Electronic Supplementary Information

Organometallic Ionic Liquids from Octamethylferrocenium Cations: Preparation, Thermal Properties, Crystal Structures, and Magnetic Properties

Yusuke Funasako,[a] Takashi Inagaki,[a] Tomoyuki Mochida,*[a] Toshihiro Sakurai,[b] Hitoshi Ohta,[c] Ko Furukawa[d] and Toshikazu Nakamura[d]

[a]*Department of Chemistry, Graduate School of Science, Kobe University, Rokkodai, Nada, Hyogo 657-8501, Japan*

[b]*Center for Supports to Research and Education Activities, Kobe University, Rokkodai, Nada, Hyogo 657-8501, Japan*

[c]*Molecular Photoscience Research Center, Kobe University, Rokkodai, Nada, Hyogo 657-8501, Japan*

[d]*Institute for Molecular Science, Myodaiji, Okazaki, Aichi 444-8585, Japan*

1. Preparation of alkyloctamethylferrocenes

Alkyloctamethylferrocenes were prepared in a similar manner to that described for propyloctamethylferrocene in the text, and the data are shown below.

Pentyloctamethylferrocene: a) 1-Hydroxypentyloctamethylferrocene. Yellow-orange solid, 72.6% yield. b) Pentyloctamethylferrocene. Yellow oil, 64.5% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 0.88 (t, 3H, J = 6.8 Hz), 1.29 (br, 6H), 1.63–1.70 (br, 24H), 2.14 (s, 2H), 3.23 (s, 1H). Anal. Calcd (%) for $C_{23}H_{36}Fe$ (368.4): C, 74.99; H, 9.85. Found: C, 74.58; H, 9.96. **Hexyloctamethylferrocene:** a) 1-Hydroxyhexyloctamethylferrocene. Yellow solid, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 0.87 (t, 3H, J = 6.8 Hz), 1.26 (br, 6H), 1.43 (br, 2H), 1.65–1.76 (m, 21H), 1.90 (s, 3H), 2.31 (s, 1H), 3.55 (s, 1H), 4.40 (br, 1H). b) Hexyloctamethylferrocene. Yellow oil, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 0.87 (t, 3H, J = 6.8 Hz), 1.29 (br, 8H), 1.65 (s, 6H), 1.73 (m, 18H), 2.17 (t, 2H, J = 7.2 Hz), 3.20 (s, 1H). Anal. Calcd (%) for $C_{24}H_{38}Fe$ (382.4): C, 75.38; H, 10.02. Found: C, 75.39; H, 10.13. **Octyloctamethylferrocene:** a)

1-Hydroxyoctyloctamethylferrocene. Yellow solid, 76.5% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 0.88 (t, 3H, J = 6.8 Hz), 1.25 (br, 8H), 1.43 (br, 2H), 1.68–1.76 (m, 21H), 1.89 (s, 3H), 2.31 (s, 1H), 3.55 (s, 1H), 4.35 (br, 1H). b) Octyloctamethylferrocene. Yellow oil, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 0.88 (t, 3H, J = 6.8 Hz), 1.26 (br, 12H), 1.66 (s, 6H), 1.73 (m, 18H), 2.18 (br, 2H), 3.21 (s, 1H). Anal. Calcd (%) for $C_{26}H_{42}Fe$ (382.4): C, 76.08; H, 10.31. Found: C, 76.01; H, 10.32. **Decyloctamethylferrocene:** a) 1-Hydroxydecyloctamethylferrocene. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 0.89 (t, 4.3H, J = 6.2 Hz), 1.26 (br, 18H), 1.43 (br, 2H), 1.69–1.76 (m, 21H), 1.89 (s, 3H), 2.31 (s, 1H), 3.55 (s, 1H), 4.35 (br, 1H). The crude product was used for the next step without purification. b) Decyloctamethylferrocene. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 0.88 (t, 4.4H, J = 6.8 Hz), 1.26 (br, 22H), 1.68 (s, 6H), 1.73 (m, 18H), 2.18 (t, 2H, J = 7.4 Hz), 3.20 (s, 1H). The crude product was used for the salt preparation without purification. **Dodecyloctamethylferrocene:** a) 1-Hydroxydodecyloctamethylferrocene. Yellow solid, 48.5% yield (crude). The crude product was used for the next step without purification. b) Dodecyloctamethylferrocene. Yellow oil, 71% yield (crude). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 0.88 (t, 3.4H, J = 6.8 Hz), 1.25 (br, 22H), 1.63–1.70 (m, 24H), 2.14 (br, 2H), 3.22 (s, 1H). The crude product was used for the salt preparation without purification. **Heptadecyloctamethylferrocene:** a) 1-Hydroxyheptadecyloctamethylferrocene. Yellow solid. The crude product was used for the next step without purification. b) Heptadecyloctamethylferrocene. Yellow oil. The crude product was used for the salt preparation without purification. ***trans*-1-Pentenyloctamethylferrocene:** 1-Hydroxypentyloctamethylferrocene (0.531 g), prepared similarly, was distilled under vacuum at 130 °C to give the product within an hour as a dark-brown oil (0.268 g, 53%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 0.94 (m, 3H), 1.47 (m, 2H), 1.65 (s, 6H), 1.70 (s, 6H), 1.77 (s, 6H), 1.86 (s, 6H), 2.11 (m 2H), 3.55 (s, 1H), 5.87 (m, 1H), 6.04 (d, 1H, J = 16.0 Hz). Anal. Calcd (%) for $C_{23}H_{34}Fe$ (354.4): C, 75.40; H, 9.35. Found: C, 75.34; H, 9.44.

2. Thermal behavior of [C5Fc][Tf_2N]

The DSC trace of [**C5Fc**][Tf_2N] is shown in Figure S1. When cooled from the melt, crystallization occurred at around –2.3 °C to give phase I, and with further cooling, a phase transition to phase II occurred at around –11.5 °C (ΔS = 44.2 J K^{-1} mol^{-1}). In the heating run, phase I melted at 20.2 °C (Figure S1c), but an unprecedented, exothermal transition to phase III often occurred (Figures S1a and S1b). In the heating run, a transition from phase II to III occurred at –8.5 °C (Figure S1a). In the run shown in Figure S1b, a transition from phase II to I occurred at 0.4 °C, followed by an exothermal transition to phase III, which melted at 30.0 °C.

3. Figures

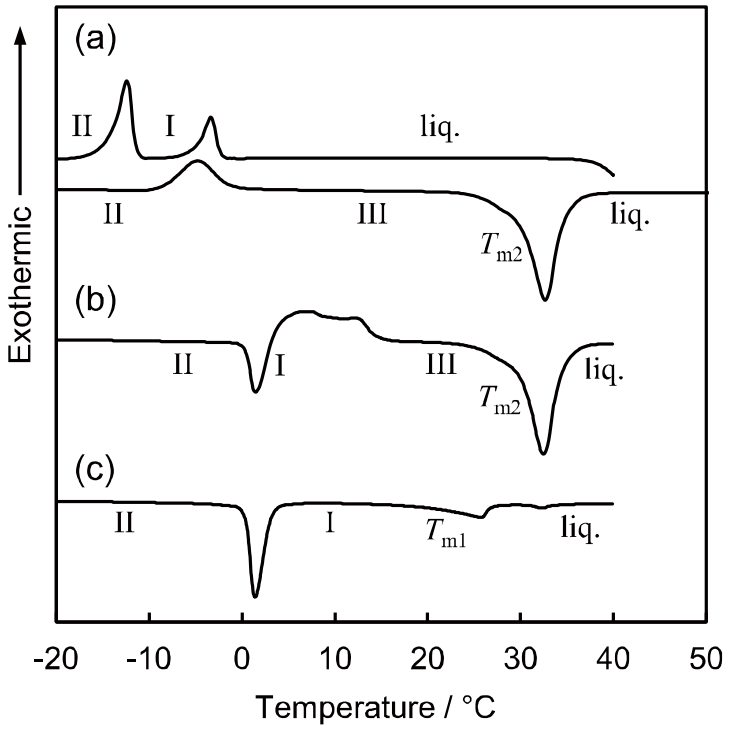

Fig. S1 DSC traces of [pentyloctamethylferrocenium][Tf_2N] ([**C5Fc**][Tf_2N]) measured at 10 °C min^{-1}. Only the heating runs are shown in (b) and (c).

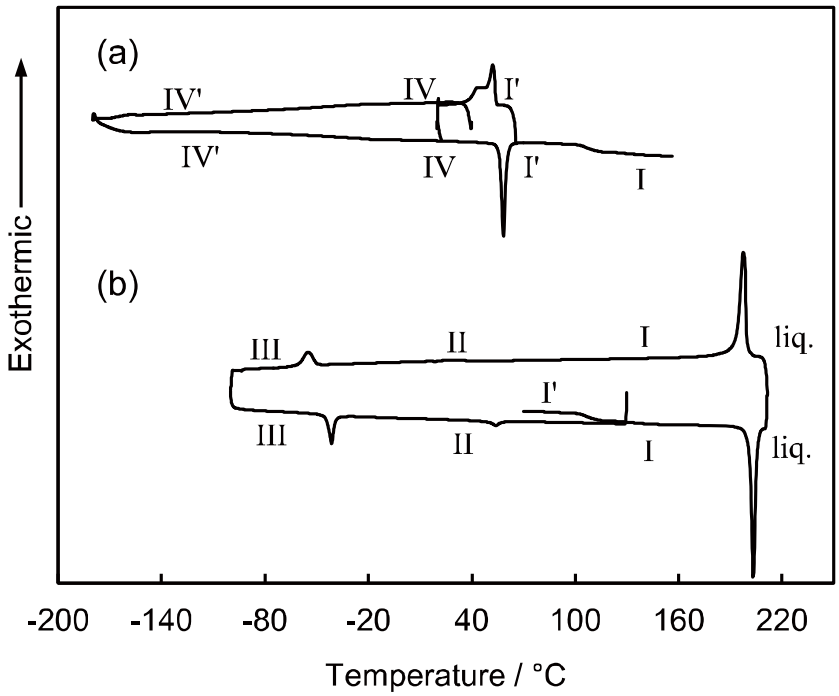

Fig. S2 DSC traces of [decyloctamethylferrocenium][PF_6] ([**C10Fc**][PF_6]) measured at 10 °C min^{-1}. Cycles (a) before and (b) after experiencing glass transition from phase I' to phase I are shown.

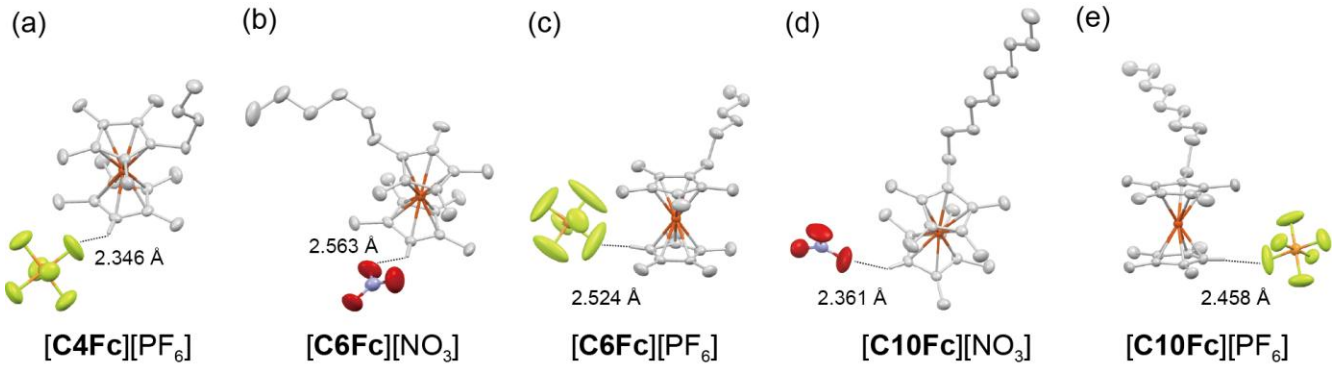

Fig. S3 Molecular structures of (a) [**C4Fc**][PF_6], (b) [**C6Fc**][NO_3], (c) [**C6Fc**][PF_6], (d) [**C10Fc**][NO_3], and (e) [**C10Fc**][PF_6]. C–H...X contacts are indicated by dotted lines.

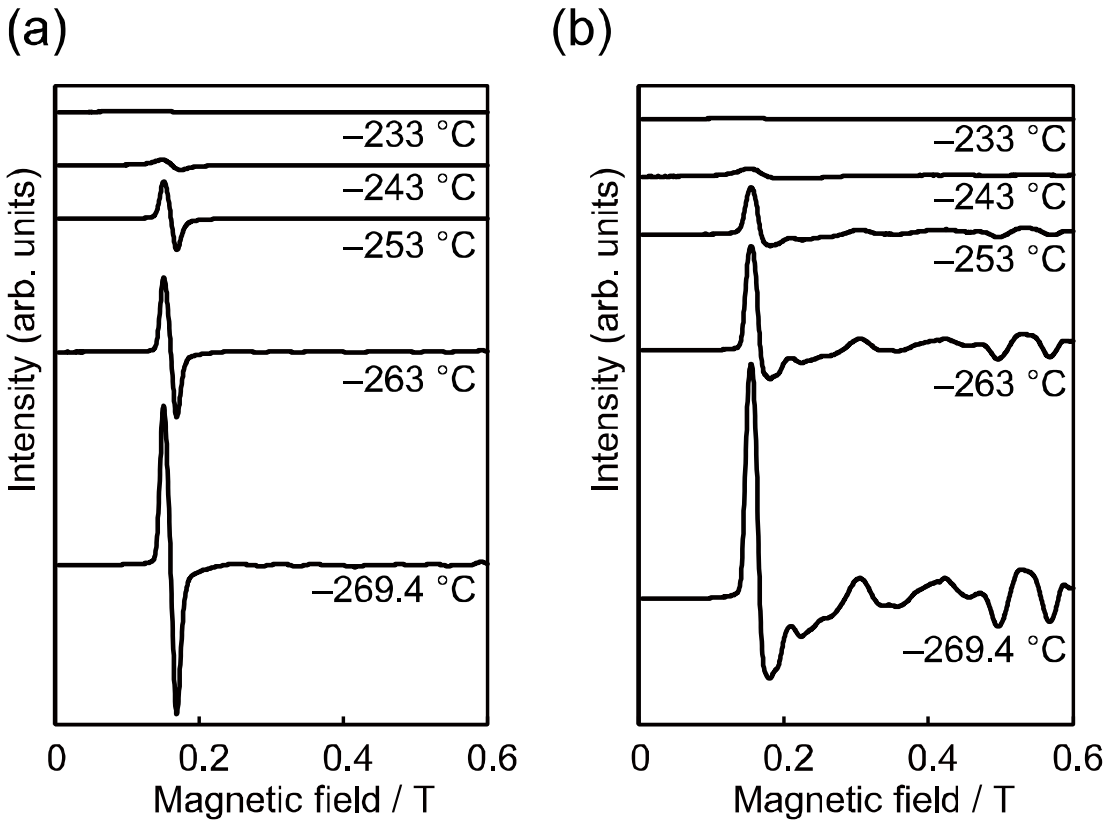

Fig. S4 Temperature dependences of ESR spectra of [**C4Fc**][Tf_2N] crystallized (a) under a magnetic field of 0.8 T and (b) without a magnetic field.

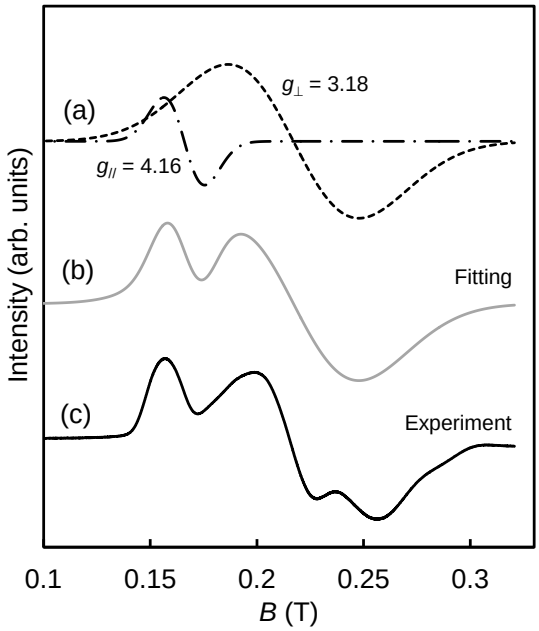

Fig. S5 (a) ESR spectra of [**C4Fc**][Tf_2N] crystallized under a magnetic field of 0.8 T recorded at –269.4 °C (θ = 50°). (b), (c) Simulated spectra (dotted line: oriented component; broken line: nonoriented component).

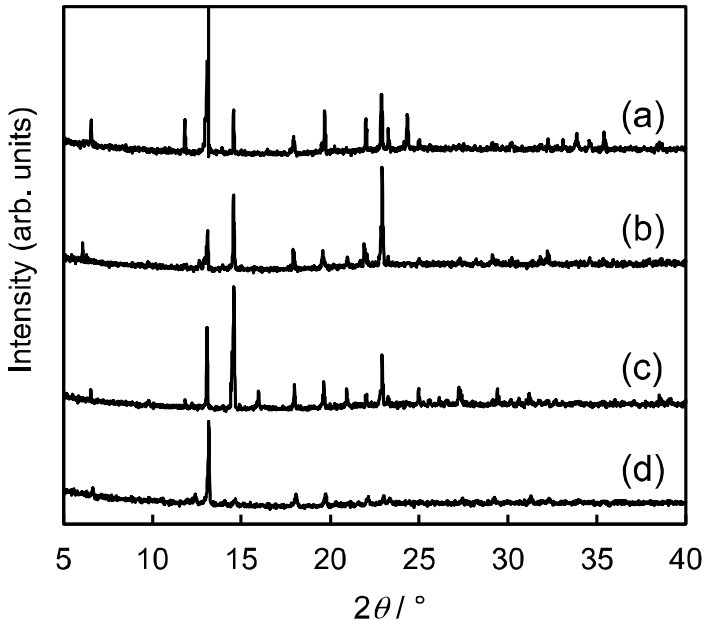

Fig. S6 Powder XRD patterns of [**C4Fc**][Tf_2N] crystallized under a magnetic field of 0.36 T (a–c) and without a magnetic field (d).

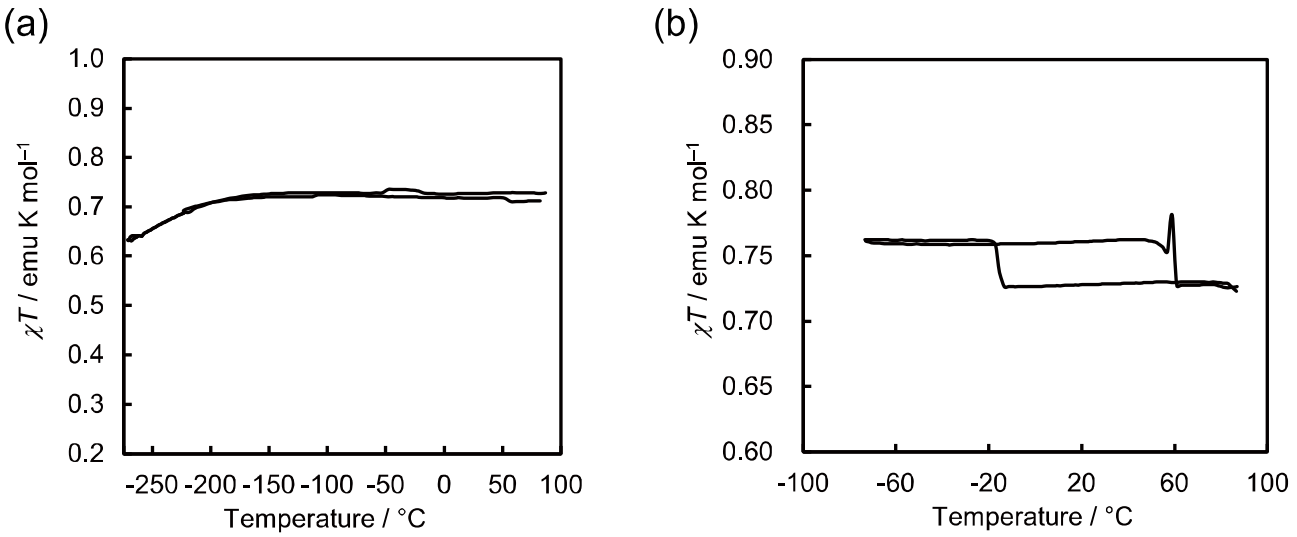

Fig. S7 Temperature dependences of magnetic susceptibilities of [**C5'Fc**][Tf_2N] measured under (a) 0.1 T and (b) 2 T at a scan rate of 2 °C min^{-1}.