

Electronic Supplementary Information

Synthesis and size-dependent spin crossover of the coordination polymer $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)^\dagger$

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1 Introduction

Introduction to spin crossover

The phenomenon of spin crossover was observed for the first time in 1931 by Cambi and his co-workers in N,N'-substituted tris (dithiocarbomates) Fe(III) compound L. Cambi [1931]Real et al. [2005]. Pauling initially attributed their results to a change in the bond type from covalent to ionic Coryell et al. [1937]. However, it was Orgel who was able to explain the phenomenon on the basis of change in the spin state of the ion Orgel [1956]. During the 1950s the development in the field of ligand field theory (which was originally given in 1930s by an American physicist John Hasbrouck Van Vleck) and the discovery of Mössbauer effect (Nobel prize in Physics in 1961 to Robert Hofstadter and R.L.Mössbauer) further enhanced the research in this field Boukheddaden [1992].

In 1964, Baker and Bobonich found an unusual cooperative behaviour observed for the

complexes $[\text{Fe}(\text{phen})_2(\text{NCX})_2]$ ($\text{X} = \text{S}, \text{Se}$) and $[\text{Fe}(\text{bipy})_2(\text{NCS})_2]$. This marked the first ever reported spin crossover system in iron (II) complex Long and Baker [1971]. Later, the hypothesis associated with a spin transition between the $S = 0$ and 2 spin states of iron(II) was proposed by Konig and Madeja based on detailed magnetic and Mössbauer spectroscopic studies Koenig and Madeja [1967]. Barefield, Busch, Nelson and also Sacconi reviewed in depth and extended the work in other transition metal ions including iron, cobalt and nickel complexes having interesting results and anomalous magnetic moments Barefield et al. [1968], Sacconi [1971].

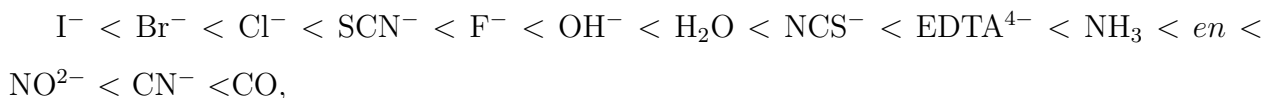
In the last two decades, there was an increasing research interest in this field due to molecular bistability Gutlich P. [2004] of the compounds and their utilisation in molecular switches, information storage and various other potential applications Halcrow [2013], Bousseksou et al. [2011].

Several studies were carried out to characterise the spectroscopic, magnetic, structural and dynamic properties of Fe(II) complexes with different ligands, aiming at identifying the parameters that are crucial in determining potential applications of these complexes. All of these studies were comprehensively discussed and collected in three volumes published in 2004 that were dedicated to spin crossover complexes Gutlich P. [2004]. The fascinating fact from these studies is that several electronic and structural properties are common to nearly all Fe(II)-based spin crossover complexes.

In a perfect octahedral coordination geometry, the five “ d ” orbitals of a transition metal ion are split into a subset of three orbitals, namely d_{xy} , d_{yz} and d_{zx} , which are basis to the irreducible representation t_{2g} , and a subset of two orbitals, namely d_{z^2} and $d_{x^2-y^2}$, which are basis to the irreducible representation e_g . The t_{2g} orbitals are non-bonding and are therefore at lower energy than the anti-bonding e_g orbitals. The splitting between the two sets is referred to as ligand field splitting and is symbolized by the parameter of the ligand field strength Shriver and Atkins [1999].

In the case of octahedral complexes, the ligand approaches along the axis (the lobes of e_g orbitals are along the axis) as a consequence, the energy is raised, whereas t_{2g} lobes are present between the axes so they experience less repulsive force and hence, their energy is lower. This splitting of the d orbital into t_{2g} and e_g sets in the presence of an octahedral

ligand field provides the possibility for octahedral coordination compounds to exhibit dual nature i.e. the tendency to exist in low spin (LS) state or high spin (HS) state. The nature of the ligands plays an important role in determining the spin state of the complex. The ligand can be strong or weak according to the spectrochemical series:



The stronger the ligand is, the larger the magnitude of ligand-field splitting gets. The ligand-field splitting energy relative to the spin pairing energy determines whether the complex can exist in HS or LS Tanabe and Sugano [1954]:Sorai and Seki [1974]. When strong-field ligands are coordinated to the metal ion, LS is the ground state. In the case of octahedral ligand geometry, electrons fill the t_{2g} set first and then occupy the e_g set. In the case of weak field ligands, HS is the ground state where the d orbitals are occupied by electrons according to Hund's rule of maximum multiplicity, thus both t_{2g} and e_g sets can be partially occupied. When the external factors such as temperature, pressure or light irradiation are applied, the spin state of a metal complex can switch between LS and HS state, referred to as spin crossover.

Polymeric Structure of $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$

The lattice structure of $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ at the LS spin state was taken from the Cambridge Crystallographic Data Centre (CCDC)-900726 Grosjean et al. [2013].

Thermochromism

The spin crossover in $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ is accompanied by the colour change from purple in LS at room temperature to white in HS at a temperature above 100°C as shown in Video 1.

Materials

All the chemicals, Iron(II) tetrafluoroborate hexahydrate $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, 99%, Aldrich), 1H-1,2,4-triazole (99%, Alfa Aesar), and Methanol (99.9 %, Merck), were used as received without

further purification.

Synthesis at higher precursor concentrations

With increase in concentration the quality with regard to size homogeneity degrades. At $C=0.5\text{M}$ or higher no large crystals were grown, as shown in Fig. S1.

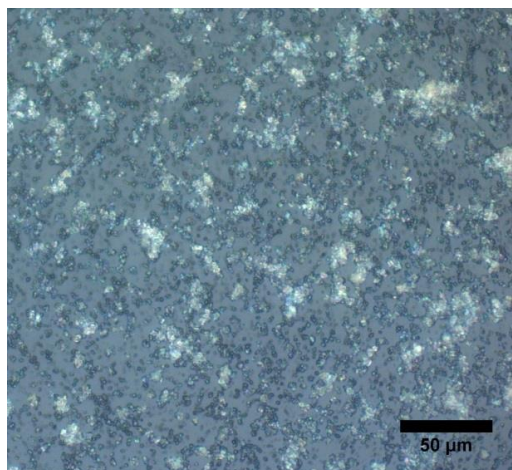


Figure S1: Optical micrograph of $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ crystals synthesized in water at 45°C with a $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ concentration of 0.5M .

Powder X-ray diffraction analysis

Rietveld refinement was done using the Full Prof Suite program with the Pseudo-Voigt profile function for the well-crystalline (Crystal) $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ and the Thompson-Cox-Hastings pseudo-Voigt Axial divergence asymmetry profile function for the least-crystalline (Powder) $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$. See the results in Fig. S2, S3 and the corresponding parameters in Table S1. The initial lattice parameters and the required information for the refinement procedure was taken from the LS state crystallographic information file (cif) CCDC-900726 Grosjean et al. [2013]

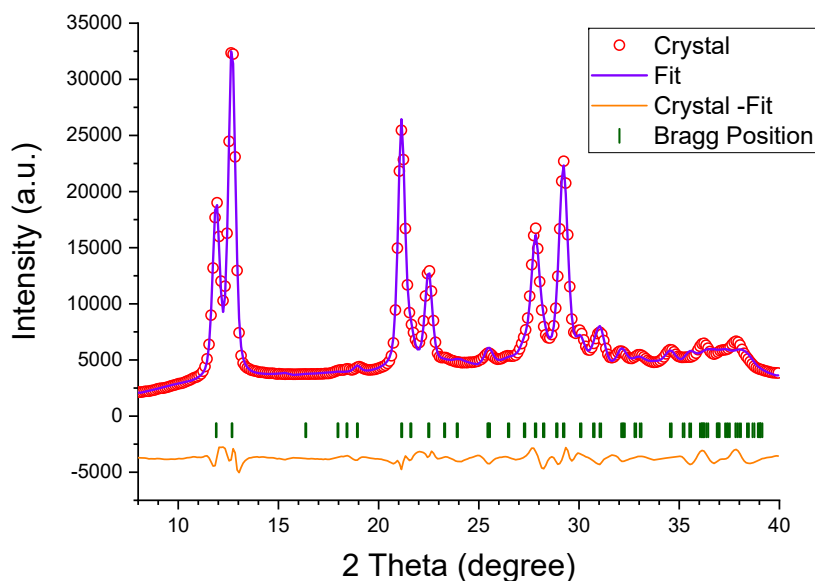


Figure S2: Powder X-ray diffraction profile of the well-crystalline (Crystal) $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ and the best-fit after Rietveld refinement.

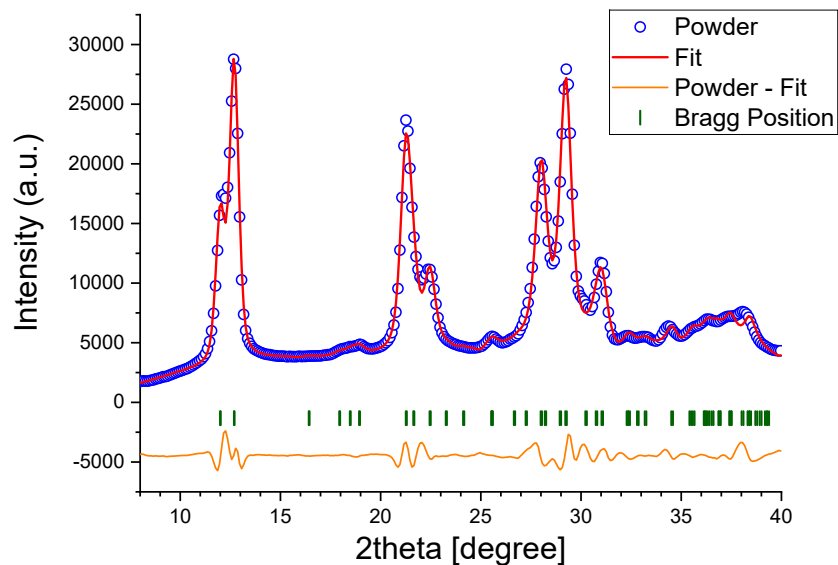


Figure S3: Powder X-ray diffraction profile of well-crystalline (Crystal) $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ and the best-fit after Rietveld refinement.

	Crystal	Powder
Crystal system	orthorhombic	orthorhombic
Space group	P n m a	P n m a
Temperature (K)	300	300
a (Å)	17.283865	17.129097
b (Å)	7.343238	7.346150
c (Å)	9.180679	9.192760
Wavelength, Cobalt K_α (Å)	1.789	1.789
2 Θ Angular range (°)	8-40	8-40
Rwp (%)	9.21	8.74
Rp (%)	9.03	7.85

Table S1: Lattice parameters obtained after Rietveld refinement.

Spectroelectrochemistry

Raman spectroscopy (using Horiba Jobin Yvon, LabRAM HR800 with an excitation wavelength of 514.5nm) and electrochemistry (using PGSTAT 204 with Nova 2.1 software by Metrohm autolab) were combined in order to characterise changes in lattice structure upon redox reactions of $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$.

In our setup, a silver-silver chloride (Ag/AgCl) and platinum (Pt) wires were used as reference electrode (RE) and counter electrode (CE), respectively. The electrolyte used was 0.2M acetonitrile (methyl cyanide CH_3CN) solution of lithium perchlorate LiClO_4 . The powder sample that was prepared in methanol was drop-casted on a Pt wire used as working electrode (WE). A electrochemical cell with an quartz optical window was used for spectroelectrochemistry. The Raman spectra in Fig. S4 were recorded first at 0 V and then at 1.2 V. No change was observed in the spectrum upon biasing. This demonstrates that the spin transition is not induced by electrochemical doping.

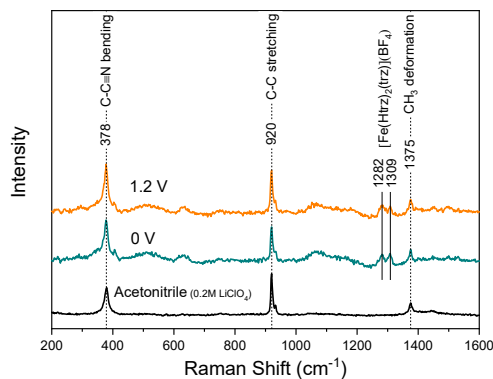


Figure S4: Raman spectra of the $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ film biased at 0 V and 1.2 V in 0.2M acetonitrile solution of lithium perchlorate LiClO_4 , measured at a laser wavelength of $\lambda=514.5$ nm.

Current-voltage characteristics

The I-V characteristics recorded at 300 K, 330 K and 400 K showed a non-linear behaviour.

See Fig. S5

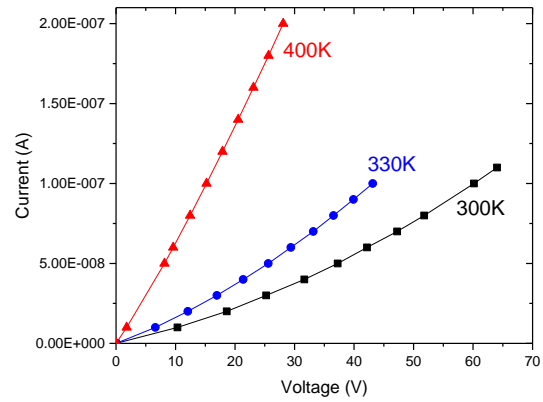


Figure S5: The Current-Voltage characteristics of the sample recorded at three different temperatures.

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