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ARTICLE TYPE

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

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A paramagnetic ferrocenium-based ionic liquid that exhibits a magnetic memory effect coupled with a liquid-solid phase transformation has been developed. Based on field alignment of the magnetically anisotropic ferrocenium cation, the magnetic susceptibility in the solid state can be tuned by the weak magnetic fields (< 1 T) of permanent magnets.

For many years, molecular magnetic materials, whose properties can be controlled by external stimuli, have attracted considerable interest for their potential use in electronic devices.[1] In practice, magnetic changes and phase-change mechanisms have been used for reversible recording of information.[2] In this study, we aimed to design materials that exhibit a magnetic memory effect coupled with a liquid-solid phase change. It is known that very strong magnetic fields can control the orientation of inorganic materials, polymers, and molecular materials during the solidification process.[3] We expected that magnetic fields would efficiently affect solidification of magnetically anisotropic molecular liquids. Among such fluids, we have focused on ionic liquids, which are defined as salts that melt below 100 °C.[4] Several intriguing ionic liquids comprising onium cations and magnetic anions such as MX_n (M = transition metal or rare-earth metal)[5] and nitroxides[6] have been reported, and their magnetic properties have attracted special attention. These magnetic anions, however, are magnetically isotropic. We recently found that ferrocenium salts with fluorinated anions form ionic liquids,[7] and that these materials contain paramagnetic cations with magnetic anisotropy. Here we report that a paramagnetic ferrocenium-based ionic liquid, [butyloctamethylferrocenium][TFSA] (**1**, TFSA = bis(trifluoromethanesulfonyl)amide, Fig. 1), exhibits a magnetic memory effect coupled with a liquid-solid phase transformation near room temperature.

Fig. 1 Chemical formula of [butyloctamethylferrocenium][TFSA] (**1**).

A dark green ionic liquid of **1** was obtained in almost quantitative yield by reacting butyloctamethylferrocene with AgTFSA in CH_2Cl_2.[8] The temperature dependence of the magnetic susceptibility of **1** was measured with a SQUID magnetometer, which showed that **1** was paramagnetic in the measured temperature range of 2–330 K.[8] The susceptibility around room temperature is shown in Fig. 2. The χT value in the liquid state (0.78 emu K mol^{-1}), which is typical of ferrocenium cations, is larger than the spin-only value because of the orbital contribution.[9] When the liquid was cooled under 0.5 T (Fig. 2, filled circles), a significant increase in the susceptibility was observed in association with solidification at 299 K. Heating the solid led to melting at a higher temperature, 309 K, where the magnetic susceptibility decreased and returned to the initial value. Thus, the magnetic response accompanies the thermal hysteresis based on phase changes.[10] Under 0.1 T, however, only a small change was observed at the phase change (Fig. 2, open circles). This result shows that the magnetic susceptibility in the solid state can be controlled by the intensity of the magnetic field that is applied upon solidification.

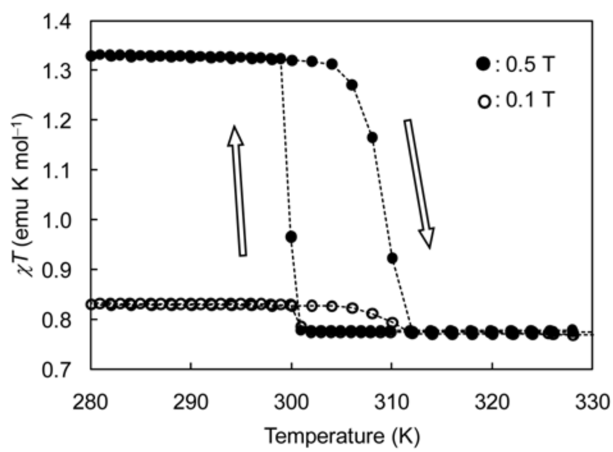

Fig. 2 Temperature dependence of magnetic susceptibilities of 1 shown as a χT–T plot measured under 0.5 T (filled circles) and 0.1 T (open circles).

Next, the detailed field dependence of the magnetic susceptibility changes was investigated, the results of which are plotted in Fig. 3 (open circles). The value increases as a function of the magnetic field, exhibiting saturation above 2 T. Therefore, the material can record the applied magnetic field up to about 1 T. The dependencies of the magnetic susceptibility on the temperature and magnetic field were independent of the scan rate in the range of 0.5–10 K min^{-1}.

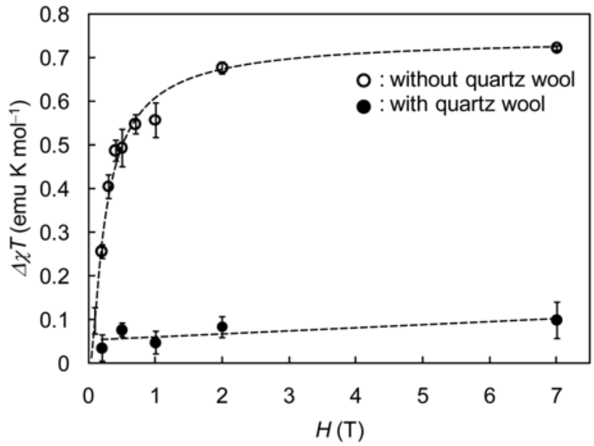

Fig. 3 Magnetic susceptibility changes of **1** ($\Delta\chi T = \chi T_{270\ \mathrm{K}} - \chi T_{310\ \mathrm{K}}$) plotted as a function of magnetic field strength (open circles). Data are also shown for a sample filled with quartz wool (filled circles).

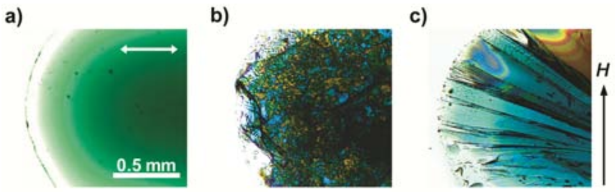

Fig. 4 Polarized optical microscopy images of **1** under plain-polarized light on a glass plate at RT. a) Liquid state, b) after solidification without magnetic field, and c) after solidification under a magnetic field of 0.6 T applied parallel to the surface. The optical axis is indicated by the arrow in a).

The magnetic response is attributed to the magnetic-field orientation of the material upon solidification, which can be observed directly by polarized optical microscopy (POM). Fig. 4a shows the POM image of a liquid of **1** on a glass plate at room temperature. Solidification of the liquid in the absence of magnetic fields resulted in the formation of microscopic domains (Fig. 4b). However, under a magnetic field of permanent magnets (0.6 T), the liquid crystallized into needles arranged perpendicular to the field (Fig. 4c). The magnetic orientation was quantitatively confirmed by observing angle-dependent ESR spectra at 3.8 K on a sample crystallized under a magnetic field of 0.8 T. The anisotropic g values obtained from the angular dependence were $g_{\perp} = 4.3$, $g_{//} = 1.7$, and $g_{\mathrm{av}} = 2.8$. The SQUID magnetic susceptibilities were well reproduced by these values. When quartz wool (14 wt.%) was added to the liquid sample to inhibit magnetic orientation during solidification, the susceptibility change $\Delta\chi T$ was effectively suppressed (Fig. 3, filled circles).

For magnetic orientation to occur, it is important that the crystal structure is magnetically anisotropic. Therefore, the molecular arrangement of **1** in the solid state was determined at 100 K (Fig. 5).[11] In the unit cell, the C_5 axes of ferrocenium cations are aligned parallel to the *c*-axis. Given that the largest principal value of the *g*-tensor of a ferrocenium cation is along its C_5 axis,[12] this arrangement produces the largest magnetic susceptibility along the *c*-axis. Out-of-plane XRD patterns for samples crystallized under magnetic fields exhibited a significant increase in the intensities of peaks corresponding to [0 0 2], indicating that the *c*-axis is oriented perpendicular to the surface. These results demonstrate that the field orientation is consistent with the magnetic anisotropy of the crystal.

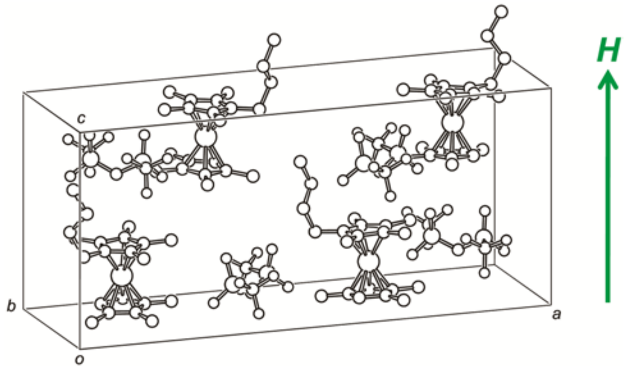

Fig. 5 Crystal structure of **1** at 100 K. This figure also illustrates the direction of the field orientation of the crystal with respect to the external field (*H*) indicated by the arrow.

In this study, control of the magnetic response near room temperature was achieved using a paramagnetic ionic liquid with magnetic anisotropy. Without using magnetic ordering, the memory mechanism cannot be realized by typical molecular magnets, inorganic materials, or conventional magnetic fluids. In particular, it is highly advantageous that the phenomenon is (i) observable near room temperature, (ii) accompanied by hysteresis, and (iii) controllable by weak magnetic fields (< 1 T). Although the magnetic-field alignment of materials upon solidification has been widely investigated,[3a–c] very strong magnetic fields or field gradients are required. To our knowledge, the remarkable magnetic orientation we observed under weak magnetic fields is hitherto unknown. Magnetic susceptibility changes coupled with a liquid-solid transformation are also observed in several molecular materials. For example, slight susceptibility changes are observed for paramagnetic ionic liquids such as [ethylmethylimidazolium][$FeCl_4$] ($\Delta\chi T_{\mathrm{solid\text{-}liquid}}$ ~ 0.05 emu K mol^{-1}).[5a] Another example is the transformation of diamagnetic organic solids composed of radical dimers to a paramagnetic liquid upon melting.[13] In these cases, however, the magnetic changes are smaller and cannot be controlled by external fields.

In summary, a paramagnetic ferrocenium-based ionic liquid [butyloctamethylferrocenium][TFSA] that exhibits a magnetic response due to field-oriented solidification near room temperature has been developed. This phenomenon was achieved by a room-temperature ionic liquid and a ferrocenium ion with magnetic anisotropy. The physical chemistry of liquids, in addition to the characteristic magnetic features as well as the flexibility of the material, may lead to novel molecular electronic applications using molecular liquids.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental procedures, preparation, details on thermal and magnetic properties, cif file and crystallographic data for compounds **1**. CCDC 775548. For ESI and crystallographic data in CIF or other electronic format See DOI: 10.1039/b000000x/

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11 Crystallographic parameters for **1**: $Pna2_1$, a = 26.602(3) Å, b = 8.773(5) Å, c = 11.901(6) Å, V = 2777.8(5) Å^3, Z = 4, and R_1 = 0.0254. See Supporting Information for detail.

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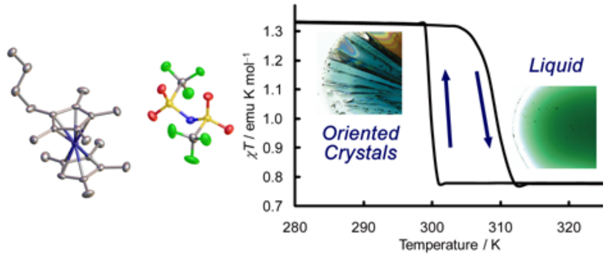

Magnetic Memory Based on Magnetic Alignment of a Paramagnetic Ionic Liquid near Room Temperature

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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[S1] and AgTFSA[S2], 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 Kα radiation (λ = 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_4Cl solution (10 mL) and extracted with Et_2O. The organic layer was dried over magnesium sulfate and concentrated under reduced pressure. The crude product was purified by column chromatography (silica, CH_2Cl_2). The product was obtained as a yellow solid (0.447 g, 78.4% yield). ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 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).

Butyloctamethylferrocene. To a stirred solution of 1-hydroxybutyloctamethylferrocene (0.670 g, 1.75 mmol) in THF (15 mL) was added a solution of $BH_3 \cdot SMe_2$ (2.6 mL, 5.24 mmol) in THF (2 M). After refluxing the solution for 1 hour, the reaction was quenched with aqueous NH_4Cl (10 mL), and the solution extracted with CH_2Cl_2. 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, $CDCl_3$, 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 $C_{22}H_{34}Fe$ (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.

[Butyloctamethylferrocenium][TFSA] (1). Under dark, AgTFSA (76.0 mg, 0.20 mmol) was added to a solution of butyloctametylferrocene (60.4 mg, 0.18 mmol) in CH_2Cl_2 (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, $CDCl_3$, TMS): δ = 3.18 (s, 24H), 7.43 (br., 1H), 16.72 (br., 9H). Anal. Calcd. for $C_{24}H_{34}F_6FeNO_4S_2$ (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: M_{W} = 634.49, orthorhombic, space group $Pna2_1$, with unit cell a = 26.602(3) Å, b = 8.773(5) Å, c = 11.901(6) Å, and V = 2777.8(5) Å^3. Z = 4, $D_{\mathrm{calcd.}}$ = 1.517 gcm^{-3}, $R1(I > 2\sigma(I))$ = 0.0254, $wR2$ = 0.0617, $R1$(all data) = 0.0237, $wR2$ = 0.0596, 4875 independent reflections (R(int) = 0.0239), 352 parameters refined on F^2. 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 poperties of 1

DSC measurements revealed that **1** melted at 34.3 $^{\mathrm{o}}$C (ΔH = 26.7 kJ mol^{-1}, ΔS = 86.3 JK^{-1}mol^{-1}) on heating and crystallized at 18.9 $^{\mathrm{o}}$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 behevior, while a slight decrease was observed below about 70 K, which is ascribed to the decrease of orbital contribution.

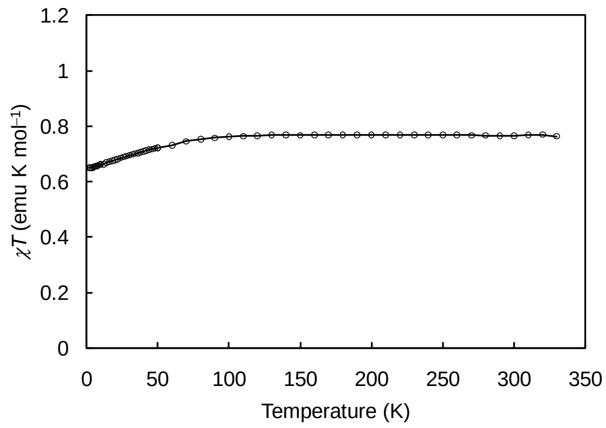

Figure S1. Temperature dependence of magnetic susceptibility of **1** measured under 0.1 T.

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