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Doping cobalt into a [Zn₇] cluster-based MOF for tuning magnetic behaviours and inducing fluorescence signal mutation

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An in situ doping strategy was successfully applied to tune the magnetic behaviours and induce the fluorescence signal mutation of a spindle heptanuclear zinc cluster-based MOF by only modifying its structural composition. The Co II-doped ZnII-MTV-M′MOF exhibits canted antiferromagnetism and weaker fluorescence properties.

The exploration of new Metal–Organic Frameworks (MOFs) species with improved physical and chemical properties is a permanent prerequisite and aim due to their application in various sectors like nanoscale magnetism,1 catalysis,2 gas storage and separation,3 drug delivery,4 and sensor devices.5 Regarding the rational design of physical properties and chemical activity of a MOF, the type and properties of incorporated metal ions are important. Consequently, the incorporation of different metal centers into one unique structure to construct Mixed-Metal-Organic Frameworks (M′MOFs) might be advantageous. In this kind of materials, various types of metal ions can assume respective tasks or synergistic effects, for example, rare earth metal ions (such as Sm3+ and Eu3+) can act as luminescent candidates, and paramagnetic metal ions (such as Cu2+ and Co2+) can be responsible for the magnetic characteristic.6 Up to now, current research focuses on three effective strategies to construct M′MOFs with enhanced or multivariate (MTV) functionalities.7 The most common strategy is ligand expansion which directly introduces bifunctional organic linkers containing mixed O- and N-donors into their frameworks usually to form lanthanide–transition metal (4f–3d) heterobimetallic compounds.8 The second strategy is cations exchange by inserting cations into well-defined environments to obtain similar M′MOFs with various composition.5e,9,14 The new strategy emerging in recent years is direct doping of another metal ion in the in situ synthesis system to construct MTV-M′MOFs.9b Our group had successfully implemented this approach to construct several Co II-doped ZnII-tetrazole-benzoate M′MOFs and systematically studied their spectroscopy.9b In our continuing efforts to explore these Co II-doped ZnII-tetrazole system, we deliberately consider a charmingly spindle heptanuclear zinc cluster-based MOF ([Zn₇(OH)₈(DTA)₃]·H₂O)n (here denoted as Zn-MOF) (DTA₂⁻ = 9,10-ditetrazoloxanthracene) characterized in our previous paper as presynthesized precursor to elaborate a Co II-doped ZnII-MTV-M′MOFs.9b Our aim is to develop this new strategy to tune the magnetic behaviours and induce the fluorescence signal mutation of a Zn-MOF by only modifying its structural composition. Here we fortunately isolated a Co II-doped ZnII-MTV-M′MOF, namely {([Co₂Zn₇OH)₈(DTA)₃]·H₂O)n (here denoted as Co-Zn-MOF), by doping Co II ions into the Zn-MOF. It exhibits canted antiferromagnetism and weaker fluorescence properties.

Block-like red crystals of Co-Zn-MOF were obtained via solvothermal reaction of 9,10-dicyanoanthracene (DCA) with ZnCl₂, CoCl₂·6H₂O and NaN₃ in H₂O/EtOH mixed solution at 160 ºC.‡ Phase purity of the bulky crystals was confirmed by the similarity between the experimental and simulated powder X-ray diffraction (PXRD) patterns (Fig. S1).

Fig. 1 (a) The capsule shaped heptanuclear [Co₂Zn₇] cluster in Co-Zn-MOF (M=Co₂/Zn₇); (b) the 3D structure of Co-Zn-MOF viewing from the c direction; (c) the tiling of the Co-Zn-MOF framework; (d) the Co-Zn-MOF crystals with red colour showing the existence of Co II in the compound.

The single-crystal X-ray diffraction study revealed that Co-Zn-MOF crystallizes in the trigonal space group R-3c (For details see X-ray Crystallography section, ESI). The basic structural feature of Co-Zn-MOF is similar to our previously reported Zn-MOF, which presents a 3D MOF exhibits a pcu-type topology formed by DTA₂⁻ bridging unprecedented heptanuclear spindle [Co₂Zn₇] clusters as secondary building units (SBUs) (Fig. 1a-c).11 A comparison of the bond lengths and angles for the Co-Zn-
MOF and its parent Zn-MOF have been made in Tables S1 and S2 in ESI. It was shown that the metal bonds M-O and M-N all changed obviously after replaced. So we can conclude that seven Zn atoms are partly replaced by two Co atoms through the site-occupancy disorder of the two metal centers in the same position. So the substituted sites by Co atoms in Co-Zn-MOF cannot be directly determined by X-ray Crystallography. Thus, the CoII centers are confirmed by the inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis and magnetic measurements (see ESI and magnetic analysis section). The red colour of Co-Zn-MOF crystals is further proved the CoII ions have been doped into the compound (Fig. 1d). The structural analysis has been carried out in our previous studies, so we do not discuss in detail here.11

The magnetic data of Co-Zn-MOF were measured on the pure microcrystals sample. The temperature dependence of magnetic susceptibility $\chi_M T$ for Co-Zn-MOF at an applied field of 1000 Oe is shown in Fig. 2a. The value of $\chi_M T$ at 300 K is 3.68 emu K mol$^{-1}$ (4.57 µB), which is much smaller than usually observed value (5.06-5.76 emu K mol$^{-1}$) for two high-spin tetrahedral CoII ions due to the strong antiferromagnetic coupling between CoII ions. As the temperature decreases, the $\chi_M T$ gradually decreases to 2.29 emu K mol$^{-1}$ at 42 K, then increases abruptly to reach a maximum 4.05 emu K mol$^{-1}$ at 9 K, and finally, decreases to 1.47 emu K mol$^{-1}$ at 2 K. Co-Zn-MOF obeys Curie–Weiss law in the range of 150–300 K with $C = 5.15$ emu K mol$^{-1}$ and $\theta = -121.95$ K. The $C$ value corresponds to $g = 2.34$, being normal for the tetrahedral CoII ion with spin–orbit coupling,12 and the large negative $\theta$ value suggests antiferromagnetic interactions between CoII ions. Notably, the spin-orbit coupling makes a contribution to the large negative $\theta$ value.

It is noteworthy that magnetic research for high spin Co system is fairly complicated and difficult because many factors, especially the spin-orbital coupling, can influence the magnetic behaviours.13 For Co-Zn-MOF, the first decrease for $\chi_M T$ value (300–42 K) may be mainly due to the spin-orbital coupling of the single-ion behaviour and strong antiferromagnetic interactions. The abrupt increase of $\chi_M T$ (42–9 K) can be interpreted by spin canting, which is strong enough to compensate for the single-ion behaviour resulting from spin-orbital coupling. The next decrease for $\chi_M T$ value (9–2 K) suggests the magnetic saturation and/or zero field splitting.

To further characterize the canted antiferromagnetism, ac susceptibility for Co-Zn-MOF was measured for variable frequencies (Fig. 2b).14 The three curves of $\chi_M'$ vs. $T$ superpose at higher temperature. They increase abruptly below 12.5 K and then diverge at around 9 K for Co-Zn-MOF, which is consistent with the antiferromagnetic order temperature $T_N = 9$ K. No peaks of $\chi_M''$ vs. $T$ were observed, which is further indicated that canted antiferromagnetism exists in Co-Zn-MOF. It is well-known that $\chi_M = \chi_M' + i\chi_M''$, if $\chi_M' = 0$, $\chi_M'' = \chi_M$. If we compare the $\chi_M' $ values (at ca. 0 Oe) with those obtained in a dc measurement (Fig. S5), we realize that they are very similar but with the important difference: at ca. 0 Oe there is possibility of a saturation effect at low temperature in $\chi_M''$ values, whereas at 0.1 T no saturation affects the $\chi_M''$ values.

The spin canting of Co-Zn-MOF is further confirmed by field-dependent isothermal magnetization (Fig. 2c). $M$ increases quickly at very low field, reaching about 1.18 N$\beta$ at 20 kOe. In the high field region the increase of magnetization is slow and linear, reaching to 1.53 N$\beta$ for the formula Co-Zn-MOF unit at 70 kOe, which is far from the expected for a total alignment of spin saturation ($M_s$) value of 7.02 N$\beta$ ($M_s = 2gS N\beta$, where $S = 3/2$ and $g = 2.34$). The canting angles of Co-Zn-MOF at 2 K is about 9.4° estimated with the equation $\sin(\gamma) = M_R/M_S$ ($M_R$ obtained by extrapolating the high-field linear part of the magnetization curve at 2 K to zero field).15 As shown in Fig. S3, upon the demagnetization process, a small hysteresis is observed for Co-Zn-MOF at 2 K. In summary, compound Co-Zn-MOF displays canted antiferromagnetic behaviour.

Fig. 2 (a) Temperature dependence of magnetic susceptibilities in the forms of $\chi_M T$ (●) at an applied field of 1 kOe for Co-Zn-MOF; (b) the $\chi_M'$ vs. $T$ and $\chi_M''$ vs. $T$ plots (inset) between 2 and 20 K for variable frequencies; (c) $M$ vs. $H$ plot for Co-Zn-MOF (★) measured at 2 K.
fluorescence spectra, respectively. The absorption bands also clearly confirm the successful CoII-doping of Co atoms in Co-Zn-MOF. Fig. 3b shows a comparison of the absorption bands of high spin tetra-coordinated tetrahedral CoII species, being well in accord with the coordination environment of Co atoms in Co-Zn-MOF. The presence of these multiple absorption bands also clearly confirms the successful CoII-doping in Co-Zn-MOF.10b,14 Fluorescence measurements of the Co-Zn-MOF were also carried out in the solid state at room temperature. Fig. 3b shows a comparison of the Zn-MOF and Co-Zn-MOF fluorescence spectra, respectively. Co-Zn-MOF displays mild blue fluorescent emissions at 483 nm upon excitation at 396 nm, which is different from that of Zn-MOF at the same excitation and emission position. In contrast to Zn-MOF, the CoII-doping product of Co-Zn-MOF shows weak fluorescent emission, only exhibits an abrupt suppression of the fluorescence intensity (Fig. 3b), which indicates that metal ions play important roles in the compounds fluorescent properties and also confirms that paramagnetic ions (such as CoII and CuII) can quench fluorescence emission.10b,16 As we can see that pre- and post-CoI-substituted, the fluorescence signals of Zn-MOF and Co-Zn-MOF hold the same peaks only associated with intensity modification. Accordingly, this conclusion indicates that metalsubstituted strategy can be an effective route for designing and preparing photoactive materials with expected fluorescence properties. Moreover, the mechanism of fluorescence spectra in Co-Zn-MOF is similar to Zn-MOF, which has been discussed in our previous studies, so we do not discuss in detail here.11

In conclusion, a CoII-doped ZnII-MTV-MOF has been constructed from an in situ doping strategy. The result compound Co-Zn-MOF presents the same structural features with the spindle heptanuclear zinc cluster-based MOF but only modifying its structural composition. The performance measurement demonstrated that it exhibits canted antiferromagnetism and weaker fluorescence properties compared to its parent Zn-MOF. The results further highlighted the importance of metal doping on tuning the material properties. More research work will focus on doping some special type metal ions into the classical MOFs (such as MOF-5, HKUST-1, ZIF-8 and MIL-101) in order to isolate new MTV-MMOF species with interesting properties and functionalities.

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Notes and references


An *in situ* doping strategy was successfully applied to tune the magnetic behaviours and induce the fluorescence signal mutation of a spindle heptanuclear zinc cluster-based MOF, which leads to a new Co$^{II}$-doped Zn$^{II}$-MTV-M$'$MOF with canted antiferromagnetism and weaker fluorescence emission.