**Magnetic Memory Based on Magnetic Alignment of a Paramagnetic Ionic Liquid near Room Temperature**

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**Supporting Information**

**General methods**

All regents and solvents were commercially available and have been used without further purification except for octamethylformylferrocene and AgTFSA, which were synthesized according to a literature method. $^1$H NMR spectra were recorded by using a JEOL JNM-ECL-400 spectrometer operating at 400 MHz. Elemental analyses were performed with a Yanaco CHN corder MT5. Magnetic measurements were carried out using a Quantum Design MPMS-XL7 SQUID susceptometer. ESR measurements were performed with a JEOL TE-260 X-band ESR spectrometer at 3.8 K. X-ray Diffraction (XRD) measurements were performed using Rigaku SmartLab X-ray Diffractometer equipped with Cu $\alpha$ radiation ($\lambda = 1.54056$ Å). DSC measurements were performed using a TA Instrument Q100 differential scanning calorimeter at a rate of 10 K min$^{-1}$.

**Preparation of [butyloctamethylferrocenium][TFSA] (1)**

1-Hydroxybutyloctamethylferrocene. All the manipulations were carried out under a nitrogen atmosphere. Propyl bromide (1.0 mL, 11.0 mmol) was added dropwise to a stirred mixture of magnesium turnings (0.312 g, 12.8 mmol) and diethyl ether (15 mL), and the solution was stirred until most of the magnesium dissolve. The Grignard reagent thus prepared was added slowly to a solution of octamethylformylferrocene (0.502 g, 1.54 mmol) in dry THF (20 mL) cooled at –78 °C, and the solution was stirred for 30 min. The reaction mixture was quenched at –78 °C with saturated NH$_4$Cl solution (10 mL) and extracted with Et$_2$O. The organic layer was dried over magnesium sulfate and concentrated under reduced pressure. The crude product was purified by column chromatography (silica, CH$_2$Cl$_2$). The product was obtained as a yellow solid (0.447 g, 78.4% yield). $^1$H NMR (400 MHz, CDCl$_3$, TMS): $\delta = 0.88$ (m, 3H), 1.27 (m, 2H), 1.44 (m, 2H), 1.69–1.76 (br., 23H), 1.90 (s, 3H), 2.30 (s, 1H), 3.55 (s, 1H), 4.33 (s, 1H).

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**Butyloctamethylferrocene.** To a stirred solution of 1-hydroxybutyloctamethylferrocene (0.670 g, 1.75 mmol) in THF (15 mL) was added a solution of BH₃·SMe₂ (2.6 mL, 5.24 mmol) in THF (2 M). After refluxing the solution for 1 hour, the reaction was quenched with aqueous NH₄Cl (10 mL), and the solution extracted with CH₂Cl₂. The organic layer was dried over magnesium sulfate and concentrated under reduced pressure. The crude product was purified by column chromatography (alumina, pentane). The product was obtained as a yellow oil (0.449 g, yield 70.0%). ¹H NMR (400 MHz, CDCl₃, TMS): δ = 0.88 (t, 3H, J = 7.2 Hz), 1.25–1.30 (m, 4H), 1.65 (s, 3H), 1.72 (m, 18H), 2.18 (t, 2H, J = 7.6 Hz), 3.21 (s, 1H). Anal. Calcd. for C₂₂H₃₄Fe (354.4): C, 74.57; H, 9.67. Found: C, 74.37; H, 9.77. The other compounds were prepared in a similar manner as described above.

**[Butyloctamethylferroacenium][TFSA] (1).** Under dark, AgTFSA (76.0 mg, 0.20 mmol) was added to a solution of butyloctamethylferrocene (60.4 mg, 0.18 mmol) in CH₂Cl₂ (10 mL). After stirring the solution for a few minutes, the mixture was filtered via a syringe equipped with a membrane filter to remove silver deposits and unreacted AgTFSA. Removal of the solvent from the filtrate under reduced pressure gave the product as a dark green solid (82.4 mg, 72% yield). Product of the reaction was dried under vacuum at 80 °C for 24 hours. Recrystallization from ethanol / hexane gave analytically pure product. Dark green plate crystal. ¹H NMR (400 MHz, CDCl₃, TMS): δ = 3.18 (s, 24H), 7.43 (br., 1H), 16.72 (br., 9H). Anal. Calcd. for C₂₄H₃₄F₆FeNO₄S₂ (634.5): C, 45.43; H, 5.40; N, 2.21. Found: C, 45.58; H, 5.50; N, 2.42. The other TFSA salts were prepared in a similar manner.

**Single crystal X-ray structure determination of 1**

Single crystal of 1 for X-ray structure determination was obtained by recrystallization from ethanol / hexane at −14 °C. X-ray diffraction data were collected on a Bruker Smart1000 CCD diffractometer using Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct method and refined by using SHELXTL. Crystallographic parameters: Mᵣ = 634.49, orthorhombic, space group Pna₂₁, with unit cell a = 26.602(3) Å, b = 8.773(5) Å, c = 11.901(6) Å, and V = 2777.8(5) Å³. Z = 4, D_calcd = 1.517 gcm⁻³, R(I > 2σ(I)) = 0.0254, wR2 = 0.0617, R1(all data) = 0.0237, wR2 = 0.0596, 4875 independent reflections (R(int) = 0.0239), 352 parameters refined on F². Crystallographic data (excluding structure factors) for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 775548.

**Thermal and magnetic properties of 1**

DSC measurements revealed that 1 melted at 34.3 °C (ΔH = 26.7 kJ mol⁻¹, ΔS = 86.3 JK⁻¹mol⁻¹) on heating and crystallized at 18.9 °C on cooling, and no other phase transitions were observed down to 93 K. Temperature dependence of magnetic susceptibility for 1 measured under 0.1 T is shown in Figure S1. This salt showed a simple paramagnetic behavior, while a slight decrease was observed below about 70 K, which is ascribed to the decrease of orbital contribution.
Figure S1. Temperature dependence of magnetic susceptibility of 1 measured under 0.1 T.