ChemComm

Cite this: *Chem. Commun.*, 2011, **47**, 2697–2699

www.rsc.org/chemcomm

COMMUNICATION

Synthesis of bimagnetic ionic liquid and application for selective aerobic oxidation of aromatic alcohols under mild conditions†

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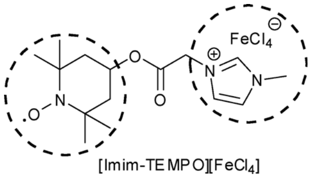
Received 27th October 2010, Accepted 20th December 2010
DOI: 10.1039/c0cc04644b

The first bimagnetic ionic liquid based on Fe and TEMPO with cooperative functionalities not only exhibited strong paramagnetic behaviour at room temperature under an applied magnetic field of 5000 Oe but also proved to be an effective catalyst for selective aerobic oxidation of aromatic alcohols under mild and clean conditions.

Ionic liquids (ILs) are salts being composed of distinct cations and anions that are capable of facilely tuning, and whereby can be designed for task-specific applications through a smart choice of the respective cation and/or anion. Nowadays, ILs have been extensively investigated with a wide range of interesting applications,[1] because of their limitless attractive properties, such as wide liquid temperature ranges, good thermal stabilities, high ionic conductivity, wide electrochemical potential windows, and high solvation interactions with both polar and nonpolar compounds.

On the other hand, the magnetic behaviour of ILs with metal-containing anions has been less known until Hayashi and Hamaguchi[2] found paramagnetic behaviour of $[C_4mim][FeCl_4]$ with effective magnetic moment (μ_{eff} = 5.8 μ_B) and high conductivity ($<2.0 \times 10^{-2}$ S cm^{-1}). Subsequently, magnetic ILs have been attracting more and more attention in view of special properties and applications.[3] A series of imidazole- or tetraalkylphosphonium-based gadolinium(III), manganese(II), iron(III) and cobalt(II) ILs have become available in Del Sesto's group, which show potential applications for magnetic and electrochromic switching as well as magnetic transport.[4] Furthermore, dysprosium(III)-based ILs exhibited strong luminescence and response to magnetic fields (μ_{eff} = 10.4 μ_B).[5] Even the $FeCl_4$-based magnetic chiral ILs derived from amino acids and their magnetic properties were also investigated.[6] In addition, non-metal organic magnetic IL based on a radical ion, such as 2,2,6,6-tetramethyl-1-piperidinyl-oxy-4-sulfate with potential as conductive material, was also reported.[7] Interestingly, based on positive effects of ILs[8] and rapid development of iron catalysis,[9] metal magnetic IL *i.e.* $[C_4min][FeCl_4]$ combining attractive properties of both ionic liquid and $FeCl_3$ was found to have great application in catalysis.[10] Despite those successes with the magnetic ILs, the bimagnetic ILs with more potential functionality were never found in the literature. In this context, developing task-specific bimagnetic ILs would be much promising.[11] As a continuation of our interests on ILs,[12] we herein would like to report the first bimagnetic imidazolium salt based on Fe and organic radical ion (Scheme 1), which showed strong paramagnetic behaviour (χ_g = 37.8 × 10^{-6} emu g^{-1}) and attractive catalytic properties.



Scheme 1 Novel Fe/TEMPO-based bimagnetic IL with cooperative functionalities.

The target bimagnetic IL was successfully synthesized from commercially available 4-hydroxy-TEMPO, chloroacetic acid, 1-methylimidazole and $FeCl_3$.[3,13] The magnetic properties of the ILs such as [Imin-TEMPO]$[FeCl_4]$ and [Imin-TEMPO][Cl] were examined by using the SQUID (superconducting quantum interference device) method. The results are shown in Fig. 1A and 1B and Fig. S3–S13 (see ESI†). The magnetizations for [Imim-TEMPO]$[FeCl_4]$ and [Imim-TEMPO][Cl] at 298 K were measured in the magnetic field range of −50 000 to 50 000 Oe, revealing an expected linear response to the applied magnetic field (Fig. 1A and Fig. S13 (ESI†)). As a result, the gram and molar magnetic susceptibilities of [Imim-TEMPO]$[FeCl_4]$ at 298 K were determined to be 37.8 × 10^{-6} emu g^{-1} and 0.0187 emu mol^{-1}, respectively, being in well agreement with the expected value of Fe(III).[2] On the other hand, the effective magnetic moment (μ_{eff}) for [Imim-TEMPO][Cl] was found to be 1.39 μ_B, being well consistent with the expected value for TEMPO.[7] Interestingly, the effective magnetic moment (μ_{eff}) for [Imim-TEMPO]$[FeCl_4]$ was found to be 6.66 μ_B, suggesting the cooperative contribution from both the S = 5/2 high-spin

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† Electronic supplementary information (ESI) available: General experimental part, characterization of magnetic imidazolium salts and its intermediates, supporting tables and figures, ^1H NMR and ^{13}C NMR data for products identification. See DOI: 10.1039/c0cc04644b

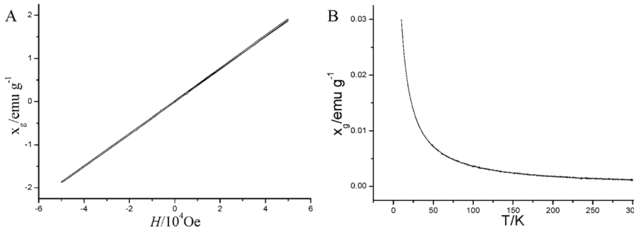


Fig. 1 A: Field dependence of the mass susceptibility χ_g for [Imim-TEMPO][$FeCl_4$] at 298 K; B: Temperature dependence of the mass susceptibility χ_g at a field of 500 Oe for [Imim-TEMPO][$FeCl_4$]:

electronic state of iron(III) (5.92 μ_B)^2 and the $S = 1/2$ radical spin of TEMPO (1.73 μ_B).[7] In comparison with the bimagnetic ILs [Imim-TEMPO][$FeCl_4$], [Imim-TEMPO][Cl] gave much smaller values of the gram and molar magnetic susceptibilities at 298 K, *i.e.* 24.5 × 10^{-7} emu g^{-1} and 0.000816 emu mol^{-1}, respectively.

The catalytic application of the task-specific bimagentic imidazolium salts [Imim-TEMPO][$FeCl_4$] for aerobic oxidation of alcohols was further investigated. An initial experiment was carried out by using benzyl alcohol as the substrate in the presence of 5 mol% of the bimagnetic imidazolium salts under organic solvent-free conditions. The results are summarized in Table 1. The reaction did not occur in the absence of any component of the catalytic system (entries 1–6, Table 1). Furthermore, $FeCl_3$/$NaNO_2$ shows no activity without any TEMPO and the IL (entry 6). In other words, [Imim-TEMPO][$FeCl_4$], $NaNO_2$ and O_2 are prerequisite to performing those reactions smoothly. In particular, [Imim-TEMPO][Cl] and [Imim][$FeCl_4$] were found to be inactive, indicating that combination of both [$FeCl_4$] and TEMPO parts probably plays a crucial role in promoting the aerobic oxidation (entries 4 and 5). After rough optimization of the reaction conditions, quantitative yields with excellent selectivity could be achieved at mild conditions (30 °C, 0.2 MPa O_2, 1.5 h) (entries 7–10, Table 1; entries 12 and 13, Table S1 (ESI†)). It is worth mentioning that the reaction also performed well even while using air as an oxidant, and was totally immune to moisture (entries 11 and 12).

Table 1 Oxidation of benzylic alcohol catalyzed by the designed bimagnetic imidazolium salt[a]

Entry	PO_2/Mpa	t/h	Conv.[b]/%	Yield[b]/%
1	0	1	1	1
2[c]	1	1	0.4	0.3
3[d]	1	1	1	1
4[e]	1	1	0.5	0.5
5[f]	1	1	0	0
6[g]	1	1	0	0
7	1	2	100	99
8	0.6	1	69	68
9	0.2	1.5	100	99
10	0.1	24	100	99
11[h]	0.1	48	65	63
12[i]	0.2	1.5	100	99

[a] Reaction conditions: benzyl alcohol (1.93 mmol), [Imim-TEMPO][$FeCl_4$] (5 mmol%), $NaNO_2$ (5 mmol%), 30 °C. [b] Yields determined by GC. [c] Without [Imim-TEMPO][$FeCl_4$]. [d] Without $NaNO_2$. [e] [Imim-TEMPO][$FeCl_4$] was replaced by [Imim-TEMPO][Cl]. [f] [Imim][$FeCl_4$] was used instead of [Imim-TEMPO][$FeCl_4$]. [g] $FeCl_3$ (5 mmol%), $NaNO_2$ (5 mmol%) in the absence of any TEMPO and the IL. [h] Air as oxygen resource. [i] 0.3 mL H_2O was added.

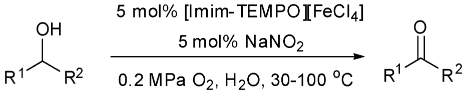
Encouraged by those results, we further examined the utility and generality of this approach for transformation of various alcohols including the benzyl alcohols and heterocyclic alcohols to carbonyl compounds by performing the reaction under the given conditions (Table 2). Notably, the activities of the substituted benzyl alcohols were promoted by addition of water (entries 2 *vs.* 3, 4 *vs.* 5, Table 2). Fortunately, all primary benzylic alcohols were converted into the corresponding aldehydes in high yield and excellent selectivity (entries 1, 3, 5–9) and the secondary benzylic alcohols also gave high to moderate yields by prolonging the reaction time (entries 10 and 11). It is noteworthy that the heterocyclic alcohols are compatible in this bimagnetic imidazolium IL-catalyzed oxidation reaction (entries 12–14), which are generally problematic with other transition metal-mediated aerobic oxidation protocols; and the reactivity follows the order 2-furfuryl alcohol > 2-thiophenemethanol > 2-pyridinylmethanol. Unfortunately, allylic and aliphatic alcohols were inert to this catalytic system (entries 1–5, Table S2, ESI†).

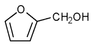
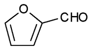
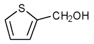
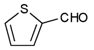
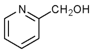
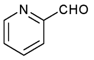
Furthermore, one feature of this bimagnetic IL-catalyzed aerobic oxidation of alcohols would be facile separation of the catalyst. In each run, [Imim-TEMPO][$FeCl_4$] was readily recovered by ether extraction, then was subjected to a subsequent run of the reaction by charging a fresh substrate and $NaNO_2$. The results show that the catalyst can be reused for at least five times with retention of high activity and selectivity.[14]

Although the mechanism for the present catalytic oxidation is not yet clear, valuable insight and discussion would be herein presented. The control experiments reveal that TEMPO and [$FeCl_4$]$^-$ species/$NaNO_2$ are indispensable parts of this efficacious catalytic system (entries 1–6, Table 1). Additionally, $NaNO_2$ as the electron-transfer-medium is required for completing the catalytic cycle.[15] In other words, $NaNO_2$ could release NO and NO_2, and the oxidation of NO into NO_2 undergoes easily with O_2. On the other hand, the aliphatic alcohol was inert in this study (Table S2, ESI†), suggesting that the reaction could not undergo an 'oxoammonium' mechanism[16] or a $FeCl_3$/TEMPO/$NaNO_2$ process.[17] ILs were reported to stabilize the anionic oxygen radical intermediate and thus accelerate electron transfer reactions.[18] Indeed, the EPR (electron paramagnetic resonance) experiment could show the existence of the radical species *in situ* generated in the reaction (Fig. S1, ESI†).[19] Moreover, the iron valence could be changeable during the reaction being detected by the ESI-MS technique (electrospray ionization mass spectrometry, Fig. S2, ESI†). In short, the oxidation would go through an electron transfer process mediated by [Imim-TEMPO][$FeCl_4$] and $NaNO_2$.

In conclusion, a type of novel bimagnetic imidazolium salt ([Imim-TEMPO][$FeCl_4$]) was developed and its paramagnetic properties were confirmed by the use of SQUID measurements. Notably, [Imim-TEMPO][$FeCl_4$] with cooperative functionalities proved to be a highly effective catalyst for selective oxidation of a variety of aromatic alcohols under mild conditions without utilization of any organic solvent. Thus, the bimagnetic imidazolium salt able to be designed for specific applications through the choice of the respective magnetic core appears to be very appealing in view of creating novel chemistry as well as developing extremely valuable

Table 2 Oxidation of various alcohols[a]



Entry	Alcohol	Product	T/°C	t/h	Conv.[b] (%)	Yield[b] (%)
1[c]	$PhCH_2OH$	PhCHO	30	1.5	100	99
2[c]	4-MeO–$C_6H_4CH_2OH$	4-MeO–C_6H_4CHO	30	10	7	6
3	4-MeO–$C_6H_4CH_2OH$	4-MeO–C_6H_4CHO	30	3	80	80(78)
4[c]	3-MeO–$C_6H_4CH_2OH$	3-MeO–C_6H_4CHO	30	10	3	2
5	3-MeO–$C_6H_4CH_2OH$	3-MeO–C_6H_4CHO	30	3	88	87(83)
6	2-MeO–$C_6H_4CH_2OH$	2-MeO–C_6H_4CHO	30	14	90	90
7	4-Me–$C_6H_4CH_2OH$	4-Me–C_6H_4CHO	60	3	91	91
8	4-NO_2–$C_6H_4CH_2OH$	4-NO_2–C_6H_4CHO	100	2	100	100(94)
9	2-NO_2–$C_6H_4CH_2OH$	2-NO_2–C_6H_4CHO	100	2	82	81(80)
10	$PhCH(OH)CH_3$	$PhC(O)CH_3$	30	24	100	> 99
11	PhCH(OH)Ph	PhC(O)Ph	100	24	67	64
12			30	4	100	98
13			30	12	100	98
14			30	24	73	71

[a] Reaction conditions: alcohol (1.93 mmol), [Imim-TEMPO][$FeCl_4$] (5 mol%), $NaNO_2$ (5 mol%), H_2O (0.3 mL), O_2 (0.2 MPa). [b] Determined by GC, values in parentheses refer to isolated yields. [c] In the absence of H_2O.

materials with great potential applications. Further studies on mechanistic investigations and the use of a magnet to recover magnetic ILs are in progress and will be reported in due course.

Support by the grant from the National Natural Sciences Foundation of China (No. 20672054, 20872073), National Natural Science Funds for Distinguished Young Scholar (20625618) and National Basic Research Program of China (973 program, 2009CB219901) is gratefully acknowledged.

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