

Bis[*E*-2,6-bis(1*H*-pyrazol-1-yl)-4-styrylpyridine]iron(II) Complex: Relationship between Thermal Spin Crossover and Crystal Solvent

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S Supporting Information



ABSTRACT: The crystal structures and thermal spin-crossover (SCO) behavior of $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{X}$ [E-dpsp = (*E*)-2,6-bis(1*H*-pyrazol-1-yl)-4-styrylpyridine; X = crystal solvent] are investigated. The titled iron(II) complex features polymorphology induced by crystal solvents, which is identified by means of single-crystal X-ray diffraction analysis: For $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{acetone}$ and $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot 4\text{MeNO}_2$, detailed analyses at various temperatures are conducted. The magnetic properties of bulk microcrystalline samples of $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{X}$ are assessed using a SQUID magnetometer. Among the series, only $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{acetone}$ undergoes peculiar thermal SCO, such as a precipitous and hysteretic spin-state change ($T_{1/2\uparrow} = 179$ K, $T_{1/2\downarrow} = 164$ K, and $\Delta T_{1/2} = 15$ K) and frozen-in effect. All single crystals of $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{X}$ are free from intermolecular interaction except for $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{acetone}$: One of the phenyl rings in $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{acetone}$ is twisted appreciably and features an intermolecular H–H short contact with one of the neighboring complexes to form a one-dimensional network. The twisted phenyl group also participates in π – π stacking with one of the pyrazolyl rings of another neighboring molecule, constructing a dimeric couple. These intermolecular interactions would induce cooperative effects, which leads to the good thermal SCO phenomenon of $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{acetone}$.

INTRODUCTION

Thermal spin crossover (SCO)^{1,2} is a phenomenon in which the spin state of a metal center is switched between low-spin (LS) and high-spin (HS) states under external heat stimuli. Octahedral first-row transition-metal complexes with electronic configurations of d^4 – d^7 are known to exhibit thermal SCO, and among those, iron(II) complexes with nitrogen-containing ligands are studied vigorously. It has been suggested that not only intramolecular structures (e.g., coordination sphere and ligand-field strength) but also intermolecular interaction in crystal lattices, such as an intermolecular contact, hydrogen bonding, and π – π stacking, play important roles in the fabrication of high-end thermal SCO materials (i.e., abrupt spin-state change and wide thermal hysteresis): Such solid-state intermolecular interaction is expected to induce cooperative effects.^{1d} Polymorphology, including those induced by crystal-solvent inclusion, can perturb such intermolecular interaction, thereby affecting SCO phenomena greatly.^{1d} This series of solid-state interaction is difficult to control at will and has still been investigated keenly.²

The $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$ type of iron(II) complex [dpp = 2,6-bis(1*H*-pyrazol-1-yl)pyridine; Figure 1a] has been intensively

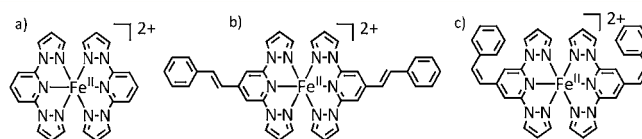


Figure 1. Molecular structures of (a) $[\text{Fe}(\text{dpp})_2]^{2+}$, (b) $[\text{Fe}(\text{E-dpsp})_2]^{2+}$, and (c) $[\text{Fe}(\text{Z-dpsp})_2]^{2+}$.

studied from the viewpoint of SCO chemistry.³ A tridentate dpp ligand produces a ligand field suitable for thermal SCO, and the tetrafluoroborate anions tend to show good crystallinity. Another intriguing point of these types of complexes is inclusion of crystal solvents.

Iron(II) complexes with dpp ligands and their derivatives with small substituents seldom encapsulate crystal solvents.^{3a,b} On the other hand, the dpsp types of ligands with bulky substituents such as mesityl, ferrocenylethylenyl, and 4-cyanophenyl groups are prone to include crystal solvents.^{3c,d} Among the instances, Ruben and co-workers reported that

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thermal SCO behavior was tunable upon desorption of the crystal solvent molecules.^{3c}

In the previous papers, we synthesized a new class of $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$ complexes, $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2$ and $[\text{Fe}(Z\text{-dpsp})_2](\text{BF}_4)_2$ [$E\text{-dpsp} = (E)\text{-}2,6\text{-bis}(1H\text{-pyrazol-}1\text{-yl})\text{-}4\text{-styrylpyridine}$, $Z\text{-dpsp} = (Z)\text{-}2,6\text{-bis}(1H\text{-pyrazol-}1\text{-yl})\text{-}4\text{-styrylpyridine}$; Figure 1b,c] so that we observed solid-state ligand-driven light-induced spin change⁴ upon one-way Z -to- E photoisomerization.⁵ In the course of the investigation, we found that $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2$ was very prone to hold various crystal-solvent molecules, giving rise to polymorphology, whereas $[\text{Fe}(Z\text{-dpsp})_2](\text{BF}_4)_2$ was unlikely to encapsulate them. This is rationalized by the fact that $E\text{-dpsp}$ and $Z\text{-dpsp}$ correspond to the “extended” and “shrunken” forms, respectively.

Under the background described above, we have noticed that $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2$ is a good sample for gaining insight into a correlation between thermal SCO and cooperative effects induced by intermolecular interaction in crystal lattices. In the present full paper, we prepare five types of single crystals of $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2 \cdot X$ (X = crystal solvent), which are analyzed by means of temperature-variable single-crystal X-ray diffraction (XRD) analysis to determine both intramolecular structures and intermolecular interaction. The thermal SCO behavior of microcrystalline samples of $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2 \cdot X$ is quantified using a superconducting quantum interference device (SQUID) magnetometer. A correlation between thermal SCO and crystal structures is discussed.

EXPERIMENTAL SECTION

Materials. Syntheses of $E\text{-dpsp}$, $Z\text{-dpsp}$, and $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2$ were reported in our previous paper.^{5a} Reagents and solvents commercially available were used as received unless otherwise noted.

Preparation of Single Crystals of $E\text{-dpsp}$ and $Z\text{-dpsp}$. Recrystallization from dichloromethane and hexane gave single crystals of $E\text{-dpsp}$ and $Z\text{-dpsp}$ suitable for XRD analysis.

Preparation of Single Crystals of $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2 \cdot \text{acetone}$. Under a nitrogen atmosphere, $E\text{-dpsp}$ (67 mg, 0.21 mmol) and $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (35 mg, 0.10 mmol) were slowly diffused in acetone (17 mL) in H-shaped glassware. After 2 weeks, large crystals formed on the bottom of the tube. The crystals were collected by filtration and washed with 50 mL of hexane.

Preparation of Single Crystals of $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2 \cdot X$ ($X = 4\text{MeNO}_2$, $\text{H}_2\text{O} \cdot 3\text{MeCN}$, $0.5\text{Et}_2\text{O}$, 2PC ; $\text{PC} = \text{propylene carbonate}$). Solvent-free $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2$, which was prepared from $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2 \cdot \text{acetone}$ by vacuuming at 393 K, was dissolved in soluble solvents. The solutions were layered with insoluble solvents, which afforded single crystals of $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2 \cdot X$. The pairs of soluble and insoluble solvents are as follows: nitromethane and diethyl ether for $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2 \cdot 4\text{MeNO}_2$; acetonitrile and diethyl ether for $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2 \cdot \text{H}_2\text{O} \cdot 3\text{MeCN}$ and $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2 \cdot 0.5\text{Et}_2\text{O}$ (the two crystals were easy to separate because of their different appearances from one another); propylene carbonate, ethyl acetate, and diethyl ether for $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2 \cdot 2\text{PC}$.

Single-Crystal XRD Analysis. Diffraction data were collected using a Rigaku AFC8 diffractometer coupled with a Rigaku Saturn CCD system and a rotating-anode X-ray generator [graphite-monochromated $\text{Mo } K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$)]. A single crystal suitable for the measurement was mounted on a loop fiber with liquid paraffin or on a glass capillary with petroleum jelly. The measurements with temperatures above 173 K always employed petroleum jelly. A numerical correction was applied with the program NUMABS.⁶ The structures were solved using either SIR-97 ⁷ or SIR-2004 ⁸ and were refined using SHELXL-97 ⁹ by full-matrix least-squares techniques on F^2 . All calculations were performed using the WinGX-1.70.01 software package.¹⁰ All non-hydrogen atoms were refined anisotropically.

Hydrogen atoms were refined using a set of riding models with fixed thermal parameters.

Differential Scanning Calorimetry (DSC). DSC was carried out using a Rigaku ThermoPlus DSC 8230 under a nitrogen atmosphere. Single crystals of $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2 \cdot \text{acetone}$ (1.55 mg) were put in aluminum pans, which were sealed by press. To avoid damage to the sample, the measurement began with a scan from 123 to 298 K at a rate of 5 K min^{-1} .

Magnetic Susceptibility Measurements. Magnetic susceptibilities in the solid state were measured with an applied magnetic field of 0.5 T in a temperature range of 5–300 K at a rate of 1 K min^{-1} (sweep mode) with a Quantum Design MPMS SQUID magnetometer. Sheets of aluminum foil (Nippaku, Inc.) were used as sample containers, whose magnetic contributions were subtracted by measuring their own magnetic susceptibilities in all measurements. The typical weights of the aluminum foil and $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2 \cdot X$ were 10 and 3 mg, respectively, and the average height of the sample was 4 mm. The molar magnetic susceptibilities of $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2 \cdot X$ were corrected with their diamagnetic susceptibilities, which were calculated from Pascal's constants: $-358 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ for $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2 \cdot \text{acetone}$; $-424 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ for $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2 \cdot 4\text{MeNO}_2$; $-403 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ for $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2 \cdot \text{H}_2\text{O} \cdot 3\text{MeCN}$; $-353 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ for $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2 \cdot 0.5\text{Et}_2\text{O}$; $-424 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ for $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2 \cdot 2\text{PC}$.

RESULTS AND DISCUSSION

Crystal Structures of $E\text{-dpsp}$ and $Z\text{-dpsp}$. Figure 2 shows an ORTEP drawing of the $E\text{-dpsp}$ ligand: As a reference,

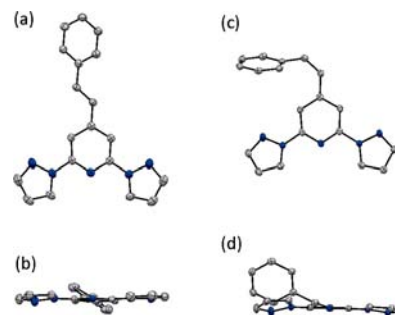


Figure 2. ORTEP drawings of (a and b) $E\text{-dpsp}$ and (c and d) $Z\text{-dpsp}$ with the thermal ellipsoid set at the 50% probability level. Hydrogen atoms are omitted. Color code: C, gray; N, blue.

that of $Z\text{-dpsp}$ is also shown. Table S1 in the Supporting Information collects their crystallographic parameters. One of the most curious structural features lies in the fact that the styryl group is not coplanar with the 2,6-bis(1H-pyrazol-1-yl)pyridine moiety even in the E form. The dihedral angles between the phenyl and pyridyl rings are 33.48° and 64.32° for $E\text{-dpsp}$ and $Z\text{-dpsp}$, respectively. The large dihedral angle of $Z\text{-dpsp}$ can be rationalized by intramolecular steric hindrance between the two rings. On the other hand, the E form is free from such intramolecular repulsion. Therefore, crystal packing affords the relatively large distortion in the E form. The tolerance of the styryl group toward distortion leads to the intermolecular interaction of $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2 \cdot \text{acetone}$ in the crystal phase (vide infra).

Crystal Structures of $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2 \cdot \text{acetone}$. Variable-temperature single-crystal XRD analysis was conducted for $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2 \cdot \text{acetone}$. Figure 3a shows an ORTEP drawing of the complex measured at 190 K. Table S2 in the Supporting Information collects the crystallographic parameters, and representative bond lengths and angles are

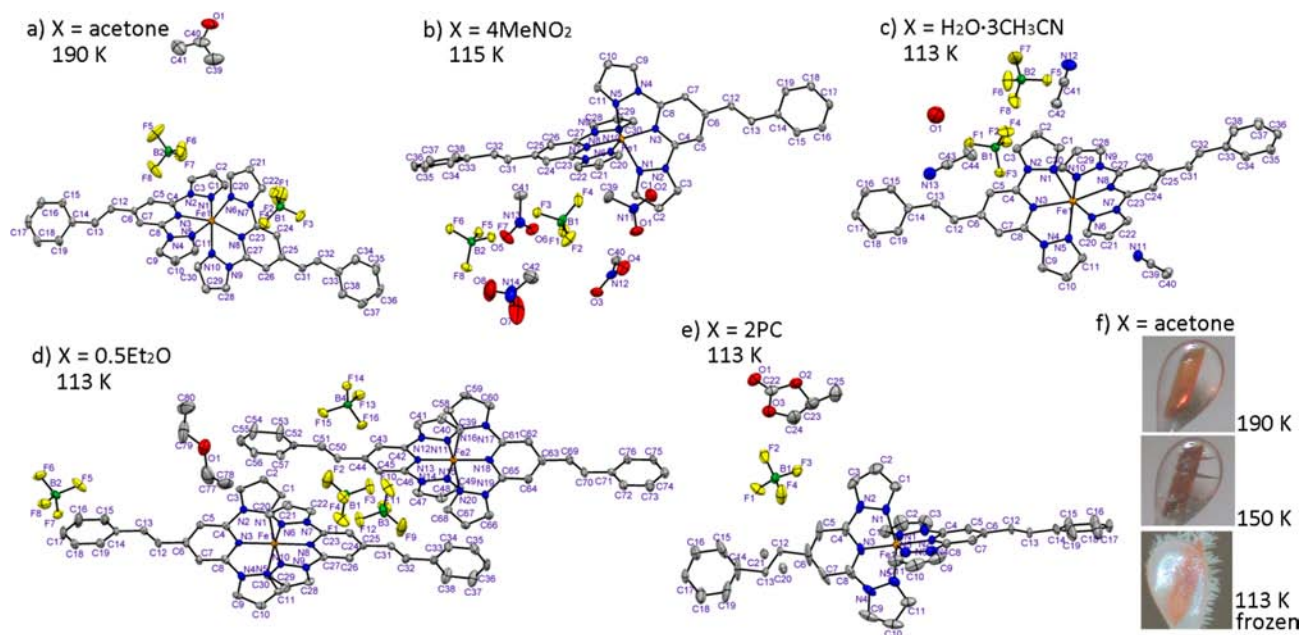


Figure 3. ORTEP drawings of $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{X}$ with the thermal ellipsoid set at the 50% probability level: (a) $\text{X} = \text{acetone}$; (b) $\text{X} = 4\text{MeNO}_2$; (c) $\text{X} = \text{H}_2\text{O} \cdot 3\text{MeCN}$; (d) $\text{X} = 0.5\text{Et}_2\text{O}$; (e) $\text{X} = 2\text{PC}$. Hydrogen atoms are omitted. Color code: C, gray; N, blue; O, red; Fe, orange; B, green; F, yellow. For (d) $\text{X} = 2\text{PC}$, the two *E-dpsp* ligands are crystallographically equivalent to one another. (f) Photographs of a single crystal of $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{acetone}$ at different temperatures and conditions.

Table 1. Selected Bond Distances, Σ Parameters, and Dihedral Angles for $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{acetone}$ at Various Temperatures

	temperature/K				
	240(2)	190(2)	175(2) ^a	150(2)	113(2) ^b
Fe–N1/Å	2.172(3)	2.173(2)	1.976(4)	1.984(3)	2.1171(16)
Fe–N3/Å	2.128(2)	2.124(2)	1.898(4)	1.900(3)	2.1255(14)
Fe–N5/Å	2.192(3)	2.193(2)	1.960(4)	1.979(3)	2.1949(16)
Fe–N6/Å	2.163(3)	2.161(2)	1.979(4)	1.984(3)	2.1599(16)
Fe–N8/Å	2.133(2)	2.128(2)	1.892(4)	1.897(3)	2.1308(14)
Fe–N10/Å	2.205(3)	2.203(2)	1.976(4)	1.990(3)	2.1972(16)
average Fe–N/Å	2.166	2.164	1.947	1.956	2.1542
Σ/deg	168.36	170.31	97.22	95.80	172.00
θ/deg^c	40.65	40.59	45.48	45.88	40.65
	9.70	9.59	8.66	8.58	9.91

^aCooled first and then warmed at a rate of 1 K min^{-1} . ^bFrozen by a rapid cooling process at a rate of 60 K min^{-1} . ^cThe dihedral angle between the pyridyl and phenyl rings in the stilbene unit.

Table 2. Selected Bond Distances, Σ Parameters, and Dihedral Angles for $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot 4\text{MeNO}_2$ at Various Temperatures

	temperature/K						
	243(2)	217(2)	192(2)	165(2)	140(2)	115(2)	113(2) ^a
Fe–N1/Å	2.138(4)	2.067(4)	2.000(3)	1.987(2)	1.987(3)	1.989(2)	1.986(2)
Fe–N3/Å	2.084(3)	2.005(3)	1.926(2)	1.904(2)	1.899(2)	1.899(2)	1.8991(19)
Fe–N5/Å	2.144(4)	2.070(4)	1.995(2)	1.980(2)	1.974(3)	1.972(2)	1.971(2)
Fe–N6/Å	2.140(4)	2.068(4)	2.001(3)	1.991(2)	1.990(3)	1.990(2)	1.992(2)
Fe–N8/Å	2.079(4)	2.004(3)	1.924(2)	1.902(2)	1.900(2)	1.900(2)	1.901(2)
Fe–N10/Å	2.139(4)	2.071(4)	1.999(2)	1.975(2)	1.975(3)	1.971(2)	1.972(2)
average Fe–N/Å	2.121	2.048	1.974	1.958	1.954	1.954	1.954
Σ/deg	140.16	119.52	96.39	90.40	89.48	90.00	89.00
θ/deg^b	10.43	10.76	11.46	12.2	12.59	13.16	12.68
	5.67	5.58	5.40	5.14	4.78	4.50	4.06

^aFrozen by a rapid cooling process at a rate of 60 K min^{-1} . ^bThe dihedral angle between the pyridyl and phenyl rings in the stilbene unit.

Table 3. Selected Bond Distances, Σ Parameters, and Dihedral Angles for $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2 \cdot \text{X}$ at Various Temperatures

	X = 0.5Et ₂ O					
	X = H ₂ O·3MeCN		113(2) K		X = 2PC	
	113(2) K		Fe1 site	Fe2 site	283(2) K	113(2) K
Fe–N1/Å	2.182(2)		1.971(3)	1.961(3)	1.956(3)	1.956(3)
Fe–N3/Å	2.1305(19)		1.890(3)	1.886(3)	1.878(3)	1.878(3)
Fe–N5/Å	2.181(2)		1.975(3)	1.964(3)	1.965(3)	1.965(3)
Fe–N6/Å	2.1726(19)		1.972(3)	1.970(3)		
Fe–N8/Å	2.1186(19)		1.887(3)	1.884(3)		
Fe–N10/Å	2.200(2)		1.964(3)	1.967(3)		
average Fe–N/Å	2.164		1.943	1.939	1.933	1.933
Σ /deg	156.43		88.65	85.62	85.49	85.49
θ /deg ^a	7.17		21.56	20.44	6.77	6.77
	6.72		10.48	5.95		

^aThe dihedral angle between the pyridyl and phenyl rings.

Table 4. Elemental Analysis for $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2 \cdot \text{X}$ (X = acetone, 4MeNO₂, H₂O·3MeCN, and 2PC)

	X											
	acetone			4MeNO ₂			H ₂ O·3MeCN			2PC		
	C	H	N	C	H	N	C	H	N	C	H	N
found	53.67	3.95	15.35	51.06	3.62	15.60	52.98	4.51	14.86	52.04	4.20	13.10
calcd	53.86	3.97	15.32	45.85	3.85	17.82	52.99	4.14	18.26	52.11	3.99	13.21

assembled in Table 1. The color of the crystal changed drastically from orange to brown upon cooling (Figure 3f), implying that $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2 \cdot \text{acetone}$ should undergo thermal SCO around the temperatures. The Fe–N bond length and bite angle around the coordination sphere are known to be good indicators of the spin state of iron(II) complexes.^{1a,11,12} The $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$ types of complexes are reported to possess an average Fe–N bond distance of 1.93–1.97 Å in the LS state and 2.14–2.20 Å in the HS state.^{3,5,13} Also, the Σ parameter, which is the summation of the deviations from 90° of the 12 bite angles around the central Fe^{II} ion, can range from 85° to 96° in the LS state and from 145° to 197° in the HS state.^{1d,14} Table 1 includes the two key parameters, which tells us that thermal SCO occurs at 175–190 K. We note that a single crystal subjected to rapid refrigeration at a rate of 60 K min^{−1} from 293 to 113 K retains its original color, indicating that the HS state is thermally trapped (frozen-in effect; Figure 3f). In fact, its average Fe–N bond distance (2.1542 Å) and Σ parameter (172.00°) correspond to the HS state (Table 1).

Another noteworthy feature of the crystal structure is that one of the stilbene units loses planarity, so that the pyridyl and phenyl rings compose relatively a large dihedral angle (θ in Table 1). This feature is observed only in the titled compound among the $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2 \cdot \text{X}$ series.

Crystal Structures of $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2 \cdot 4\text{MeNO}_2$. Variable-temperature single-crystal XRD analysis is also conducted using $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2 \cdot 4\text{MeNO}_2$ (Figure 3b and Tables 2 and S3 in the Supporting Information). A single crystal of $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2 \cdot 4\text{MeNO}_2$ was very prone to effloresce in ambient conditions so it must be coated with either liquid paraffin or petroleum jelly immediately after isolation from the mother liquid. The Fe–N distance and Σ parameter change gradually from 2.121 Å and 140.86° (at 243 K) to 1.954 Å and 90.00° (at 115 K), respectively (Table 2), suggesting an occurrence of SCO. The values at 243 K are slightly deviated from the average values of the $[\text{Fe}(\text{dpp})_2](\text{BF}_4)_2$ types of complexes in the HS state (2.14–2.20 Å^{3,5,13}

and 145–197°^{1d,14}), suggesting that the LS state would still remain even at the temperature. In contrast to $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2 \cdot \text{acetone}$, $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2 \cdot 4\text{MeNO}_2$ does not show the frozen-in effect (Table 2). The gradual thermal SCO and absence of the frozen-in effect imply that a cooperative effect is absent in the crystal system of $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2 \cdot 4\text{MeNO}_2$.

Crystal Structures of $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2 \cdot \text{X}$ (X = H₂O·3MeCN, 0.5Et₂O, 2PC). A single crystal of $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2 \cdot \text{H}_2\text{O} \cdot 3\text{MeCN}$ is also efflorescent under an ambient atmosphere. It includes three acetonitrile molecules and one water molecule as crystal solvents in the asymmetric unit (Figure 3c and Tables 3 and S4 in the Supporting Information). In this crystal system, the HS state is retained even at low temperatures such as 113 K: Its average Fe–N bond distance (2.164 Å) and Σ parameter (156.43°) at 113 K can be categorized to those of the HS species (Table 3).

The asymmetric unit of $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2 \cdot 0.5\text{Et}_2\text{O}$ consists of two independent $[\text{Fe}(E\text{-dpsp})_2]^{2+}$ units, four BF₄ anions, and one Et₂O molecule as a crystal solvent (Figure 3d and Tables 3 and S4 in the Supporting Information). The average Fe–N distance and Σ parameter at 113 K are 1.943 Å and 88.65° for the Fe1 unit and 1.939 Å and 85.62° for the Fe2 unit, respectively, indicating that both complex entities take the LS state (Table 3). The crystal structure at ambient temperature is not disclosed because of the low quality of the diffraction data.

The asymmetric unit of $[\text{Fe}(E\text{-dpsp})_2](\text{BF}_4)_2 \cdot 2\text{PC}$ comprises half of the $[\text{Fe}(E\text{-dpsp})_2]^{2+}$ moiety, one BF₄ anion, and one PC molecule as a crystal solvent (Figure 3e and Tables 3 and S4 in the Supporting Information). The iron atom is located at the crystallographic special position with an occupancy of 1/2. As shown in Table 3, the Fe–N distance and Σ parameter also reveal that the complex is in the LS state throughout 113–283 K (1.935 Å and 84.64° at 113 K and 1.933 Å and 85.49° at 283 K).

Elemental Analysis for Bulk Microcrystalline Samples.

The results of elemental analysis for $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{X}$ are assembled in Table 4. Those of $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{acetone}$ and $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot 2\text{PC}$ are in good agreement with the calculated values. In sharp contrast, those of $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot 4\text{MeNO}_2$ and $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{H}_2\text{O} \cdot 3\text{MeCN}$ substantially deviate from the values predicted from the composition formulas. This series of results is perfectly consistent with whether the crystal system is efflorescent or not. In combination with the results of elemental analysis, the collapse of the single crystals should be derived from the disengagement of the crystal-solvent molecules. We note that elemental analysis for $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot 0.5\text{Et}_2\text{O}$ could not be carried out because of the low production yield: Concomitant $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{H}_2\text{O} \cdot 3\text{MeCN}$ is the major product.

Magnetic Susceptibilities. Magnetic susceptibilities of $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{X}$ in the microcrystalline state were measured using a SQUID magnetometer. As expected from the results of single-crystal XRD and elemental analyses, their magnetic properties are significantly dependent on X. $\chi_{\text{M}}T$ - T plots for $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{acetone}$ are shown in Figure 4a, and those of other solvated complexes are collected in Figure 4b.

At 300 K, a bulk crystalline sample of $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{acetone}$ exhibits $\chi_{\text{M}}T$ of $3.7 \text{ cm}^3 \text{ K mol}^{-1}$, which is somewhat greater than the spin-only value for a HS Fe^{II} center ($3.0 \text{ cm}^3 \text{ K mol}^{-1}$). This discrepancy is derived from the

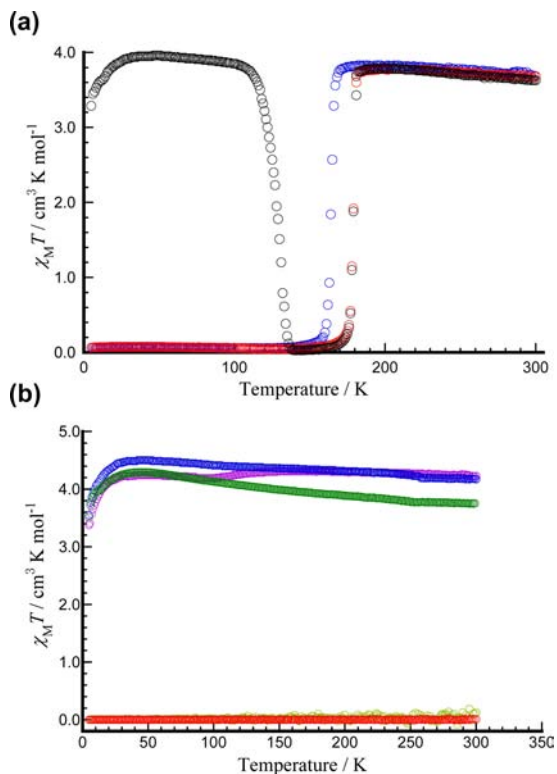


Figure 4. (a) $\chi_{\text{M}}T$ - T plots for $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{acetone}$. Blue circles: cooling process. Red circles: heating process. Black circles: “frozen” sample in the heating process. (b) $\chi_{\text{M}}T$ - T plots for $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{X}$ in the cooling process. Blue circles: X = 4MeNO_2 . Violet circles: X = 4MeNO_2 using a fresh sample. Green circles: X = $\text{H}_2\text{O} \cdot 3\text{MeCN}$. Yellow-green circles: X = $0.5\text{Et}_2\text{O}$. Red circles: X = 2PC .

presence of an orbital contribution to $\chi_{\text{M}}T$.¹⁵ When the sample is precipitously cooled to 80 K in a few seconds, it sustains the original $\chi_{\text{M}}T$ value ($3.9 \text{ cm}^3 \text{ K mol}^{-1}$). This behavior corresponds to the frozen-in effect and is consistent with single-crystal XRD analysis (Figure 3c). After further freezing to 5 K, the temperature is raised to 300 K (black circles in Figure 4a). In the early stage of the heating process, the $\chi_{\text{M}}T$ value increases because of the zero-field splitting of the HS species complex with a distorted octahedral coordination sphere. The subtle change reaches a plateau at around 30 K. Afterward, a rapid decrease in $\chi_{\text{M}}T$ appears at around 120 K, reaching $0.05 \text{ cm}^3 \text{ mol}^{-1}$ at 140 K. This stems from relaxation of the thermally trapped HS state to the LS state. A remaining fraction of the HS species at this temperature is estimated to be no more than 0.013. After relaxation, an abrupt increase of the $\chi_{\text{M}}T$ value takes place in a temperature range of 176–181 K. This corresponds to thermal SCO to the HS state with a $T_{1/21}$ of 179 K. Finally, the sample obeys the Curie law in 181–300 K, returning to the initial $\chi_{\text{M}}T$ of $3.7 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 K.

Upon cooling, $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{acetone}$ undergoes thermal SCO toward the LS state at a $T_{1/21}$ of 164 K (blue circles in Figure 4a); therefore, $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{acetone}$ features a 15 K hysteresis. A heating process, starting from the thermodynamically stabilized LS state at 5 K, traces the same track as the “frozen-in” sample, except for the range of 5–140 K, where the frozen HS fraction is alive (red circles in Figure 4a).

Bulk crystalline samples of $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot 0.5\text{Et}_2\text{O}$ and $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot 2\text{PC}$ are entirely diamagnetic in the temperature range of 5–300 K, revealing that these samples take the LS state (yellow-green and red circles of Figure 4b).

A bulk crystalline sample of $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot 4\text{MeNO}_2$ stored under an ambient atmosphere for a couple of days exhibits $\chi_{\text{M}}T$ of $4.2 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 K, indicative of the HS state. However, this value is too high even if the orbital contribution is taken into consideration. In addition, the $\chi_{\text{M}}T$ - T plot does not show a gradual thermal SCO implied in single-crystal XRD analysis (blue circles of Figure 4b): The sample retains the HS state throughout the whole temperature range. This series of discrepancies should stem from the efflorescence of the crystal structure of $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot 4\text{MeNO}_2$ and resultant liberation of nitromethane molecules. This idea is supported by the results of elemental analysis (Table 4) and also by an experiment as follows. A more “flesh” bulk crystalline sample of $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot 4\text{MeNO}_2$, which was separated from the mother liquid and introduced in a SQUID cavity within a few hours, undergoes incomplete thermal SCO (violet circles in Figure 4b). The fresh sample is expected to be more intact than the old one; however, we cannot determine the intact fraction quantitatively.

The $\chi_{\text{M}}T$ - T plot for $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{H}_2\text{O} \cdot 3\text{MeCN}$ suggests that the sample is in the HS state up to 5 K (green circles in Figure 4b). Upon first glance, the magnetic behavior is consistent with the results of single-crystal XRD analysis; however, we cannot answer to the question of whether the crystal lattice and crystal-solvent molecules are sustained or not during the measurement: In fact, elemental analysis suggests that a single crystal of $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{H}_2\text{O} \cdot 3\text{MeCN}$ collapses easily (Table 4).

DSC of $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{acetone}$. Heat capacity calorimetry is a convenient experimental tool to detect the existence of phase transitions. Here $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{acetone}$ was subjected to DSC (Figure 5 and Table

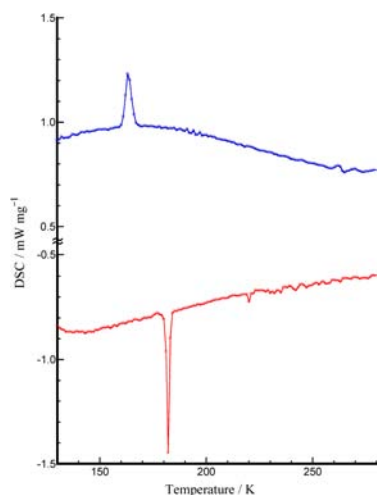


Figure 5. DSC chart of $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{acetone}$ in cooling (blue) and heating (red) processes at a rate of 5 K min^{-1} .

5). First, a bulk crystalline sample of $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{acetone}$ is cooled from 298 to 123 K at a rate of 5 K

Table 5. Transition Temperatures and Thermodynamic Parameters of $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{acetone}$

	$\Delta H/\text{kJ mol}^{-1}$	$\Delta S/\text{J K}^{-1} \text{ mol}^{-1}$	T_{T}^a	$T_{1/2}^b$
cooling	10.0	61.4	163	164
heating	11.0	60.3	182	179

^aTransition temperatures giving the peaks in DSC. ^b $T_{1/2\downarrow}$ and $T_{1/2\uparrow}$ given by the magnetic susceptibility measurement shown in Figure 4a.

min^{-1} . As depicted in Figure 5, an exothermic peak is found at 163 K with $\Delta H = 10.0 \text{ kJ mol}^{-1}$ and $\Delta S = 61.4 \text{ J K}^{-1} \text{ mol}^{-1}$. On the other hand, the backward heating process featured an endothermic peak at 182 K with $\Delta H = 11.0 \text{ kJ mol}^{-1}$ and $\Delta S = 60.3 \text{ J K}^{-1} \text{ mol}^{-1}$. These transition temperatures are in good agreement with $T_{1/2\downarrow}$ and $T_{1/2\uparrow}$ observed in the SQUID measurement (Table 5); therefore, the transitions in Figure 5 can be associated with the thermal SCO phenomenon. The thermodynamic parameters of $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{acetone}$ are comparable to those of the iron(II) SCO complexes reported thus far.^{3a} We note that the ΔS values are far greater than the ideal value for a conversion from the LS state to the HS state, $13.4 \text{ J K}^{-1} \text{ mol}^{-1}$. This fact suggests that the ΔS values involve substantial contributions from nonelectronic vibrations and lattice heat capacity.¹⁶

Correlation between the Magnetic Property and Intermolecular Interaction in the Crystal Lattice. The previous sections have revealed that $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{acetone}$ alone undergoes a profound thermal SCO phenomenon (an abrupt spin-state change with a thermal hysteresis and frozen-in effect). Hereafter a correlation between the magnetic property and intermolecular interaction is discussed. Figure 6 shows intermolecular packing structures of $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{X}$. All crystal systems lack interaction between the $[\text{Fe}(\text{E-dpsp})_2]^{2+}$ entity and solvent molecules. Similarly, that between $[\text{Fe}(\text{E-dpsp})_2]^{2+}$ and counteranions is found to be negligible.

On the other hand, interaction among $[\text{Fe}(\text{E-dpsp})_2]^{2+}$ themselves is found in $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{acetone}$ (Figure 7 and Table 6), whereas the other crystal systems possess no such interaction. One of the phenyl rings (C14–C19 in Figure

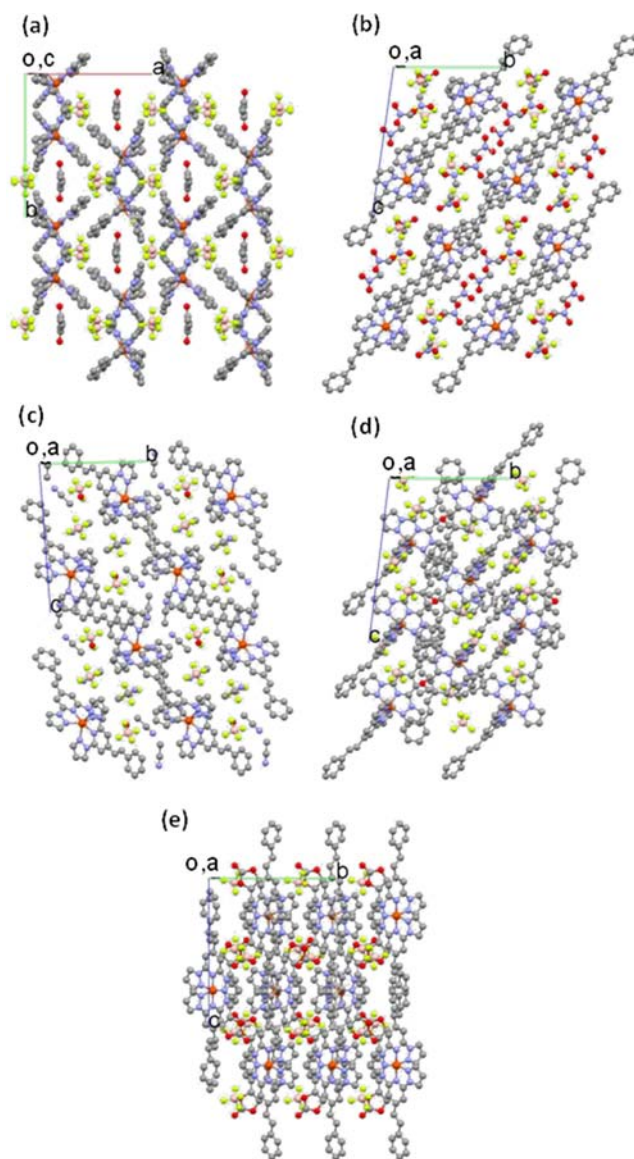


Figure 6. Intermolecular packing structures of $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{X}$ in single crystals: (a) $\text{X} = \text{acetone}$ at 150 K; (b) $\text{X} = 4\text{MeNO}_2$ at 113 K; (c) $\text{X} = \text{H}_2\text{O} \cdot 3\text{MeCN}$ at 113 K; (d) $\text{X} = 0.5\text{Et}_2\text{O}$ at 113 K; (e) $\text{X} = 2\text{PC}$ at 113 K. Color code: B, pink; C, gray; N, blue; O, red; F, yellow-green; Fe, orange. Hydrogen atoms are omitted. Part a is looking down upon the c axis, whereas the others are upon the a axis.

3a–c) plays a main role in the interaction. The phenyl group is twisted to avoid steric repulsion with one of the pyrazolyl rings (N6, N7, and C20–C22 in Figure 3a–c) of a nearby complex along the c axis throughout all temperature ranges. Despite the distortion, they still contact with each other to form an H–H short contact. The shortest distance between the hydrogen atoms of the two rings, H16 and H22, is $2.390\text{--}2.590 \text{ \AA}$ (Table 6). This interaction continues along the c axis of the crystal lattice, forming a one-dimensional network. The twisted phenyl ring also produces $\pi\text{--}\pi$ stacking with one of the pyrazolyl rings of another neighboring molecule (Figure 7 and Table 6). The $\pi\text{--}\pi$ interaction forms a dimeric pair of the $[\text{Fe}(\text{E-dpsp})_2]^{2+}$ entities. These two types of intermolecular interactions are expected to induce cooperative effects, leading to the profound thermal SCO phenomenon in $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{acetone}$.

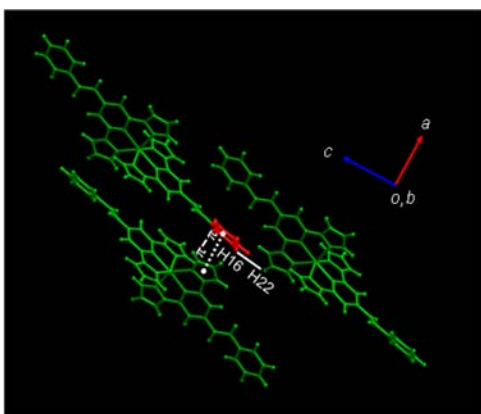


Figure 7. Intermolecular H–H contact and π – π interaction in a single crystal of $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{acetone}$. The key phenyl ring (C14–C19) is highlighted in red. Counteranions and solvent molecules are omitted for clarity.

Table 6. Short contact distances and noncovalent interactions in $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{acetone}$

temp/K	short contact distance between H16 and H22/Å	π – π interaction	
		distance ^a /Å	dihedral angle ^b /deg
240(2)	2.390	3.480	31.12
190(2)	2.376	3.434	30.39
175(2)	2.582	3.372	29.74
150(2)	2.590	3.373	28.81

^aBetween C18 and C21, corresponding to the shortest distance between the phenyl group (C14–C19) and pyrazolyl group (N6, N7, and C20–C22). ^bBetween the phenyl and pyrazolyl groups.

CONCLUSIONS

We clarified the crystal structures and thermal SCO behavior of $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{X}$. The iron(II) complex was very likely to include crystal solvents, affording various kinds of single crystals. Single crystals of $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{acetone}$, $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot 4\text{MeNO}_2$, $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{H}_2\text{O} \cdot 3\text{MeCN}$, $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot 0.5\text{Et}_2\text{O}$, and $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot 2\text{PC}$ were investigated by means of XRD analysis. Especially as to $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{acetone}$ and $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot 4\text{MeNO}_2$, crystal structures at various temperatures spanning 110–240 K were analyzed. Bulk microcrystalline samples were investigated using a SQUID magnetometer to disclose that their magnetic properties changed drastically by the crystal solvents. Their spin states were consistent with those predicted from the average Fe–N length and Σ parameter in the crystal structures, except for $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot 4\text{MeNO}_2$, the crystal lattice of which proved to be effluorescent. A noteworthy magnetic feature was observed in $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{acetone}$. This sample underwent abrupt thermal SCO with hysteresis ($T_{1/2\uparrow} = 179$ K, $T_{1/2\downarrow} = 164$ K, and $\Delta T_{1/2} = 15$ K) and frozen-in effect. One of the phenyl rings in $[\text{Fe}(\text{E-dpsp})_2](\text{BF}_4)_2 \cdot \text{acetone}$ adopted a twisted configuration and experienced a H–H short contact with one of the neighboring complex molecules to form a one-dimensional network along the c axis of the crystal lattice. The twisted phenyl ring also featured π – π stacking with the pyrazolyl ring of another neighboring complex cation, resulting in a dimeric pair of $[\text{Fe}(\text{E-dpsp})_2]^{2+}$ entities. These

intermolecular interactions would trigger cooperative effects, which led to the peculiar thermal SCO phenomenon.

ASSOCIATED CONTENT

Supporting Information

Crystallographic parameters for single-crystal XRD analysis (Tables S1–S4) and CIF files (CCDC 811071 and 911427–911443). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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