Supporting Information

Dicationic magnetic ionic liquids with tunable heteroanions

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General Comments

Materials: 1-butylimidazole (98%), 1,2-dibromoethane (99%) and iron (III) chloride (≥ 99.99%) were purchased from Sigma-Aldrich and used as received. Aerosol-OT (AOT) was purchased from Sigma-Aldrich and purified by Soxhlet extraction using dry acetone and subjected to repeated centrifugation.[1]

Instruments: Melting points were measured using a TA instruments DSC Q200. The heating and cooling ramp for each sample was 10 ˚C min^{-1} and cyclic profiles were repeated three times. ^{1}H-NMR spectra were carried out on a Varian 400 MHz spectrometer. Visible absorption spectra were recorded on a Nicolet Eco 300 UV-Vis spectrometer in acetonitrile (0.1 M, 500 – 900 nm). A Bohlin CVO (Malvern Instruments), fitted with a cone and plate (4˚ / 20 mm), was used to determine viscosities at 75 ˚C. Repeat scans of viscosity as a function of shear stress (10-1000 Pa) were carried out to ensure the materials gave linear responses with no shear history. Viscosities were fitted using a power law, $\sigma = \eta \cdot \gamma^n$, with σ shear stress, η viscosity and γ shear rate. Magnetic susceptibility data were collected using a PPMS (physical properties measurement system) made by Quantum Design and varying the temperature from room temperature down to 2 K and applying a high magnetic fields (85 kOe). A gel capsule was used to fix small amounts (10-20 mg) of the samples on the sample holder of the PPMS extraction magnetometer.

Synthesis

[1,2-Bis[N-(N'-butylimidazolium)ethane] [dibromide] (**$[C_4mim_2][Br]_2$**) was synthesized according to literature.[2] A solution of 1-butylimidazole (8.213 g, 66.20 mM) and 1,2-dibromoethane (6.2155 g, 33.10 mM) in MeCN (40 mL) was refluxed for 3 days. The white crystalline precipitate was filtered after cooling, and washed with tetrahydrofuran (THF) three times before being dried *in vacuo* at 80 ˚C for 2 days. mp 167˚C. ^{1}H-NMR (400 MHz, methanol-d_4 23 ˚C): δ 0.98 (s, 6H), 1.33 – 1.44 (m, 4H), 1.86 – 1.94 (m, 4H), 4.28 (m 4H), 4.90 (s, 4H), 7.74 (t, 4H), 9.28 (s, 2H). Elemental Analysis (*theoretical value in brackets*): H = 6.32 (6.42), C = 44.05 (44.07), N = 12.53 (12.85), Br = 37.04 (36.65).

[1,2-Bis[N-(N'-butylimidazolium)ethane] [bis-bromotrichloroferrate (III)] (**$[C_4mim_2]$ $[FeCl_3Br]_2$**) was synthesized by mixing $[C_4mim_2][Br]_2$ (2.864 g, 6.57 mM, 1 eq.) with iron (III) chloride (2.131 g, 0.0131 moles, 2 eq.) and stirring in MeOH for 2 hrs. mp 52 ˚C. Elemental Analysis (*theoretical value in brackets*): H = 3.71 (3.68), C = 25.35 (25.27), N = 7.35 (7.37), Br = 20.95 (21.02), Cl = 27.87 (27.97). Visible spectroscopy also revealed the three characteristic bands of the $[FeCl_3Br]^-$ ion similar to those expected for $[FeBr_4]^-$ ion at around 534, 619 and 688 nm.[3, 4]

[1,2-Bis[N-(N'-butylimidazolium)ethane] [bis-[1,4-bis(2-ethylhexoxy)-1,4-dioxobutane-2-sulfonate]] (**$[C_4mim_2]$ $[AOT]_2$**) was synthesized by dissolving sodium 1,4-bis(2-ethylhexoxy)-1,4-dioxobutane-2-sulfonate (Aerosol-OT, AOT, 3.862g, 8.686 mM, 2 eq.) in EtOH/H_2O (1:1 v/v) and passing it through a column containing a strong ion exchange resin (Amberlite IR 120 H^+ form). The free sulfonic acid formed on passing the sodium salt through the resin was then immediately neutralized with an ethanolic solution $[C_4mim_2][Br]_2$ (1.894 g, 4.34 mM, 1 eq.) that had been passed through a hydroxide exchange resin (Dowex Monosphere 550A). The solvent was then removed by evaporation and drying *in vacuo* for 36hrs. mp 68 ˚C. ^{1}H-NMR (400 MHz, chloroform-

d_1 23 ˚C): δ 0.75 - 0.92 (m, 24H), δ 0.93 – 1.01 (t, 6H), δ 1.11 – 1.70 (m, 40H), δ 3.08 – 3.34 (m, 4H), δ 3.85 – 4.10 (m, 8H), δ 4.11 – 4.27 (m, 6H), δ 4.88 (s, 4H), δ7.11 (s, 2H), δ 8.41 (s, 2H), δ 9.74 (s, 2H). Elemental Analysis (*theoretical value in brackets*): H = 9.10 (9.12), C = 60.28 (60.60), N = 5.37 (5.44), Br = 0.00 (0), Na = 0.00 (0).

[1,2-Bis[N-(N'-butylimidazolium)ethane] [1,4-bis(2-ethylhexoxy)-1,4-dioxobutane-2-sulfonate] [bromotrichloroferrate (III)] (**[C_4mim$_2$][AOT][$FeCl_3Br$]**) was synthesized by mixing 1 eq. (0.698 g, 0.623 mM) [C_4mim$_2$] [$FeCl_3Br$]$_2$ and 1eq. (0.698 g, 0.623 mM) [C_4mim$_2$][AOT]$_2$ in MeOH for 2 hours followed by removing the solvent by evaporation: mp <-25 ˚C. Elemental Analysis (*theoretical value in brackets*): H = 6.86 (6.92), C = 45.95 (46.02), N = 6.07 (5.96), S = 3.41 (3.43), Na = 0.00 (0.00). Visible spectroscopy again revealed the characteristic bands of the [$FeCl_3Br$]$^-$ ion.

Squid Magnetometry

In the magnetometry analysis (Figure 2, main paper) a diamagnetic contribution, which is typical of organic materials, was not taken into consideration. Therefore, when χT was calculated the actual obtained value was $T(-\chi_{diamag}+\chi)= \chi T-T\chi_{diamag}$. This accounts for the slight increase in χT as the temperature decreases. The negative slope above ~60 K yields a diamagnetic susceptibility (χ_{diamag}) of $-2x10^{-6}$ emu/(g Oe).

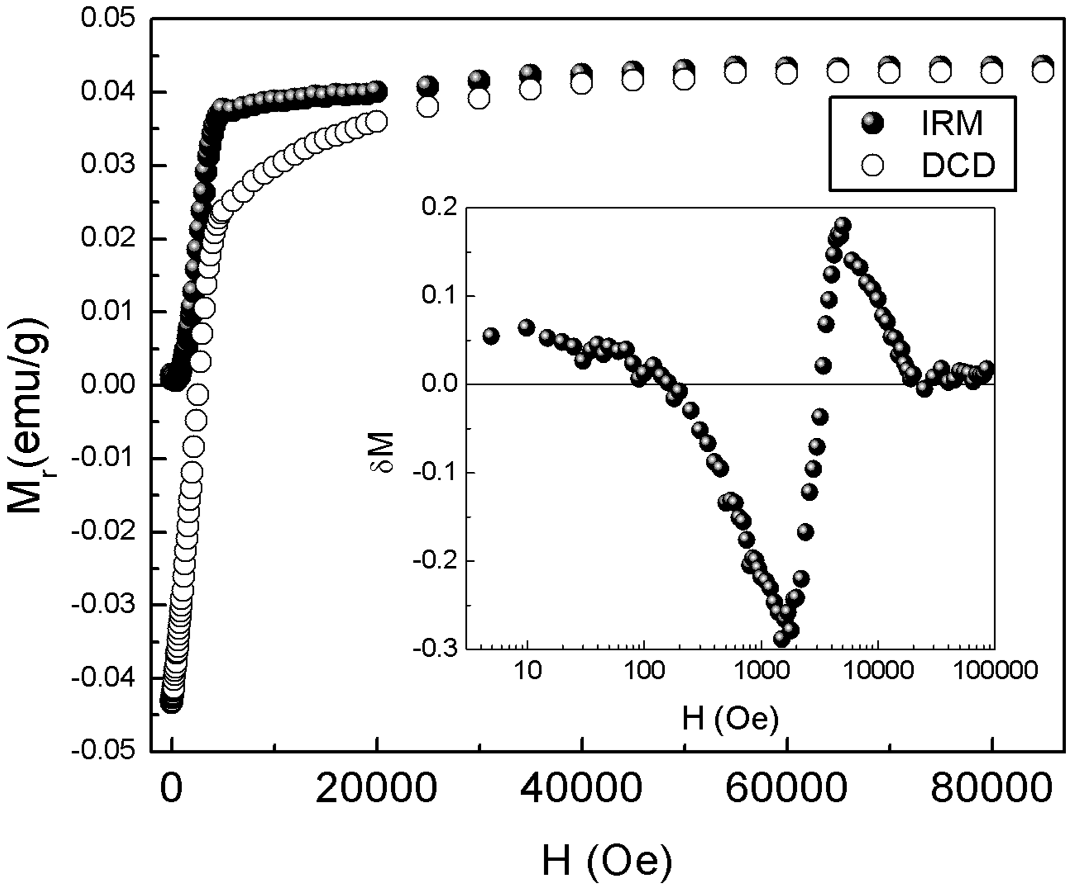

Figure S1: Isothermal remanent magnetization (IRM) and demagnetizing remanence (DCD) for the magnetic compound $[C_4mim_2][FeCl_3Br]_2$ as a function of applied magnetic field. Inset: Corresponding Henkel plot for T = 5 K.

References

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