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Enantiopure 1,1′-Binaphthyl-Based Polyoxometalate-Containing Molecular Hybrids

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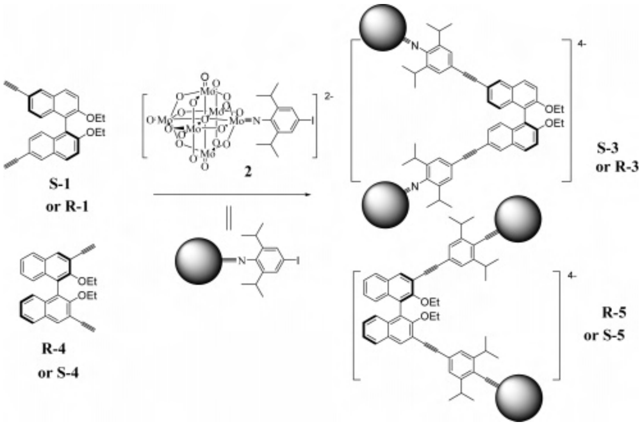
The first chiral molecular hybrids based on covalently linked polyoxometalate clusters and enantiopure 1,1′-binaphthyl units have been prepared. Their structures have been confirmed by ^{1}H NMR, FTIR, and ESI-MS measurements. Such hybrids show moderate chiroptical behavior in solutions, and Cotton effects are observed up to 450 nm, indicating chiral extension from the binaphthyl core to the cluster-containing π-conjugated arms.

Because of their potential applications in asymmetric catalysis and medicine, chiral polyoxometalates (POMs) have long been actively pursued.[1] While a number of chiral metal−oxide microporous solids have been reported, enantiopure POMs stable in both solution and solid state have not been realized until very recently.[2] Chiral POMs are generally obtained in two approaches; one utilizes a chiral template, usually an organic ligand or metal−organic complex, to direct the cluster assembly.[3] The chiral transfer from the template to the final cluster framework can be remarkable, as demonstrated recently by Hill et al.[2] Another approach brings chirality to POM complexes by associating chiral organic ligands to otherwise nonchiral POM clusters.[4] The combination of chiral amino acids with chiral POMs has also led to NMR-distinguishable diastereomers.[5] The research on the second approach, however, has so far been limited to interactions between amino acids with POMs. The weak association of amino acids with POMs in solution prevents chirality extension to the POM clusters.[5b] Herein, we report the first chiral molecular hybrids based on covalently linked POM clusters and enantiopure 1,1′-binaphthyl units. 1,1′-Binaphthyl derivatives are among the most extensively studied chiral organic ligands for asymmetric catalysis.[6] The covalent anchoring of such a chiral ligand to a POM cluster may lead to not only new catalysts but also new electronic materials.

Scheme 1. Synthesis of Chiral Molecular Hybrids



Besides the potential for asymmetrical catalysis, the reported chiral hybrids may exhibit interesting nonlinear optical properties. As shown in Scheme 1, both hybrids **3** and **5** contain electron-donating ethoxy groups and electron-withdrawing POM clusters linked through π-conjugated bridges.[7] The donor−π-acceptor structure makes them

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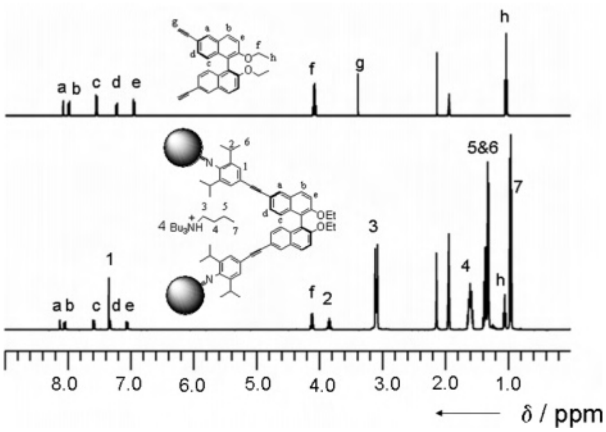

Figure 1. ^{1}H NMR spectra of (*S*)-**1** and (*S*)-**3** in CD_3CN. The two unlabeled peaks are solvent signals (acetone and acetonitrile).

second-order nonlinear optical chromophores.[8] On the other hand, single crystals of enantiopure **3** and **5** should possess noncentrosymmetry, thus possessing bulk nonlinearity.[8a,9] The unique combination of molecular nonlinearity due to its noncentral symmetrical electronic structure with bulk nonlinearity resulting from noncentral symmetrical packing makes them interesting new hybrid systems for nonlinear optics.

The chiral hybrids were synthesized by direct coupling of an iodo-functionalized hexamolybdate cluster (compound **2**)[10] with an enantiopure 1,1′-bi-2-naphthyl derivative carrying two ethynyl groups,[11] at either the 6,6′ positions [compounds (*R*)-**1** and (*S*)-**1**] or the 3,3′ positions [compounds (*R*)-**4** and (*S*)-**4**].[12] The resulting four hybrids are soluble in common organic solvents such as acetonitrile, acetone, and dimethylformamide. Their structures have been confirmed by ^{1}H NMR, Fourier transform infrared (FTIR), and mass spectrometry.

Figure 1 shows the ^{1}H NMR spectra of (*S*)-**1** and (*S*)-**3**. (*S*)-**1** has five signals in the aromatic region, which can be assigned to the five different types of protons on the binaphthyl skeleton. The singlet at 3.39 ppm is attributed to the ethynyl protons. After coupling with **2**, the ^{1}H NMR spectrum of hybrid (*S*)-**3** shows signals corresponding to both the binaphthyl unit and tetrabutylammonium counterions. Except for slight downfield shifts, particularly for protons e (see Figure 1 for proton labeling), protons in the binaphthyl unit of (*S*)-**3** show signals otherwise identical with those in (*S*)-**1**. The aryl protons in the phenyl ring appear as a singlet (proton 1). The ethynyl proton signal (signal g) in (*S*)-**1** completely disappeared, indicating that both ethynyl groups have reacted. The integration ratio of signals associated with the arylimido−POM cluster segment (signals labeled as 1−7) versus those of the binaphthyl units (labeled as a−h) also confirms that two POM clusters linked to one binaphthyl unit. Compounds (*R*)-**1** and (*R*)-**3** show ^{1}H NMR spectra identical with those of (*S*)-**1** and (*S*)-**3**, respectively.

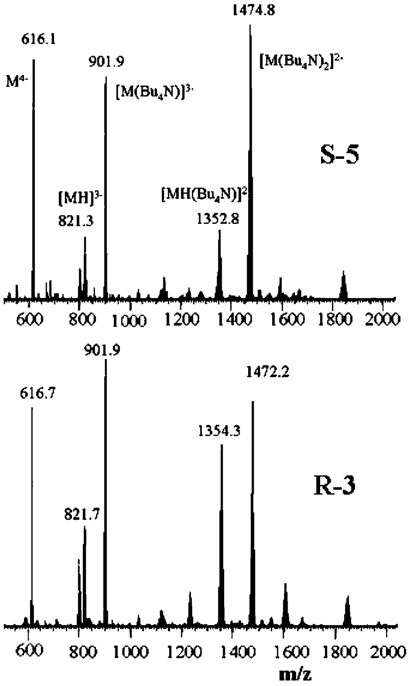

Figure 2. ESI-MS spectra of (*S*)-**5** and (*R*)-**3**.

The ^{1}H NMR spectra of **4** [(*S*)-**4** and (*R*)-**4**] again show five aromatic signals. The four ethylene protons (protons f), unlike **1** where they appear as one quartet, give two quartets at 4.01 and 3.71 ppm (see the Supporting Information for their NMR spectra). The ethynyl proton signal is again missing in the spectrum of **5**. All signals can be unambiguously assigned in accordance with the targeted structures.

The FTIR spectra of **3** and **5**, like that of **2**, are dominated by two strong bands at 790 and 950 cm^{-1} and a shoulder band at 975 cm^{-1}, all of which are typical absorptions of imido derivatives of hexamolybdates.[13] One weak band at 2196 cm^{-1} can be identified for both **3** and **5**, which are consistent with the stretching absorptions of internal alkyne bonds. Absorptions associated with terminal alkynes are not observed, confirming again that both terminal alkyne bonds in **1** and **3** have coupled with cluster **2**.

The structures of the two enantiomer pairs of **3** and **5** were also studied by electrospray ionization mass spectrometry (ESI-MS), an analytical tool that has been increasingly applied not only for the purpose of confirming the structure of functionalized POMs but also from the perspective of gaining insight into the stability of these hybrid anions.[14] As shown in Figure 2, all four hybrids [see the Supporting

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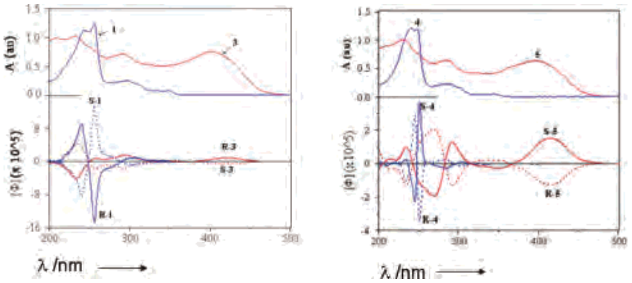

Figure 3. UV/vis absorption spectra (top) of hybrids **1** and **3**−**5** and CD spectra (bottom) of their enantiomers.

Information for the ESI-MS spectra of (*R*)-**5** and (*S*)-**3**] show five dominant bands centered at *m*/*z* 616, 821, 902, 1353, and 1473. These signals can be assigned to the molecular ions M^{4-} (615), $M^{4-} + H^+$ (820), $M^{4-} + Bu_4N^+$ (901), $M^{4-} + H^+ + Bu_4N^+$ (1352), and $M^{4-} + 2Bu_4N^+$ (1473), respectively, unambiguously confirming their chemical compositions. It should be mentioned that great effort has been made in growing single crystals out of **3** and **5**. Unfortunately, good quality single crystals have not yet been produced.

Hybrids **3** and **5** show excellent thermal stability. Thermal gravimetric analysis (TGA) indicates that they are thermally stable up to 250 °C, at which temperature counterions start to decompose. The optical properties of these hybrids were studied by UV/vis absorption and circular dichroism (CD) spectroscopy. As shown in Figure 3, binaphthyl derivatives **1** and **4** show strong ^1L_a absorptions around 250 nm and weak ^1L_b absorptions around 300 nm. After the anchoring of POM clusters, the resulting hybrids **3** and **5** show one broad, significantly red-shifted absorption band around 400 nm. Both the ligand-to-metal charge-transfer transition associated with the Mo−N bond and the $\pi-\pi^*$ transition of the extended π system may contribute to this absorption band. The CD spectra of **1** and **4** show a high-intensity bisignate absorption couplet associated with their ^1L_a transition and a minor one at longer wavelengths corresponding to the ^1L_b transition.[15] The two enantiomers of hybrid **3** (and **5**) show mirror-symmetry CD spectra, confirming their enantiopurity. Compared to the CD spectra of **1**, those of hybrid **3** show similar Cotton effects in the UV range, except for a slight blue shift in wavelength and a notable decrease in intensity, indicating that the binaphthyl core may not be significantly altered after the attachment of the two clusters. On the contrary, the CD spectra of **5** show very different bands from those of **4** in the wavelength range of 200−350 nm. It is likely that the dihedral angle of the two naphthyl rings is further twisted significantly in **5** because of the close proximity of the two attached bulk clusters, leading to varied Cotton effects.

In conclusion, two pairs of enantiopure hybrids containing covalently linked POMs and 1,1′-bi-2-naphthyl units have been prepared. Their structures have been confirmed by ^1H NMR, FTIR, and ESI-MS measurements. Such hybrids show moderate chiroptical behavior in solutions, and Cotton effects are observed up to 450 nm, indicating chiral extension from the binaphthyl core to the cluster-containing π-conjugated arms.

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Supporting Information Available: Detailed procedures for the preparation of **1** and **3**−**5**, ^1H NMR spectra of **4** and **5**, FTIR spectra of **2**, **3**, and **5**, and TGA curves of **3** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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