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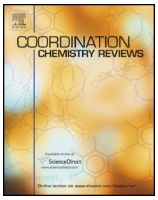

Review

# Crystalline central-metal transformation in metal-organic frameworks

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## ABSTRACT

Recently, there has been considerable interest in the transformation of metal nodes in metal-organic frameworks (MOFs) because this transformation can yield favorable changes in their chemical or physical properties. In this review, we provided an overview of crystalline central-metal transformation in MOFs, including central-metal spin-state transformation, central-metal oxidation-state transformation, and central-metal exchange in a single-crystal-to-single-crystal manner. Investigations of this concept suggest that crystalline central-metal transformation will play an emerging role in the exploration of novel MOFs for use in further applications in the near future.

## 1. Introduction

Metal-organic frameworks (MOFs) fabricated *via* the reticular synthesis of metal nodes with organic struts comprise impressively versatile scaffolds [1–3] with attractive features, including long-range organization and order, relatively stable nano-sized cavities, well-defined two-dimensional (2D) or three-dimensional (3D) crystalline architectures, record-high surface areas, and a modular nature. These features, as well as the endless variability of the organic and central-metal components, make MOFs interesting for potential applications in different fields, especially catalysis [4–6], gas storage and separation [7–9], metal sensing and sequestration [10,11], optics [12–16], and biomedical imaging [17,18]. Thus, the functionalization of target architectures

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with specific properties and applications has become one of the hottest topics in MOFs research. In principle, specific potential applications are tightly linked to the ability to present a corresponding functionality within MOFs.

At present, MOF materials are being produced with more sophisticated properties to integrate functionalities into these materials in a straightforward manner [19]. Functionalized organic building blocks have been employed as linkers for MOFs to obtain multi-functional MOFs. For instance, bodipy-porphyrin-based MOF (BOP MOF) can be used as an antenna-type light harvester because the 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (BODIPY) struts serve as antenna chromophores to allow the excitation of the porphyrin struts [20]. In practice, the synthetic of a MOF designed with functional linkers may often be a tedious process, which normally hinders the use of "pre-functionalized" linkers. In addition to the use of functionalized linkers, postsynthetic modification or substitution reactions based on linkers of precursor MOFs can also be an optimal choice to facilitate the functionalization of MOFs [21–23].

As well as the use of versatile connectors during construction, central-metal ions undoubtedly play crucial roles in determining the properties of MOFs. Previous reports have shown that central-metal ions can govern the magnetic exchange coupling interaction [24,25]. In particular, isostructural MOFs, which have identical architectures and linkers but different central-metal ions, can exhibit distinctly different properties [26,27]. This means that forming isostructural MOFs by central-metal transformation is also an efficient strategy for integrating functionalities into MOF materials. Excluding the effects of ligands and geometries, research into isostructural MOFs is beneficial for determining the relationships between metal ions and the corresponding properties of MOFs (such as electrical conductivity [28]). Series of isostructural M-MOF-74 (M = Mg, Mn, Fe, Co, Ni, Cu, Zn) [29–33], M-BTT (M = Mn, Fe, Co, Ni, Cu or Cd) [34,35], M-HKUST-1 (M = Cr, Cu, Zn, Mo, or Ru) [36–38], and lanthanide MOFs [39,40] have been constructed, but it is still difficult to obtain isostructural MOFs *via* a self-assembly synthetic pathway [41]. This is because the conventional synthetic pathway is relatively time-consuming or it is often challenging to diversify central-metal nodes. Thus, it would be more predictable and controllable to transform central-metal nodes in a precursor MOF where the structural integrality is maintained. Thanks to the advantages of single-crystal X-ray diffraction (SCXRD) for monitoring the structural transformations of MOFs, various metal ions that have been incorporated in specific positions throughout the MOFs can be visualized directly [42,43]. In this review, we provide an exhaustive investigation of the structure-property relationships of the corresponding MOFs, which indicates that single crystals are always conducive before and after the transformation.

We provide a detailed literature survey that highlights the new concept of crystalline central-metal transformation, which only occurs at metal nodes in the framework, rather than in the pores or at the metallo-ligands. This review comprises three main sections: central-metal spin-state transformation, central-metal oxidation-state transformation, and central-metal exchange (CME). The first section describes the interesting spin crossover (SCO) phenomenon in MOFs, which is ascribed to the transition between low-spin (LS) and high-spin (HS) states. Our discussion focuses only on the SCO induced by host-guest interactions. The second section considers central-metal oxidation-state transformations, which originate from electron gains and losses by central-metal ions. In the final section, we discuss the crystalline CME, as follows: (i) divalent CME, (ii) monovalent CME, (iii) trivalent and tetravalent CME, and (iv) the mechanisms of CME. In particular, we describe the mechanisms responsible for CME on a case-by-case basis.

## 2. Crystalline central-metal spin-state transformation

It is well known that in some $d^4$–$d^7$ transition metal complexes, the electronic configuration can be characterized by two low-lying electronic states with different spin-multiplicities. The LS state with a maximum number of paired electrons is found in the $t_{2g}$ sub-shell as the electronic ground state, and the HS state with the electrons entering the d-orbital is a thermally accessible state at relatively low temperatures in accordance with Hund's rule. Under external stimuli (*e.g.*, temperature, pressure, or light) [44,45], SCO occurs between the HS and LS states in such complexes. For instance, the so-called thermal SCO is a transition from the LS state populated at low temperatures to an almost quantitative, entropy-driven population in the HS state at elevated temperatures [46]. In particular, when SCO centers are incorporated into the MOFs, phenomena such as guest-sensing may exploit the interaction between SCO behaviors and host-guest processes [47]. In fact, the guest molecules in the cavities of these materials are not free, which is usually due to non-covalent host-guest interactions, such as $\pi$–$\pi$ stacking, hydrogen bonds, and Van der Waals forces [48,49]. Host-guest interactions can cause perturbations that lead to a switch in the spin state at constant (ideally ambient) temperature, but without disrupting the framework structure [50]. Alterations of guest molecules significantly change intermolecular cooperative interactions, which play important roles in the tuning of SCO behaviors [51–55].

For octahedral Fe(II) complexes, the LS $^1A_1$ ($t_{2g}{}^6$) state is diamagnetic and the HS $^5T_2$ ($t_{2g}{}^4eg^2$) state is paramagnetic. The SCO behavior in octahedral Fe(II) complexes always results in large changes in the molecular volume and dramatic color differences. Due to the difference $\Delta r_{HL} = r_{HS} - r_{LS} \approx 0.2$ Å in the metal–ligand bond length, there is a concomitant large difference in the molecular volume ($\Delta V_{HL} = V_{HS} - V_{LS}$), which is approximately 25 Å$^3$ per six-coordinated unit [56]. In addition, there is a color change from almost colorless at 293 K to deep purple at 10 K (such as the well-known example of $[Fe(ptz)_6](BF_4)_2$ (ptz = 1-propyltetrazole). In particular, the comparatively weak absorption band in the near infrared (NIR) range corresponds to the spin-allowed transition of the HS species ($^5T_2 \rightarrow {}^5E$) at 293 K. There are two absorption bands for the LS species (spin-allowed transitions $^1A_1 \rightarrow {}^1T_1$ and $^1A_1 \rightarrow {}^1T_2$) in the visible range, and two very weak absorption bands for the LS species (spin-forbidden transitions $^1A_1 \rightarrow {}^3T_1$ and $^1A_1 \rightarrow {}^3T_2$) in the NIR range at 10 K [46]. Hence, SCO octahedron $Fe^{II}$ MOFs have been investigated widely [57–60].

A simple approach for obtaining SCO MOFs is the insertion/removal of solvent guests (*e.g.*, $H_2O$, MeOH, and aromatic molecules) and gas molecules (*e.g.*, $CO_2$ and $SO_2$). The solvent guests can penetrate the pores to induce changes in the crystal structures [61–66] and the gas molecules can be chemisorbed or physically absorbed to influence the SCO behavior of MOFs [67–69]. Since Kepert et al. first reported a guest-dependent SCO in a nanoporous MOF $[Fe_2(azpy)_4(NCS)_4]_3$ (guest) (azpy = trans-4,4′-azopyridine) in 2002 [70], numerous notable examples of guest-activated SCO frameworks have emerged, such as porous pillared-Hofmann-type frameworks $[Fe(L)M(CN)_4]\cdot$(guest) (L = pyrazine; M = $Ni^{II}$, $Pd^{II}$, $Pt^{II}$), which exhibit both guest-exchange-induced SCO changes and SCO-induced changes in their host-guest properties [71–76].

To explore the influences of different guest molecules, Kitagawa et al. used a dehydration guest-free framework $Fe(pz)[Pt(CN)_4]$ (**1**; pz = pyrazine) in a guest-responsive SCO study [72]. The yellow HS clathrate was stabilized by guest molecules, such as $H_2O$, alcohols, acetone, and five- and six-membered aromatic molecules, while the red LS clathrate was stabilized by $CS_2$ at 298 K (Fig. 1). Smaller gas molecules such as $N_2$, $O_2$, and $CO_2$ did not stabilize each spin state (HS or LS), which was ascribed to the lack of obvious interactions between the guest and the host framework. In this framework, the

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