Synthesis and Characterization of the Physicochemical and Magnetic Properties for Perfluoroalkyl Ester and Fe(III) Carboxylate-based Hydrophobic Magnetic Ionic Liquids

Omprakash Nacham, Kevin D. Clark, and Jared L. Anderson*

Department of Chemistry, Iowa State University, Ames, IA 50011 USA

Abstract

Magnetic ionic liquids (MILs) are a new class of ionic liquids (ILs) that incorporate a paramagnetic component in their chemical structure. Although imidazolium-based MILs can be synthesized using inexpensive and relatively straightforward procedures, these compounds often are water soluble which limits their usefulness in aqueous applications. In this study, two classes of hydrophobic MILs, including perfluorobutyl ester-based and Fe(III) carboxylate-based MILs, were synthesized and characterized. Functionalization of the cation with fluorinated substituents yielded MILs that were insoluble in aqueous solution at concentrations as low as 0.1% (w/v). In contrast to conventional MILs that rely on paramagnetic anions, Fe(III) carboxylate-based MILs were prepared featuring carboxylate ligands in the cationic moiety capable of chelating a paramagnetic Fe(III) center. The hydrophobic character of the Fe(III) carboxylate-based MILs was subsequently controlled by incorporating the bis[(trifluoromethyl)sulfonyl]imide ($\text{[NTf}_2^-$]) anion, resulting in MILs that were insoluble in aqueous solutions at 0.1% (w/v). This synthetic strategy has the potential to impart dual functionality to MILs by providing the flexibility to incorporate a task specific anion without sacrificing paramagnetic properties. The molar magnetic susceptibilities ($\chi_m$) and effective magnetic moments ($\mu_{\text{eff}}$) of the studied MILs were determined using superconducting quantum interference device (SQUID) magnetometry. Consistent with the Curie-Weiss law, a linear relationship between temperature and inverse magnetic susceptibility ($\chi_m^{-1}$) was observed for the hydrophobic MILs. The $\mu_{\text{eff}}$ values of the MILs examined in this study ranged from 3.56 to 8.06 Bohr magnetons ($\mu_B$).

Corresponding Author:

Jared L. Anderson
Department of Chemistry
Iowa State University
Ames, IA 50011
Tel.: +1 515-294-8356
E-mail address: andersoj@iastate.edu
Introduction

Ionic liquids (ILs) are a class of non-molecular solvents with low melting points ($\leq 100$ °C) and are typically comprised of unsymmetrical organic cations and symmetrical/unsymmetrical inorganic/organic anions. ILs possess a number of intriguing physicochemical properties including negligible vapor pressure at ambient temperatures, high thermal stabilities, wide electrochemical windows, and unique solvation capabilities.\(^1\) By choosing different combinations of cations and anions, the properties of ILs can be readily modified. Magnetic ionic liquids (MILs) are a subclass of ILs and are produced by incorporating a high spin metal complex in either the cationic or anionic component.\(^2\) MILs can be designed to contain most if not all of the desirable features of conventional ILs, but also exhibit a paramagnetic property. As a result, their motion can be easily manipulated in the presence of an external magnetic field. MILs have been featured in a wide range of applications including solvents for DNA extraction,\(^5\) CO$_2$ absorption media,\(^6\) switchable electrochromic materials,\(^7\) and magnetic stimuli responsive surfactants.\(^8\)

Although transition metal-based ILs were reported decades ago, the magnetic properties of these materials were initially overlooked.\(^9\)\textsuperscript{-}\textsuperscript{11} However, Hayashi \textit{et al.} reported in 2004 the synthesis of the 1-butyl-3-methylimidazolium tetrachloroferrate(III) [BMIM$^+$][FeCl$_4^-$] MIL and demonstrated this compound’s paramagnetic behavior in an external magnetic field.\(^2\) Subsequently, a variety of MILs have been prepared using imidazolium cations and transition metal or lanthanide-based anions.\(^12\)\textsuperscript{-}\textsuperscript{14} By incorporating different metal complexes into the anion, it is possible to modify the physicochemical and magnetic properties of imidazolium-based MILs. However, the
hydrophilic nature of the imidazolium cation has limited the application of MILs in aqueous systems. Lee et al. have studied the phase separation behavior of the [BMIM][FeCl₄] MIL in aqueous solution. At concentrations lower than 20% (v/v) MIL, no observable phase separation occurred upon the application of a 1 T external magnetic field. To address this challenge, heavily alkylated phosphonium and ammonium cations have been shown to increase the hydrophobic character of MILs. Nonetheless, the synthesis and structural modification of imidazolium-based MILs is often preferred due to their lower cost and lower complexity when compared to MILs with functionalized phosphonium or ammonium cations.

Present strategies for enhancing the hydrophobic nature of MILs include modifying the structure of the cation (e.g., increasing the alkyl chain length of substituent groups) or by mixing equimolar quantities of weakly coordinating anions, such as bis[(trifluoromethyl)sulfonyl]imide ([NTf₂]). In these approaches, the choice of anion is often fixed because the paramagnetic properties of the MIL are governed by the anionic component. As a result, the MIL cation represents the primary basis for structural customization, greatly limiting the tunability of hydrophobic MILs. However, this can be overcome through the preparation of either magnetoactive cations or through the synthesis of ILs that are capable of chelating paramagnetic metals, thereby providing flexibility in tuning the anion of the resulting MIL. Very recently, the synthesis and magnetic properties of ferrocenium-based MILs possessing [NTf₂] and hexafluorophosphate [PF₆] anions were reported. By incorporating a magnetoactive cation in the MIL structure, greater flexibility in the choice of anion was achieved.
Unfortunately, the instability of ferrocenium complexes in air as well as the multiple step synthesis involved in preparing these compounds presents substantial challenges.

In this study, two different classes of hydrophobic MILs were synthesized, as shown in Figure 1. Within each class, unique synthetic strategies were exploited to enhance the hydrophobic nature and impart paramagnetic properties to the resulting MIL. The first class features hydrophobic imidazolium-based MILs with fluorinated substituents as the side chain of the cation. In the second class, imidazolium-based cations capable of chelating the paramagnetic iron(III) center were prepared. In this case, carboxylate groups appended to the imidazolium cation act as ligands for the paramagnetic center, thereby providing the flexibility to incorporate the \([\text{NTf}_2^-]\) anion into the MIL structure. The thermal properties of all MILs were investigated using differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). Within the first class, the melting point of IL intermediates were found to be significantly reduced through esterification with perfluorobutyryl chloride. The paramagnetic properties of the synthesized MILs were examined using superconducting quantum interference device (SQUID) magnetometry and the effective magnetic moment (\(\mu_{\text{eff}}\)) values of the MILs synthesized in this study were between 3.56–8.03 Bohr magnetons (\(\mu_B\)).

**Materials and Measurements**

Benzimidazole (98%), benzylbromide (98%), 1,12-dibromododecane (98%), and perfluorobutyryl chloride (98%) were purchased from Acros Organics (Morris Plains, NJ, USA). 6-bromohexanol (97%), benzylimidazole (99%), 2-bromoethanol (95%), 1-bromohexadecane (99%), thionyl chloride (99.5%), iron (III) chloride (FeCl₃·6H₂O)
(97%), and dimethyl sulfoxide (DMSO) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Acetonitrile, chloroform, acetone, methanol, hexanes, and ethyl acetate were obtained from Fisher Scientific (Fair Lawn, NJ, USA). Lithium bis(trifluoromethyl)sulfonylimide (98%) was purchased from Synquest Labs (Alachua, FL, USA). All solvents and reagents were used as received without any additional purification. Deuterated chloroform, methanol, and DMSO were obtained from Cambridge Isotope Laboratories (Andover, MA, USA) and were used as received without any further drying.

NMR spectra (\(^1\)H, \(^13\)C, and \(^19\)F) were recorded using either a Varian 400 MHz or Bruker 500 MHz nuclear magnetic resonance spectrometer. Solvents peaks were used as reference values for reporting the chemical shifts. Mass spectra were obtained using an Esquire-LC-MS/MS from Bruker Daltonics. A Perkin Elmer PYRIS Diamond Differential Scanning Calorimeter was used to evaluate the phase transition behavior of MILs and selected intermediates. Thermal decomposition temperatures of the MILs were probed using a Netzsch STA449 F1 thermogravimetric analyzer under nitrogen gas flow of 60 mL min\(^{-1}\) at a thermal rate of 20 °C min\(^{-1}\). The evolved gases from the thermogravimetric analyzer were examined using Netzsch QMS 403 D Aeolos mass spectrometer. Magnetic susceptibility measurements were determined using a magnetic susceptibility balance (MSB) from Johnson Matthey. The MSB was calibrated using CuSO\(_4\)•5H\(_2\)O. Prior to MIL measurements, the instrument was validated using the previously reported data for the \(\left[\text{P}_{6,6,6,14}^+\right] \left[\text{FeCl}_4^-\right]\) MIL. Visible absorption spectra of MILs were recorded in acetonitrile using a Thermo Scientific Evolution 300 UV-vis spectrophotometer. IR spectra of MILs were obtained using a Frontier FT-IR.
spectrometer from Perkin Elmer. The spectra were collected by dissolving a small amount of MIL in chloroform followed by evaporation to a thin film on the sample platform.

**Preparation of Monocationic and Dicationic Perfluorobutyryl Ester-based Hydrophobic MILs**

MIL 1 was synthesized as shown in Scheme 1. Benzimidazole (1 mmol) and potassium hydroxide (5 mmol) were dissolved in DMSO (30 mL) at room temperature and stirred for 12 h. A desired amount of alkyl/aryl bromide was added to the reaction mixture and stirred at 30-35 °C for 12 h. Water (35 mL) was added to the reaction mixture and the contents transferred to a separatory funnel. Compound 1a/1b was extracted from the reaction mixture using chloroform (3 x 35 mL). The organic phases were washed several times with excess water until a neutral pH was observed. The combined organic phases were dried over sodium sulfate for 20 min and filtered using vacuum filtration. After evaporation of the chloroform, compound 1a/1b was dried at 75 °C for 3 h under reduced pressure. Compound 1a (1 mmol) and 6-bromohexanol (1.5 mmol) were dissolved in acetonitrile (30 mL) and stirred for 72 h under reflux conditions. The solvent was evaporated under reduced pressure. Crude compound 1c was washed with hexanes (3 x 30 mL) and dried at 60 °C under reduced pressure for 5 h. Compound 1d was synthesized by reacting 1c (1 mmol) with perfluorobutyryl chloride (2.1 mmol) in dichloromethane at 0-5 °C for 6 h. Following solvent evaporation, the crude compound was washed with ethyl acetate and dried at 60 °C for 4 h under vacuum to remove residual solvents and excess perfluorobutyryl chloride. Finally, MIL 1 was prepared by
reacting 1d (1 mmol) with FeCl₃•6H₂O (1.3 mmol) in acetone (10 mL) at room temperature under a nitrogen atmosphere for 6 h. After solvent evaporation, compound 1 was dissolved in dichloromethane and washed several times with water to remove unreacted FeCl₃. The solvent was evaporated and MIL 1 was dried at 60 °C for 5 h under vacuum.

MIL 2 was prepared using a previously reported procedure from the literature with some modifications, as shown in Scheme 1. Compound 2b was prepared by reacting previously synthesized compound 2a (1 mmol) with 6-bromohexanol (2.4 mmol) in acetonitrile/chloroform 9:1 ratio (40 mL) at 50-55 °C for 4 days. The reaction mixture was partially evaporated and acetone was added to precipitate compound 2b. The precipitate was then washed with chloroform (10 mL) followed by diethylether (30 mL). Compound 2b was dried under reduced pressure for 5 h at 60 °C to remove residual solvents. Compound 2c was synthesized by reacting 2b (1 mmol) with perfluorobutyryl chloride (3 mmol) in dichloromethane at 0-5 °C for 5 h. Following solvent evaporation, compound 2c was washed with ethyl acetate and dried at 70 °C for 6 h under reduced pressure. MIL 2 was prepared by reacting 2c (1 mmol) with FeCl₃•6H₂O (1.3 mmol) in acetone at room temperature under a nitrogen atmosphere for 6 h. Followed by solvent evaporation the compound was dissolved in chloroform (10 mL) and washed with water (3 x 10 mL) to remove the unreacted FeCl₃. Chloroform was evaporated under reduced pressure and MIL 2 was dried at 60 °C for 5 h under vacuum.

NMR Analysis of 1a. A dark brown solid. Yield 87%. ¹H NMR (400 MHz, DMSO-d₆) δ (ppm) 8.20 (s, 1H), 7.63 (d, J = 7.8 Hz, 1H), 7.55 (d, J = 7.9 Hz, 1H), 7.19
(dt, $J = 20.0, 7.3$ Hz, 2H), 4.20 (t, $J = 7.0$ Hz, 2H), 1.75 (p, $J = 7.0$ Hz, 2H), 1.19 (d, $J = 10.5$ Hz, 26H), 0.82 (t, $J = 6.5$ Hz, 3H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ (ppm) 144.72, 143.46, 143.18, 133.76, 123.03, 122.09, 121.18, 120.33, 120.08, 119.25, 118.75, 110.92, 109.93, 109.61, 44.05, 30.36, 29.66, 29.40, 29.09, 28.97, 28.79, 28.54, 26.14, 22.14. 13.30. ESI-MS: m/z (+) 342.3.

**NMR Analysis of 1b.** A white solid. Yield 91%. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ (ppm) 7.85 (s, 1H), 7.76 – 7.71 (m, 1H), 7.27 – 7.12 (m, 6H), 7.08 (dd, $J = 7.2, 2.5$ Hz, 2H), 5.25 (s, 2H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ (ppm) 143.02, 135.27, 133.73, 128.82, 128.05, 126.86, 122.85, 122.04, 120.05, 109.81, 48.64. ESI-MS: m/z (+) 209.4.

**NMR Analysis of 1c.** A dark brown solid. Yield 75%. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ (ppm) 11.44 (s, 1H), 7.80 – 7.63 (m, 4H), 4.64 (m, 4H), 3.65 (t, $J = 5.8$ Hz, 2H), 2.09 (m, 4H), 1.68 – 1.11 (m, 32H), 0.87 (t, $J = 6.6$ Hz, 3H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ (ppm) 143.44, 131.79, 131.73, 127.58, 127.55, 113.61, 113.54, 62.55, 48.33, 47.91, 32.38, 32.35, 30.16, 30.11, 30.06, 29.98, 29.87, 29.82, 29.54, 29.33, 27.08, 26.28, 25.33, 23.16, 14.61.

**NMR Analysis of 1d.** A light brown viscous liquid. Yield 90%. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ (ppm) 10.54 (s, 1H), 7.75 – 7.65 (m, 4H), 4.52 (dt, $J = 18.4, 7.6$ Hz, 4H), 4.36 (t, $J = 6.4$ Hz, 2H), 2.01 (m, 4H), 1.74 (m, 2H), 1.50 – 1.19 (m, 30H), 0.87 (t, $J = 6.6$ Hz, 3H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ (ppm) 142.78, 131.41, 127.33, 113.20, 113.02, 68.39, 47.87, 47.51, 32.07, 29.81, 29.77, 29.71, 29.62, 29.51, 29.49, 29.47, 29.20, 29.09, 27.89, 26.63, 25.99, 25.07, 22.85, 14.28. $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ (ppm) 65.15.
Chloroform-\(d\) \(\delta\) (ppm) -81.28 (dt, \(J = 24.6, 8.7\) Hz, 3F), -119.76 (dq, \(J = 107.6, 9.0\) Hz, 2F), -127.56 (d, \(J = 21.4\) Hz, 2F).

**Visible Spectrum of MIL 1.** A dark brown viscous liquid. Yield 83%. Characteristic bands for the \([\text{FeCl}_3\text{Br}^-]\) anion were observed at 534, 619, and 688 nm.

Elem. Anal. Calcd (%) for \(\text{C}_{33}\text{H}_{50}\text{BrCl}_3\text{F}_7\text{FeN}_2\text{O}_2\) \(\cdot\) \(\text{H}_2\text{O}:\) C, 44.05; H, 5.82; N, 3.11. Found: C, 43.91; H, 5.82; N, 3.04;

**NMR Analysis of 2b.** White powder. Yield 74%. \(^1\text{H}\) NMR (500 MHz, Methanol-\(d_4\)) \(\delta\) 9.65 (s, 2H), 8.01 (dp, \(J = 7.6, 4.3\) Hz, 4H), 7.73 (dt, \(J = 6.3, 3.6\) Hz, 4H), 4.55 (q, \(J = 7.0\) Hz, 8H), 3.54 (t, \(J = 6.3\) Hz, 4H), 2.10 – 1.97 (m, 8H), 1.54 (s, 4H), 1.49 – 1.36 (m, 16H), 1.29 (s, 8H). \(^{13}\text{C}\) NMR (125 MHz, Methanol-\(d_4\)) \(\delta\) 142.13, 132.46, 127.76, 114.11, 62.10, 48.94, 48.77, 48.54, 48.02, 47.93, 32.77, 30.12, 30.06, 29.72, 29.68, 27.06, 26.78, 25.87.

**NMR Analysis of 2c.** A light brown viscous liquid. Yield 87%. \(^1\text{H}\) NMR (400 MHz, Chloroform-\(d\)) \(\delta\) (ppm) 10.54 (s, 2H), 7.75 – 7.65 (m, 8H), 4.52 (dt, \(J = 18.4, 7.6\) Hz, 8H), 4.36 (t, \(J = 6.4\) Hz, 4H), 2.01 (m, 8H), 1.74 (m, 4H), 1.50 – 1.19 (m, 24H). \(^{13}\text{C}\) NMR (100 MHz, Chloroform-\(d\)) \(\delta\) (ppm) 142.78, 131.41, 127.33, 113.20, 113.02, 68.39, 47.87, 47.51, 32.07, 29.81, 29.77, 29.71, 29.62, 29.51, 29.49, 29.47, 29.20, 29.09, 27.89, 26.63, 25.99, 25.07, 22.85, 14.28. \(^{19}\text{F}\) NMR (376 MHz, Chloroform-\(d\)) \(\delta\) -78.57 (dt, \(J = 31.4, 8.8\) Hz, 6F), -116.71 (dq, \(J = 206.7, 8.7\) Hz, 4F), -124.65 (d, \(J = 43.0\) Hz, 4F).

**Visible Spectrum of MIL 2.** A brown viscous liquid. The \([\text{FeCl}_3\text{Br}^-]\) anion of MIL 2 showed the characteristic bands at 534, 619, and 688 nm which were similar to the
previously reported compounds.\textsuperscript{16, 17} Elem. Anal. Calcd (%) for C\textsubscript{46}H\textsubscript{58}Br\textsubscript{2}Cl\textsubscript{6}F\textsubscript{14}Fe\textsubscript{2}N\textsubscript{4}O\textsubscript{4} 6.0H\textsubscript{2}O: C, 34.76; H, 4.44; N, 3.53; Found: C, 34.95; H, 4.09; N, 3.80.

**General Procedure for the Synthesis of Fe(III) Carboxylate-based Hydrophobic MILs**

MIL 3 was synthesized as shown in Scheme 2. Benzylimidazole (1 mmol) was reacted with an excess of 10-bromodecanoic acid (2.1 mmol) in acetonitrile (35 mL) for 72 h under reflux conditions. The solvent was evaporated under reduced pressure followed by washing of the crude product with ethyl acetate (4 x 35 mL) under sonication to remove excess 10-bromodecanoic acid. The bromide salt 3a was then dried at 60 °C for 2 h under reduced pressure to remove residual solvents. Compound 3b was synthesized by reacting 3a (1 mmol) with lithium bis[(trifluoromethyl)sulfonyl]imide (1.5 mmol) in water at room temperature for 12 h. After solvent evaporation, compound 3b was washed with an excess of water and the bromide impurities were monitored by adding silver nitrate to the aqueous phase. Compound 3b was then dried at 65 °C under reduced pressure for 12 h to remove residual water. Compound 3c was prepared by reacting 3b (1 mmol) with sodium hydroxide (1.8 mmol) in methanol at room temperature for 24 h. The solvent was evaporated under reduced pressure and compound 3c was washed with dichloromethane. After solvent evaporation, compound 3c was dried under vacuum at 60 °C for 4 h to remove residual solvents. Compound 3 was synthesized by reacting 3c (3 mmol) with FeCl\textsubscript{3}·6H\textsubscript{2}O (1.3 mmol) in acetone (10 mL) at room temperature for 12 h. The ensuing precipitate was separated using vacuum filtration and the filtrate evaporated under reduced pressure to yield compound 3. Compound 3 was
washed with water to remove any excess FeCl$_3$ and dried under reduced pressure to remove residual water.

MILs 4 and 5 were synthesized as shown in Scheme 2. Compound 4b/5b was prepared by reacting previously prepared 1a/1b with excess of 10-bromodecanoic acid in acetonitrile (40 mL) for 72 h under reflux conditions. Followed by solvent evaporation, the crude compound was washed with ethyl acetate to remove the unreacted 10-bromodecanoic acid. Compound 4b/5b was dried at 60 °C under vacuum for 2 h to remove residual solvents. Compound 4c/5c was prepared by reacting lithium bis[(trifluoromethyl)sulfonyl]imide (1.5 mmol) with 4b/5b (1 mmol) in methanol at room temperature for 12 h. The solvent was evaporated under reduced pressure and the crude compound washed several times with water to remove excess lithium bis[(trifluoromethyl)sulfonyl]imide. Compound 4c/5c was dried at 65 °C under vacuum for 5 h to evaporate residual water. Compound 4d/5d was prepared by reacting 4c/5c (1 mmol) with sodium hydroxide (1.8 mmol) in methanol at room temperature for 24 h. Following solvent evaporation, the crude product was washed with dichloromethane. Compound 4d/5d was dried at 60 °C under vacuum for 4 h to remove the residual solvent from the product. Finally, compound 4/5 was synthesized by reacting 4d/5d (3 mmol) with FeCl$_3$•6H$_2$O (1.3 mmol) in acetone (10 mL) at room temperature for 12 h. The reaction mixture was filtered using vacuum filtration to separate the precipitate; the filtrate was then evaporated under reduced pressure to yield crude compound 4/5. The final product was washed with excess water to remove unreacted FeCl$_3$ and dried under vacuum at 60 °C for 6 h to remove residual solvent.
**NMR Analysis of 3a.** A light brown solid. Yield 83%. $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ (ppm) 11.99 (s, 1H), 9.38 (t, $J = 1.6$ Hz, 1H), 7.84 (p, $J = 1.9$ Hz, 2H), 7.46 – 7.34 (m, 5H), 5.44 (s, 2H), 4.17 (t, $J = 7.2$ Hz, 2H), 2.18 (t, $J = 7.3$ Hz, 2H), 1.78 (p, $J = 7.3$ Hz, 2H), 1.52 – 1.42 (m, 2H), 1.31 – 1.15 (m, 10H). $^{13}$C NMR (100 MHz, DMSO-d$_6$) $\delta$ (ppm) 174.50, 136.12, 134.94, 129.01, 128.75, 128.24, 122.81, 122.59, 51.93, 48.97, 33.68, 29.25, 28.70, 28.64, 28.53, 28.29, 25.49, 24.50.

**NMR Analysis of 3b.** A dark brown viscous liquid. Yield 92%. $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ (ppm) 11.99 (s, 1H), 9.29 (d, $J = 1.7$ Hz, 1H), 7.81 (d, $J = 1.6$ Hz, 2H), 7.47 – 7.35 (m, 5H), 5.41 (s, 2H), 4.16 (t, $J = 7.2$ Hz, 2H), 2.18 (t, $J = 7.3$ Hz, 2H), 1.78 (p, $J = 7.2$ Hz, 2H), 1.46 (q, $J = 7.1$ Hz, 2H), 1.23 (q, $J = 8.7$, 7.4 Hz, 10H). $^{13}$C NMR (100 MHz, DMSO-d$_6$) $\delta$ (ppm) 174.50, 136.12, 134.89, 129.01, 128.76, 128.20, 122.81, 122.61, 121.07, 117.87, 51.99, 48.98, 33.67, 29.24, 28.69, 28.63, 28.53, 28.28, 25.49, 24.49.

**FT-IR Characterization of MIL 3.** A dark reddish brown viscous liquid. IR spectra of metal carboxylates are usually characterized in the range of 1650-1510 cm$^{-1}$. MIL 3 showed two distinctive bands at 1596 and 1443 cm$^{-1}$ which are similar to the previously reported iron carboxylate compounds. \(^{20}\) Elem. Anal. Calcd (%) for C$_{66}$H$_{84}$F$_{18}$FeN$_9$O$_{18}$S$_6$·2H$_2$O: C, 41.34; H, 4.63; N, 6.57; Found C, 41.37; H, 4.22; N, 6.16;

**NMR Analysis of 4b.** A dark brown solid. Yield 83%. $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ (ppm) 11.98 (s, 1H), 9.82 (s, 1H), 8.10 (dd, $J = 6.4$, 3.1 Hz, 2H), 7.69 (dd, $J = 6.3$, 3.1 Hz, 2H), 4.48 (t, $J = 7.1$ Hz, 4H), 2.16 (t, $J = 7.3$ Hz, 2H), 1.90 (t, $J = 7.1$ Hz,
**NMR Analysis of 4c.** A dark brown liquid. Yield 93%. $^1$H NMR (400 MHz, DMSO-$d_6$) δ (ppm) 11.98 (s, 1H), 9.98 (s, 1H), 8.14 – 8.05 (m, 2H), 7.69 (dt, $J = 6.3$, 3.6 Hz, 2H), 4.48 (t, $J = 7.1$ Hz, 4H), 2.16 (t, $J = 7.3$ Hz, 2H), 1.90 (t, $J = 7.0$ Hz, 4H), 1.45 (t, $J = 6.8$ Hz, 2H), 1.28 (t, $J = 5.1$ Hz, 36H), 0.89 – 0.79 (m, 3H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ (ppm) 174.50, 142.38, 134.10, 131.30, 130.84, 128.89, 128.72, 128.21, 126.71, 126.66, 113.93, 49.87, 46.93, 33.72, 29.17, 28.82, 28.36, 28.06, 25.78, 24.43.

**FT-IR Characterization of MIL 4.** A dark brown viscous liquid. IR spectrum of MIL 4 showed two characteristics bands at 1596 and 1443 cm$^{-1}$. Elem. Anal. Calcd (%) for C$_{105}$H$_{168}$F$_{18}$FeN$_{9}$O$_{18}$S$_6$ 6.0H$_2$O: C, 49.60; H, 7.14; N, 4.96; Found: C, 49.29; H, 6.30; N, 5.15.

**NMR Analysis of 5b.** A light brown solid. Yield 86%. $^1$H NMR (400 MHz, DMSO-$d_6$) δ (ppm) 11.99 (s, 1H), 9.98 (s, 1H), 8.14 – 8.09 (m, 1H), 7.97 (dd, $J = 7.3$, 2.1 Hz, 1H), 7.71 – 7.61 (m, 2H), 7.54 – 7.49 (m, 2H), 7.45 – 7.34 (m, 3H), 5.77 (s, 2H), 4.51 (t, $J = 7.2$ Hz, 2H), 2.18 (t, $J = 7.3$ Hz, 2H), 1.92 (p, $J = 7.3$ Hz, 2H), 1.46 (p, $J = 7.0$ Hz, 2H), 1.35 – 1.19 (m, 10H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ (ppm) 174.50, 142.38, 134.10, 131.30, 130.84, 128.89, 128.72, 128.21, 126.71, 126.66, 113.93, 49.87, 46.93, 33.72, 29.17, 28.82, 28.36, 28.06, 25.78, 24.43.
NMR Analysis of 5c. $^1$H NMR (400 MHz, DMSO-d$_6$) δ (ppm) 11.99 (s, 1H), 9.99 (s, 1H), 8.14 – 8.09 (m, 1H), 7.97 (dd, $J = 7.3, 1.9$ Hz, 1H), 7.71 – 7.61 (m, 2H), 7.53 – 7.48 (m, 2H), 7.44 – 7.33 (m, 3H), 5.77 (s, 2H), 4.51 (t, $J = 7.2$ Hz, 2H), 2.18 (t, $J = 7.4$ Hz, 2H), 1.92 (p, $J = 7.1$ Hz, 2H), 1.45 (q, $J = 7.2$ Hz, 2H), 1.38 – 1.16 (m, 10H).

$^{13}$C NMR (100 MHz, DMSO-d$_6$) δ (ppm) 198.95, 177.63, 142.79, 134.21, 131.34, 130.88, 129.00, 128.73, 128.26, 126.71, 126.67, 121.12, 117.92, 113.90, 49.88, 46.83, 38.46, 29.38, 28.96, 28.85, 28.41, 26.46, 25.78.

FT-IR Characterization of MIL 5. A dark brown viscous liquid. IR spectrum of compound 5 showed the characteristic bands at 1593 and 1443 cm$^{-1}$. Elem. Anal. Calcd (%) for C$_{78}$H$_{90}$F$_{18}$FeN$_9$O$_{18}$S$_6$ 3.0H$_2$O: C, 44.91; H, 4.64; N, 6.04; Found: C, 44.44; H, 4.33; N, 5.98.

Results and Discussion

Structural Tuning and Optimization of Reaction Conditions for Synthesis of Perfluorobutyryl Ester-based MILs

In liquid-liquid extraction (LLE) approaches, a water immiscible extraction solvent is often employed to isolate analytes of interest from the aqueous phase. Subsequently, recovery of the extraction phase is often achieved via a time consuming and laborious centrifugation process prior to sample analysis. MILs possess a significant advantage over conventional extraction solvents in the ease with which they can be manipulated by external magnetic fields. Using a MIL-based LLE technique, the paramagnetic properties of MILs can be exploited to enable rapid recovery of the analyte-enriched MIL extraction phase. However, previous studies have revealed that
imidazolium-based MILs are soluble in aqueous solution at compositions less than 20% (v/v) MIL. As a result of their solubility, they can no longer be manipulated using an external magnetic field. Therefore, disadvantages associated with imidazolium-based MILs can be addressed by tuning the structure of the MIL to impart sufficient hydrophobic nature to the resulting compound.

In order to improve the hydrophobicity of the resulting MILs, a relatively hydrophobic benzimidazole core as well as alkyl and perfluoroalkyl groups were selected and utilized for the synthesis of MILs (1-2), as shown in Scheme 1. The initial strategy employed for the synthesis of MIL 1 involved the preparation of a bromo-substituted perfluoroalkyl ester followed by reaction with hexadecylbenzimidazole to generate the bromide salt. Following this approach, 2-bromoethanol was reacted with perfluorobutyryl chloride to produce a bromo-substituted perfluorobutyryl ester. Unfortunately, when this compound was reacted with 1a, low product yields (< 21%) were observed with most of the hexadecylbenzimidazole remaining unreacted (based on $^1$H NMR). This may be attributed to the strong inductive effect from the perfluoroalkyl ester functional group. In order to overcome this challenge, a bromide salt with terminal hydroxyl groups on the benzimidazolium cation was prepared prior to the esterification reaction. Firstly, a 2:1 mole ratio of 2-bromoethanol was reacted with compound 1a. The resulting bromide salt was then esterified with perfluorobutyryl chloride in an effort to incorporate fluorinated substituents, but the esterification reaction did not progress to completion (< 45% based on $^1$H NMR). However, substantially improved product formation (90.1%) was observed under similar reaction conditions when 1c was reacted with perfluorobutyryl chloride. The bromide salt was subsequently reacted with FeCl$_3$$\cdot$6H$_2$O to generate the
paramagnetic iron(III) center in MIL 1. In order to remove unreacted FeCl₃, the final
product was dissolved in dichloromethane and washed several times with water. When
the same conditions were applied for reaction of 1c with longer perfluoroacid chlorides
(e.g. hexyl and octyl), the final products were isolated as room temperature solids.

The general synthetic strategy utilized for the preparation of MIL 2 is described in
Scheme 1. In an attempt to reduce the melting point of the MIL products, a precursor
comprised of two benzimidazole moieties separated by a dodecyl linkage chain (2a) was
prepared. Initially, 2a was reacted with 6-bromohexanol in neat chloroform for 7 days
under reflux. However, the desired dibromide salt was not formed using these conditions.
When a mixture of acetonitrile/chloroform (9:1) was employed as the reaction solvent, 2b
was generated with 74% yield. The hydroxyl groups of the dibromide salt were
subsequently reacted with excess perfluorobutyryl chloride to form compound 2c.
Finally, the perfluorobutyryl-ester based dibromide salt was reacted with FeCl₃·6H₂O to
incorporate the paramagnetic anion [FeCl₃Br⁻] in the resulting MIL 2.

The solubilities of perfluorobutyryl ester-based monocationic and dicationic MILs
in water and hexanes are shown in Table 1. Due to the presence of fluorinated
substituents as well benzimidazole moieties, MILs 1-2 were found to be immiscible in
aqueous solutions at compositions as low as 0.1% (w/v) of MIL and were found to be
miscible with hexane. Perfluoroalkyl ester-based hydrophobic MILs may be useful
candidates for liquid-liquid microextractions, where low volumes of extraction solvent
are often employed.

**Preparation of Fe(III) Carboxylate-based Hydrophobic MILs**
The most common approach employed in the preparation of MILs involves the pairing of a functionalized cation with a paramagnetic anion. While it is possible to impart hydrophobic character to the MIL by incorporating long alkyl chains/perfluoroalkyl or benzyl groups in the cationic component, the anion must remain unchanged in order to maintain the paramagnetic susceptibility of the compound. This paradigm severely limits the opportunity to include functional or task-specific anions other than those that impart paramagnetic properties to the MIL. To overcome this challenge and expand the variety of anions that can be incorporated into the MIL structure, the synthesis of imidazolium-based cations capable of chelating a paramagnetic iron(III) center was explored.

The general synthetic strategy employed for the preparation of Fe(III) carboxylate-based hydrophobic MILs is described in Scheme 2. With the aim of incorporating carboxylate functional groups into the imidazolium cation, a n-bromo-substituted alkyl carboxylic acid was reacted with an alkyl or aromatic substituted imidazole/benzimidazole. Initial attempts to react 5-bromovaleric acid with benzylimidazole resulted in low product yields (<30% based on $^1$H NMR) with most of the starting material remaining unreacted. In contrast, similar reaction conditions with 10-bromodecanoic acid resulted in substantially improved product formation (83-86%). Following preparation of the bromide salt, the carboxyl group was deprotonated with sodium hydroxide. Initially, $3\text{a}$ was reacted with sodium hydroxide in methanol, but the deprotonation reaction did not progress to completion (based on $^1$H NMR). However, similar reaction conditions with $3\text{b}$ resulted in complete formation of the desired sodium carboxylate. After dissolving the deprotonated compound in acetone, FeCl$_3$·6H$_2$O was added to the reaction mixture. A white precipitate was observed during the reaction that
corresponded to the formation of NaCl and was separated from the product by filtration. The final product was washed several times with water to remove unreacted FeCl$_3$.

Compound 3 exhibited a water solubility below 0.25% (w/v). In order to improve upon the hydrophobic character of 3, the imidazolium cation was replaced with the benzimidazolium cation to produce MILs 4 and 5, as shown in Scheme 2. Significant enhancement in the hydrophobicity for 4 and 5 was observed, and these compounds were found to be insoluble in water at 0.1% (w/v) of MIL.

**Thermal Properties of Perfluoroalkyl Ester-based and Fe(III) Carboxylate-based Hydrophobic MILs**

The thermal properties of the five hydrophobic MILs prepared in this study were investigated using DSC and TGA. As shown in Table 1, the only MIL to exhibit a melting point ($T_m$) above −45 °C was the monocationic perfluoroalkyl ester-based MIL 1. Although phase transitions were not observed for MILs 2–5 under the temperatures studied, these compounds existed as room temperature liquids. Interestingly, the dicationic MIL 2 was found to be a viscous liquid despite having a component of symmetry. Further investigation of the intermediates used to generate MIL 2 revealed that the perfluoroalkyl ester group had a profound influence on the melting point of the salt. While 2b was isolated as a room temperature solid with a melting point of 119 °C, esterification with fluorobutyryl chloride generated compound 2c with no detectable phase transition above −45 °C. This may be explained by the higher propensity of 2b to participate in hydrogen bonding when compared to the ester-functionalized compound 2c. Thermal stabilities for the perfluoroalkyl ester-based MILs 1 and 2 were found to be 254 °C and 225 °C, respectively.
Hydrophobic MILs derived from carboxylate-functionalized imidazolium and benzimidazolium cations (MILs 3–5) did not exhibit phase transitions above −45 °C. This behavior is likely due to the incorporation of the non-coordinating [NTf₂⁻] anion in the MIL structure. Compared to the perfluoroalkyl ester-based MILs, compounds 3–5 possessed enhanced thermal stabilities as high as 314 °C in the case of MIL 3. TGA coupled with mass spectrometry (TGA-MS) enabled the analysis of volatile components released from the MILs during temperature ramping. When heated beyond 250 °C, a prominent peak at \( m/z \) 44 was observed for all three Fe(III) carboxylate-based MILs corresponding to the release of CO₂. These results indicate that the decomposition of MILs 3-5 initially proceeds through a decarboxylation pathway.

**Magnetic Properties of Hydrophobic MILs**

The ability to precisely control the motion of MILs by application of a magnetic field represents a significant advantage for these compounds over conventional ILs. Due to the presence of unpaired electrons in the valence orbitals of metal ions, MILs align their spins in response to an external magnetic field and exhibit a net magnetization. When the magnetic field is removed, thermal motion causes the spins to orient themselves randomly resulting in the loss of net magnetization. The Curie-Weiss law describes the inverse relation between the magnetic susceptibility and the temperature of paramagnetic materials.

Imidazolium-based MILs comprised of high-spin d⁵ Fe(III) centers have been well studied as a result of their relative ease of preparation and the low cost of iron materials.²,¹⁴ Table 1 shows \( \mu_{\text{eff}} \) values at 295 K for the five hydrophobic MILs prepared
in this study. The $\mu_{\text{eff}}$ values of the perfluorobutyryl ester-based MILs containing the [FeCl$_3$Br$^{-}$] anion (1-2) were determined according to previously reported procedures using an Evans magnetic susceptibility balance$^{17,21}$ and SQUID magnetometer.$^{18}$ The $\mu_{\text{eff}}$ values of the monocationic and dicationic perfluorobutyryl ester-based MILs were 5.36 and 8.03 $\mu_B$, respectively, and found to be in good agreement with previously reported high-spin d$^5$ Fe(III)-based MILs.$^{17,18}$ Figures 2a and b show the temperature dependence of molar magnetic susceptibilities ($\chi_m$) and the reciprocal magnetic susceptibilities ($\chi_m^{-1}$) for the dicationic MIL 2 as a representative example of [FeCl$_3$Br$^{-}$]-based MILs. The linear relationship between $\chi_m^{-1}$ and temperature for MIL 2 indicates that this compound follows the Curie-Weiss law.

The paramagnetic properties of MIL solvents often depend on the incorporation of a magnetoactive anion into the MIL structure. However, the synthesis of Fe(III) carboxylate-based MILs provides an alternative method for generating MILs in which the choice of anion is greatly expanded. Figures 3a and b show the temperature dependence of $\chi_m$ and $\chi_m^{-1}$ for the Fe(III) carboxylate-based MIL 4 (for MILs 3 and 5, see the Supporting Information). A linear relationship between $\chi_m^{-1}$ and temperature was observed from room temperature down to approximately 50 K, providing evidence of paramagnetic behavior for MIL 4. The $\mu_{\text{eff}}$ values of the Fe(III) carboxylate-based hydrophobic MILs ranged from 3.56 to 4.71 $\mu_B$ at 295 K, which is in line with previously reported Fe(III) complexes possessing carboxylate ligands.$^{22,23}$ Although the $\mu_{\text{eff}}$ values are considerably less than those observed for MILs containing high spin Fe(III) centers (e.g., tetrahaloferrates(III)), the Fe(III) carboxylate-based MILs can nonetheless be readily manipulated by application of an external magnetic field.
Conclusions

In this study, two classes of hydrophobic MILs were successfully synthesized and characterized. Within each class, unique synthetic strategies were employed to control the hydrophobicity, melting point, and magnetic susceptibility of the resulting MILs. In the first class, imidazolium cations were functionalized with fluorinated substituents in an effort to improve the hydrophobic character of the MIL. Both mono and dicationic perfluoroalkyl ester-based MILs were insoluble in aqueous solution at concentrations as low as 0.1% (w/v) MIL. Interestingly, reaction of the intermediates bearing hydroxyl groups with perfluorobutyryl chloride significantly lowered the melting points of the esterified products. Within the second class, the structure of the imidazolium cation was designed to possess carboxylate ligands as chelators for a paramagnetic iron(III) center. This novel approach generated MILs with a paramagnetic component in the cationic moiety, thereby allowing incorporation of [NTf$_2^-$] anions into the MIL structure without sacrificing paramagnetic properties. The magnetic properties of the MILs were investigated using SQUID magnetometry. The highest $\mu_{\text{eff}}$ (8.03 $\mu_B$, 295 K) was obtained for the dicationic MIL possessing two [FeCl$_3$Br$^-$] anions, while the Fe(III) carboxylate-based MILs exhibited $\mu_{\text{eff}}$ values ranging from 3.56 to 4.71 $\mu_B$ at 295 K. Despite the lower $\mu_{\text{eff}}$ values, the Fe(III) carboxylate-based MILs are readily manipulated by application of an external magnetic field. The hydrophobic MILs synthesized in this study may be intriguing candidates for extraction solvents in liquid-liquid microextraction techniques or in catalytic applications wherein the MIL can be easily isolated using a magnetic field, circumventing the need for time-consuming centrifugation steps.
Acknowledgments

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Supporting information:

NMR spectra, absorbance spectra, IR spectra, Figure S1-S7 are available in supporting information.

References

Scheme 1. Synthesis of monocationic and dicationic perfluorobutyryl ester-based hydrophobic magnetic ionic liquids
Scheme 2. Synthesis of Fe(III) carboxylate-based hydrophobic magnetic ionic liquids
Table 1. Physicochemical and magnetic properties of hydrophobic MILs and intermediates synthesized in this study.

<table>
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<th>Entry</th>
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<th>Melting point (°C)</th>
<th>$\mu_{\text{eff}}$ ($\mu_B$)</th>
<th>Thermal stability (°C)</th>
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$^a$ $\mu_{\text{eff}}$ = effective magnetic moment measured at 295 K using magnetic susceptibility balance; $^b$ $\mu_{\text{eff}}$ = effective magnetic moment measured at 295 K using SQUID; $^c$ Thermal gravimetric analysis (TGA) = temperature at which 5% wt loss of MIL is observed; I = insoluble; $^c$ Insoluble at 0.1% (w/v); $^d$ Insoluble at 0.25% (w/v); S = soluble.
Figure 1. Chemical structures of perfluorobutyryl ester (1-2) and Fe(III) carboxylate-based hydrophobic magnetic ionic liquids (3-5).
Figure 2. Temperature dependence of the (a) molar magnetic susceptibility and the (b) reciprocal molar susceptibility for MIL 2 using a field of 20,000 Oe.
Figure 3. Temperature dependence of the (a) molar magnetic susceptibility and the (b) reciprocal molar susceptibility for MIL 4 using a field of 20,000 Oe.
The hydrophobic and magnetic properties of magnetic ionic liquids can be controlled using cation functionalization or anion modification.