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and supplied fundamental data to application of magnetic ILs.

# Synthesis and characterization of the iron-containing magnetic ionic liquids

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ABSTRACT

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## 1. Introduction

lonic liquids (ILs) are used as green solvents or excellent media due to their unique physicochemical properties [1–4], such as wide liquid range, higher ionic conductivity, excellent solubility, thermal stability and designability by appropriate modifications of cations or anions in structures. Magnetic ILs not only have the above excellent properties but also exhibit an unexpectedly strong response to an additional magnet. These properties make magnetic ILs have more advantages and potential application prospects than conventional ILs in the fields of catalytic reactions [5–8], solvent effects [9–11] and separation processes [12,13].

1-butyl-3-methylimidazolium tetrachloroferrate ([bmim]FeCl<sub>4</sub>) with magnetism was synthesized and first reported by Hayashi et al. [14] in 2004. Since then, the syntheses of magnetic ILs have been focused on expanding synthesis with different alkyl chain length of imidazole cations or different magnetic metal anions. Metal-containing ILs and ionic liquid crystals based on imidazolium moiety were prepared by Ivan J. B. Lin et al. [15] in 2005. A series of imidazolium-based magnetic ILs with different alkyl substituent groups of cations were synthesized by Sesto et al. [16] in 2007. Furthermore, a series of imidazolium-based magnetic ILs with different complexing dysprosium metal anions were prepared by Mallick et al. [17] in 2008. In 2010, it was reported that 1-ethyl-3-methylimidazolium tetrachloroferrate ([emim]FeCl<sub>4</sub>) clearly showed a long-range antiferromagnetic ordering when it was frozen [18]. All these studies were confined to synthesis the magnetic ILs

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with the same imidazole cationic rings. Therefore, it is necessary to exploit novel magnetic ILs with different cationic structures.

In this paper, two novel magnetic ILs with pyridine and pyrrolidine cationic rings were synthesized and tested to show the same paramagnetism, which hasn't been reported in the literatures. Their magnetic susceptibilities are close to the imidazolium-based magnetic ILs in the same test conditions. Furthermore, they possess the same paramagnetism at 5 K–300 K. This study will provide references for further synthesizing magnetic ILs with stronger magnetism and offer many potential chances for magnetic ILs in practical application in the near future.

# 2. Experimental

# 2.1. Materials

FeCl<sub>3</sub>·6H<sub>2</sub>O, pyridine, *N*-methylpyrrolidine, *n*-chlorobutane, acetonitrile and ethyl acetate were of analytical grade and were used without further purification. Crystalline 1-butyl-3-methylimidazolium chloride ([bmim]Cl) with purity 99% was purchased from Henan Lihua Pharmaceutical Co., Ltd.

# 2.2. Preparation of magnetic ionic liquids

Three species of room temperature magnetic ionic liquids (ILs) including 1-butyl-3-methylimidazolium

tetrachloroferrate ([bmim]FeCl<sub>4</sub>), N-butylpyridium tetrachloroferrate ([bPy]FeCl<sub>4</sub>) and 1-butyl-1-methyl-

pyrrolidium tetrachloroferrate ([bmP]FeCl4) were synthesized via two-step in this paper. The intermedi-

ates and magnetic ILs were characterized by ultimate analysis, <sup>1</sup>H NMR, ESI-MS, FT-IR and Raman. In

addition, the three magnetic ILs were quantitatively tested by magnetic property measurement system (superconducting quantum interference device), and the results indicated that they had similar magnet-

ic susceptibilities and paramagnetic properties. This research expanded cationic types of magnetic ILs,

The preparation of magnetic ILs, such as [bmim]FeCl<sub>4</sub>, *N*-butylpyridium tetrachloroferrate ([bPy]FeCl<sub>4</sub>) and 1-butyl-1-methyl-pyrrolidium tetrachloroferrate ([bmP]FeCl<sub>4</sub>), were prepared using the following methods (shown in Scheme 1).

Firstly, intermediates *N*-butylpyridium chloride ([bPy]Cl) and 1-butyl-1-methylpyrrolidium chloride ([bmP]Cl) were prepared by reaction of equimolecular of pyridine (or *N*-methylpyrrolidine) and *n*-chlorobutane

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Scheme 1. synthetic pathway to [bmim]FeCl<sub>4</sub>, [bPy]FeCl<sub>4</sub> and [bmP]FeCl<sub>4</sub>.

at 80 °C ([bmP]Cl at 100 °C) with a magnetic stirring for five days. The intermediate products were repeatedly recrystallized from acetonitrile, subsequently washed three times with ethyl acetate and dried in vacuum at last.

Secondly, the intermediates including [bmim]Cl [19], [bPy]Cl and [bmP]Cl were respectively mixed with equimolecular of FeCl<sub>3</sub>·6H<sub>2</sub>O together under N<sub>2</sub> atmosphere with a mechanical stirring at room temperature ([bPy]FeCl<sub>4</sub> at 50 °C, [bmP]FeCl<sub>4</sub> at 30 °C). The products were washed with ether and deionized water, purified by reduced pressure distillation and dried in vacuum successively. Then the magnetic ILs, [bmim]FeCl<sub>4</sub>, [bPy]FeCl<sub>4</sub> and [bmP]FeCl<sub>4</sub>, were obtained.

## 2.3. Characterization

Nitrogen, carbon and hydrogen element contents of the synthesized intermediates were determined by combustion analysis in a Vario EL-III elemental analyzer (Germany, Elementar). <sup>1</sup>H NMR spectra of the intermediates were recorded on a BRUKER AVANCE 600 MHz spectrometer (Germany, Bruker) using DMSO- $d_6$  as an internal reference. Chemical shifts ( $\delta$ ) are given in ppm and coupling constants (J) are given in Hz. The multiplicities of signals in <sup>1</sup>H NMR are given with chemical shifts (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet).

ESI-MS analysis of the magnetic ILs was performed using a Bruker Daltonics APEX-II (America, Bruker Daltonics Inc). FT-IR spectra were registered with a Nicolet Magna-IR-560 Spectrometer infrared spectrophotometer (America, Nicolet). Raman spectra were detected by a microscopic confocal Raman spectrometer LabRAM HR-800 (France, Horiba Jobin Yvon) using a 785 nm laser beam and a charge-coupled detector (CCD) with 4 cm<sup>-1</sup> resolution. The magnetic susceptibilities of magnetic ILs were measured by a MPMS (SQUID) (America, Quantum Design) in Peking University.

## 3. Results and discussion

The physical properties of magnetic ILs are mainly affected by their structures, and their purities also have great influence on their physical parameters. Therefore, structures and purities of the ILs are characterized by some analytical methods so as to achieve the aims of the study. In the experiment, the intermediates were mainly characterized by ultimate analysis, <sup>1</sup>H NMR, and the synthetic magnetic ILs were characterized by ESI-MS, FT-IR, Raman and MPMS (SQUID).

#### 3.1. Ultimate analysis of the intermediates

The intermediates [bPy]Cl and [bmP]Cl are extremely easy to absorb water. This phenomenon will result in the test values of hydrogen contents of the intermediates greater than the theoretical values. To avoid such deviation appearing, experimental treatment and sample handling should be done as soon as possible in the analytical process. In data processing, the test values of N, C and H elements are compared with the theoretical values, and the test N/C ratios of intermediates are also compared with theoretical N/C ratios. Test data are as follow: Anal. calcd for C<sub>9</sub>H<sub>14</sub>ClN: C, 62.97%; H, 8.22%; N, 8.16%; found: C, 62.95%; H, 8.26%; N, 8.14%; Anal. calcd for C<sub>9</sub>H<sub>20</sub>ClN: C, 60.83%; H, 11.34%; N, 7.88%; found: C, 60.81%; H, 11.37%; N, 7.85%. The results manifest that the test values of intermediates are basically consistent with the theoretical values.

## 3.2. <sup>1</sup>H NMR spectra of the intermediates

The cationic structures and purities of the intermediates [bPy]Cl and [bmP]Cl are primarily confirmed using the  $^{1}$ H NMR spectra, and the data are listed as follow.



**Fig. 1.** ESI-MS spectra of [bmim]<sup>+</sup>(1), [bPy]<sup>+</sup>(2), [bmP]<sup>+</sup>(3) and [FeCl<sub>4</sub>]<sup>-</sup>(4).

[bPy]Cl, <sup>1</sup>H NMR (DMSO- $d_6$ ,  $\delta$ , ppm): 0.96 (3H, t, J = 7 Hz); 1.34–1.43 (2H, m); 1.98–2.06 (2H, m); 4.64 (2H, t, J = 7 Hz); 8.09 (2H, t, J = 6 Hz); 8.57 (1H, t, J = 8 Hz); 8.88 (2H, d, J = 6 Hz).

[bmP]Cl, <sup>1</sup>H NMR (DMSO- $d_6$ ,  $\delta$ , ppm): 0.97 (3H, t, J=7.4 Hz); 1.36–1.46 (2H, m); 1.76–1.84 (2H, m); 2.23 (4H, s); 3.06 (3H, s); 3.33–3.37 (2H, m); 3.52 (4H, s).

The <sup>1</sup>H NMR spectra show that the approximate ratios of integral peak area are concordant with the ratios of the number of hydrogen atoms at different shift in an allowable error range. Meanwhile, there are not additional peaks existing in the <sup>1</sup>H NMR spectra of the intermediates. Therefore, it can be concluded that [bPy]Cl and [bmP] Cl have been synthesized successfully.

# 3.3. ESI-MS spectra of the magnetic ILs

In order to analyze and determine the structures and purities of the synthesized magnetic ILs, they were tested by ESI-MS spectra (Fig. 1). In Fig. 1, it can be seen that the characteristic ionic peaks appear at m/z139.1, m/z136.1 and m/z142.1 successively corresponding to the cationic molecular weight of the magnetic ILs. Therefore, the information about the cationic structures of magnetic ILs is definitely determined. The anions of magnetic ILs have the very similar ESI-MS spectra, which appears one characteristic ionic peak at m/z198.8. Furthermore, there are rarely impurity peaks in the ESI-MS spectra of anions and cations of magnetic ILs. Therefore, it can be inferred that the magnetic ILs have been synthesized with high purities. Test results are as follow: Electrospray  $MS^+m/z$ : 136.1 [bPy]<sup>+</sup>;  $MS^-m/z$ : 198.8 [FeCl<sub>4</sub>]<sup>-</sup>; Electrospray  $MS^+m/z$ : 136.1 [bPy]<sup>+</sup>;  $MS^-m/z$ : 198.8 [FeCl<sub>4</sub>]<sup>-</sup>.

# 3.4. FT-IR spectra of the magnetic ILs

Compared FT-IR spectra of intermediates with their corresponding complexes, it can be found that spectra of intermediates are quite similar to their corresponding complexes. From fingerprint area  $(400-1300 \text{ cm}^{-1})$  to characteristic frequency area (13004000 cm<sup>-1</sup>), there are no differences except the sharper peaks appearing in the complexes spectra. The analysis indicates that the intermediates corresponding complexes have the same cationic structures with the intermediates and the anions of complexes have little effect on the chemical displacements of complexes.

## 3.5. Raman spectra of the magnetic ILs

Raman spectra were recorded from  $50 \text{ cm}^{-1}$  to  $1600 \text{ cm}^{-1}$  on a laboratory made near-infrared multichannel Raman system. The 785 nm laser was used as the excitation source in order to avoid fluorescence from impurities. The Raman spectra of magnetic ILs [bmim]FeCl<sub>4</sub>, [bPy]FeCl<sub>4</sub> and [bmP]FeCl<sub>4</sub> are very well in keeping with each other in  $50-500 \text{ cm}^{-1}$  (see Fig. 2). In Fig. 2, the two peaks appear at  $113.24 \text{ cm}^{-1}$  and  $333.20 \text{ cm}^{-1}$  in the spectra of three magnetic ILs. Those peaks were reported and assigned to the symmetric Fe–Cl bond stretch vibrations of [FeCl<sub>4</sub>]<sup>-</sup> in the literature [14]. Thus, it can be confirmed that the tested samples contain the same [FeCl<sub>4</sub>]<sup>-</sup> anions.



Fig. 2. Raman spectra of  $[bmim]FeCl_4(a)$ ,  $[bPy]FeCl_4(b)$  and  $[bmP]FeCl_4(c)$  at room temperature.



Fig. 3. Magnetization of [bmim]FeCl<sub>4</sub>, [bPy]FeCl<sub>4</sub> and [bmP]FeCl<sub>4</sub> as a function of applied magnetic field at 300 K.

 Table 1

 The magnetic susceptibilities of magnetic ionic liquids.

Compound	Temperature/K	Magnetic susceptibility $\times10^{5}/emu~g^{-1}$
[bmim]FeCl4	300	4.04
[bPy]FeCl4	300	4.11
[bmP]FeCl4	300	0.95

#### 3.6. Magnetic property analysis of the magnetic ILs

The magnetic susceptibilities of the three magnetic ILs were measured by the MPMS (SQUID). A small amount of [bmim]FeCl<sub>4</sub> (45.72 mg), [bPy]FeCl<sub>4</sub> (27.45 mg) or [bmP]FeCl<sub>4</sub> (42.23 mg) was contained respectively in a pharmaceutical cellulose capsule and measured at 300 K in the magnetic field range from -10,000 Oe to 10,000 Oe. The results are shown in Fig. 3. It can be seen that magnetization intensities of the three magnetic ILs show linear response to the magnetic field. From the slopes of the three fitted lines, the magnetic susceptibilities of [bmim]FeCl<sub>4</sub>, [bPy]FeCl<sub>4</sub> and [bmP]FeCl<sub>4</sub> are determined (see Table 1). From Table 1, it can be seen that [bmim] FeCl<sub>4</sub> and [bPy]FeCl<sub>4</sub> have the same order of magnitude. In an allowable error range, the experimental value of [bmim]FeCl<sub>4</sub> is in accord with literature value [14]. The interdependencies between magnetic moment and magnetic field indicate that the three magnetic ILs are paramagnetic and there are no strong couplings among the spin angular momenta of the cations.

Furthermore, the temperature dependence of the magnetization was tested from 5 K to 300 K (see Fig. 4). As is shown in Fig. 4, the magnetic susceptibilities of [bmim]FeCl<sub>4</sub>, [bPy]FeCl<sub>4</sub> and [bmP]FeCl<sub>4</sub> versus temperature changes are in perfect accord with Curie–Weiss law. The result demonstrates that the three kinds of magnetic ILs have the same magnetic characteristics under the testing temperature.

# 4. Conclusions

Two novel types of magnetic ILs with pyridine and pyrrolidine cationic rings were synthesized via two-step, and varieties of magnetic ILs were expanded and enriched. The structures and major existing forms of the synthesized magnetic ILs were ascertained in detail by <sup>1</sup>H NMR, ESI-MS, FT-IR and Roman analytical methods.

Magnetic susceptibilities of the three species magnetic ILs were measured at a certain temperature or with proper intension of magnetic



Fig. 4. Magnetization of [bmim]FeCl<sub>4</sub>, [bPy]FeCl<sub>4</sub> and [bmP]FeCl<sub>4</sub> as a function of temperature under an applied magnetic field at 10,000 Oe.

field. The results show that the magnetic susceptibility of [bmP]FeCl<sub>4</sub> is the lowest among the three ILs and the magnetic susceptibility of [bPy] FeCl<sub>4</sub> is a little higher than that of [bmim]FeCl<sub>4</sub> at the same order of magnitude. In addition, the magnetic properties of [bmim]FeCl<sub>4</sub>, [bPy] FeCl<sub>4</sub> and [bmP]FeCl<sub>4</sub> are paramagnetic from 5 K to 300 K.

Predictably, iron-containing magnetic ILs [bPy]FeCl<sub>4</sub> and [bmP] FeCl<sub>4</sub> will be applied as solvent and catalyst in chemical reactions or separation technology as well as [bmim]FeCl<sub>4</sub> system in the near future.

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