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Stable chiral salen Mn(III) complexes with built-in phase-transfer capability for the asymmetric epoxidation of unfunctionalized olefins using NaOCl as an oxidant

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ABSTRACT

A series of novel chiral salen Mn(III) complexes with inherent phase-transfer capability were prepared by covalent linkage of the limidazolium IL moieties containing various PEG chains with chiral salen ligand at two sides of 5,5′-position. Technologies of characterization well suggested the presence of polyether chain, the IL linker, and the intact active sites in the complexes. The amphipathic nature of the PEG chain allowed the PEG-based catalysts to undergo built-in phase transfer, which in turn increased the reaction rates in water/organic biphasic systems. Enantioselective epoxidation of styrene, α-methylstyrene, indene, 1,2-dihydronaphthalene, 6-cyano-2,2-dimethylchromene, and 6-nitro-2,2-dimethylchromene catalyzed by the complexes with NaOCl gave >99% conversions within 60 min. The enantiomeric excess (*ee*) for the epoxides was in the range of 68–93%, except for styrene (*ee*, 35%) and α-methylstyrene (*ee*, 42%). Furthermore, the PEG-based complexes were stable and could be separated from the reaction mixture by control of the solvent.

1. Introduction

Enantiopure epoxides are very useful synthetic intermediates for the synthesis of fine chemicals and many pharmaceuticals, which can be further converted into many important chiral building blocks via stereoselective ring-opening or functional group transformations [1,2]. The asymmetric epoxidation of unfunctionalized olefins catalyzed by chiral salen Mn(III) complex is one of the most efficient strategies for obtaining enantiopure epoxides [3–15]. Sodium hypochlorite (NaOCl) used as an oxygen source has been drawn much attention in the asymmetric epoxidation of non-functionalized olefins, since it is reasonably stable, readily available, environment friendly, and inexpensive. Kureshy et al. have reported the catalytic asymmetric epoxidation of non-functionalized alkenes catalyzed by dimeric or polymeric chiral salen Mn (III) complexes using NaOCl as an oxidant. Longer reaction time (2.5–10 h) is required due to the limited solubility of the catalysts in the aqueous NaOCl solution, although high epoxide conversions and enantioselectivities were obtained [16,17]. The reaction rates can be increased by the addition of surfactants [18]. Polyethylene glycol (PEG) is commonly used, which enhances mutual solubility or mobility of the components across the phase boundary or increases the concentration of the catalyst to the interface [19]. The phase-transfer capability of PEG is dependent upon the amphipathic nature of the polymer chain with its hydrophobic methylene groups interspersed with ether groups which can compliment the hydrogen bonded structure of water. The remarkable enhancement of reaction rates with the addition of PEG is explained by the assumption of the formation of microcapsule in the water/oil biphasic condition. The microcapsule may act as "microreactors", and thus adjusts the catalyst-substrate orientation similar to that featured in homogenous system.

Furthermore, the chiral salen Mn(III) complexes with built-in phase-transfer capability have been developed for the biphasic condition by introducing the hydrophilic substituents, such as the tertiary amino alkyl group [16,21–24] or methyl (triphenylphosphonium chloride) group [20] into the frame of the salen ligand. This type of complexes showed high epoxidation activity under biphasic condition, but the separation of the catalysts is often unfavorable. We have earlier found that ionic liquids (ILs) with the tunable miscibility can be used as phase tags to facilitate recycling and reuse of the chiral salen Mn(III) catalyst in the asymmetric epoxidation of unfunctionalized olefins [25,26]. Furthermore, the special 'ionophilicity' and polarity of the ILs played positive effects on stabilizing the complex. The microcapsule-forming concept of the PEG and the reusability of the IL-functionalized catalyst encourage us to develop IL containing PEG chain grafted chiral salen Mn(III) complexes, which provides the lipophilic metal

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center, the amphiphilic polyether-long chain, and the hydrophilic IL linker. We envisage that the amphipathic nature of the PEG chain can allow PEG-based catalysts to undergo inherent phase transfer, which is in turn expected to increase the reaction rates in two-phase systems. Furthermore, the solubility properties of the PEG, that is, it is soluble in CH_2Cl_2, but can be precipitated with *n*-hexane, potentially endow the novel complexes with the feature of solvent-regulated separation.

Herein, the N-polyether-substituted imidazol was synthesized and successfully introduced into the two sides of 5,5′ positions in the salen ligand of (R,R)-{N-(3-tert-butyl-5-chloromethyl-salicylidine)-N′-(3′-tert-butyl-5′-chloromethyl-salicylidine)}-1,2-cyclohexanediamine, which provided the imidazolium IL containing polyether chain functionalized chiral salen Mn(III) complex (**PICC**). It has proved that the new catalysts could achieve the process of phase-transfer catalysis (PTC) in the asymmetric epoxidation of unfunctionalized olefins using NaOCl as an oxidant and could be facilely separated for reuse by control of the solvent. Thus, the problems associated with the phase-transfer limitation in the biphasic reaction and the separation of the catalysts can be well resolved. In addition, the total length of polyether chain significantly affected the catalytic performances of the novel complexes.

2. Experimental

2.1. Materials and reagents

(±)-1,2-diaminocyclohexane and 3-chloroperoxybenzoic acid (*m*-CPBA) were purchased from Alfa Aesar. Indene and 1,2-dihydronaphthalene were obtained by TCI. Pyridine-N-oxide (PyNO) was bought from Aldrich. Other commercially available chemicals were laboratory grade reagents from local suppliers. All of the solvents were purified by standard procedures [27]. Styrene and indene were passed through a pad of neutral alumina before use. 6-cyano-2,2-dimethylchromene and 6-nitro-2,2-dimethylchromene were synthesized according to the literature procedures [28]. [(R,R′)-(N,N′-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminato] manganese(III) chloride (the neat complex) was prepared according to the procedures described in Ref. [29]. 3-tert-butyl-2-hydroxybenzaldehyde and 3-tert-butyl-5-chloromethyl-2-hydroxy benzaldehyde were prepared according to the procedures described in Refs. [30,31], respectively.

2.2. Methods

FT-IR spectra were obtained as potassium bromide pellets with a resolution of 4 cm^{-1} and 32 scans in the range 400–4000 cm^{-1} using an AVATAR 370 Thermo Nicolet spectrophotometer. The ultraviolet–visible light (UV–vis) spectra were recorded on a UV–vis Agilent 8453 spectrophotometer. The solution of samples in dichloromethane (*ca.* 1.0 mM) was poured into a 1 cm quartz cell for UV–vis adsorption with dichloromethane as the reference. The thermogravimetric and differential thermogravimetric (TG–DTG) curves were obtained on a NETZSCH STA 449C thermal analyzer. Samples were heated from room temperature up to 700 °C under flowing air using alumina sample holders. The sample weight was *ca.* 10 mg and the heating rate was 10 K/min. ^{1}H NMR spectra of samples were recorded on a Varian-500 spectrometer with TMS as an internal standard. Thin layer chromatography (TLC) was conducted on glass plates coated with silica gel GF_{254}. Mn ion contents were measured by the method of complexometry with ethylenediamine tetraacetic acid (EDTA) according to Ref. [32]. Mass spectrometry analyses were performed using an API 3000 tandem mass spectrometer (Applied Biosystems, USA) with electrospray interface (ESI-MS/MS in MeOH). The operating conditions in positive ionization mode were optimized using a +5500 V ion spray voltage, 8 psi for curtain gas, 8 psi for drying gas heated to 100 °C, 7 psi for nebulizing gas, respectively. The optical rotation of catalysts was measured in dichloromethane on a WZZ-2A Automatic Polarimeter. The conversions and the *ee* values were measured by a 6890 N gas chromatograph (Agilent Co.) equipped with the chiral capillary column (HP19091G-B213, 30 m × 0.32 mm × 0.25 μm) and the FID detector.

2.3. Preparation of PICC-n (n = 5, 15, 25)

The preparation of **PICC-n** (*n* = 5, 15, 25) was outlined in Scheme 1.

2.3.1. Synthesis of N-polyoxyethyleneimidazole A

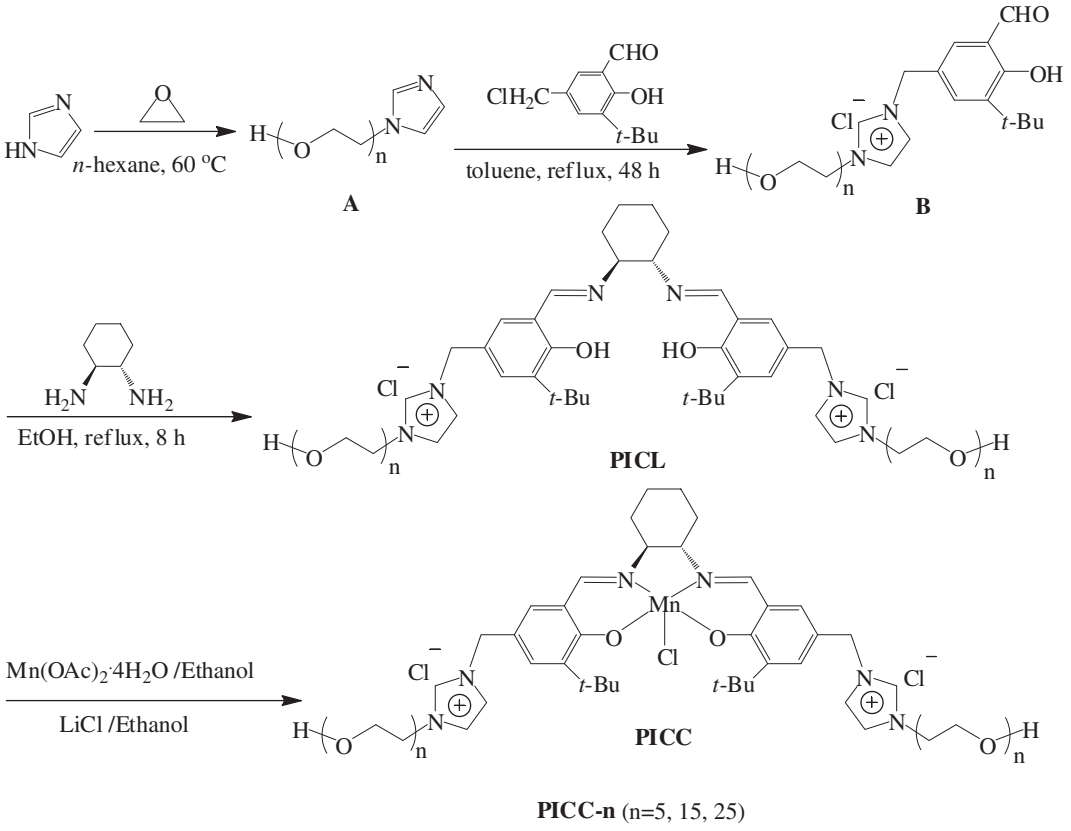
Frozen imidazole (1.7 g, 25 mmol) and *n*-hexane (15 mL) were added into an autoclave (100 mL). Different amount of the frozen ethylene oxide liquid (EO, 10 mL for *n* = 5; 20 mL for *n* = 15; 30 mL for *n* = 25) was subsequently added into the autoclave with a magnetic stirrer. The resulted mixture was kept at room temperature under N_2 overnight, and then stirred for 5 h at 60 °C. After removing solvent, the mixture was dried under vacuum to afford the compound **A** as a dark brown viscous liquid. The average numbers of ethylene oxide unit of the polyether chain were calculated from the weight increase of products [33]. Compound **A** (*n* = 15): ^{1}H NMR (D_2O, 500 MHz) δ_H, ppm: 7.65 (s, 1H, ring NC*H*N), 7.15 (s, 1H, ring C═NC*H*), 6.96 (s, 1H, ring N—C═C*H*), 4.15 (t, 2H, *J* = 10 Hz, O—CH_2—CH_2—N_{ring}), 3.55–3.63 (m, 58H, H(O—C_2H_4—O)$_{14}$ CH_2). FT-IR (KBr): γ_{max}/cm^{-1} 3369, 2871, 1655, 1510, 1455, 1351, 1291, 1249, 1107, 947, 887, 833, 747, 668, 626.

2.3.2. Synthesis of modified salicylaldehyde B

N-polyoxyethylene imidazole **A** (10 mmol) in dry benzene (20 mL) was added dropwise into the benzene solution of 3-tert-butyl-5-chloromethylsalicylaldehyde (10 mmol, 2.27 g) under stirring. The obtained mixture was refluxed for 48 h. After the completion of the reaction, the lower viscous liquid was washed three times with dry benzene. The solvent was removed to obtain the compound **B** as the dark brown viscous liquids. Compound **B** (*n* = 15): ^{1}H NMR (D_2O, 500 MHz) δ_H, ppm: 9.76 (s, 1H, C*H*═O), 7.48–7.60 (m, 5H, ring NC*H* and Ar*H*), 5.33 (s, 2H, Ar—CH_2—N_{ring})), 4.34 (t, 2H, *J* = 9.8 Hz, O—CH_2—CH_2—N_{ring}), 3.48–3.82 (m, 58H, H(O—C_2H_4—O)$_{14}$$CH_2$), 1.11–1.28 (s, 9H, t-butyl). FT-IR (KBr): γ_{max}/cm^{-1} 3378, 2948, 2873, 1647, 1560, 1440, 1351, 1390, 1323, 1272, 1238, 1213, 1188, 1106, 946, 887, 835, 775, 705, 528.

2.3.3. Synthesis of the PEG-IL-functionalized chiral salen ligand (PICL)

(1*R*, 2*R*)-(−)-1, 2-diaminocyclohexane mono-(+)-tartrate salt (2.5 mmol, 0.660 g) was treated with saturated potassium hydroxide (5.0 mmol, 0.280 g) in 20 mL dichloromethane under vigorously stirring at room temperature. The resulted cloudy mixture was stirred for another 2 h. The liberated diamine was dried over anhydrous Na_2SO_4. After removal of the solvent in vacuum, the (1*R*, 2*R*)-(−)-1, 2-diaminocyclohexane was dissolved in anhydrous ethanol and added dropwise into the solution of PEG-IL modified salicylaldehyde **B** (5 mmol) in anhydrous ethanol (10 mL) at room temperature. The resulting mixture was refluxed for another 8 h to synthesize the PEG-IL-functionalized chiral salen ligand (**PICL**). **PICL** (*n* = 15): ^{1}H NMR (D_2O, 500 MHz): δ_H, ppm: 8.35 (s, 2H, C*H*═N), 7.02–7.57 (s, 10H, ring NC*H* and Ar*H*), 5.42 (s, 4H, Ar—CH_2—N_{ring}), 4.60 (m, 4H, O—CH_2—CH_2—N_{ring}), 3.66–3.91 (m, 116H, H(O—C_2H_4—O)$_{14}$$CH_2$), 3.60–3.62 (m, 2 H, C═NC*H*), 1.44–1.83 (m, 8H, cyclohexyl-*H*), 1.20–1.28 (s, 18H, t-butyl). FT-IR (KBr): γ_{max}/cm^{-1} 3341, 2941, 2868, 1629, 1445, 1353, 1246, 1211, 1105, 942, 842, 776, 649.



Scheme 1. Synthesis of the catalysts of **PICC-n** (n = 5, 15, 25).

2.3.4. Synthesis of PICC-n (n = 5, 15, 25)

Under nitrogen protection and stirring at 50 °C, a solution of $Mn(OAc)_2{\cdot}4H_2O$ (5 mmol, 1.225 g) in anhydrous ethanol (20 mL) was added dropwise into the above-obtained PICL solution. The resulting brown mixture was refluxed for 12 h, then cooled to room temperature, followed by addition of solid LiCl (12 mmol, 0.504 g), and stirred for additional 5 h. The mixture was bubbled with a gentle stream of air for another 2 h, and then exposed to air overnight. After removal of the solvent in vacuum, the mixture was washed with ether for several times. The gummy residue was dissolved in dichloromethane (100 mL). The organic phase was washed with saturated sodium chloride and dried over anhydrous Na_2SO_4, and then dried at 40 °C in vacuum to obtain the sticky-brown products **PICC-n** (where n is the average numbers of ethylene oxide unit in the PEG chains, n = 5, 15, 25). The **PICC** containing the average numbers of ethylene oxide unit in the PEG chains of 5, 15, and 25 were denoted as **PICC-5, PICC-15,** and **PICC-25**, respectively. **PICC-5**: FT-IR (KBr): γ_{max}/cm^{-1} 3390, 2918, 2867, 1616, 1545, 1519, 1457, 1388, 1348, 1307, 1246, 1205, 1108, 1035, 946, 834, 570, 481, 420; UV–vis (CH_2Cl_2): λ_{max}/nm (ε_{max}/L mol^{-1} cm^{-1}) 506 (1594), 410 (4681), 322 (13,218); Mn ion content: 1.02 mmol/g; $\alpha_D^{25} = +960$ (C = 0.02, CH_2Cl_2); ESI-MS: m/z = 488 (M-2(CH_2 + IL))$^+$. **PICC-15**: FT-IR (KBr): γ_{max}/cm^{-1} 3390, 2918, 2867, 1616, 1545, 1519, 1457, 1388, 1348, 1307, 1246, 1205, 1108, 1035, 946, 834, 570, 481, 420; UV–vis (CH_2Cl_2): λ_{max}/nm (ε_{max}/L mol^{-1} cm^{-1}) 506 (1589), 410 (3929), 322 (12,930); Mn ion content: 0.48 mmol/g; $\alpha_D^{25} = +955$ (C = 0.02, CH_2Cl_2); ESI-MS: m/z = 488 (M-2(CH_2 + IL))$^+$. **PICC-25**: FT-IR (KBr): γ_{max}/cm^{-1} 3390, 2918, 2867, 1616, 1545, 1519, 1457, 1388, 1348, 1307, 1246, 1205, 1108, 1035, 946, 834, 570, 481, 420; UV–vis (CH_2Cl_2): λ_{max}/nm (ε_{max}/L mol^{-1} cm^{-1}) 506 (2015), 410 (6563), 322 (13,756); Mn ion content: 0.34 mmol/g; $\alpha_D^{25} = +950$ (C = 0.02, CH_2Cl_2); ESI-MS: m/z = 488 (M-2(CH_2 + IL))$^+$.

2.4. Preparation of the IL-complex

For comparison, the 1-methyl-3-methyleneimidazolium chlorine-functionalized chiral salen Mn(III) complex (denoted as IL-complex) was also prepared by the similar preparation procedure of **PICC-n** (n = 5, 15, 25). During the procedure, N-methylimidazole was used instead of the material of N-polyoxyethyleneimidazole. The structures of the IL-complex and the neat complex were shown in Chart 1.

2.5. Catalyst testing

The catalysts of the **PICC-n** (n = 5, 15, 25) (4 mol%), unfunctionalized alkene (0.25 mmol), and PyNO (0.05 mmol, 0.0005 g) were added into 1 mL dichloromethane under stirring. The buffered NaOCl as an oxidant (0.5 mmol, pH = 11.5) was added in four equal portions at 0 °C. The progress of the epoxidation reaction was monitored on GC. After the reaction, the reaction mixture was separated by separatory funnel. The aqueous phase was extracted with CH_2Cl_2 for several times. The extract was combined with the organic phase, and dried over anhydrous sodium sulfate. After the evaporation of volatile solvents, the catalysts of **PICC-n** (n = 5, 15, 25) could be separated from the mixture by the addition of n-hexane. The upper organic phase with the epoxides was separated from the lower polyether-based catalyst by simple decantation. Further purification of the n-hexane layer by flash column chromatography afforded the epoxides. The conversions and *ee* values were measured by a 6890N gas chromatograph (Agilent Co.) equipped with the chiral capillary column (HP19091G-B213, 30 m × 0.32 mm × 0.25 μm) and the FID detector. The retention times of the corresponding epoxides are as follows: (a) styrene epoxide: T = 90 °C, t_R = 15.2 min, t_S = 15.7 min; (b) α-methylstyrene epoxide: T = 80 °C, t_S = 16.3 min, t_R = 16.5 min; (c) indene epoxide:

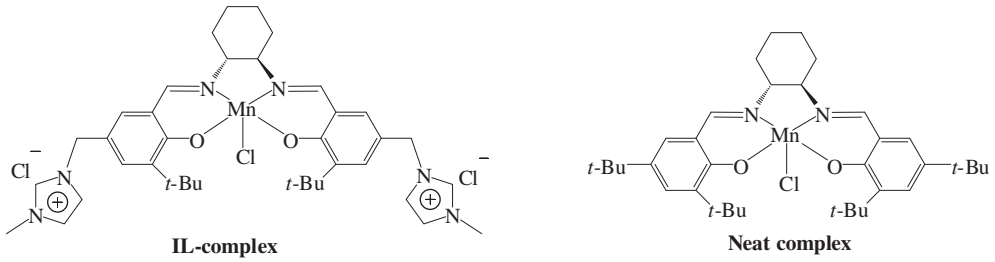


Chart 1. The structures of the IL-complex and the neat complex.

T = 80–180 °C, t_{SR} = 11.5 min, t_{RS} = 11.9 min; (d) 1,2-dihydronaphthalene epoxide: T = 80–180 °C, t_{SR} = 13.4 min, t_{RS} = 13.6 min; (e) 6-cyano-2,2′-dimethylchromene epoxide: T = 80–200 °C, t_{SS} = 24.0 min, t_{RR} = 24.3 min; (f) 6-nitro-2,2′-dimethylchromene epoxide: T = 80–200 °C, t_{SS} = 30.3 min, t_{RR} = 30.8 min. The lower catalyst could be recycled by adding fresh solvents and reaction substrates.

3. Results and discussion

3.1. Preparation and characterization of PICC-n (n = 5, 15, 25)

We have found that the ILs derived from N,N-dialkylimidazolium can stabilize the chiral salen Mn(III) complex during the process of the epoxidation or can act as a modifier that accelerates the reaction and enhances the selectivity [25,26]. Thus, we chose IL containing imidazolium moiety as the linker to combine the chiral salen Mn(III) complex with the polyether chain. A strategy that we have designed here is to append covalently the limidazolium IL moieties containing PEG chain at two sides of 5,5′ position in the salen ligand to make the PEG-based IL-functionalized chiral ligand (**PICL**) resemble PEG.

The synthesis route for the **PICC-n** (n = 5, 15, 25) was outlined in Scheme 1. At first, N-polyoxyethyleneimidazole (**A**) with different numbers of polymerized ethylene oxide unit (n = 5, 15, 25), which was provided by ethoxylation between imidazol and ethylene oxide, directly reacted with 3-tert-butyl-5-chloromethyl-2-hydroxybenzaldehyde to afford PEG-based IL-substituted 3-tert-butyl-2-hydroxybenzaldehyde (**B**). The successive condensation between the aldehyde (—CHO) group of the compound **B** and the amino ($—NH_2$) groups of (R,R′)-1,2-cyclohexanediamine was used to form the **PICL**. Treatment of the **PICL** with manganese (II) acetate tetrahydrate under nitrogen gave the dianionic complex. The acetic ion was replaced by chloride ion with lithium chloride at room temperature. The dianionic complex was readily oxidized by oxygen, affording the **PICC-n** (n = 5, 15, 25). The catalysts newly synthesized are brown and viscous liquids at room temperature. The viscosity increases with the length of polyether chain.

The numbers of ethylene oxide unit of the polyether chain were determined on the basis of the weight increase amount of imidazol after ethoxylation and the molecular weight of one ethylene oxide unit [33]. It is interested that all the **PICC-n** (n = 5, 15, 25) is soluble in water at room temperature. We speculated that the water-solubility of the complex was related with the total length of polyether chain. Moreover, it is also found that the **PICC-n** (n = 5, 15, 25) are miscible in some organic solvents, *e.g.,* CH_2Cl_2 and DMF, but can be precipitated with other organic solvents, *e.g.,* Et_2O and n-hexane. It is suggested that the amphipathic **PICC-n** (n = 5, 15, 25) should be an easily recoverable catalyst for asymmetric epoxidation of alkenes by simple phase separation techniques *via* change of solvents.

3.2. Characterization of samples

3.2.1. FT-IR spectra

The synthesized **PICC-n** (n = 5, 15, 25), as well as the neat chiral salen Mn(III) complex for comparison, were characterized by FT-IR spectra (Fig. 1). The FT-IR spectra of the neat complex show characteristic vibration bands at around 1613, 1535, 569, and 413 cm^{-1}, which are associated with the stretching vibration modes of C═N, C—O, Mn—O, and Mn—N, respectively (Fig. 1a) [25,26,34], while the characteristic bands in the FT-IR spectra of **PICC-n** (n = 5, 15, 25) appear as red shift from 1613 cm^{-1}, 1535 cm^{-1}, 569 cm^{-1}, and 413 cm^{-1} to 1616 cm^{-1}, 1545 cm^{-1}, 570 cm^{-1}, and 420 cm^{-1}, respectively, compared with those of neat complex (Fig. 1b–d vs. a). It is mainly due to the election-deficient substitutes of the imidazolium cations at the 5,5′-positions in the salen ligands [10]. The new stretching vibration ν(C—N) of C—N bond at around 1457 cm^{-1} further suggests the grafting of imidazolium IL moiety on the salen ligand (Fig. 1b–d). In addition, the FT-IR spectra of the **PICC-n** (n = 5, 15, 25) show another new bands at 1108 cm^{-1}, which is assigned to stretching vibration of C—O—C groups in the PEG chain [35]. The very broad band centered at 3390 cm^{-1} is assigned to the terminal hydroxyl group of the PEG chains for the **PICC-n** (n = 5, 15, 25) (Fig. 1b–d). The results suggest that the neat complex is functionalized by the PEG modified-imidazolium IL through covalent bonds, and the functionalization presented here does not change the structure of catalytic active sites.

3.2.2. UV–vis spectra

Fig. 2 showed UV–vis spectra of the **PICC-n** (n = 5, 15, 25) and neat chiral salen Mn(III) complex. UV–vis spectra give more obvious evidence for the successful grafting based on the fact that

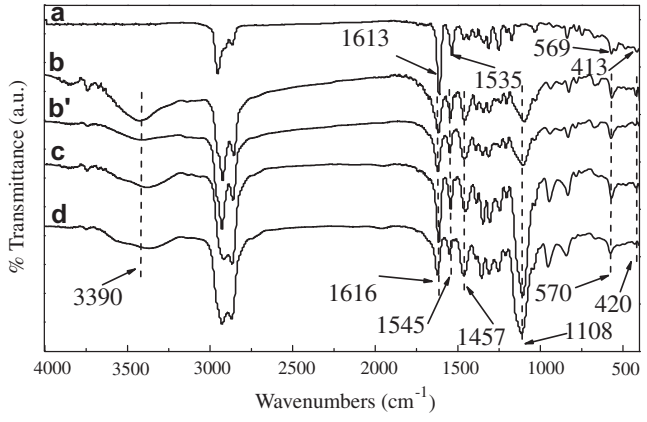


Fig. 1. FT-IR spectra of the neat complex (a), **PICC-5** (b), the recovered **PICC-5** after the 5th reuse in the aqueous NaClO oxidant system at 0 °C (b′), **PICC-15** (c), and **PICC-25** (d).

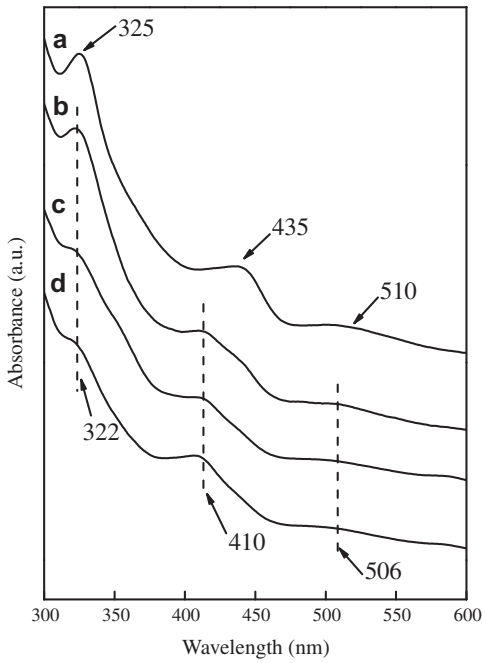


Fig. 2. UV–vis spectra of the neat complex (a), **PICC-5** (b), **PICC-15** (c), and **PICC-25** (d).

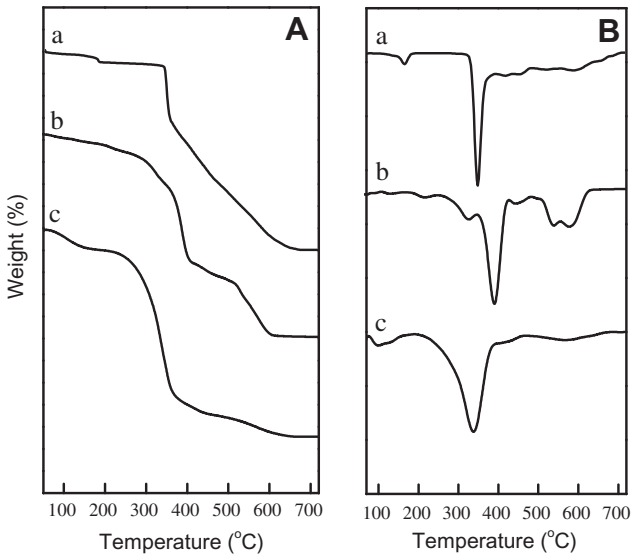


Fig. 3. Thermogravimetric (A) and differential thermogravimetric (B) results of the neat complex (a), **PICC-15** (b), and N-polyoxyethyleneimidazole (c).

the characteristic bands of the neat complex at around 325, 435, and 510 nm are shifted to 322, 410, and 506 nm for **PICC-n** (n = 5, 15, 25), respectively (Fig. 2a vs. b–d). The band at 322 nm is due to the charge transfer transition of the salen ligand, the band at 410 nm is due to the ligand-to-metal charge transfer transitions in the chiral salen Mn(III) complex, and the band at 510 nm is due to the metal-to-metal charge transfer band between the chiral salen Mn(III) complexes [36]. The shifts of the characteristic band also show the presence of the imidazolium cations at 5,5′ positions.

3.2.3. Thermal analysis

Thermal analysis had been used to monitor the decomposition profiles of the neat complex as well as PEG-IL grafted complex of **PICC-15**, and the results obtained are depicted in Fig. 3. The neat complex shows two distinct steps of weight loss in the combined TG–DTG curves (Fig. 3a). The first loss in weight centers at 160 °C. As mentioned, this weight loss is due to a release of chloride anions as hydrogen chloride. A second large weight loss appeared at 350 °C, which is assigned to the successive cleavage of the salen ligand moieties. The decomposition profiles of the neat complex get complete at 400 °C with the residues amounting to manganese oxides. Fig. 3b displays the TG–DTG curves of **PICC-15**, in which four major weight losses are observed. The first weight loss centered at 335 °C is logical to assign to the decomposition of the polyether chain parts of the **PICC-15**, since the N-polyoxyethyleneimidazole shows similar major weight loss at around 340 °C (Fig. 3c). Notably, the temperature of the successive cleavage of the salen ligand moieties in the **PICC-15** gets increased up to 390 °C, due to the mutual stabilization of the salen ligand part and the ILs moieties. It is indirect proof for the successful grafting of PEG-ILs moiety on the chiral salen ligand. The third weight loss appeared 556 °C and was followed by an additional weight loss at 594 °C which extended up to *ca.* 628 °C. The two steps were well distinguished in the corresponding DTG curve. We tentatively assigned these steps to the complete decomposition of the ILs. The non-removable residue belonged to the formation of manganese oxide in air atmosphere at high temperature [37,38].

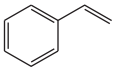
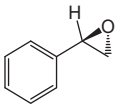
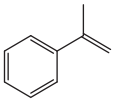
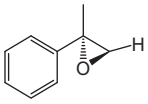
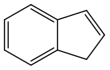
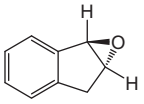
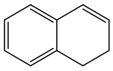
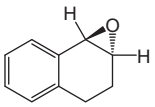
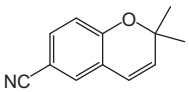
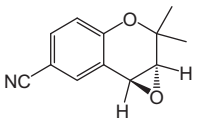
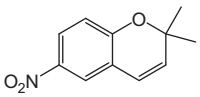
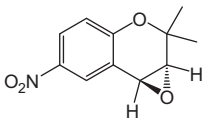
3.3. Catalytic performances

Since the complexes of **PICC-n** (n = 5, 15, 25) are miscible in dichloromethane, we chose dichloromethane as reaction medium in the asymmetric epoxidation. The results of the enantioselective epoxidation of different substrates at 0 °C, using **PICC-n** (n = 5, 15, 25) as catalysts and aqueous NaOCl as oxygen source in dichloromethane, are summarized in Table 1. To investigate the built-in phase-transfer capability originated the PEG moiety, the PEG-free counterpart (denoted as **IL-complex**) was prepared as the control catalyst by introducing the IL of 1-methyl-3-methyleneimidazolium chlorine salt into the two sides of 5,5′ positions in the salen ligand.

As expected, the catalyst of IL-complex offered higher conversion than neat complex (Table 1, entry 2 vs. 1) due to the positive effect of the IL moieties derived from N,N-dialkylimidazolium on enhancing the catalytic activity of chiral salen Mn(III) complex [25,26]. However, we noticed that the catalyst of IL-complex was far less active than the catalysts of **PICC-n** (n = 5, 15, 25) (Table 1, entry 2 vs. entries 3–5). Using aqueous NaOCl as oxygen source, the novel complexes gave excellent conversions (in the range of 80–99%) with 35% enantioselectivity (*ee* values) in the asymmetric epoxidation of styrene at 0 °C within 40 min (Table 1, entries 3–5). While the IL-complex gave only 72% conversion of the styrene under the identical reaction conditions (Table 1, entry 2). The **PICC-n** (n = 5, 15, 25) catalysts bearing the amphipathic PEG chains indeed showed the phase-transfer capability in the dichloromethane/water biphasic reaction. Besides their amphiphilicity, the remarkable enhancement of reaction rates with the employment of the **PICC-n** (n = 5, 15, 25) catalysts might be due to their ether groups in PEG chain as well, which can transport the real oxidant HOCl from aqueous to organic phase through the formation of hydrogen bonds. Slightly lower *ee* value (35%) upon the **PICC-n** (n = 5, 15, 25) and the IL-complex is due to the variation of the electronic nature of the 5,5′-substituents of the ligand (Table 1, entries 2–5). Complex bearing electron-deficient substituents, such as imidazolium cations, at the 5,5′-positions afford slight lower *ee* value [39]. The result provided further proof for successful grafting.

Furthermore, Table 1 also showed that various length of polyether chain of **PICC** has crucial effects on the catalytic activity of the corresponding complex in dichloromethane/water biphasic

Table 1
The results of the enantioselective epoxidation of styrene over different chiral salen Mn(III) complexes[a].

Entry	Catalyst	Substrate	Product	t (min)	Conv. [b] (%)	ee [b] (%)	Yield [c] (%)	TOF [d] $\times 10^{-3}$ (s^{-1})
1	Neat complex			40	65	39	60	6.77
2	IL-complex			40	72	35	66	7.50
3	**PICC-5**		 *(R)*	40	>99	35	93	10.42
4	**PICC-15**			40	92	35	88	9.58
5	**PICC-25**			40	80	35	75	8.33
6	Neat complex			30	75	45	68	10.42
7	**PICC-5**		 *(R)*	30	>99	42	92	13.89
8	Neat complex			60	70	70	63	4.86
9	**PICC-5**		 *(1R, 2S)*	60	>99	68	95	6.94
10	Neat complex			60	65	80	61	4.51
11	**PICC-5**		 *(1R, 2S)*	60	>99	78	96	6.94
12	Neat complex			60	55	95	49	3.82
13	**PICC-5**		 *(3R, 4R)*	60	>99	93	94	6.94
14	Neat complex			60	55	95	50	3.82
15	**PICC-5**		 *(3R, 4R)*	60	>99	93	93	6.94

[a] Reaction condition: catalyst (0.01 mmol), substrate (0.25 mmol), PyNO (0.05 mmol), NaOCl (0.5 mmol, added in four equal parts), CH_2Cl_2 (1 mL), $T = 0$ °C.
[b] Determined by GC.
[c] Isolated yields.
[d] Turnover frequency (TOF) is calculated by the expression of [product]/[catalyst] × time (s^{-1}).

reaction. Clearly, the **PICC-5** showed the highest catalytic activity, which gave the styrene epoxide in quantitative conversions with 35% *ee* value within 40 min (Table 1, entry 3). When the numbers of ethylene oxide unit of the polyether chain increased from 5 to 15, and further increased to 25, the conversion decreased accordingly (Table 1, entries 3–5). The possible explanation might be that the total length of polyether chain directly affects the inherent phase-transfer capability of the corresponding complex. However, there is no change in enantioselectivity.

Remarkable enhancement of reaction rates with the employment of the **PICC-5** is also observed in the case of the α-methylstyrene, indene, 1,2-dihydronaphthalene, 6-cyano-2,2-dimethylchromene, and 6-nitro-2,2-dimethylchromene, as shown by TOF in Table 1 (Table 1, entries 7, 9, 11, 13, and 15). The TOF values for the **PICC-5** were notably high in the epoxidation of the substrates, which are significant higher than that of the neat complex in the corresponding epoxidations (Table 1, entry 7 vs. 6, entry 9 vs. 8, entry 11 vs. 10, entry 13 vs. 12, entry 15 vs. 14). Excellent conversions (>99%) were obtained with all the alkenes used in this work but the highest chiral induction (93%) was observed for the electron-deficient 6-cyano-2,2-dimethylchromene and 6-nitro-2,2-dimethylchromene (Table 1, entries 13 and 15). The relatively bulkier olefins, such as indene and 1,2-dihydronaphthalene, show the moderate *ee* values (68% and 78%, respectively) (Table 1, entries 9 and 11), while the *ee* values were not encouraging in the case of the terminal-olefins, such as styrene and α-methylstyrene (Table 1, entries 2 and 7).

It is known that the **PICC-5** is selectively soluble in some organic solvents, reaction medium should play a crucial role in the catalytic performance of the **PICC-5** in the asymmetric epoxidation of non-functionalized alkenes. Table 2 summarizes the results of

Table 2
The results of the asymmetric epoxidation of styrene in different solvent over the **PICC-5**[a].

Entry	Solvent	Conv. (%) [b]	ee (%) [b]	TOF [c] $\times 10^{-3}$ (s^{-1})
1	*n*-hexane	34	22 (R)	3.54
2	Ether	38	23 (R)	3.96
3	Dichloromethane	>99	35 (R)	10.42
4	Acetone	71	30 (R)	7.40
5	Acetonitrile	56	27 (R)	5.83
6	Methanol	42	10 (R)	4.38
7	Water	39	3 (R)	4.06

[a] Reaction condition: catalyst (0.01 mmol), styrene (0.25 mmol), PyNO (0.05 mmol), NaOCl (0.5 mmol, added in four equal parts), CH_2Cl_2 (1 mL), $t = 40$ min, $T = 0$ °C.
[b] Same as in Table 1.
[c] Same as in Table 1.

comparative study of the enantioselective epoxidation of styrene over the **PICC-5** catalyst in various solvents.

As shown in Table 2, the epoxidation results for styrene over the **PICC-5** indicated differences in the catalytic activity and enantioselectivity depending on the solvent. The **PICC-5** is difficultly soluble in *n*-hexane and ether, poor conversions and *ee* values were obtained when the reaction was performed in *n*-hexane (34% of conversion with 22% *ee* value) or in ether (38% conversion with the 23% *ee* value) (Table 2, entries 1 and 2). If the **PICC-5** can be dissolved completely in the reaction medium, the conversion and the *ee* value should be high. In the case of dichloromethane, >99% conversion and 35% *ee* could be obtained within 40 min (Table 2, entry 3). However, the catalytic activities of the **PICC-5** were not encouraging in acetone, acetonitrile, methanol, and water (Table 2, entries 4, 5, 6, and 7). The principal explanation for this difference is that the solvent containing oxygen or nitrogen atom with lone electron pair can induce probably coordination with metal center of the chiral salen Mn(III) complex, suppressing the ability of the formation of the active oxygen transfer species (Mn(V)-oxo) in the epoxidation of styrene [40]. Especially, only 39% of conversion with 3% *ee* value was obtained in water (Table 2, entry 7). The lower activity is attributed to the limited solubility of the styrene in the aqueous solution of the catalyst and oxidant, and the poor enantioselectivity is partially due to the solvation of water. Therefore, dichloromethane is a suitable solvent for the catalytic asymmetric epoxidation of styrene presented here, which gave the highest conversion (>99%) and *ee* value (35%).

3.4. Recycling

The solubility of the **PICC-n** ($n = 5, 15, 25$) potentially allows them to combined the advantages of homogeneous catalysis with an easy way of catalyst separation. The PEG-based catalyst could be separated from the reaction mixture by the addition of *n*-hexane. The upper organic phase with the product was separated from the lower PEG-based catalyst by simple decantation. The lower catalyst can be recycled by adding fresh solvents and reaction substrates.

Fig. 4 shows the results of the recovery and reusability of these complexes. Unfortunately, the catalytic activity of the recycled **PICC-n** ($n = 5, 15, 25$) gradually decreased upon successive use mainly due to the leaching loss of the water-soluble complexes in the dichloromethane/water biphasic system, and this was also observed by other groups for similar catalytic system [41,27]. We noticed that the reusability of the **PICC-n** ($n = 5, 15, 25$) was associated with the total length of polyether chain of corresponding complex. The **PICC-5** gave progressive decrease of styrene epoxide conversion (approximately 50%) during the reuse for four times (Fig. 4A), whereas there is only 12% progressive drop in styrene epoxide conversion if **PICC-25** is used as catalyst (Fig. 4C). The retention of *ee* value suggests that there is no apparent change in the catalyst structure during epoxidation reaction. FT-IR spectra of the typical **PICC-5** with fresh and reused five times (see Fig. 1b vs. b′) further confirmed the perfect stability of **PICC-5** during the oxidation presented here. Short reaction time (within 60 min) and low temperature (0 °C) used in our studies would prevent or at least slow catalyst degradation. Furthermore, the imidazolium IL linker moiety plays a positive effect on stabling the complex [25,26].

The **PICC-n** ($n = 5, 15, 25$) should not suffer activity loss, when the complexes are used in the anhydrous catalytic system. To test this hypothesis, 0.01 mmol catalyst was recycled in the asymmetric epoxidation of styrene using *m*-CPBA as an oxidant and using

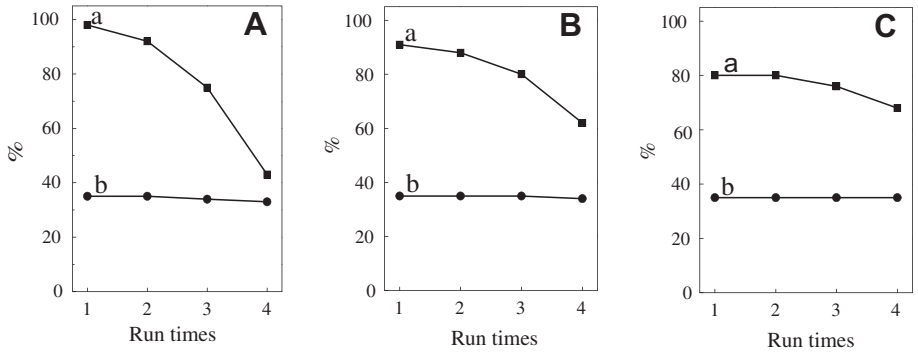


Fig. 4. The reuse of **PICC-5** (A), **PICC-15** (B), and **PICC-25** (C) in the asymmetric epoxidation of styrene with NaClO/PyNO as oxidant system at 0 °C (a: conversion; b: *ee* value).

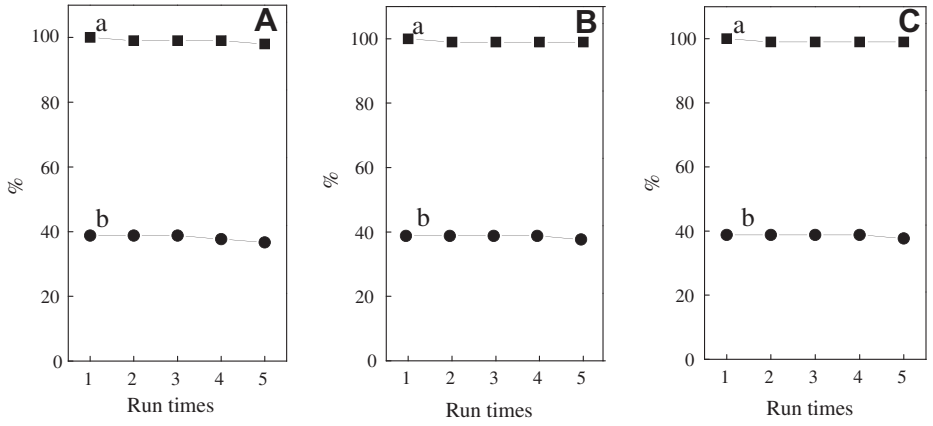


Fig. 5. The reuse of **PICC-5** (A), **PICC-15** (B), and **PICC-25** (C) in the asymmetric epoxidation of styrene with *m*-CPBA/PyNO as oxidant system at 0 °C (a: conversion; b: *ee* value).

dichloromethane as solvent. The conversion and the *ee* value of the epoxide for both runs are summarized in Fig. 5. As seen in the figure, all of the **PICC-n** (n = 5, 15, 25) could be recycled up to five times with no appreciable loss in conversion and enantioselectivity of styrene epoxides. The negligible activity loss of the catalysts upon recycle is completely consistent with the proposed idea that the leaching loss of the water-soluble complexes in the dichloromethane/water biphasic system causes a decrease of the catalytic activity. It is further confirm that the catalysts of **PICC-n** (n = 5, 15, 25) are stable in the epoxidation.

4. Conclusions

In conclusion, chiral salen Mn(III) complexes functionalized by polyether chain-modified-imidazolium IL (**PICC-n** (n = 5, 15, 25)) were first prepared and acted as the inherent phase-transfer catalysts in the enantioselective epoxidation of unfunctionalized olefins with aqueous NaOCl as an oxidant. Remarkable enhancement of the reaction rates was observed over the catalysts of **PICC-n** (n = 5, 15, 25) in the water-CH_2Cl_2 biphasic system due to the built-in phase-transfer capacity originated from the amphiphilic polyether-long chain. Among them, the catalyst of **PICC-5** showed the best catalytic activity, which gave >99% of conversions with 93% of enantioselectivity for the epoxidation of nitro- and cyano-chromene within 60 min. Furthermore, the synthesized **PICC-n** (n = 5, 15, 25) was stable in the epoxidation, since the imidazolium IL linker moiety plays a positive effect on stabling the complex.

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