ChemComm

Cite this: *Chem. Commun.*, 2011, **47**, 4475–4477

www.rsc.org/chemcomm

COMMUNICATION

Magnetic memory based on magnetic alignment of a paramagnetic ionic liquid near room temperature†

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

Received 28th December 2010, Accepted 23rd February 2011
DOI: 10.1039/c0cc05820c

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.

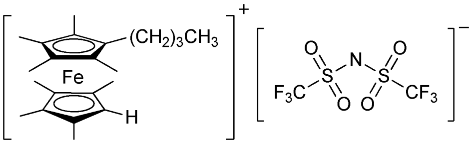

Fig. 1 Chemical formula of [butyloctamethylferrocenium][TFSA] (**1**).

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

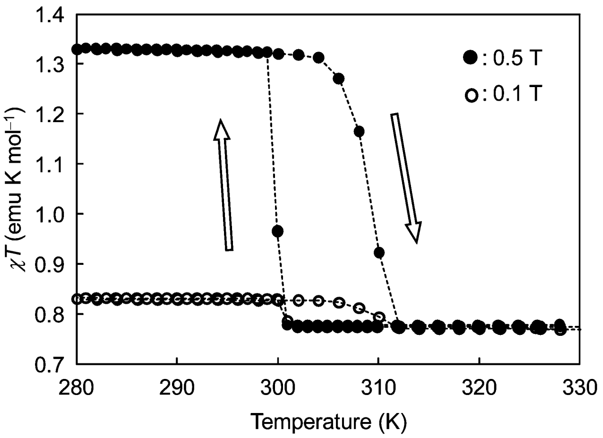

Fig. 2 Temperature dependence of magnetic susceptibilities of **1** shown as a χT–T plot measured under 0.5 T (filled circles) and 0.1 T (open circles).

---

[a] *Department of Chemistry, Graduate School of Science, Kobe University, Rokkodai, Nada, Hyogo 657-8501, Japan. E-mail: tmochida@platinum.kobe-u.ac.jp; Fax: +81 78 803 5679; Tel: +81 78 803 5679*
[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*

† Electronic supplementary information (ESI) available: Experimental procedures, preparation, details on thermal and magnetic properties for compound **1**. CCDC 775548. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0cc05820c

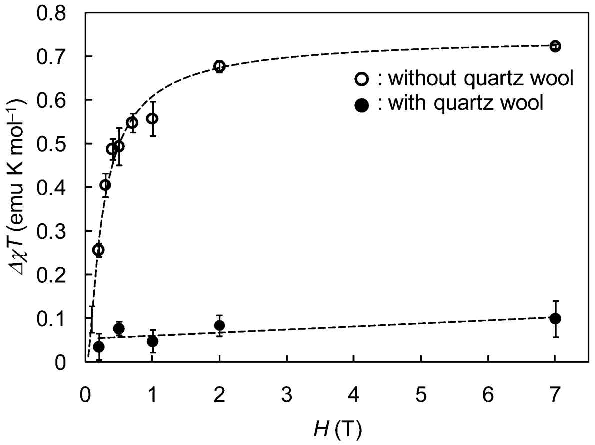

Fig. 3 Magnetic susceptibility changes of **1** ($\Delta\chi T = \chi T_{270\ \mathrm{K}} - \chi T_{310\ \mathrm{K}}$) plotted as a function of magnetic field strength (open circles). Data are also shown for a sample filled with quartz wool (filled circles).

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.

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}.

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 $g_{\perp} = 4.3$, $g_{\parallel} = 1.7$, 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).

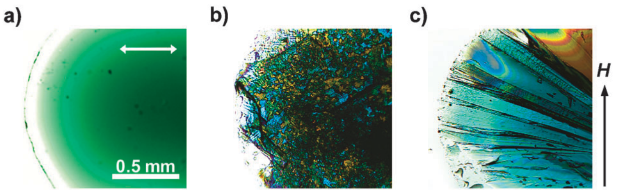

Fig. 4 Polarized optical microscopy images of **1** under plain-polarized light on a glass plate at RT. (a) Liquid state, (b) after solidification without magnetic field, and (c) after solidification under a magnetic field of 0.6 T applied parallel to the surface. The optical axis is indicated by the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

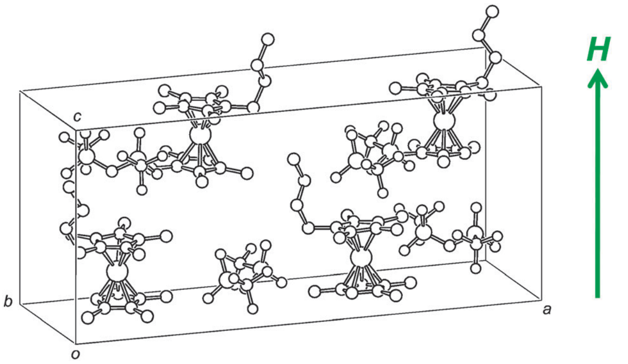

Fig. 5 Crystal structure of **1** at 100 K. This figure also illustrates the direction of the field orientation of the crystal with respect to the external field (H) indicated by the arrow.

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.

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$_4$] ($\Delta\chi T_{\mathrm{solid-liquid}} \approx 0.05$ 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.

This work was supported by a Grant-in-Aid for Scientific Research (No. 21350077) from the Japan Society for the Promotion of Science; Research for Promoting Technological Seeds A (No. 11-145, 2009) from the Japan Science and Technology Corporation, and the IMS (Institute for Molecular Science) Joint Studies Program. We thank Prof. Y. Shinoda (Waseda University) for his English support and Y. Furuie (Kobe University) for the elemental analysis.

Notes and references

1 (*a*) J. S. Miller and A. J. Epstein, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 385; (*b*) O. Kahn, *Molecular Magnetism*Wiley-VCH, New York, 1993; (*c*) W. Fujita and K. Awaga, *Science*, 1999, **286**, 261; (*d*) M. E. Itkis, X. Chi, A. W. Cordes and R. C. Haddon, *Science*, 2002, **296**, 1443; (*e*) O. Sato, J. Tao and Y.-Z. Zhang, *Angew. Chem., Int. Ed.*, 2007, **46**, 2152.

2 (*a*) J. Feinleib, J. P. deNeufville, S. C. Moss and S. R. Ovshinsky, *Appl. Phys. Lett.*, 1971, **18**, 254; (*b*) A. Hamada, T. Kurosu, M. Saito and M. Kikuchi, *Appl. Phys. Lett.*, 1972, **20**, 9.

3 (*a*) P. de Rango, M. Lees, P. Lejay, A. Sulpice, R. Tournier, M. Ingold, P. Germi and M. Pernet, *Nature*, 1991, **349**, 770; (*b*) A. E. Mikelson and Y. K. Karklin, *J. Cryst. Growth*, 1981, **52**, 524; (*c*) T. Sugiyama, M. Tahashi, K. Sassa and S. Asai, *ISIJ Int.*, 2003, **43**, 855; (*d*) H. Ezure, T. Kimura, S. Ogawa and E. Ito, *Macromolecules*, 1997, **30**, 3600; (*e*) S. Takami, Y. Shirai, Y. Wakayama and T. Chikyow, *Thin Solid Films*, 2008, **516**, 2438.

4 (*a*) A. Stark and K. R. Seddon, in *Kirk-Othmer Encyclopedia of Chemical Technology*, ed. A. Seidel, Wiley-Interscience, Hoboken, New Jersey, 5th edn, 2007, vol. 26, p. 836; (*b*) *Ionic Liquids: Industrial Applications to Green Chemistry*, ed. R. D. Rogers and K. R. Seddon, ACS Symposium Series, American Chemical Society, Washington, DC, 2002; (*c*) M. Armand, F. Endres, D. R. MacFarlane, H. Ohno and B. Scrosati, *Nat. Mater.*, 2009, **8**, 621; (*d*) P. Hapiot and C. Lagrost, *Chem. Rev.*, 2008, **108**, 2238; (*e*) N. V. Plechkova and K. R. Seddon, *Chem. Soc. Rev.*, 2008, **37**, 123; (*f*) H. Weingärtner, *Angew. Chem., Int. Ed.*, 2008, **47**, 654; (*g*) S. Lee, *Chem. Commun.*, 2006, 1049; (*h*) Y. Yoshida and G. Saito, *Phys. Chem. Chem. Phys.*, 2010, **12**, 1675; (*i*) T. Torimoto, T. Tsuda, K. Okazaki and S. Kuwabata, *Adv. Mater.*, 2010, **22**, 1196.

5 (*a*) Y. Yoshida, A. Otsuka, G. Saito, S. Natsume, E. Nishibori, M. Takata, M. Sakata, M. Takahashi and T. Yoko, *Bull. Chem. Soc. Jpn.*, 2005, **78**, 1921; (*b*) M. Okuno, H. Hamaguchi and S. Hayashi, *Appl. Phys. Lett.*, 2006, **89**, 132506; (*c*) B. Mallick, B. Balke, C. Felser and A.-V. Mudring, *Angew. Chem., Int. Ed.*, 2008, **47**, 7635; (*d*) T. Peppel, M. Köckerling, M. Geppert-Rybczyńska, R. V. Ralys, J. K. Lehmann, S. P. Verevkin and A. Heintz, *Angew. Chem., Int. Ed.*, 2010, **49**, 7116; (*e*) B. M. Krieger, H. Y. Lee, T. J. Emge, J. F. Wishart and E. W. Castner, Jr., *Phys. Chem. Chem. Phys.*, 2010, **12**, 8919.

6 Y. Yoshida, H. Tanaka and G. Saito, *Chem. Lett.*, 2007, **36**, 1096.

7 T. Inagaki and T. Mochida, *Chem. Lett.*, 2010, **39**, 572.

8 See ESI† for details.

9 J. S. Miller, D. T. Glatzhofer, D. M. O'Hare, W. M. Reiff, A. Chakraborty and A. J. Epstein, *Inorg. Chem.*, 1989, **28**, 2930.

10 Y. Funasako, K. Abe and T. Mochida, *Thermochim. Acta*, 2011, DOI: 10.1016/j.tca.2011.01.013.

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 ESI† for details.

12 J. S. Miller, J. C. Calabrese, H. Rommelmann, S. R. Chittipeddi, J. H. Zhang, W. M. Reiff and A. J. Epstein, *J. Am. Chem. Soc.*, 1987, **109**, 769.

13 (*a*) K. Nishimura and G. Saito, *Synth. Met.*, 2005, **153**, 385; (*b*) W. Fujita, K. Awaga, Y. Nakazawa, K. Saito and M. Sorai, *Chem. Phys. Lett.*, 2002, **352**, 348.