

Electronic Supplementary Information (ESI)

Thermoresponsive Magnetic Ionic Liquids: Synthesis and Temperature Switchable Magnetic Separation

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Experimental Section

Materials. Chemicals and solvents, including trimethyl-1-octylammonium bromide (N_{1,1,1,8}Br, Alfa Aesar, 97%), dodecyltrimethylammonium chloride (N_{1,1,1,12}Cl, Fluka, ≥98%), (1-tetradecyl)trimethylammonium bromide (N_{1,1,1,14}Br, Alfa Aesar, 98%), tetrabutylphosphonium bromide (P_{4,4,4,4}Br, Aldrich, 98%), tributyl-*n*-octylphosphonium bromide (P_{4,4,4,8}Br, TCI, >98%), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, Aldrich, 98%), 1-bromobutane (Sigma-Aldrich, 99%), iron (III) chloride hexahydrate (FeCl₃•6H₂O, Sigma-Aldrich, ≥98%), ethylenediaminetetraacetic acid iron (III) sodium salt (Na[FeEDTA], Sigma, 99%), dichloromethane (Sigma-Aldrich, ≥99.8%), ethanol (Fisher, HPLC grade), diethyl ether (Fisher, 99%), were used as received. Deionized (DI) water (18 MΩ·cm) was produced with a Milli-Q system (Millipore, USA).

Synthesis of DBU-BuBr. The synthesis of DBU-BuBr followed the procedures described in literature.¹ Briefly, 50 mmol of DBU was mixed with 50 mmol of 1-bromobutane at room temperature. The mixture was stirred at 500 rpm for 10 min to ensure fully mixing. Then the mixture was heated to 90 °C and kept stirring at 500 rpm for 24 hr. The colorless liquid turned brownish after the completion of reaction. The viscous liquid was washed with diethyl ether twice to remove the unreacted reactants. The final product was obtained after vacuum drying at 40 °C.

Synthesis of MILs. The synthesis of MILs is conducted according to a modified method.^{2,3} Briefly, 2 mmol of ammonium/amidine/phosphonium salts were dissolved in 5 mL of dichloromethane, followed by adding 2 mmol of FeCl₃•6H₂O powder. After stirring at room temperature for 24 hr, the aqueous phase was removed before evaporating the solvent of dichloromethane. The residual was washed with diethyl ether twice. The final products were obtained after vacuum drying at 40 °C. The synthesis of [FeEDTA]⁻ complex-based MILs can be found in literature.⁴

Characterizations. Fourier transformation infrared (FT-IR) spectroscopy measurements of the MILs and their correspondent ammonium/amidine salts were accomplished with a Bio-Rad spectrometer (FTS 3500). Raman studies of the MILs were performed on an XploRA PLUS Raman microscope (Horiba/JY, France) with the excitation wavelength of 785 nm. UV-Vis spectra of the MILs were recorded using a Shimadzu UV-1800 spectrometer in plastic cuvettes with a 1 cm path length at room temperature. Elemental analysis of each MIL was conducted with a PHI Quantera X-ray photoelectron spectroscopy (XPS) with a chamber pressure of 5×10⁻⁹ torr, a spatial resolution of 30 μm and an Al cathode as the X-ray source. The magnetic properties of the MILs were examined by using SQUID (superconducting quantum interference device, Quantum Design) magnetometer in the magnetic field range of -20000 to 20000 Oe at 300 K. The lower critical solution temperatures (LCSTs) of the MILs were determined with turbidity measurement using a UV-Vis spectrophotometer (Shimadzu, UV-3600). Thermogravimetric analysis (TGA) of the MILs after phase separation was performed with a thermogravimetric analyzer (Shimadzu, DTG-60AH) under N₂ from 30 to 120 °C at a temperature ramping rate of 2 °C min⁻¹.

Table S1. Elemental analysis of the MILs.

<i>Atomic Concentration (%)</i>	<i>N_{1,1,1,8}[FeBrCl₃]</i>	<i>N_{1,1,1,12}[FeCl₄]</i>	<i>N_{1,1,1,14}[FeBrCl₃]</i>	<i>DBU-Bu[FeBrCl₃]</i>
<i>Fe</i>	19.1	15.2	14.6	11.7
<i>N</i>	15.4	18.1	17.4	29.2
<i>Cl</i>	52.7	66.7	49.9	45.2
<i>Br</i>	12.8	-	18.1	13.9

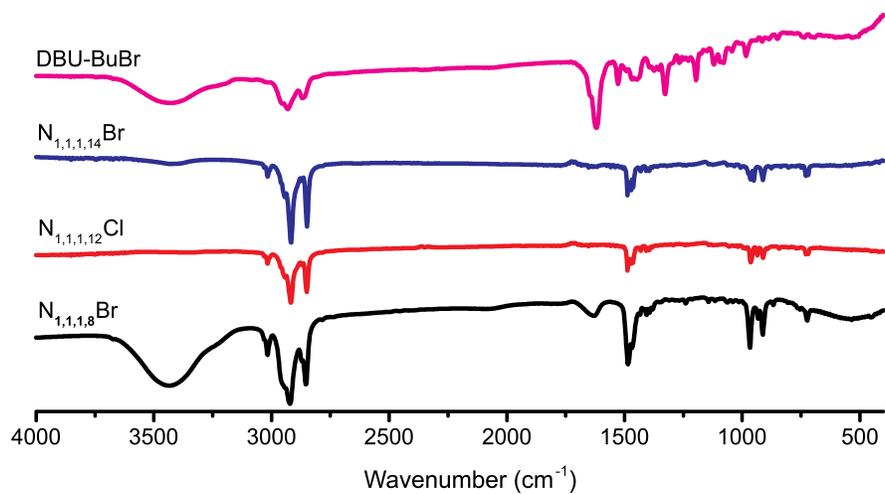


Fig. S1 FT-IR spectra of ammonium/amidine salts.

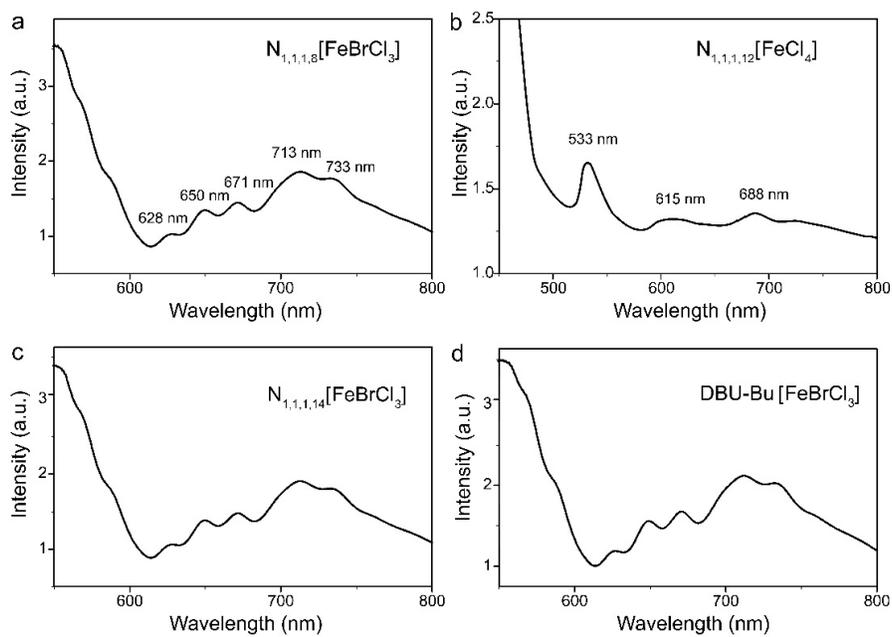


Fig. S2 UV-Vis spectra of (a) $N_{1,1,1,8}[FeBrCl_3]$, (b) $N_{1,1,1,12}[FeCl_4]$ (c) $N_{1,1,1,12}[FeBrCl_3]$, and (d) DBU-Bu[FeBrCl₃].

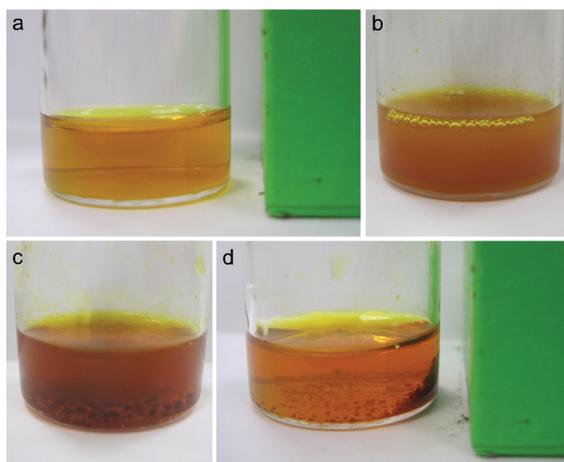


Fig. S3 Photographs of LCST behaviour of $N_{1,1,1,12}[FeCl_4]$ solution (a) at 24 °C, (b) heated to 60 °C for 20 min, (c) at 60 °C for 10 more minutes, and (d) response to magnetic field at 60 °C.

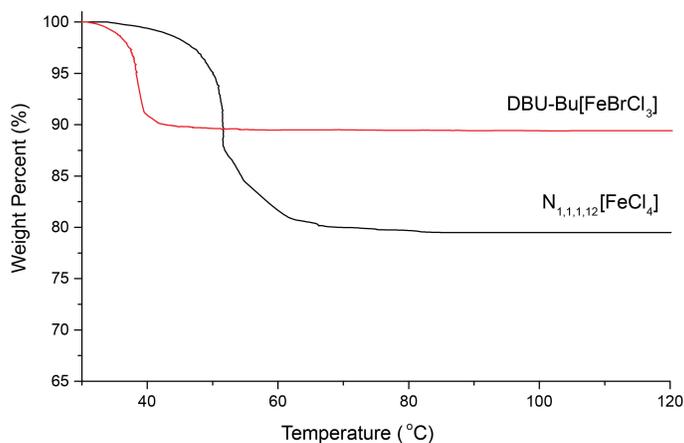


Fig. S4 TGA curves of DBU-Bu[FeBrCl₃] and $N_{1,1,1,12}[FeCl_4]$ in the separated MIL phase.

References

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