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COMMUNICATION

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 Zn^{II}-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 Sm^{3+} and Eu^{3+}) can act as luminescent candidates, and paramagnetic metal ions (such as Cu^{2+} and Co^{2+}) 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.[10] Our group had successfully implemented this approach to construct several Co^{II}-doped Zn^{II}-tetrazole-benzoate M′MOFs and systematically studied their spectroscopy.[10b] In our continuing efforts to explore these Co^{II}-doped Zn^{II}-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**) (DTA^{2-} = 9,10-ditetrazoleanthracene) characterized in our previous paper as presynthesized precursor to elaborate a Co^{II}-doped Zn^{II}-MTV-M′MOFs.[11] 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 Zn^{II}-MTV-M′MOF, namely {[Co₂Zn₅(OH)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 °C.[‡] Phase purity of the bulky crystals was confirmed by the similarity between the experimental and simulated powder X-ray diffraction (PXRD) patterns (Fig. S1).
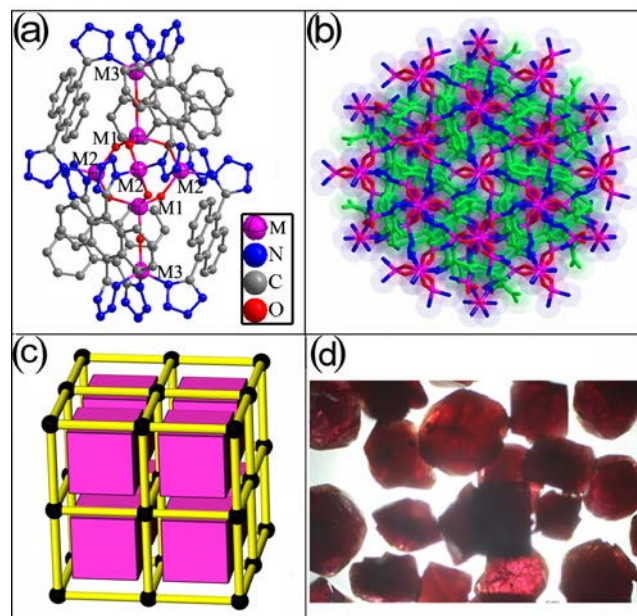

Fig. 1 (a) The capsule shaped heptanuclear **[Co₂Zn₅]** cluster in **Co-Zn-MOF** (M=Co$_{2/7}$Zn$_{5/7}$); (b) the 3D structure of **Co-Zn-MOF** viewing from the *c* direction; (c) the tiling of the **Co-Zn-MOF** framework; (d) the **Co-Zn-MOF** crystals with red colour showing the existence of Co^{II} in the compound.

The single-crystal X-ray diffraction study revealed that **Co-Zn-MOF** crystallizes in the trigonal space group *R*-3*c* (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 DTA^{2-} bridging unprecedented heptanuclear spindle **[Co₂Zn₅]** 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 Co^{II} 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 Co^{II} 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]
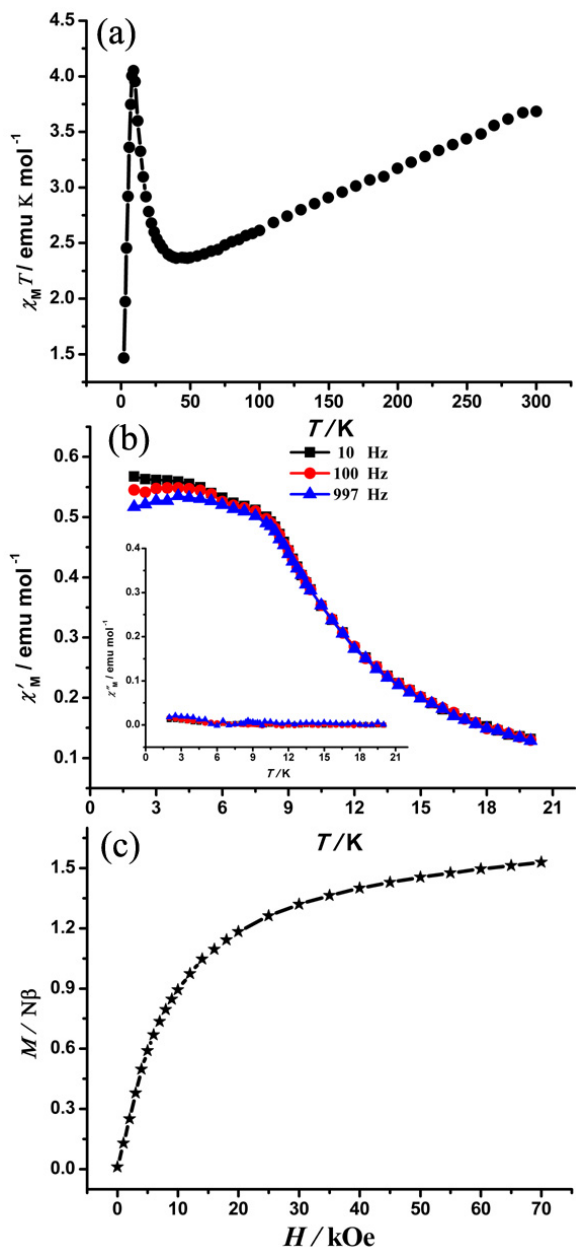

Fig. 2 (a) Temperature dependence of magnetic susceptibilities in the forms of $\chi_M T$ (●) at an applied field of 1 kOe for **Co-Zn-MOF**; (b) the χ'_M vs. T and χ''_M vs. T plots (inset) between 2 and 20 K for variable frequencies; (c) M vs. H plot for **Co-Zn-MOF** (★) measured at 2 K.

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 μ_B), which is much smaller than usually observed value (5.06-5.76 emu K mol^{-1}) for two high-spin tetrahedral Co^{II} ions due to the strong antiferromagnetic coupling between Co^{II} 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 θ = –121.95 K. The C value corresponds to g = 2.34, being normal for the tetrahedral Co^{II} ion with spin–orbit coupling,[12] and the large negative θ value suggests antiferromagnetic interactions between Co^{II} ions. Notably, the spin-orbit coupling makes a contribution to the large negative θ 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 χ'_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 χ''_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 χ'_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 χ_M values, whereas at 0.1 T no saturation affects the χ_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 Nβ at 20 kOe. In the high field region the increase of magnetization is slow and linear, reaching to 1.53 Nβ 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 Nβ ($M_S = 2gS$ Nβ, 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.
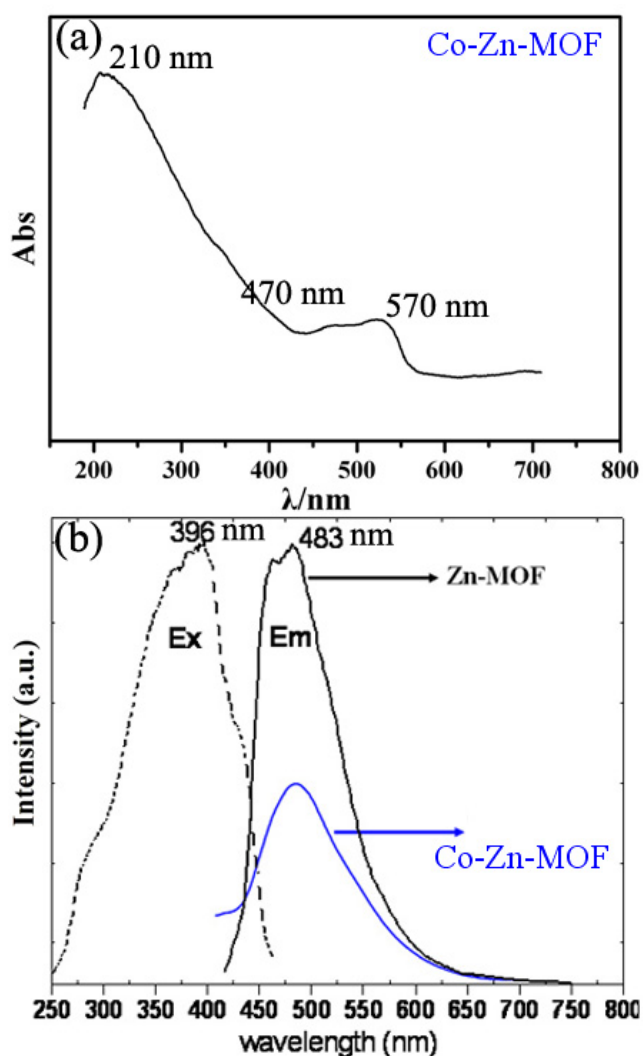
Fig. 3 (a) Solid-state UV-visible spectrum of **Co-Zn-MOF**; (b) solid-state fluorescent spectra of **Zn-MOF** and **Co-Zn-MOF** at room temperature.

UV-Visible electronic spectrum of phase-pure crystal samples of **Co-Zn-MOF** is shown in Fig. 3a. It is shown that there are two broad absorption bands: one centered at 210 nm (ligands n-π*); the second at 470 nm $[^4T_{1g}(F) \rightarrow ^4T_{2g}(F)]$ with a shoulder at 570 nm $[^4T_{1g}(F) \rightarrow ^4T_{1g}(P)]$, and the two bands are typical absorption bands of high spin tetra-coordinated tetrahedral Co^{II} species,[14] 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 Co^{II}-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 Co^{II}-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 Co^{2+} and Cu^{2+}) can quench

fluorescence emission.[10b,16] As we can see that pre- and post-Co^{II}-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 metals-substituted strategy can be an effective route for designing and preparing photoactive materials with expected fluorescence properties.[16] 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 Co^{II}-doped Zn^{II}-MTV-M′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-M′MOF species with interesting properties and functionalities.

Notes and references

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‡ Synthesis of **Co-Zn-MOF**: A mixture of $ZnCl_2$ (0.109 g, 0.8 mmol), $CoCl_2 \cdot 6H_2O$ (0.048 g, 0.2 mmol), DCA (0.013 g, 0.057 mmol), NaN_3 (0.052 g, 0.8 mmol), and $H_2O/EtOH$ (8 mL, V:V = 1:1) was sealed in a 23 mL Teflonlined stainless steel container, which was heated at 160 °C for 3 days and then cooled to room temperature at a rate of 10 °C·h^{-1}. Red block shaped crystals of **Co-Zn-MOF** were collected. Yield: 24% based on Zn. ICP-AES analysis of **Co-Zn-MOF** gave the contents of Zn and Co as 16.72 and 6.02 wt% respectively, indicating a Zn/Co ratio of 5:2. Elemental analysis (%) for $C_{48}H_{34}N_{24}O_9Zn_5Co_2$ (M = 1535.85): *Calcd.*: C, 37.54; H, 2.23; N, 21.89; *Found*: C, 36.98; H, 2.29; N, 21.57.

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Graphic Abstract

Doping cobalt into a [Zn$_7$] cluster-based MOF for tuning magnetic behaviours and inducing fluorescence signal mutation

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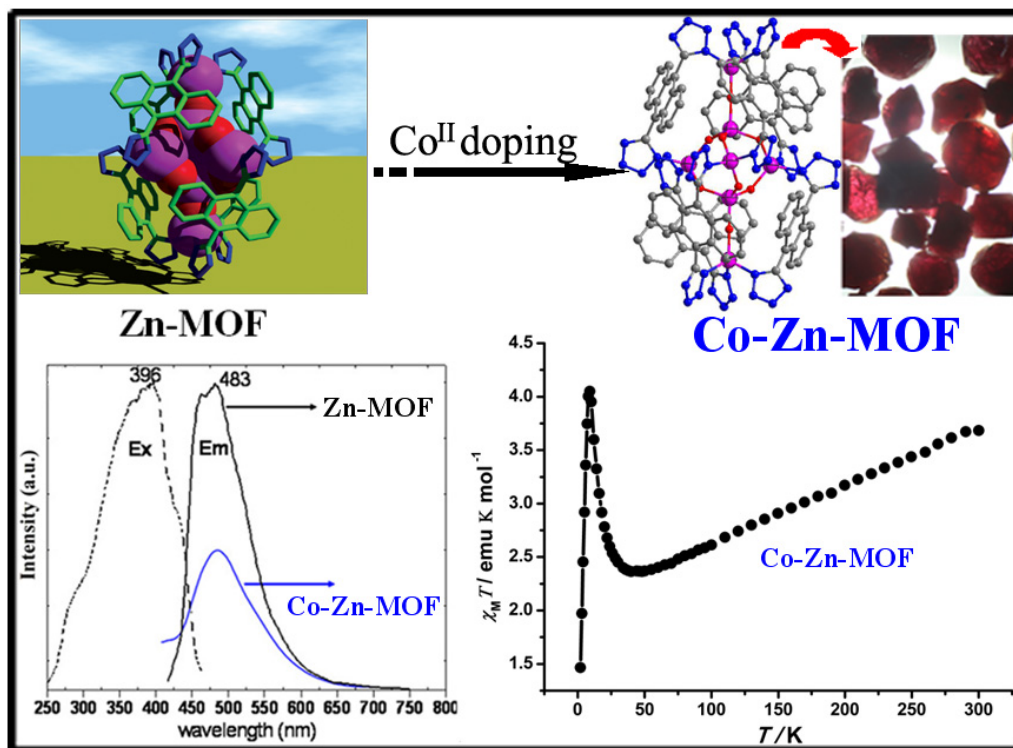
An *in situ* doping strategy was successfully applied to tune the magnetic behaviours and induce the fluorescence signal mutation of a spindle heptanuclear zinc cluster-based MOF, which leads to a new Co^{II}-doped Zn^{II}-MTV-M′MOF with canted antiferromagnetism and weaker fluorescence emission.