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Unusual High Thermal Stablility of a 2D → 3D Polycatenated Fe(II) Metal–Organic Framework Showing Guest-Dependent Spin-Crossover Behavior and High Spin-Transition Temperature

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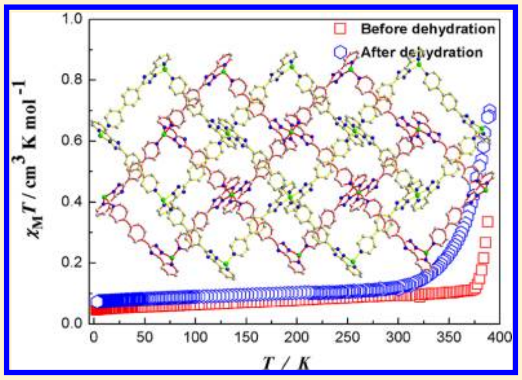
Ⓢ *Supporting Information*

ABSTRACT: A novel three-dimensional (3D) Fe(II) metal–organic framework (MOF), $[Fe_2(pptp)_4{\cdot}2H_2O]_n$ (**1**), constructed from the rigid 2-(3-(4-(pyridin-4-yl)phenyl)-1*H*-1,2,4-triazol-5-yl)pyridine (Hpptp) ligand was synthesized and structurally characterized. Complex **1** exhibits a two-dimensional (2D) → 3D polycatenated framework based on inclined interlocked 2D 4^4-**sql** grids. Variable-temperature magnetic susceptibility measurements reveal that **1** is a rare example exhibiting a thermal-driven dehydration and consequently accompanied by a dramatic change of spin crossover (SCO) behaviors. Its spin transition temperature is as high as 390 K with ~20% high-spin character. Moreover, the framework of **1** shows unusual thermal stability to nearly 500 °C.



The spin crossover (SCO) phenomenon mainly observed in octahedrally coordinated first-row d^4–d^7 transition metal (most commonly Fe(II), $3d^6$) complexes has drawn great attention due to its bistable nature of spin states, namely, high spin (HS) and low spin (LS), which can be triggered by external stimuli such as light irradiation and variation in temperature or pressure.[1] Since the first observation of a SCO compound in 1931,[2] many fascinating spin-transition compounds showing room-temperature hysteresis,[3] large hysteresis loops,[4] and photo- and pressure-induced spin transitions[5] have been obtained. Among them, discrete mononuclear Fe(II) or low-dimensional species historically dominated SCO research; however, organic ligands linked SCO centers in polynuclear Fe(II) or high-dimensional framework are rare.[5] On the other hand, the search for spin transition (ST) materials with a transition temperature ($T_{1/2}$) around room temperature with a large hysteresis loop has continued since the first revelation of a "ST based display device" by Kahn.[6] Although recent years have witnessed a great advance in the elevation of transition temperature, compounds with $T_{1/2}$ in the range of room temperature and above are still scarce.[7] As we know, $T_{1/2}$, is not only affected by local coordination of metal ions but also by counteranions and sometimes even by solvent molecules.[8] According to previous reports, three-dimensional (3D) SCO frameworks could increase the molecular cooperativity,[9] and $T_{1/2}$ might be shifted to the higher temperature region, accompanying a simultaneously widened hysteresis loop, which may be due to the enhanced rigidity in higher dimensional architectures. So design and synthesis of novel ligand to construct and modulate SCO compounds are still the hot topics in this field. Recently, Tong et al., designed a dipyridinyl triazole ligand, 2-(3-(pyridin-4-yl)-1*H*-1,2,4-triazol-5-yl)-pyridine, and used it to construct a series of Fe(II) compounds showing tunable SCO behaviors accompanying the *cis*-to-*trans* transformation behavior and supramolecular isormer phenomenon.[10]

Following the above ideas and our previously work on SCO compounds,[11] we designed and synthesized a longer dipyridinyl triazole ligand, 2-(3-(4-(pyridin-4-yl)phenyl)-1*H*-1,2,4-triazol-5-yl)pyridine (Hpptp), which could provide a suitable ligand field supporting the occurrence of SCO and could be used to construct high-dimensional interpenetrated networks,[12] thus enhancing cooperation between SCO sites. In this contribution, we report the crystal structure and physical properties of a 2D → 3D polycatenated Fe(II) MOF based on inclined interlocked 2D 4^4-**sql** grids. This MOF is a rare example exhibiting a thermal-driven dehydration and consequently accompanied by dramatic change of SCO behaviors. Our focus is directed toward a fundamental insight of the structural and magnetic properties relationship to elucidate the solvent effect on the spin transition behavior.

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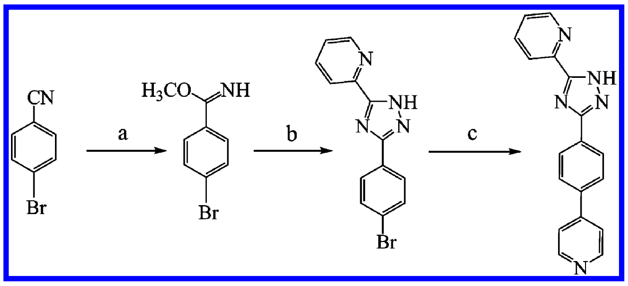
Ligand Hpptp was synthesized using Suzuki cross-coupling reaction of 4-pyridinylboronic acid and 2-(3-(4-bromophenyl)-1*H*-1,2,4-triazol-5-yl)pyridine (Scheme 1 and see Supporting Information). Black crystals of **1** were synthesized by solvothermal reaction of iron(II) sulfate and Hpptp in the presence of sodium hydroxide in DMF-H_2O (14 mL, v:v = 1:6, 170 °C). Repeated attempts to synthesize the complex **1** using different solvents resulted only in intractable precipitate. Phase purity of is sustained by the powder X-ray diffraction patterns (Figure S1 in the Supporting Information). For **1**, the most peak positions of simulated and experimental patterns are in good agreement with each other. The dissimilarities in intensity may be due to the preferred orientation of the crystalline powder samples.

Scheme 1. Synthetic Procedures of the Hpptp[a]



[a](a) Na/CH_3OH; (b) 2-picolinyl hydrazide; (c) $Pd(PPh_3)_4$, K_3PO_4, 1,4-dioxane, 4-pyridinylboronic acid.

The crystal structure of **1** was determined by single-crystal X-ray diffraction analysis at 298 K (see Supporting Information). Compound **1** crystallizes in the orthorhombic space group of *Pbcn* and is a neutral 3D framework based on inclined interlocked 2D 4^4-**sql** grids. In the asymmetric unit, there is one crystallographically independent Fe(II) ion located on an inversion center, one anionic pptp ligand and one lattice water molecule passed through by a 2-fold axis. As shown in Figure 1a, the Fe(II) ion is coordinated by two chelating pptp ligands and two bridging pptp ligands at equatorial and apical directions, respectively, as a result, a perfect FeN_6 octahedron is formed imposed by crystallographic inversion center (Fe1−N1 = 2.006(3), Fe1−N2 = 1.953(2) and Fe1−N5^{ii} = 2.000(2)). The average Fe−N bond length is 1.986(3) Å within a 1.953(2)−2.006(3) Å range, in accordance with the typical low spin state Fe(II)−N bond length.[13] The pptp ligands use the 4-position N-donor to connect the Fe(II) centers to form a 2D 4^4-**sql** network incorporating square grids with a dimension of 14.46 × 14.46 Å based in Fe···Fe separation (Figure 1b). The ligand pptp is very similar to that of 2-(3-(pyridin-4-yl)-1*H*-1,2,4-triazol-5-yl)pyridine;[10] however, it has longer dimension and is more rigid in a bent conformation. Structurally equivalent 2D grids are interlocked at an angle of 46° (Figure 2a), resulting in a 2D → 3D polycatenated framework (Figure 2b).[14] This structure is geometrically similar and topologically identical to nanoporous MOF $[Fe_2(azpy)_4(NCS)_4 \cdot (EtOH)]$ (azpy is *trans*-4,4′-azopyridine and EtOH is ethanol),[9a] which exhibits an interesting change in magnetic behavior upon absorption−desorption of guest molecules in the crystal lattice, and such a phenomenon is reversible and highly dependent on the guest molecules.

An appealing feature of **1** is its unusual high thermal stability. Thermogravimetric analysis of **1** was conducted under a

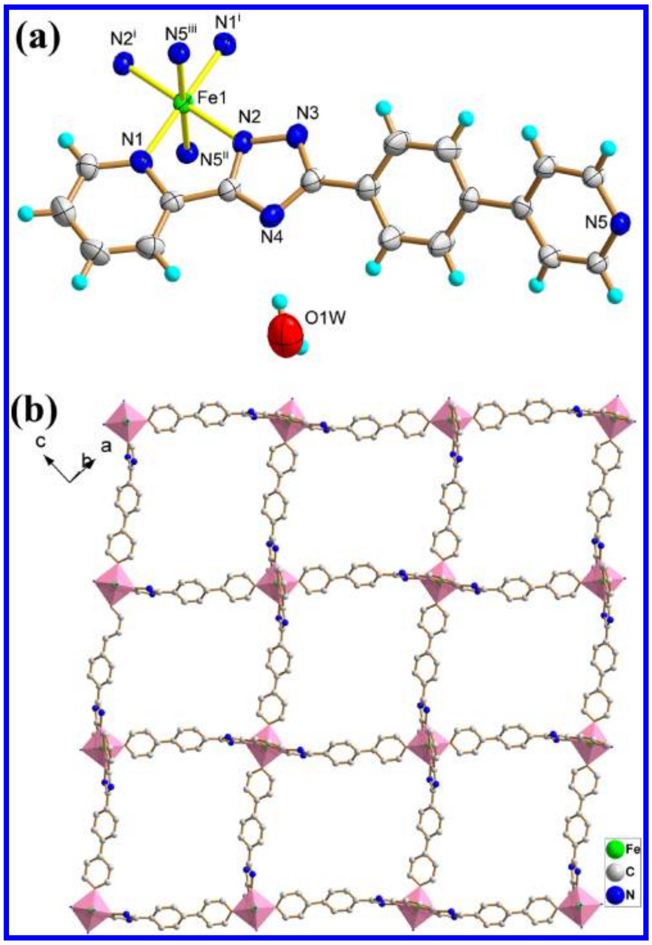


Figure 1. (a) Octahedral coordination geometry around the Fe center of **1**; thermal ellipsoids are at 30% probability (symmetry codes: (i) $-x, -y, -z$; (ii) $x - 1/2, y - 1/2, -z + 1/2$; (iii) $-x + 1/2, -y + 1/2, z - 1/2$). (b) Perspective view of the 2D network in **1**.

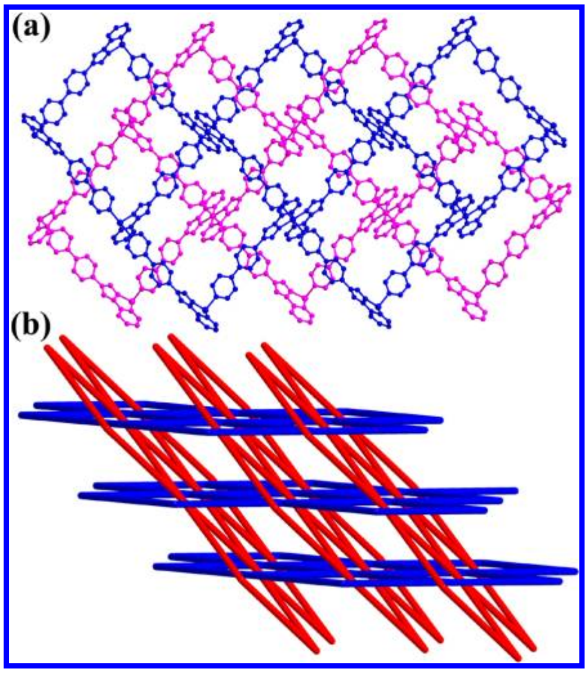


Figure 2. (a) A diagrammatic representation of the polycatenation of infinite $Fe_2(pptp)_4$ square grids. (b) Schematic representation of simplified 3D polycatenated networks.

nitrogen atmosphere (Figure 3) and showed that the first weight loss of 2.91% in the range of 65−108 °C corresponds to two H_2O molecule per formula unit (calcd. 2.69%) with a small exothermic peak observed at 95 °C. After that, a plateau appears and the dehydrated sample is thermally stable up to 490 °C. The framework starts to collapse with the loss of pptp ligands at 490 °C accompanying one strong exothermic peak at 500 °C. Generally speaking, degradation of the organic components of porous MOFs typically starts at moderate temperatures (200−350 °C),[15] leading to the decomposition of the frameworks. There are only limited MOFs which are reported to be stable near 500 °C.[16] To the best of our knowledge, the present MOF is a rare example with both high thermal stability, which may highly facilitate their functional applications. It is assumed that the polycatenated networks tighten the backbone of the ligands and enhance their resistance to pyrolysis.

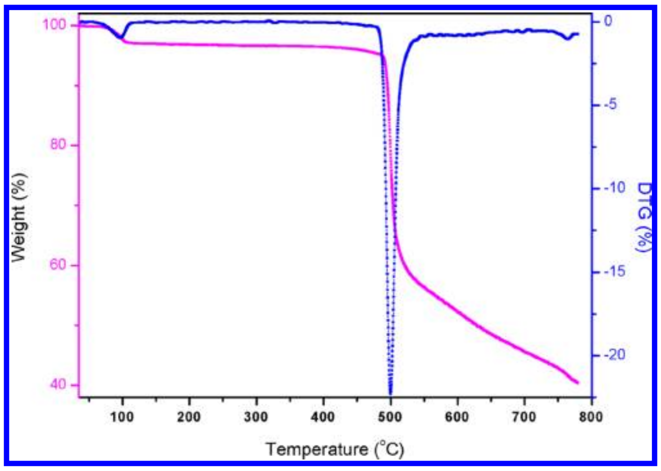


Figure 3. The TG-DSC plots of **1**.

Variable temperature magnetic susceptibility measurements of **1** revealed a relatively abrupt one-step incomplete spin transition (Figure 4) induced by dehydration. First, the $\chi_M T$ value displays 0.04−0.12 cm^3 K mol^{-1} from 2 to 375 K, indicating that the spin equilibrium favors the diamagnetic LS state at this temperature range. Then the $\chi_M T$ value starts to increase successively and get to the value of 0.33 cm^3 K mol^{-1}. According to the TG trace, we found that **1** becomes a dehydrated phase above 375 K. Therefore, the increased $\chi_M T$ values might be ascribed to the spin transition of the iron(II) ions in the solvent-free framework. Staying at 390 K for about 10 min, the $\chi_M T$ value reaches a maximum value of 0.7 cm^3 K mol^{-1}. Then cooling the temperature, the $\chi_M T$ value decreases gradually and reaches 0.12 cm^3 K mol^{-1} at 300 K. After heating the temperature to 390 K, the $\chi_M T$ values repeat again and no obvious hysteresis could be observed. The whole tendency of the $\chi_M T$ values indicates the occurrence of SCO behavior of the solvent-free sample with $T_{1/2}$ larger than 390 K. Compared to the $\chi_M T$ value of 3.50 cm^3 K mol^{-1} attributed to the HS state of Fe(II), only about 20% HS Fe(II) was captured at 390 K. A higher percentage of trapped HS Fe(II) species may be possible here with the use of a higher temperature.

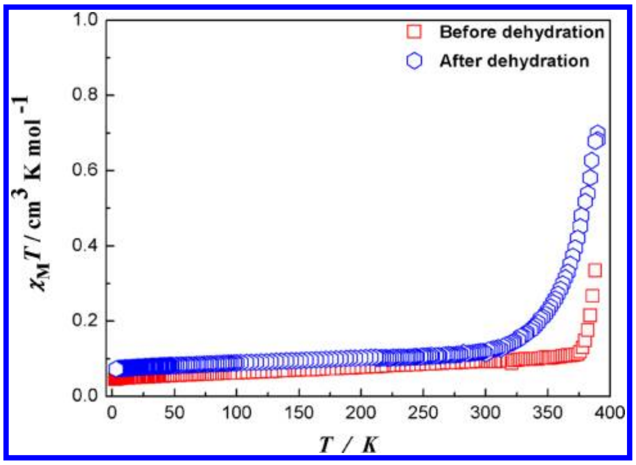


Figure 4. Temperature dependence of the solid state magnetic susceptibilities for **1** before and after dehydration.

In summary, we have successfully prepared a novel 3D Fe(II) metal−organic framework based on inclined interlocked 2D 4^4-**sql** grids. This MOF is a rare example exhibiting a thermal-driven dehydration and consequently accompanied by a dramatic change of SCO behaviors. The magnetic measurements of **1** reveal spin transitions at a temperature higher to 390 K with 20% high-spin character. Because of the increasing cooperativity through hydrogen bonds, or in the synergy of dehydration and spin transition, lattice water molecule plays a dominant role in the SCO behaviors. Moreover, the framework of **1** shows unusual thermal stability to nearly 500 °C.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The preparation of ligand and **1**, Tables S1−S2, IR, and powder XRD patterns. X-ray crystallographic file in cif format for **1**. 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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