Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


## Supporting Information

# Paramagnetic ionic plastic crystals containing the octamethylferrocenium cation: counteranion dependence of phase transitions and crystal structures

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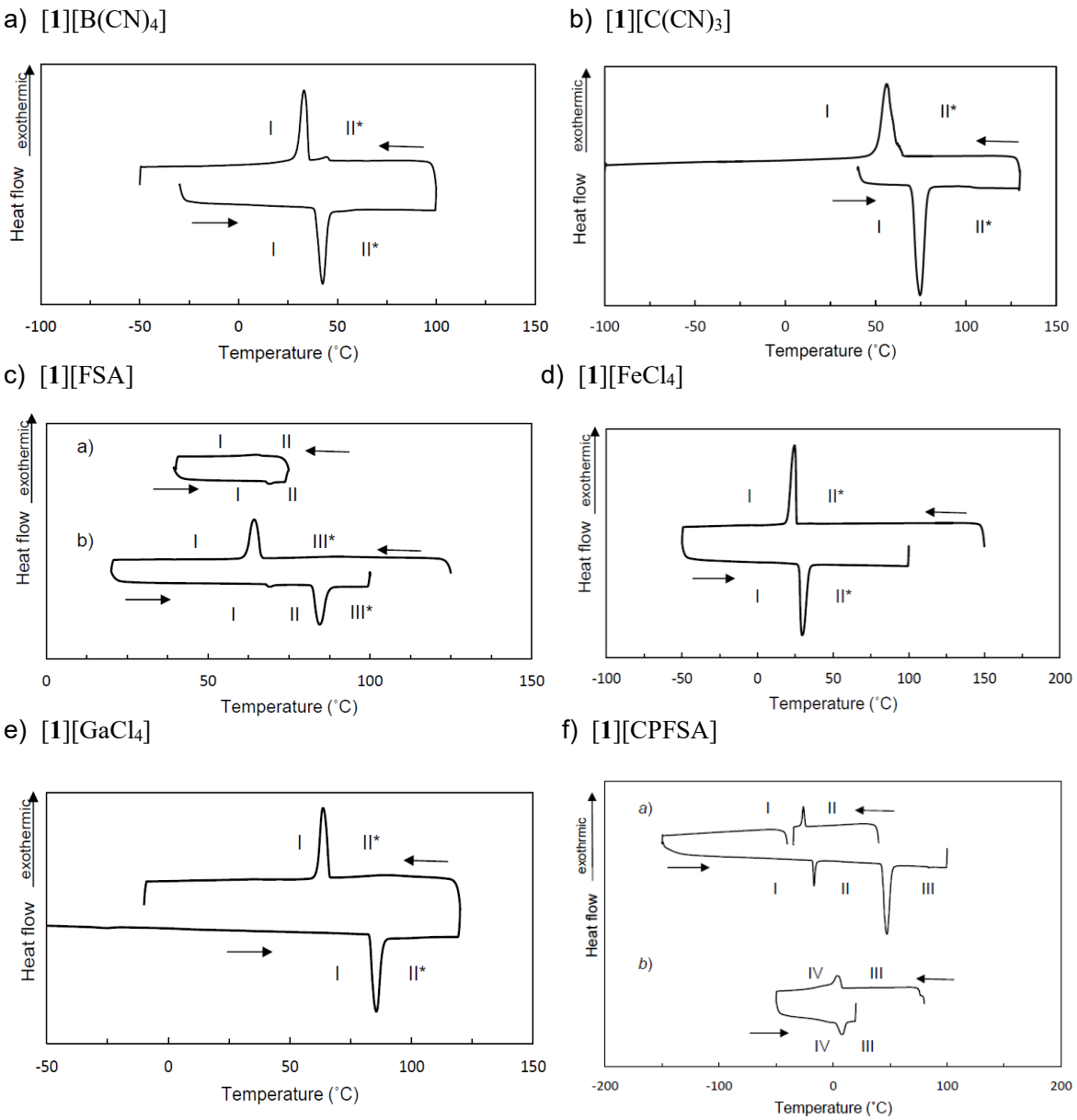
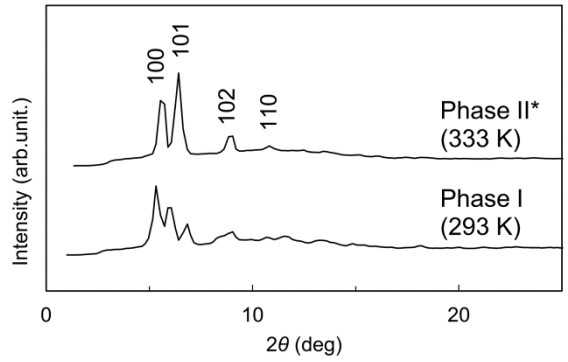
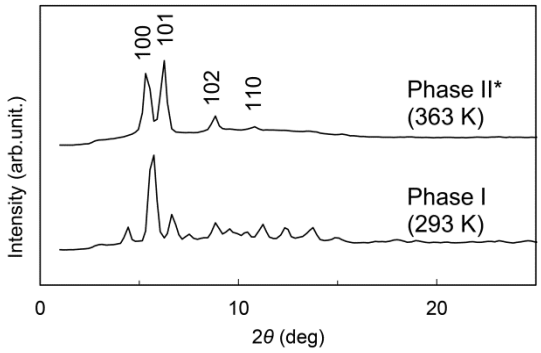



**Fig. S1** DSC traces of the salts; *a* and *b* denote the 1st and 2nd cycles, respectively. Asterisks indicate plastic phases.

a) [**1**][$B(CN)_4$]




b) [**1**][$C(CN)_3$]




c) [**1**][$FeCl_4$]

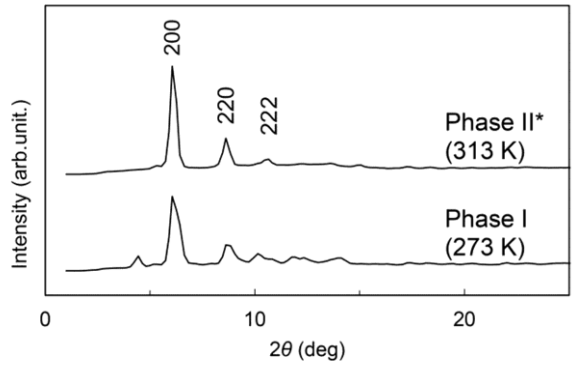
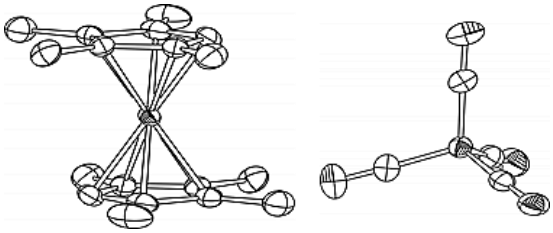
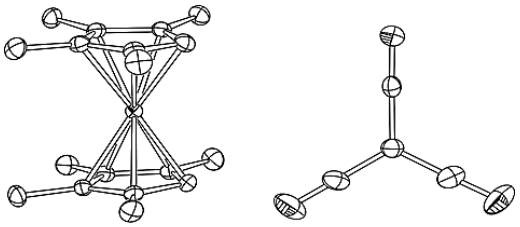



**Fig. S2** Powder X-ray diffraction patterns of (a) [**1**][$B(CN)_4$], (b) [**1**][$C(CN)_3$], and (c) [**1**][$FeCl_4$] (MoKα radiation, $\lambda$ = 0.71073 Å).

a) [**1**][$B(CN)_4$]

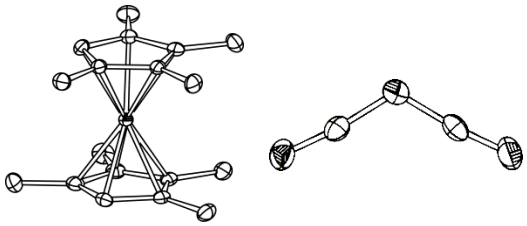


b) [**1**][$C(CN)_3$]

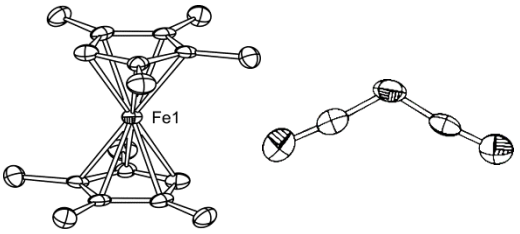


c) [**1**][$N(CN)_2$]

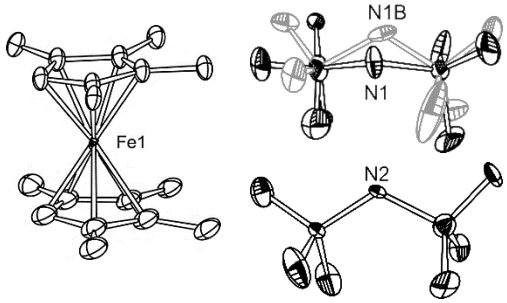
Phase I



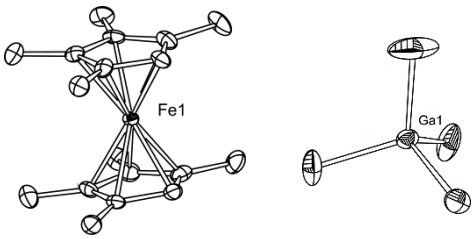
Phase II




d) [**1**][FSA]

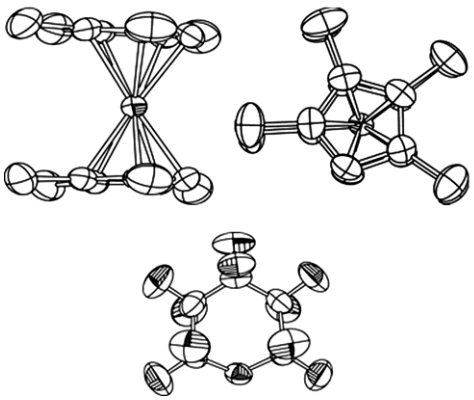



e) [**1**][$GaCl_4$]




f) [**1**][CPFSA]

293 K



100 K

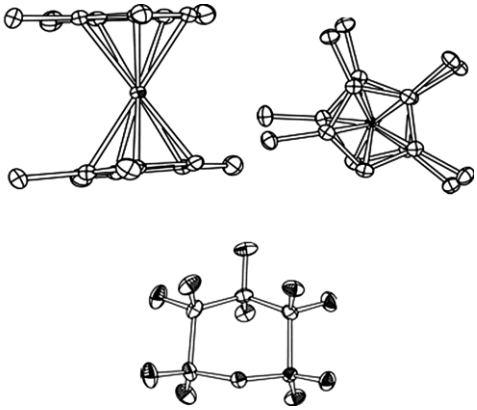


**Fig. S3** ORTEP drawings of the cations and anions in each salt at 100 K. Hydrogen atoms have been omitted for clarity. Only one of the two crystallographically independent cations or anions are shown for [**1**][$N(CN)_2$] (phase II), [**1**][FSA], and [**1**][$GaCl_4$], since the molecules are almost identical.

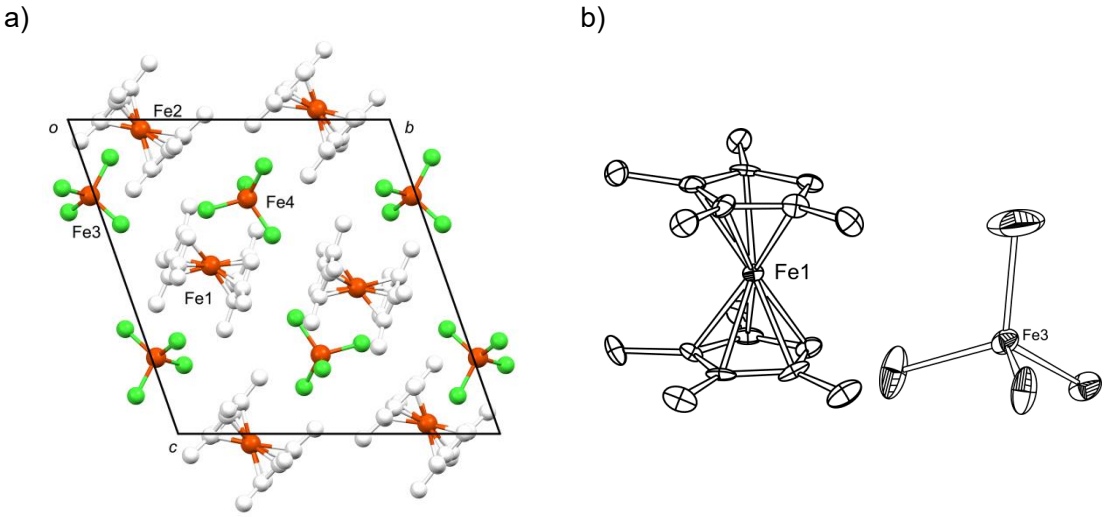



**Fig. S4** (a) Packing diagram, and (b) ORTEP drawing of [**1**][$FeCl_4$] at 100 K. In (b), only molecules containing Fe1 and Fe3 are shown, because those containing Fe2 and Fe4 are structurally almost identical. Hydrogen atoms have been omitted for clarity.

**Table S1** Anion volumes, van der Waals radii of anions, and radius ratios of the salts estimated from DFT calculations

| | Anion volume (Å$^3$) | van der Waals radius (Å) | Radius ratio ($r^-/r^+$) |
|---|---|---|---|
| [**1**][$BF_4$][a] | 54.9 | 2.36 | 0.559 |
| [**1**][$N(CN)_2$] | 64.5 | 2.49 | 0.590 |
| [**1**][$PF_6$][a] | 74.9 | 2.61 | 0.620 |
| [**1**][OTf][a] | 85.4 | 2.73 | 0.647 |
| [**1**][$C(CN)_3$] | 90.8 | 2.79 | 0.660 |
| [**1**][$FeCl_4$] | 98.0 | 2.86 | 0.677 |
| [**1**][FSA] | 98.7 | 2.87 | 0.679 |
| [**1**][$GaCl_4$] | 103.4 | 2.91 | 0.689 |
| [**1**][$B(CN)_4$] | 117.2 | 3.03 | 0.719 |
| [**1**][$Tf_2N$][a] | 157.5 | 3.35 | 0.794 |
| [**1**][CPFSA] | 162.3 | 3.38 | 0.801 |

[a]Mochida, *et al*., *Chem. Eur. J*., **22**, 15725 (2016).