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# Ligand field and intermolecular interactions tuning the magnetic properties of spin-crossover Fe(II) polymer with 4,4′-bipyridine

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ABSTRACT

A new spin crossover coordination polymer (SCO-CPs) of Fe(II)-4,4′-bipyridine (4,4′-bipy) family: {Fe(4,4′-bipy)$_2$(H$_2$O)$_2$}·(4,4′-bipy)· 8(H$_2$O)·2(ClO$_4$) (**3**), which displays half spin transitions between 100 and 300 K, has been synthesized and structurally characterized. Compound **3** featured with two-dimensional (2-D) grids connected by hydrogen bonds and $\pi\ldots\pi$ packing between one-dimensional (1-D) chains, the 2-D grids expand to three-dimensional (3-D) architecture supported by a "S-shaped holder" involving lattice 4-4′-bipy, water molecules and perchlorate anion. We compared **3** with the other two analogous complexes: ({Fe(4,4′-bipy)(H$_2$O)$_2$ (NCS)$_2$}·4,4′-bipy, **1** and {Fe(4,4′-bipy)$_2$(NCS)$_2$}·mSolv, **2**) through Hirshfeld surfaces analysis, which revealed that the low ligand field strength (NCS$^-$) and lone-pair…H contacts contribute to the stabilization of HS (high-spin) state of the Fe(II) ion, while the high ligand field strength (4,4′-bipy) and strong intermolecular contacts (hydrogen bonds and $\pi\ldots\pi$ packing interactions) make for the LS (low-spin) state.



## 1. Introduction

The design and characterization of the six-coordinated iron(II) complexes that show spin-crossover (SCO) properties remains one of the most spectacular questions in the field of magnetic materials chemistry due to their molecular bi-stability and potential applications for the development of display and memory devices, electrical and electroluminescent devices, MRI contrast agents, switchable liquid crystals, and so on [1–5]. The phenomenon of transitions between high-spin (HS) and low-spin (LS) electronic states have been extensively studied during a few past decades and the results have been summarized in several reviews [6]. The pronounced SCO properties were related to cooperative interactions (hydrogen-bonding, $\pi\ldots\pi$ stacking, *van der Waals* contacts) between the active metal ions in the crystal [7]. An effectively approach to explore these interactions is the self-assembly of spin changing centre with suitable bridging ligands into extended one-, two-, and three -dimensional (1D, 2D, 3D) spin crossover coordination polymers (SCO-CPs). Since the first reported two series of 1D triazole-based complexes of SCO-CPs [8], a large number of 1D, 2D and 3D SCO-CPs based on triazoles, tetrazoles and pyridine-like bridging ligands combined with anionic bridges (cyanom etallates, dicyanamide, and polynitriles) have been reported [9,10].

Among the pyridine-like bridging ligands, the well-known bis-mono-dentate building block 4,4′-bipyridine has been widely used as an ancillary bridging ligands for the synthesis of a variety of Fe(II) SCO compounds ranging from discrete binuclear to 1D, 2D, and 3D coordination polymers [11]. These reported 1D SCO-CPs bridged by 4,4′-bipyridine can be generically formulated as {Fe(4,4′-bipy)(*L*)*n*}·mSolv (*L*=quadridentate, *n*=1; *L*=bidentate, *n*=2 and *L*=monodentate, *n*=4) [11]. While 2D SCO-CPs bridged by 4,4′-bipyridine usually formulated as {Fe(4,4′-bipy)$_2$(*L*)$_2$}·mSolv (*L*=monodentate) [12]. For example, Real [11a] and co-workers have synthesized a 1D compound {Fe(4,4′-bipy)(H$_2$O)$_2$(NCS)$_2$}·4,4′-bipy (**1**), where, the 1D chains held together by strong hydrogen bonds between the guest bi-pyridine ligands and the coordinated water molecules, which giving a 2D supramolecular array. Latter, they substituted the water molecules in **1** by nitrogen-donor bidentate ligand 2,2′-bithiazoline (bt), and obtained another 1D SCO-CP {Fe(4,4′-bipy)(bt)(NCS)$_2$} [11b], which undergo 12% HS–LS transition. Real and co-workers further heated the complex **1** at about 110 °C, which resulting the concerted loss of the coordinated water molecules and the coordination of the uncoordinated guest bi-pyridine molecules, and affording a 2D coordination polymer with stoichiometry {Fe(4,4′-bipy)$_2$(NCS)$_2$} (**2**). Compound **2** featured infinite 2D (4,4) iron-bi-pyridine grids, which act as excellent solvent host, Real. et al. have introduced nine different solvent molecules into this 2D grids, and have obtained eight HS (**2**$_{1–8}$) host–guest complexes [12b]: **2**·2(trichloroethene) (**2**$_1$), **2**·2(toluene) (**2**$_2$), **2**·2(nitrobenzene) (**2**$_3$), **2**·2(ether) (**2**$_4$), **2**·4(acetone) (**2**$_5$), **2**·3(CS$_2$) (**2**$_6$), **2**·3(methanol)

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($\mathbf{2}_7$), $\mathbf{2}\cdot 2$(nitromethane · methanol) ($\mathbf{2}_8$) and a spin-crossover host–guest complex $\mathbf{2}\cdot 4(CHCl_3)$ ($\mathbf{2}_9$). [12c] $\mathbf{2}_9$ displays complete two steps SCO transitions attribute to cooperative interactions between the iron-bi-pyridine grids and $CHCl_3$ molecules. From the viewpoint of crystal engineering, we substituted the $NCS^-$ anions in **2** by water molecules, and we obtained a new 1D SCO-CP $\{Fe(4,4'\text{-bipy})_2(H_2O)_2\}\cdot(4,4'\text{-bipy})\cdot 4(H_2O)\cdot 2(ClO_4)$ (**3**). The connecting motif around the iron(II) centre of complexes **1–3** were shown in Scheme 1. The 1D chain in **3** held together by strong hydrogen bonds and $\pi\ldots\pi$ packing interactions between the coordinated bi-pyridine ligands and water molecules into 2D grids, the 2D grids further expand to 3D architecture supported by a "S-shaped holder" composed of guest 4-4′-bipy, water and perchlorate anions. The "S-shaped holder" display efficient cooperative interactions with the 2D iron-bi-pyridine grids, which may play a key role for the half SCO transition of **3**. We further studied the magnetic properties of **3** and compared the intermolecular interactions of with **1** and $\mathbf{2}_{1-9}$ through Hirshfeld surfaces analysis [13–15].

## 2. Results and discussions

### 2.1. Crystal structures

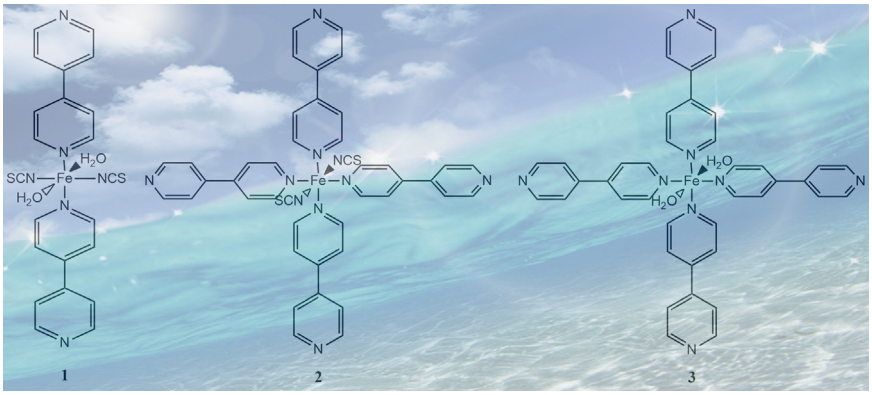
The basic structures of complexes **1**–**3** were shown in Fig. 1, the selected bond distances and angles around the octahedron centre of complexes **1**,$\mathbf{2}_9$ (we choose complex $\mathbf{2}_9$ for the structural description of **2** series for the reason that it undergoes SCO transition) and **3** were tabulated in Table 1 and hydrogen bonds interactions were tabulated in Table 2. Complex **3** crystallizes in the monoclinic (*C*2/*c*) space group (Table S1), the basic unit of it composed of a $\{Fe(4,4'\text{-bipy})_4(H_2O)_2\}^{2+}$ complex cation, two uncoordinated $ClO_4^-$ anions, four uncoordinated water molecules and one uncoordinated 4,4′-bipy (Scheme 1). For the complex cation, two of the 4,4′-bipy ligands serves as a bridge ligand connecting the adjacent ions forming a linear chain and the other two are terminal ones which are mono-coordinated to the iron together with two water molecules. The coordination of Fe is thus $FeN_4O_2$. The 1D linear chain structure of the complex cation along *a*-axis was shown in Fig. 1, the Fe–N distances for the bridged and mono-coordinated ligand are 2.29, 2.25 and 2.22 Å for N1, N2 and N3, respectively (Table 1), the value of which is similar with **1** and **2**, and is typical of HS Fe(II) centres. The Fe–O distance is 2.08 Å, which is much shorter than that in **1** (2.12 (5) Å). All the N–Fe–N and N–Fe–O angles are in the range of 87.83–92.17°, which is also typical coordination geometry for HS Fe(II) centres. The distortion parameter $\sum$ [15] for the coordination octahedron in **3** is 40°, which is similar with $\mathbf{2}_9$ (38.5° for Fe2, the Fe2 atom at 120 K is in HS state while Fe1 is in LS state. So, we compared the geometry of around Fe2 with complex **3**) and much smaller than **1** (52.6°), and indicting that **3** may undergo SCO transition.

It is noteworthy that the double-coordinated and single-coordinated 4,4′-bipy have different level of distortion, and the guest 4,4′-bipy are co-planar in complex **3**, which may attribute to the strong intermolecular interactions. The angle between the pyridine rings containing the atoms N1 and N2, N3 and N4 being 28.987 (2 2 1)° and 7.684 (1 5 1)°, respectively. While the angle between adjacent 4,4′-bipys containing the atoms N1 and N2 in the 1D linear chain is 79.181 (1 1 5)°, which is larger than that in **2**. The adjacent 1D linear chains in **3** then connected *via* strong O–H···N hydrogen bonds (O–N distance of 2.743 Å) interactions between the mono-coordinated 4,4′-bipy ligands and coordinated water molecules into 2D layer structure (Figs. 1–3). It is noticeable that the 4,4′-bipy ligands between the adjacent chains are nearly parallel to each other by $\pi\ldots\pi$ interactions with plane separation of 3.674 Å. The Fe…Fe distances through bridged and mono-coordinated 4,4′-bipy ligands are 11.648(5) and 12.483(5) Å, respectively. The value of which within one linear chain is a little longer than that in **1** and **2**, while the distance between adjacent chains is much shorter than in **1** while a little longer than in **2**. These distances may have a close relationship with the magnetic properties, the closer distances between adjacent 1D linear chains contribute to the cooperative between active iron(II) center.

There are eight uncoordinated water molecules (O6, O7, O8 and O9), two perchlorate anions and one uncoordinated 4,4′-bipy (N7) in the lattice of 3 (Figs. 2 and 3), which form an "*S*-shaped holder" bridged by O–H···O and O–H···N hydrogen bonds contacts (O–O distances are of 2.83(5), 2.73(10) and 2.81(5) Å, O–N distance of 2.773(15) Å). The "*S*-shaped holder" connects to the $\{Fe(4,4'\text{-bipy})_4(H_2O)_2\}^{2+}$ complex cation through O–H···O hydrogen bonds interaction (O–O distances are of 2.651(11) Å) between uncoordinated water O6 and coordinated O1, and $\pi\ldots\pi$ packing interactions (plane…plane separation 3.830 Å) between coordinated and uncoordinated 4,4′-bipy (Fig. 2a). For the "*S*-shaped holder", the uncoordinated water molecules and perchlorate anions are distributed symmetrically on the two ends of the uncoordinated 4,4′-bipy molecule (Fig. 2b). Every "*S*-shaped holder" binds to two different coordinated water molecules in adjacent 2D layers, connecting the structures into 3D architecture (Fig. 3) with $\pi\ldots\pi$ packing interactions (plane…plane separation 3.830 and 3.758 Å). It is the "*S*-shaped holder" that plays a key role for the stabilization of the 3D architecture and SCO transition.

### 2.2. Magnetic properties

Shown in Fig. 4 was the temperature dependent magnetic profiles of complexes **1** [11b] $\mathbf{2}_9$ [12c] and **3**. The magnetic properties of complexes $\mathbf{2}_{1-8}$ were all in HS state (paramagnetic),




**Scheme 1.** Molecular structures of one iron(II) centre for complexes **1**, **2** and **3**.