Epoxidations catalyzed by an ionic manganese(III) porphyrin and characterization of manganese(V, IV)-oxo porphyrin complexes by UV–vis spectrophotometer in ionic liquid solution

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ABSTRACT

An ionic metalloporphyrin of manganese tetrakis-(4-*N*-trimethylaminophenyl)porphyrin hexafluorophosphate ([Mn^{III}TTMAPP][PF$_6$]$_5$, **1c**), resided in the mixed ionic liquids (ILs) of [BzMIM]BF$_4$ and [BMIM]BF$_4$, proved to be an efficient and recyclable catalytic system for styrene (derivative) epoxidations without the involvement of the auxiliary axial ligands. The epoxidation rate in **1c**–IL could be dramatically promoted by addition of water. In the built-up **1c**–IL–H$_2$O system, the active manganese(V)-oxo porphyrin intermediate (**1d**, 444 nm) was stabilized to facilitate its detection by a UV–vis spectrophotometer. And the formation of the μ-oxo Mn(IV) porphyrin dimer (**1e**, 416 nm) was completely suppressed due to the counteraction between **1c** and the IL.

1. Introduction

The development of metalloporphyrin catalysts is inspired by biological systems such as cytochrome P450 family of monooxygenases [1]. The heart of the native enzyme of P450s is an iron porphyrin, which serves as the reactive site of oxygen activation and transfer. Thus, the interest in mimicking P450 chemistry with abiotic systems is focused on constructions of novel metalloporphyrin systems and investigations toward the elucidation of the mechanism [1–3]. Manganese porphyrins have been described as good catalysts for alkene epoxidations [1,4]. In most cases, the catalytic behaviour is believed to derive from a hypervalent manganese(V)-oxo porphyrin species, which has been suggested as the active intermediate in charge of oxygen activation and transfer [5–8]. Anyway, the active manganese(V)-oxo porphyrin complexes are few and their intermediacy has long been implicated from reactivity patterns and ^{18}O-exchange into products from water [5–10]. The most encouraging work on characterization of manganese(V)-oxo porphyrin complexes was achieved by Groves et al., using the rapid-mixing stopped-flow UV–vis spectrophotometer, with the ionic manganese porphyrin as the pre-catalyst and the phosphate as the buffer [8]. On the other hand, suppression of the formation of the low reactive μ-oxo Mn(IV) porphyrin dimmer coming from π–π interaction of porphyrin itself has been explored by introduction of bulky and/or electronegative substituents into the porphyrino ring to improve the activity and stability of manganese porphyrins [11–13]. The techniques of metalloporphyrin immobilization on mesoporous molecular sieve (MCM-41) [14], Merrifield's peptide resin [15], or highly cross-linked polymer [16], are also proved to be good means toward oxidative degradation/self aggregation of metalloporphyrins due to efficient porphyrin site-isolation. Anyway, these heterogeneous catalyses showed quite slow reaction rate, owing to mass transfer interface.

It is noteworthy that, in a metalloporphyrin system, the axial ligand plays an important role for the pre-catalyst activation and oxygen-transfer to the substrates. The nature of the added axial ligand greatly influenced the product distribution, the rate of the overall reaction, and the stability of the catalyst toward degradation [17]. The conventional axial ligands like pyridine/imidazole or their derivatives could stabilize metalloporphyrins, and promote the catalytic reaction in a selective and desirable manner. However, the strategy of adding exogenous axial ligands led to the formation of inactive 6-coordinate bis-ligated complexes, which may result in retardation for reaction rates. Another problem is the sacrifice of axial ligands by the oxidants, which is the reason for excess amount of axial ligands required [18].

Inspired by the efficient activity of metalloporphyrin towards alkene epoxidations, remarkable roles of the axial ligands, and the attractive features of ionic liquids (ILs), we incorporated the quaternized ammonium tags into a neutral manganese porphyrin (tetrakis(4-*N*-dimethylaminophenyl)porphyrin, Mn^{III}TDMAPP, **1a**),

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along with PF_6^- as the counterions, to achieve an ionic manganese porphyrin of tetrakis-(4-N-trimethylaminophenyl) porphyrin hexafluorophosphate ([Mn^{III}TTMAPP][PF$_6$]$_5$, **1c**), which could be compatibly dissolved in the ILs ([BzMIM]BF$_4$, 1-benzyl-3-methylimidazoulim tetrafluoroborate; [BMIM]BF$_4$, 1-n-butyl-3-methylimidazoulim tetrafluoroborate [19]) (Scheme 1). The resultant ionic **1c**–IL system, triply as the catalyst, the solvent and the axial ligand, was investigated onto the epoxidations of styrene and its derivatives. The formation of an active manganese(V)-oxo porphyrin intermediate (**1d**) and μ-oxo Mn(IV) porphyrin dimer (**1e**), derived from the oxidation of **1c** by PhIO, was characterized by a UV–vis spectrophotometer.

2. Experimental

2.1. Measurement and analysis

The ^{1}H NMR (500 MHz, 298 K) spectra were recorded on a Bruker Avance 500 spectrometer. The elemental analyses were performed by the Analytical Center in ECNU (Elementar Vario EL III). GC analyses were performed on a SHIMADZU-14B chromatography equipped with HP-1 capillary column (30 m × 0.25 mm). GC-MS analyses were recorded on an Agilent 6890 instrument equipped with Agilent 5973 mass selective detector.

2.2. Synthesis of manganese tetrakis-(4-N-trimethylaminophenyl)porphyrin hexafluorophosphate ([Mn^{III}TTMAPP][PF$_6$]$_5$, 1c) [20]

Tetrakis(4-N-dimethylaminophenyl)porphyrin (H$_2$TDMAPP, **1**) and manganese tetrakis-(4-N-dimethylaminophenyl)porphyrin (Mn^{III}TDMAPP, **1a**) were prepared according to the reported work [21].

In N$_2$ atmosphere, into a three-neck round-bottom bottle were added DMF (50 mL), H$_2$TDMAPP (**1**, 1.0 g), and CH$_3$I (3.0 g, excess). The resulting mixture was stirred at 120 °C for 1 h. After cooled to room temperature, the mixture was added with diethyl ether to precipitate a solid, which was thoroughly washed with acetone and diethyl ether. The collected red-brown solid was then dried *in vacuo* to yield the product of tetrakis(N-methyl-4-pyridinium)-porphyrin iodide ([H$_2$T(N-Me-4-Py)P][I]$_4$, **1b**) (0.6 g, Yield: 35%). ^{1}H NMR (DMSO-d_6): δ=−2.97 (2H, s, 2NH), 3.92 (36H, br, 12N$^+$CH$_3$), 8.43 (8H, d, benzyl (CH)$_2$), δ = 8.49 (8H, s, pyrrolyl, β-H), 8.85 (8H, benzyl N$^+$–C(CH)$_2$) ppm. UV–vis (in CH$_3$CN): λ_{max} (nm) = 418 (s, Soret band), 520 (w, Q band), 580 (w, Q band), 650 (w, Q band). FT-IR (KBr disc, cm^{-1}): 3339 (s, stretching vibration of N–H of pyrrolyl), 1623 (s), 1400 (s). TG-DTA analysis: thermal decomposition temperature 210 °C (in N$_2$ flow). Elemental analysis found (calculated, MW 1354.2) for C$_{56}$H$_{62}$N$_8$I$_4$ (**1b**): C 49.83 (49.63), H 4.39 (4.58), N 8.14 (8.27).

The mixture of 1.36 g [H$_2$TTMAPP][I]$_4$ (**1b**, 1.0 mmol) and 1.97 g Mn(OAc)$_2$·4H$_2$O (8.0 mmol) in 100 mL acetic acid was heated at 80 °C for 6 h. After removal of the solvent in vacuo, the left residue was recrystallized with methanol/diethyl ether to yield a dark-purple solid as [Mn^{III}T(N-Me-4-Py)P][I]$_{5-x}$[OAc]$_x$ (x = 0–5). The obtained solid was then dissolved in deionized water, and then treated with excess NH$_4$PF$_6$ aqueous solution. The purple solids precipitated readily. By washing with deionized water and methanol, the purple solids of manganese tetrakis(4-N-trimethylaminophenyl)porphyrin hexafluorophosphate ([Mn^{III}TTMAPP][PF$_6$]$_5$, **1c**) were obtained with yield of 75%. Due to influence of ^{55}Mn quadrupolar nucleus and the

[Mn^{III}TMAPP][PF$_6$]$_5$ (1c)

[Mn^{III}DMAPP][OAc] (1a)

ILs: [BzMIM]BF$_4$ - [BMIM]BF$_4$
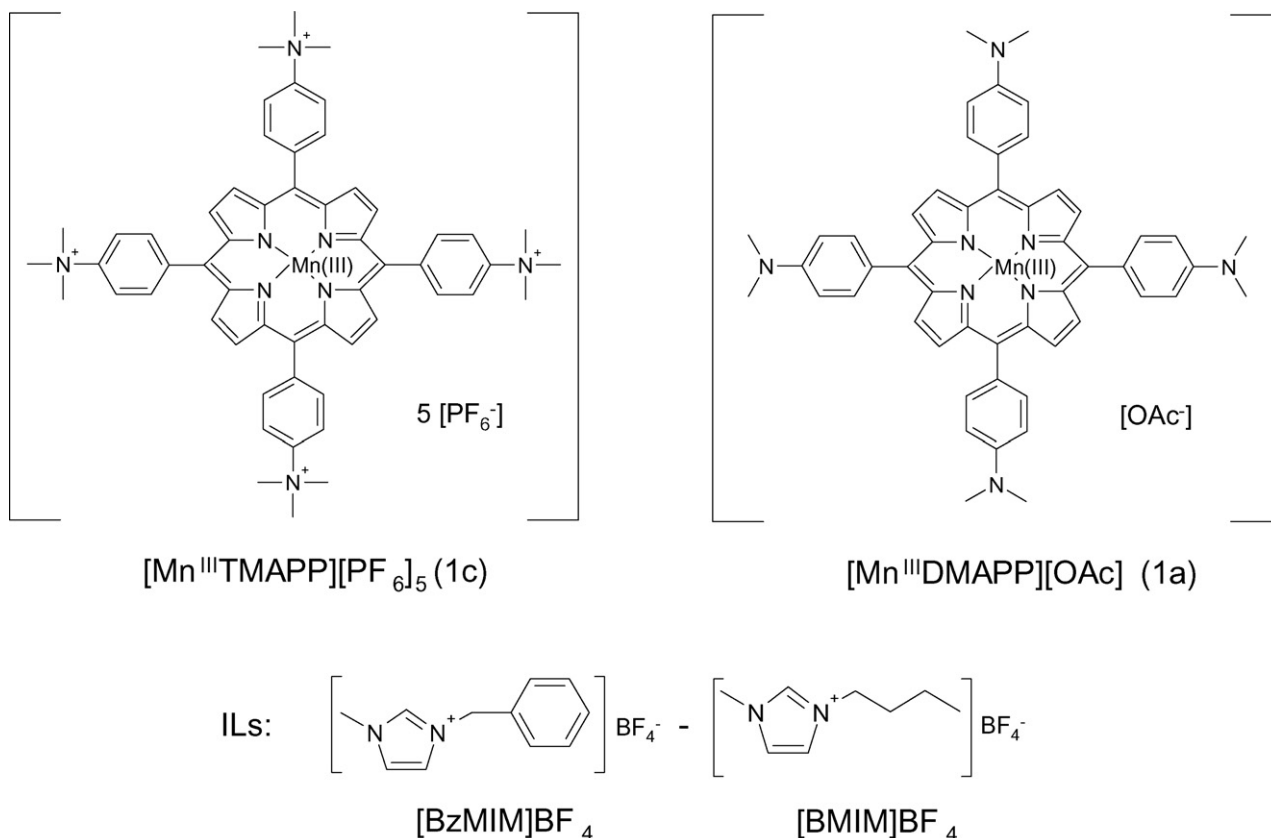
Scheme 1. Manganese porphyrin-IL system.

Table 1
Comparison of **1c** and **1a** in the ILs and organic solvents for styrene epoxidation[a]

No.	Cat.	Sol.	Axial ligand	Conv (%)	Sel. (%)		
					Styrene oxide	Phenyl acetaldehyde	Benzaldehyde
1	**1c**	[BMIM]BF$_4$–[BzMIM]BF$_4$	–	96	96	0	4
2	**1c**	[BMIM]BF$_4$–[BzMIM]BF$_4$	Pyridine	96	96	0	4
3	**1c**	CH$_3$CN[b]	–	61	97	0	3
4	**1c**	CH$_3$CN[b]	Pyridine	100	97	0	3
5[c]	**1c**	CH$_2$Cl$_2$[b]	–	12	84	0	10
6[c]	**1c**	CH$_2$Cl$_2$[b]	Pyridine	18	90	0	16
7	**1a**	[BMIM]BF$_4$–[BzMIM]BF$_4$	–	74	80	16	4
8	**1a**	[BMIM]BF$_4$–[BzMIM]BF$_4$	Pyridine	97	90	8	2
9	**1a**	CH$_3$CN[b]	–	69	85	12	3
10	**1a**	CH$_3$CN[b]	Pyridine	99	90	8	2
11	**1a**	CH$_2$Cl$_2$[b]	–	40	84	10	6
12	**1a**	CH$_2$Cl$_2$[b]	Pyridine	69	90	7	3

[a] Cat. 1.6 μmol (0.4 mol%), styrene 400 μmol, pyridine 130 μmol, PhIO 800 μmol, ILs [BMIM]BF$_4$ (1 mL) + [BzMIM]BF$_4$ (1 g), organic solvent 2 mL, reaction temperature 30 °C, reaction time 1 h.
[b] CH$_3$CN and CH$_2$Cl$_2$ were distilled with CaO before use.
[c] The catalyst was insoluble in CH$_2$Cl$_2$.

paramagnetism of Mn^{III} porphyrin **1c**, the signals of ^{1}H NMR of **1c** were broadened to flatness. UV–vis (**1c** in CH$_3$CN): λ_{max} (nm) = 463 (s, Soret band), 565 (w, Q band), 598 (w, Q band) nm. FT-IR (**1c**, KBr disc, cm^{-1}): 3133 (C-H stretching vibration), 1622, 1624, 1495, 1403, 1132, 1012, 835 (PF$_6^-$). TG-DTA analysis of **1c**: thermal decomposition temperature 160 °C (in N$_2$ flow).

2.3. General procedures for epoxidations of styrene (derivatives) catalyzed by **1c**–IL system

In the open air, to the mixture of 1 g 1-benzyl-3-methylimidazolium tetrafluoroborate ([BzMIMPy]BF$_4$), 1 mL 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF$_4$), and 400 μmol styrene (analytical grade reagent used as received) was added [Mn^{III}TTMAPP][PF$_6$]$_5$ (**1c**), yielding a totally homogeneous light-purple solution in which PhIO was added afterwards to take up the epoxidation at 30 °C. Upon completion, diethyl ether was used to extract the organic compounds (2 mL ×3). The conversions of substrates were based on GC analyses with 1-dodecane as internal standard. The selectivities of products were based on GC analyses with normalization method. The products were further identified by GC-mass analysis.

The left ionic liquid phase was dried *in vacuo* to remove trace of diethyl ether and used without further treatment for next run. In each run, due to the stoichiometric consumption of the oxidant, PhIO was added (400 μmol) additionally besides the substrate.

2.4. UV–vis spectra

All the UV–vis spectra were recorded on a SHIMADZU-UV 2550 spectrophotometer. The spectral resolution was about 1 nm. The reactions between [Mn^{III}TTMAPP][PF$_6$]$_5$ (**1c**), PhIO, and styrene in the presence of the ILs or CH$_3$CN were performed by single mixing, and the concentrations presented were the final concentrations after mixing.

3. Results and discussion

3.1. Catalytic performance of **1c** for styrene (derivative) epoxidations

In this work we used the ionic manganese porphyrin of **1c** as the pre-catalyst for styrene epoxidation along with the ILs ([BzMIM]BF$_4$ and [BMIM]BF$_4$) as the solvent and the axial ligand (Scheme 1). In order to compare difference in terms of activity, selectivity, and sta-

bility, the neutral manganese porphyrin **1a** was used in the parallel experiments. The selection of ILs as the solvent of **1c** was based on the principle of structural similarity. The IL of [BzMIM]BF$_4$ was supposed to be the matched solvent for **1c**. Unfortunately, [BzMIM]BF$_4$ is not an ambient liquid, and unsuitable for ambient epoxidation and UV detection. So the ambient IL of [BMIM]BF$_4$ was used as a co-solvent with [BzMIM]BF$_4$ together. The counterion of BF$_4^-$ was preferred in the ILs of [BMIM]BF$_4$ and [BzMIM]BF$_4$ because of its inertness to hydrolysis compared to PF$_6^-$. Consequently, the formation of HF, which may cause the breakdown of porphyrino ring, derived from the hydrolysis of the ILs was ruled out if the trace of water was in the presence of the system [22–25].

The reaction conditions were optimized in terms of temperature, reaction time, oxidant (PhI(OAc)$_2$, PhIO, NaIO$_4$, HOOAc, H$_2$O$_2$), and ratio of oxidant to styrene. Under the optimal reaction conditions (**1c** 1.6 μmol, PhIO 800 μmol, reaction temperature 30 °C, reaction time 1 h), the epoxidations of styrene catalyzed by **1c** or **1a** in the ILs ([BMIM]BF$_4$–[BzMIM]BF$_4$) or organic solvents (CH$_3$CN, CH$_2$Cl$_2$) were presented in Table 1. In the **1c**–IL system, the excellent yield of styrene oxide was obtained under mild conditions without additional involvement of auxiliary axial ligands (No. 1). The use of pyridine as the exogenous axial ligand showed negligible impact on the activity (No. 2). Whenever CH$_3$CN or CH$_2$Cl$_2$ was applied as the solvent to replace the ILs, the efficient epoxidations of styrene definitely required the participation of an axial ligand (pyridine), no matter in the cases of ionic **1c** or neutral **1a** as the catalyst (Nos. 4, 6, 8, 10, and 12). Due to poor solubility of **1c** in CH$_2$Cl$_2$, the low conversion of styrene was obtained (Nos. 5 and 6) under the same conditions.

The recycling uses of **1c**–IL, **1c**-CH$_3$CN, and **1a**-CH$_3$CN systems were further investigated to elucidate their difference in activity and stability (Table 2). In the **1c**–IL system, after four runs the

Table 2
The recycling uses of **1c** and **1a** in the ILs and CH$_3$CN for styrene epoxidation[a]

No.	Cat.	Sol.[b]	Conv. (%)[c]			
			Run 1	Run 2	Run 3	Run 4
1	**1c**	[BMIM]BF$_4$–[BzMIM]BF$_4$	96 (96)	72 (97)	41 (96)	20 (99)
2	**1c**	CH$_3$CN	61 (97)	20 (90)	9 (86)	–
3	**1a**	CH$_3$CN	69 (85)	38 (40)	4 (6)	–

[a] Cat. 0.4 μmol, styrene 400 μmol, PhIO 400 μmol which was additionally added per pass, temperature 30 °C, reaction time 1 h.
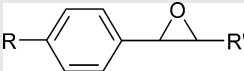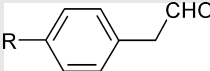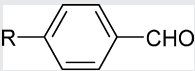[b] ILs [BMIM]BF$_4$ 1 mL, [BzMIM]BF$_4$ 1 g, CH$_3$CN 2 mL.
[c] The selectivity of styrene epoxide was indicated in parentheses.
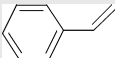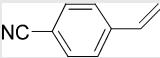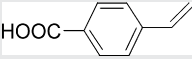
styrene conversion decreased to 20% with >96 epoxide selectivity. Afterwards, the characteristic Soret peak of **1c** at ca. 470 nm still existed in UV–vis spectra, although the degradation of **1c** coming from the oxidative destruction of porphyrino ring was also observed. Whenever CH$_3$CN was used as the solvent, the catalyst **1c** or **1a** was oxidatively broken down after four runs, leading to the total loss of the activity and disappearance of the Soret peak in the UV–v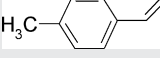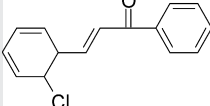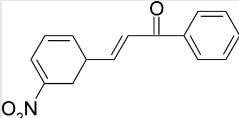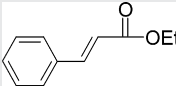is profiles. During the recycling use of **1c**–IL, the selectivity of styrene epoxide maintained at >96%, better than that in the systems of **1c**-CH$_3$CN and **1a**-CH$_3$CN with more phenyl acetaldehyde formed.

The generality of **1c**–IL to the substrates was demonstrated in Table 3, in which a wide array of styrene derivatives with different electronic and steric effects was selected. Obviously, whenever the substitute group was introduced into styrene, the extended reaction time was required to reach the acceptable conversions due to the bulky steric hindrance. With the electron-withdrawing group in *para*-position of styrene (–CN, –COOH, –Cl, –Br), the selectivities for oxides were remarkable, indicating that the decreased electron density at α-C of the styrene derivatives suppressed the formation of the rearranged products (epoxide sel. >95%, Nos. 2–5). However, for the electron-donor group of –CH$_3$, the increased electron-density at α-C of C=C bond resulted into the formation of the rearranged product (No. 6) [26,27]. While for the substrates (Nos. 7–9) with internal C=C bond, the epoxides were the only products, implicating the facial access of the substrate to manganese(V)-oxo porphyrin domain [28]. The more accessibility of the substrate to the catalytic center, the more favorable conversion was achieved (Nos. 7 and 8 *vs.* No. 9). For the olefins with saturated alkyl group, such as 1-hexene, 1-chloropropene, cyclohexene, the poor conver-

Table 3
Epoxidations of styrene and its derivatives catalyzed by the **1c**–IL system[a]

No.	Subs.	Conv. (%)	Sel. (%)		
			R—⬡—epoxide—R'	R—⬡—CH$_2$CHO	R—⬡—CHO
1	styrene	96 (1 h)[b]	96	0	4
2	NC—styrene	98 (3 h)[b]	100	0	0
3	HOOC—styrene	96 (3 h)[b]	100	0	0
4	Cl—styrene	96 (4 h)[b]	96	0	4
5	Br—styrene	95 (4 h)[b]	98	0	2
6	H$_3$C—styrene	97 (3 h)[b]	87	9	4
7	(Cl-chalcone)-trans	76 (6 h)[b]	100	0	0
8	(O$_2$N-chalcone)-trans	75 (6 h)[b]	100	0	0
9	(ethyl cinnamate)-trans	42 (6 h)[b]	100	0	0

[a] **1c** 1.6 μmol, substrate 400 μmol, PhIO 600 μmol, ILs [BMIM]BF$_4$ (1 mL) + [BzMIM]BF$_4$ (1 g), reaction temperature 30 °C.
[b] Reaction time was indicated in parentheses.

Table 4
Effects of water on the catalytic performance of **1c** and **1a**[a]

No.	Cat.	Time (min)	Sol.[b]	H_2O[c] (mmol)	Conv. (%)	Sel. (%)		
						Styrene oxide	Phenyl acetaldehyde	Benzaldehyde
1	**1c**	5	IL	5	93	99	0	1
2	**1c**	10	IL	5	96	99	0	1
3	**1c**	20	IL	5	98	98	0	2
4	**1c**	5	IL	–	4	100	0	0
5	**1c**	20	IL	–	36	99	0	1
6	**1c**	60	IL	–	96	96	0	4
7	**1c**	5	CH_3CN	5	5	100	0	0
8	**1c**	5	CH_3CN	–	7	100	0	0
9	**1c**	60	CH_3CN	5	63	96	0	4
10	**1c**	60	CH_3CN	–	61	97	0	3
11[d]	**1c**	5	IL	5	53	99	0	1
12[d]	**1c**	60	IL	–	67	96	0	4
13	**1a**	5	IL	5	54	80	16	4
14	**1a**	5	IL	–	–	–	–	–
15	**1a**	5	CH_3CN	5	–	–	–	–
16	**1a**	5	CH_3CN	–	–	–	–	–

[a] Cat. 1.6 μmol, styrene 400 μmol, PhIO 800 μmol, and reaction temperature 30 °C.
[b] ILs [BMIM]BF_4 (1 mL) + [BzMIM]BF_4 (1 g), CH_3CN 2 mL.
[c] The content of water was optimized to 5 mmol.
[d] Cat. **1c** 0.4 μmol.

sions were obtained because of the severe mass transfer limitation, mainly ascribing to the immiscibility of such kind of substrates with the conjugated **1c**–IL system.

As some literatures found that hydrolysis could occur in IL systems, leading to the decomposition of ILs and formation of HF [22–25], which would be poisonous to the metalloporphyrin catalysts. On the other hand, water has been considered to participate the activation of metalloporphyrin catalysts with the evidence from $H_2{}^{18}O$-exchange experiments [5–10]. Hence, the influence of water on the catalytic performance of **1c**–IL was investigated in Table 4. Surprisingly it was found that the presence of water in the **1c**–IL system led to the dramatically enhanced reaction rate. In ca. 5–10 min, the conversions of styrene were comparative to the case obtained in 60 min if free of water (Nos. 1 and 2 *vs.* No. 6). Even with neutral manganese porphyrin **1a** as the pre-catalyst, the positive effect of water also was observed if the ILs applied as the solvent (Nos. 13 and 14). However, the effect of water could not be observed when CH_3CN was applied as the solvent (Nos. 7–10, 15, and 16). These results implied that water could accelerate the formation rate of the active manganese(V)-oxo porphyrin intermediate derived from **1c** or **1a** with mediation of the IL.

3.2. Detection and characterization of manganese-oxo(V, IV) porphyrin complexes by UV–vis spectrophotometer

The unexpectantly promoted effect of water on the reaction rate evoked us to understand the formation and stabilization of the active manganese(V)-oxo porphyrin intermediate or the other complexes derived from **1c** or **1a** in the IL system. The reaction of **1c**–IL with PhIO was analyzed by a SHIMADZU-UV 2550 spectrophotometer at ambient temperature (ca. 25 °C). The mixture compositions were completely the same as those for the real catalytic epoxidation of styrene in Table 1(No. 1), except for the much low concentration of **1c** (1.3×10^{-5} M) required for UV detection. The UV–vis spectra obtained upon mixing **1c**, [BzMIM]BF_4, [BMIM]BF_4, deionized water, PhIO and styrene consecutively into a UV cuvette (3 mL) was presented in Fig. 1. As can be seen, the maximum absorbance of **1c**–IL in presence of H_2O was observed at 470 nm as a typical Soret band of Mn(III)-porphyrin (**1c**, PMn(III)). Whenever PhIO was added into **1c**–IL, after ca. 2 min, a new peak at 444 nm was gradually growing to reach the maximum intensity

(lines 3–9), which was identified as an active manganese(V)-oxo porphyrin intermediate (**1d**, PMn(V)=O) according to the previously reported work [8]. When the formed **1d** subsequently mixed with styrene, the absorbance peak at 444 nm decayed rapidly due to epoxidation of styrene to afford epoxide in good yield (96% in 5 min), accompanied by a concurrent recovery of Mn(III) porphyrin monitored at 470 nm (lines 10 and 11) and decreased intensity at 380 nm. These results suggested the direct diversion of intermediate **1d** back to the starting pre-catalyst of **1c** through two-electron redox catalytic pass. If excess PhIO was additionally added into the mixture of **1c**–IL–H_2O–styrene (line 11 of Fig. 1), the pre-catalyst **1c** and the corresponding intermediate **1d** were totally
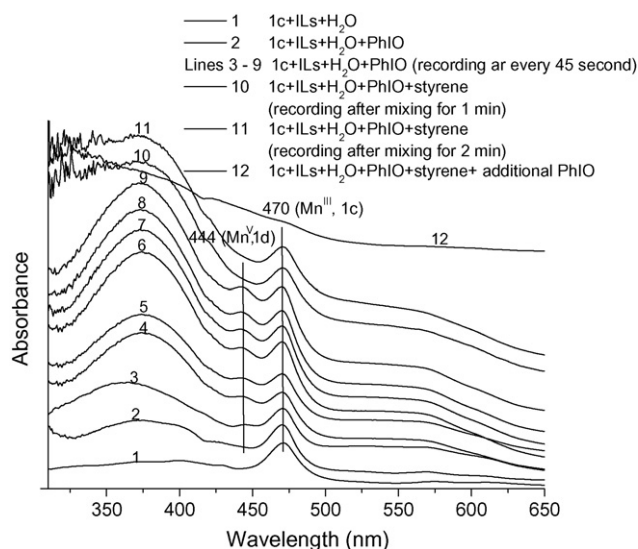
Fig. 1. UV–vis absorption spectra recorded: (1) line 1, for the mixture of **1c**–ILs–H_2O; (2) line 2, after adding PhIO into **1c**–ILs–H_2O immediately; (3) lines 3–9, for the mixture of **1c**–ILs–H_2O–PhIO recorded continuously at every 45 s; (4) line 10, after adding styrene into the mixture corresponding to spectrum of line 9 and standing by for 1 min; (5) line 11, after adding styrene into the mixture corresponding to spectrum of line 9 and standing by for 2 min; (6) line 12, after adding PhIO (60 μmol) additionally into the mixture corresponding to the spectrum of line 11 (conditions: **1c** 1.3×10^{-5} M, ILs 3 mL ([BMIM]BF_4 1.5 mL + [BzMIM]BF_4 1.5 g), H_2O 5 mmol, PhIO 60 μmol, styrene 30 μmol).
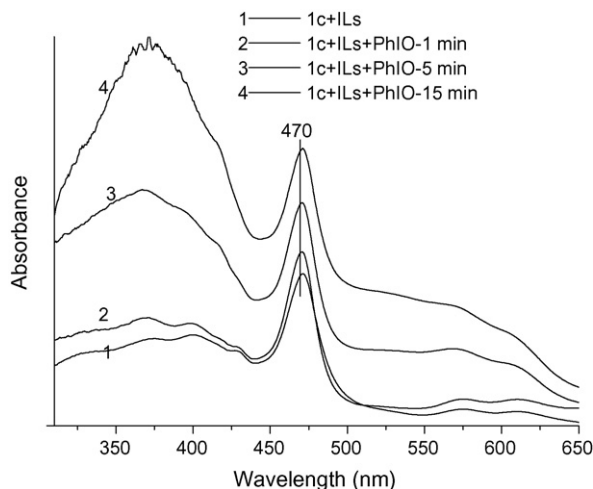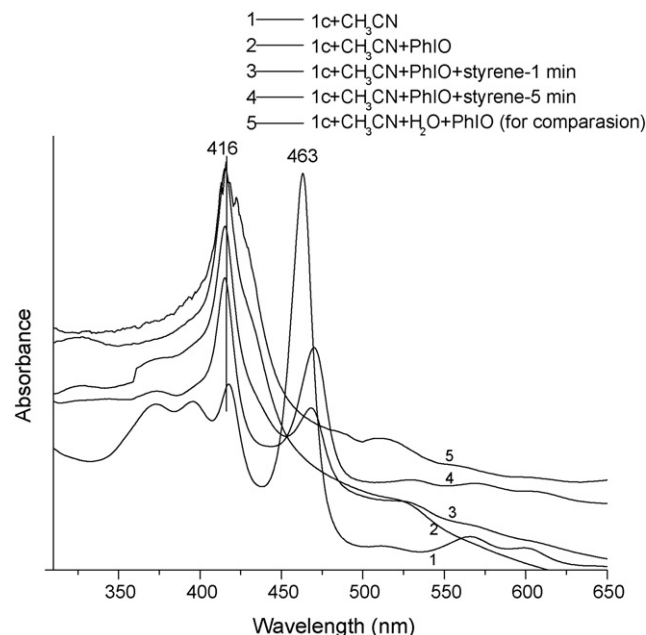
Fig. 2. UV–vis absorption spectra recorded: (1) for **1c**–ILs free of water; (2) after mixing **1c**–ILs with PhIO for 1 min; (3) after mixing **1c**–ILs with PhIO for 5 min; (4) after mixing **1c**–ILs with PhIO for 15 min; (5) after mixing **1c**–ILs with PhIO for 25 min (conditions: **1c** 1.3×10^{-5} M, ILs 3 mL ([BMIM]BF$_4$ 1.5 mL + [BzMIM]BF$_4$ 1.5 g), H$_2$O 5 mmol, PhIO 60 μmol, styrene 30 μmol).

destructed into non-super conjugated fragments as shown in line 12. The similar active manganese(V)-oxo porphyrin intermediate with the life-time <30 ms has been captured by Groves et al. by a (time-resolved) stopped-flow spectrophotometer [8]. In our work, the peak at 444 nm could stand for at least 5 min, indicating the improved stability (life-time) of **1d** in the presence of the IL and H$_2$O. The stabilized **1d** could accumulate to reach the concentration for the common UV–vis detection. In Fig. 2, a large blue-shift band at 380 nm grew rapidly after mixing **1c**–IL and PhIO together. It has been reported that the absorbance at 380 nm was ascribed to the ring-to-metal charge transfer (CT) transition [29–35]. According to Gouterman and Boucher's work, it was claimed that with involvement of the ionic salts or the polar solvent, the CT transition at 380 nm was allowed when the metal e$_g$(dπ) orbital mixed strongly with the porphyrin e$_g$*(π) orbital. As a kind of "hyperporphyrins" [31], the manganese porphyrin (**1c**) showed such extra optical absorption band (Q band) at 380 nm in the presence of the IL and PhIO, suggesting that the highly polar IL act not only as the solvent, but also as the axial ligand to influence manganeseporphyrin d(π) interactions dramatically through π−π force.

Whenever water was in the absence of the **1c**–IL system, the absorbance peak ascribed to the short-lived **1d** (444 nm) could not been observed (Fig. 2). This result indicated that the formation and stability of **1d** in the **1c**–IL system was not favored as that happened in the **1c**–IL-H$_2$O one, and then the concentration of **1d** could not be accumulated highly enough for the UV–vis detection. Such information supported the catalytic results obtained in Table 4, in which the epoxidation rate was greatly promoted by addition of 5 mmol H$_2$O.

If not considering the appearance of **1d** (444 nm), it can be seen that the very similar profiles are presented in Figs. 1 and 2. The μ-oxo Mn(IV) porphyrin dimer (**1e**, PMn(IV)–O–Mn(IV)P), with strong Soret maximum at around ~420 nm as reported before [32,36,37], was unobservable. This result indicated that, due to the common ionic nature, the similar conjugated feature, and the repulsive force between the positive charges in the **1c**–IL system, the interaction between **1c** and the IL counteracted the π−π stacking of metalloporphyrin itself, suppressing the formation of the μ-oxo porphyrin dimer as we supposed [38].

In comparison with CH$_3$CN as the solvent of **1c**, the UV–vis spectra of **1c**-CH$_3$CN in Fig. 3 totally differed to those of the

Fig. 3. UV–vis absorption spectra recorded (1) for **1c**–CH$_3$CN; (2) after adding PhIO into **1c**–CH$_3$CN immediately; (3) after adding styrene into the mixture corresponding to line 2 for 1 min; (4) after adding styrene into the mixture corresponding to line 2 for 5 min; (5) after mixing **1c**–CH$_3$CN–H$_2$O with PhIO immediately (conditions: **1c** 1.3×10^{-5} M, CH$_3$CN 3 mL, H$_2$O 5 mmol, PhIO 60 μmol, styrene 30 μmol).

1c–IL system. Clearly, water showed no impact on the formation of manganese(V)-oxo porphyrin intermediate (**1d**). Whenever the oxidant PhIO was added, the monitored processes revealed sharp increase in absorbance at around 416 nm, which is assigned to μ-oxo Mn(IV) porphyrin dimer (**1e**), accompanied by the rapid absorbance disappearance at around 463 nm (**1c**). The reaction of **1e** with styrene in the presence of PhIO led to the recovery of Mn(III) porphyrin (**1c**, 470 nm) as shown in lines 3 and 4 of Fig. 3, with a 54% epoxide yield in 3 h. Coincident to the reported work [11–13], the μ-oxo Mn(IV) porphyrin dimer (**1e**) proved to be a low-reactive pre-catalyst for epoxidation compare to **1c**, which could undergo disproportionation through one-electron transfer to result in the recovery of Mn(III) porphyrin complex (**1c**) and the formation of active manganese(V)-oxo intermediate (**1d**) corresponding to styrene epoxidation (PMn(IV)–O–Mn(IV)P → PMn(III) + PMn(V)=O).

As can been seen in Figs. 1–3, the most obvious features were concluded as follows: (1) the formation and lifetime of manganese(V)-oxo porphyrin intermediate (**1d**) derived from the reaction of **1c** and PhIO was facilitated by the involvement of the IL and H$_2$O (Fig. 1); (2) when the IL was applied as the solvent for **1c** oxidation, the CT transition at 380 nm actively occurred due to the strong influence of the IL on d(π) interactions of the manganese porphyrin (Figs. 1 and 2); (3) the formation of μ-oxo Mn(IV) porphyrin dimer (**1e**, 416 nm) was suppressed completely in the presence of the IL (Figs. 1 and 2); (4) When CH$_3$CN was applied as the solvent, **1c** converted to **1e** rapidly. The latter can disproportionate to PMn(III) (**1c**) and PMn(V)=O (**1d**) complexes when intervened by styrene (Fig. 3).

4. Conclusions

The ionic manganese porphyrin of **1c** dissolved in the mixed ILs of [BzMIM]BF$_4$ and [BMIM]BF$_4$ proved to be an efficient catalytic system for styrene (derivatives) epoxidations without the involvement of the auxiliary axial ligands. The degradation of **1c** coming

from the porphyrin self-aggregation and the oxidative destruction was greatly suppressed in the **1c**–IL system. The epoxidation rate in **1c**–IL could be dramatically promoted by addition of water. The UV–vis analysis supported the facts including that (1) the formation rate and the lifetime of the active manganese(V)-oxo intermediate (**1d**) was improved remarkably with mediation of the IL and H_2O; (2) the μ-oxo Mn(IV) dimer (**1e**) was thoroughly suppressed and the CT transition became rather active in the **1c**–IL system, due to the strong interaction between the ionic manganese porphyrin and the IL.

Acknowledgements

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