimido ligands have been found in oligonuclear or polynuclear early-transitional-metal complexes,[19–21] and the isoelectronic alkoxo groups in the bridging mode have been widely observed in polyoxoalkoxometalates.[10a] It seems that bridging organoimido-substituted POMs are not as stable as their terminal analogues, especially in the case of the mono- and difunctionalized derivatives. During our efforts to pursue multisubstituted organoimido POMs, we observed that the bridging oxo group between two terminal organoimido ligands could be replaced by a third organoimido ligand. Herein, we report the synthesis and structural characterization of two such unprecedented organoimido-functionalized hexamolybdates, $[\mathrm{Mo_6O_{16}}(2,6\text{-}\mathrm{Me_2\text{-}NC_6H_3})_2(\mu_2\text{-}2,6\text{-}\mathrm{Me_2\text{-}NC_6H_3})]^{2-}$ (**3-Ar-III**) and $[\mathrm{Mo_6O_{14}}(2,6\text{-}\mathrm{Me_2\text{-}NC_6H_3})_4(\mu_2\text{-}2,6\text{-}\mathrm{Me_2\text{-}NC_6H_3})]^{2-}$ (**5-Ar-II**, co-crystallized with the corresponding terminally substituted isomer **5-Ar-I**, Scheme 1). This work extends the range of organoimido–POM coordination chemistry, providing insight into the mechanism of oxo metathesis in the Lindqvist polymolybdate and opportunities for the further modification of POM surfaces.



Scheme 1. Synthesis of compounds **3-Ar-III** and [**5-Ar-I**][**5-Ar-II**].

In light of Errington's discovery, using *N,N'*-dicyclohexylcarbodiimide (DCC, a common dehydrating reagent in organic synthesis) we developed a convenient "DCC protocol" to afford organoimido-functionalized hexamolybdates with aromatic amines as the imido-releasing reagents by formal removal of the water formed in the reaction.[17] While

---

[*] J. Hao, Dr. L. Wang, Dr. Y. Zhu, Dr. Q. Li, P. Yin, Prof. Dr. Y. Wei
Department of Chemistry
Tsinghua University, Beijing 100084 (China)
E-mail: yonggewei@mail.tsinghua.edu.cn
Homepage: http://chem.tsinghua.edu.cn/english/info/szdw_info.php?sessid=&infoid=74

J. Hao, Prof. Dr. L. Ruhlmann
Laboratoire de Chimie Physique
Université de Paris Sud 11, 91405 Orsay cedex (France)

Dr. Y. Xia, Prof. H. Guo
Department of Chemistry
Beijing University of Chemical Technology, Beijing 102413 (China)

Dr. Y. Xia
Department of Science and Technology Information
China Institute of Atomic Energy, Beijing 102413 (China)

[**] This work is supported by NFSC No. 20671054 and 20373001, by the CNRS, by the JCqn2005039 and THSJZ, the University Paris-Sud 11, and by the ANR agency (grant No. ANR-05-52437). The authors thank Prof. Yadong Li for helpful suggestions in preparing this manuscript. Special thanks are dedicated to Prof. Zheming Wang for XRD data collection.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

monosubstituted arylimidohexamolybdates are easily prepared by the reaction of $(TBA)_2[Mo_6O_{19}]$ (TBA = $[nBu_4N]^+$), arylamines, and DCC in a molar ratio of 1:1:1 (0.02–0.04 mol L^{-1}) in refluxing aqueous acetonitrile (25 mL), pure *cis*-disubstituted arylimidohexamolybdates can be selectively synthesized by reaction of $(TBA)_4[\alpha\text{-}Mo_8O_{26}]$, arylamines, and DCC in a molar ratio of 1:2:2. Interestingly, we have observed that amine hydrochlorides can effectively promote this kind of imidoylization reaction. However, in the presence of amine hydrochloride, $(TBA)_4[\alpha\text{-}Mo_8O_{26}]$ only affords monosubstituted complexes, even if it reacts with excess arylamine.[17b] In the case of $(TBA)_2[Mo_6O_{19}]$ as starting material, by increasing the molar ratio of arylamines and DCC to two equivalents, both *cis*- and *trans*-disubstituted complexes can be recovered by careful control of the reaction temperature.[17d] In a recent attempt to save reaction time by reducing solvent volumes, we unexpectedly observed that there were also some trace polysubstituted products formed during the preparation of di(organoimido)-substituted hexamolybdates. With this discovery, we further increased the molar ratio of arylamines and DCC in an attempt to synthesize multiply functionalized imido derivatives of hexamolybdate. As shown in Scheme 1, **3-Ar-III** was obtained by reaction of $(TBA)_2[Mo_6O_{19}]$, 2,6-dimethylaniline (DMA), and DCC in a molar ratio of 1:3.2:3.5, while clusters **5-Ar-I** and **5-Ar-II** were yielded by reaction of $(TBA)_2[Mo_6O_{19}]$, DMA, and DCC in a molar ratio of 1:6:6. According to our test, approximately 0.1 equivalent DMA·HCl is essential for the synthesis of **3-Ar-III**, which can remarkably increase the yield of the product. However, it does not improve the yield of [**5-Ar-I**][**5-Ar-II**]. Obviously, being different from Maatta and co-workers' methodology,[14b] our case indicates that this DCC protocol not only yields terminally multifunctionalized imido derivatives of POMs but also affords an unprecedented modification pattern for organoimido derivatives of POMs: the imido group acts as a bridging ligand in the multifuctionalized derivatives.

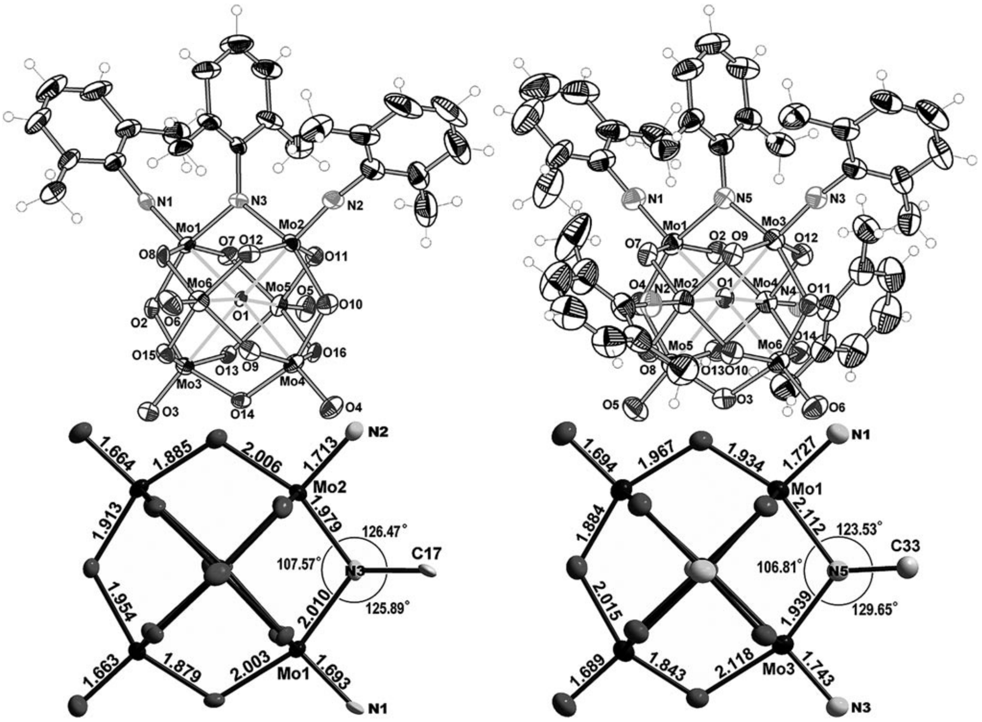


Figure 1. ORTEP showing of the cluster anions **3-Ar-III** (left) and **5-Ar-II** (right). Thermal ellipsoids are set at 25% probability. Selected bond lengths and angles are given in the depictions of the cores (bottom).

X-ray single crystal diffraction studies show that **3-Ar-III** and [**5-Ar-I**][**5-Ar-II**] crystallize in the triclinic space group $P\bar{1}$ and the orthorhombic space group *Pbca*, respectively (see Table S1 in the Supporting Information). As shown in Figure 1, the asymmetric unit of cluster **3-Ar-III** contains one novel triply functionalized Lindqvist hexamolybdate, which features two terminal and one bridging organoimido ligand and is quite different from the other known isomers of anion **3-Ar-III** (tripod-type **3-Ar-I**[14b] and T-type **3-Ar-II**[17e]). The asymmetric unit of [**5-Ar-I**][**5-Ar-II**] holds two quintuply functionalized cluster anion isomers, **5-Ar-I** and **5-Ar-II**. The former possesses five terminally substituted organoimido ligands (see Figure S1 in the Supporting Information), while the latter contains four terminal and one bridging organoimido ligand.

The most distinctive feature of the bridging imido ligands in **3-Ar-III** and **5-Ar-II** is that the bridging nitrogen atom shows typical sp^2 hybridization on account of its three-coordinate linking mode. Furthermore, the bridging nitrogen atom is coplanar with the three atoms to which it bonds. The dihedral angle between the phenyl ring of the bridging ligand and the Mo-N_{br}-Mo plane is 75.0° for **3-Ar-III** and 74.6° for **5-Ar-II**, suggesting that the unhybridized p orbitals of the N_{br} atoms are not conjugated with the phenyl rings. This situation would result in the relaxation of conjugative interaction between the bridging imido ligand and the hexamolybdates cage, because the ligand is confined in the scanty space between the flanking terminal imido ligands and could not freely rotate to a position allowing facile conjugation with the $\{Mo_4O_3N\}$ plane. Such a feature has also been observed by Errington and co-workers in a trinuclear tungsten complex containing a bridging imido ligand.[19] However, in the dinuclear complex $[Mo_2O_3(Cp)_2(\mu_2\text{-}p\text{-Me-}C_6H_4N)]$ (Cp = C_5H_5),[20a] the phenyl ring is comfortably coplanar with its $\{Mo_2N\}$ ring. The C–N bond lengths of bridging imido ligands (1.487(15) Å for **3-Ar-III** and 1.469(7) Å for **5-Ar-II**) are obviously longer than those of terminal imido ligands (1.38–

1.44 Å) and of the bridging imido ligand in $[Mo_2O_3(Cp)_2(\mu_2\text{-}p\text{-}Me\text{-}C_6H_4N)]$ (1.395 Å) owing to their different strengths of conjugation and different hybridizations of the nitrogen atoms. Moreover, the $Mo{-}N_{br}$ bond lengths (1.94–2.11 Å) in **3-Ar-III** and **5-Ar-II** are close to that of a reported decanuclear complex also containing a bridging organoimido ligand, $[Mo_{10}(p\text{-}Me\text{-}C_6H_4N)_{12}(py)_2O_{18}]$ (1.99–2.03 Å, py = pyridine).[21] As for the nitrogen atoms of the terminal organoimido ligands in both compounds, they all show typical sp hybridization, consistent with that of other organoimido-substituted hexamolybdates.[14–17] The $Mo{-}N_t$ bonds demonstrate substantial triple-bond character, evidenced by the short bond length (1.69–1.74 Å) and nearly liner $Mo\text{-}N_t\text{-}C$ angle (171.1–179.8°).[22]

Besides the novel structure, the UV/Vis absorption spectra of **3-Ar-III** and **5-Ar-II** also demonstrate interesting changes (see Figure S2 in the Supporting Information). It is well known that the lowest energy electronic absorption band shifts toward red with an increasing number of terminal imido ligands on the hexamolybdate cage (as shown in Table 1).[14b] However, the lowest energy electronic absorption bands for **3-Ar-III** and **[5-Ar-I][5-Ar-II]** appear at 353 and 365 nm, respectively, which are closer to the terminally disubstituted $[Mo_6O_{17}(NAr')_2]^{2-}$ (**2-Ar′-*cis***, Ar′ = 2,6-diisopropylphenyl) and tetrasubstituted $[Mo_6O_{15}(NAr')_4]^{2-}$ (**4-Ar′-I**) than to the corresponding unbridged isomers $[Mo_6O_{16}(NAr')_3]^{2-}$ (**3-Ar′-I**) and $[Mo_6O_{14}(NAr')_5]^{2-}$ (**5-Ar′-I**). This result implies that the bridging arylimido ligand is not conjugated with the delocalized $\{Mo_4O_3N\}$ ring, which is in good agreement with the above X-ray structure study; hence, the bridging ligand has no obvious effect on the electronic levels of the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of the cluster anions.

Table 1: Summary of UV/Vis data for multiply substituted complexes $[Mo_6O_{19-x}(NAr)_x]^{2-}$.

Compound	Label	λ_{max} [nm]	Reference
$[Mo_6O_{18}(NAr')]^{2-}$	**1-Ar′**	351	[14b]
$[Mo_6O_{17}(NAr')_2]^{2-}$	**2-Ar′-*cis***	356	[14b]
$[Mo_6O_{16}(NAr')_3]^{2-}$	**3-Ar′-I**	361	[14b]
$[Mo_6O_{15}(NAr')_4]^{2-}$	**4-Ar′-I**	364	[14b]
$[Mo_6O_{14}(NAr')_5]^{2-}$	**5-Ar′-I**	364	[14b]
$[Mo_6O_{16}(NAr)_3]^{2-}$	**3-Ar-III**	353	this work
$[Mo_6O_{14}(NAr)_5]^{2-}$	**[5-Ar-I][5-Ar-II]**	365	this work

^1H NMR spectra of the two compounds show clearly resolved signals (Figure 2 and Figure S3 in the Supporting Information). The integration matches well with their structures. Compared to the corresponding mono- and disubstituted clusters, all the aromatic hydrogen atoms in **3-Ar-III** and **[5-Ar-I][5-Ar-II]** exhibit smaller chemical shifts, and the more organoimido ligands in the cluster, the more appreciable the upfield shift of the signals in the ^1H NMR spectra, owing to the stronger electron-donating nature of organoimido ligands than oxo groups.[14b] Futhermore, the aromatic protons on bridging imido ligands demonstrate further upfield resonance signals relative to the corresponding terminal ligands. As the bridging imido group is sandwiched between two aryl rings and its rotation is restricted, the combined effect of the diamagnetic anisotropy of two such terminal arylimido groups has a significant effect on the ^1H NMR chemical shifts of the protons of the bridging ligand; a similar effect has been reported by Errington and co-workers.[19] In addition, the bridging imido groups possess higher π electron density than terminal ligands, because they cannot effectively conjugate with the electron-withdrawing hexamolybdate cluster, which also accounts for their lower ^1H NMR chemical shifts. We also noticed that the aromatic protons on the terminal imido groups near the bridging imido ligand show lower chemical shifts than those on other terminal imido groups, because they are situated at the aryl-ring shielding region of the bridging imido ligands.

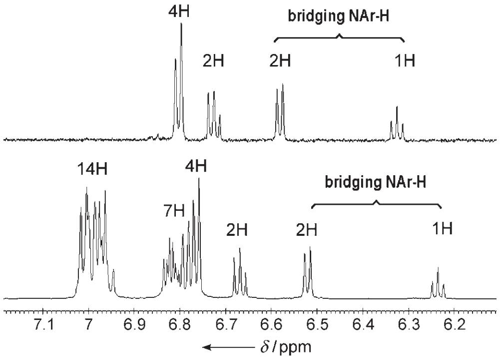


Figure 2. ^1H NMR spectra of $(TBA)_2$[**3-Ar-III**] (top) and $(TBA)_4$[**5-Ar-I**][**5-Ar-II**] (bottom) in the downfield region.

IR spectra of the two compounds (Figure 3) show similar characteristics in the Mo–O stretching region of 1000–700 cm^{-1}. The peaks located at 946 and 939 cm^{-1} for **3-Ar-III** and **[5-Ar-I][5-Ar-II]**, respectively, are ascribed to the stretching vibration of Mo=O groups; the reduction of peak intensity derives from the decrease in the number of terminal oxo ligands owing to their gradual replacement by imido ligands. The asymmetric Mo-O-Mo stretching vibration is found near 772 and 765 cm^{-1} for **3-Ar-III** and **[5-Ar-I][5-Ar-**

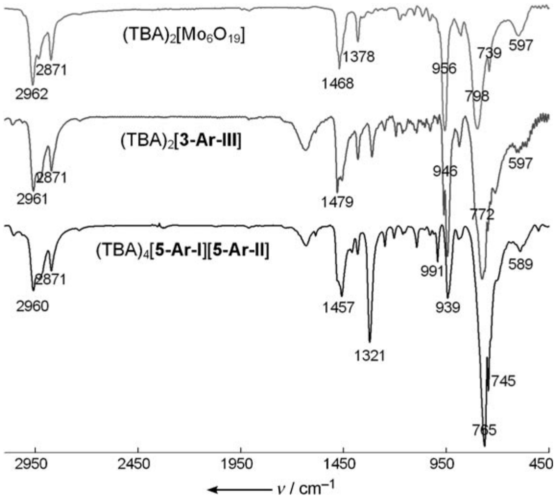


Figure 3. IR spectra of $(TBA)_2[Mo_6O_{19}]$, $(TBA)_2$[**3-Ar-III**], and $(TBA)_4$[**5-Ar-I**][**5-Ar-II**].

II], respectively. Compared to the parent hexamolybdate, the above vibrations both demonstrate the obvious red shift; the more terminal imido groups in the derivatized hexamolybdate, the more remarkable the red shift becomes, which implies that these Mo–O bonds are weakened to some extent owing to the incorporation of electron-donating arylimido groups. Moreover, there is a shoulder at 963 cm^{-1} in **3-Ar-III**, which might be principally associated with the Mo–N vibration.[22] As shown in Figure 3, with the further incorporation of imido ligands, the C–N vibration band, which appears at 1311–1321 cm^{-1}, becomes more intense in [**5-Ar-I**][**5-Ar-II**] than in **3-Ar-III**, in agreement with the degree of substitution of the cluster.

The imido-bridged anions **3-Ar-III** and **5-Ar-II** are stable enough to be recrystallized from acetonitrile or acetone solutions, although **5-Ar-II** always cocrystallizes with its **5-Ar-I** isomer. As to their formation, the oxo group between the two imido ligands is easily replaced by a bridging arylimido ligand, presumably owing to its higher electronic density compared to oxo ligands between two terminal oxo groups or between one terminal oxo group and one terminal arylimido ligand. On the other hand, compared to the assumed compound with a single, bridging arylimido ligand, the bridging arylimido groups in compounds **3-Ar-III** and **5-Ar-II** are stabilized, owing to steric effects, by the two neighboring arylimido groups, which can prevent nucleophilic attacking of the bonding Mo atoms. However, much more effort will be needed to shed light on the real mechanism.

In conclusion, we have successfully synthesized two novel arylimido derivatives of hexamolybdate that contain unprecedented bridging imido ligands. Our current work provides not only an example that the bridging imido ligand could exist in derivatives of polyoxometalates but also offers a chance to explore thoroughly the whole family of organoimido derivatives involving these previously unexpected species containing bridging imido ligands.

Experimental Section

All synthetic operations were performed in nitrogen atmosphere. Infrared (IR) spectra were recorded on a Perkin–Elmer FTIR spectrometer. UV/Vis absorption spectra were recorded on a UV-2100S spectrometer. The electrospray mass spectra (ESI-MS) were measured on a Finngan LCQ Deca XP Plus ion-trap mass spectrometer (San Jose, CA), and all experiments were carried out in the negative-ion mode using CH_3CN as solvent. ^1H NMR spectra were obtained on a JOEL JNM-ECA300 spectrometer and are reported in ppm. Splitting patterns are indicated as s singlet, d doublet, t triplet, q quartet, m multiplet. Tetramethylsilane (TMS) was used as internal standard, and coupling constants (J) are reported in Hz. Suitable crystals of $(TBA)_2$[**3-Ar-III**] and $(TBA)_4$[**5-Ar-I**][**5-Ar-II**] were covered with mineral oil, mounted onto glass fibers, and transferred directly to a Rigaku RAXIS-SPIDER IP diffractometer at room temperature. Data collection, data reduction, cell refinement, and experimental absorption correction were performed with the software package of Rigaku RAPID AUTO (Rigaku, 1998, Ver2.30). Structures were solved by direct methods and refined against F^2 by full matrix least squares. All non-hydrogen atoms, except disordered atoms, were refined anisotropically. Hydrogen atoms were generated geometrically. All calculations were performed using the SHELXS-97 program package.[23]

$(TBA)_2$[**3-Ar-III**]: A mixture of DMA (0.388 g, 3.2 mmol), DCC (0.722 g, 3.5 mmol), DMA·HCl (0.016 g, 0.1 mmol) and $(TBA)_2[Mo_6O_{19}]$ (1.325 g, 1.0 mmol) was heated at reflux in anhydrous MeCN (50 mL) under nitrogen in an oil bath at 106 °C for about 16.5 h. The white precipitates were removed, solvent was removed under vacuum, and the residue was washed with Et_2O. The crude product was recrystallized from MeCN/EtOH (1:1) to yield dark red plate-like crystals in approximately 30% yield. Elemental analysis calcd (%) for $C_{56}H_{99}Mo_6N_5O_{16}$ (1674.04): C 40.18, H 5.96, N 4.18; found: C 40.05, H 5.93, N 4.19. ESI-MS, most intense peaks, m/z: 594.5 (93%, [**3-Ar-III**]$^{2-}$, calcd 594.6), 1190.2 (87%, [H(**3-Ar-III**)]$^-$, calcd 1190.1), 1432.1 (100%, [TBA(**3-Ar-III**)]$^-$, calcd 1431.6). ^1H NMR (600 MHz, CD_3CN): $\delta = 0.93$ (t, 24H, TBA-H), 1.32 (sextet, 16H, TBA-H), 1.57 (quintet, 16H, TBA-H), 2.23 (s, 6H, CH_3-Ar), 2.36 (s, 12H, CH_3-Ar), 3.05 (t, 16H, TBA-H), 6.32 (t, 1H, ArH), 6.58 (d, 2H, ArH), 6.72 (t, 2H, ArH), 6.80 ppm (d, 4H, ArH). UV/Vis (MeCN): $\lambda_{max} = 220$, 236, 270, 353 nm. IR (KBr): $\tilde{\nu} = 772$ (s), 946 (s), 963 (m), 990 (w), 1092 (w), 1194 (w), 1206 (w), 1249 (w), 1311 (w), 1379 (m), 1457 (m), 1479 (m), 1584 (w), 1632 (w), 2871 (m), 2961 (m) cm^{-1}.

Crystal data for $(TBA)_2$[**3-Ar-III**]: $Mo_6O_{16}N_5C_{56}H_{99}$, $M_r = 1674.06$, $0.15 \times 0.1 \times 0.05$ mm^3, triclinic, space group $P\bar{1}$, $a = 11.745(2)$, $b = 12.534(3)$, $c = 23.488(5)$ Å, $\alpha = 91.01(3)$, $\beta = 92.84(3)$, $\gamma = 92.59(3)°$, $V = 3449.2(12)$ Å^3, $T = 293$ K, $2\theta_{max} = 45°$, $Z = 2$, $\rho_{calcd} = 1.612$ Mgm^{-3}, $\mu = 1.120$ mm^{-1}, $F(000) = 1700$, 17441 reflections collected, 8895 unique ($R_{int} = 0.0899$), Final R indices ($I > 2\sigma(I)$) $R_1 = 0.0958$, $wR_2 = 0.1464$, max/min residual electron density = 0.738/−1.021 e Å^{-3}.

$(TBA)_4$[**5-Ar-I**][**5-Ar-II**]: A mixture of DMA (0.727 g, 6.0 mmol), DCC (1.240 g, 6.0 mmol), and $(TBA)_2[Mo_6O_{19}]$ (1.325 g, 1.0 mmol) was heated at reflux in anhydrous MeCN (15 mL) under nitrogen for about 24 h. The white precipitates were removed, solvent was removed under vacuum, and the residue was washed successively with Et_2O, toluene, and MeCOOEt. The crude product was recrystallized twice from EtOH and twice from acetone/ethyl acetate (1:1) to yield dark red block crystals. Elemental analysis calcd (%) for $C_{144}H_{234}Mo_{12}N_{14}O_{28}$ (3760.73): C 45.99, H 6.27, N 5.21; found: C 46.23, H 6.18, N 5.15. ESI-MS, most intense peaks, m/z: 697.7 (100%, [**5-Ar-I/II**]$^{2-}$, calcd 697.7), 1638.8 (15%, [TBA(**5-Ar-I/II**)]$^-$, calcd 1637.9). ^1H NMR (300 MHz, CD_3CN): $\delta = 0.93$ (t, 48H, TBA-H), 1.33 (sextet, 32H, TBA-H), 1.56 (quintet, 32H, TBA-H), 2.36 (s, 6H, CH_3-Ar), 2.38 (s, 12H, CH_3-Ar), 2.57 (m, 30H, CH_3-Ar), 2.62 (s, 12H, CH_3-Ar), 3.06 (t, 32H, TBA-H), 6.24 (t, 1H, ArH), 6.52 (d, 2H, ArH), 6.67 (t, 2H, ArH), 6.76 (d, 4H, ArH), 6.77–6.83 (m, 7H, ArH), 6.95–7.02 ppm (m, 14H, ArH). UV/Vis (MeCN): $\lambda_{max} = 222$, 245, 268, 365 nm. IR (KBr): $\tilde{\nu} = 745$ (m), 765 (s), 939 (m), 991 (w), 1023 (w),1091 (w), 1206 (w), 1248 (w), 1321 (s), 1380 (w), 1457 (m), 1479 (m), 1585 (w), 1631 (w), 2871 (m), 2960 cm^{-1} (m).

Crystal data for $(TBA)_4$[**5-Ar-I**][**5-Ar-II**]: $Mo_{12}O_{28}N_{14}C_{144}H_{234}$, $M_r = 3760.79$, $0.5 \times 0.5 \times 0.2$ mm^3, orthorhombic, space group $Pbca$, $a = 21.730(4)$, $b = 29.582(6)$, $c = 51.647(10$ Å, $V = 33200(11)$ Å^3, $T = 296$ K, $2\theta_{max} = 50°$, $Z = 8$, $\rho_{calcd} = 1.505$ Mgm^{-3}, $\mu = 0.939$ mm^{-1}, $F(000) = 15392$, 184176 reflections collected, 27878 unique ($R_{int} = 0.0664$), final R indices ($I > 2\sigma(I)$) $R_1 = 0.0491$, $wR_2 = 0.1051$, max/min residual electron density = 1.560/−0.892 e Å^{-3}.

CCDC-671815 ($(TBA)_4$[**5-Ar-I**][**5-Ar-II**]) and CCDC-671814 ($(TBA)_2$[**3-Ar-III**]) 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.

Received: October 2, 2007
Revised: November 22, 2007

Keywords: bridging groups · imido ligands · organic–inorganic hybrid composites · polyoxometalates

[1] a) M. T. Pope in *Comprehensive Coordination Chemistry II*, *Vol. 4* (Ed.: A. G. Wedd), Elsevier, Oxford **2004**, pp. 635–679; b) C. L. Hill in *Comprehensive Coordination Chemistry II*, *Vol. 4* (Ed.: A. G. Wedd), Elsevier, Oxford, **2004**, pp. 679–759.

[2] a) *Chem. Rev.* **1998**, *98*, 1–389 (Guest Ed.: C. L. Hill); b) *Polyoxometalate Chemistry: From Topology via Self-Assembly to Applications* (Eds.: M. T. Pope, A. Müller), Kluwer, Dordrecht, **2001**; c) *Polyoxometalate Chemistry for Nano-Composite Design*, (Eds.: T. Yamase, M. T. Pope), Kluwer Academic, New York, **2002**.

[3] a) A. Müller, P. Kogerler, H. Bogge, *Struct. Bonding (Berlin)* **2000**, *96*, 203–236; b) A. Müller, P. Kogerler, A. W. M. Dress, *Coord. Chem. Rev.* **2001**, *222*, 193–218.

[4] D. L. Long, E. Burkholder, L. Cronin, *Chem. Soc. Rev.* **2007**, *36*, 105–121.

[5] For selected examples of nanosized POMs, see: a) L. Cronin, C. Beugholt, E. Krickemeyer, M. Schmidtmann, H. Bögge, P. Kogerler, T. K. K. Luong, A. Müller, *Angew. Chem.* **2002**, *114*, 2929–2932; *Angew. Chem. Int. Ed.* **2002**, *41*, 2805–2808; b) K. Wassermann, M. H. Dickman, M. T. Pope, *Angew. Chem.* **1997**, *109*, 1513–1516; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1445–1448; c) B. Botar, P. Kögerler, C. L. Hill, *J. Am. Chem. Soc.* **2006**, *128*, 5336–5337; d) B. S. Bassil, M. H. Dickman, I. Römer, B. Von der Kammer, U. Kortz, *Angew. Chem.* **2007**, *119*, 6305–6308; *Angew. Chem. Int. Ed.* **2007**, *46*, 6192–6195.

[6] a) T. Liu, E. Diemann, H. Li, A. Dress, A. Müller, *Nature* **2003**, *426*, 59–62; b) G. Liu, T. B. Liu, S. S. Mal, U. Kortz, *J. Am. Chem. Soc.* **2006**, *128*, 10103–10110.

[7] a) S. Liu, H. Möhwald, D. Volkmer, D. G. Kurth, *Langmuir* **2006**, *22*, 1949–1951; b) S. Liu, D. G. Kurth, B. Bredenkötter, D. Volkmer, *J. Am. Chem. Soc.* **2002**, *124*, 12279–12287.

[8] L. Cronin, *Angew. Chem.* **2006**, *118*, 3656–3658; *Angew. Chem. Int. Ed.* **2006**, *45*, 3576–3578.

[9] a) A. Müller, D. Rehder, E. T. K. Haupt, A. Merca, H. Bögge, M. Schmidtmann, G. Heinze-Brückner, *Angew. Chem.* **2004**, *116*, 4566–4570; *Angew. Chem. Int. Ed.* **2004**, *43*, 4466–4470; b) D. Rehder, E. T. K. Haupt, H. Bögge, A. Müller, *Chem. Asian J.* **2006**, *1*, 76–81; c) A. Müller, L. Toma, H. Bogge, M. Henry, E. T. K. Haupt, A. Mix, F. L. Sousa, *Chem. Commun.* **2006**, 3396–3398.

[10] a) P. Gouzerh, A. Proust, *Chem. Rev.* **1998**, *98*, 77–111; b) "New classes of functionalized polyoxometalates: Organo-nitrogen derivatives of Lindqvist systems": A. R. Moore, H. Kwen, C. G. Hamaker, T. R. Mohs, A. M. Beatty, B. Harmon, K. Needham, E. A. Maatta in *Polyoxometalate Chemistry for Nano-Composite Design* (Eds.: T. Yamase, M. T. Pope), Kluwer Academic, New York **2002**, pp. 129; c) Z. Peng, *Angew. Chem.* **2004**, *116*, 948–953; *Angew. Chem. Int. Ed.* **2004**, *43*, 930–935.

[11] R. Ho, W. Klemperer, *J. Am. Chem. Soc.* **1978**, *100*, 6772–6774.

[12] F. Zonnevijlle, M. Pope, *J. Am. Chem. Soc.* **1979**, *101*, 2731–2732.

[13] W. Knoth, R. Harlow, *J. Am. Chem. Soc.* **1981**, *103*, 4265–4266.

[14] a) Y. Du, A. L. Rheingold, E. A. Maatta, *J. Am. Chem. Soc.* **1992**, *114*, 345–346; b) J. B. Strong, G. P. A. Yap, R. Ostrander, L. M. Liable-Sands, A. L. Rheingold, R. Thouvenot, P. Gouzerh, E. A. Maatta, *J. Am. Chem. Soc.* **2000**, *122*, 639–649.

[15] a) W. Clegg, R. J. Errington, K. Fraser, S. A. Holmes, A. Schäfer, *J. Chem. Soc. Chem. Commun.* **1995**, 455–456; b) W. Clegg, R. J. Errington, K. Fraser, C. Lax, D. G. Richards in *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity* (Eds.: M. T. Pope, A Müller), Kluwer, Dordrecht, **1994**, pp. 105–114.

[16] A. Proust, R. Thouvenot, M. Chaussade, F. Robert, P. Gouzerh, *Inorg. Chim. Acta* **1994**, *224*, 81–95.

[17] a) Y. Wei, B. Xu, C. L. Barnes, Z. Peng, *J. Am. Chem. Soc.* **2001**, *123*, 4083–4084; b) P. Wu, Q. Li, N. Ge, Y. Wei, Y. Wang, P. Wang, H. Guo, *Eur. J. Inorg. Chem.* **2004**, 2819–2822; c) L. Xu, M. Lu, B. Xu, Y. Wei, Z. Peng, D. R. Powell, *Angew. Chem.* **2002**, *114*, 4303–4306; *Angew. Chem. Int. Ed.* **2002**, *41*, 4129–4132; d) Y. Xia, Y. Wei, Y. Wang, H. Guo, *Inorg. Chem.* **2005**, *44*, 9823–9828; e) J. Hao, Y. Wei, L. Ruhlmann, unpublished results.

[18] I. Bar-Nahum, K. V. Narasimhulu, L. Weiner, R. Neumann, *Inorg. Chem.* **2005**, *44*, 4900–4902.

[19] D. C. Bradley, R. J. Errington, M. B. Hursthouse, R. L. Short, *J. Chem. Soc. Dalton Trans.* **1990**, 1043–1051.

[20] a) H. Alper, J. F. Petrignani, F. W. B. Einstein, A. C. Willis, *J. Am. Chem. Soc.* **1983**, *105*, 1701–1702; b) J. Robbins, G. C. Bazan, J. S. Murdzek, M. B. O'Regan, R. R. Schrock, *Organometallics* **1991**, *10*, 2902–2907.

[21] A. Proust, S. Taunier, V. Artero, F. Robert, R. Thouvenot, P. Gouzerh, *Chem. Commun.* **1996**, 2195–2196.

[22] W. Nugent, J. E. Mayer, *Metal–Ligand Multiple Bonds*, Wiley-VCH, New York, **1988**.

[23] G. M. Sheldrick, SHELXTL v. 5.10, Structure Determination Software Suite, Bruker AXS, Madison, Wisconsin (USA), **1998**.