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

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6       **Abstract**

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

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## 36 Introduction

37 Ionic liquids (ILs) are a class of non-molecular solvents with low melting points  
38 ( $\leq 100$  °C) and are typically comprised of unsymmetrical organic cations and  
39 symmetrical/unsymmetrical inorganic/organic anions. ILs possess a number of intriguing  
40 physicochemical properties including negligible vapor pressure at ambient temperatures,  
41 high thermal stabilities, wide electrochemical windows, and unique solvation  
42 capabilities.<sup>1</sup> By choosing different combinations of cations and anions, the properties of  
43 ILs can be readily modified. Magnetic ionic liquids (MILs) are a subclass of ILs and are  
44 produced by incorporating a high spin metal complex in either the cationic or anionic  
45 component.<sup>2-4</sup> MILs can be designed to contain most if not all of the desirable features of  
46 conventional ILs, but also exhibit a paramagnetic property. As a result, their motion can  
47 be easily manipulated in the presence of an external magnetic field. MILs have been  
48 featured in a wide range of applications including solvents for DNA extraction,<sup>5</sup> CO<sub>2</sub>  
49 absorption media,<sup>6</sup> switchable electrochromic materials,<sup>7</sup> and magnetic stimuli responsive  
50 surfactants.<sup>8</sup>

51 Although transition metal-based ILs were reported decades ago, the magnetic  
52 properties of these materials were initially overlooked.<sup>9-11</sup> However, Hayashi *et al.*  
53 reported in 2004 the synthesis of the 1-butyl-3-methylimidazolium tetrachloroferrate(III)  
54 [BMIM<sup>+</sup>][FeCl<sub>4</sub><sup>-</sup>] MIL and demonstrated this compound's paramagnetic behavior in an  
55 external magnetic field.<sup>2</sup> Subsequently, a variety of MILs have been prepared using  
56 imidazolium cations and transition metal or lanthanide-based anions.<sup>12-14</sup> By  
57 incorporating different metal complexes into the anion, it is possible to modify the  
58 physicochemical and magnetic properties of imidazolium-based MILs. However, the

59 hydrophilic nature of the imidazolium cation has limited the application of MILs in  
60 aqueous systems. Lee *et al.* have studied the phase separation behavior of the  
61 [BMIM<sup>+</sup>][FeCl<sub>4</sub><sup>-</sup>] MIL in aqueous solution. At concentrations lower than 20% (v/v) MIL,  
62 no observable phase separation occurred upon the application of a 1 T external magnetic  
63 field.<sup>15</sup> To address this challenge, heavily alkylated phosphonium and ammonium cations  
64 have been shown to increase the hydrophobic character of MILs.<sup>16,17</sup> Nonetheless, the  
65 synthesis and structural modification of imidazolium-based MILs is often preferred due  
66 to their lower cost and lower complexity when compared to MILs with functionalized  
67 phosphonium or ammonium cations.

68 Present strategies for enhancing the hydrophobic nature of MILs include  
69 modifying the structure of the cation (e.g., increasing the alkyl chain length of substituent  
70 groups) or by mixing equimolar quantities of weakly coordinating anions, such as  
71 bis[(trifluoromethyl)sulfonyl]imide ([NTf<sub>2</sub><sup>-</sup>]).<sup>17, 18</sup> In these approaches, the choice of  
72 anion is often fixed because the paramagnetic properties of the MIL are governed by the  
73 anionic component. As a result, the MIL cation represents the primary basis for structural  
74 customization, greatly limiting the tunability of hydrophobic MILs. However, this can be  
75 overcome through the preparation of either magnetoactive cations or through the  
76 synthesis of ILs that are capable of chelating paramagnetic metals, thereby providing  
77 flexibility in tuning the anion of the resulting MIL. Very recently, the synthesis and  
78 magnetic properties of ferrocenium-based MILs possessing [NTf<sub>2</sub><sup>-</sup>] and  
79 hexafluorophosphate [PF<sub>6</sub><sup>-</sup>] anions were reported.<sup>3, 19</sup> By incorporating a magnetoactive  
80 cation in the MIL structure, greater flexibility in the choice of anion was achieved.

81 Unfortunately, the instability of ferrocenium complexes in air as well as the multiple step  
82 synthesis involved in preparing these compounds presents substantial challenges.

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

## 99 **Materials and Measurements**

100 Benzimidazole (98%), benzylbromide (98%), 1,12-dibromododecane (98%), and  
101 perfluorobutyryl chloride (98%) were purchased from Acros Organics (Morris Plains, NJ,  
102 USA). 6-bromohexanol (97%), benzylimidazole (99%), 2-bromoethanol (95%), 1-  
103 bromohexadecane (99%), thionyl chloride (99.5%), iron (III) chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ )

104 (97%), and dimethylsulfoxide (DMSO) were purchased from Sigma-Aldrich (St. Louis,  
105 MO, USA). Acetonitrile, chloroform, acetone, methanol, hexanes, and ethyl acetate were  
106 obtained from Fisher Scientific (Fair Lawn, NJ, USA). Lithium  
107 bis(trifluoromethyl)sulfonylimide (98%) was purchased from Synquest Labs (Alachua,  
108 FL, USA) All solvents and reagents were used as received without any additional  
109 purification. Deuterated chloroform, methanol, and DMSO were obtained from  
110 Cambridge Isotope Laboratories (Andover, MA, USA) and were used as received without  
111 any further drying.

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

127 spectrometer from Perkin Elmer. The spectra were collected by dissolving a small  
128 amount of MIL in chloroform followed by evaporation to a thin film on the sample  
129 platform.

### 130 **Preparation of Monocationic and Dicationic Perfluorobutyryl Ester-based** 131 **Hydrophobic MILs**

132 MIL **1** was synthesized as shown in Scheme 1. Benzimidazole (1 mmol) and  
133 potassium hydroxide (5 mmol) were dissolved in DMSO (30 mL) at room temperature  
134 and stirred for 12 h. A desired amount of alkyl/aryl bromide was added to the reaction  
135 mixture and stirred at 30-35 °C for 12 h. Water (35 mL) was added to the reaction  
136 mixture and the contents transferred to a separatory funnel. Compound **1a/1b** was  
137 extracted from the reaction mixture using chloroform (3 x 35 mL). The organic phases  
138 were washed several times with excess water until a neutral pH was observed. The  
139 combined organic phases were dried over sodium sulfate for 20 min and filtered using  
140 vacuum filtration. After evaporation of the chloroform, compound **1a/1b** was dried at 75  
141 °C for 3 h under reduced pressure. Compound **1a** (1 mmol) and 6-bromohexanol (1.5  
142 mmol) were dissolved in acetonitrile (30 mL) and stirred for 72 h under reflux conditions.  
143 The solvent was evaporated under reduced pressure. Crude compound **1c** was washed  
144 with hexanes (3 x 30 mL) and dried at 60 °C under reduced pressure for 5 h. Compound  
145 **1d** was synthesized by reacting **1c** (1 mmol) with perfluorobutyryl chloride (2.1 mmol) in  
146 dichloromethane at 0-5 °C for 6 h. Following solvent evaporation, the crude compound  
147 was washed with ethyl acetate and dried at 60 °C for 4 h under vacuum to remove  
148 residual solvents and excess perfluorobutyryl chloride. Finally, MIL **1** was prepared by

149 reacting **1d** (1 mmol) with FeCl<sub>3</sub>·6H<sub>2</sub>O (1.3 mmol) in acetone (10 mL) at room  
150 temperature under a nitrogen atmosphere for 6 h. After solvent evaporation, compound **1**  
151 was dissolved in dichloromethane and washed several times with water to remove  
152 unreacted FeCl<sub>3</sub>. The solvent was evaporated and MIL **1** was dried at 60 °C for 5 h under  
153 vacuum.

154 MIL **2** was prepared using a previously reported procedure from the literature  
155 with some modifications,<sup>17</sup> as shown in Scheme 1. Compound **2b** was prepared by  
156 reacting previously synthesized compound **2a** (1 mmol) with 6-bromohexanol (2.4 mmol)  
157 in acetonitrile/chloroform 9:1 ratio (40 mL) at 50-55 °C for 4 days. The reaction mixture  
158 was partially evaporated and acetone was added to precipitate compound **2b**. The  
159 precipitate was then washed with chloroform (10 mL) followed by diethylether (30 mL).  
160 Compound **2b** was dried under reduced pressure for 5 h at 60 °C to remove residual  
161 solvents. Compound **2c** was synthesized by reacting **2b** (1 mmol) with perfluorobutyryl  
162 chloride (3 mmol) in dichloromethane at 0-5 °C for 5 h. Following solvent evaporation,  
163 compound **2c** was washed with ethyl acetate and dried at 70 °C for 6 h under reduced  
164 pressure. MIL **2** was prepared by reacting **2c** (1 mmol) with FeCl<sub>3</sub>·6H<sub>2</sub>O (1.3 mmol) in  
165 acetone at room temperature under a nitrogen atmosphere for 6 h. Followed by solvent  
166 evaporation the compound was dissolved in chloroform (10 mL) and washed with water  
167 (3 x 10 mL) to remove the unreacted FeCl<sub>3</sub>. Chloroform was evaporated under reduced  
168 pressure and MIL **2** was dried at 60 °C for 5 h under vacuum.

169 **NMR Analysis of 1a.** A dark brown solid. Yield 87%. <sup>1</sup>H NMR (400 MHz,  
170 DMSO-*d*<sub>6</sub>) δ (ppm) 8.20 (s, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.19

171 (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,  $J =$   
172 10.5 Hz, 26H), 0.82 (t,  $J = 6.5$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  (ppm) 144.72,  
173 143.46, 143.18, 133.76, 123.03, 122.09, 121.18, 120.33, 120.08, 119.25, 118.75, 110.92,  
174 109.93, 109.61, 44.05, 30.36, 29.66, 29.40, 29.09, 28.97, 28.79, 28.54, 26.14, 22.14.  
175 13.30. ESI-MS:  $m/z$  (+) 342.3.

176 **NMR Analysis of 1b.** A white solid. Yield 91%.  $^1\text{H}$  NMR (400 MHz,  
177 Chloroform- $d$ )  $\delta$  (ppm) 7.85 (s, 1H), 7.76 – 7.71 (m, 1H), 7.27 – 7.12 (m, 6H), 7.08 (dd,  $J$   
178 = 7.2, 2.5 Hz, 2H), 5.25 (s, 2H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform- $d$ )  $\delta$  (ppm) 143.02,  
179 135.27, 133.73, 128.82, 128.05, 126.86, 122.85, 122.04, 120.05, 109.81, 48.64. ESI-MS:  
180  $m/z$  (+) 209.4.

181 **NMR Analysis of 1c.** A dark brown solid. Yield 75%.  $^1\text{H}$  NMR (400 MHz,  
182 Chloroform- $d$ )  $\delta$  (ppm) 11.44 (s, 1H), 7.80 – 7.63 (m, 4H), 4.64 (m, 4H), 3.65 (t,  $J = 5.8$   
183 Hz, 2H), 2.09 (m, 4H), 1.68 – 1.11 (m, 32H), 0.87 (t,  $J = 6.6$  Hz, 3H).  $^{13}\text{C}$  NMR (100  
184 MHz, Chloroform- $d$ )  $\delta$  (ppm) 143.44, 131.79, 131.73, 127.58, 127.55, 113.61, 113.54,  
185 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,  
186 27.08, 26.28, 25.33, 23.16, 14.61.

187 **NMR Analysis of 1d.** A light brown viscous liquid. Yield 90%.  $^1\text{H}$  NMR (400  
188 MHz, Chloroform- $d$ )  $\delta$  (ppm) 10.54 (s, 1H), 7.75 – 7.65 (m, 4H), 4.52 (dt,  $J = 18.4, 7.6$   
189 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  
190 (t,  $J = 6.6$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform- $d$ )  $\delta$  (ppm) 142.78, 131.41, 127.33,  
191 113.20, 113.02, 68.39, 47.87, 47.51, 32.07, 29.81, 29.77, 29.71, 29.62, 29.51, 29.49,  
192 29.47, 29.20, 29.09, 27.89, 26.63, 25.99, 25.07, 22.85, 14.28.  $^{19}\text{F}$  NMR (376 MHz,

193 Chloroform-*d*)  $\delta$  (ppm) -81.28 (dt,  $J = 24.6, 8.7$  Hz, 3F), -119.76 (dq,  $J = 107.6, 9.0$  Hz,  
194 2F), -127.56 (d,  $J = 21.4$  Hz, 2F).

195 **Visible Spectrum of MIL 1.** A dark brown viscous liquid. Yield 83%.  
196 Characteristic bands for the  $[\text{FeCl}_3\text{Br}^-]$  anion were observed at 534, 619, and 688 nm.  
197 Elem. Anal. Calcd (%) for  $\text{C}_{33}\text{H}_{50}\text{BrCl}_3\text{F}_7\text{FeN}_2\text{O}_2 \cdot 1.0\text{H}_2\text{O}$ : C, 44.05; H, 5.82; N, 3.11.  
198 Found: C, 43.91; H, 5.82; N, 3.04;

199 **NMR Analysis of 2b.** White powder. Yield 74%.  $^1\text{H}$  NMR (500 MHz,  
200 Methanol-*d*<sub>4</sub>)  $\delta$  9.65 (s, 2H), 8.01 (dp,  $J = 7.6, 4.3$  Hz, 4H), 7.73 (dt,  $J = 6.3, 3.6$  Hz, 4H),  
201 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  
202 – 1.36 (m, 16H), 1.29 (s, 8H).  $^{13}\text{C}$  NMR (125 MHz, Methanol-*d*<sub>4</sub>)  $\delta$  142.13, 132.46,  
203 127.76, 114.11, 62.10, 48.94, 48.77, 48.54, 48.02, 47.93, 32.77, 30.12, 30.06, 29.72,  
204 29.68, 27.06, 26.78, 25.87.

205 **NMR Analysis of 2c.** A light brown viscous liquid. Yield 87%.  $^1\text{H}$  NMR (400  
206 MHz, Chloroform-*d*)  $\delta$  (ppm) 10.54 (s, 2H), 7.75 – 7.65 (m, 8H), 4.52 (dt,  $J = 18.4, 7.6$   
207 Hz, 8H), 4.36 (t,  $J = 6.4$  Hz, 4H), 2.01 (m, 8H), 1.74 (m, 4H), 1.50 – 1.19 (m, 24H).  $^{13}\text{C}$   
208 NMR (100 MHz, Chloroform-*d*)  $\delta$  (ppm) 142.78, 131.41, 127.33, 113.20, 113.02, 68.39,  
209 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,  
210 26.63, 25.99, 25.07, 22.85, 14.28.  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -78.57 (dt,  $J =$   
211 31.4, 8.8 Hz, 6F), -116.71 (dq,  $J = 206.7, 8.7$  Hz, 4F), -124.65 (d,  $J = 43.0$  Hz, 4F).

212 **Visible Spectrum of MIL 2.** A brown viscous liquid. The  $[\text{FeCl}_3\text{Br}^-]$  anion of  
213 MIL 2 showed the characteristic bands at 534, 619, and 688 nm which were similar to the

214 previously reported compounds.<sup>16, 17</sup> Elem. Anal. Calcd (%) for C<sub>46</sub>H<sub>58</sub>Br<sub>2</sub>Cl<sub>6</sub>F<sub>14</sub>Fe<sub>2</sub>N<sub>4</sub>O<sub>4</sub>  
215 6.0H<sub>2</sub>O: C, 34.76; H, 4.44; N, 3.53; Found: C, 34.95; H, 4.09; N, 3.80.

### 216 **General Procedure for the Synthesis of Fe(III) Carboxylate-based Hydrophobic** 217 **MILs**

218 MIL **3** was synthesized as shown in Scheme 2. Benzylimidazole (1 mmol) was  
219 reacted with an excess of 10-bromodecanoic acid (2.1 mmol) in acetonitrile (35 mL) for  
220 72 h under reflux conditions. The solvent was evaporated under reduced pressure  
221 followed by washing of the crude product with ethyl acetate (4 x 35 mL) under sonication  
222 to remove excess 10-bromodecanoic acid. The bromide salt **3a** was then dried at 60 °C  
223 for 2 h under reduced pressure to remove residual solvents. Compound **3b** was  
224 synthesized by reacting **3a** (1 mmol) with lithium bis[(trifluoromethyl)sulfonyl]imide  
225 (1.5 mmol) in water at room temperature for 12 h. After solvent evaporation, compound  
226 **3b** was washed with an excess of water and the bromide impurities were monitored by  
227 adding silver nitrate to the aqueous phase. Compound **3b** was then dried at 65 °C under  
228 reduced pressure for 12 h to remove residual water. Compound **3c** was prepared by  
229 reacting **3b** (1 mmol) with sodium hydroxide (1.8 mmol) in methanol at room  
230 temperature for 24 h. The solvent was evaporated under reduced pressure and compound  
231 **3c** was washed with dichloromethane. After solvent evaporation, compound **3c** was dried  
232 under vacuum at 60 °C for 4 h to remove residual solvents. Compound **3** was synthesized  
233 by reacting **3c** (3 mmol) with FeCl<sub>3</sub>•6H<sub>2</sub>O (1.3 mmol) in acetone (10 mL) at room  
234 temperature for 12 h. The ensuing precipitate was separated using vacuum filtration and  
235 the filtrate evaporated under reduced pressure to yield compound **3**. Compound **3** was

236 washed with water to remove any excess FeCl<sub>3</sub> and dried under reduced pressure to  
237 remove residual water.

238 MILs **4** and **5** were synthesized as shown in Scheme 2. Compound **4b/5b** was  
239 prepared by reacting previously prepared **1a/1b** with excess of 10-bromodecanoic acid in  
240 acetonitrile (40 mL) for 72 h under reflux conditions. Followed by solvent evaporation,  
241 the crude compound was washed with ethyl acetate to remove the unreacted 10-  
242 bromodecanoic acid. Compound **4b/5b** was dried at 60 °C under vacuum for 2 h to  
243 remove residual solvents. Compound **4c/5c** was prepared by reacting lithium  
244 bis[(trifluoromethyl)sulfonyl]imide (1.5 mmol) with **4b/5b** (1 mmol) in methanol at room  
245 temperature for 12 h. The solvent was evaporated under reduced pressure and the crude  
246 compound washed several times with water to remove excess lithium  
247 bis[(trifluoromethyl)sulfonyl]imide. Compound **4c/5c** was dried at 65 °C under vacuum  
248 for 5 h to evaporate residual water. Compound **4d/5d** was prepared by reacting **4c/5c** (1  
249 mmol) with sodium hydroxide (1.8 mmol) in methanol at room temperature for 24 h.  
250 Following solvent evaporation, the crude product was washed with dichloromethane.  
251 Compound **4d/5d** was dried at 60 °C under vacuum for 4 h to remove the residual solvent  
252 from the product. Finally, compound **4/5** was synthesized by reacting **4d/5d** (3 mmol)  
253 with FeCl<sub>3</sub>•6H<sub>2</sub>O (1.3 mmol) in acetone (10 mL) at room temperature for 12 h. The  
254 reaction mixture was filtered using vacuum filtration to separate the precipitate; the  
255 filtrate was then evaporated under reduced pressure to yield crude compound **4/5**. The  
256 final product was washed with excess water to remove unreacted FeCl<sub>3</sub> and dried under  
257 vacuum at 60 °C for 6 h to remove residual solvent.

258 **NMR Analysis of 3a.** A light brown solid. Yield 83%.  $^1\text{H}$  NMR (400 MHz,  
259 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  
260 – 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,  $J =$   
261 7.3 Hz, 2H), 1.52 – 1.42 (m, 2H), 1.31 – 1.15 (m, 10H).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  
262  $\delta$  (ppm) 174.50, 136.12, 134.94, 129.01, 128.75, 128.24, 122.81, 122.59, 51.93, 48.97,  
263 33.68, 29.25, 28.70, 28.64, 28.53, 28.29, 25.49, 24.50.

264 **NMR Analysis of 3b.** A dark brown viscous liquid. Yield 92%.  $^1\text{H}$  NMR (400  
265 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,  
266 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),  
267 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).  $^{13}\text{C}$   
268 NMR (100 MHz, DMSO- $d_6$ )  $\delta$  (ppm) 174.50, 136.12, 134.89, 129.01, 128.76, 128.20,  
269 122.81, 122.61, 121.07, 117.87, 51.99, 48.98, 33.67, 29.24, 28.69, 28.63, 28.53, 28.28,  
270 25.49, 24.49.

271 **FT-IR Characterization of MIL 3.** A dark reddish brown viscous liquid. IR  
272 spectra of metal carboxylates are usually characterized in the range of 1650-1510  $\text{cm}^{-1}$ .  
273 MIL 3 showed two distinctive bands at 1596 and 1443  $\text{cm}^{-1}$  which are similar to the  
274 previously reported iron carboxylate compounds.<sup>20</sup> Elem. Anal. Calcd (%) for  
275  $\text{C}_{66}\text{H}_{84}\text{F}_{18}\text{FeN}_9\text{O}_{18}\text{S}_6 \cdot 2.0\text{H}_2\text{O}$ : C, 41.34; H, 4.63; N, 6.57; Found C, 41.37; H, 4.22; N,  
276 6.16;

277 **NMR Analysis of 4b.** A dark brown solid. Yield 83%.  $^1\text{H}$  NMR (400 MHz,  
278 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,  $J$   
279 = 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,

280 4H), 1.52 – 1.10 (m, 38H), 0.85 (t,  $J = 6.6$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$   
281 (ppm) 198.91, 174.46, 142.06, 131.11, 126.57, 113.75, 46.69, 33.66, 31.33, 29.08, 29.05,  
282 28.92, 28.87, 28.75, 28.67, 28.54, 28.47, 28.44, 28.41, 25.74, 24.49, 22.14, 14.02.

283 **NMR Analysis of 4c.** A dark brown liquid. Yield 93%.  $^1\text{H}$  NMR (400 MHz,  
284 DMSO- $d_6$ )  $\delta$  (ppm) 11.98 (s, 1H), 9.80 (s, 1H), 8.14 – 8.05 (m, 2H), 7.69 (dt,  $J = 6.3, 3.6$   
285 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  
286 (t,  $J = 6.8$  Hz, 2H), 1.28 (t,  $J = 5.1$  Hz, 36H), 0.89 – 0.79 (m, 3H).  $^{13}\text{C}$  NMR (100 MHz,  
287 DMSO- $d_6$ )  $\delta$  (ppm) 198.91, 174.46, 142.06, 131.11, 126.57, 113.75, 117.14, 46.69,  
288 33.66, 31.33, 29.08, 29.05, 28.92, 28.87, 28.75, 28.67, 28.54, 28.47, 28.44, 28.41, 25.74,  
289 24.49, 22.14, 14.02.

290 **FT-IR Characterization of MIL 4.** A dark brown viscous liquid. IR spectrum of  
291 MIL 4 showed two characteristics bands at 1596 and 1443  $\text{cm}^{-1}$ . Elem. Anal. Calcd (%)  
292 for  $\text{C}_{105}\text{H}_{168}\text{F}_{18}\text{FeN}_9\text{O}_{18}\text{S}_6 \cdot 6.0\text{H}_2\text{O}$ : C, 49.60; H, 7.14; N, 4.96; Found: C, 49.29; H, 6.30;  
293 N, 5.15.

294 **NMR Analysis of 5b.** A light brown solid. Yield 86%.  $^1\text{H}$  NMR (400 MHz,  
295 DMSO- $d_6$ )  $\delta$  (ppm) 11.99 (s, 1H), 9.98 (s, 1H), 8.14 – 8.09 (m, 1H), 7.97 (dd,  $J = 7.3, 2.1$   
296 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  
297 (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,  
298 2H), 1.35 – 1.19 (m, 10H).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  (ppm) 174.50, 142.38,  
299 134.10, 131.30, 130.84, 128.89, 128.72, 128.21, 126.71, 126.66, 113.93, 49.87, 46.93,  
300 33.72, 29.17, 28.82, 28.36, 28.06, 25.78, 24.43.

301 **NMR Analysis of 5c.**  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  (ppm) 11.99 (s, 1H),  
302 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),  
303 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,  $J$   
304 = 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).  
305  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  (ppm) 198.95, 177.63, 142.79, 134.21, 131.34,  
306 130.88, 129.00, 128.73, 128.26, 126.71, 126.67, 121.12, 117.92, 113.90, 49.88, 46.83,  
307 38.46, 29.38, 28.96, 28.85, 28.41, 26.46, 25.78.

308 **FT-IR Characterization of MIL 5.** A dark brown viscous liquid. IR spectrum of  
309 compound **5** showed the characteristic bands at 1593 and 1443  $\text{cm}^{-1}$ . Elem. Anal. Calcd  
310 (%) for  $\text{C}_{78}\text{H}_{90}\text{F}_{18}\text{FeN}_9\text{O}_{18}\text{S}_6 \cdot 3.0\text{H}_2\text{O}$ : C, 44.91; H, 4.64; N, 6.04; Found: C, 44.44; H,  
311 4.33; N, 5.98.

## 312 **Results and Discussion**

### 313 **Structural Tuning and Optimization of Reaction Conditions for Synthesis of** 314 **Perfluorobutyryl Ester-based MILs**

315 In liquid-liquid extraction (LLE) approaches, a water immiscible extraction  
316 solvent is often employed to isolate analytes of interest from the aqueous phase.  
317 Subsequently, recovery of the extraction phase is often achieved via a time consuming  
318 and laborious centrifugation process prior to sample analysis. MILs possess a significant  
319 advantage over conventional extraction solvents in the ease with which they can be  
320 manipulated by external magnetic fields. Using a MIL-based LLE technique, the  
321 paramagnetic properties of MILs can be exploited to enable rapid recovery of the analyte-  
322 enriched MIL extraction phase. However, previous studies have revealed that

323 imidazolium-based MILs are soluble in aqueous solution at compositions less than 20%  
324 (v/v) MIL. As a result of their solubility, they can no longer be manipulated using an  
325 external magnetic field. Therefore, disadvantages associated with imidazolium-based  
326 MILs can be addressed by tuning the structure of the MIL to impart sufficient  
327 hydrophobic nature to the resulting compound.

328 In order to improve the hydrophobicity of the resulting MILs, a relatively  
329 hydrophobic benzimidazole core as well as alkyl and perfluoroalkyl groups were selected  
330 and utilized for the synthesis of MILs (**1-2**), as shown in Scheme 1. The initial strategy  
331 employed for the synthesis of MIL **1** involved the preparation of a bromo-substituted  
332 perfluoroalkyl ester followed by reaction with hexadecylbenzimidazole to generate the  
333 bromide salt. Following this approach, 2-bromoethanol was reacted with perfluorobutyryl  
334 chloride to produce a bromo-substituted perfluorobutyryl ester. Unfortunately, when this  
335 compound was reacted with **1a**, low product yields (< 21%) were observed with most of  
336 the hexadecylbenzimidazole remaining unreacted (based on  $^1\text{H}$  NMR). This may be  
337 attributed to the strong inductive effect from the perfluoroalkyl ester functional group. In  
338 order to overcome this challenge, a bromide salt with terminal hydroxyl groups on the  
339 benzimidazolium cation was prepared prior to the esterification reaction. Firstly, a 2:1  
340 mole ratio of 2-bromoethanol was reacted with compound **1a**. The resulting bromide salt  
341 was then esterified with perfluorobutyryl chloride in an effort to incorporate fluorinated  
342 substituents, but the esterification reaction did not progress to completion (< 45% based  
343 on  $^1\text{H}$  NMR). However, substantially improved product formation (90.1%) was observed  
344 under similar reaction conditions when **1c** was reacted with perfluorobutyryl chloride.  
345 The bromide salt was subsequently reacted with  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  to generate the

346 paramagnetic iron(III) center in MIL **1**. In order to remove unreacted FeCl<sub>3</sub>, the final  
347 product was dissolved in dichloromethane and washed several times with water. When  
348 the same conditions were applied for reaction of **1c** with longer perfluoroacid chlorides  
349 (e.g. hexyl and octyl), the final products were isolated as room temperature solids.

350 The general synthetic strategy utilized for the preparation of MIL **2** is described in  
351 Scheme 1. In an attempt to reduce the melting point of the MIL products, a precursor  
352 comprised of two benzimidazole moieties separated by a dodecyl linkage chain (**2a**) was  
353 prepared. Initially, **2a** was reacted with 6-bromohexanol in neat chloroform for 7 days  
354 under reflux. However, the desired dibromide salt was not formed using these conditions.  
355 When a mixture of acetonitrile/chloroform (9:1) was employed as the reaction solvent, **2b**  
356 was generated with 74% yield. The hydroxyl groups of the dibromide salt were  
357 subsequently reacted with excess perfluorobutyryl chloride to form compound **2c**.  
358 Finally, the perfluorobutyryl-ester based dibromide salt was reacted with FeCl<sub>3</sub>·6H<sub>2</sub>O to  
359 incorporate the paramagnetic anion [FeCl<sub>3</sub>Br<sup>-</sup>] in the resulting MIL **2**.

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

### 367 **Preparation of Fe(III) Carboxylate-based Hydrophobic MILs**

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

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

391 corresponded to the formation of NaCl and was separated from the product by filtration.  
392 The final product was washed several times with water to remove unreacted FeCl<sub>3</sub>.  
393 Compound **3** exhibited a water solubility below 0.25% (w/v). In order to improve upon  
394 the hydrophobic character of **3**, the imidazolium cation was replaced with the  
395 benzimidazolium cation to produce MILs **4** and **5**, as shown in Scheme 2. Significant  
396 enhancement in the hydrophobicity for **4** and **5** was observed, and these compounds were  
397 found to be insoluble in water at 0.1% (w/v) of MIL.

### 398 **Thermal Properties of Perfluoroalkyl Ester-based and Fe(III) Carboxylate-based** 399 **Hydrophobic MILs**

400 The thermal properties of the five hydrophobic MILs prepared in this study were  
401 investigated using DSC and TGA. As shown in Table 1, the only MIL to exhibit a  
402 melting point ( $T_m$ ) above  $-45\text{ }^\circ\text{C}$  was the monocationic perfluoroalkyl ester-based MIL **1**.  
403 Although phase transitions were not observed for MILs **2–5** under the temperatures  
404 studied, these compounds existed as room temperature liquids. Interestingly, the  
405 dicationic MIL **2** was found to be a viscous liquid despite having a component of  
406 symmetry. Further investigation of the intermediates used to generate MIL **2** revealed  
407 that the perfluoroalkyl ester group had a profound influence on the melting point of the  
408 salt. While **2b** was isolated as a room temperature solid with a melting point of  $119\text{ }^\circ\text{C}$ ,  
409 esterification with perfluorobutyryl chloride generated compound **2c** with no detectable  
410 phase transition above  $-45\text{ }^\circ\text{C}$ . This may be explained by the higher propensity of **2b** to  
411 participate in hydrogen bonding when compared to the ester-functionalized compound  
412 **2c**. Thermal stabilities for the perfluoroalkyl ester-based MILs **1** and **2** were found to be  
413  $254\text{ }^\circ\text{C}$  and  $225\text{ }^\circ\text{C}$ , respectively.

414 Hydrophobic MILs derived from carboxylate-functionalized imidazolium and  
415 benzimidazolium cations (MILs 3–5) did not exhibit phase transitions above  $-45\text{ }^{\circ}\text{C}$ .  
416 This behavior is likely due to the incorporation of the non-coordinating  $[\text{NTf}_2]^-$  anion in  
417 the MIL structure. Compared to the perfluoroalkyl ester-based MILs, compounds 3–5  
418 possessed enhanced thermal stabilities as high as  $314\text{ }^{\circ}\text{C}$  in the case of MIL 3. TGA  
419 coupled with mass spectrometry (TGA-MS) enabled the analysis of volatile components  
420 released from the MILs during temperature ramping. When heated beyond  $250\text{ }^{\circ}\text{C}$ , a  
421 prominent peak at  $m/z\ 44$  was observed for all three Fe(III) carboxylate-based MILs  
422 corresponding to the release of  $\text{CO}_2$ . These results indicate that the decomposition of  
423 MILs 3–5 initially proceeds through a decarboxylation pathway.

#### 424 **Magnetic Properties of Hydrophobic MILs**

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

433 Imidazolium-based MILs comprised of high-spin  $d^5$  Fe(III) centers have been  
434 well studied as a result of their relative ease of preparation and the low cost of iron  
435 materials.<sup>4, 14</sup> Table 1 shows  $\mu_{\text{eff}}$  values at 295 K for the five hydrophobic MILs prepared

436 in this study. The  $\mu_{\text{eff}}$  values of the perfluorobutyryl ester-based MILs containing the  
437  $[\text{FeCl}_3\text{Br}^-]$  anion (**1-2**) were determined according to previously reported procedures  
438 using an Evans magnetic susceptibility balance<sup>17, 21</sup> and SQUID magnetometer.<sup>18</sup> The  $\mu_{\text{eff}}$   
439 values of the monocationic and dicationic perfluorobutyryl ester-based MILs were 5.36  
440 and 8.03  $\mu_{\text{B}}$ , respectively, and found to be in good agreement with previously reported  
441 high-spin  $d^5$  Fe(III)-based MILs.<sup>17, 18</sup> Figures 2a and b show the temperature dependence  
442 of molar magnetic susceptibilities ( $\chi_{\text{m}}$ ) and the reciprocal magnetic susceptibilities ( $\chi_{\text{m}}^{-1}$ )  
443 for the dicationic MIL **2** as a representative example of  $[\text{FeCl}_3\text{Br}^-]$ -based MILs. The  
444 linear relationship between  $\chi_{\text{m}}^{-1}$  and temperature for MIL **2** indicates that this compound  
445 follows the Curie-Weiss law.

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

## 459 Conclusions

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

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486 measurements using the SQUID magnetometer. The authors thank the Iowa State  
487 University Chemical Instrumentation Facility and staff member Steve Veysey for training  
488 and assistance pertaining to Netzsch TGA and MS instruments.

## 489 Supporting information:

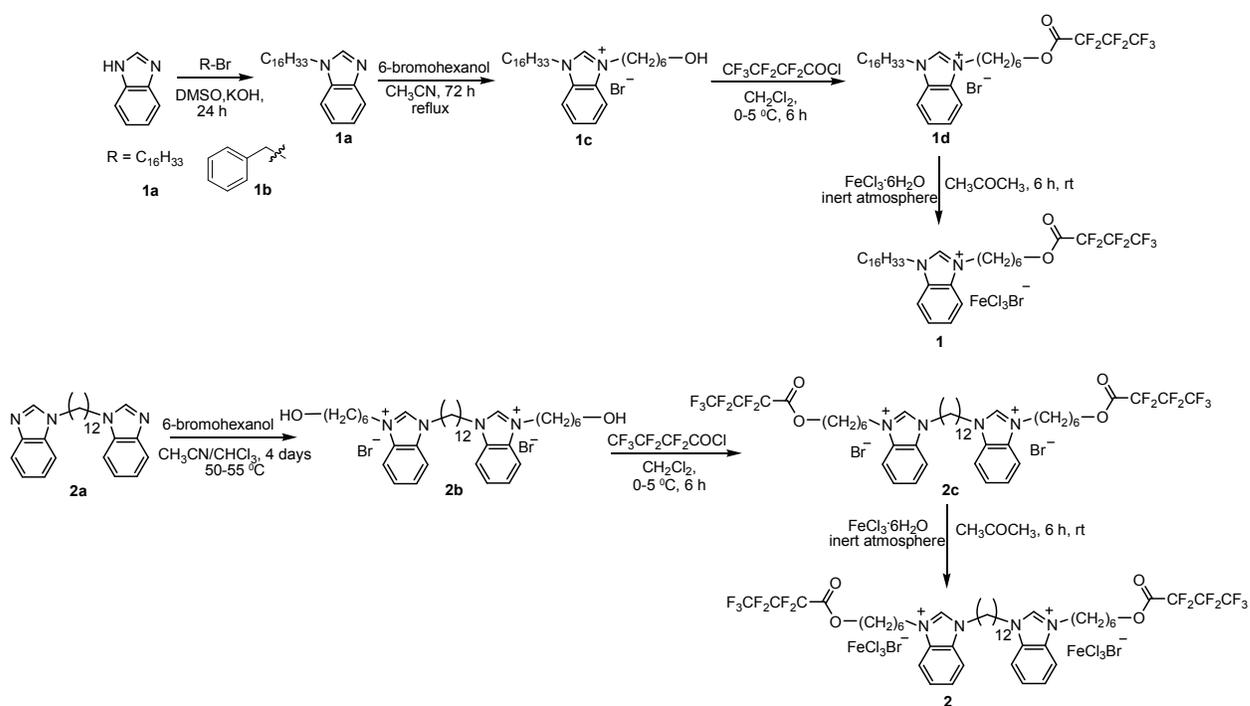
490 NMR spectra, absorbance spectra, IR spectra, Figure S1-S7 are available in supporting  
491 information.

## 492 References

- 493 1. J. P. Hallett and T. Welton, *Chem. Rev.*, 2011, **111**, 3508-3576.
- 494 2. S. Hayashi and H.-o. Hamaguchi, *Chem. Lett.*, 2004, **33**, 1590-1591.
- 495 3. T. Inagaki and T. Mochida, *Chem. Lett.*, 2010, **39**, 572-573.
- 496 4. E. Santos, J. Albo and A. Irabien, *RSC Adv.*, 2014, **4**, 40008-40018.
- 497 5. K. D. Clark, O. Nacham, H. Yu, T. Li, M. M. Yamsek, D. R. Ronning and J. L.  
498 Anderson, *Anal. Chem.*, 2015, **87**, 1552-1559.
- 499 6. E. Santos, J. Albo, C. I. Daniel, C. A. M. Portugal, J. G. Crespo and A. Irabien, *J.*  
500 *Membr. Sci.*, 2013, **430**, 56-61.
- 501 7. A. Branco, L. C. Branco and F. Pina, *Chem. Commun.*, 2011, **47**, 2300-2302.
- 502 8. P. Brown, T. A. Hatton and J. Eastoe, *Curr. Opin. Colloid Interface Sci.*, 2015,  
503 doi:10.1016/j.cocis.2015.08.002.
- 504 9. M. Lipsztajn and R. A. Osteryoung, *Inorg. Chem.*, 1985, **24**, 716-719.
- 505 10. S. A. Bolkan and J. T. Yoke, *J. Chem. Eng. Data.*, 1986, **31**, 194-197.
- 506 11. M. S. Sitze, E. R. Schreiter, E. V. Patterson and R. G. Freeman, *Inorg. Chem.*,  
507 2001, **40**, 2298-2304.
- 508 12. B. Mallick, B. Balke, C. Felser and A.-V. Mudring, *Angew. Chem. Int. Ed.*, 2008,  
509 **47**, 7635-7638.
- 510 13. P. Nockemann, B. Thijs, N. Postelmans, K. Van Hecke, L. Van Meervelt and K.  
511 Binnemans, *J. Am. Chem. Soc.*, 2006, **128**, 13658-13659.
- 512 14. Y. Yoshida and G. Saito, *J. Mater. Chem.*, 2006, **16**, 1254-1262.

- 513 15. S. H. Lee, S. H. Ha, S.-S. Ha, H.-B. Jin, C.-Y. You and Y.-M. Koo, *J. Appl.*  
514 *Phys.*, 2007, **101**, 09J102-103.
- 515 16. R. E. Del Sesto, T. M. McCleskey, A. K. Burrell, G. A. Baker, J. D. Thompson,  
516 B. L. Scott, J. S. Wilkes and P. Williams, *Chem. Commun.*, 2008, 447-449.
- 517 17. O. Nacham, K. D. Clark, H. Yu and J. L. Anderson, *Chem. Mater.*, 2015, **27**, 923-  
518 931.
- 519 18. P. Brown, C. P. Butts, J. Eastoe, E. Padron Hernandez, F. L. d. A. Machado and  
520 R. J. de Oliveira, *Chem. Commun.*, 2013, **49**, 2765-2767.
- 521 19. Y. Funasako, T. Inagaki, T. Mochida, T. Sakurai, H. Ohta, K. Furukawa and T.  
522 Nakamura, *Dalton Trans.*, 2013, **42**, 8317-8327.
- 523 20. L. M. Bronstein, X. Huang, J. Retrum, A. Schmucker, M. Pink, B. D. Stein and B.  
524 Dragnea, *Chem. Mater.*, 2007, **19**, 3624-3632.
- 525 21. D. Evans, *J. Phys. E: Sci. Instrum.*, 1974, **7**, 247.
- 526 22. J. Catterick, P. Thornton and B. W. Fitzsimmons, *Dalton Trans.*, 1977, 1420-  
527 1425.
- 528 23. A. K. Boudalis, C. P. Raptopoulou, A. Terzis and S. P. Perlepes, *Polyhedron*, 2004,  
529 **23**, 1271-1277.

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532

533 Scheme 1. Synthesis of monocationic and dicationic perfluorobutyryl ester-based  
 534 hydrophobic magnetic ionic liquids

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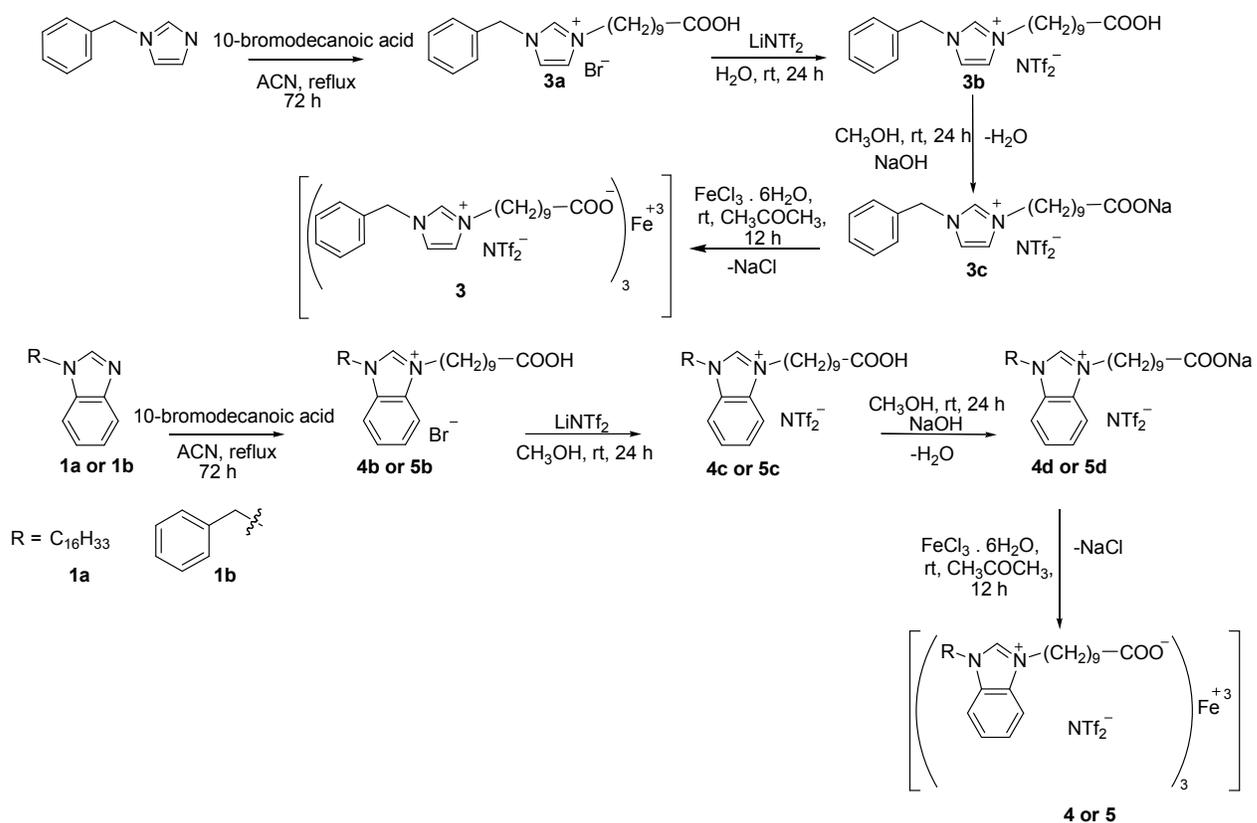
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544 Scheme 2. Synthesis of Fe(III) carboxylate-based hydrophobic magnetic ionic liquids

545

546

547 Table 1. Physicochemical and magnetic properties of hydrophobic MILs and  
 548 intermediates synthesized in this study.

Entry	MW (g/mol)	Melting point (°C)	$\mu_{\text{eff}}$ ( $\mu_{\text{B}}$ )	Thermal stability <sup>c</sup> (°C)	Solubility in hexanes	Solubility in water
<b>1</b>	881.85	-18	5.36 <sup>a</sup>	254	S	I <sup>d</sup>
<b>2</b>	1480.21	<-45	8.03 <sup>b</sup>	225	S	I <sup>d</sup>
<b>2b</b>	764.73	119	-----		I	I <sup>e</sup>
<b>2c</b>	691.81	<-45	-----		I	I <sup>d</sup>
<b>3</b>	1881.46	<-45	3.56 <sup>b</sup>	314	I	I <sup>e</sup>
<b>4</b>	2437.96	<-45	4.16 <sup>b</sup>	311	I	I <sup>d</sup>
<b>5</b>	2037.96	<-45	4.71 <sup>b</sup>	309	I	I <sup>d</sup>

549

550 <sup>a</sup> $\mu_{\text{eff}}$  = effective magnetic moment measured at 295 K using magnetic susceptibility  
 551 balance; <sup>b</sup> $\mu_{\text{eff}}$  = effective magnetic moment measured at 295 K using SQUID; <sup>c</sup> Thermal  
 552 gravimetric analysis (TGA) = temperature at which 5% wt loss of MIL is observed; I =  
 553 insoluble; <sup>c</sup> Insoluble at 0.1% (w/v); <sup>d</sup> Insoluble at 0.25% (w/v); S = soluble.

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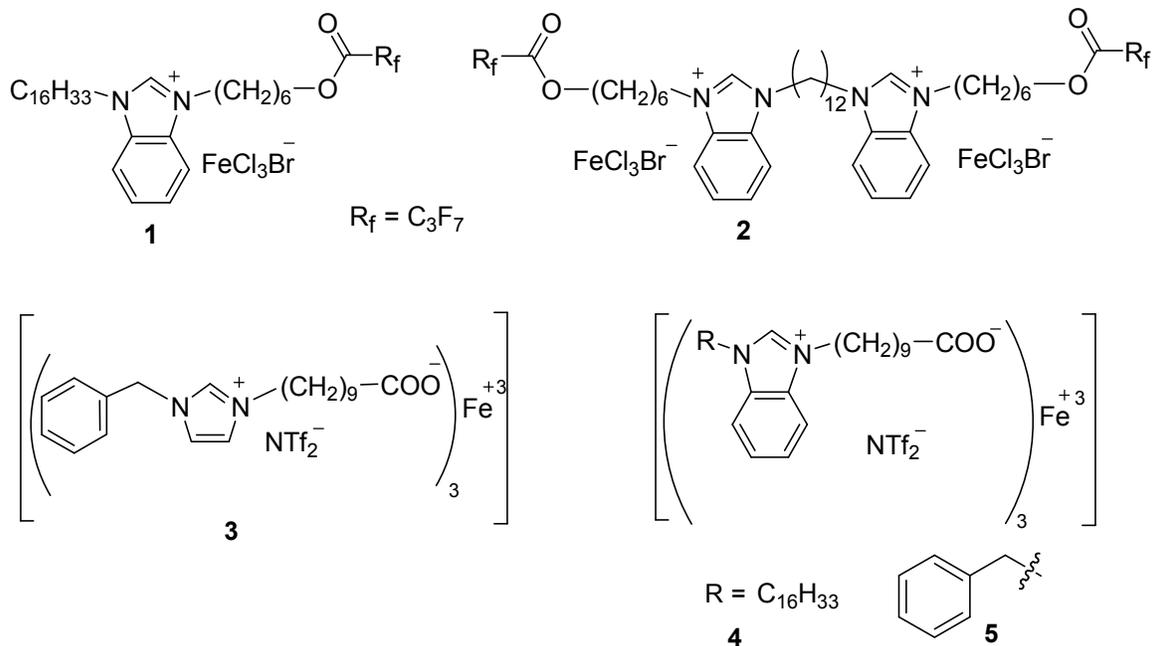
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562 Figure 1. Chemical structures of perfluorobutyryl ester (1-2) and Fe(III) carboxylate-  
563 based hydrophobic magnetic ionic liquids (3-5).

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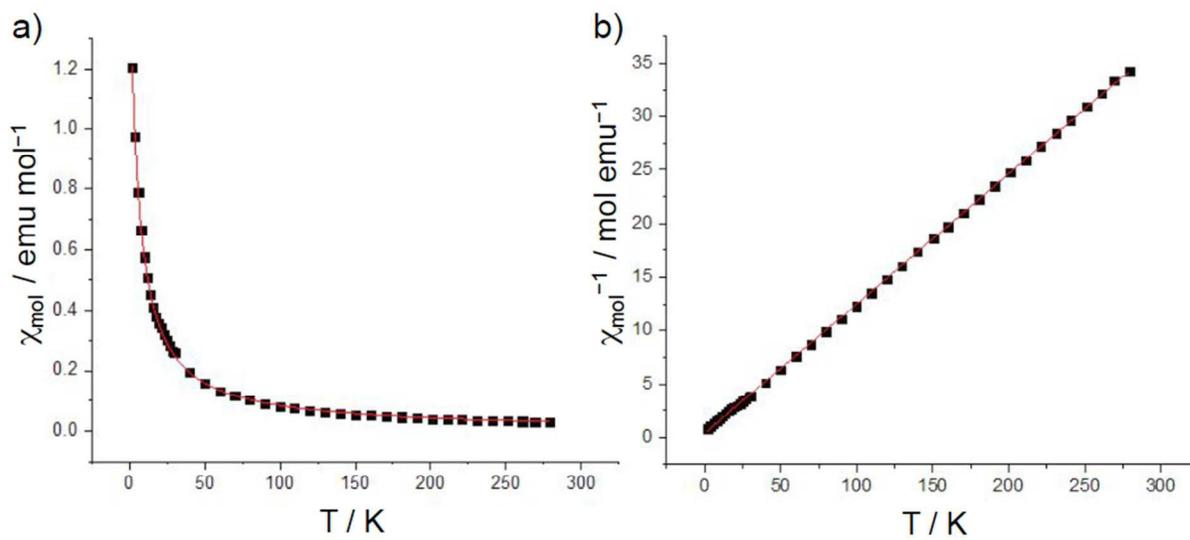
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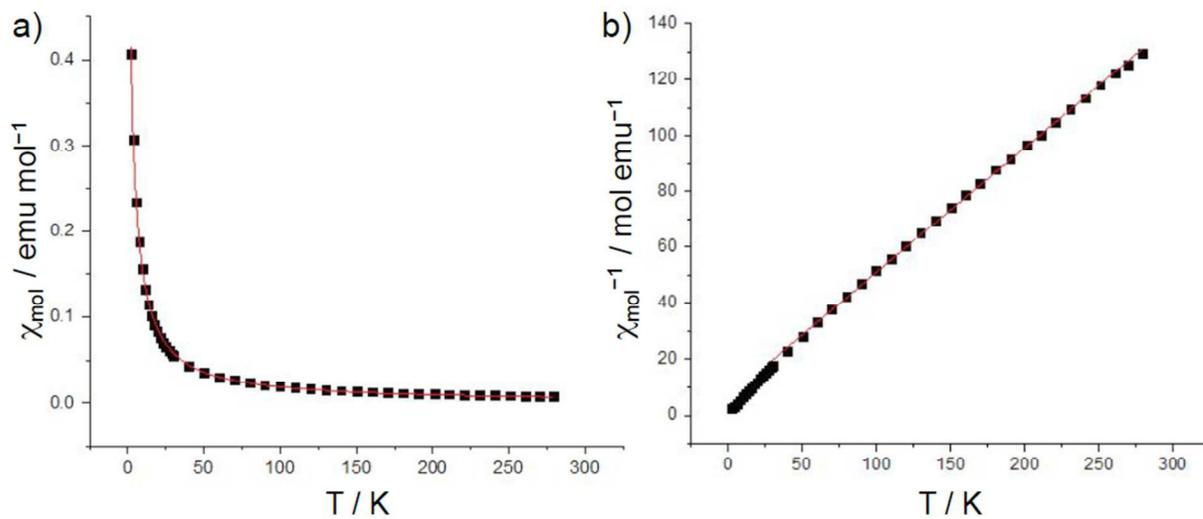
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574 Figure 2. Temperature dependence of the (a) molar magnetic susceptibility and the (b)  
575 reciprocal molar susceptibility for MIL 2 using a field of 20,000 Oe.

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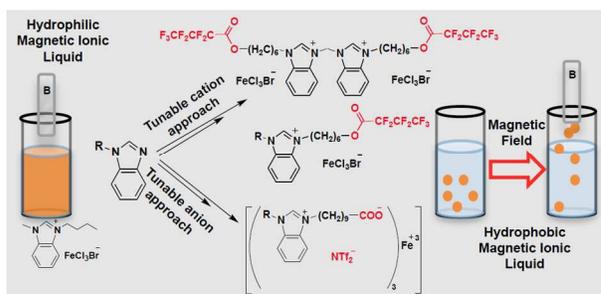


577

578 Figure 3. Temperature dependence of the (a) molar magnetic susceptibility and the (b)  
579 reciprocal molar susceptibility for MIL 4 using a field of 20,000 Oe.

580

581 For TOC use only



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583

584 **Text highlighting our work:**

585 The hydrophobic and magnetic properties of magnetic ionic liquids can be controlled  
 586 using cation functionalization or anion modification.