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COMMUNICATION

A spin-Crossover ionic liquid from the cationic iron(III) Schiff base complex†

Megumi Okuhata, Yusuke Funasako, Kazuyuki Takahashi, Tomoyuki Mochida*

A thermochromic magnetic ionic liquid containing a cationic iron(III) Schiff-base complex has been developed, whose color and magnetic moment change with temperature because of spin crossover in the liquid state. This spin-crossover behavior closely resembles that of a solid having the same cation.

Ionic liquids are salts with melting points below 373 K, and they have attracted much attention because of their various functionalities.¹ In recent years, magnetic ionic liquids, having the advantageous properties of ionic liquids as well as magnetic fluids, have been prepared.^{2–5} They are mostly onium salts with magnetic anions such as MX_n^- ,³ organic radicals,⁴ and metal complexes,⁵ and their magnetic moments are usually temperature independent. This paper reports the preparation and properties of a magnetic ionic liquid that exhibits thermochromism and temperature-dependent magnetic properties.

We have recently developed a series of ionic liquids with functional cationic metal complexes.⁶ In this study, we employed an iron(III) acacen complex (acacen = *N,N'*-bis (acetylaceton) ethylenediamine) as the cation. Acacen is one of the representative Schiff base ligands that are used in the preparation of various metal complexes.⁷ Several iron(III) acacen complexes show a spin-crossover phenomenon in the solid state, namely a reversible transformation between high-spin and low-spin states with change in temperature or pressure.^{8,9} In this context, we prepared $[\text{Fe}(\text{acacen})(1\text{-butylimidazole})_2][\text{Tf}_2\text{N}]$ (**1-Tf₂N**, shown in Fig. 1), which turned out to be an ionic liquid that exhibits spin-crossover behavior in the liquid state.

1-Tf₂N was prepared by the reaction between $[\text{Fe}(\text{acacen})\text{Cl}]$, 1-butylimidazole, and $\text{Ag}[\text{Tf}_2\text{N}]$. The resulting salt was a blue paramagnetic liquid at room temperature, which undergoes only a glass transition at low temperature ($T_g = 242$ K). The salt was stable for more than a few days under nitrogen atmosphere, although it gradually decomposed by desorption of the axial ligands. Heating above 323 K also led to decomposition. We also prepared $[\text{Fe}(\text{acacen})(1\text{-butylimidazole})_2][\text{PF}_6]$ (**1-PF₆**) in a similar fashion, which produced a crystalline solid.

The temperature dependence of the magnetic moment (μ_{eff}) of **1-Tf₂N** is shown in Fig. 2. This salt exhibited a spin-crossover phenomenon in the liquid state and a rapid decrease in magnetic susceptibility when cooled from room temperature to 203 K. The

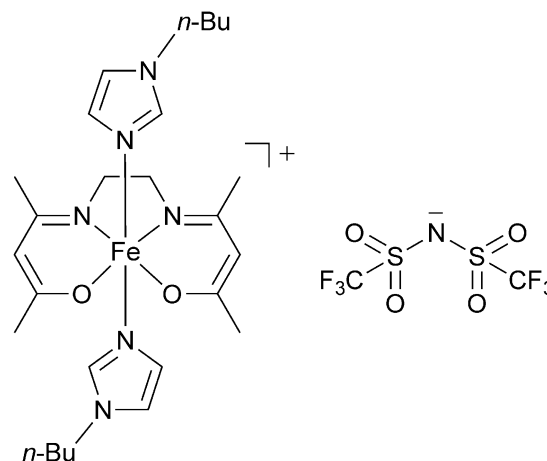


Fig. 1 Structural formula of $[\text{Fe}(\text{acacen})(1\text{-butylimidazole})_2][\text{Tf}_2\text{N}]$ (**1-Tf₂N**).

magnetic moment at 310 K was $3.06 \mu_B$, which is an intermediate value between that for a high-spin state ($S = 5/2$, $5.92 \mu_B$) and a low-spin state ($S = 1/2$, $1.73 \mu_B$). The magnetic moment below 203 K was a low-spin value, and there was no anomaly observed at around the glass transition temperature. No thermal hysteresis was observed for the spin-crossover behavior. Furthermore, because of spin crossover, this salt showed thermochromism, in which its color reversibly changes between blue-green (248 K) and violet-blue (313 K) (Fig. 3a). The effects of temperature on the UV-vis spectra can be seen in Fig. 3b. As the temperature was increased, the absorption band at around 650 nm decreased, which is a ligand-to-metal charge transfer band of the low-spin state;¹⁰ this was accompanied by an increase in absorption at around 510 nm, showing an isosbestic point at 591 nm.

For comparison, the molecular structures and magnetic properties of **1-PF₆** were investigated. Despite being a solid, the magnetic susceptibility of this salt closely resembled that of **1-Tf₂N** (Fig. 2b). The value of μ_{eff} at 310 K was $2.76 \mu_B$, which is slightly smaller than that of **1-Tf₂N**, probably because of the effect of crystal packing. The value of μ_{eff} below 200 K was a low-spin value. This crystal also exhibited thermochromism, displaying color changes between blue-green (233 K) and blue (333 K) (†ESI, Fig. S2). The structure of the cation was

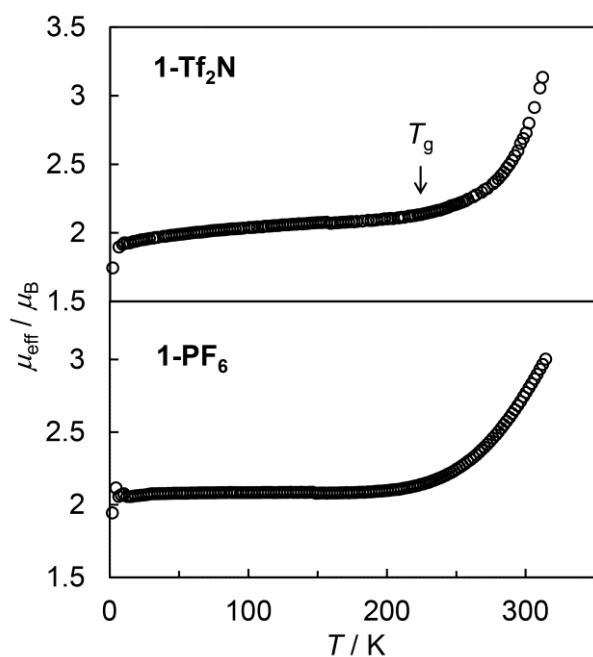


Fig. 2 Temperature dependence of magnetic susceptibilities of **1-Tf₂N** and **1-PF₆**.

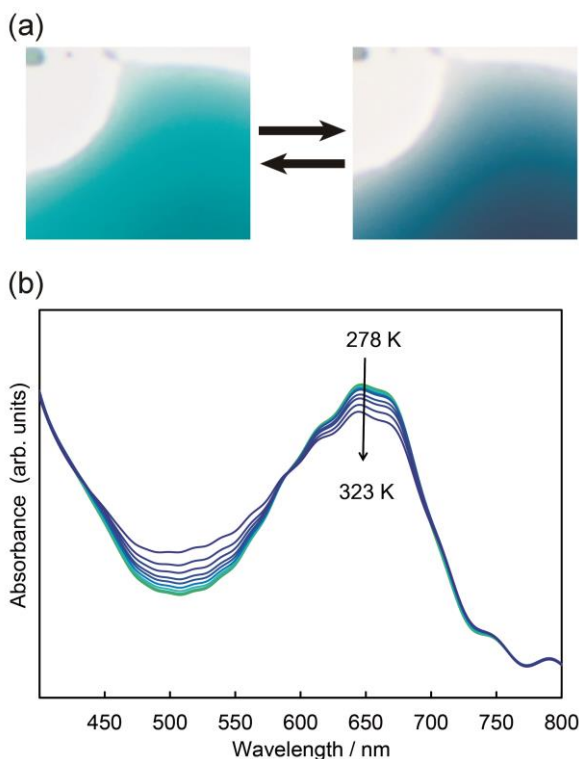


Fig. 3 (a) Photographs of **1-Tf₂N** at different temperatures. (b) Temperature dependence of UV-vis absorption spectra of **1-Tf₂N** measured at intervals of 5 K.

confirmed by X-ray structure analysis at 298 K and 100 K. The molecular structure at 298 K is shown in Fig. 4. The bond lengths between the metal ions and the ligand donor atoms (Fe–N_{Im}: 2.013(4), 2.019(4) Å; Fe–N_{acacen}: 1.930(4), 1.932(4) Å; Fe–O: 1.898(4), 1.906(3) Å) were intermediate between those of high-spin and low-spin species,^{9a} which is consistent with magnetic susceptibility. These bonds became shorter at 100 K (Fe–N_{Im}:

1.975(2)–1.995(2) Å; Fe–N_{acacen}: 1.901(2)–1.916(2) Å; Fe–O: 1.900(2)–1.914(2) Å), adopting low-spin bond lengths.^{9a} Hence, spin crossover was structurally confirmed. The absence of cooperative effects in the spin crossover of **1-PF₆** is probably ascribed to the absence of any strong intermolecular interactions; hence, the gradual spin crossover in **1-PF₆** and **1-Tf₂N** is inherent to the cation, which results in their comparable magnetic behaviors. In fact, spin-crossover complexes often display gradual spin crossover in solutions, although their color and magnetism are usually much less prominent. [Fe(acacen)(1-methyl imidazole)₂][BPh₄]^{9a} also shows a gradual spin crossover in the solid state, although it occurs at lower temperatures than the present salts.

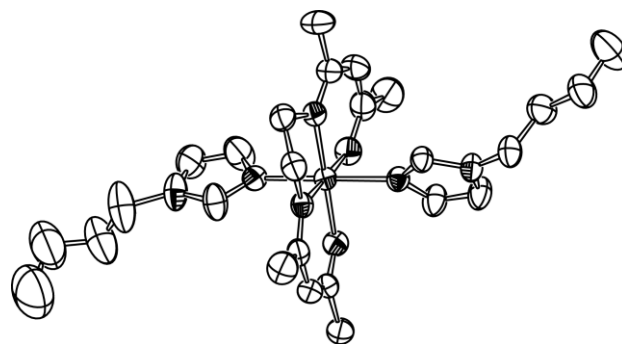


Fig. 4 Ortep drawing of cation in **1-PF₆** at 298 K.

In conclusion, we have developed a magnetic fluid that exhibits temperature-dependent magnetic and thermochromic properties by liquefying a spin-crossover complex. Previously, we prepared Tf₂N salts of cationic salen complexes (salen = *N,N'*-bis(salicylideneamino)ethylene), also containing a Schiff base ligand, though their melting points were relatively high.¹¹ In the iron(III) acacen complex, the lower molecular weight and weaker intermolecular interactions of the acacen ligand are responsible for the formation of the ionic liquid state. Although there are soft matter such as liquid crystals that exhibit spin crossover,¹² ionic liquids that show temperature-dependent magnetic properties are scarce.^{5b} Spin-state switching in the liquid phase leads to various applications.¹³ Utilization of the magnetic function of metal complexes is an effective strategy in the functionalization of ionic liquids, which expands the scope of liquid science.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental procedures, crystallographic data, packing diagrams and photographs of **1-PF₆**. CCDC 939975–939976. See DOI: 10.1039/b000000x/

‡ **1-Tf₂N**: All manipulations were performed under nitrogen atmosphere. 1-Butylimidazole (0.1 mL, 0.94 mmol) was added to a dichloromethane solution (5 mL) of [Fe(acacen)Cl]¹⁴ (100 mg, 0.31 mmol), and the solution was stirred for 30 min, and then the solution was filtered. An ether solution (3 mL) of Ag[Tf₂N]¹⁵ (121.5 mg, 0.31 mmol) was added to this filtrate and stirred for 1 h. The solution was concentrated by evaporation, and the solution was filtered to remove silver chloride. After evaporation of the solvent, the residual blue liquid was washed with a mixture of ether and pentane and then dried by repeated freeze-pump-

thaw cycling. The liquid was sensitive to air and moisture. Yield: 157 mg, 61.0%. Anal. Calcd. For $C_{28}H_{42}F_6FeN_7O_6S_2$: C, 41.69; H, 5.25; N, 12.15. Found: C, 41.66; H, 5.35; N, 12.38.

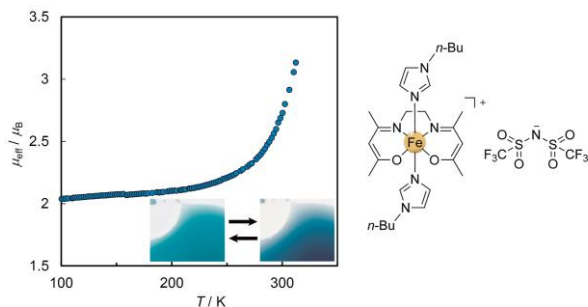
1-PF₆: 1-butylimidazole (0.13 mL, 1.04 mmol) was added to a methanol solution of [Fe(acacen)Cl] (108.4 mg, 0.347 mmol), and the solution was stirred for 10 min. Then the solvent was removed by evaporation, and the residue was dissolved in dichloromethane and filtered. Evaporation of the filtrate gave the product as dark blue block crystals, which were further purified by slow diffusion of hexane into concentrated dichloromethane solutions. Yield: 70.3 mg, 65.4%. Anal. Calcd. For $C_{26}H_{42}F_6FeN_6O_2P$: C, 46.51; H, 6.30; N, 12.52. Found: C, 46.08; H, 6.40; N, 12.53.

- 1 (a) *Ionic Liquid: Industrial Applications to Green Chemistry*, eds. R. D. Rogers, K. R. Seddon, American Chemical Society, Washington, D.C., ACS Symposium Series, 2002; vol. 818, (b) A. Stark, K. R. Seddon, in *Kirk-Othmer Encyclopedia of Chemical Technology*, Wiley-Interscience, New York, 5th ed., 2007, vol. 26, pp 836–919; (c) S. -g. Lee, *Chem. Commun.*, 2006, 1049–1063; (d) M. Armand, F. Endres, D. R. MacFarlane, H. Ohno and B. Scrosati, *Nat. Mater.*, 2009, **8**, 621–629; (e) M. Pucheault, M. Vaultier, *Top. Curr. Chem.*, 2010, **290**, 83–126.
- 2 (a) Y. Yoshida and G. Saito, *Phys. Chem. Chem. Phys.*, 2010, **12**, 1675–1684; (b) Y. Yoshida and G. Saito in *Ionic Liquids—Theory, Properties, New Approaches*, ed. A. Kokorin, INTECH, 2011, ch. 29, pp.723–738.
- 25 3 (a) S. Hayashi and H. Hamaguchi, *Chem. Lett.*, 2004, **33**, 1590–1591; (b) 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**, 1921–1928; (c) P. Nockemann, B. Thijs, N. Postelmans, K. Van Hecke, L. Van Meervelt and K. Binnemans, *J. Am. Chem. Soc.*, 2006, **128**, 13658–13659; (d) B. Mallick, B. Balke, C. Felser and A. -V. Mudring, *Angew. Chem. Int. Ed.*, 2008, **47**, 7635–7638; (e) T. Peppel, M. Köckerling, M. Geppert-Rybaczynska, R. V. Ralys, J. K. Lehmann, S. P. Verevkin and A. Heintz, *Angew. Chem. Int. Ed.*, 2010, **49**, 7116–7119; (f) B. M. Krieger, H. Y. Lee, T. J. Emge, J. F. Wishart and E. W. Castner, Jr., *Phys. Chem. Chem. Phys.*, 2010, **12**, 8919–8925; (g) D. Prodius, F. Macaeve, E. Stingaci, V. Pogrebnoi, V. Mereacre, G. Novitchi, G. E. Kostakis, C. E. Anson and A. K. Powell, *Chem. Commun.*, 2013, **49**, 1915–1917.
- 4 Y. Yoshida, H. Tanaka and G. Saito, *Chem. Lett.*, 2007, **36**, 1096–1097.
- 5 (a) R. E. Del Sesto, C. Corley, A. Robertson and J. Wilkes, *J. Organomet. Chem.*, 2005, **690**, 2536–2542; (b) Y. Yoshida, H.

- Tanaka, G. Saito, L. Ouahab, H. Yoshida and N. Sato, *Inorg. Chem.*, 2009, **48**, 9989–9991; (c) A. Branco, L. C. Branco and F. Pina, *Chem. Commun.*, 2011, 2300–2302; (d) P. Zhang, Y. Gong, Y. Lv, Y. Guo, Y. Wang, C. Wang and H. Li, *Chem. Commun.*, 2012, **48**, 2334–2336.
- 6 (a) T. Inagaki and T. Mochida, *Chem. Lett.*, 2010, **39**, 572–573; (b) Y. Funasako, T. Mochida, T. Inagaki, T. Sakurai, H. Ohta, K. Furukawa and T. Nakamura, *Chem. Commun.*, 2011, **47**, 4475–4477; (c) T. Inagaki, T. Mochida, M. Takahashi, C. Kanadani, T. Saito and D. Kuwahara, *Chem. Eur. J.*, 2012, **18**, 6795–6804; (d) T. Inagaki, T. Mochida, *Chem. Eur. J.*, 2012, **18**, 8070–8075; (e) Y. Funasako, T. Mochida, T. Inagaki, T. Sakurai, H. Ohta, K. Furukawa and T. Nakamura, *Dalton Trans.*, 2013, **42**, 8317–8327.
- 55 7 A. D. Garnovskii, A. L. Nivorozhkin and V. I. Minkin, *Coord. Chem. Rev.*, 1993, **126**, 1–69.
- 8 (a) M. Nihei, T. Shiga, Y. Maeda and H. Oshio, *Coord. Chem. Rev.*, 2007, **251**, 2606–2621; (b) P. Gütllich, *Eur. J. Inorg. Chem.*, 2013, 581–591.
- 60 9 (a) B. J. Kennedy, A. C. McGrath, K. S. Murray, B. W. Skelton and A. H. White, *Inorg. Chem.*, 1987, **26**, 483–495; (b) H. Ohshio, Y. Maeda and Y. Takashima, *Inorg. Chem.*, 1983, **22**, 2684–2689; (c) S. Imatomi, R. Kitashima, T. Hamamastu, M. Okeda, Y. Ogawa and N. Matsumoto, *Chem. Lett.*, 2006, **35**, 502–503; (d) S. Imatomi, S. Hashimoto and N. Matsumoto, *Eur. J. Inorg. Chem.*, 2009, 721–726; (e) T. M. Ross, S. M. Neville, D. S. Innes, D. R. Turner, B. Moubaraki and K. S. Murray, *Dalton Trans.*, 2010, **39**, 149–159.
- 10 S. Schenker, A. Hauser and R. M. Dyson, *Inorg. Chem.*, 1996, **35**, 4676–4682.
- 70 11 M. Okuhata and T. Mochida, *Polyhedron*, 2012, **43**, 153–158.
- 12 (a) Y. Galyametdinov, V. Ksenofontov, A. Prosvirin, I. Ovchinnikov, G. Ivanova, P. Gütllich and W. Haase, *Angew. Chem. Int. Ed.*, 2001, **40**, 4269–4271; (b) S. Hayami, M. R. Karim and Y. H. Lee, *Eur. J. Inorg. Chem.*, 2013, 683–696.
- 75 13 (a) C. Gandolfi, G. G. Morgan and M. Albrecht, *Dalton Trans.*, 2011, **41**, 3726–3730. (b) M. P. Shores, C. M. Klug, S. R. Fiedler, in *Spin-Crossover Materials: Properties and Applications*, ed. M. A. Halcrow, Wiley, 2013, Chap. 10.
- 14 Y. Nishida, S. Oshio and S. Kida, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 119–122.
- 80 15 A. Vij, Y. Y. Zheng, R. L. Kirchmeier and J. M. Shreeve, *Inorg. Chem.*, 1994, **33**, 3281–3288.

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A thermochromic magnetic ionic liquid containing a cationic iron(III) Schiff-base complex has been developed. The color and magnetic moment change with temperature due to spin crossover in the liquid state.

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Spin-Crossover Magnetic Fluid: Magnetic and Thermochromic Ionic Liquid from Cationic Iron(III) Schiff-Base Complex

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General methods

¹H NMR spectra were recorded on a JEOL JNM-ECL-400 spectrometer. Elemental analysis was performed using a Yanaco CHN MT-5 analyzer. DSC measurements were performed using a TA instruments Q100 differential scanning calorimeter at 10 K min⁻¹ in a temperature range down to 100 K. Magnetic susceptibilities were measured using a Quantum Design MPMS-XL7 SQUID susceptometer under a magnetic field of 0.1 T. Temperature dependence of the UV-Vis-NIR spectra were recorded on a JASCO V-570 UV/VIS/NIR spectrometer with a Linkam LTS350 hot stage.

Crystal structures

Single crystals of [Fe(acacen)(1-butylimidazole)₂][PF₆] (**1-PF₆**) suitable for X-ray crystallography was obtained by diffusion of hexane into a dichloromethane solution of the compound. X-ray diffraction data were collected at 298 K and 100 K on a Bruker APEX II Ultra CCD diffractometer using MoK α radiation ($\lambda = 0.71073$ Å). Crystallographic parameters are listed in Table S1. The structures were solved by direct method and refined on F^2 using SHELX-97.^{S1} Empirical absorption correction was applied (SADABS^{S2}). The non-hydrogen atoms were refined anisotropically. The ORTEP-3 program^{S3} was used for molecular graphics.

The packing diagram of **1-PF₆** at 298 K is depicted in Figure S1a. This salt crystallized in a space group $P4_2/n$. The unit cell contains one crystallographically independent cation. The imidazole rings of the two axial ligands are twisted by 68.6(4)°. The packing diagram and the molecular structure of the cations determined at 100 K are shown in Figures S1b and S1c. The space group was $I4_1/a$. The change of the space group indicates the occurrence of a phase transition at low temperature, which is independent of spin crossover. The phase transition could not be detected by DSC measurement probably due to its small transition entropy and/or distribution of transition temperatures. Although the unit cell was different, the packing structure was almost the same as that in 298 K. In this phase, there are two crystallographically independent cations (molecules 1 and 2, Fig. S1c) having different torsion angles between the imidazole rings, which are 83.7° and 30.9°, respectively.

Table S1. Crystallographic parameters for **1-PF₆**.

	298 K	100 K
Empirical formula	C ₂₆ H ₄₂ F ₆ Fe N ₆ O ₂ P	C ₂₆ H ₄₂ F ₆ Fe N ₆ O ₂ P
Formula weight (g mol ⁻¹)	671.48	671.48
Crystal system	Tetragonal	Tetragonal
Space group	<i>P</i> 4 ₂ / <i>n</i>	<i>I</i> 4 ₁ / <i>a</i>
Crystal size (mm ³)	0.4×0.34×0.26	0.4×0.34×0.26
<i>a</i> (Å)	18.012(2)	25.255(3)
<i>b</i> (Å)	18.012(2)	25.255(3)
<i>c</i> (Å)	20.474(2)	39.511(4)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
Volume (Å ³)	6642.3(14)	25201(4)
<i>Z</i>	8	32
<i>d</i> _{calcd.} (g cm ⁻³)	1.343	1.416
λ (Å)	0.71073	0.71073
μ (mm ⁻¹)	0.568	0.599
Reflections collected	31753	60475
Independent reflections	5888 (<i>R</i> (int) = 0.0262)	11115 (<i>R</i> (int) = 0.0264)
<i>F</i> (000)	2808	11232
<i>R</i> ₁ ^[a] , <i>wR</i> ₂ ^[b] (<i>I</i> > 2σ(<i>I</i>))	0.0789, 0.2418	0.0390, 0.0970
<i>R</i> ₁ ^[a] , <i>wR</i> ₂ ^[b] (all data)	0.0958, 0.2663	0.0457, 0.1028
Goodness-of-fit on <i>F</i> ²	1.052	1.017
Completeness to θ (%)	100	99.9
Parameters	386	769
Largest diff. peak and hole (e Å ⁻³)	0.892 and -0.662	0.711 and -0.473
[a] $R_1 = \sum F_o - F_c / \sum F_o $, [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$		

References

- S1 G. M. Sheldrick, *SHELXL: Program for the Solution for Crystal Structures*; University of Göttingen, Germany, 1997.
- S2 G. M. Sheldrick, *SADABS: Program for Semi-empirical Absorption Correction*, University of Göttingen, Germany, 1997.
- S3 L. J. Farrugia, *J. Appl. Cryst.* 1999, **32**, 837–838.

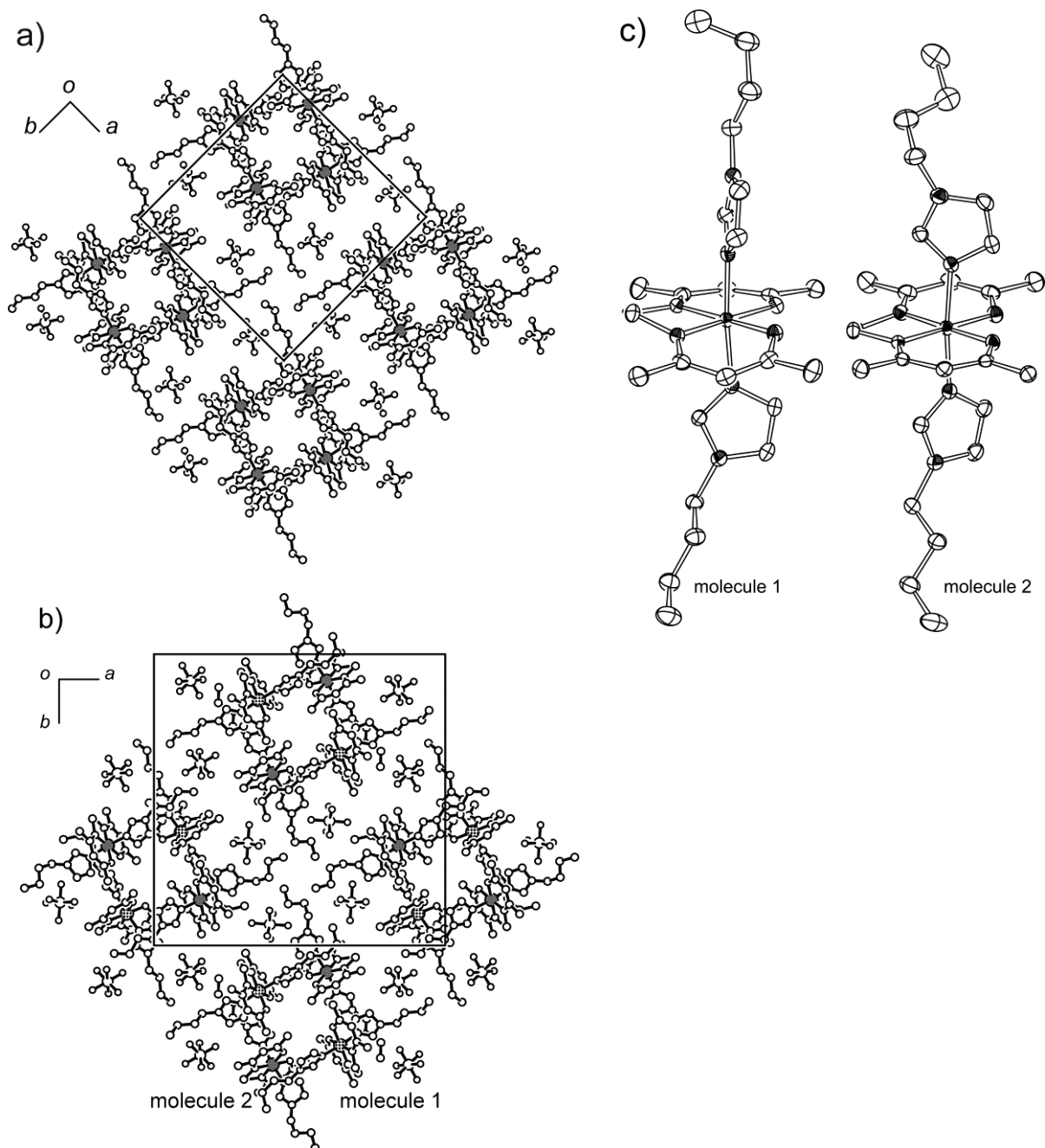


Fig. S1. Packing diagram of **1-PF₆** determined at (a) 298 K and (b) 100 K. Cations I and II in (b) are indicated by different hatching patterns of the iron atoms. (c) Ortep drawing of the cations in **1-PF₆** at 100 K.

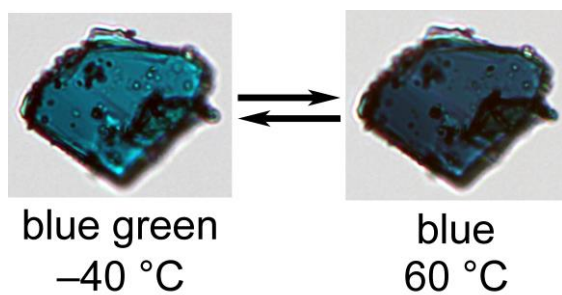


Fig. S2. Photographs of **1-PF₆** at different temperatures.