Advances in Chemical Engineering

Chapter 1

POM-based Chiral Hybrids Synthesis via Organoimidization Covalent Modification of Achiral Precursors

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Abstract In this chapter, covalent modification of POMs (polyoxometalates) clusters especially by organo imidization via the well-developed DCC(N,N′-dicyclohexylcarbodiimide)-dehydrating protocol by our group is briefly reviewed. The functionalization of POMs with covalently organic moiety is one of the effective ways to increase the diverse POMs family and incorporate exceptional properties that these organic molecules attach to POM clusters in a reliable and predefined manner, which is expected to be applied to the design of molecular functionalized materials. The combination chirality with POMs is a crucial but challenging issue since POMs usually possess high symmetry. Organo imidization covalent modification of achiral precursors Lindquist $[Mo6O19]^{2-}$ has been proved to be a flexible strategy for applying in the generation of POM-based chiral hybrids. The organic ligands offer great opportunities to install stereogenic elements to POMs structure as structure directing-agents to remove symmetric elements in POM clusters, and some special POM clusters bearing amino group on its surface serves as special imido ligands. This takes full advantage of the intrinsic hindrance of the bulky and heavy POMs,Which will greatly extend chirality in polyoxometalate chemistry since the primary chiral POM anions are rare. In consideration of the fact that there exist plenty of chiral natural products L- amino acids and many POM clusters anchor amino group as remote group on the surface. It can foresee that more and more POM-based chiral hybrids will be generated by organo imidization covalent modification of achiral precursors Lindquist $[Mo6O19]^{2-}$ in the future.

Graphical abstract

1. Introduction

Polyoxometalates (POMs) are an exceptional family of inorganic oxide anions consisting of early transition metal ions such as Mo, W, V, etc. at their highest oxidization states bridging by oxide anions with structural versatility and a wide range of properties including catalysis, medicine and materials science [1-3]. Since the first salt of POM, ammonium 12-molybdophosphate, $(NH_4)_3[PMo_{12}O_{40}]$ was reported by Berzelius in 1826, the chemistry of POMs has gained dramatic development, with the development of structure characterization technology, especially single X-ray diffraction, the structure of POMs cluster can be precisely

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confirmed. Since Keggin reported the famous Keggin structure in 1934. The topology structure of Keggin [4], Anderson [5], Dawson [6], Waugh [7], Silverton [8], Lindqvist [9] were discovered sequentially and formed into the six basic structure of POMs. In 1970s-1980s, several novel structures including Weakley [10], Standberg [11], Finke [12], and Preyssler [13] were reported (**Figure 1**). POMs, as inorganic multidentate ligands, are prime candidates for the design and construction of different dimensional architectures with judicious selection of appropriate cations and organic molecules and POMs can serve as electron containers due to the property of multi-electron reduction without loss of the architecture. These aspects make POMs more valuable with charming electrical and optical properties such as electrochromism, photochromism, conductivity, and redox activities that suitable in a wide range of potential application [14-21] such as reversible redox activity that can be utilized as efficient solid-acid catalysts and electron-transfer catalysts for diverse organic reactions.

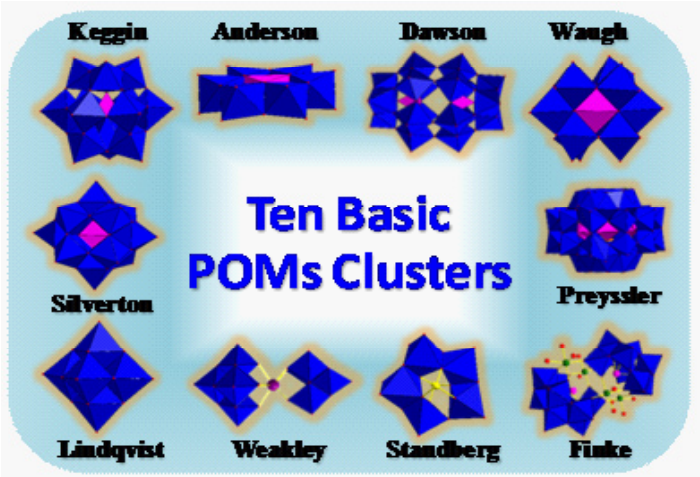


Figure 1: Ten basic structural topology of POM clusters.

Chirality has become an increasingly crucial issue in many fields, ranging from pharmaceuticals to asymmetric catalysis and clinical analysis [22-23]. The synthesis and resolution of chiral polyoxometalates (POMs) is an interesting but challenging area since POMs usually possess high symmetry. Chemists are urgent to break this symmetry so as to get chiral POMs. Preparation of POMs' chiral structures would provide ultimate control of the synthesis of those nanosized objects. Generally speaking, chirality of POMs-based inorganic-organic hybrids

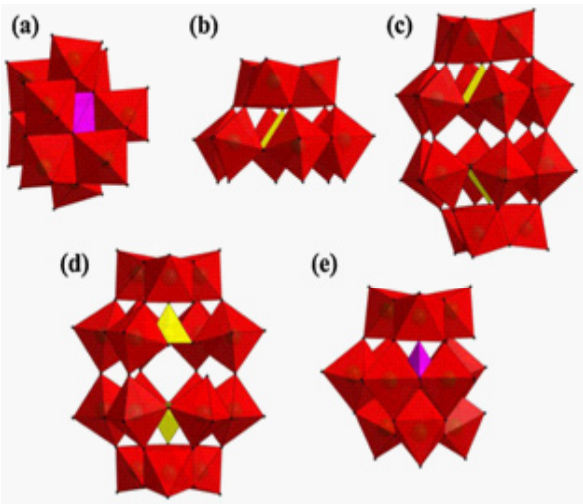


Figure 2: Classical intrinsic chiral POM frameworks.

can manifest itself in two distinct ways [24-26] : (1) They can be intrinsically chiral in the framework of POMs by bond length alteration, geometrical distortion, the formation of structural lacunae and replacement with other metals. Classical intrinsic chiral POM frameworks are $[MnMo_9O_{32}]^{6-}$ (**Figure 2a**), $[PMo_9O_{31}(OH)_3]^{3-}$ (**Figure 2b**), α-$[P_2Mo_{18}O_{62}]^{6-}$ (**Figure 2c**), α1-$[P_2W_{17}O_{61}]^{10-}$ (**Figure 2d**) and β2-$[SiW_{11}O_{39}]^{8-}$ (**Figure 2e**). However, such enantiomers are very easily racemized and difficult to beseparated and isolated. Such a problem has seriously hindered the application of chiral POM-based materials. (2) POMs are chemically modified through coordination bonding, electrostatic interaction and covalent modification. Since metal ions, organic cation especially chiral organic cation and surfactants, organic ligands can dramatically affect the final architectures. Such strategy may lead to the rational design and synthesis of chiral POM-based materials in enantiopure forms.

Organic–inorganic POMs hybrids can be categorized into two classifications [20,27], classification I and classification II (**Figure 3**), which are well-defined according to the interactions between the organic and inorganic moieties, to be exact, non-covalent and covalent interactions, respectively. Classification I organic–inorganic hybrids can be assembled by electrostatic interactions, hydrogen bonding, as well as/or van der Waals interactions.

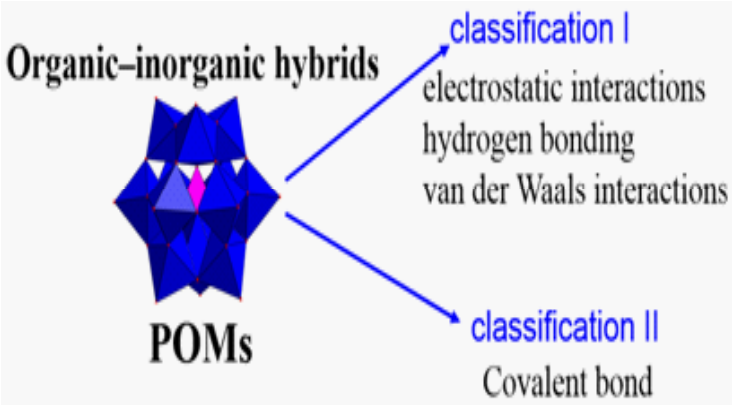


Figure 3: Definition of the two classifications (I and II) of organic/inorganic hybrid POMs

Covalent modification, by grafting organic moieties onto POMs framework, namely, the organic ligand can substitute an oxo group of the POM and be directly linked to the metallic center, resulting in the formation of classification II hybrids. The later has gained much attentional though they are vastly different in molecular structures, POMs and conjugated organic molecule are both electrically active materials with similar electrical and optical properties such as photochromism, electrochromism, and conductivity. The fundamental mechanisms of these properties are, however, different for these two types of materials, with dπ electrons responsible for the inorganic POM clusters, and delocalized pπ electrons responsible for the organic counter part. While both areas have been enjoying considerable success, there has been only a few success in bringing these two types of materials together through covalent bonds to make novel POM-based organic-inorganic hybrids owing to the lacks of reliable strategy to functionalize POMs and prepare their organic derivatives in high yield. As could be expected,

however, such organic-inorganic hybrid materials will not only combine the advantages of organic materials: such as good process ability and fine-regular structure and electronic properties, with those of inorganic POM clusters, such as good chemical stability and strong electron acceptability, to produce so-called "value-adding properties", but also may bring exciting synergistic effects due to the close interaction of delocalized organic pπ orbits with the inorganic POM cluster's dπ orbits.

Compared with such organic-inorganic hybrids, POMs are conventionally prepared by coordination bonding or electrostatic interaction approaches, which lack predictability and controllability. However, the ability of covalently modify the POM clusters in a reliable and predefined manner holds promise for the development of molecular materials that bridge the gap between molecular organic and bulk semiconducting POMs cluster. Furthermore, giving exceptional physical and structural properties intrinsic to POM superstructures can be achieved by post-functionalized through common organic reactions and apply organically functionalized POM clusters as building blocks [28-29].

Grafting organic moieties onto a POMs cluster requires an anchorage point ensuring the link between the two components. This link is closely dependent on the chemical structure nature and electronic properties of the POMs cluster. The nucleophilic character of the oxygen atoms localized on the surface of the POMs can lead to covalent interactions with electrophilic groups bearing organic groups. The presence of the negative charge borne by the POMs cluster is an important point that needs to be considered for the grafting of the organic moieties. Neutral or negatively charged organic moieties will be chosen in order to favor covalent grafting over electrostatic interactions. The functionalization of POMs through oxygen atoms located at the periphery of the POM structure is the most conventional route. Organic ligand which is the isoelectronic of O^{2-} can substitute an oxo group of the POM and be directly linked to the metallic center [30].

Based on the coordination modes to covalently link organic moieties onto the POM cluster surface. The commonly synthetic strategies can be categorized into the following main classifications: Organoimidization [28,31-34], Organoalkoxylation [35-48], Organotin [49-54], Organosilylation [55-63], Organophosphonylation and organoarsonylation [64-72] (**Figure 4**). Organically functionalized POMs applying specific organic ligands as linkers make POMs-based inorganic-organic chiral hybrids more accessible and flexible. In this review, we specially focus on the issue that such POMs-based inorganic-organic chiral hybrids were obtained by the covalent modification of achiral POM cluster precursors applying organic ligands as structure-directing agents by symmetry reduction or breaking the achiral POM cluster.

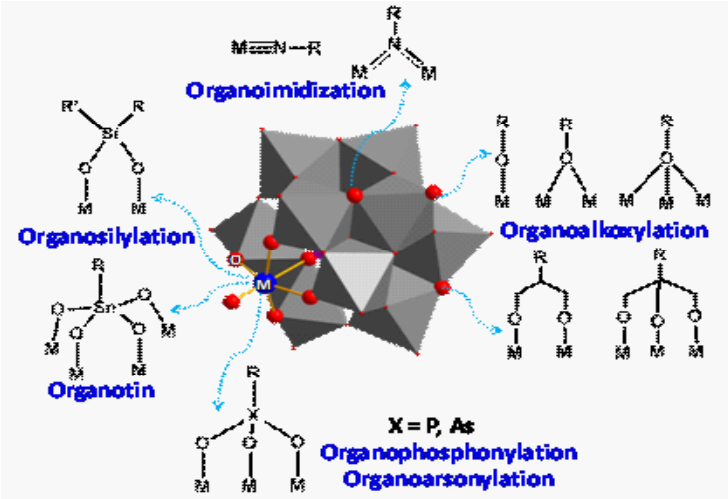


Figure 4: Current existed synthetic strategies and main coordination modes to covalently link organic moieties onto surface of the POM clusters.

2. Organoimidization by the DCC-dehydrating protocol

Among the above mentioned synthetic strategies concerning covalent modification of POM clusters, organoimidization has attracted particular interest. Strictly speaking, the direct covalent modification of the POM cluster without the bridging through the transition metal the organoimidization of $[Mo_6O_{19}]^{2-}$ is the only system. Various synthetic approaches to prepare organoimido derivatives of $[Mo_6O_{19}]^{2-}$ using different organoimido-releasing reagents have-been summarized in a previous book chapter by us [31]. Recently, a lot of arylimido derivatives including polymers of the Lindqvist hexamolybdate cluster, $[Mo_6O_{19}]^{2-}$, have been synthesized continuously [28]. Since the π electrons in the organic component of such derivatives may extend their conjugation to the inorganic POM framework via the N atoms of the imido groups, thus result in strong d–pπ interactions and dramatically modify the electronic structure and redox properties of the corresponding parent POMs.

In addition, organoimido derivatives of POMs with a remote active functional group can be exploited as building blocks to conveniently and controllably fabricate the complicated covalently-linked POM-based organic-inorganic hybrids, including the nano-dumbbells, polymeric chains and even networks of POMs [28]. This modular building block approach brings rational design and structure regulation into the synthesis of organic-inorganic hybrid molecular materials.

In this review, we will just focus on organoimidization of $[Mo_6O_{19}]^{2-}$ by the DCC-dehydrating protocol in brief which has also been well reviewed by our group [28,34] and demonstrated how this protocol can be applied in chiral POMs hybrids synthesis through covalent modification. As it can be expected, the reaction chemistry of organoimido derivatives of POMs stands for the fascinating future of the chemistry of organoimido derivatives of POMs since it opens not only a new road to the chemical modification of POMs, but also an exciting research arena where a variety of hybrid materials containing covalently bonded POM clusters

and organic conjugated segments can be prepared in more controllable and rational manner.

The hexamolybdate ion, $[Mo_6O_{19}]^{2-}$, is amongst the most well-known POM clusters for its thermal and chemical robust and easy to be prepared, which has the so-called Lindqvist structure. As it is depicted in **Figure 5**, the Lindqvist structure consists of a central oxyanion surrounded in an octahedral cage formed by six metal atoms. All the six metal atoms also have an octahedral environment.

Besides the central oxygen atom, they each coordinate triply to one terminal oxygen atom, forming a terminal metal-oxo group (M≡O), and share an additional four double-bridging oxygen atoms (μ_2-O atoms) with neighboring metal atoms. Generally speaking, a Lindqvist ion has a super-octahedral structure approach to O_h point group and features its six terminal metal-oxo groups aligned along the Cartesian axes. For the hexamolybdate, these molybdyl groups (Mo≡O) are reactive enough for the terminal oxygen atoms to be directly replaced by various nitrogenous species. The organoimido derivatives of $[Mo_6O_{19}]^{2-}$ is generated by the substitution of one or more $Mo{=}O_{term}$ bond(s) by one or more Mo≡NR bond(s). Monosubstituted derivatives can be obtained with a variety of organoimido ligands using the hexamolybdate anion $[Mo_6O_{19}]^{2-}$ directly or starting from the octamolybdate anion $[Mo_8O_{26}]^{4-}$ involving the POM reconstruction both in the presence of the N,N′-dicyclohexylcarbodiimide (DCC) dehydrating agent.

2.1. Monosubstituted Derivatives

In the presence of one equivalent of DCC, one equivalent of primary amines reacts smoothly with stoichiometric $(n\text{-}Bu_4N)_2[Mo_6O_{19}]$ under dry N_2 gas and refluxing acetonitrile, to give the corresponding mono-substituted imido derivatives usually in excellent yield of more than 90%. Not only a variety of primary amines occur this reaction, but also it is usually completed in less than 12 hours, and pure *crystalline* products can be readily obtained with convenient bench manipulations. Moreover, this reaction can be carried out in the open air without nitrogen protection if slightly over one equivalent of DCC (1.2 equivalent) is added. (**Scheme 1**)

$$[Mo_6O_{19}]^{2-} + RNH_2 + DCC \longrightarrow [Mo_6O_{18}(NR)]^{2-} + DCU$$

Scheme 1. The Monosubstituted organoimido derivatives $[Mo_6O_{18}(NR)]^{2-}$ synthesis by $[Mo_6O_{19}]^{2-}$ directly functionalization.

Moreover, in our recent attempts to functionalize the octamolybdtates with organoimido groups, we discovered that in the presence of DCC, a proton could dramatically speed up the reaction of α-$[Mo_8O_{26}]^{4-}$ with primary amines under much milder condition. Mean while, monofunctionalized organoimido derivatives of $[Mo_6O_{19}]^{2-}$ were selectively synthesized in high purity and moderate yield with easy workup. This acid-assisting route has allowed the facile

synthesis of a large number of mono-imido hexamolybdates. It is worth pointing out that, the proton was crucial to the above route for the formation of monofunctionalized derivatives. It was observed that in the absence of hydrochloride salt–which offer the protons, amines reacted with α-$[Mo_8O_{26}]^{4-}$ to yield only the bifunctionalized arylimido derivatives of hexamolybdate. (**see Scheme 2**)

$$3(N\text{-}Bu_4)_4[Mo_8O_{26}]+4RNH_2.HC1+6DCC \xrightarrow{CH_3CN\ refluxing} 4(Bu_4N)_2[Mo_6O_{18}(NR)]+6DCU+4Bu_4NC1$$

Scheme 2. The Monosubstituted organoimido derivatives $[Mo_6O_{18}(NR)]^{2-}$ synthesis by $[Mo_8O_{26}]^{4-}$ reconstruction.

2.2. Disubstituted Derivatives

A characteristic feature of the derivatization of $[Mo_6O_{19}]^{2-}$ with organoimido ligands is the capacity for polyfunctionalization. Among organoimido derivatives of $[Mo_6O_{19}]^{2-}$, the bifunctionalized ones are the easiest and most common potential building blocks for constructing POM-based hybrids.

$$2RNH_2+(N\text{-}Bu_4)_4[Mo_8O_{26}]+2DCC \xrightarrow{CH_3CN\ refluxing} (Bu_4N)_2[Mo_6O_{17}(NR)_2]+2DCU+(Bu_4N)_2[Mo_2O_7]$$

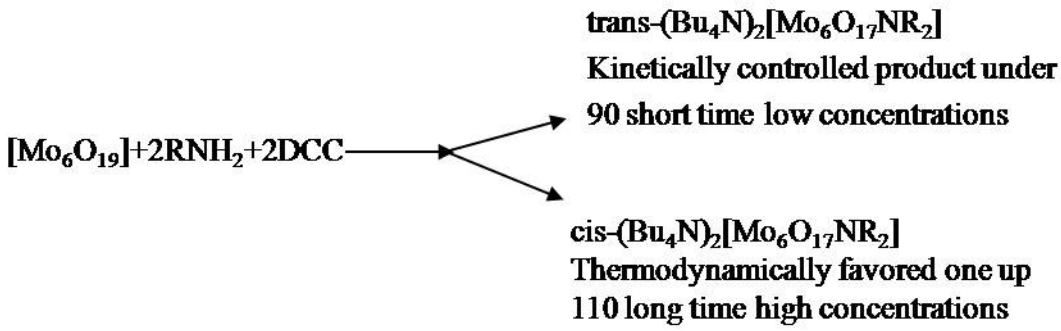
Scheme 3: The disubstituted organoimido derivatives $[Mo_6O_{17}(NR)_2]^{2-}$ synthesis by $[Mo_8O_{26}]^{4-}$ reconstruction.

In the past years, we also checked the possibility of our DCC-dehydrating protocol in the preparation of di-organoimido derivatives of the hexamolybdate. In most cases, attempts to use the same route as for the mono-substituted derivatives but with astoichiometric ratio of two equivalent aromatic primary amines failed to obtain the disubstituted derivatives in high yields. Instead, mixture of various polysubstituted hexamolybdates were generated since there are six equally reactive sites on a hexamolybdate ion, and thus repeated recrystallization is needed for purification of the anticipant product.

However, an attempt to functionalize the α-isomer of octamolybdate ion α-$[Mo_8O_{26}]^{4-}$, with this reaction routine resulted in the selective synthesis of difunctionalized arylimido derivatives of hexamolybdate with good yield and high purity. The reaction of $(n\text{-}Bu_4N)_2$ [α-Mo_8O_{26}] with DCC and organoimido ligands at the ratio of 1 : 2 : 2 in refluxing dry acetonitrile for 6 to 12 hours afforded the corresponding disubstituted organoimido derivatives $[Mo_6O_{17}(NR)_2]^{2-}$. This novel route allowed the efficient and selective synthesis of a number of di-organoimido hexamolybdates with more convenient and simple bench operations in good yield and high purity [73] (**Scheme 3**).

Considering exclusively steric hindrance, the trans structure of the disubstituted hexamolybdate is expected to be the principal product compared with the cis isomer. However, the trans-disubstituted hexamolybdates have hardly been detected in the above reaction route. Such a result is amazing, which suggests that the steric effect is less important here and the

presence of an excessive imido substituent induces an activating effect on the adjacent molybdyl groups. A DFT study on hexamolybdate derivatives reveals that the cis-disubstituted derivatives are more stable in energy than the corresponding trans-isomers [74].



Scheme 4: The disubstituted organoimido derivatives $[Mo_6O_{17}(NR)_2]^{2-}$ synthesis by $[Mo_6O_{19}]^{2-}$ directly functionalization.

We conducted our DCC-dehydrating protocol for the direct functionalization of $[Mo_6O_{19}]^{2-}$ with stoichiometric ratios of $(n\text{-}Bu_4N)_2[Mo_6O_{19}]$ and the corresponding organoimido ligands [75-76]. Both the cis- and trans-disubstituted imido derivatives could be obtained in reasonable yields, respectively, by careful control of the refluxing time, reaction temperature and concentration. It should be noted that the cis-isomer is by far the most common structure among the disubstituted species even if the kinetically controlled trans isomer has been recently isolated [75-77]. In general, prolonged refluxing time at high concentration and high temperature promotes the formation of the cis-isomer, while the trans-isomer can be isolated from a relative short-time at low concentration and low temperature reaction system (see **Scheme 4 and Figure 5**).

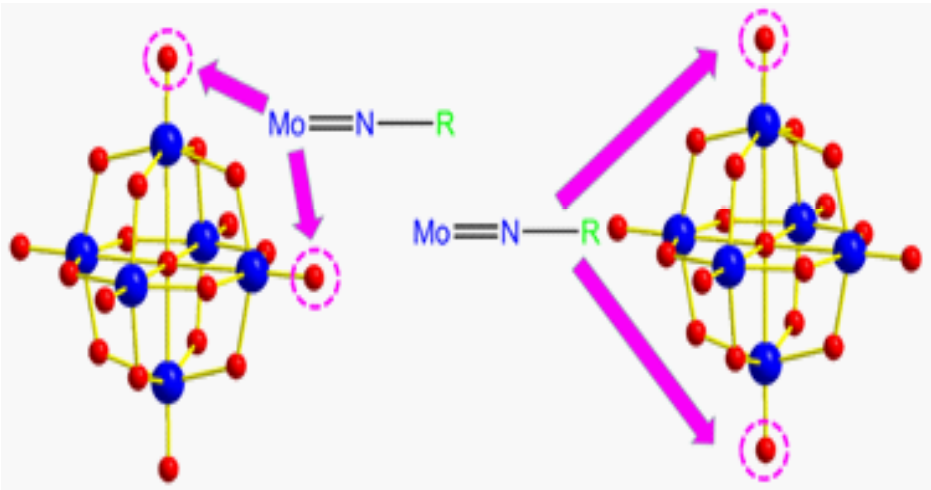


Figure 5: The cis- and trans-disubstituted mode imido derivatives of $[Mo_6O_{19}]^{2-}$.

2.3. Polysubstituted Derivatives

We are also interested in the preparation of the polysubstituted hexamolybdates in the context of our DCC-dehydrating protocol using primary amines as the imido-releasing agents. In a recent attempt to synthesize the fac-tri-2,6-dimethylanilido hexamolybdate, contrary to our expectation, the as-resulted tri-imido derivative, $(Bu_4N)_2[cis\text{-}Mo_6O_{16}\mu_2\text{-}(NAr)(NAr)_2]$, was not exclusively terminal-oxo replaced complex, and instead, one of bridging-oxo groups was substituted. This indicated a very important fact that not only the terminal oxo group can be substituted, but also the bridging oxo groups can be replaced by amine groups [78] (**Figure 6**).

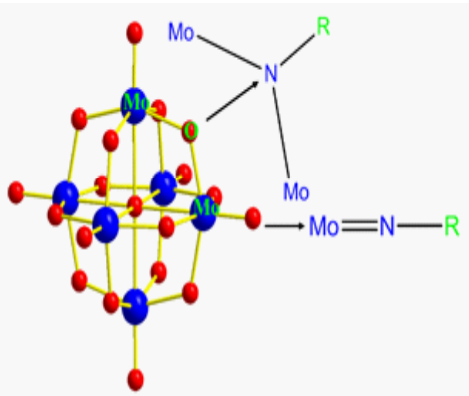


Figure 6: Two substitution modes of terminal or bridging oxygen by organoimido ligands.

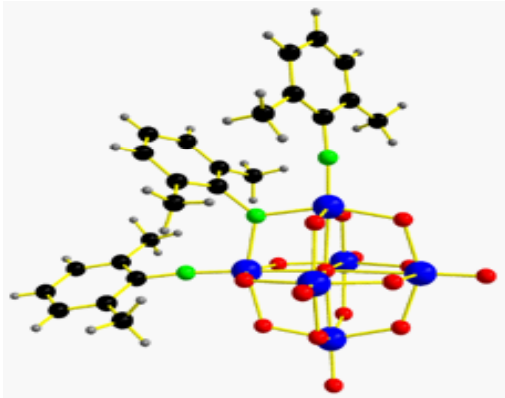


Figure 7: Ball-and-stick model of the trisubstituted hexamolybdate.

This compound has a feature that the μ_2-bridging oxygen atom sharing by the two imido-bearing Mo atoms in a cis-diimido hexamolybdate is substituted with a μ_2-bridging organoimido ligand. It suggests that such oxygen atoms in the cis-diimido hexamolybdates have been doubly activated by the neighboring imido groups and become more negative (nucleophilic) than other oxygen atoms, resulting in the easy electrophilic attack by DCC. It stands for the first example of a bridging oxygen atom in POMs replaced by the bridging imido groups. It breaks the myth that only the terminal oxo groups can be directly replaced with imido ligands before and brings us a wonderful prospect in the chemistry of organoimido derivatives of POMs (**Figure 7**).

2.4. Organoimido Derivatives of other POMs

While there are fruitful developments in the synthetic chemistry of hexamolybdate, related studies on other POMs keep scarcely well developed. So far, there only has been obtained quite limited success in extending the above approaches to the other Lindqvist POMs.

Attempts to directly functionalize the hexatungstate anion, $[W_6O_{19}]^{2-}$, another important Lidquvist homopolyoxometalate besides the hexamolybdate, have failed to utilize all the existing approaches, since $[W_6O_{19}]^{2-}$ does not react at all with phosphinimines, isocyanates or aromatic primary amines under the present developed conditions. It seems that compared to

the molybdyl groups in the hexamolybdate, the tungstyl groups in the hexatungstate is rather unreactive. The only one example of imidosubstituted hexatungstates, $(Bu_4N)_2[W_6O_{18}(NAr)]$, Ar = 2,6-diisopropyl-$C_6H_3$, was obtained about twenty years ago by Maatta [79].

Although the hexatungstate cluster is less labile, replacement of tungstyl groups with reactive molybdyl groups will exert an activate effect on the cluster. Surely, we discovered that the pentatungstenmolybdate ion, $[MoW_5O_{19}]^{2-}$, a Lidquvist heteropolyoxometalate, could be directly functionalized with primary amines using the DCC-dehydrating protocol [80].

$$[MoW_5O_{19}]^{2-} + RNH_2 + DCC \longrightarrow [W_5O_{18}(MoNR)]^{2-} + DCU$$

Scheme 5. The Monosubstituted organoimido derivatives $[W_5O_{18}(MoNR)]^{2-}$ synthesis by $[MoW_5O_{19}]^{2-}$ directly functionalization.

In addition of one and a half equivalents of DCC, the reaction of one equivalent of 2,6-dimethylaniline with one equivalent of $(Bu_4N)_2[MoW_5O_{19}]$ does occur in hot acetonitrile under nitrogen, affording the mono-imido derivatives $(Bu_4N)_2$ $[W_5O_{18}(MoNR)]^{2-}$. Indeed as expected, the terminal oxygen atom bonded to the molybdenum atom was selectively replaced by an imido substituent. This result opens a general road for the synthesis of organo imido derivatives of less reactive POM clusters, namely, by replacement one of the inert terminal metal-oxo groups with a functionalizable Mo-O group.

3. POM-Based Chiral Hybrids Synthesis via Organo imidization

The organo imidization strategy is applying in POM-based chiral hybrids synthesis through covalent modification of achiral precursors POM cluster $[Mo_6O_{19}]^{2-}$ mainly focuses on the construction of chiral axle species. The determination criterion of whether organic-inorganic POM hybrids have chirality or not depends on the overlapping with their mirror structure. Even there does not exist a chiral carbon in organic-inorganic POM hybrids structure, they can still be chiral if there is a chiral axle in the structure. Chirality that results from chiral axle can be catalogued into three types: propadiene-type, biphenyl-type and handle-type.

For the biphenyl-type chiral axle containing POM-based chiral hybrids design. Peng designed two pairs of enantiopure C_2-symmetric 1,1'-binaphthyl units based organic ligand. Through the post-functionalization, achiral precursors monosubstituted organo imido derivatives $[Mo_6O_{18}(NR)]^{2-}$covalently linked to such chiral organic ligand and the chirality transfer from organic ligand to the whole POM-based hybrids [81]. Such hybrids showed moderate chiroptical behaviour in solution, and Cotton effects are observed up to 450 nm, indicating chiral extension from the binaphthyl core of the cluster-containing π-conjugated arms (**Figure 8**).

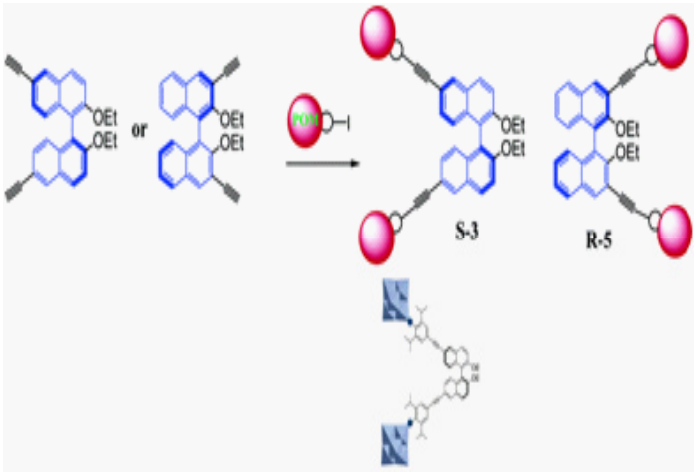


Figure 8 : The 1,1'-binaphthyl units based chiral organic ligand covalent modification of achiral precursors monosubstituted organoimido derivatives $[Mo_6O_{18}(NR)]^{2-}$.

In the view of applying chiral organic ligands as structure-directing agents to transfer chirality to the whole POM-based hybrids strategy, chiral species are still consumed. This organoimidization covalent modification would be more valuable if applying intrinsic hindrance of the bulky and heavy POMs. Then we further promoted this strategy. POM–organic hybrid chiral molecular nanorods were obtained through organo imidization of achiral precursors Lindquist $[Mo_6O_{19}]^{2-}$ applying achiral precursors Anderson type POMs as special imido ligands. They also displayed biphenyl-type chiral axle and C_2-symmetry due to the hindrance of the bulky and heavy POMs to the rotation around the N–C single bond, which stabilized a chiral conformation [82] (**Figure 9**).

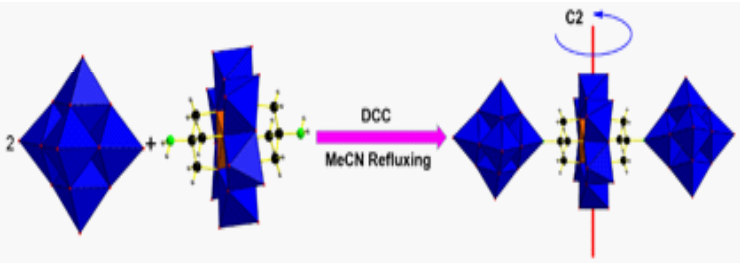


Figure 9: The chiral nanorods synthesis through organoimidization of $[Mo_6O_{19}]^{2-}$ applying Anderson type POMs as special imido ligands.

Such chiral nanorods were obtained in enantioenriched forms by spontaneous resolution. Their chirality was confirmed by the single crystal X-ray diffraction analyses and solid CD spectroscopy measurements. Although such C_2-symmetric frameworks do not possess stereogenic metal ions, the synthetic strategy provides an original route for the development of novel chiral POM architectures. We also extended this strategy to design another type of chiral axle POM-based chiral hybrids such as handle-type POM-based chiral hybrids.

We applied anthranilic alkyl ether as imidization reagent, which is moderately flexible and non-plane organic molecule. By removing symmetric plane and symmetric centers in POM clusters and the formation of ring, we couldobtain chiral metal macro-cyclic compo unds$[Mo_6O_{17}(C_{18}H_{20}N_2O_2)]_2(\pm)$ through organoimidizationcovalent modification by reacting

$[Bu_4N]_4[\alpha\text{-}Mo_8O_{26}]$, binary aromatic amines (1,4 - bis (o- amino- phenoxy)-butane, 1,6 - bis (o - amino- phenoxy) hexane, 1,8 - bis (o - amino- phenoxy)-octane), their hydrochloride and DCC in anhydrous acetonitrile [83].

The flexible alkyl chains which connect two benzene rings in organic ligand can result in the creation of chirality. Since the two ends of organic ligand are fixed on the $Mo_6O_{18}^{2-}$ by Mo-N triple bond, the flexible chain cannot be wiggle freely, so that an asymmetric chain is formed and the symmetry of the original $Mo_6O_{19}^{2-}$ can be broken. In this way, the whole metal macro-cycle turns to be chiral. This isan important breakthrough in POM metal macro-cyclic compounds synthesis (**Figure 10**).

Taking the advantage of disubstituted organoimidization strategy, we also attempt to design multifunctional hybrid materials by introducing aromatic and aliphatic organic amine moieties simultaneously, indeed in such *cis*-disubstituted imido derivatives the symmetry was reduced to C_i point group from reactants $Mo_6O_{19}^{2-}$ cluster which has high symmetry O_h point group. Unfortunately spontaneous resolution and chiral separation of such disubstituted imido derivatives have not yet achieved, however this indicated the important issue that disubstituted/polysubstituted organoimidization strategy should also be an effective strategy in chiral POM-based multifunctional hybrid materials design [84] (**Figure 11**).

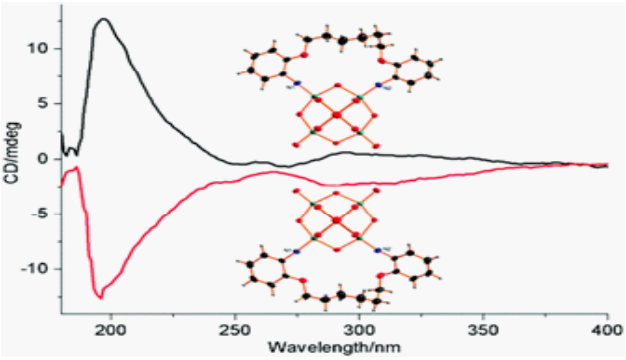


Figure 10: Chiral metal macro-cyclic compounds $[Mo_6O_{17}(C_{18}H_{20}N_2O_2)]_2(\pm)$ through organoimidization covalent modification and their solid CD spectroscopy.

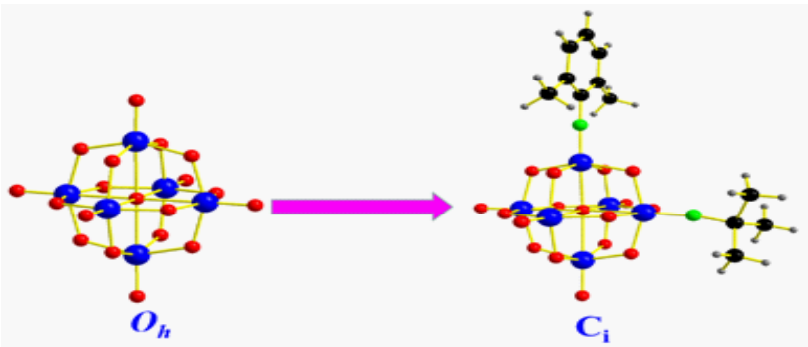


Figure 11: The symmetry reduction by mix disubstituted organoimidization.

Recently, we also attempted to synthesize trisubstituted imido derivatives by introducing the bioactive amine molecule- amantadine, and this is the first reported trisubstituted derivatives using aliphatic organoimido ligands. Similarly, such fac-trisubstituted imido derivatives the symmetry was reduced to D3d point group which couldserve as a potential chiral synthon [85] (**Figure 12**).

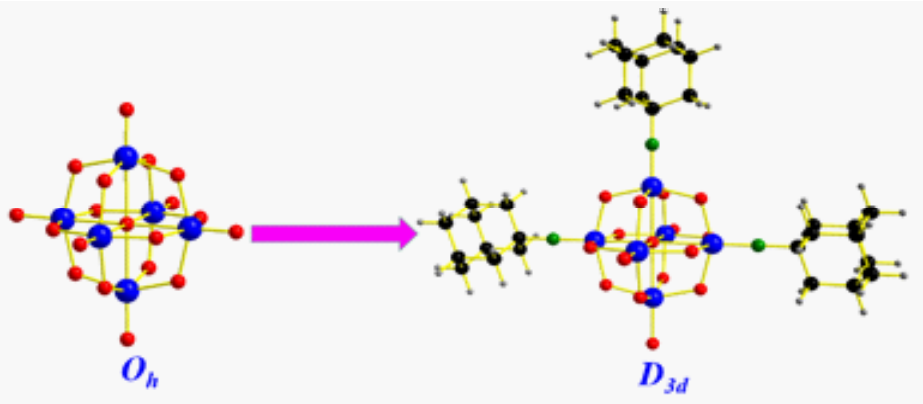


Figure 12: The symmetry reduction by trisubstituted organoimidization

Considering the polyfunctionalization capacity character of the derivatizational $[Mo_6O_{19}]^{2-}$, this strategy designing through the post-functionalization monosubstituted organoimido derivatives as building block becomes more accessible and flexible. We have proved that the remaining terminal reactive oxygen atoms in such organoimido derivatives can be further functionalized by other imido ligands [86]. Since the fact that there exist plenty of chiral natural products L- amino acids and remote amino groups on the surface in POM clusters including $\{[NH_2C(CH_2O)_3]_2V_6O_{13}\}^{2-}$ [87], δ-$\{[NH_2CC(CH_2O)_3]Cr(OH)_3Mo_6O_{18}\}^{3-}$ [88], $\{[C_2H_5C(CH_2O)_3]MMo_6O_{18}[(OCH_2)_3CNH_2]\}^{3-}$ [89], χ-$\{[NH_2CC(CH_2O)_3]Cr(OH)_3Mo_6O_{18}\}^{3-}$ [90], $\{[NH_2C(CH_2O)_3]_2P_2V_3W_{15}O_{59}\}^{6-}$ [43], $\{Ni_6O_{12}[NH_2C(CH_2O)_3](a\text{-}PW_9O_{34})\}$ [91]. (**Figure 13**)

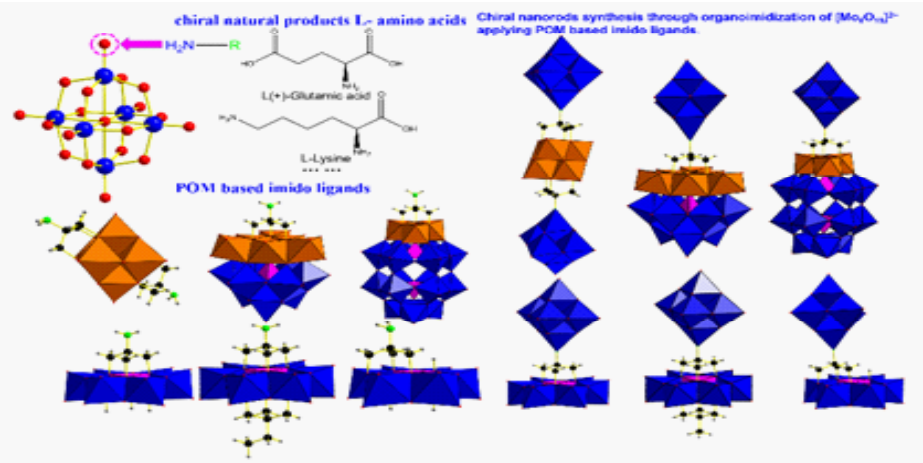


Figure 13: The perspective of POM-based chiral hybrids synthesis by organoimidizationcovalent modification of achiral precursors Lindquist $[Mo_6O_{19}]^{2-}$ strategy.

4. Conclusion and Outlook

Organoimidization covalent modification of achiral precursors Lindquist $[Mo_6O_{19}]^{2-}$ is a flexible strategy applying in the generation of POM-based chiral hybrids. It possesses steric hindrance to remove symmetric elements in POM clusters, by introducing specific customized organic ligands, which includes chiral organic ligands as structure-directing agents or POM clusters that bear amino group on the POM surface and serve as special imido ligands takingfull advantage of intrinsic hindrance of the bulky and heavy POMs. It can fore see that more and more POM-based chiral hybrids will be generated by organoimidization covalentmodifi-

cation in the future and some related investigation is being conducted in our lab now

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