Discovery of a Magnetic Ionic Liquid [bmim]$FeCl_4$

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A magnetic ionic liquid, which shows a strong response to magnetic field, has been discovered. We synthesized an ionic liquid by mixing 1-butyl-3-methylimidazolium chloride ([bmim]Cl) and $FeCl_3$, in anticipation of unique magnetic properties due to the possible local ordering of the magnetic anions. The visible absorption spectroscopy has shown that this liquid contains the high spin $FeCl_4^-$ as the anion. Raman spectroscopy has indicated that it contains $bmim^+$ as the cation. It has thus been confirmed that the prepared liquid is [bmim]$FeCl_4$. The liquid [bmim]$FeCl_4$ responded strongly to magnetic field. The SQUID measurements have shown that it is paramagnetic having a large magnetic susceptibility of 40.6×10^{-6} emu g^{-1}. The present discovery of a magnetic ionic liquid has opened up a new research area of the magnetism of liquids.

Liquids that are composed solely of ions are called ionic liquids. In contrast to ordinary organic liquids, in which the dipolar or higher order multipolar interactions are dominating, the Coulomb interaction plays a major role in ionic liquids. Because of the long-range nature of the Coulomb interaction, ionic liquids may possibly have higher structural ordering than organic liquids. In fact, our recent studies on the crystal and liquid structures of the 1-butyl-3-methylimidazolium salts ([bmim]X, where X is Cl, Br, I, BF_4, and PF_6) have revealed a few unexpected features of these ionic liquids that suggest the existence of a local ordering of the constituent ions.[1–4] X-ray crystallography has shown that, in [bmim]Cl and [bmim]Br crystals, the $bmim^+$ cations form columns extending along the *a* axis and the halogen anions are accommodated in the channels surrounded by four cation columns to form linear chains.[1,5] The Raman spectra of the $bmim^+$ cation in crystalline and liquid [bmim]X highly resemble each other, indicating that their structures in the liquid state are similar to those in the crystalline state.[2,3] Most recent wide-angle X-ray scattering experiment on [bmim]I has shown a few clear peaks in the radial distribution. This finding is indicative of the local ordering of the iodide anions.[4] If the ions are locally ordered as suggested by these results, it will give rise to many unique physical properties of ionic liquids. With this expectation in mind, we started the preparation and the characterization of [bmim]X ionic liquids having magnetic anions. In the present letter, we report on the first compound [bmim]$FeCl_4$.

The synthesis of [bmim]$FeCl_4$ has already been reported in the literature.[6] In the present study, we prepared [bmim]$FeCl_4$ by mixing crystal powder of [bmim]Cl with two ferric chlorides, anhydrous $FeCl_3$ and $FeCl_3 \cdot 6H_2O$. Crystalline [bmim]Cl was prepared according to the standard procedure[7] followed by repeated recrystalization from dry acetonitrile. By mixing equimolar amount of [bmim]Cl (1.16 g) and $FeCl_3$ (1.07 g) in a dry box with N_2 atmosphere, a dark brown liquid (Liquid 1) was obtained as a result of an exothermic solid-state reaction. Similarly, by mixing [bmim]Cl (1.46 g) and $FeCl_3 6H_2O$ (2.31 g), a dark brown liquid (Liquid 2) was obtained endothermically. Liquid 2 is immiscible with water and the reaction ended with two layers of liquids, Liquid 2 and water. Both Liquid 1 and Liquid 2 show strong response to a magnet. Pictures in Figure 1 show how Liquid 2 responds to a magnet. Without a magnet (Figure 1a), the layer of Liquid 2 spreads beneath the water layer. As a magnet approaches, the Liquid 2 layer is attracted toward the magnet (Figure 1b) and is finally distorted to make a concave curve (Figure 1c).

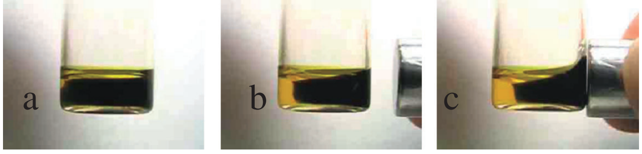

Figure 1. Pictures showing the response of [bmim]$FeCl_4$ (Liquid 2) to a magnet.

In order to spectroscopically characterize Liquids 1 and 2, we first measured their visible absorption spectra. A Hitachi U-3500 spectrometer was used. The results are given in Figure 2. Both Liquid 1 (full line) and Liquid 2 (dotted line) show three absorption peaks at 534, 619, and 688 nm. These peaks are well known as characteristic peaks of $FeCl_4^-$.[8] We therefore conclude that both Liquid 1 and 2 contain the $FeCl_4^-$ ion.

We then measured the Raman spectra of Liquids 1 and 2 so as to obtain information about the cation structure. A laboratory made near-infrared multichannel Raman spectrometer[9] was used. The excitation wavelength was 1064 nm. The use of near-infrared excitation enabled the collection of high S/N Raman spectra from dark colored liquids. The Raman spectra of Liquids 1 and 2 agree very well with each other. Figure 3

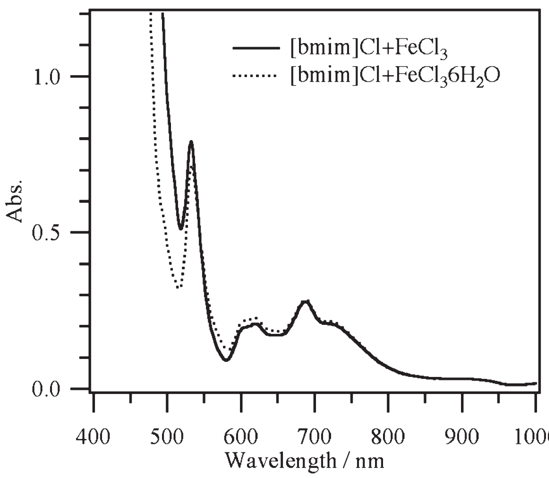

Figure 2. Visible absorption spectra of [bmim]$FeCl_4$ (Liquids 1 and 2).

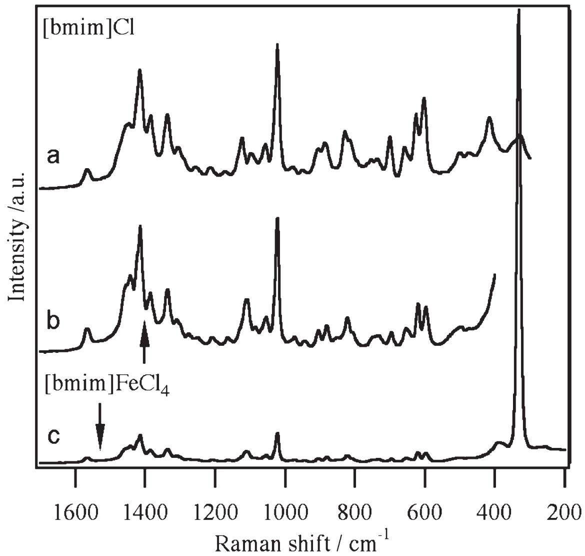

Figure 3. Raman spectra of [bmim]Cl (a) and $[bmim]FeCl_4$ (Liquid 1, b and c).

compares the Raman spectrum of liquid [bmim]Cl (super-cooled liquid at room temperature, Figure 3a) and those of Liquid 1 (Figures 3b and 3c). The spectrum of Liquid 1 in Figure 3c shows a strong band at $330\,cm^{-1}$. This band is already reported and is assigned to the totally symmetric Fe–Cl stretch vibration of $FeCl_4^-$.[6] The expanded Raman spectrum of Liquid 1 in Figure 3b is very similar to that of [bmim]Cl in Figure 3a. Since the chloride anion gives no Raman bands, the Raman bands observed in Figure 3a are all assigned to the vibrations of the $bmim^+$ cation. The Raman spectrum in Figure 3b then indicates that the $bmim^+$ cation, which has a structure similar to that in [bmim]Cl, exists in Liquid 1. Combining these results with the visible absorption data, it is confirmed that Liquids 1 and 2 are the same ionic liquid consisting of $[bmim]FeCl_4$.

The magnetic properties of $[bmim]FeCl_4$ were examined by using the SQUID method. A small amount (0.101 g) of $[bmim]FeCl_4$ was contained in a pharmaceutical cellulose capsule and its magnetic moment was measured in the magnetic field range of -10000 to 10000 Oe using a MPMS SQUID measuring system. The results are shown in Figure 4. Although the container capsule itself showed no magnetic response (crosses), the capsule containing $[bmim]FeCl_4$ showed a beautiful linear response to the magnetic field (circles). From the slope of the magnetic field dependence, the magnetic susceptibility of $[bmim]FeCl_4$ is determined to be $40.6 \times 10^{-6}\,emu\,g^{-1}$. Preliminary measurements (results not given) showed that $[bmim]FeCl_4$ exhibited ordinary paramagnetic temperature dependence in the temperature range between 5 and 300 K. The value of magnetic moment and its temperature dependence indicate that $[bmim]FeCl_4$ is paramagnetic and that there is no strong coupling among the spin angular momenta of the $FeCl_4^-$ anions.

It is known that concentrated aqueous solutions of magnetic salts like $FeCl_3$ and $CuSO_4$ respond to a magnet. Colloidal suspensions of powdered magnets are also known to respond to magnetic field. The presently discovered $[bmim]FeCl_4$ is entirely distinct from those conventional magnetic fluids. It possesses all characteristics of ionic liquids including high temperature stability, nonvolatility (no measurable vapor pressure), high viscosity, and so on. More importantly, we are able to design and create a number of new magnetic ionic liquids by combining a wide variety of cations and anions containing magnetic metal ions. It is even expected that a ferromaginetic ionic liquid will be synthesized in the near future. Studies along this line are in progress in our laboratory.

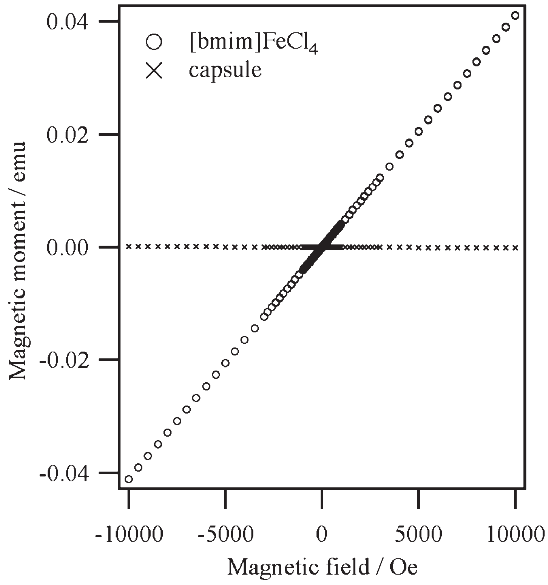

Figure 4. Relationship between the magnetic moment and the applied magnetic field, $[bmim]FeCl_4$ in a capsule (circle) and empty capsule (cross).

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