Electronic Supplementary Information

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

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General methods

^{1}H 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)$_2$][PF$_6$] (**1-PF$_6$**) 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 MoKα radiation (λ = 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-PF$_6$** 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-PF_6**.

	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	$P\,4_2/n$	$I\,4_1/a$
Crystal size (mm^3)	0.4×0.34×0.26	0.4×0.34×0.26
a (Å)	18.012(2)	25.255(3)
b (Å)	18.012(2)	25.255(3)
c (Å)	20.474(2)	39.511(4)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
Volume ($Å^3$)	6642.3(14)	25201(4)
Z	8	32
$d_{calcd.}$ (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 (R(int) = 0.0262)	11115 (R(int) = 0.0264)
F(000)	2808	11232
R_1[a], wR_2[b] ($I > 2\sigma$(I))	0.0789, 0.2418	0.0390, 0.0970
R_1[a], wR_2[b] (all data)	0.0958, 0.2663	0.0457, 0.1028
Goodness-of-fit on F^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] $R_1 = \Sigma\, ||F_o| - |F_c|| \,/\, \Sigma\, |F_o|$, [b] $wR_2 = [\, \Sigma\, w(F_o^2 - F_c^2)^2 \,/\, \Sigma\, w(F_o^2)^2 \,]^{1/2}$

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.

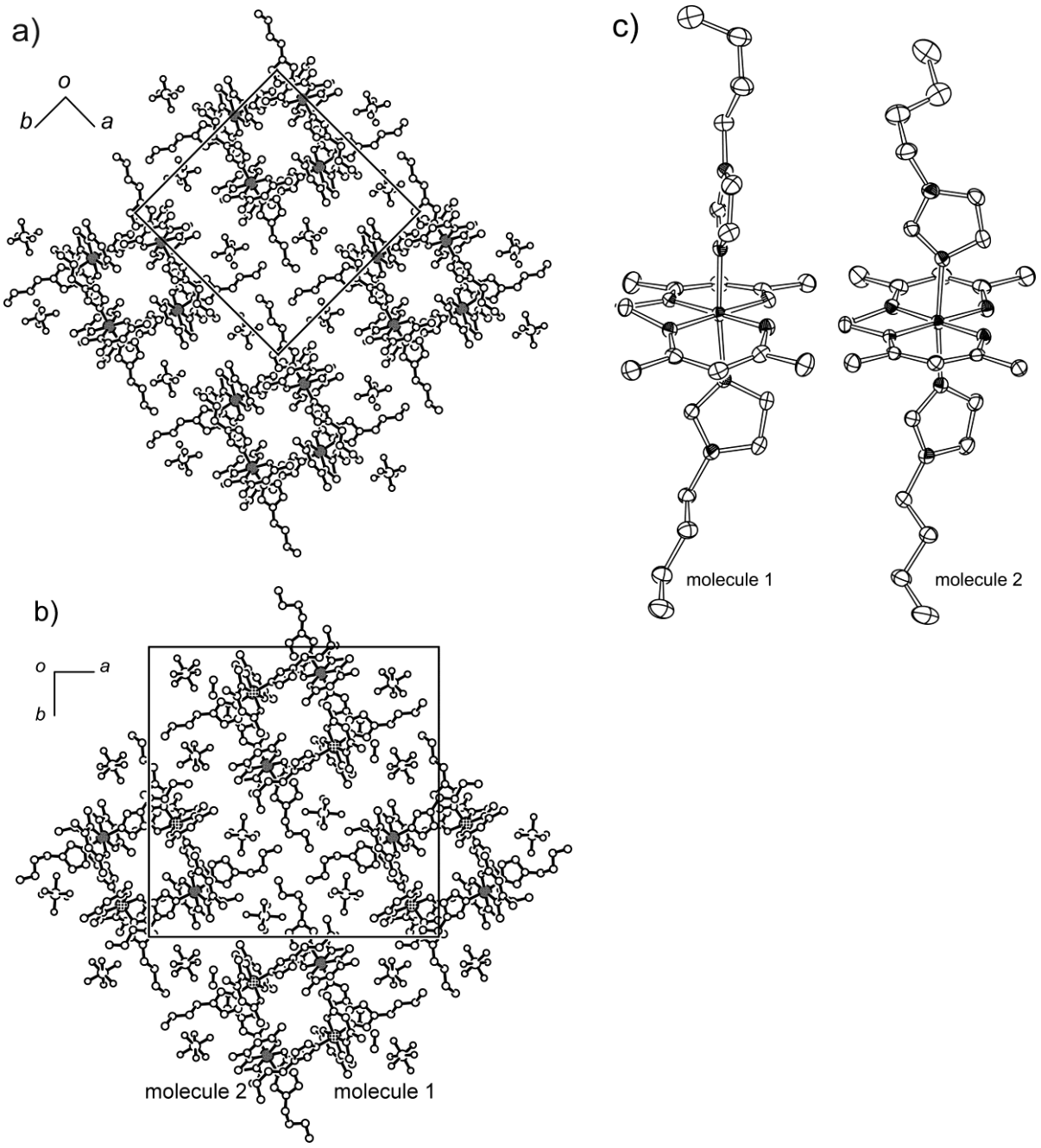

Fig. S1. Packing diagram of **1-PF$_6$** determined at (a) 298 K and (b) 100 K. Cations I and II in (b) are indicated by different hatching patterns of the iron atoms. (c) Ortep drawing of the cations in **1-PF$_6$** at 100 K.

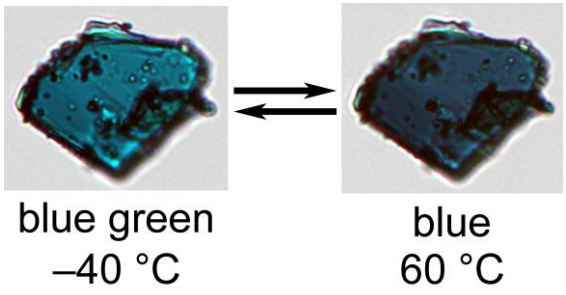

Fig. S2. Photographs of **1-PF$_6$** at different temperatures.