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Synthetic Strategies for Tailoring the Physicochemical and Magnetic Properties of Hydrophobic Magnetic Ionic Liquids

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ABSTRACT: Magnetic ionic liquids (MILs) are a subclass of ionic liquids (ILs) containing paramagnetic components and are readily manipulated by an external magnetic field. Due to their hydrophobic nature, very few applications of MILs in aqueous systems have been reported. In this study, three general classes of hydrophobic MILs including monocationic, symmetrical/unsymmetrical dicationic, and symmetrical/unsymmetrical tricationic MILs were synthesized and characterized. By tuning the structure of the MIL, various physicochemical properties including water solubility, magnetic susceptibility, and melting point were regulated. MILs synthesized with the benzimidazolium cation were shown to exhibit lower water solubility (0.1% (w/v)) when compared to those containing imidazolium cations (0.25% (w/v)). By incorporating asymmetry into the cationic component of the MIL, the melting point of dicationic MILs was lowered while the effective magnetic moment ($\mu_{\text{eff}}$) and magnetic susceptibility remained unchanged. Tricationic MILs paired with three $[\text{FeCl}_3\text{Br}^-]$ anions exhibited an $\mu_{\text{eff}}$ as high as 11.76 Bohr magnetons ($\mu_B$), the highest ever reported for MILs. The synthetic strategies employed in this study facilitate the generation of hydrophobic MILs that show great promise for liquid–liquid extraction and catalytic studies where the MIL can be easily removed or in microfluidic applications where the MIL microdroplet can be manipulated by an external field.

INTRODUCTION

Ionic liquids (ILs) are molten organic salts composed of organic cations and inorganic/organic anions with low melting points ($\leq 100 \, ^\circ \text{C}$). These solvents have garnered much attention due to their low vapor pressure at ambient temperatures, high thermal stability, wide electrochemical window, and multiple solvation capabilities. Furthermore, the physicochemical properties of ILs can be modulated through careful design of the cation/anion pair. By incorporating high-spin transition metals into the IL structure, an intriguing subclass of ILs called magnetic ionic liquids (MILs) has been generated. In addition to the unique and tunable properties of conventional ILs, MILs exhibit susceptibility to external magnetic fields. Owing to their paramagnetic nature, MILs have been exploited in a wide range of applications including reusable catalysts in synthesis, electroactive species in electrochemistry, magnetic hydraulics in engineering, and materials for gas absorption. The excellent thermal stability of some MILs has been exploited when used as stationary phases in multidimensional gas chromatography.

The 1-butyl-3-methylimidazolium tetrachloroferrate(III) ([BMIM$^+$][FeCl$_4$$^-]$) MIL represents the earliest example of magnetooactive ILs and was prepared by mixing equimolar amounts of the halide salt and neutral metal halide complex. The popular imidazolium cation has since appeared in MIL structures paired with lanthanide-containing anions synthesized by metathesis reaction. Using a similar approach, dysprosium-(III)-based MILs with enhanced magnetic susceptibilities and, in some cases, luminescent properties have been prepared. An investigation of the [BMIM$^+$][FeCl$_4$] MIL showed that phase separation of the MIL from aqueous solutions (greater than 20% (v/v) MIL) was possible upon application of a strong magnetic field (1 T). The study demonstrated the ease with which MILs can be manipulated by a magnetic field and has been noted as an important advantage when compared to traditional solvents, particularly in separation processes. Traditional liquid–liquid extraction relies on the partitioning of analytes between two immiscible phases followed by a recovery step (e.g., centrifugation or evaporation) in which the extraction phase is isolated for purification or analysis. Employing MILs as extraction solvents has the potential to rapidly recover the MIL extraction phase by simply applying an external magnetic field. Unfortunately, the high phase ratio required for recovery of the imidazolium-based MILs precludes their use in aqueous microextraction systems. This is likely a consequence of the intrinsic hydrophilic nature associated with imidazolium-based MILs.

Similar to conventional ILs, the water miscibility of MILs can be controlled by inclusion of nonpolar moieties into the MIL structure. Typical noncoordinating, hydrophobic anions such as the bis(trifluoromethyl)sulfonyl imide ($[\text{NTf}_2^-]$) anion cannot be used in the design of monocationic MILs due to a lack...
of paramagnetic properties, thus confining structural modifications to the cationic portion. The heavily alkylated trihexyl(tetradecyl)phosphonium ([P$_{6,6,6,14}$]$^+$) cation has been paired with [MnCl$_4$]$^{2-}$, [CoCl$_4$]$^{2-}$, and [GdCl$_6$]$^{3-}$ anions to form MILs that are relatively hydrophobic when compared to their imidazolium counterparts.\textsuperscript{18} Although aqueous solutions containing less than 1% (v/v) of the [P$_{6,6,6,14}$]$^+$$[FeCl_4]^{-}$ MIL have reportedly achieved phase separation upon application of an external magnetic field,\textsuperscript{19} the production of stable and inexpensive functionalized phosphonium-based cations is not easy or straightforward. An alternate route for tuning the physicochemical properties of MILs involves a dicationic platform incorporating both paramagnetic and hydrophobic anions produced through the mixing of homoanion precursors.\textsuperscript{20}

Figure 1. Chemical structures of the three general classes of hydrophobic magnetic ionic liquids synthesized in this study.
In an effort to further understand the interplay of hydrophobicity and magnetic susceptibility in MILs, 11 novel hydrophobic MILs were synthesized in this study. Figure 1 groups the MILs into the following three classes: monocationic ammonium-based MILs (1−3), symmetrical/unsymmetrical dicationic MILs with heteroanions (4a, 4b, and 6−8), and symmetrical/unsymmetrical tricationic MILs (10−12). Each synthetic route undertaken offers a unique approach toward incorporating hydrophobicity and magnetic susceptibility to the MIL structure. By designing MILs with multiple paramagnetic iron(III) centers, high effective magnetic moments (μeff) were achieved. The tricationic MIL 12 exhibited an μeff of 11.76 Bohr magnetons (μB), which is, to our knowledge, the highest μeff reported for a MIL. Moreover, the low water solubility observed for the MILs in this study (less than 0.25% (w/v)) are ideal for employing these compounds in magnet-based aqueous biphasic systems. The thermal properties of each MIL were evaluated using thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC).

# EXPERIMENTAL SECTION

## Materials and Measurements.

Imidazole (99%), 2-methylimidazole (99%), benzimidazole (98%), trioctylamine (97%), benzyl bromide (98%), 3-methoxybenzene (98%), 4-(tert-butyl)benzene (97%), octanethiol (≥98.5%), 2,2-dimethoxy-2-phenylacetophenone (99%), lithium bis(trifluoromethyl)sulfonylimide, and 1,12-dibromododecane (98%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). All reagents were used as received without any further purification.

1H NMR and 13C NMR spectra were recorded using a Varian 400 MHz nuclear magnetic resonance spectrometer. Chemical shifts reported in this work are relative to tetramethylsilane. Mass spectra were obtained using an Esquire-LC-MS/MS from Bruker Daltonics. Thermogravimetric analyses were performed using a TA Instruments TGA Q600 thermogravimetric analyzer. All samples were loaded in platinum pans and heated at a rate of 5 °C min−1 under nitrogen flow (50 mL min−1). Differential scanning calorimetry (DSC) traces were obtained using a Diamond differential scanning calorimeter from PerkinElmer. Magnetic susceptibility measurements were determined using a magnetic susceptibility balance (MSB) from Johnson Matthey. The MSB was calibrated with CuSO4·5H2O and validated using the previously reported data for the [P6,6,6,14+][FeCl4−] MIL.19 Visible absorption spectra were obtained using a Thermo Scientific Evolution 300 UV−vis spectrophotometer. Absorption spectra of MILs were collected using acetonitrile as the solvent.

11H NMR and 13C NMR spectra were recorded using a Varian 400 MHz nuclear magnetic resonance spectrometer. Chemical shifts reported in this work are relative to tetramethylsilane. Mass spectra were obtained using an Esquire-LC-MS/MS from Bruker Daltonics. Thermogravimetric analyses were performed using a TA Instruments TGA Q600 thermogravimetric analyzer. All samples were loaded in platinum pans and heated at a rate of 5 °C min−1 under nitrogen flow (50 mL min−1). Differential scanning calorimetry (DSC) traces were obtained using a Diamond differential scanning calorimeter from PerkinElmer. Magnetic susceptibility measurements were determined using a magnetic susceptibility balance (MSB) from Johnson Matthey. The MSB was calibrated with CuSO4·5H2O and validated using the previously reported data for the [P6,6,6,14+][FeCl4−] MIL.19 Visible absorption spectra were obtained using a Thermo Scientific Evolution 300 UV−vis spectrophotometer. Absorption spectra of MILs were collected using acetonitrile as the solvent.

## General Procedure for the Synthesis of Monocationic Hydrophobic MILs.

As shown in Scheme 1, the synthesis of MILs 1−3 involved the reaction of trioctylamine (1 mmol) with bromomethyl substituents (R-CH2Br; R = benzene, methoxybenzene, and tert-butylbenzene; 1.1 mmol) in chloroform (50 mL) under reflux conditions. The solvent was evaporated under reduced pressure followed by washing the crude compound with hexanes (4 × 25 mL) under sonication to remove the unreacted starting materials. The bromide salt was then dried under vacuum at 60 °C for 12 h. Characterization of compounds 1a−3a was performed using 1H NMR, 13C NMR, and ES-MS. After confirming the purity of the intermediates, compounds 1a−3a were reacted with equimolar amounts of FeCl3·6H2O in methanol at room temperature under nitrogen atmosphere for 2 h. After evaporation of solvent, the crude...
MIL was washed with an excess of deionized water to remove unreacted FeCl₃ from the final product. The MILs 1–3 were then dried under vacuum at 80 °C for 48 h and characterized using visible spectrophotometry and elemental analysis. All spectra are provided in the Supporting Information (SI).

**Characterization of 1a.** Yield 92%. 1H NMR (400 MHz; CDCl₃; ppm): δ 0.86 (t, J_H,H = 6.35 Hz, 9H); 1.25 (m, 30H); 1.75 (m, 6H); 3.29 (t, J_H,H = 8.06 Hz, 6H); 4.92 (s, 2H); 7.42 (m, 3H); 7.53 (m, 2H). 13C NMR (400 MHz; CDCl₃; ppm): δ 14.31; 22.81; 22.97; 26.61; 29.21; 31.84; 59.08; 63.51; 127.68; 129.60; 130.97; 132.76. ESI-MS: m/z 279.1. Yield 91%. 1H NMR (400 MHz; CDCl₃; ppm): δ 0.86 (t, J_H,H = 6.23 Hz, 9H); 1.32 (m, 39H); 1.75 (m, 6H); 4.48 (t, J_H,H = 6.84 Hz, 4H); 7.18 (m, 2H); 7.52 (m, 4H); 7.66 (m, 4H); 7.97 (m, 2H); 8.11 (m, 2H); 10.10 (s, 2H). 13C NMR (400 MHz; CDCl₃; ppm): δ 14.17; 22.71; 22.94; 26.62; 29.30; 29.36; 31.36; 31.87; 58.86; 63.12; 124.33; 126.61; 132.38; 154.50.

**Characterization of 2a.** Yield 93%. 1H NMR (400 MHz; CDCl₃; ppm): δ 0.87 (t, J_H,H = 6.35 Hz, 9H); 1.25 (m, 30H); 1.92 (m, 8H); 4.52 (t, J_H,H = 6.14 Hz, 4H); 7.74 (m, 8H); 9.42 (s, 2H). 13C NMR (400 MHz; CDCl₃; ppm): δ 14.40; 22.92; 26.39; 26.69; 29.07; 29.74; 29.95; 32.19; 48.05; 113.33; 113.60; 127.76; 131.61; 141.09. ESI-MS: m/z 292.4 (+) 426.7.

**Characterization of 3a.** Yield 89%. 1H NMR (400 MHz; CDCl₃; ppm): δ 0.88 (t, J_H,H = 6.07 Hz, 9H); 1.32 (m, 39H); 1.75 (m, 6H); 4.48 (t, J_H,H = 6.84 Hz, 4H); 7.18 (m, 4H); 7.52 (m, 4H); 7.66 (m, 4H); 7.97 (m, 2H); 8.11 (m, 2H); 10.10 (s, 2H). 13C NMR (400 MHz; CDCl₃; ppm): δ 14.40; 22.92; 26.39; 26.69; 29.07; 29.74; 29.95; 32.19; 48.05; 113.33; 113.60; 127.76; 131.61; 141.09. ESI-MS: m/z 292.4 (+) 426.7; m/z (−) 279.1.

**Characterization of Compound 5.** Compound 5 was synthesized as shown in Scheme 1. Benzimidazolium [(+) 426.7; m/z 426.7; m/z (+) 292.4. Synthetic H NMR (400 MHz; CDCl₃; ppm): δ 0.87 (t, J_H,H = 6.07 Hz, 9H); 1.32 (m, 39H); 1.75 (m, 6H); 4.48 (t, J_H,H = 6.84 Hz, 4H); 7.18 (m, 4H); 7.52 (m, 4H); 7.66 (m, 4H); 7.97 (m, 2H); 8.11 (m, 2H); 10.10 (s, 2H). 13C NMR (400 MHz; CDCl₃; ppm): δ 14.40; 22.92; 26.39; 26.69; 29.07; 29.74; 29.95; 32.19; 48.05; 113.33; 113.60; 127.76; 131.61; 141.09. ESI-MS: m/z 292.4 (+) 426.7; m/z (−) 279.1.

**Characterization of MIL 6.** Yield 91%. The presence of the paramagnetic anion, [FeCl₃Br−], was confirmed using visible spectrophotometry. Elem. Anal. Calcd (%) for C₉₆H₉₆Br₃Cl₃FeN₉O₄S₂ (931): C, 52.38; H, 7.33; N, 5.09. Found: C, 53.28; H, 7.30; N, 5.06.

**Characterization of 7a.** Yield 92%. 1H NMR (400 MHz; DMSO-d₆; ppm): δ 1.21 (m, 16H); 1.92 (m, 4H); 4.52 (t, J_H,H = 7.14 Hz, 4H); 5.80 (s, 4H); 7.39 (m, 6H); 7.52 (m, 4H); 7.66 (m, 4H); 7.97 (m, 2H); 8.11 (m, 2H); 10.10 (s, 2H). 13C NMR (400 MHz; DMSO-d₆; ppm): δ 25.28; 28.45; 28.49; 28.94; 46.84; 49.83; 113.90; 126.64; 128.23; 128.96; 131.29; 134.12; 142.38. ESI-MS: m/z 292.4 (+) 292.4.

**Characterization of 7b.** Yield 90%. 1H NMR (400 MHz; CDCl₃; ppm): δ 1.24 (m, 16H); 1.99 (m, 4H); 4.48 (t, J_H,H = 7.32 Hz, 4H);
Scheme 3. Synthesis of Symmetrical Tricationic Alkylated and Thiaalkylated-Based Hydrophobic Magnetic Ionic Liquids

**Characterization of MIL 7.** Yield 88%. A dark brown viscous liquid. Characteristic bands for the \(\text{[FeCl}_3\text{Br}^-]\) anion were observed at 534, 619, and 688 nm using visible spectroscopy. Elem. Anal. Calcd (%) for \(\text{C}_47\text{H}_72\text{Br}_3\text{Cl}_9\text{Fe}_3\text{N}_6\) (1549.66): C, 41.85; H, 6.09; N, 5.42. Found: C, 41.65; H, 6.22; N, 5.82.

**Characterization of MIL 8.** As shown in Scheme 2, compound 8 was synthesized using a reported procedure from the literature with some modifications. Briefly, a solution of 1,12-dibromododecane (8.20 g, 25.0 mmol) in chloroform (40 mL) was added dropwise using a syringe to a stirred solution of N-benzylimidazole (1.00 g, 6.32 mmol) in chloroform (40 mL) for 2 h. The reaction mixture was allowed to stir for 12 h under reflux. The crude compound 8a, was obtained by evaporating the solvent under reduced pressure and washed with excess of hexanes and ethyl acetate (1:1; 3 × 30 mL) under sonication to remove the unreacted starting materials. Compound 8a was dried in vacuum at 70 °C for 16 h to remove the residual solvents. Compound 8b was obtained by anion exchange of 8a with LiNTf2 in water at room temperature for 24 h. After drying, compound 8b (0.30 g, 0.44 mmol) was reacted with \(\text{FeCl}_3\cdot\text{H}_2\text{O} (1.1\text{ mmol})\) in dichloromethane at room temperature for 6 h to yield crude compound 8. After evaporation of the solvent, compound 8 was washed several times with water to remove the unreacted iron chloride and dried under vacuum for 4 h at 70 °C.

**Characterization of 8b.** Yield 65%. \(^1\)H NMR (400 MHz; DMSO; ppm): \(\delta\) 1.23 (m, 16H); 1.78 (m, 4H); 3.52 (t, \(J_{\text{H}-\text{H}} = 6.59\text{ Hz}, 2H\)); 4.16 (t, \(J_{\text{H}-\text{H}} = 6.96\text{ Hz}, 2H\)); 5.41 (s, 2H); 7.41 (m, 5H); 7.81 (m, 3H); 8.11 (m, 2H); 8.62 (m, 6H); 10.41 (s, 3H). \(^1\)C NMR (400 MHz; CDCl3; ppm): \(\delta\) 26.17; 28.19; 28.79; 29.89; 29.49; 29.55; 29.90; 32.88; 39.12; 49.64; 52.63; 123.28; 123.49; 128.87; 129.69; 136.79. ESI-MS: m/z + (+) 407.3.

**Characterization of 8c.** Yield 82%. \(^1\)H NMR (400 MHz; DMSO; ppm): \(\delta\) 0.84 (t, \(J_{\text{H}-\text{H}} = 6.59\text{ Hz}, 3H\)); 1.21 (m, 42H); 1.76 (m, 2H); 1.89 (m, 4H); 4.15 (t, \(J_{\text{H}-\text{H}} = 6.80\text{ Hz}, 2H\)); 4.48 (t, \(J_{\text{H}-\text{H}} = 6.59\text{ Hz}, 4H\)); 5.41 (s, 2H); 7.40 (m, 5H); 7.70 (m, 2H); 7.83 (m, 3H); 8.11 (m, 2H); 9.29 (s, 1H); 9.80 (s, 1H). \(^1\)C NMR (400 MHz; DMSO; ppm): \(\delta\) 13.98; 22.13; 25.58; 25.72; 28.83; 29.06; 29.31; 31.32; 46.69; 48.89; 51.98; 113.74; 122.61; 122.80; 126.57; 128.21; 129.01; 131.10; 134.48; 136.10; 142.04. ESI-MS: m/z (+) 334.7; m/z (--) 279.1.

**Characterization of MIL 8.** Yield 91%. A dark brown viscous liquid. Characteristic bands for the \(\text{[FeCl}_3\text{Br}^-]\) anion were observed at 534, 619, and 688 nm using visible spectroscopy. Elem. Anal. Calcd (%) for \(\text{C}_54\text{H}_90\text{Br}_3\text{Cl}_9\text{Fe}_3\text{N}_6\) (1549.66): C, 41.85; H, 6.09; N, 5.42. Found: C, 41.65; H, 6.22; N, 5.82.

**Synthesis of Compound 9.** Compound 9 was synthesized according to a previously reported procedure. A detailed synthetic procedure is available in the Supporting Information. Yield 70–75%. \(^1\)H NMR (400 MHz; CDCl3; ppm): \(\delta\) 5.08 (s, 6H); 6.84 (m, 6H); 7.12 (s, 3H); 7.52 (s, 3H). \(^1\)C NMR (400 MHz; CDCl3; ppm): \(\delta\) 50.37; 119.40; 125.77; 130.45; 137.61; 138.65.

**Synthesis of Compound 10.** As shown in Scheme 3, compound 10a was synthesized from compound 9 by following a procedure from the literature. Compound 10a was prepared by mixing compound 10a (1 mmol) with \(\text{FeCl}_3\cdot\text{H}_2\text{O} (3.1\text{ mmol})\) in methanol under nitrogen atmosphere at room temperature for 4 h. After evaporation of solvent, compound 10 was washed with water (4 × 10 mL) and dried under vacuum at 60 °C for 12 h.

**Characterization of 10a.** Yield 87%. \(^1\)H NMR (400 MHz; CDCl3; ppm): \(\delta\) 0.88 (t, \(J_{\text{H}-\text{H}} = 6.59\text{ Hz}, 9H\)); 1.26 (m, 54H); 1.89 (m, 6H); 4.22 (t, \(J_{\text{H}-\text{H}} = 7.32\text{ Hz}, 6H\)); 5.55 (s, 6H); 7.08 (s, 3H); 8.62 (m, 6H); 10.41 (s, 3H). \(^1\)C NMR (400 MHz; CDCl3; ppm): \(\delta\) 14.36; 22.91; 26.51; 29.19; 29.55; 29.59; 29.81; 32.12; 50.45; 52.21; 121.46; 124.62; 132.72; 135.77; 136.58.

**Characterization of MIL 10.** Yield 94%. A dark brown viscous liquid. The \(\text{[FeCl}_3\text{Br}^-]\) anion was characterized using visible spectroscopy showing characteristic bands at 534, 619, and 688 nm. Elem. Anal. Calcd (%) for \(\text{C}_47\text{H}_72\text{Br}_3\text{Cl}_9\text{Fe}_3\text{N}_6\) (1549.66): C, 41.85; H, 6.09; N, 5.42. Found: C, 41.65; H, 6.22; N, 5.82.

**Synthesis of MIL 11.** For the synthesis of MIL 11, shown in Scheme 3, allyl bromide (0.590 g, 4.89 mmol) was added to a stirred solution of compound 9 (0.50 g, 1.6 mmol) in acetonitrile (15 mL) at 40–50 °C and stirred for 48 h. After evaporating the solvent in vacuo, the residue was washed with hexanes (3 × 15 mL) and dried under vacuum at 60 °C for 6 h to yield compound 11a. A mixture of 11a (0.30 g, 0.44 mmol), 1-octanethiol (0.579 g, 3.96 mmol), and 2,2-dimethoxy-2-phenylacetophenone (0.169 g, 0.659 mmol) in 10 mL of methanol/dichloromethane (1:1) was then transferred to a quartz tube and stirred until homogeneity. The contents were then exposed to UV radiation (254 nm) for 16 h. The solvent was evaporated and the crude compound was washed with hexanes (4 × 30 mL) under sonication. Removal of residual solvent under vacuum yielded compound 11b.

Finally, 11b (1 mmol) was mixed with \(\text{FeCl}_3\cdot\text{H}_2\text{O} (3.10\text{ mmol})\) in...
methanol at room temperature under nitrogen atmosphere for 4 h to form compound 11. Methanol was evaporated, and MIL 11 was washed with deionized water and dried at 70 °C for 12 h.

Characterization of 11a. Yield 91%. 1H NMR (400 MHz; CDCl3; ppm): δ 4.89 (d, JH-H = 6.59 Hz, 6H); 5.45 (m, 3H); 5.48 (d, JH-H = 4.76 Hz, 3H); 5.58 (s, 6H); 5.99 (m, 3H); 7.16 (s, 3H); 8.46 (s, 3H); 8.52 (s, 3H); 10.34 (s, 3H). 13C NMR (400 MHz; CDCl3; ppm): δ 52.28; 52.50; 121.42; 123.23; 124.58; 129.68; 131.91; 135.71; 136.74.

Characterization of 11b. Yield 85%. 1H NMR (400 MHz; CDCl3; ppm): δ 0.88 (t, JH-H = 6.23 Hz, 9H); 1.27 (m, 35H); 1.55 (m, 6H); 2.21 (m, 6H); 2.49 (t, JH-H = 7.32 Hz, 6H); 2.55 (t, JH-H = 6.59 Hz, 6H); 4.39 (t, JH-H = 6.96 Hz, 6H); 5.56 (s, 6H); 7.17 (s, 3H); 8.58 (m, 6H); 10.42 (s, 3H). 13C NMR (400 MHz; CDCl3; ppm): δ 14.67; 23.20; 28.82; 29.43; 29.74; 30.03; 32.35; 32.71; 49.18; 52.66; 122.25; 124.88; 132.53; 136.02; 136.93; 139.77; 140.08.

Characterization of MIL 11. Yield 91%. A dark brown viscous liquid. Characteristic bands for the [FeCl3Br\textsuperscript−] anion were observed at 534, 619, and 688 nm using visible spectroscopy. Elem. Anal. Calcd (%) for C\textsubscript{36}H\textsubscript{57}Br\textsubscript{3}Cl\textsubscript{9}Fe\textsubscript{3}N\textsubscript{6}S\textsubscript{3} (1460.43): C, 37.83; H, 4.76; N, 7.67. Found: C, 39.10; H, 5.62; N, 5.44.

Synthesis of MIL 12. The synthesis of MIL 12 is shown in Scheme 4. Compound 9 (0.60 g, 1.9 mmol) was dissolved in acetonitrile (30 mL) and added dropwise to a solution of bromobutane (0.517 g, 3.78 mmol) in acetonitrile (20 mL). The reaction mixture was stirred under reflux for 72 h. After evaporation of the solvent, the crude compound was washed with diethyl ether (3 × 30 mL) under nitrogen atmosphere. The resulting MIL was then dissolved in water and allowed to react with Li\textsubscript{NTf\textsubscript{2}} (2.20 mmol) in H\textsubscript{2}O at room temperature for 72 h. Finally, MIL 12 was synthesized by reacting 12c with FeCl\textsubscript{3}, 6H\textsubscript{2}O. Characterization of MIL 12. Yield 90%. A dark brown viscous liquid. The [FeCl\textsubscript{3}Br\textsuperscript−] anion was characterized using visible spectroscopy showing absorption bands at 534, 619, and 688 nm. Elem. Anal. Calcd (%) for C\textsubscript{61}H\textsubscript{93}Br\textsubscript{3}Cl\textsubscript{9}Fe\textsubscript{3}N\textsubscript{6}O\textsubscript{8}S\textsubscript{4} (1606.8): C, 37.83; H, 4.76; N, 7.67. Found: C, 37.33; H, 4.37; N, 7.39.

Results and Discussion

Preparation of Monocationic Ammonium-Based Hydrophobic MILs. The general strategy used to prepare MILs in this study is based on the synthesis of bromide salt precursors and their subsequent reaction with FeCl\textsubscript{3}, 6H\textsubscript{2}O. Coordination of bromide to the iron(III) center produces the [FeCl\textsubscript{3}Br\textsuperscript−] anion, which imparts paramagnetic properties to the resulting MIL.

Imidazolium-based MILs are an extensively studied class of compounds due to relatively low reagent costs and ease of functionalization. Initial attempts were made to enhance the hydrophobicity of MILs by incorporating long hydrocarbon chains and/or bulky aromatic moieties to the imidazolium cation, as shown in SI Table S1. However, entries 1−4 were soluble in water below 5% (w/v) and were room-temperature solids with higher melting points. In addition to van der Waals and π−π interactions, it has been suggested that the presence of the acidic proton on the 2-position of the imidazolium ring favors hydrogen bonding with the MIL anion and discourages the formation of lower melting point MILs. Therefore, the strategy employed in this study involved the design of monocationic MILs that lack acidic protons and could be readily functionalized.

Quaternary ammonium cations are commonly exploited in IL structures due to their ease of customization and control over physicochemical properties. To improve the hydrophobic character of the resulting MIL, trioctylamine was chosen.
and quaternized with alkyl halides. The reaction of trioctylamine and butyl/decyl bromide resulted in low yields of the bromide salt (<20%) with most of the starting materials left unreacted, even after 7 days (based on $^1$H NMR spectroscopy). In contrast, the same reaction conditions with benzylic bromide produced higher yields (>90%) and proceeded to completion within 72 h, as shown in Scheme 1. This may be due to resonance stabilization of the carbocation by the aromatic moiety. It was also possible to incorporate functionalized benzylic substituents including 3-methoxybenzyl and 4-tert-butylbenzyl into the quaternary ammonium structure, demonstrating the ability to generate unique substitutions within the monocation MIL framework.

The solubility of the ammonium-based MILs in water and hexane is shown in Table 1. Independent of the substituent functional groups imparted by the quaternization reaction, MILs 1–3 were immiscible with water at compositions as low as 0.1% (w/v) MIL. The hydrophobic properties of the monocationic MILs are thus ideal for applications such as aqueous liquid–liquid microextraction, where extremely low phase ratios of extraction solvent are employed.

**Structural Tuning of Symmetrical/Unsymmetrical Dicationic Hydrophobic MILs.** Dicationic ILs provide more opportunities for control of physical and chemical properties compared to conventional monocationic ILs. The dicationic IL platform is especially relevant and useful for MILs, which require at least a paramagnetic anion to provide sufficient magnetic susceptibility. Previous work by Brown et al. prompted an investigation in this study to pair one cation in a dicationic system with the $\text{[NTf}_2^-\text{]}$ anion and produce functionalized hydrophobic MILs based on imidazolium cations.20 In general, the synthesis of symmetrical imidazolium-based dicationic MILs was performed in three steps. First, a dicaticonic bromide salt was synthesized with alkyl/aromatic substituents on the cation. A dodecyl linkage chain between the imidazolium-based cations was employed to increase the conformational degrees of freedom, thus improving the likelihood of forming low-melting MILs. Two homoanion precursors were then synthesized from the dibromide salt, either by anion exchange to incorporate hydrophobic [FeCl$_3$·6H$_2$O] to generate paramagnetic [FeCl$_3$·Br$^-$] anions. Finally, mixing equimolar quantities of the [NTf$_2^-$] and [FeCl$_3$·Br$^-$] salts produced dicationic MILs with heteroanions.

When functionalized with benzyl substituents, the imidazolium-based dicationic MIL 4A exhibited water solubility below 0.25% (w/v), as shown in Table 1. Blocking the acidic C-2 proton of the hexadecyl functionalized imidazolium dication with a methyl group (4B) resulted in similar water solubility to 4A. The hydrophobicity of this class of MILs was significantly improved by replacing the imidazolium cation with the benzimidazolium cation. MILs 6 and 7 were synthesized according to Scheme 1. Improved hydrophobic character was observed for 6 and 7, which were insoluble in water at 0.1% (w/v) MIL.

Another important structural feature that has profound implications on the physicochemical properties of ILs is the presence of asymmetry in the molecule.29,30 Dicationic ILs are uniquely amenable to unsymmetrical archetypes since it is possible to independently functionalize the cationic moieties.29,30 Drawing on the improved hydrophobicity obtained for dicationic MILs 6 and 7, a MIL that tethers benzimidazolium and imidazolium cations was produced. Scheme 2 illustrates the synthesis of the heterocationic MIL 8. Initially, reaction of 1,12-dibromododecane with benzylimidazole in a 1:1 mole ratio resulted in formation of 20% (based on $^1$H NMR) of the dibromide salt. However, increasing the mole ratio of 1,12-dibromododecane to 4:5:1 significantly reduced the formation of the dibromide salt to <5%, based on $^1$H NMR. The metathesis reaction of compound 8a with 1.2 mol equiv of LiNTf$_2$ formed a precipitate (8b) while the dicationic [Br$^-$]/[NTf$_2^-$] analogue remained in the aqueous phase.30 After the incorporation of the hydrophobic anion, compound 8b was reacted with previously synthesized hexadecylbenzimidazole to generate the unsymmetrical dicationic [Br$^-$]/[NTf$_2^-$] salt 8c. Finally, hydrophobic MIL 8 was synthesized by reacting compound 8c with FeCl$_3$·6H$_2$O. Similar to MILs 1–3, 6, and 7, the heterocationic MIL 8 was insoluble in water down to 0.1% (w/v) MIL.

**Synthesis of Symmetrical Alkylated/Thiaalkylated and Unsymmetrical Tricationic Hydrophobic MILs.** The synthesis of symmetrical tricationic hydrophobic MILs 10 and 11 is shown in Scheme 3. With the aim of minimizing water solubility of the resulting MILs, a relatively hydrophobic benzoic core functionalized with three imidazol moieties (9) was selected from the literature as a precursor and prepared accordingly.21 Compound 9 was then alkylated by reaction with 1-bromododecane for 5 days in acetonitrile to generate compound 10a. Subsequent mixing with FeCl$_3$·6H$_2$O produced...

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**Table 1. Physicochemical and Magnetic Properties of Hydrophobic MILs Synthesized in This Study**

<table>
<thead>
<tr>
<th>MIL</th>
<th>MW (g/mol)</th>
<th>melting point (°C)*</th>
<th>$\mu_{\text{eff}}$ (μB)</th>
<th>thermal stability (°C)</th>
<th>solubility in hexanes</th>
<th>solubility in water</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>686.9</td>
<td>−53.2 (T$_g$)</td>
<td>5.26</td>
<td>258</td>
<td>1</td>
<td>I&lt;sup&gt;4&lt;/sup&gt;</td>
</tr>
<tr>
<td>2</td>
<td>716.9</td>
<td>&lt;−65</td>
<td>5.60</td>
<td>203</td>
<td>1</td>
<td>I&lt;sup&gt;4&lt;/sup&gt;</td>
</tr>
<tr>
<td>3</td>
<td>743.01</td>
<td>−50.7 (T$_g$)</td>
<td>5.68</td>
<td>222</td>
<td>1</td>
<td>I&lt;sup&gt;4&lt;/sup&gt;</td>
</tr>
<tr>
<td>4A</td>
<td>1035.0</td>
<td>−32.6 (T$_g$)</td>
<td>5.40</td>
<td>310</td>
<td>1</td>
<td>I&lt;sup&gt;4&lt;/sup&gt;</td>
</tr>
<tr>
<td>4B</td>
<td>1303.6</td>
<td>&lt;−25</td>
<td>5.37</td>
<td>294</td>
<td>1</td>
<td>I&lt;sup&gt;4&lt;/sup&gt;</td>
</tr>
<tr>
<td>6c</td>
<td>1338.9</td>
<td>&lt;−25</td>
<td>7.58</td>
<td>299</td>
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<td>I&lt;sup&gt;4&lt;/sup&gt;</td>
</tr>
<tr>
<td>6</td>
<td>1375.7</td>
<td>&lt;−0.6</td>
<td>5.69</td>
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<td>1</td>
<td>I&lt;sup&gt;4&lt;/sup&gt;</td>
</tr>
<tr>
<td>7</td>
<td>1107.1</td>
<td>−6.7 (T$_g$)</td>
<td>5.45</td>
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<td>1</td>
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<td>8</td>
<td>1191.3</td>
<td>−16.7</td>
<td>5.30</td>
<td>312</td>
<td>1</td>
<td>I&lt;sup&gt;4&lt;/sup&gt;</td>
</tr>
<tr>
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<td>1549.6</td>
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<td>11.25</td>
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<td>I&lt;sup&gt;4&lt;/sup&gt;</td>
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<td>1</td>
<td>I&lt;sup&gt;4&lt;/sup&gt;</td>
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<tr>
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<td>1460.4</td>
<td>5.0</td>
<td>5.10</td>
<td>276</td>
<td>1</td>
<td>I&lt;sup&gt;4&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

*“T$_g$ = glass transition temperature. $\mu_{\text{eff}}$ = effective magnetic moment measured at 295 K. *Thermal gravimetric analysis (TGA) = temperature at which 5 wt % loss of MIL is observed; I = insoluble. *Insoluble at 0.1% (w/v). *Insoluble at 0.25% (w/v).
hydrophobic MIL 10. From Scheme 3, it is clear that synthesis of the tribromide salt 10a was the most time-consuming step. In an effort to reduce the time required for the generation of a MIL with similar magnetic susceptibility and hydrophobicity to MIL 10, thiol–ene click chemistry was employed. The thiol-based approach has been shown to provide a convenient route for modification of the cationic portion of monocationic ILs but has been unexplored in tricationic IL systems. Using a similar synthetic route, the tricationic hydrophobic MIL 11 was synthesized as shown in Scheme 3.

For synthesis of MIL 11, intermediate 9 was reacted with allyl bromide for 48 h in acetonitrile to produce compound 11a. In comparison to the sluggish formation of the bromide salt 10a, compound 11a was more rapidly generated, possibly due to the resonance stabilization of allylic carbocation. Compound 11b was prepared by reacting 11a with octanethiol in a methanol/dichloromethane (1:1) solvent mixture in the presence of UV irradiation for 16 h. Exclusive formation of anti-Markovnikov-oriented products as previously noted by Davis et al.24 was confirmed by 1H NMR. Excess amounts of unreacted starting materials were easily removed by washing the crude product with hexanes. Thus, the total reaction time required for the generation of the thiaalkyl-based tribromide salt (11b) was significantly less in comparison with 10a. Finally, the hydrophobic MIL 11 was prepared by reacting 11b with FeCl3·6H2O. From Table 1, MILs 10 and 11 were shown to be insoluble in aqueous solution down to 0.25% (w/v) MIL.

In an effort to improve the hydrophobic character of the tricationic MILs, hydrophobic [NTf2−] anions were incorporated into the molecular structure, as shown in MIL 12. Previous studies indicated that when intermediate 9 was reacted with alkyl halides such as 1-bromooctane, subsequent anion exchange with [NTf2−] led to the formation of room-temperature solids (Tm = 51.1 °C).25 Formation of MILs with lower melting points involved reacting intermediate 9 with 1-bromobutane to yield the dibromide salt (12a), as shown in Scheme 4. Hydrophobic [NTf2−] anions were then incorporated by metathesis reaction of 12a. Generation of the unsymmetrical tricationic IL was accomplished by reacting 12b with 1-bromohexadecane to produce compound 12c. Finally, MIL 12 was generated by reacting compound 12c with FeCl3·6H2O in dichloromethane for 4 h. As shown in Table 1, MIL 12 exhibited improved hydrophobicity in comparison to MILs 10 and 11.

**Thermal Properties of Hydrophobic MILs.** The phase transition behavior and thermal stability of the 11 hydrophobic MILs were studied using DSC and TGA and the results compiled in Table 1. Monocationic MILs 1 and 3 exhibited glass transition temperatures (Tg) of −53.2 and −50.7 °C, respectively. A melting point (Tm) for MIL 2 could not be detected above −65 °C. These values were much lower in comparison with ammonium-based MILs possessing only linear alkyl substituents. Previous reports dictate that the total number of carbon atoms and asymmetry of the cation structure govern the Tm of quaternary ammonium salts.27 Hence, the relatively low Tm of MILs 1 and 3 may be explained by the asymmetry resulting from incorporation of aromatic moieties within the cation structure. Interestingly, while MIL 1 was thermally stable up to 258 °C, similar weight loss (5%) was observed at lower temperatures for the methoxy (2) and tert-butyl (3) functionalized monocationic MILs.

Symmetrical dicaticonic MILs with heteroanions (4A, 4B, 6, and 7) exhibited higher phase transition temperatures than the monocaticonic MILs but were nonetheless liquids at room temperature. Despite similar cation substituents, MIL 7 exhibited a higher Tg than 4A which may be attributed to enhanced π–π interactions as a consequence of the benzimidazolium cation. The dicaticonic MILs exhibited no more than 5% weight loss below temperatures ranging from 294 to 312 °C. No significant enhancement in thermal stability was observed for the dicaticonic MILs containing [NTf2−]/[FeCl3Br−] heteroanions compared to those containing 2[FeCl3Br−] homoanions.

The effect of dissimilar cationic moieties on the melting point of dicaticonic MILs is shown in SI Figure S1. Unsymmetrical replacement of the hexadecylbenzimidazolium cation with the benzylimidazolium cation lowered the Tm from −0.6 to −16.7 °C (MILs 6 and 8, respectively), an outcome that may be attributed to diminished π–π interactions as well as removal of the dication symmetry component.29 Analogous to conventional dicaticonic ILs, endothermic peaks in DSC traces were quite broad with observable shouldering. This may be due to the highly flexible nature of the MIL cations, which allows different conformations and multiple step phase transitions.29

Phase transitions were not observed above −65 °C for the heavily alkylated/thiaalkylated symmetrical tricationic MILs 10 and 11. Both compounds 10 and 11 are room temperature liquids in contrast to their corresponding bromide salts. This is most certainly a function of incorporating the weaker coordinating [FeCl3Br−] anion. The thermal decomposition temperatures varied significantly between the alkylated (10) and thiaalkylated (11) hydrophobic tricationic MILs. Possessing a more thermally labile C–S bond, MIL 11 exhibited 5% weight loss at 225 °C compared to 312 and 275 °C for MIL 10 and 11, respectively.

**Magnetic Properties of Hydrophobic MILs.** The paramagnetic properties of MILs provide a unique advantage over conventional ILs by permitting control over substrate motion through the application of an external magnetic field. MILs containing high-spin d5 iron(III) centers are well characterized owing to the abundance and low cost of iron materials and have repeatedly been shown to exhibit paramagnetism at ambient temperatures.3,7,20,31 Table 1 shows the effective magnetic moments for all 11 MILs, determined using an Evans magnetic susceptibility balance.23 The general expression for molar magnetic susceptibility using the Evans balance is shown in eq 1:

\[
X_M = \frac{C_{bal}LM(R - R_o)}{10^3m}
\]

where \(X_M\) represents the molar magnetic susceptibility, \(C_{bal}\) is the balance calibration constant, \(L\) corresponds to the length of the sample in the tube, \(M\) is the molecular weight of the compound being measured, \(R\) is the instrument reading for the sample in the tube, \(R_o\) is the instrument reading for the empty sample tube, and \(m\) is the mass of sample introduced into the Evans’s balance. From \(X_M\) it is possible to calculate \(\mu_{eff}\) according to eq 2:

\[
\mu_{eff} = 2.83\sqrt{X_MT}
\]

where \(T\) is the absolute temperature. The \(\mu_{eff}\) for ammonium-based monocationic MILs ranged from 5.26 to 5.68 \(\mu_B\) and were comparable to those determined for heteroanionic MILs possessing a single [FeCl3Br−] anion (4A, 4B, 6, 7, 8, and 12). A video showing the magnetic manipulation of MIL 1 in...
aqueous solution is available in the SI. In an effort to increase the magnetic susceptibility of MILs, multiple paramagnetic iron(III) centers were incorporated into the MIL structure. For example, dicaticonic MIL 6c was designed to possess two paramagnetic iron(III) centers providing an increase in $\mu_{\text{eff}}$ to nearly 7.6 $\mu_B$. Further enhancement of magnetic susceptibility was observed in tricationic MILs 10 and 11, which exhibited $\mu_{\text{eff}} = 11.25$ $\mu_B$ and 11.76 $\mu_B$ respectively. The iron(III)-based MILs represent an inexpensive and readily available alternative to MILs based on lanthanides, such as Dy(III) ($\mu_{\text{eff}} = 10.6$ $\mu_B$).\(^{15}\) Moreover, the higher response of MILs 10 and 11 toward magnetic fields enables the use of smaller magnets with lower field strength for their manipulation in solution, which may prove useful in miniaturized magnet-based systems.\(^{34}\)

## CONCLUSION

In this study, three general classes of hydrophobic MILs were successfully synthesized and characterized. Within each class, unique synthetic approaches were exploited to control the magnetic and physicochemical properties of MILs. The incorporation of benzyl substituents within the MIL structure of monocationic quaternary ammonium-based hydrophobic MILs produced lower melting point compounds compared to linear alkyl substituents. The hydrophobicity of dicaticonic MILs was enhanced by replacing imidazolium cations with benzimidazolium cations, resulting in MILs that are insoluble in water down to 0.1% (w/v). Moreover, the inclusion of asymmetry within the cationic portion of dicationic MILs lowered the melting point without sacrificing hydrophobicity or magnetic susceptibility. Additionally, increasing the number of paramagnetic iron(III) centers in the MIL structure resulted in higher $\mu_{\text{eff}}$ values. Throughout the preparation of tricationic MILs, a common intermediate was chosen and modified to alter the hydrophobicity and magnetic properties of resulting MILs. Tricationic MILs containing three [FeCl$_3$Br$^{-}$] anions exhibited $\mu_{\text{eff}}$ values as high as 11.76 $\mu_B$ representing the highest known value reported for MILs. The synthesis of iron(III)-based tricationic hydrophobic MILs possessing large $\mu_{\text{eff}}$ is an inexpensive alternative to MILs based on lanthanides.

## ASSOCIATED CONTENT

Supporting Information

Figures showing NMR spectra, the absorbance spectrum of [FeCl$_3$Br$^{-}$], and DSC traces of dicaticonic hydrophobic MILs (Figure S1), text describing the synthesis of compound 9, table listing MILs and their corresponding water solubilities (Table S1), and multimedia videos demonstrating the magnetic manipulation of the hydrophobic MILs in water. This material is available free of charge via the Internet at http://pubs.acs.org.

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