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Short Communication

Preparation of chiral oxovanadium (IV) Schiff base complex functionalized by ionic liquid for enantioselective oxidation of methyl aryl sulfides

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ABSTRACT

Chiral oxovanadium (IV) Schiff base complex covalently grafted with ionic liquid (IL: 1-(3-aminopropyl)-3-methylimidazolium tetrafluoroborate) has been reported first time. The *IL*-functionalized complex was found to be an efficient catalyst in the enantioselective oxidation of methyl aryl sulfides to sulfoxides with hydrogen peroxide as an oxidant. Especially, the *IL*-functionalized complex could be recovered conveniently by simple precipitation with addition of hexane and reused at least six cycles without loss of activity and enantioselectivity.

1. Introduction

The optically active sulfoxides are of great important chiral auxiliaries in organic synthesis and bioactive ingredients in the pharmaceutical industry [1,2]. The catalytic asymmetric oxidation of prochiral sulfides is often the efficient methodology to synthesize enantiopure sulfoxides [3]. Bolm and Bienewald first described enantioselective oxidation of sulfides catalyzed by the *in situ* formed vanadyl complex of the substituted salicylidene derivatives of (S)-tert-leucinol (1.5 mol%) utilizing aqueous 30% H_2O_2 as stoichiometric oxidant [4]. However, the recovery of the *in situ* formed vanadyl complex often becomes difficulty. To address the issue, much effort has been made to immobilize the chiral oxovanadium (IV) Schiff base complex onto insoluble solid supports [5,6]. Unfortunately, the nature of the insoluble supports often suffers from poor activity and low accessibility of the substrates. Recently, ionic liquids (ILs) bonded to the chiral salen Mn(III) complex have been found to enhance catalysts efficiency and recovery [7,8]. Thus, immobilization of the complex using ILs might provide a means to develop reusable catalysts with high activity.

Herein, a hydrophilic IL of 1-(3-aminopropyl)-3-methylimidazolium tetrafluoroborate was first applied to functionalize the chiral oxovanadium (IV) Schiff base complex. The amphiphilic *IL*-functionalized chiral oxovanadium (IV) Schiff base complex can improve the yield and enantioselectivity of sulfoxides in the asymmetric oxidation of methyl aryl sulfides. Furthermore, a facile product isolation and catalyst recycle were also enjoyed upon introduction of the IL moiety into the chiral oxovanadium (IV) Schiff base complex.

2. Experimental

2.1. Reagents

2-tert-butyl phenol, L-leucinol and methyl aryl sulfides were purchased from Alfa Aesar. Other laboratory grade reagents were obtained from the local suppliers. 1-(3-aminopropyl)-3-methylimidazolium tetrafluoroborate [7], 3-tert-butyl-2-hydroxybenzaldehyde [9], 5-chloromethyl-2-hydroxy-3-nitrobenzaldehyde [10] and 3-tert-butyl-5-chloromethyl-2-hydroxybenzaldehyde [11] were prepared by the procedures described in the literature, respectively.

2.2. Characterizations

Fourier transform infrared (FT-IR) spectra were obtained at 400–4000 cm^{-1} region on an AVATAR 370 Thermo Nicolet spectrophotometer, using KBr pellets. UV–vis spectra were obtained on a UV–vis Agilent 8453 spectrophotometer at 200–800 nm. The contents of vanadium in the samples were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) using a BAIRD PS-6 analyzer.

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2.3. Preparation of IL-functionalized chiral oxovanadium (IV) Schiff base complex **1**, **2,** *and the neat chiral oxovanadium (IV) Schiff base complex* **3**

The procedure for synthesis of the complex **1** and **2** was outlined in Scheme 1.

To a stirred solution of L-leucinol (1.17 g, 10 mmol) in dry ethanol (20 mL), an equivalent amount of 3-tert-butyl-5-chloromethyl-2-hydroxybenzaldehyde or 3-nitro-5-chloromethyl-2-hydroxybenzaldehyde in dry ethanol (20 mL) was added dropwise. The mixture was stirred for 48 h at 0 °C, and then the solvent was evaporated under vacuum. Recrystallization from ethanol gave a yellow solid of CL1 (2.96 g, yield of 91%) or CL2 (2.74 g, yield of 87%).

A solution of the CL1 (2.61 g, 8 mmol) or CL2 (2.52 g, 8 mmol) and an equivalent amount of IL in dry toluene (20 mL) was refluxed for 48 h under nitrogen protection. After cooled to 5 °C overnight, the obtained compound was collected by removal of toluene, washed completely with hexane. Drying in vacuum gave a deep yellow solid of IL-CL1 (3.4 g, yield of 82%) or IL-CL2 (3.09 g, yield of 79%).

To a stirred solution of the IL-CL1 (2.58 g, 5 mmol) or IL-CL2 (2.52 g, 5 mmol) in dry methnol (20 mL), VO(acac)$_2$ (1.22 g, 3.5 mmol) in dry methnol (15 mL) was added dropwise at 40 °C under nitrogen protection. The mixture was stirred for 1 h, and then heated to reflux for additional 8 h. After exposed to air overnight, the above mixture was cooled to 5 °C for 2 h, filtered and washed with 50 mL of water and 50 mL of hexane. The obtained solid was dried under vacuum at 40 °C to give a light brown powder of *IL*-functionalized chiral oxovanadium (IV) Schiff base complex **1** (2.51 g, 86%) or complex **2** (2.74 g, 83%).

The structure identification of the synthesized ligands of CL1, CL2, IL-CL1, IL-CL2, as well as the complex **1** and **2** were presented in supplementary information.

The neat chiral oxovanadium (IV) Schiff base complex **3** was synthesized according to the above similar method.

2.4. Asymmetric oxidation of the methyl aryl sulfides

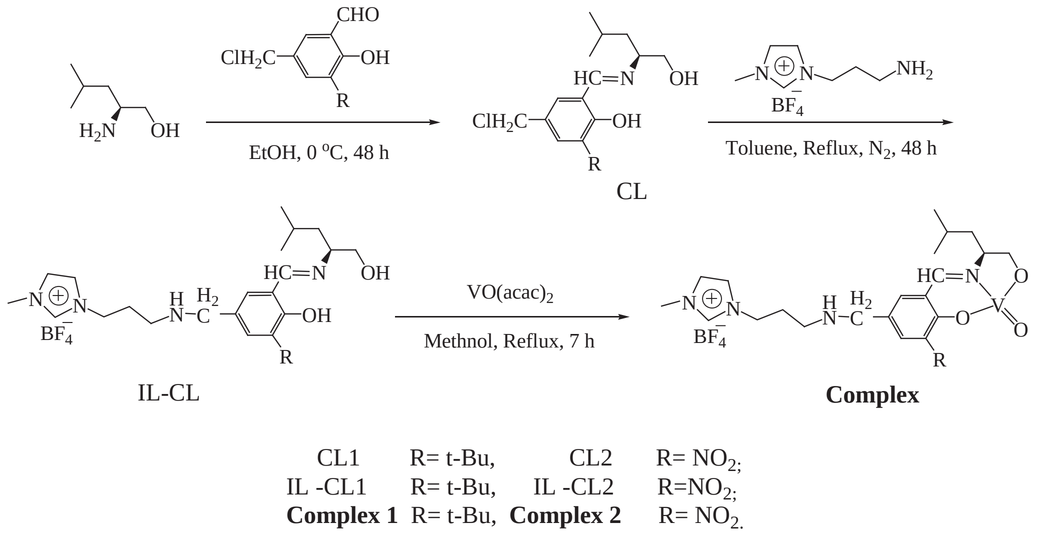
Methyl aryl sulfide (1 mmol) was added into the mixture of catalyst (0.02 mmol) and dichloromethane (1 mL) at 20 °C under stirring. Aqueous 30% H_2O_2 (0.17 g, 1.5 mmol) was added dropwise. Gas chromatography (Agilent Technologies 6890) was employed to monitor the progress of the reaction. After the reaction, the mixture was extracted with hexane to make the catalyst precipitate out from the reaction system. The combined extract layer was dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 1.5/1, *V/V*) using ethyl acetate as the eluent. The *e.e* value of methyl aryl sulfoxides was determined by HEWLETT PACKARD SERIES 1050 HPLC analysis with chiral columns of Daicel Chiracel OD-H or OB-H (0.46 cm i.d. × 25 cm) using hexane/ i-PrOH as eluent according to the method presented in supplementary information.

3. Results and discussions

3.1. Preparation and characterization of samples

As described in Scheme 1, the tridentate chiral Schiff base ligand (CL) was prepared by the condensation of the substituted salicylaldehydes with optical L-leucinol. Then, the –CH_2Cl group in the resultant CL was reacted with –NH_2 of the IL to give the *IL*-functionalized chiral Schiff base ligand (IL-CL). Lastly, the IL-CL was treated with VO(acac)$_2$ under nitrogen, and then exposed to air overnight to afford the expected *IL*-functionalized chiral oxovanadium (IV)-Schiff-base complexes **1** and **2**.

The synthesized *IL*-functionalized complexes **1** and **2**, as well as the neat complex **3**, were characterized by FT-IR and UV–vis spectra (Figs. 1 and 2). It was found that the *IL*-functionalized complex **1** displayed the υ(V=O) stretching band at 996 cm^{-1}, the υ(O–Ph) stretching band at the range of 1290–1320 cm^{-1}, and the υ(C=N) stretching band at 1628 cm^{-1} , respectively [12], which were in agreement with the neat complex **3** (Fig. 1b vs.Fig. 1a). While, in the case of the complex **2**, theυ(C=N) and the υ(V=O) stretching band shifted to 1634 cm^{-1} and 974 cm^{-1} due to the electron-withdrawing effect of the nitro group in the aryl group (Fig. 1c). It has been reported that the oxovanadium (IV) complexes with coordination numbers 5 and 6 haveυ(V=O) values higher than and lower than about 990 cm^{-1}, respectively [13]. As shown in Fig. 1, the complex **1** in the solid state should be penta coordinated oxovanadium (IV) complex due to theυ(V=O) stretching band at 996 cm^{-1}. The complex **2**, whose υ(V=O) value is around 974 cm^{-1}, should be hexa-coordination in the solid state. The neat complex **3** in the solid state exhibited another characteristic band at 820 cm^{-1}, which assigned to V–O–V bond [13]. The result indicated that the neat complex **3** should be dimer in the solid state [14]. Furthermore, the *IL*-functionalized complex **1** and **2** showed additional signals at 621 and 3389 cm^{-1}, assigned to the characteristic bands of imidazole fragment and stretching vibration of N–H group of the second amine group, respectively (Fig. 1a and c) [7]. The second amine should be



Scheme 1. Synthesis and the idealized structure of the complexes **1** and **2.**

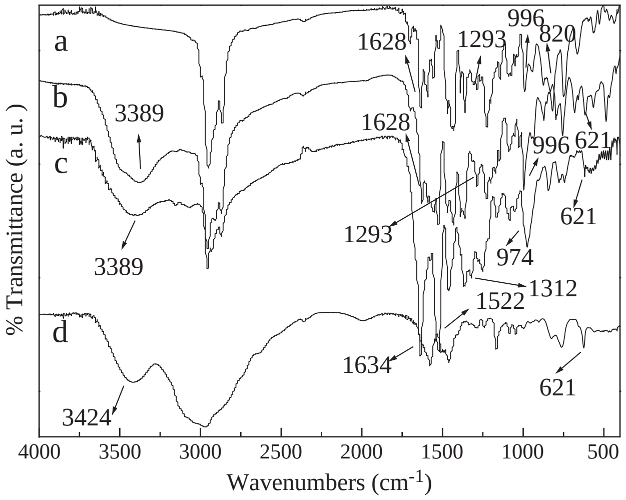
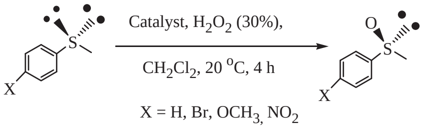


Fig. 1. FT-IR spectra of the neat complex **3** (a), the complex **1** (b), the complex **2** (c), and the IL (d).

Table 1
Results of the asymmetric oxidation of methyl aryl sulfide over various catalysts[a].



Entry	X	Catalyst	Run times	Yield (%)[b]	e.e (%)[c]	TOF[d] × 10^{-3} (s^{-1})
1	H	No	/	2.7	0	/
2	H	The neat Complex **3**	fresh	66	39 (S)	2.3
3	H	Complex **1**	fresh	85	43 (S)	3.0
4	H		2nd	85	43 (S)	3.0
5	H		6th	83	42 (S)	2.9
6	H	Complex **2**	fresh	76	38 (S)	2.6
7	Br	Complex **1**	fresh	87	40 (S)	3.1
8	OCH_3	Complex **1**	fresh	75	39 (S)	2.6
9	NO_2	Complex **1**	fresh	64	32 (S)	2.3

[a] Catalyst (0.02 mmol), substituted sulfide (1 mmol), dropwise addition of aqueous 30% H_2O_2 (0.17 g, 1.5 mmol), 1 mL CH_2Cl_2, 4 h, 20 °C.
[b] Determined by GC.
[c] Determined by HLPC.
[d] Turnover frequency (TOF) is calculated by the expression of (product)/[(catalyst) × time].

formed by the reaction between the end amino group of IL and chloromethyl group of the chiral Schiff base ligand.

The UV–vis electronic spectra of the *IL*-functionalized complex **1** exhibited the benzene ring π–π* transitions at near 274 nm, the d–π transitions from alkoxys oxygen to vanadium (IV) at 367 nm and the d–d transitions between the vanadium (IV) and vanadium (IV) of the complexes at 538 nm (Fig. 2b) [15]. The three distinct peaks were identical with those of the neat complex **3** (Fig. 2a). The observation implied that the active site of the complex **1** was intact provided that the IL was covalently bonded onto chiral Schiff base ligand. However, in the spectrum of the complex **2**, the peaks around 274, 367 and 538 nm shifted to 265, 352 and 443 nm, respectively, due to the strong electron-withdrawing ability of nitro group in the complex **2** (Fig. 2c).

3.2. Catalytic performances

Table 1 showed the catalytic performances of the *IL*-functionalized chiral oxovanadium (IV) Schiff base complexes in the enantioselectivity oxidation of methyl aryl sulfides to sulfoxides. Only 2.7% of methyl phenyl sulfide conversion with racemic sulfoxide (0% *e.e*) was obtained without catalyst (entry 1). In comparison with the neat complex **3**, the complex **1** bearing the hydrophilic IL moiety increased catalytic activity (TOF) and *e.e* value (entry 3 *vs.* 2). The hydrophilic IL moiety and the hydrophobic catalytic species in the complex structure were able to transfer the hydrogen peroxide from aqueous phase to organic phase, which overcame the mass transfer disadvantage. Furthermore, the IL moiety was thought to activate hydrogen peroxide and stabilize the catalytic active sites [16], and therefore enhanced the catalytic activity. A possible mechanism for the catalytic asymmetric oxidation of sulfide by the complex **1** was presented in supplementary information.

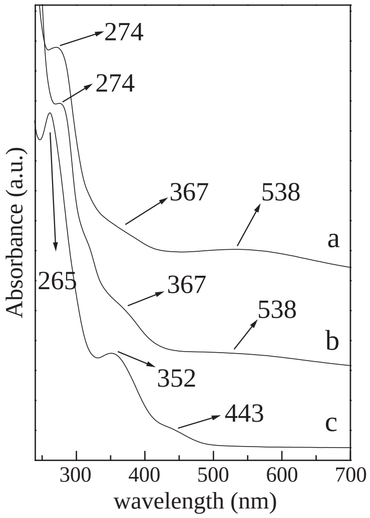


Fig. 2. UV-vis spectra of the neat complex **3** (a), the complex **1** (b), and the complex **2** (c).

The influence of the substitutes at the 3 position of the salicylidenyl moiety of the ligand on the enantioselective oxidation of methyl phenyl sulfide has also been studied. The complex **1** bearing *tert*-butyl group gave better conversion and enantioselectivity than the complex **2** bearing the nitro group (entry 3 vs. 6). The poor performance of catalyst **2** is due to the electron-withdrawing effect as well as the slight steric hindrance of nitro group at the 3-position in the complex **2** [17]. Understandably, the complex **1** was more effective than the complex **2** in the enantioselective oxidation reaction.

The interesting soluble feature of the complexes depends on their inherent tendency to precipitate in n-hexane, since the IL moiety has selective solubility in the solvent. After the reaction, the complex **1** could be recovered conveniently from the reaction system by simply adding n-hexane and used for the subsequent catalytic runs. Table 1 described the reuse of the complex 1 after six catalytic cycles. Obviously, the complex **1** could be reused at least 6 times without significant loss of activity and enantioselectivity (entries 3, 4 and 5). The recovered complex **1** had been characterized by FT-IR spectra which were presented in supplementary information. No significant changes in the FT-IR spectra of the complex **1** had been observed even after reused for six times. The results indicated the stability of the obtained complex **1** towards organic solvents, water and oxidative agents (H_2O_2). In addition, no vanadium leaching was detected in the supernatants extracted from the catalyst separation, which clearly indicated that the complex was readily recyclable from the reaction system and resistant against leaching during the reaction.

More substrates of other methyl aryl sulfides were used to test the catalytic activity of complex **1** (entries 3 vs. 7–9). Surprisingly, the complex **1** was efficient in the oxidation of methyl aryl sulfides having both electron-donating as well as electron-withdrawing substituents with good sulfoxides yield and satisfactory ee values, which indicated the synthetic value of the *IL*-functionalized complex.

4. Conclusions

In summary, a new strategy using IL to functionalize the chiral oxovanadium (IV) Schiff base complexes has been developed. The IL moiety endowed the *IL*-functionalized chiral oxovanadium (IV) Schiff base complex **1** with unique solubility and improved catalytic activity in the catalytic asymmetric oxidation of sulfide. Moreover, the complex could be readily recovered from reaction system by simple precipitation and reused without significant loss of activity and enantioselectivity.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.catcom.2011.06.006.

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