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A Chiral Spin Crossover Metal-Organic Framework

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A chiral metal-organic framework exhibiting spin crossover (SCO) property, [Fe^{II}(mptpy)₂·EtOH·0.2DMF (1-solv), has been solvothermally synthesized through spontaneous resolution. It displays remarkable stability and two-step SCO under ($T_{c1} = 200$ K) and above ($T_{c2} = 357$ K) room temperature.

As a consequence of the splitting of the energy of the d orbitals into t_{2g} and e_g sets in octahedral field, metal ions with configuration d^4 to d^7 , particularly the Fe^{II} ion, can undergo SCO if appropriate ligand field strength is afforded. The switching between the high-spin (HS) and low-spin (LS) states may be driven by external stimuli such as temperature, pressure, light and magnetic field, resulting in alterable chemical and physical properties and thus offering potential applications as molecular switches, molecular sensors, data storage and display devices.^{1, 2} Furthermore, developing SCO materials exhibiting multi-step spin transition around room temperature, which enables a larger information storage capacity, would be of great interest towards application.

Particularly, the synthesis of new multi-functional materials is one of the most important trends in the SCO field, in which the SCO properties may be combined with other physical or chemical properties, such as magnetic coupling, liquid crystalline properties, non-linear optical properties and electrical conductivity.³ In order to obtain novel magneto-optical materials, integrating chirality into SCO complexes would be a promising strategy. With conventional achiral optical recording media based on photochromic SCO compounds, the already stored data can be erased when the compounds are exposed to the light used to read the data by UV/Vis spectroscopy (destructive readout). The chiral SCO materials can provide nondestructive readout property by using an optical rotation measurement.^{4a} Although several combination of SCO cation with anionic chiral magnetic framework⁴, chiral mononuclear SCO complexes⁵ and a

cyanide-bridged [CoFe] chain^{3b} have been investigated, 2D or 3D SCO materials with chirality which always possess higher stability are rare until now. A recent breakthrough was achieved by Ohkoshi et al. in a chiral structured iron-octacyanoniobate where photomagnetism and chiral structure are coupled.^{3c}

With the aim to explore multi-dimensional SCO system with chirality and higher critical temperature, we elaborately chose 3-methyl-2-(5-(4-(pyridin-4-yl)phenyl)-4H-1,2,4-triazol-3-yl)pyridine (Hmptpy) as the ligand to coordinate with Fe^{II} ion. Hmptpy can be viewed as a lengthened analogue of 3-(2-pyridyl)-5-(4-pyridyl)-1,2,4-triazolate which was demonstrated previously as an appropriate ligand to construct highly stable SCO-MOFs.⁶ It is expected an additional benzene ring could enhance intermolecular interaction without disturbing ligand field strength and coordination behaviour a lot. Moreover, this kind of asymmetric ligands has rich coordination modes, in particular, chiral ones (Scheme S1) that may result in optical active SCO materials, which makes it more fascinating.

Crystals of 1-solv (Figure 1) were synthesized by reacting Hmptpy and FeCl₂·4H₂O in the mixture of EtOH and DMF at 160°C. Single crystals of 1-solv crystallize in chiral space group (either $P3_112$, 1-P or $P3_212$, 1-M) through spontaneous resolution, while the bulk sample is a racemic mixture. Each asymmetric unit contains half of the formula and the coordination environments of the Fe atoms have either Δ (1-P) or Λ (1-M) form (inset of Figure 2a). Each Fe^{II} ion is *cis* coordinated to six N atoms from four μ -mptpy ligands and is further connected to four other Fe^{II} ions, thus forming a 4-connected 3D network. Topologically, every Fe^{II} ion can be seen as a four-connected node and every mptpy ligand acts as a linker. The 3D framework is characteristic of quartz (*qtz*) net topology with Fe point symbol of $6^4.8^2.7$. In contrast to the silica prototype, 1-solv also contains a 3-fold screw axis in the *c* direction and the Fe^{II} ions running along this axis produce a right-handed helix in 1-P (or a left-handed helix in 1-M). The six helices are put together by sharing Fe^{II} ions. A consequence

of lengthening the Si-O-Si connections by the replacement with Fe-mptpy-Fe is that there is room for the interpenetration of three identical but independent nets. The three nets are related to each other by a rotation along the threefold c axis of 120° and they all have the same handedness. In spite of the interpenetration there are still voids along the c axis that accommodate disordered guests. These guests cannot be refined well in our crystallographic analysis, but can be determined by thermogravimetric-mass spectroscopy and elemental analysis as 1 EtOH and 0.2 DMF (Figure S1).

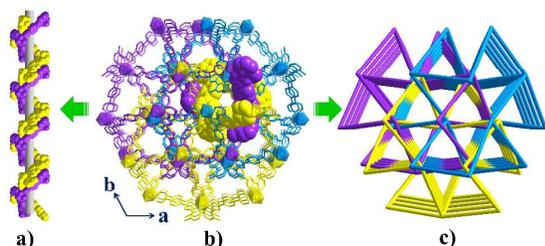


Figure 1 a) The 3_1 helical chains (1-P) viewing from a-axis. b) The 3-fold interpenetrated structure in 1-P with a hexagonal helical channel along the c -axis highlighted (H atoms and guests are omitted for clarity). c) The 3D framework of 1-P possessing the qtz net topology.

The occurrence of SCO was detected by comparing structural features of 1-P as a representative at 150 K, 293 K and 373 K (Table S1). The effective indicators, octahedral distortion parameter Σ and variation of $\text{Fe-N}_{\text{average}}$, are listed in Table S2. The $\text{Fe-N}_{\text{average}}$ bond length of 2.021 Å at 150 K denotes most Fe^{II} are in the LS states. Upon warming to 293 K, the bond length increases to 2.077 Å. While at 373 K, the value showed sizable increase to 2.165 Å, indicating that most Fe^{II} are in the HS states.

In order to confirm the supramolecular enantiomeric nature of 1-solv, both individual crystals and bulk samples were characterized with solid-state circular dichroism (CD) spectra in KCl pellets (Figure 2a and S2). The signal of bulk samples is hardly recognized, while obvious cotton effects are observed for individual crystals, showing two positive peaks at 299 nm and 536 nm, as well as three negative peaks at 355 nm, 405 nm and 610 nm for 1-P. Opposite signals at the same wavelengths for 1-M are observed too, indicating the spontaneous resolution process. As for the framework's stability, TG analysis shows no occurrence of decomposition until 735 K except weight loss of guests (6.7%) centred at 432 K while the variable temperature powder X-ray diffraction patterns (Figure S3) reveal that its framework remains unaltered at least to 653 K which is the upper limit of experimental condition.

The magnetic susceptibilities of both the as-synthesized sample 1-solv and the desolvated sample 1 were measured in an applied field of 2000 Oe. The results are shown in Figure 2b in the form of $\chi_M T$ versus T plots, showing the occurrence of two-step SCO behaviour ($T_{c1} = 200$ K, $T_{c2} = 357$ K) without thermal hysteresis. The measurement for 1-solv was carried out below 390 K in order to avoid the escape of solvent. The $\chi_M T$ value at 390 K is 3.19 $\text{emu mol}^{-1} \text{K}$, indicating that most Fe^{II} ions are in the HS state. Upon cooling, the $\chi_M T$ value continuously

decreases and then reaches a pseudo-plateau between 310 K and 270 K, with a value of about 1.75 $\text{emu mol}^{-1} \text{K}$, which is expected for an approximately 50% distribution of the HS and LS states (intermediate state, IP). With further decrease of the temperature, the $\chi_M T$ value decreases to a minimum value below 80 K of approximately 0.2 $\text{emu mol}^{-1} \text{K}$, implying the completion of SCO. Such behaviour is consistent with the variable-temperature Raman spectra in which the peak at 1223 cm^{-1} exhibits blue shift to 1233 cm^{-1} upon heating rather than the ordinary red shift due to the lattice expansion (inset of Figure 2b, Figure S5). The desolvated sample, 1, shows highly similar SCO behaviour to 1-solv with the $\chi_M T$ value reaching 3.54 $\text{emu mol}^{-1} \text{K}$ at 480 K, demonstrating that almost all Fe^{II} ions are in the HS state.

The two-step SCO nature of this 3D framework presents a case with crystallographically equivalent metal centers undergo stepped SCO.⁸ One possibility for this phenomenon is symmetry breaking in the IP phase (long range order).^{8d} But no crystallographic evidence for such an event was observed. While the evidence for symmetry breaking can be very subtle that it is not always possible to detect a symmetry breaking phase transition using a standard laboratory X-ray diffraction setup, thus, this type of transition cannot be eliminated here. The other possibility is random arrangement of HS and LS irons at IP states.^{8e} As the crystal data at 293 K show no distinct changes compared to those at 373 K and 150 K, variable temperature RAMAN experiment was undertaken to find some message.⁹ Apparent discontinuities are observed from 80 K to 390 K (Figure S5), indicating that a synergetic structural rearrangement of the whole lattice may be responsible.

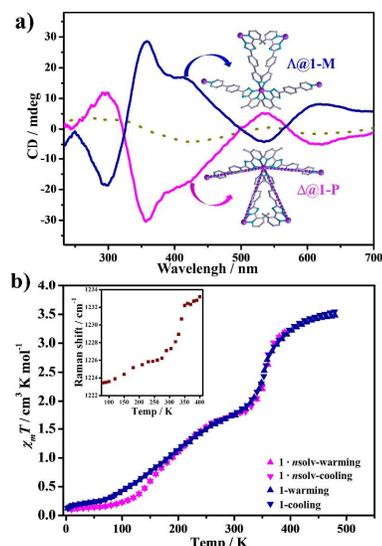


Figure 2 a) Bulk samples and single-crystal CD spectra. 1-M (navy), 1-P (magenta) and bulk samples (dark yellow); inset: Ball and stick drawing of the coordination environments of the Fe atoms and Hmptpy ligand in 1-solv (H atoms are omitted for clarity). Color code: Fe^{II} , pink; N, blue; C, grey. b) $\chi_M T$ vs. T for 1-solv and 1; inset: Blue shift at 1222 cm^{-1} vs. T obtained from variable Raman spectra.

In differential scanning calorimetry (DSC) measurement, the sample of 1-solv was first heated from 300 K to 720 K (Figure S4). It gives two peaks centred at 358 K and 445 K ($\Delta H_1 = 10.5$ kJ mol^{-1} , $\Delta S_1 = 29.1$ $\text{J K}^{-1} \text{mol}^{-1}$; $\Delta H_2 = 37.6$ kJ mol^{-1} ,

$\Delta S_2 = 84.5 \text{ J K}^{-1} \text{ mol}^{-1}$), corresponding to the second step transition and the loss of guest molecules respectively. The subsequent measurement upon cooling and the second circle of heating and cooling represent only the spin transition for **1**.

In order to get a deeper insight into the spin state and the corresponding transition process, the ^{57}Fe Mössbauer spectra of **1**-solv were recorded at 60 K, 300 K, and 400 K (Figure 3, Table S3). At 60 K, the spectrum can be fitted with one doublet ($\delta = 0.46$ and $\Delta E_Q = 0.83 \text{ mm s}^{-1}$, where δ is the isomer shift and ΔE_Q the quadrupole splitting), the hyperfine parameters values of which being characteristic for a single LS Fe^{II} site. Upon warming, the 300 K Mössbauer spectrum (i.e., at a temperature in the plateau) shows emergence of an additional doublet corresponding to HS Fe^{II} sites, implying that about half (45%) of the iron centres have undergone the LS \rightarrow HS transition (LS Fe^{II} : $\delta = 0.42$, $\Delta E_Q = 0.93 \text{ mm s}^{-1}$; HS Fe^{II} : $\delta = 0.93$, $\Delta E_Q = 2.04 \text{ mm s}^{-1}$). On warming to 400 K, most Fe^{II} sites accomplish spin transition, however, some LS Fe^{II} sites were still observed (LS Fe^{II} : $\delta = 0.33$, $\Delta E_Q = 0.61 \text{ mm s}^{-1}$; HS Fe^{II} : $\delta = 0.83$, $\Delta E_Q = 1.42 \text{ mm s}^{-1}$), which agrees with the magnetic susceptibility data.

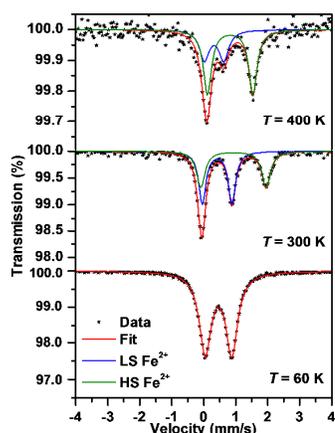


Figure 3 Mössbauer spectra of **1**-solv at 60 K, 300 K, and 400 K.

In summary, we have demonstrated the first example of chiral 3D SCO-active MOF materials. The structure has triply interpenetrated coordination network with quart-like chiral topology. Magnetic study shows it undergoes two-step spin transition behaviour with a plateau spanning room temperature. Such SCO behaviour is further confirmed by Raman spectra, DSC analysis and ^{57}Fe Mössbauer spectra.

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Notes and references

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Electronic Supplementary Information (ESI) available: Synthesis, crystallographic information, TG-MS analysis, DSC, XRD patterns, variable temperature Raman spectra, and additional figures. CCDC 972750-972753. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c000000x/

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