Bi-functionalized PEG1000 ionic liquid [Imim-PEG1000-TEMPO][CuCl2-]：An efficient and reusable catalytic system for solvrent-free aerobic oxidation of alcohols

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ARTICLE TYPE

Bi-functionalized PEG$_{1000}$ ionic liquid [Imim-PEG$_{1000}$-TEMPO][CuCl$_2^-$]：An efficient and reusable catalytic system for solvent-free aerobic oxidation of alcohols

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An efficient and reusable catalytic system for aerobic oxidation of alcohols with bi-functionalized PEG$_{1000}$ ionic liquid ([Imim-PEG$_{1000}$-TEMPO][CuCl$_2^-$]) was described. This ionic liquid shows catalyst properties similar to those of non-supported counterpart in terms of activity and selectivity affording the target products in good yield, moreover, [Imim-PEG$_{1000}$-TEMPO][CuCl$_2^-$] could be recycled and reused without significant loss of catalytic activity after five runs. Notably, the protocol presented here provides an efficacious strategy to achieve both catalysts recycling and product isolation from a viewpoint of green chemistry.

Introduction

The selective oxidation of primary and secondary alcohols into the corresponding aldehydes or ketones is one of the most important and challenging transformations in organic chemistry[1-3]. A large variety of methods have been reported to accomplish this transformation efficiently and selectively[4-5]. These methods usually require stoichiometric amounts of chemical oxidants, however, most of these oxidants are toxic, hazardous, or large amount of waste formed. From an economical and environmental viewpoint, catalytic oxidations are particularly promising, and many efforts have been devoted to the development of efficient procedures employing O_2 (or air) and hydrogen peroxide as the ultimate oxidant over the last years. These attractive catalytic systems display high atom economy and release only innocuous by-products such as H_2O. Many transition metals such as ruthenium, rhodium, palladium, gold have been utilized to catalyze this reaction, either on their nanoparticles[6-7] or salts with the assistance of co-catalysts such as stable free nitroxyl radical 2, 2, 6, 6-tetramethylpiperidine-1-oxyl (TEMPO), which has proved to be very effective for the aerobic oxidation of alcohols[8-13]. Copper as one of abundant and cheap transition metal is essential element in the human body, which is found very effective in the binding of molecular oxygen and highly selective aerobic oxidative transformations. Recently, utilization of TEMPO for oxidation of alcohols employing copper salts has been in quantity reported for the oxidation of alcohols under the aerobic conditions[14-23]. In 2004, Gamez[24] et al reported the selective and very mild aerobic oxidation of primary alcohols to aldehydes using [copper(II)-(N ligand)n] complex with TEMPO and a base as co-catalysts at room temperature. More recently, Hoover[25] et al reported a new (bpy)CuI/TEMPO/NMI catalystic system that enables efficient and selective aerobic oxidation of a broad range of primary alcohols, including allylic, benzylic, and aliphatic derivatives, to the corresponding aldehydes using readily available reagents, at room temperature with ambient air as the oxidant. However, the deficiencies of solubility of substrates, product isolation and catalyst recovery hinder the development of these systems, therefore developing a recyclable catalytic system would be a promising project.

Room temperature ionic liquids (RTILS) has drawn increasing studies over the last decades due to excellent advantages like negligible volatility, thermal stability, remarkable solubility and a variety of available structures[26-30]. Notably, functionalized ILs for specific-task has drawn many interests in the synthesis fields. In 2005, Miao[31] et al reported an effective catalytic system comprising 2, 2, 6, 6-tetramethylpiperidine-1-oxyl (TEMPO) functionalized imidazolium salt ([Imim-TEMPO]$^+$X$^-$), a carboxylic acid substituted imidazolium salt ([Imim-COOH]$^+$X$^-$), and sodium nitrite ($NaNO_2$) which was developed for the aerobic oxidation of aliphatic, allylic, heterocyclic and benzylic alcohols to the respective carbonyl compounds with excellent selectivity up to >99% at ambient conditions. In 2010, Fall[32] et al described an efficient synthesis of an ionic liquid-supported TEMPO ([Imim-TEMPO][BF$_4^-$]) which was used for the oxidation of alcohols to aldehydes and ketones. The predictable solubility of ionic liquids allows an easy separation of the oxidation products. Furthermore, the IL-supported TEMPO can be recycled and used several times without the loss of efficiency. Wu[33] et al also described a novel 2, 2, 6, 6-tetramethylpiperidine-1-oxyl (TEMPO) radical bearing an ionic liquid-type appendage and its catalytic activity for the selective oxidation of alcohols to the corresponding carbonyl compounds in ionic liquid-aqueous biphasic conditions. The ionic liquid-supported TEMPO radical shows catalyst properties similar to those of non-supported counterpart in terms of activity and selectivity, and can be easily recycled and reused without loss of activity and selectivity.

Polyethylene glycols, as a commercially available, non-toxic, and recyclable polymer, has been widely used in organic transformation as environment benign solvent and soluble support for liquid phase synthesis, which are hopeful to substitute volatile organic solvents and display excellent effect for promoting many transformations[34-41], such as N-arylation of amines, cross-coupling reaction, asymmetric dihydroxylation, aldol reaction, Baylis-Hillman reaction, multi-component condensation. In 2005, Pozzi et al[42] have reported Poly(ethylene glycol)-supported TEMPO and its catalytic activity in the chemoselective oxidation of alcohols with stoichiometric amounts of organic or inorganic oxidants. The new metal-free catalyst exhibits high activity and easy removal from the reaction mixture by filtration. Recently, Zhi and Hu[43-44] have reported a new polyethylene glycol supported ionic liquid(PEG$_{1000}$-DIL), which exhibits good compatibility of the tandem catalyst/substrate, excellent catalytic effect in promoting reaction and easy catalyst recovery from reaction system. As our interests for environmentally benign protocols for reaction, hererin, a novel catalytic system with bi-functionalized PEG$_{1000}$ ionic liquid [Imim-PEG$_{1000}$-TEMPO][CuCl$_2^-$] was described in our work (Scheme 1) and has been proved to be an effective catalyst for selective aerobic oxidation of primary and secondary alcohols into the corresponding aldehydes or ketones without the additive of base. Moreover, it was delighful that the catalytic system afforded excellent durability, which could be successfully recovered and reused without significant loss of catalytic activity. The protocol presented here provides an efficacious strategy to achieve both catalysts recycling and product isolation from a viewpoint of green chemistry.

<**Scheme 1**. Synthesis of bi-functionalized PEG$_{1000}$ ionic liquid>

Results and discussion

The synthesis steps of bi-functionalized PEG$_{1000}$ ionic liquid [Imim-PEG$_{1000}$-TEMPO][CuCl$_2^-$] are as depicted in Scheme 1. As can be seen in Fig. 1, the O-H stretching vibrations of 4-hydroxy-TEMPO at 3390 cm^{-1} has disappeared revealing PEG$_{1000}$ ionic liquid has been functionalized by TEMPO (Fig. 1b and Fig. 1c).

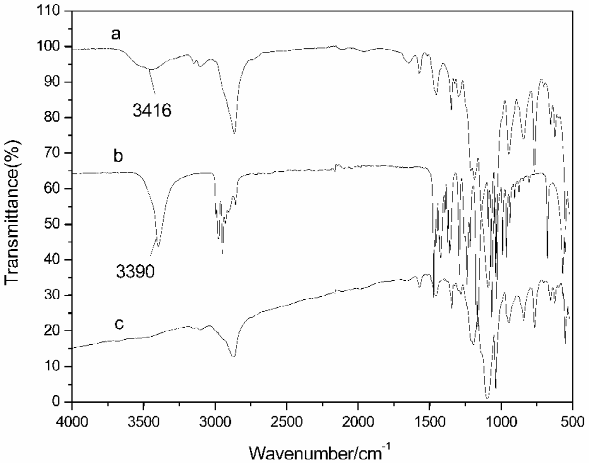

Fig. 1 IR spectra (a) PEG-1000 (b) 4-hydroxy-TEMPO (c) [Imim-PEG$_{1000}$-TEMPO][CuCl$_2^-$]

With benzyl alcohol as the model substrate, the bi-functionalized PEG$_{1000}$ ionic liquid ([Imim-PEG$_{1000}$-TEMPO][CuCl$_2^-$]) was designed for the aerobic oxidation of alcohols. The exploratory experiments were started by screening the metal salts of catalyst system and the results are summarized in Table 1. It can be seen that among the salts tested, copper salts showed much higher catalytic activity than the other transition metal salts with 60-100% conversion of benzyl alcohol (Table 1, entries 1-4 and entry 8). CuCl was found to be the best catalyst with 100% conversion, and 96% isolated yield(Table 1, entry 1). The Co containing catalyst showed no catalytic activity (Table 1, entry 5) and the Mn and Ni salts showed moderate catalytic activity with 36-41% conversion (Table 1, entries 6-7).

<**Table 1** Effects of metal salt on bi-functionalized PEG$_{1000}$ IL catalyzed oxidation of benzyl alcohol under solvent-free conditions>

This ionic liquid [Imim-PEG$_{1000}$-TEMPO][CuCl$_2^-$] shows catalyst properties similar to those of non-supported counterpart in terms of activity and selectivity affording the target products in good yield(Table 2, entries 2-3). In this respect, control experiments were carried out in other aprotic solvents like DMSO, DMF and toluene (Table 2, entries 4-6). The solubility of the catalyst would likely be more important for this reaction. As expected, DMSO, DMF and toluene could not well dissolve the catalyst and demonstrate a poor performance under identical conditions, whereas [Imim-PEG$_{1000}$-TEMPO][CuCl$_2^-$] is capable of forming a homogeneous system to enhance the reaction. One explanation was the stabilisation of Cu(I) species during the catalytic cycle caused by the coordination of N-methylimidazole molecule and the formed Cu(I) complex would intend to bind with the alcohol molecule, which is more favorable for the reaction. The other reason may be that the bi-functionalized PEG$_{1000}$ ionic liquid exhibits good compatibility of the catalyst and substrate. It was reported that organic solvents were usually used to improve the solubility of substrates[24], however, our catalytic system has a good catalytic performance without adding organic solvents. As we know, PEGs are amphiphatic molecules due to its special long chain structure. The -CH units of PEG could increase the solubility of organic compounds which is derived from gathering effect of hydrocarbon chain. Moreover, the effect of the catalyst amount was evaluated. The reaction was operative in the range of the catalyst loading from 1 to 20 mol%. The best transformation was completed within 12 h in the presence of 5 mol% catalyst (Table 2, entries 7-10). Notably, the oxidation gave the best performance at 60 ℃, and also could be carried out under mild conditions even at room temperature (Table 2, entries 11-14).

<**Table 2.** Reaction conditions on bi-functionalized PEG$_{1000}$ IL catalyzed oxidation of benzyl alcohol under solvent-free conditions>

Encouraged by those results, some other alcohols were further examined to extend the substrate scope for this methodology and the results are shown in Table 3. To our delight, the catalytic system was effective and highly selective for the oxidation of benzylic, heterocyclic and allylic alcohols to the respective carbonyl compounds at ambient conditions. The activities of primary benzylic alcohols were best, and the activities of those primary benzylic alcohols were also not significantly affected by the electronic properties and steric hindrance of the substituents on the benzene ring(Table 3, entries 1-8). Interestingly, the designed oxidation system proved to be chemoselective. In the case of double bond containing substrate, the double bond was not influenced by this method(Table 3, entry 9). Furthermore, secondary benzylic alcohols such as benzhydrol could give moderate conversion by prolonging the reaction time(Table 3, entries 10-12). Heterocyclic alcohols such as furfuryl alcohol would be also suitable to the system(Table 3, entries 13-14). Unfortunately, aliphatic alcohol such as dodecyl alcohol gave lower yields when the alcohol was added to the system(Table 3, entry 15).

< **Table 3.** Bi-functionalized PEG_{1000} IL catalyzed oxidation of various alcohols >

The recyclability of the catalytic system was also investigated. After completion of the oxidation reaction, the mixture was allowed to cool to room temperature extraction with ether. The upper layer containing product was removed by decantation. The lower layer left was dried to remove small amount of water by vacuum and fresh substrates were then recharged to react once again. With benzyl alcohol as a model substrate, IL was proved to be efficient after five times reutilization both in the view of yield and selectivity (Figure 2). There was no great loss of activity or apparent reduction of weight during the recycling process.

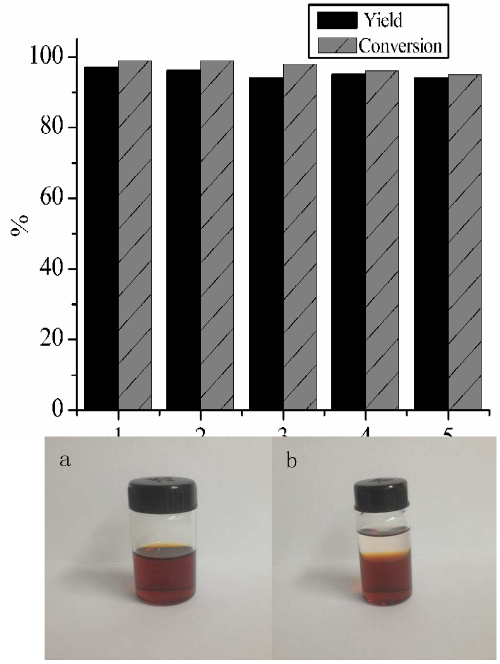

Fig 2. Cycling reaction (a) the reaction mixture (b) adding ether when cooling to room temperature

The role of TEMPO might act as a hydrogen acceptor during the proposed catalytic cycle. Firstly, species I are generated by the TEMPO-mediated oxidation of Cu(I) to Cu(II) species. Then, alcohol coordinates to the copper(II) species I to lead to alkoxy species II. The transfer of β-hydrogen to TEMPO and intramolecular one-electron transfer leads to the aldehyde, TEMPOH and Cu(I) species. The catalytic cycle is completed by the aerobic oxidation of the TEMPOH to TEMPO (Scheme 2).

< **Scheme 2.** The mechanism of aerobic oxidation of alcohols>

Conclusions

In conclusion, we have developed an efficient and reusable catalytic system for the aerobic oxidation of alcohols catalyzed by bi-functionalized PEG_{1000} ionic liquid ($[Imim\text{-}PEG_{1000}\text{-}TEMPO][CuCl_2^-]$) with good yields. Owing to the high efficiency and good compatibility, the catalytic system had a good catalytic performance to promote reaction effectively. Moreover, it could be recycled and reused without significant loss of catalytic activity after seven runs. For this environmentally catalytic system, it would find a wider application in various reactions, which is an ongoing project.

Experimental Section

All starting materials were purchased from commercial sources and used without further treatment. Analytical thin layer chromatography (TLC) was performed on precoated silica plates. Yields of the products refer to purification by silica-gel column chromatography. IR spectrum analysis were recorded on Nicolet IS-10 fourier transform infrared spectroscopy. ^{1}HNMR were recorded on a Bruker Advance III (500MHz) spectrometer with tetramethylsilane (TMS) as an internal standard. High performance liquid chromatography experiments were performed on a liquid chromatograph (Shimazhu LC-20AT, Japan).

Synthesis of bi-functionalized PEG_{1000} ionic liquid $[Imim\text{-}PEG_{1000}\text{-}TEMPO][CuCl_2^-]$: To a solution of PEG-1000 (0.06 mol, 60 g) in toluene (150 mL), pyridine(0.12 mol, 9.6 mL) was added, followed by the addition of thionyl chloride (0.12 mol, 8.7 mL) within 30 min under N_2 atmosphere at 0 ^oC. The resulting slurry was stirred for 24 h at room temperature and filtered. The toluene was then removed by rotator evaporation under reduced pressure to give intermediate **1** as a gray viscous liquid. In the next step, 4-hydroxy-TEMPO (8.6 g, 0.05mol) was added to a suspension of Na (1.15 g, 0.05 mol) in benzene (100 mL) and the resulting slurry was stirred for 8 h at room temperature. Intermediate **1** (0.025 mol) was then added and stirring resumed for 24 h at room temperature. The suspension was then filtered and the filtrate concentrated under reduced pressure. This solution was then added to ether (100 mL) that was stirred vigorously and the precipitate collected by filtration, washed twice with ether (50 mL), and dried under vacuum. The product **2** was obtained as orange red viscous solid. Then, intermediate **2** (0.025 mol) was added to N-methylimidazole (2.05 g, 0.025 mol) solution which was dissolved in toluene, and the mixture was stirred at 70 °C for 20 h. The reaction was determined by HPLC and evaporated under reduced pressure to give intermediate **3** as an orange red oil with a yield of 98.3% . In the last step, the intermediate 3 was mixed with anhydrous CuCl together under N_2 atmosphere with a mechanical stirring at room temperature. The obtained red brown liquid were washed with ether, evaporated by reduced pressure and dried in vacuum successively. Then, the ionic liquid ([Imim-PEG$_{1000}$-TEMPO][CuCl$_2^-$]) was thus obtained.

General procedure for oxidation of alcohols: To a 10 mL round-bottom flask containing the [Imim-PEG$_{1000}$-TEMPO][CuCl$_2^-$] (0.5 mmol), benzyl alcohol (10 mmol) was successively added under a constant vigorous stiring. The reaction was proceed under temperature of 60 ^{o}C and monitored by TLC. Upon completion, the reaction mixture was cooled to room temperature and extracted three times by adding ether. The organic phase was dried over anhydrous MgSO$_4$, evaporated under reduced pressure and to give benaldehyde (96% yield) with spectral data consistent with the assigned structures for the products. The next run was performed under identical reaction conditions.

Notes and references

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‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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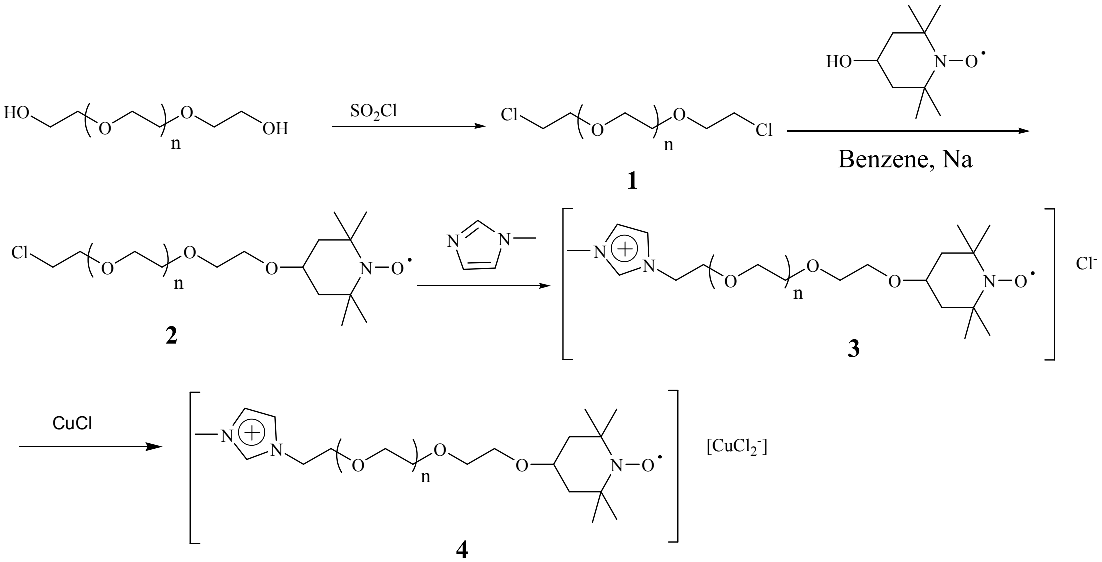


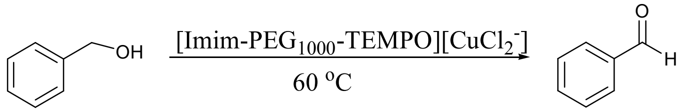
Scheme 1. Synthesis of bi-functionalized PEG$_{1000}$ ionic liquid

Table 1 Effects of metal salt on bi-functionalized PEG_{1000} IL catalyzed oxidation of benzyl alcohol under solvent-free conditions[a]

Entry	Metal salt	Conv[b] (%)	Yeild[c](%)
1	CuCl	100	96
2	CuBr	69	64
3	CuI	60	55
4	$CuCl_2$	79	72
5	$CoCl_3$	-	0
6	$NiCl_2$	36	34
7	Mn $(OAc)_2$	41	38
8	Cu $(OAc)_2$	80	71

Reaction conditions:[a] benzyl alcohol (10mmol), [Imim-PEG_{1000}-TEMPO] (0.5 mmol), metal salt(0.5 mmol), 60 ℃.
[b] Determined by HPLC
[c] Isolated yield

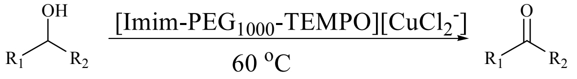
Table 2. Reaction conditions on bi-functionalized PEG$_{1000}$ IL catalyzed oxidation of benzyl alcohol under solvent-free conditions[b]

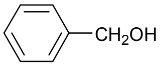
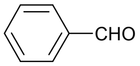
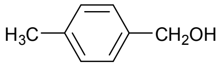
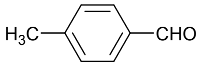
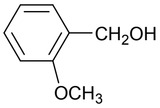
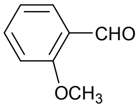
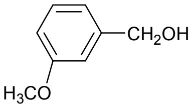
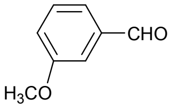
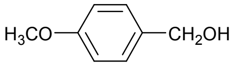
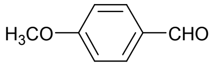
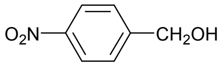
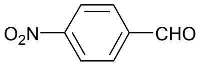
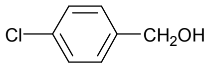
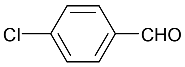
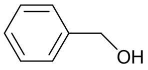
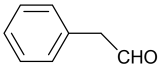
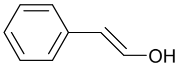
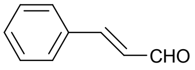
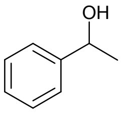
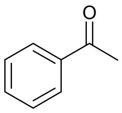
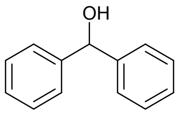
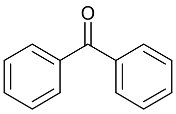
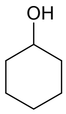
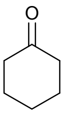
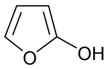
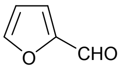
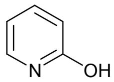
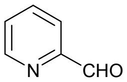
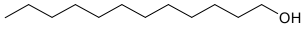
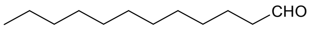


Entry	catalysts (mol%)	solvent	T /℃	Conv[b] (%)	Yeild (%)[c]
1	-	-	60	-	0
2	[Imim-PEG$_{1000}$-TEMPO][CuCl$_2^-$] (5)	CH_3CN	60	>99	95
3	CuCl(5)/TEMPO(5)	CH_3CN	60	92	90
4	CuCl(5)/TEMPO(5)	DMF	60	60	53
5	CuCl(10)/TEMPO(5)	DMSO	60	49	47
6	CuCl(5)/TEMPO(5)	Toluene	60	31	31
7	[Imim-PEG$_{1000}$-TEMPO][CuCl$_2^-$] (1)	-	60	89	84
8	[Imim-PEG$_{1000}$-TEMPO][CuCl$_2^-$] (5)	-	60	100	96
9	[Imim-PEG$_{1000}$-TEMPO][CuCl$_2^-$] (10)	-	60	100	95
10	[Imim-PEG$_{1000}$-TEMPO][CuCl$_2^-$] (20)	-	60	100	95
11	[Imim-PEG$_{1000}$-TEMPO][CuCl$_2^-$] (5)	-	rt	54	50
12	[Imim-PEG$_{1000}$-TEMPO][CuCl$_2^-$] (5)	-	40	90	85
13	[Imim-PEG$_{1000}$-TEMPO][CuCl$_2^-$] (5)	-	80	100	90
14	[Imim-PEG$_{1000}$-TEMPO][CuCl$_2^-$] (5)	-	100	100	78

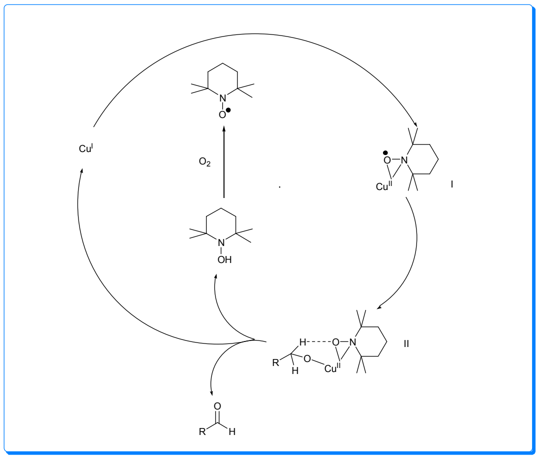
Reaction conditions:[a] benzyl alcohol (10mmol), [Imim-PEG$_{1000}$-TEMPO][CuCl$_2^-$] (0.5 mmol), 60 ℃.
[b] Determined by HPLC
[c] Isolated yield

Table 3. Bi-functionalized PEG$_{1000}$ IL catalyzed oxidation of various alcohols [a]:



Entry	Substrate	Product	Time /h	Conv[b] (%)	Yeild (%)[c]
1			12	100	96
2			10	>99	92
3			12	>99	98
4			12	>99	96
5			10	>99	98
6			13	99	95
7			12	98	93
8			12	91	88
9			14	90	85
10			16	79	78
11			20	81	75
12			20	83	80
13			20	90	88
14			16	88	87
15			16	76	72

Reaction conditions:[a] alcohols (10mmol), [Imim-PEG$_{1000}$-TEMPO][CuCl$_2^-$] (0.5 mmol), 60 ℃.
[b] Determined by HPLC
[c] Isolated yield



Scheme 2. The mechanism of aerobic oxidation of alcohols