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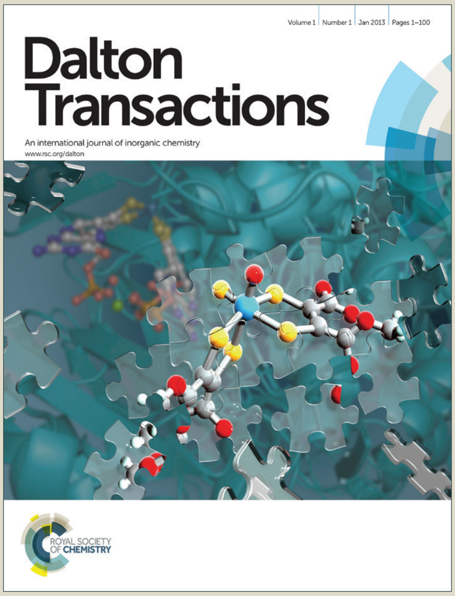

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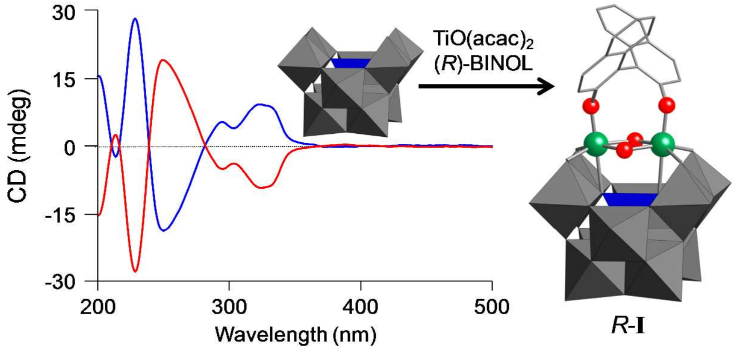

Chiral ligand-modified polyoxometalates (POMs) *R*-**I** and *S*-**I** were successfully synthesized by the introduction of BINOL into the dititanium-substituted POM.

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ARTICLE TYPE

Synthesis and structural characterization of BINOL-modified chiral polyoxometalates†

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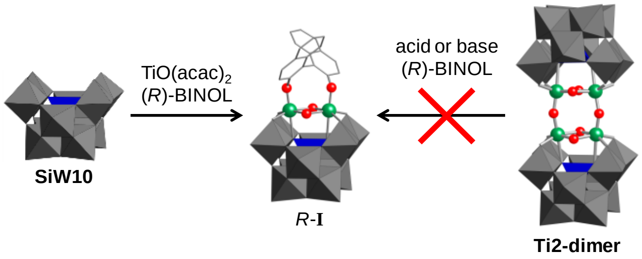
Chiral ligand-modified polyoxometalates (POMs) were successfully synthesized by introduction of BINOL into the dititanium-substituted POM in an organic medium and characterized by the X-ray crystallographic, spectroscopic, and elemental analysis. These BINOL-modified POMs were stable in the solution state and showed catalytic activity for asymmetric oxidation of thioanisole.

Polyoxometalates (POMs) are a fascinating class of metal-oxygen cluster compounds with unique structural variety and have been applied to various fields of science.[1] In addition, POMs are very attractive building blocks for functional inorganic-organic hybrids because POM-based hybrids provide additional and/or enhanced functions derived from synergy effects between POMs and organic components.[1,2] To date, various POM-based hybrids with unique electronic, catalytic, redox, and photonic properties have been synthesized.[3] Chiral molecules have become more important especially in the fine chemicals, biotechnological, pharmaceutical, and food industries.[4] Therefore, chiral POMs, which can integrate functionality from both POMs and chiral materials, have attracted particular attention in recent years due to their intriguing variety of architectures and numerous potential applications in asymmetric catalysis, inorganic medicine, non-linear optics, and chiral separation.[5–8]

In general, the synthetic methods of chiral POMs can be classified into two main routes. The first route is based on achiral ligands or skeleton of POMs without any chiral auxiliaries, and the second one is based on the use of chiral species, e.g., chiral ligands, chiral cations, or chiral metal complexes. In the first method, chiral POMs can be isolated in enantiomerically pure form by spontaneous resolution. After the spontaneous resolution for POM systems was firstly reported by Hill and co-workers in 2007, syntheses of chiral POMs by this method have extensively been investigated.[9] However, this method suffers from some drawbacks such as low probability (ca. 5–10%) of forming conglomerates which involves spontaneous resolution,[10] difficult separation of the enantiomeric crystals, and rapid racemization in the solutions. Although the use of chiral species such as chiral cations or ligands is an effective and rational method for synthesis of chiral POMs,[6,11] the modification of POMs with chiral ligands via covalent linkage has scarcely been reported and is still a challenging subject.

Several d^0-Transition metal (Ti, V, Zr, etc.)-substituted POMs have been reported to act as effective catalysts for selective oxidation reactions with hydrogen peroxide or organic hydroperoxides as the oxidant.[12] Among them, Nb-, Hf-, Zr-, and Ti-substituted POMs are prone to dimerization, and the pH-dependent interconversions between monomers and dimers have been reported.[13] We envisaged that these POM monomers and/or dimers likely act as suitable precursors for POM hybrids with chiral ligands because of the exchangeable axial coordination sites on the d^0-transition metals. In this communication, we report for the first time the successful synthesis and structural characterization of novel chiral POMs, $\mathrm{TBA_4[\gamma\text{-}SiTi_2W_{10}O_{36}(\mu\text{-}OH)_2(\mu\text{-}BINOLate)]}$ (*R*-**I** and *S*-**I**; TBA = $[(n\text{-}C_4H_9)_4N]^+$, BINOLate = $[C_{20}H_{12}O_2]^{2-}$) by the reaction of a dilacunary POM, $\mathrm{TBA_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]}$ (**SiW10**), with $\mathrm{TiO(acac)_2}$ (acac = acetylacetonate) and (*R*)- or (*S*)-1,1'-bi-2-naphthol (BINOL) (Scheme 1). While BINOL is one of the most frequently utilized and readily available chiral ligands, the modification of POMs with BINOL has never been reported, to the best of our knowledge. POMs *R*-**I** and *S*-**I** were highly stable in organic media (even in the presence of water) as the optically pure forms and showed catalytic activity for asymmetric oxidation of thioanisole with *tert*-butyl hydroperoxide (TBHP).



Scheme 1 Synthetic scheme for *R*-**I**.

To begin with, the synthesis of *R*-**I** was attempted by the reaction of $\mathrm{TBA_8[\{\gamma\text{-}SiTi_2W_{10}O_{36}(\mu\text{-}OH)_2\}_2(\mu\text{-}O)_2]}$ (**Ti2-dimer**) with (*R*)-BINOL (8 equivalents with respect to **Ti2-dimer**) in acetonitrile. Although we utilized $\mathrm{HClO_4}$ or TBAOH (2 or 4 equivalents) to monomerize **Ti2-dimer**, the synthesis was unsuccessful due to the high stability of **Ti2-dimer** against acid and base (Scheme 1, see ESI†).[14] The use of **Ti2-dimer** as the precursor should be avoided, and thus we next attempted to synthesize *R*-**I** through the one-pot procedure starting from lacunary $[\gamma\text{-}\mathrm{SiW_{10}O_{36}}]^{8-}$, titanium sources, and (*R*)-BINOL (ESI†). The introduction of titanium species into $[\gamma\text{-}\mathrm{SiW_{10}O_{36}}]^{8-}$ was hardly observed by the reaction of $\mathrm{K_8[\gamma\text{-}SiW_{10}O_{36}]}$, titanium sources ($\mathrm{TiO(acac)_2}$ or $\mathrm{TiO(SO_4)}$), and (*R*)-BINOL in aqueous media. On the other hand, the positive-ion CSI-MS spectrum of the reaction solution of organic solvent-soluble **SiW10**, TiO(acac)$_2$, and (*R*)-BINOL for 24 h in 1,2-dichloroethane showed intense signal sets at *m/z* = 4069.1 with isotopic distribution that agreed with the pattern calculated for $[TBA_5SiTi_2W_{10}O_{38}H_2(BINOLate)]^+$ (*m/z* = 4068.7) (Fig. S1, ESI†), showing the successful introduction of titanium and (*R*)-BINOL into **SiW10**. The crude products were purified by reprecipitation method followed by crystallization from nitromethane, successfully giving orange block crystals suitable for X-ray structure analysis (Tables S1–S3, ESI†). The anion structures of *R*-**I** is shown in Fig. 1(a). Similarly, *S*-**I** could also be synthesized with (*S*)-BINOL (Fig. 1(b)). An edge-shared dinuclear titanium core, $Ti_2(\mu\text{-}O)_2$, was incorporated into the lacunary site of $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$, and two titanium centers were bridged by a BINOLate ligand in the axial positions.

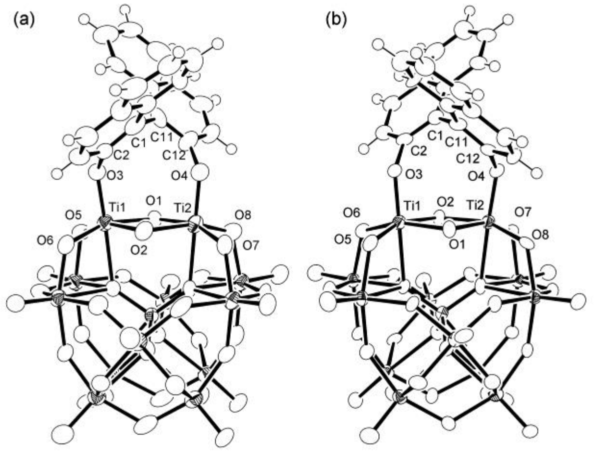


Fig. 1 ORTEP representations of the anion parts of (a) *R*-**I** and (b) *S*-**I** with thermal ellipsoids at 50% probability level. See also Fig. S2, ESI†.

The bond valence sum (BVS) values of tungsten (5.91–6.38), titanium (4.09–4.32), and silicon (3.73–3.76) atoms in **I** (*R*-**I** and *S*-**I**) indicate the respective valences of +6, +4, and +4. The existence of four TBA cations per anion implies that the charge of the anionic part of **I** is −4. Therefore, two protons are probably associated with the anion. The BVS values of bridging oxygen atoms O1 and O2 were 1.10–1.23, and these values were clearly lower than those of the other oxygen atoms (1.58–2.13), suggesting that O1 and O2 are monoprotonated. The IR spectrum of **I** did not show the strong absorbance at 661 cm^{-1} assignable to ν(Ti−O−Ti) which was observed in that of **Ti2-dimer** (Fig. S3, ESI†),[14] in agreement with the fact that **I** possessed the monomeric structure. The IR band at 3510 cm^{-1} assignable to ν(O−H) supported the existence of hydroxyl groups.

The X-ray crystallographic, spectroscopic, and elemental analysis data show that the formula of **I** is $TBA_4[\gamma\text{-}SiTi_2W_{10}O_{36}(\mu\text{-}OH)_2(\mu\text{-}BINOLate)]$. The formation can be expressed by the following equation [eqn (1)].

$$[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]^{4-} + 2TiO(acac)_2 + BINOL \\ \rightarrow [\gamma\text{-}SiTi_2W_{10}O_{36}(\mu\text{-}OH)_2(\mu\text{-}BINOLate)]^{4-} + 4acacH \qquad (1)$$

The lengths of Ti−O$_{Ti}$ (1.988–2.047 Å), Ti···Ti (3.143–3.160 Å), and Ti−O$_W$ (1.820–1.901 Å), and the angles of Ti−O−Ti (101.8–103.9°) and O$_W$−Ti−O$_W$ (95.5–96.5°) were similar to those (1.964–2.043 Å, 3.140–3.151 Å, 1.852–1.902 Å, 100.8–106.3°, and 94.5–96.7°, respectively) of **Ti2-dimer**.[14] The bond lengths of Ti−O$_C$ (1.814–1.837 Å) were also similar to those (1.753–2.020 Å) of common titanium-BINOL complexes.[15] On the other hand, the dihedral angles of binaphthyl (C2–C1–C11–C12; 84.47° and 90.39°) were larger than those (54.1–73.3°) of titanium-BINOL complexes likely due to the structural effect of the rigid POM framework on the dititanium center.

While several examples of structurally characterized POMs modified with chiral ligands have been reported until now,[11c–g] there are only a few reports on syntheses of monomeric POMs with chiral ligands.[11f–h] To the best of our knowledge, **I** was the first example of structurally characterized chiral ligand-modified monomeric Keggin-type POM.[16,17]

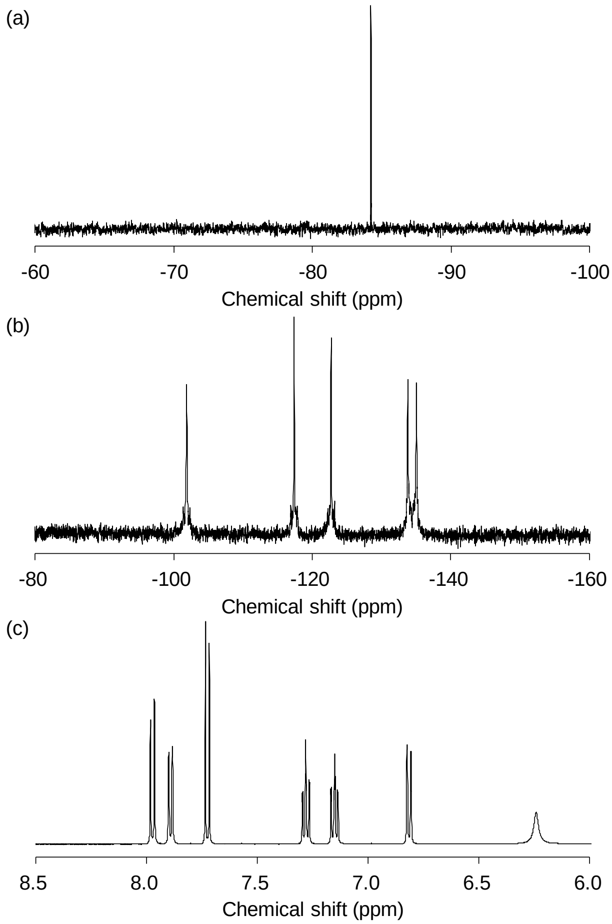


Fig. 2 (a) ^{29}Si, (b) ^{183}W, and (c) ^{1}H NMR spectra of *R*-**I** in acetonitrile-*d*$_3$. These ^{29}Si and ^{1}H NMR spectra were almost the same as those of *S*-**I** (Fig. S4, ESI†).

The ^{29}Si NMR spectrum of *R*-**I** in acetonitrile-*d*$_3$ showed a single signal at −84.22 ppm (Fig. 2(a)). The ^{183}W NMR spectrum of *R*-**I** showed five signals at −101.85, −117.38, −122.72, −133.79, and −135.03 ppm with the respective intensity ratio of 2:2:2:2:2 (Fig. 2(b)), indicating that this POM possesses C_2 symmetry which is different from that (C_{2v} symmetry) of **Ti2-dimer**. In the ^{1}H NMR spectrum of *R*-**I**, six signals due to BINOLate appeared at 7.97, 7.89, 7.72, 7.28, 7.15, and 6.81 ppm with the respective intensity ratio of 2:2:2:2:2:2, and a signal at 6.24 ppm assignable to hydroxyl ligands (Ti−OH−Ti) was also observed (Fig. 2(c)). The positive-ion CSI-MS spectrum of *R*-**I** showed intense signal sets centered at *m/z* = 2155.9 and 4069.4, which can be assigned to $[TBA_6SiTi_2W_{10}O_{38}H_2(BINOLate)]^{2+}$ and $[TBA_5SiTi_2W_{10}O_{38}H_2(BINOLate)]^{+}$, respectively (Fig. 3(a)). Water (100 equivalents with respect to *R*-**I**) was added to this solution, and the resulting solution was kept at room temperature for 24 h. Then, the CSI-MS spectrum was measured. As shown in Fig. 3(b), the CSI-MS spectrum (signal positions and intensities) was almost unchanged. All these results clearly indicate that the solid-state anion structure of *R*-**I** is maintained in the solution state and that *R*-**I** is stable even in the presence of water.

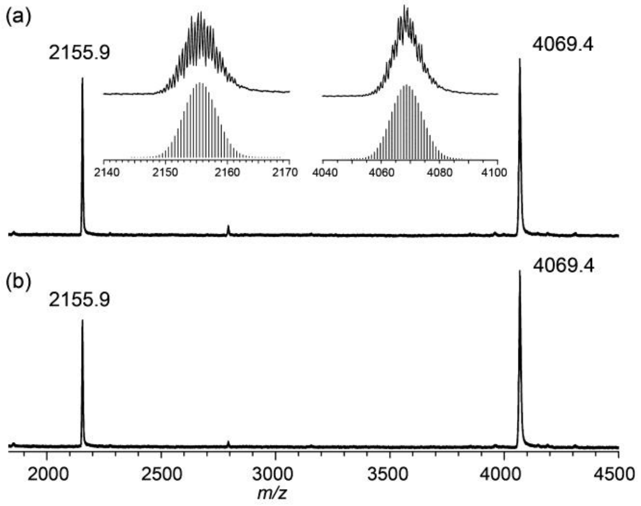


Fig. 3 Positive-ion CSI-MS spectra of *R*-**I** (0.25 mM) in acetonitrile (a) in the absence or (b) presence of water (100 equivalents with respect to *R*-**I**). Inset: calculated patterns for $[TBA_6SiTi_2W_{10}O_{38}H_2(BINOLate)]^{2+}$ (left) and $[TBA_5SiTi_2W_{10}O_{38}H_2(BINOLate)]^{+}$ (right). See also Fig. S5, ESI† for the negative-ion CSI-MS spectrum of *R*-**I**.

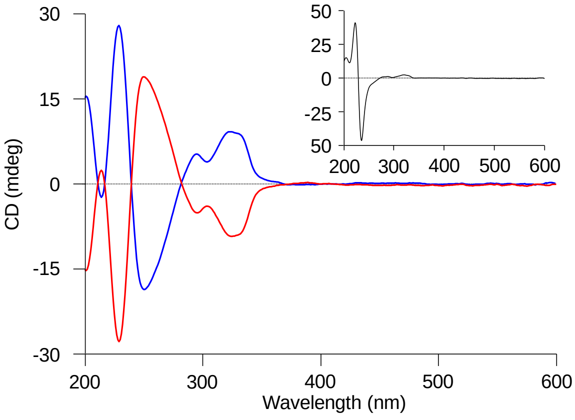
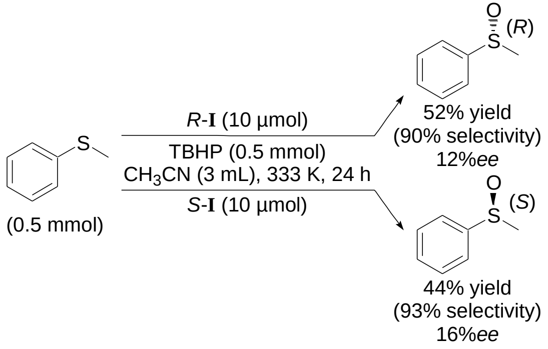


Fig. 4 CD spectra of *R*-**I** (blue line), *S*-**I** (red line), and (*R*)-BINOL (inset). Conditions: *R*-**I**, *S*-**I**, or (*R*)-BINOL (0.0725 mM) in acetonitrile.

To examine the chiroptical activities of *R*-**I** and *S*-**I**, their circular dichroism (CD) spectra in acetonitrile were measured (Fig. 4). The CD spectra of *R*-**I** and *S*-**I** showed the Cotton effects with maxima at 214, 229, 250, 295, and 324 nm and were mirror images of one another, indicating that the two compounds are a pair of enantiomers. The CD spectrum of BINOL exhibited the Cotton effects with maxima at 204, 211, 222, and 320 nm. Thus, the Cotton effects from 250 to 350 nm are in the spectral region characteristic of O→Ti^{IV} and O→W^{VI} LMCT bands (Fig. S6, ESI†).[18,19] Therefore, the chirality of BINOL is possibly transferred to the POM structure, and thereby the induced circular dichroism (ICD) is observed.[20] Such phenomena of ICD from chiral ligands to POMs have also been observed in tartrate-modified Dawson-type POMs and POM-based frameworks with helical channels.[11c,21]

To confirm the catalytic applicability of **I** to asymmetric reaction, the oxidation of thioanisole was carried out. Although we initially attempted to carry out the *R*-**I**-catalyzed oxidation of thioanisole using aqueous hydrogen peroxide as the oxidant, the oxidation did not proceed at all. In the presence of *R*-**I** using TBHP as the oxidant, thioanisole was converted into the corresponding sulfoxide in 52% yield (total yield of (*R*)- and (*S*)-isomers) for 24 h with 12%*ee* towards the (*R*)-isomer [eqn (2)]. This *ee* value for the oxidation of thioanisole was comparable to those of chiral cation exchanged POMs such as $[bis(1\text{-}phenylethyl)ammonium]_{12}[WZn_3(ZnW_9O_{34})_2]$ (18%*ee*)[6a] and $[dendritic\ ammonium]_3[PO_4\{WO(O_2)_2\}_4]$ (14%*ee*)[6b] under non-kinetic resolution conditions. In contrast, the mixtures of the raw materials such as $TiO(acac)_2$/BINOL and **SiW10**/BINOL did not show significant enantioselectivity (≤3%*ee*) for the present oxidation (Fig. S7, ESI†). The CSI-MS spectrum of the solution during the catalytic oxidation (at 3 h) showed the intense signal sets assignable to *R*-**I** (Fig. S8(b), ESI†), indicating that the molecular structure of *R*-**I** was maintained during the reaction and that *R*-**I** could act as the asymmetric oxidation catalyst. When using *S*-**I**, the corresponding sulfoxide was obtained in 44% yield with 16%*ee* towards the (*S*)-isomer [eqn (2)]. When the reaction solution was added to an excess amount of diethyl ether (50 mL), *R*-**I** dissolved in the reaction solution could spontaneously precipitate out, and thereby the used *R*-**I** after the reaction could readily be recovered by simple filtration (≥95% recovery, Fig. S8, ESI†). The CSI-MS spectrum of the recovered *R*-**I** also showed the signal sets assignable to *R*-**I** (Fig. S8(c), ESI†). Moreover, the recovered *R*-**I** could be reused for the oxidation of thioanisole without an appreciable loss of its catalytic performance (50% yield, 85% selectivity, and 12%*ee* under the conditions described in eqn (2)).



(2)

In conclusion, the novel chiral POMs *R*-**I** and *S*-**I** were successfully synthesized by introduction of BINOL into the dititanium-substituted POM. This study provides the first examples of structurally characterized Keggin-type POM monomers modified with chiral ligands. The chirality of BINOL was transferred to the POM structure through the titanium center. Compounds *R*-**I** and *S*-**I** were stable in organic media and showed the catalytic activity for the oxidation of thioanisole with TBHP.

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† Electronic supplementary information (ESI) available: Experimental details, crystallographic data, IR, UV-vis, and CSI-MS spectra. CCDC 1047984 and 1047985. See DOI: 10.1039/b000000x/

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