

Electronic Supplementary Information (ESI)

Magnetic Chiral Ionic Liquids Derived from Amino Acids

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1. Chemicals

Amino acid methyl ester hydrochlorides including L-alanine methyl ester hydrochloride, L-valine methyl ester hydrochloride, L-leucine methyl ester hydrochloride, L-isoleucine methyl ester hydrochloride, L-phenylalanine methyl ester hydrochloride, and D-phenylalanine methyl ester hydrochloride were obtained from Sigma-Aldrich (Milwaukee, WI, USA). Iron(III) chloride hexahydrate, (R)- and (S)-2,2,2-trifluoro-1-(9-anthryl)ethanol (TFAE), (R)- and (S)-1,1'-binaphthyl-2,2'-diamine (BNA), (R)- and (S)-2-(6-methoxy-2-naphthyl)propionic acid (naproxen) were also obtained from Sigma-Aldrich and used without further purification. Ethanol, methanol, acetonitrile, chloroform, and carbon tetrachloride were of anhydrous grade (Sigma-Aldrich, Milwaukee, WI), and all other organic solvents such as acetone, hexane, and water are of HPLC grade (J. T. Baker, Phillipsburg, NJ).

2. Instrumentation and methods

^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were acquired by use of a Bruker Avance 400 NMR spectrometer. The ^1H and ^{13}C chemical shifts are given in parts per million (δ) with TMS as an internal standard. Due to the paramagnetic properties of the MCILs, very dilute sample solutions in deuterated DMSO were measured for ^1H and ^{13}C NMR characterization. ^{13}C NMR spectra were acquired after overnight scan. FT-IR was measured using a Bruker Tensor 27 FT-IR spectrometer. Samples were analyzed in pure form by use of a DuraSamp IR apparatus. All spectra were obtained using 32 scans for both sample and background, with a resolution of 4 cm^{-1} . Elemental analyses were contracted to Atlantic Microlab (Atlanta, GA). A Jasco-710 spectropolarimeter was used to obtain the CD spectra of MCILs. To characterize the MCILs, their visible absorption spectra were measured using a Shimadzu UV-3101PC UV-Vis-near-IR scanning spectrometer (Shimadzu, Columbia, MD). Absorption was collected using a 1.0 cm^2 quartz cuvette at room temperature and the blank was subtracted from each spectrum.

The magnetic susceptibility and magnetization of the MCILs were measured using approximately 80 to 100 mg of the sample in a Quantum Design superconducting quantum interference device (SQUID) magnetometer (San Diego, CA, USA) for temperatures between 5 and 300 K and fields between -50 000 and 50 000 Oe.

Viscosity of the MCIL, L-PheOMeFeCl₄ was tested by use of Rheometric Scientific RFSII at room temperature. Geometry: 25mm cone and plate (25mm diameter, .04 radians cone angle, .05mm truncation). Two viscosity measurements were made using a freshly loaded sample. In the first measurement, viscosity was determined at constant shear rates (.02, .1, .5, 1., 10, 25, 50 and 100 s⁻¹), each shear rate held for 20 seconds, and the measurement averaged for a 2 second interval. In the second test, the shear rate was ramped from 0 - 100 s⁻¹, over a 300 second time interval. In each test, samples were loaded and allowed to thermal equilibrate for 15 seconds prior to the start of the test.

A TA Q50 thermal gravimetric analyzer (TA Instruments, New Castle, DE) was used to analyze the thermal stability of MCILs and their decomposition behaviour. MCIL samples (about 3-4 mg) were scanned from room temperature to 600 °C under nitrogen flow (50 ml/min) with a heating rate of 10 °C/min. Values for the onset degradation temperature and peak temperature were determined from the derivative TGA curves. Glass transition behaviour of MCILs was investigated using a Q100 differential scanning calorimeter (TA Instruments, New Castle, DE). MCIL samples (about 5 mg) were put in sealed aluminium crucibles and run under a nitrogen flow (50 ml/min). Heating - cooling - reheating cycles were performed using the following sequence: the sample was cooled to -80 °C, equilibrated at -80 °C, and isothermal for 3 min at -80 °C; then heated to 150 °C with a rate of 10 °C/min, isothermal for 3 min at 150 °C; then cooled to -80 °C with a rate of 10 °C/min, isothermal for 3 min at -80 °C; finally heated to 150 °C with a rate of 10 °C/min.

Steady-state fluorescence measurements were recorded at room temperature by use of a Spex Fluorolog-3 spectrofluorimeter (model FL3-22TAU3; Jobin Yvon, Edison, NJ) equipped with a 450-W xenon lamp and R928P photomultiplier tube (PMT) emission detector. Fluorescence emission spectra were collected in a 4-mm quartz fluorescence curvet with slit widths set for entrance exit bandwidths of 4 nm on both excitation and emission monochromators for BNA, 2 nm for TFAE, and 1.5 nm for naproxen, respectively. Fluorescence for BNA, TFAE, and naproxen were respectively monitored at excitation wavelengths of 365, 365, and 280 nm. In addition, all fluorescence spectra were blank subtracted before data analysis.

3. Synthesis of magnetic chiral ionic liquids (MCILs)

Generally, MCILs were synthesized by a reaction between L-amino acid methyl ester hydrochloride and iron(III) chloride hexahydrate in anhydrous methanol at room temperature for 12 h (Scheme 1 in the article). The evaporation of methanol and water afforded the MCIL products. A typical synthesis procedure for L-PheOMeFeCl₄ is as follows. To a solution of L-phenylalanine methyl ester hydrochloride (1.00 g, 4.6 mmol) in anhydrous methanol (10 mL) was added iron(III) chloride hexahydrate (1.26g, 4.6 mmol) in anhydrous methanol (10 mL) at room temperature. The yellow solution was stirred at room temperature for 12h. The methanol was subsequently removed by rotavapor. The viscous brownish liquid obtained after methanol removal was washed with a small amount of water. After decantation of the upper water phase, the residual water was removed by freeze-drying on a lyophilizer overnight. The final product of L-PheOMeFeCl₄ is a brownish viscous liquid.

4. Characterization of magnetic chiral ionic liquids (MCILs)

The identity and purity of the five MCILs were determined by ¹H, ¹³C NMR, FT-IR, and C, H, N elemental analysis.

L-AlaOMeFeCl₄, brownish viscous liquid, yield 88%, ¹H NMR (400 MHz, DMSO-d₆), δ (ppm): 8.47 (broad, 3H), 4.06 (m, 1H), 3.74 (s, 3H), 1.41 (d, 3H). ¹³C NMR (100 MHz, DMSO-d₆), δ (ppm): 170.6, 53.6, 48.3, 16.3. IR (neat), ν (cm⁻¹): 3197, 2945, 1747, 1571, 1433, 1263, 1174, 1176. Anal. Calcd for C₄H₁₀Cl₄FeNO₂, C, 15.92; H, 3.34; N, 4.64. Found: C, 15.27; H, 3.98; N, 5.09.

L-ValOMeFeCl₄, brownish viscous liquid, yield 90%, ¹H NMR (400 MHz, DMSO-d₆), δ (ppm): 8.45 (broad, 3H), 3.75 (m, 1H), 3.66 (s, 3H), 3.26 (m, 1H), 0.87 (d, 6H). ¹³C NMR (100 MHz, DMSO-d₆), δ (ppm): 169.7, 57.7, 53.5, 31.4, 16.9. IR (neat), ν (cm⁻¹): 3184, 2955, 1721, 1586, 1477, 1440, 1253, 1242. Anal. Calcd for C₆H₁₄Cl₄FeNO₂, C, 21.85; H, 4.28; N, 4.25. Found: C, 20.97; H, 5.23; N, 4.01.

L-LeuOMeFeCl₄, brownish viscous liquid, yield 91%, ¹H NMR (400 MHz, DMSO-d₆), δ (ppm): 8.46 (broad, 3H), 3.73 (m, 1H), 3.57 (s, 3H), 3.17 (m, 2H), 1.48 (m, 1H), 0.77 (d, 6H). ¹³C NMR (100 MHz, DMSO-d₆), δ (ppm): 168.7, 59.7, 39.4, 32.9, 29.7, 17.3. IR (neat), ν (cm⁻¹): 3175, 2956, 2866, 1724, 1575, 1471, 1438, 1367, 1249.

Anal. Calcd for $C_7H_{16}Cl_4FeNO_2$, C, 24.45; H, 4.69; N, 4.07. Found: C, 24.50; H, 5.08; N, 4.03.

L-IleOMeFeCl₄, brownish viscous liquid, yield 87%, ¹H NMR (400 MHz, DMSO-d₆), δ (ppm): 8.69 (broad, 3H), 3.67 (m, 1H), 3.72 (s, 3H), 3.34 (m, 1H), 1.23 (m, 2H), 0.86 (t, 6H). ¹³C NMR (100 MHz, DMSO-d₆), δ (ppm): 169.5, 56.4, 53.0, 36.3, 25.6, 14.7, 11.9. IR (neat), ν (cm⁻¹): 3175, 2956, 2866, 1724, 1575, 1471, 1438, 1367, 1249. Anal. Calcd for $C_7H_{16}Cl_4FeNO_2$, C, 24.45; H, 4.69; N, 4.07. Found: C, 24.16; H, 5.37; N, 3.98.

L-PheOMeFeCl₄, brownish viscous liquid, yield 92%, ¹H NMR (400 MHz, DMSO-d₆), δ (ppm): 8.46 (broad, 3H), 7.32 (d, 2H), 7.27 (d, 1H), 7.20 (m, 2H), 4.27 (m, 1H), 3.65 (s, 3H), 3.14 (d, 2H). ¹³C NMR (100 MHz, DMSO-d₆), δ (ppm): 170.2, 129.8, 129.1, 127.8, 53.7, 53.1, 31.2. IR (neat), ν (cm⁻¹): 3183, 2937, 1724, 1573, 1438, 1257, 1246. Anal. Calcd for $C_{10}H_{14}Cl_4FeNO_2$, C, 31.78; H, 3.73; N, 3.71. Found: C, 30.68; H, 4.14; N, 3.61.

5. Viscosity of magnetic chiral ionic liquids (MCILs), L-PheOMeFeCl₄ was used as a representative.

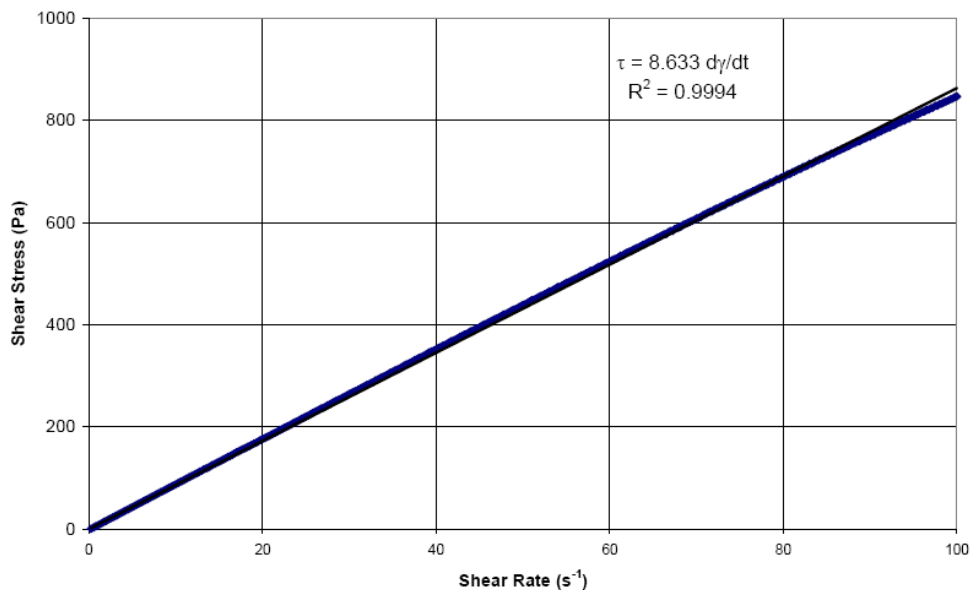


Fig. S1 Relationship between shear stress and shear rate for L-PheOMeFeCl₄. The linear relationship indicates that the sample is Newtonian flow in this shear rate range. A linear regression of the results is provided in the figure, showing that the viscosity obtained in this measurement is 8.633 Pa·s.

6. Magnetic properties of magnetic chiral ionic liquids (MCILs).

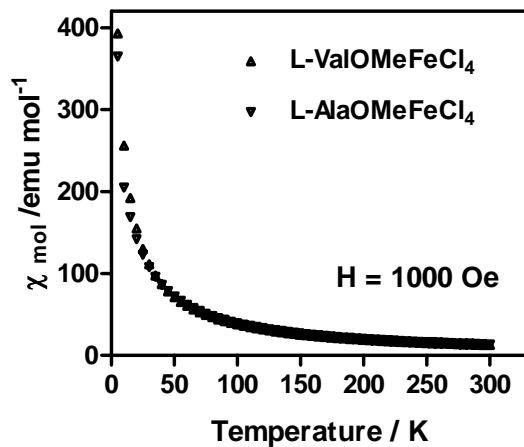


Fig. S2 Temperature dependence of the molar magnetic susceptibility of L-ValOMeFeCl₄ and L-AlaOMeFeCl₄.

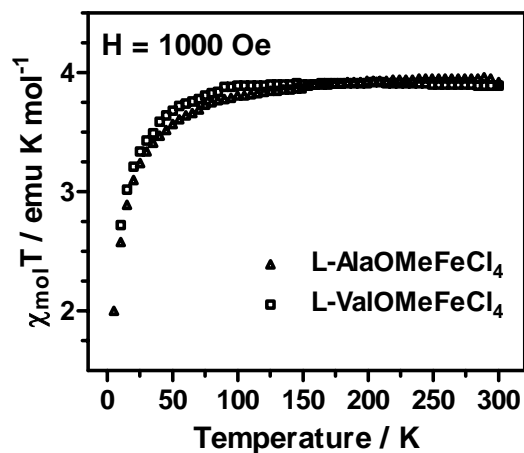


Fig. S3 Temperature dependence of the product of the temperature and the static molar susceptibility of L-ValOMeFeCl₄ and L-AlaOMeFeCl₄.

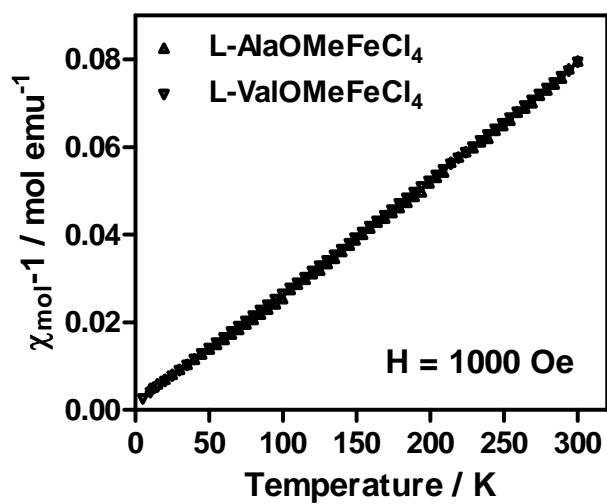


Fig. S4 Temperature dependence of reciprocal molar susceptibility of L-ValOMeFeCl₄ and L-AlaOMeFeCl₄ at a field of 1000 Oe.

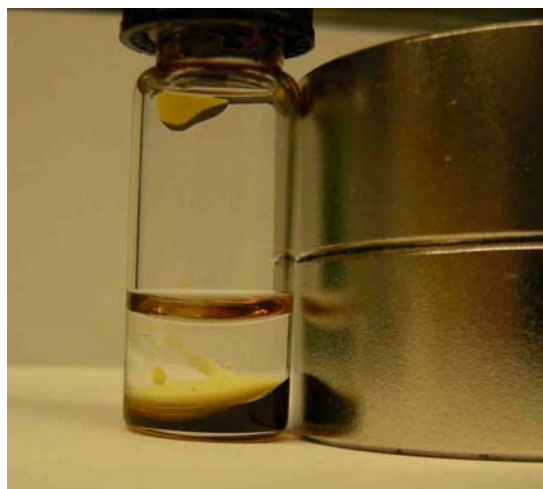


Fig. S5 Response of MCIL, L-LeuOMeFeCl₄, to a neodymium magnet. The upper transparent phase is hexane.

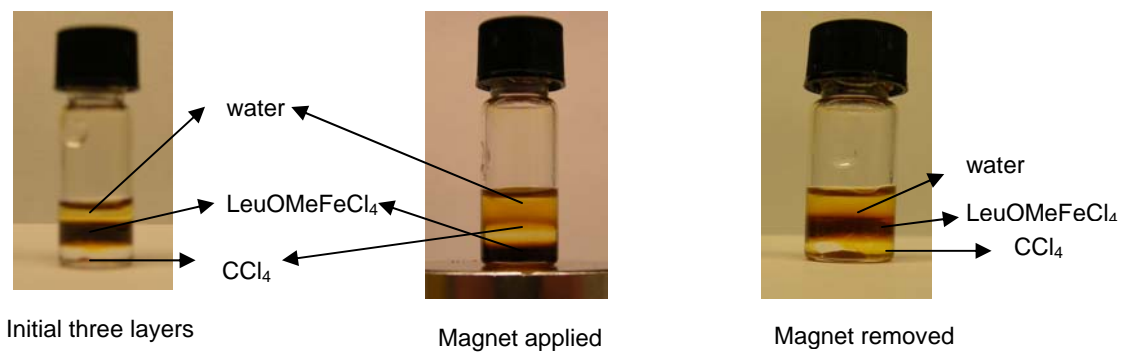


Fig. S6 Switch of phase layer distribution by a magnet.

7. Thermal gravimetric analysis of magnetic chiral ionic liquids (MCILs)

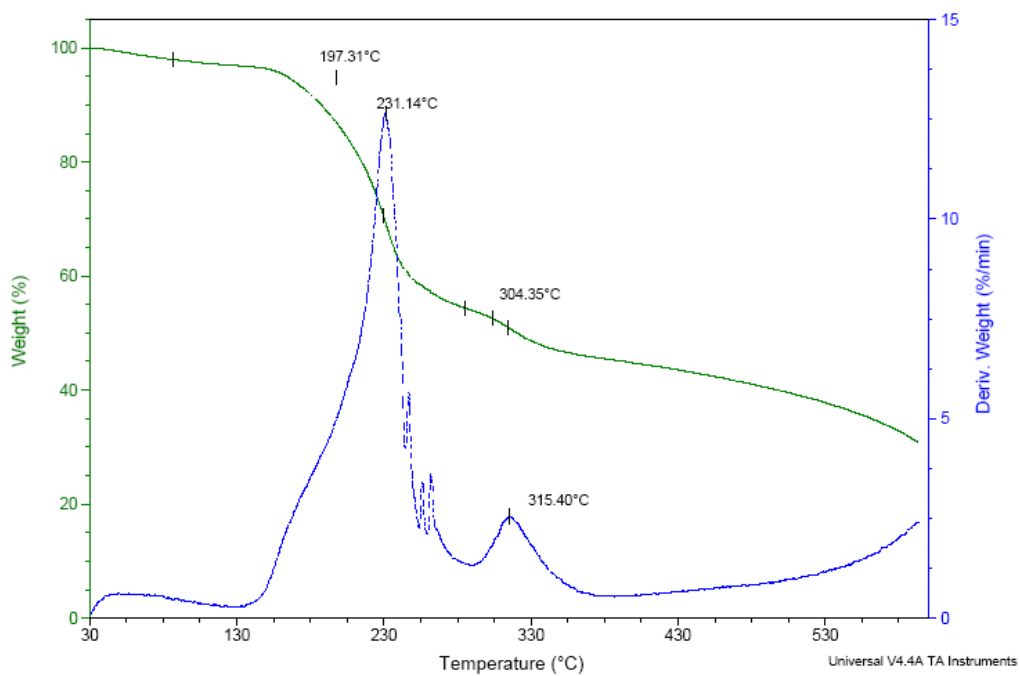


Fig. S7 Thermal gravimetric analysis scan of L-AlaOMeFeCl₄

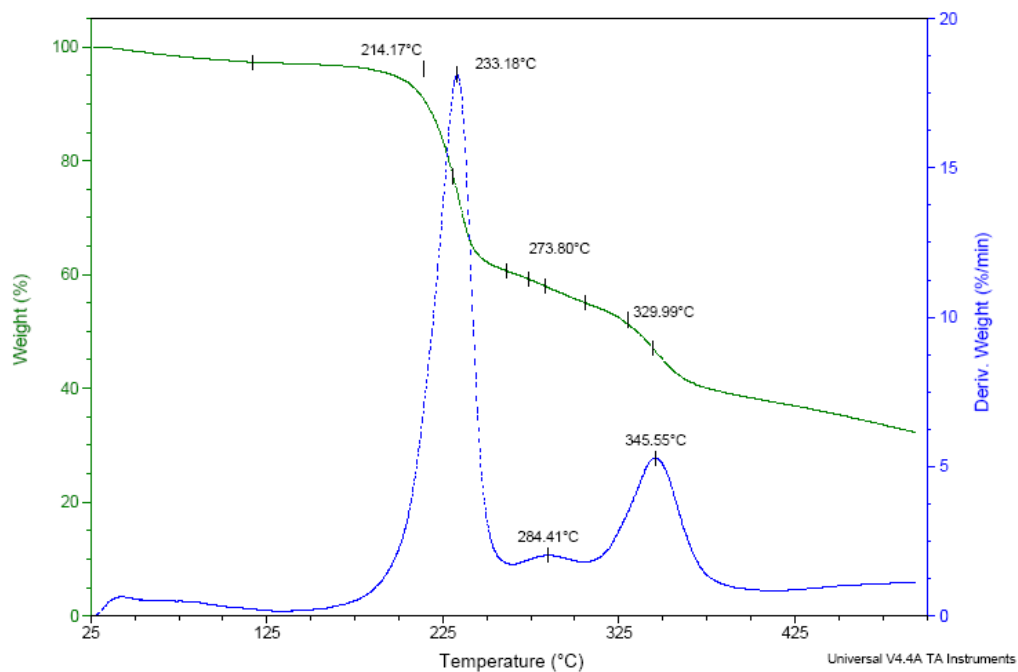


Fig. S8 Thermal gravimetric analysis scan of L-ValOMeFeCl₄

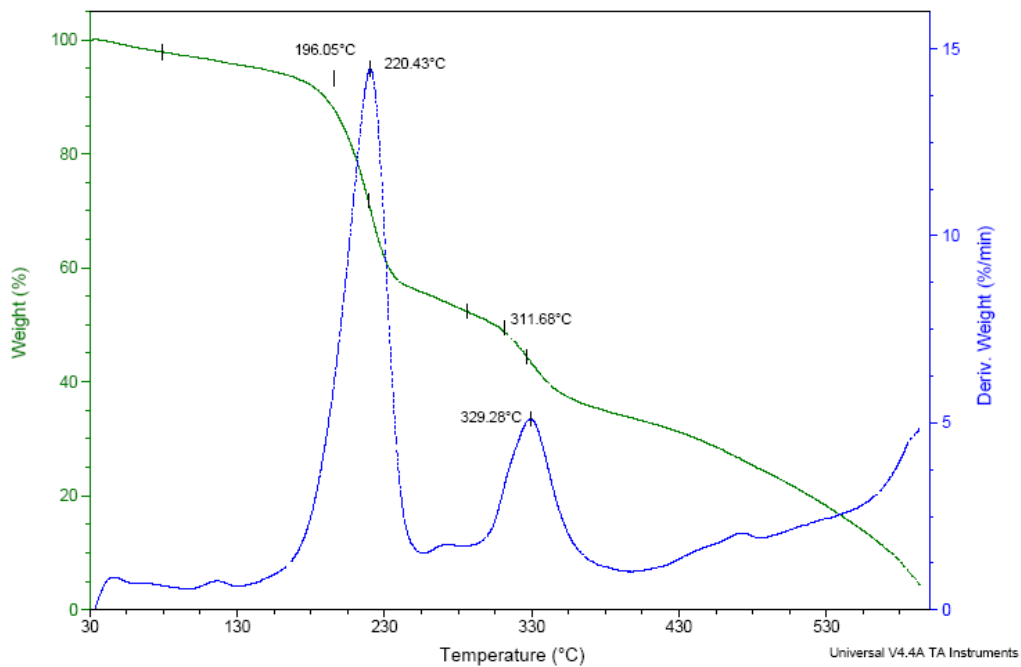


Fig. S9 Thermal gravimetric analysis scan of L-LeuOMeFeCl₄

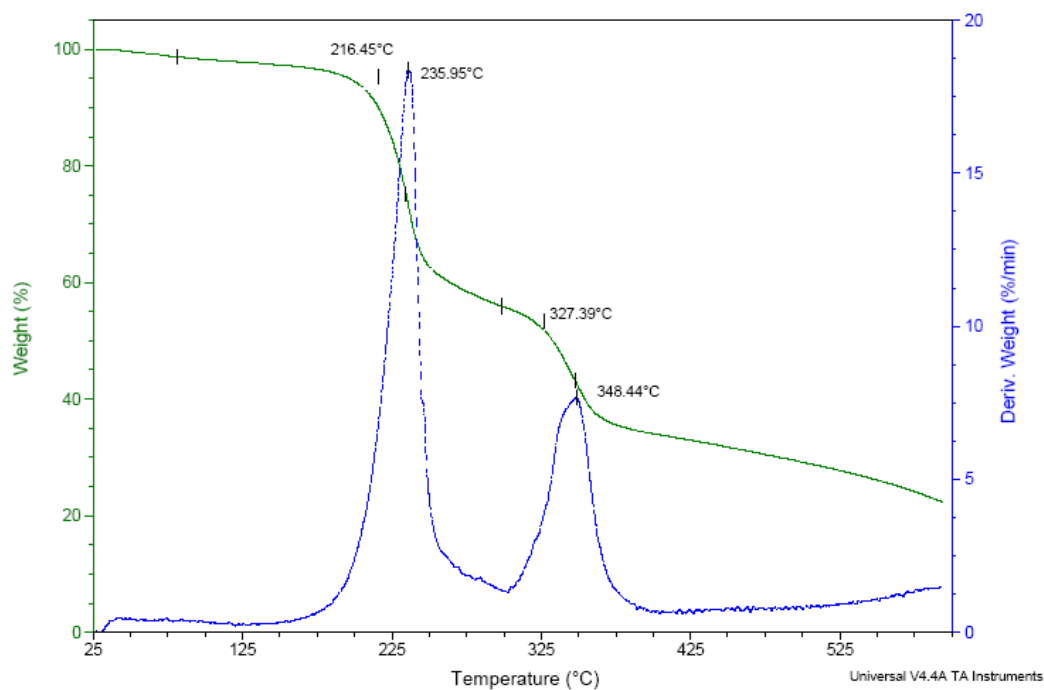


Fig. S10 Thermal gravimetric analysis scan of L-IleOMeFeCl₄

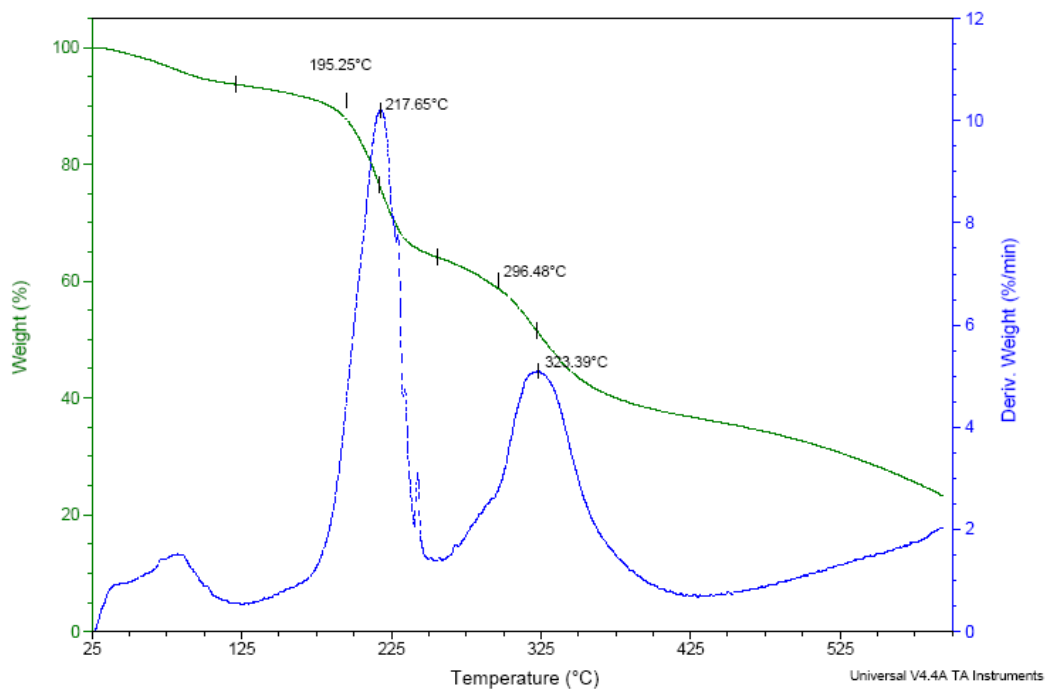


Fig. S11 Thermal gravimetric analysis scan of L-PheOMeFeCl₄

8. Differential scanning calorimetry scan of magnetic chiral ionic liquids (MCILs)

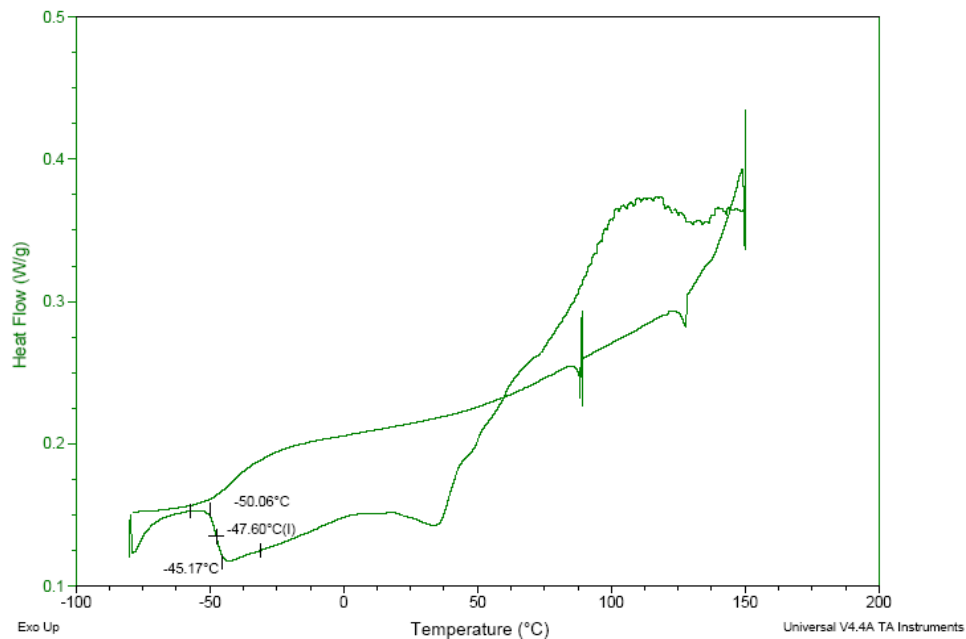


Fig. S12 Differential scanning calorimetry scan of L-AlaOMeFeCl₄

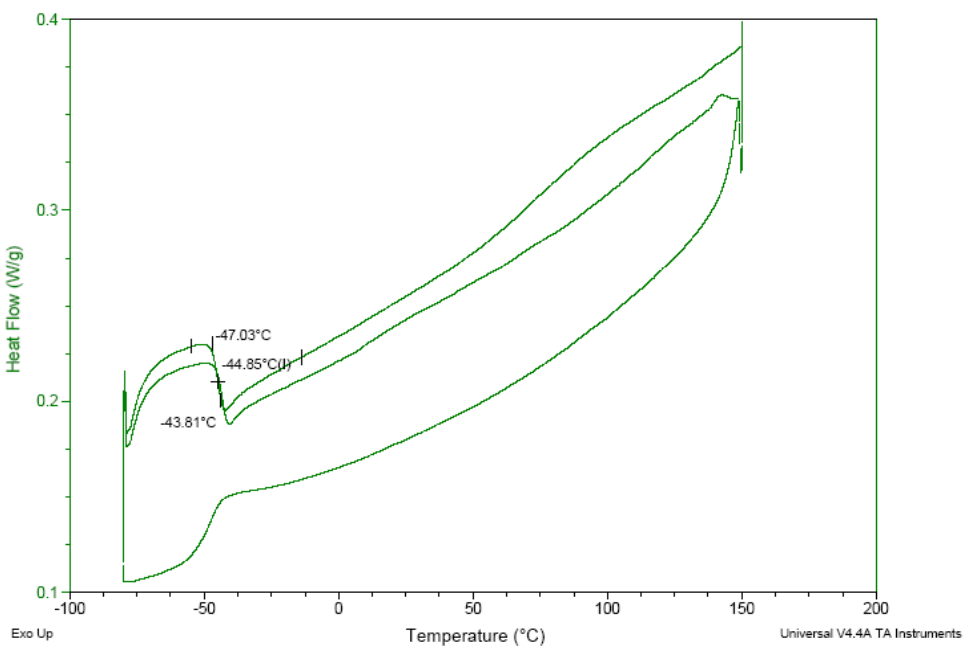


Fig. S13 Differential scanning calorimetry scan of L-ValOMeFeCl₄

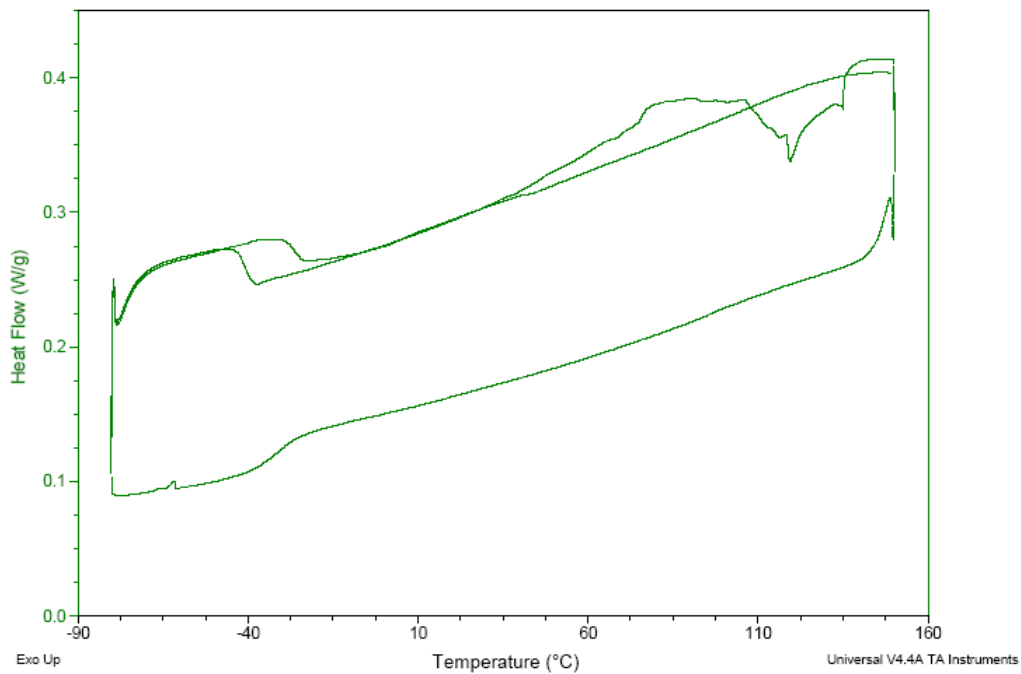


Fig. S14 Differential scanning calorimetry scan of L-LeuOMeFeCl₄

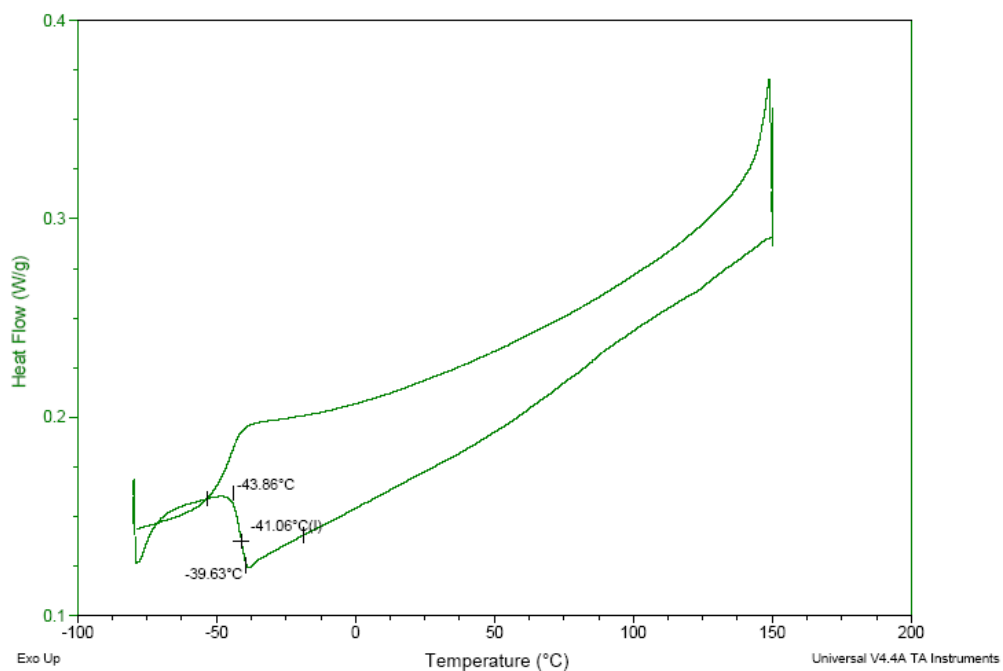


Fig. S15 Differential scanning calorimetry scan of L-IleOMeFeCl₄

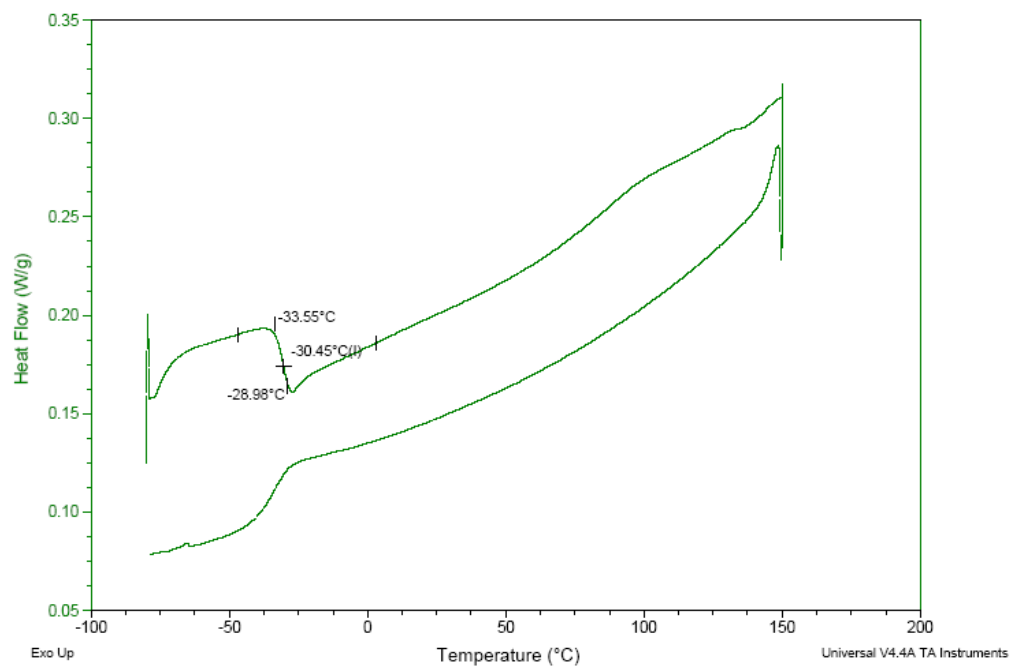


Fig. S16 Differential scanning calorimetry scan of L-PheOMeFeCl₄

9. Using steady-state fluorescence to investigate chiral recognition with L-AlaOMeFeCl₄ as chiral selector

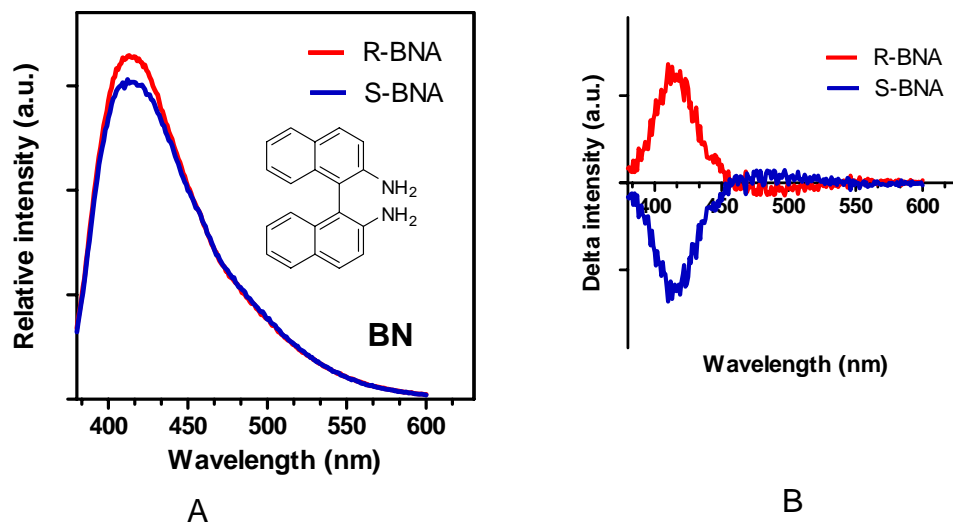


Fig. S17 Fluorescence emission (A) and mean centered spectral plot (B) of 10 μ M (R)- and (S)- BNA enantiomers in the presence of AlaOMeFeCl₄. The emission spectra of BNA were monitored at excitation wavelength of 365 nm at room temperature.

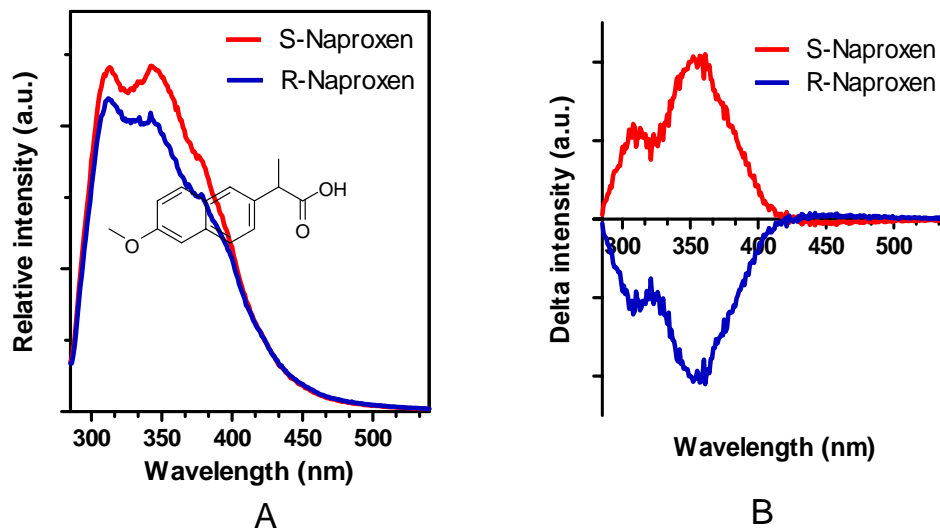


Fig. S18 Fluorescence emission (A) and mean centered spectral plot (B) of 10 μ M (R)- and (S)- Naproxen enantiomers in the presence of AlaOMeFeCl₄. The emission spectra of Naproxen were monitored at excitation wavelength of 280 nm at room temperature.