Synthesis and Application of Metal Ion Containing Ionic Liquids: A Brief Review

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Abstract: Some recent developments concerning the syntheses, physical properties and application of metal ion containing ionic liquids (ILs) with magnetic behavior are highlighted. The component ions used so far include both inorganic and organic types, and various strategies, namely not only the proper choice but also the synthesis of anions to introduce the functionality, are presented.

Keyword: Ionic liquid, magnetic, functionality, synthesis, catalysis.

1. INTRODUCTION

Ionic liquids are a group of molten salts that exist as liquids at a low temperature (<100^{o}C). An important feature of ILs is their immeasurably low vapor pressure. For this reason, they are called "green" solvents, in contrast to traditional volatile organic compounds. ILs also have many attractive properties, such as chemical and thermal stability, nonflammability, high ionic conductivity and a wide electrochemical potential window [1-4]. More importantly, ionic liquids can be designed for task-specific applications through smart choice of the respective cation/anion or by introducing different functional groups. Therefore, they have been extensively investigated with a wide range of interesting applications, such as solvents or co-catalysts in various reactions including organic catalysis [5-8], biocatalysts [9,10], liquid-liquid extraction processes, radical polymerization and so on [11].

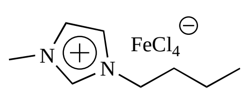
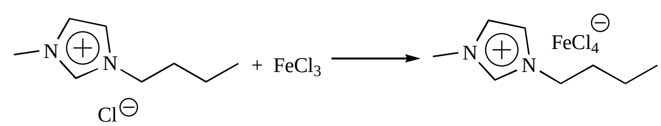


Fig. (1). The molecular structure of [Bmim][$FeCl_4$].

Although the earliest discovery of magnetic phenomena is not known for certain, magnetism is one of nature's most fascinating and evergreen phenomena. Recently, it has been proposed that the IL containing magnetic ions possesses magnetic behavior, which opens up a new research area of the magnetic liquid. The first example reported by Hamaguchi is [Bmim][$FeCl_4$] (C_4mim=1-butyl-1-methylimidazolium) (Fig. **1**) [12, 13], this kind of metal ion containing IL is primarily based on high-spin d^5 iron (III) in the form of tetrachloro- or tetrabromoferrate(III), which exhibits a strong response to magnetic fields. Since then, metal ion containing ILs with magnetic behavior are starting to attract wide interest, and some progresses on structure, physical, catalytic and even chiral properties have been published. It is important to note that both types of anions and cations provide advantages for the development of metal ion containing ILs because a wide variety of the accumulated knowledge in the common ILs field could be utilized. Unfortunately, as far as we know, only one review has referred the achievement in design of metal ion containing ILs with magnetic behavior [14], the present article provides a specific review of the recent progress that have concerning the syntheses, physical properties and catalytic application of metal ion containing ILs. Please note that this is a brief discussion on this topic, rather than a comprehensive account for developments in the area; thus, we apologize in advance to anyone who believes their contributions have been omitted.

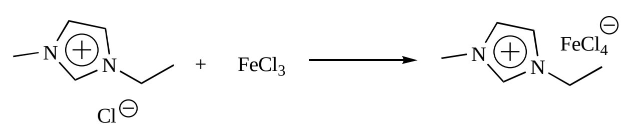
II. IRON CONTAINING IONIC LIQUIDS

Iron containing ILs are a very interesting subclass of ILs, not only they have the attractive properties of ILs, but also they may have interesting magnetic and catalytic properties. In 2004, Hamaguchi and coworkers first demonstrated the iron containing IL by mixing 1-butyl-3- methylimidazolium chloride ([Bmim][Cl]) and $FeCl_3$ (Scheme **1**) [13], which responded strongly to magnetic field. The SQUID measurements showed that it was paramagnetic having a large magnetic susceptibility of 40.6 $\times 10^{-6}$ emu g^{-1} and the effective magnetic moment (μ_{eff}) of 5.8 μB. Since then, the metal ion containing ILs based on Fe (III) focus on the design of the anions and cations.



Scheme 1. Synthesis of Bmim$FeCl_4$.

Most of the ILs containing tetrachloroferrate ion have evidenced a paramagnetic temperature dependence of the magnetic susceptibility with only small deviations from the Curie law at low temperatures. Interestingly, Fernández and coworkers reported 1-ethyl-3- methylimidazolium tetrachloroferrate [Emim][$FeCl_4$] (Scheme **2**) clearly showed a long-range antiferromagnetic ordering below the Neel temperature TN approximate to 3.8 K [15]. In addition, the field dependence of the magnetization measured at 2 K was characterized by a linear behaviour up to around 40 kOe, while above this field the magnetization became saturated with a value of 4.3 mu(B)/Fe, which was near the expected fully saturated value of 5 mu(B)/Fe for an Fe^{3+} ion. In addition, Pedro also demonstrated [Emim][$FeCl_4$] exhibited a long-range antiferromagnetic ordering below the Neel temperature TN≈3.8 K [16].



Scheme 2. Synthesis of [Emim][$FeCl_4$].

Warner and coworkers synthesized novel room temperature chiral iron containing ILs derived from amino acids and investigated their magnetic properties as well as chiral discrimination abilities (Scheme **3**) [17]. The effective magnetic moments of ILs were determined as values between 5.52 and 5.66 μB in accord with what was expected from the S = 5/2 high-spin electronic state of iron (III) (spin-only value was 5.92 μB). The chiral magnetic fluid materials with dual functionalities were expected to have great

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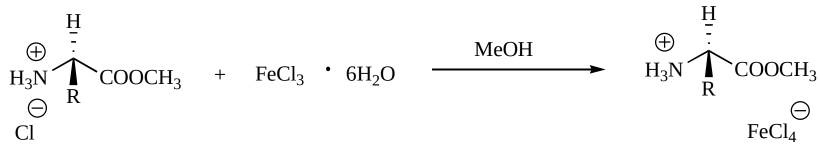


Scheme 3. Synthesis of magnetic chiral ionic liquids.

potential in a number of applications such as asymmetric catalysis and synthesis. Their strong response to a magnetic field, as well as their extremely low vapor pressure was thought to be particularly beneficial for providing an easier approach to recovering and recycling the magnetic chiral ILs used as asymmetric catalysts.

Recently, Mochida and coworkers first reported a paramagnetic ferrocenium-based ionic liquid that exhibited a magnetic memory effect coupled with a liquid-solid phase transformation (Fig. **2**) [18]. The physical chemistry of this paramagnetic ferrocenium-based ionic liquid might lead to novel molecular electronic applications using molecular liquids.

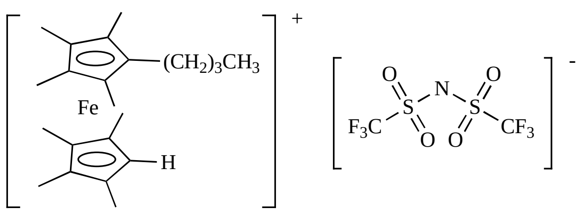
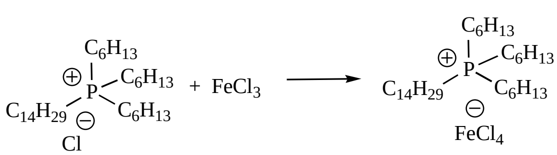


Fig. (2). Chemical formula of the paramagnetic ferrocenium-based ionic liquid.

III. OTHER METAL ION CONTAINING IONIC LIQUIDS

Quaternary phosphonium salts with short chain length are generally solids, however, utilizing large and bulky tetraalkylphosphonium cations lead to liquids. Sesto and coworkers reported several transition metal-based ILs with magnetic behavior synthesized by reaction of trihexyl(tetradecyl)phosphonium[PR_4], 1-decyl-3-methylimidazolium [C_{10}mim], or 1-butyl-3-methylimidazolium [C_4mim] halides with the corresponding metal halides, or metal-based anions ($FeCl_3$, $CoCl_2$ and $MnCl_2$) (Scheme **4**) [19]. They prepared a series of metal containing ILs containing different paramagnetic anions. Those ILs showed potential applications for magnetic and electrochromic switching as well as novel magnetic transport.



Scheme 4. Synthesis of [PR_4] [$FeCl_4$].

Mudring reported dysprosium-based ILs, synthesized from [C_6mim]SCN, KSCN, and $Dy(ClO_4)_3{\bullet}6H_2O$, showed the highest response to external magnetic fields to date, allowing magnetic manipulation of the liquid [20]. The effective magnetic moment of dysprosium (III) was calculated to be μ_{eff}=10.48 µB, which was roughly twice the value of iron (III). In addition, the liquids had excellent photophysical properties, such as long luminescence decay times and high color purity.

Köckerling and coworkers reported low-viscosity paramagnetic ILs with doubly charged [Co $(NCS)_4]^{2-}$ Ions synthesized from paramagnetic $[Co(NCS)_4]^{2-}$ anions and imidazolium-based cations had glass-transition temperatures below -60 °C (Fig. **3**) [21]. The low-viscosity paramagnetic ILs showed an effective magnetic moment of 4.40 µB, which also had unexpected ion conductivities, low heats of vaporization along with high hydrolytic stability and insensitivity to air.

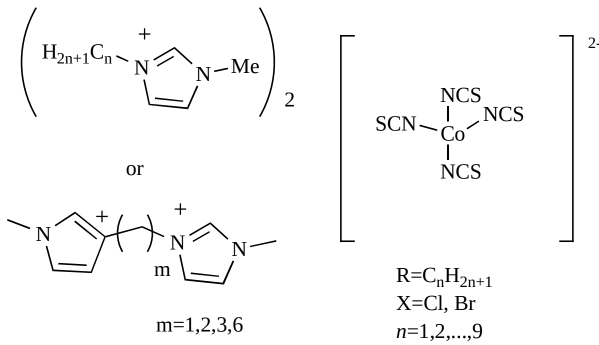


Fig. (3). The structure of doubly charged magnetic ILs.

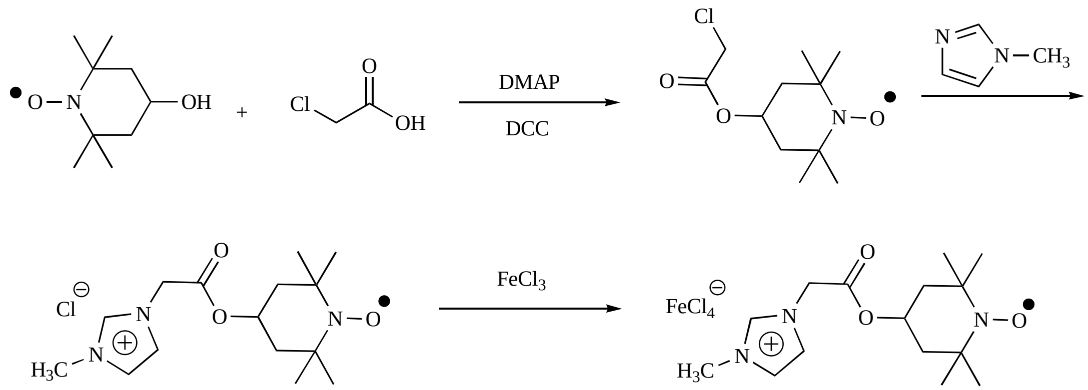
IV. APPICATION OF METAL ION CONTAINING ILS

The chemistry of room-temperature ILs is at an incredibly exciting stage in its development, however, metal ion containing IL is beginning to be used as a solvent or catalyst for a wide range of synthetic procedures. The metal ion containing ILs that combined the advantages of ILs and metal catalysis will allow those to use them for new chemistry. The application of metal ion containing IL now mainly focuses on materials synthesis, catalysis and separation.

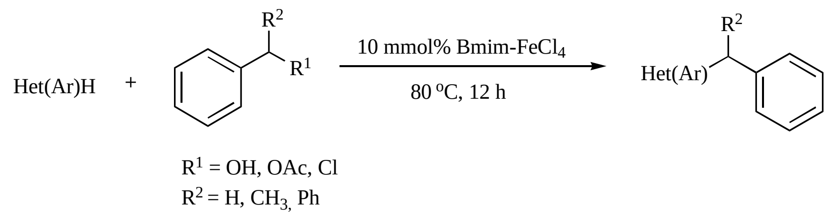
Li and coworkers reported that the synthesis of poly (3,4-ethylenedioxythiophene) nanospheres with their size ranging around 60 nm was achieved by simply adding monomers into a magnetic IL, [Bmim][$FeCl_4$] [22]. The IL led to the formation of uniform nanospheres with a relatively narrow size distribution confined to submicrometer-sized domains. The polymers produced in this magnetic IL system were compared to those synthesized in conventional solution and emulsion polymerizations.

Kim and coworkers successfully synthesized nanostructured conducting polypyrrole and poly (N-methylpyrrole) by simply adding monomers into [Bmim] [$FeCl_4$] [23]. In this process, self-organized conducting polymer nanostructures such as particles and tubes were formed without and with magnetic field. The shape of polypyrrole nanoparticles synthesized at room temperature were almost spherical with their size ranging around 60 nm with a relatively narrow size distribution. From the N-methylpyrrole monomer, more attractive nanostructured polymers were obtained. Tubes with nanoscaled inner holes and walls were synthesized using a self-assembly process for the first time. The self-assembled local structures in the solvent IL were likely to serve as templates of highly organized nanostructured polymers. External magnetic field seemed to affect these local structures and hence the resultant polymer nanostructures. The research provided a new method to synthesize various nanosized conducting polymeric materials via simple self-assembly.

Li and coworkers reported the synthesis of polypyrrole (PPy)/AgCl nanocomposites with their size ranging around 70-100 nm were achieved by using [Bmim][$FeCl_4$] as the oxidant in the interface polymerization system [24]. The interface polymerization led to the formation of uniform and unaggregated nanocomposites with a relatively narrow size distribution confined to submicrome-



Scheme 5. Synthesis of bimagnetic chiral ionic liquids.



Scheme 6. Benzylation of arenes catalyzed by iron (III)-based ionic liquid.

ter-sized domains. The morphology and structure of the nanocomposites were characterized by transmission electron microscopy, Fourier transform infrared spectroscopy, Raman spectroscopy and X-ray diffraction. The potential application of PPy/AgCl nanocomposites as a H_2O_2 biosensor was also reported.

Kim and coworkers reported [Bmim][$FeCl_4$] was highly effective catalysts for the dimerization of bicyclo- [2.2.1] hepta-2, 5-diene (2,5-norbornadiene, NBD) in the presence of diethylaluminum chloride [25]. Fe-containing ILs produced hexacyclic endo-endo NBD dimer (Hnn) in high yield and selectivity, and the yield and selectivity of Hnn were affected by the degree of reduction of Fe (III) compounds by DEAC to Fe (II) species as determined by X-ray photoelectron spectroscopy. Higher yield of Hnn was obtained with the catalytic system producing larger amounts of Fe (II) species.

Li and coworkers reported the depolymerization of poly (ethylene terephthalate) in ethylene glycol could be catalyzed by [Bmim][$FeCl_4$] [26]. This metal ion containing IL exhibited higher catalytic activity for the glycolysis of PET, compared with $FeCl_3$ or [Bmim][Cl]. Investigation also showed that the onset reaction temperature of the glycolysis process catalyzed by [Bmim] [$FeCl_4$] was much lower, being 140 degrees C. The proposed mechanism indicated that the high catalytic activity of [Bmim] [$FeCl_4$] was attributed to the synergic effect of its cation and anion.

Recently, He and Zhang reported the first bimagnetic ILs based on $FeCl_3$ and TEMPO with cooperative functionalities (Scheme **5**) [27], which exhibited strong paramagnetic behaviour at room temperature under an applied magnetic field of 500 Oe, and the effective magnetic moment (μ_{eff}) was found to be 6.66 μ_B. Moreover, the bimagnetic ILs also proved to be an effective catalyst for selective aerobic oxidation of aromatic alcohols under mild and clean conditions.

More recently, He and coworkers reported regioselective benzylation of arenes and heteroarenes catalyzed by iron (III)-based ionic liquid (Scheme **6**) [28]. Notably, this Fe (III)-based IL showed excellent stability, could be easily recovered, and reused for five times without significant loss of its catalytic activity.

Koo and coworkers investigated the possibility of a magnetic recovery system using the mixtures of [Bmim][$FeCl_4$] and water, which provided a protocol to recycle the magnetic ILs [29]. They studied the magnetic response of the mixture of [Bmim] [$FeCl_4$] and water, and the [Bmim][$FeCl_4$] rich phase in the mixture forming two phases was easily separated under an external magnetic field. The homogeneous mixtures of [Bmim][$FeCl_4$] and water were also attracted to the direction of the magnetic field. Under a gradually varied magnetic field, the concentration of the mixture varied as a function of the magnetic field strength.

V. CONCLUSIONS

Metal ion containing IL is a unique subclass of ILs which possesses a potential spectrum of utility extending far beyond that likely for more conventional ILs. By virtue of the incorporated magnetic property, these unique salts can act not only as solvents but as catalysts and reagents in an array of synthetic, separation and electrochemical applications. As has been the case for conventional ILs, the number of applications is likely to continue to expand. This review hopes to showcase some of the highlights of this exciting area, giving the reader a reasonable idea of the types of functional ILs which have been prepared, and the range of their possible applications. Future works will be concerned with developing special functionality for each ion and then combining them to form metal ion containing ILs with dual or cooperative functionalities.

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CONFLICT OF INTEREST

None declared.

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