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A series of 3D metal organic frameworks based on [24-MC-6] metallacrown clusters: structure, magnetic and luminescence properties[†]

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Four isostructural metal organic frameworks (MOFs), namely $[Co_6(HipO)_6] \cdot 6H_2O$ (1), $[Mn_6(HipO)_6] \cdot 6H_2O$ (2), $[Cd_6(HipO)_6] \cdot 6H_2O$ (3) and $[Zn_6(HipO)_6] \cdot 7H_2O$ (4) $(H_3ipO = 2$ -hydroxyisophthalic acid), were synthesized and structurally characterized. They have a 3D (4,6)-connected framework based on [24-MC-6] metallacrown clusters ([24-MC-6]-based MOFs). The arrangements of the 24-MC-6 metallacrown SBUs show a regular change indicated by the orientation of their symmetry axes, resulting in a special dense packing mode different from other [24-MC-6]-based MOFs. The analysis of SQUID measurements reveal that compound 1 displays the dominant antiferromagnetic exchanges in 300–10 K between the adjacent Co(II) ions and a ferromagnetic-like behavior at lower temperatures, whereas compound 2 shows an antiferromagnetic interaction between the adjacent Mn(II) ions. Compound 1 exhibits a magnetocaloric effect (MCE) with the resulting entropy change ($-\Delta S_{rm}$) of 15.20 J kg⁻¹ K⁻¹ for $\Delta H = 50$ kG at 6 K, which is the highest value among the cobalt-based MOFs with MCE reported so far. The luminescence properties of compounds 3 and 4 were studied, both of them exhibit photoluminescence in the solid state at room temperature which can be ascribed to intraligand $\pi \rightarrow \pi^*$ transitions.

Introduction

With intriguing structural topologies and potential applications in the areas of catalysis, ion exchange, gas separation and storage, luminescence and magnetism, metal organic frameworks (MOFs) remain an attracting research focus in coordination chemistry and materials science.¹ To design and synthesize novel functional MOFs, the construction of clusterbased MOFs using polynuclear clusters as the secondary building units (SBUs) by rational choices of organic ligands is demonstrated to be a powerful synthetic strategy.² Through

^bState Key Laboratory Cultivation Base for the Chemistry and Molecular Engineering of Medicinal Resources, School of Chemistry and Pharmacy, Guangxi Normal University, Guilin, 541004, China. E-mail: fliangoffice@yahoo.com this strategy, the resulting MOFs may combine the novel architectures with interesting properties appearing in their SBUs.³ Furthermore, the organic components of the SBUs can also be functionalized, providing an effective platform for the further development of functional molecular materials.⁴ However, compared with the common approach using the designed linkers and preselected metal centers as nodes for the rationalization of the network topology, the cluster-based SBUs are often generated *in situ* in different reactions. Thus the design and synthesis of cluster-based MOFs through this strategy is a rather complex process and it still represents a challenge in coordination chemistry.⁵

Metallacrowns are an interesting class of polynuclear clusters that draw on the crown ether analogy for its definition and nomenclature.⁶ Since Pecoraro and Lah reported the first metallacrown structure in 1989,⁷ metallacrowns with an assortment of functions including bioactivity, molecular recognition, catalysis, mimics of surface science, liquid crystals and singlemolecule magnets have been synthesized.⁶ Although it is not so easy to control the formation of metallacrown-type building blocks, they were regarded as excellent SBU candidates to tune the structural topology and function of MOFs.⁸ The reported examples tend to use primary building units to construct the metallacrown SBUs, which were linked *via* other bridging

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groups to form different coordination networks. For example, the metallacrown SBUs of the 2D $[12\mathsc{-}MC_{Cu}\mathsc{-}I^{I}\mathchar`-4]\mathchar`-4]\mathchar`-based MOFs$ were constructed with (S)- β -phenylalanine hydroxamic acid and linked via nitrate anions,^{8a} the metallacrown SBUs of the 3D [18-MC_{Mn}^{III}-6]-based MOFs were constructed with N-substituted salicylhydrazidate and linked via 1,2-bis(4-pyridyl)ethane or 1,2-bis(pyridyl)ethane,^{8b-d} the metallacrown SBUs of the 3D [24-MC_{cd}^{II}-12]-based MOFs were constructed with diphenic acid, isonicotinic acid and linked via 1,2-di(4-pyridyl)ethylene, etc.^{8e} For the [24-MC-6]-based MOFs, the metallacrown SBUs in the reported examples of Co, Mn, Fe, Ni, and Mg were both constructed and linked with some multitopic carboxylate ligands such as 1,3,5-benzenetricarboxylate,^{9a-c} 2-amino-1,4benzenedicarboxylate^{9d} and (E)-3-(pyridin-3-yl)acrylate,^{9e} while the formate groups were used as auxiliary bridging ligands in the SBU skeletons. There was only one heterometallic [24-MC_{Zp}-6]-based MOF reported to be constructed without any auxiliary ligand.^{9f} Up to now, the examples and topological nets of [24-MC-6]-based MOFs remain limited, and their properties were scarcely explored.

On the other hand, great interest has emerged over the last few years in the investigations on molecule-based magnetic cryocooling materials not only for their environmentally friendly, energy-efficient superiority, but also for their high magnetocaloric effect (MCE), synthetic tunability, and easily tailored functionality. 10 Since the first report on $\{Fe_{14}\}$ cage molecular nanomagnets with MCE,¹¹ the development of this field has moved from the discrete clusters to extended structures. As there is no need to prevent aggregations of clusters with bulky ligands, the extended structure would be advantageous for obtaining higher metal/ligand mass ratio and increased magnetic density for large MCE.^{10,12} Nevertheless, most of the current studies on MCE based on extended structures are focused on gadolinium(III) MOFs, the investigation on 3d transition metal MOFs is extremely sparse.¹³ As a matter of fact, 3d transition metal ions could generate a better free-ion MCE, and the spin frustration resulted from competing magnetic exchange-couplings between 3d transition metal ions could also be beneficial to the large MCE.^{10b,11} These special advantages suggest that it would be interesting and worth exploring the MCE of 3d transition metal MOFs.

In this contribution, we report the synthesis and structural characterization of four novel isostructural [24-MC-6]-based MOFs with a 3D (4,6)-connected pcu net, namely $[Co_6(HipO)_6]$ · $6H_2O$ (1), $[Mn_6(HipO)_6]$ · $6H_2O$ (2), $[Cd_6(HipO)_6]$ · $6H_2O$ (3) and $[Zn_6(HipO)_6]$ · $7H_2O$ (4) ($H_3ipO = 2$ -hydroxyisophthalic acid). The magnetic characterization reveals that compound 1 shows dominant antiferromagnetic interactions between adjacent $Co(\pi)$ ions and a ferromagnetic-like behavior at lower temperatures, whereas compound 2 shows overall antiferromagnetic interactions between $Mn(\pi)$ ions. Especially, compound 1 exhibits an interesting MCE with the highest $-\Delta S_m$ value among the cobalt-based MOFs reported so far. In addition, the photoluminescence of compounds 3 and 4 are presented and discussed.

Experimental

General materials and methods

All reagents were used as received without further purification. IR spectra were recorded in the range of 4000–400 cm^{-1} on a Perkin-Elmer Spectrum One FT/IR spectrometer using a KBr pellet. Elemental analyses for C, H and N were carried out on a Model 2400 II, Perkin-Elmer elemental analyzer. The ESI mass spectra were acquired using a Bruker Daltonics HCT mass spectrometer. The powder X-ray diffraction (PXRD) data were collected using a Rigaku D/max 2500v/pc diffractometer with Cu-K α radiation (λ = 1.5418 Å). The thermal analysis was performed on a Pyris Diamond TG/DTA. The crushed singlecrystal sample was heated up to 850 °C in N₂ at a heating rate of 10 °C min⁻¹. The luminescence spectra for the solid samples were measured at 293 K on a FL3-PTCSPC spectrophotometer with a xenon lamp as the light source. Magnetic susceptibility measurements were performed in the temperature range of 2-300 K, using a Quantum Design MPMS SQUIDXL-5 magnetometer equipped with a 5 T magnet. The diamagnetic corrections for these complexes were estimated using Pascal's constants, and magnetic data were corrected for diamagnetic contributions of the sample holder.

X-ray structure determination

All the data for compounds 1-4 were collected with a Bruker SMART CCD instrument by using graphite monochromatic Mo-K α radiation (λ = 0.71073 Å). The data were collected at 160(2) K. Absorption effects were corrected by semi-empirical methods. The structures were solved by direct methods with the program SHELXS-9714a and were refined by full-matrix leastsquares methods using Olex2.14b The non-hydrogen atoms were refined anisotropically. The aromatic hydrogen atoms were placed in calculated positions and refined using a riding model, but those of phenolic groups were located in the last final difference Fourier map. The hydrogen atoms bonded to the disordered water molecules were not discernible from the last final difference Fourier maps and consequently were not included in the structure refinement. The final cycle of fullmatrix least-squares refinement was based on observed reflections and variable parameters. A summary of crystal data and relevant refinement parameters, selected bond lengths and bond angles for compounds 1-4 are given in Tables S1-S5 in the ESI.† The CCDC numbers of 1, 2, 3 and 4 are 997667, 997668, 997669 and 997670, respectively.

Syntheses of the ligand

The synthetic routes for the ligand H_3ipO are presented in Scheme S1 in the ESI.† Starting from 2,6-dimethylanisole, the intermediate 2-methoxyisophthalic acid was prepared according to the reference.¹⁵ Subsequently, a suspension of 2-methoxyisophthalic acid (15 g, 76.5 mmol) in 33% HBr–AcOH (150 ml) was heated to 120 °C with vigorous stirring until the gas evolution subsided. The homogeneous orange mixture was cooled to room temperature and the precipitates appeared. The precipitates were separated *via* filtration, washed with cold

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water and then recrystallized from H₂O–MeOH, affording H₃ipO as white powder in 92% yield. M.p. 243–244 °C. ¹H NMR (500 MHz, CD₃OD): δ = 8.11 (d, 2H, *J* = 7.8), 7.00 (t, 1H, *J* = 7.7). Elemental analysis (%) calcd: C, 52.76; H, 3.32. Found: C, 52.49; H, 3.23. ESI-MS *m*/*z*: 180.80 [M – H]⁻.

Syntheses of complexes 1-4

A mixture of $M(NO_3)_2$ ·6H₂O (0.10 mmol, M = Co, Mn, Cd, Zn), H₃ipO (0.10 mmol) and 3 drops of pyridine in 1.2 mL H₂O-MeOH (V/V = 1/1, 1.2 mL of H₂O for 4) was sealed in a Pyrex tube and heated to 100 °C for 72 h followed by cooling to room temperature at a rate of 0.5 °C min⁻¹. The block-shaped crystals obtained were filtered and washed with water, to give compounds 1–4.

 $[Co_6(HipO)_6]$ - GH_2O (1). Yield: 45% (based on Co²⁺). Elemental analysis (%) calcd: C, 37.38; H, 2.35. Found: C, 37.44; H, 2.22. IR (KBr disk, cm⁻¹) selected bands: 3431 (m), 3149 (w), 2360 (w), 1603 (vs), 1481 (s), 1450 (s), 1383 (vs), 1296 (m), 757 (m), 726 (w), 612 (w), 455 (m).

 $[Mn_6(HipO)_6\cdot 6H_2O$ (2). Yield: 43% (based on Mn^{2+}). Elemental analysis (%) calcd: C, 37.97; H, 2.39. Found: C, 37.79; H, 2.17. IR (KBr disk, cm⁻¹) selected bands: 3419 (m), 3165 (w), 2364 (vw), 1602 (vs), 1482 (s), 1449 (s), 1374 (vs), 1293 (m), 757 (m), 715 (w), 609 (w), 450 (m).

 $[Cd_6(HipO)_6]$ - $6H_2O$ (3). Yield: 36% (based on Cd²⁺). Elemental analysis (%) calcd: C, 30.94; H, 1.95. Found: C, 31.15; H, 1.82. IR (KBr disk, cm⁻¹) selected bands: 3432 (m), 3178 (w), 2360 (vw), 1659 (vs), 1553 (s), 1447 (s), 1386 (vs), 1289 (m), 762 (m), 704 (w), 629 (w), 450 (m).

 $[Zn_6(HipO)_6]$ -7H₂O (4). Yield: 41% (based on Zn²⁺). Elemental analysis (%) calcd: C, 36.05; H, 2.40. Found: C, 36.18; H, 2.22. IR (KBr disk, cm⁻¹) selected bands: 3427 (w), 3093 (w), 2360 (vw), 1602 (vs), 1481 (s), 1450 (s), 1374 (vs), 1295 (m), 757 (m), 720 (m), 641 (w), 455 (m).

Results and discussion

Crystal structure

Compound 1-4 were produced from the solvothermal/hydrothermal reaction of $M(NO_3)_2 \cdot 6H_2O$ (M = Co, Mn, Cd, Zn) with H₃ipO. Single-crystal X-ray crystallography determinations reveal that they are isostructurally crystallized in a cubic space group with hexanuclear cobalt(II) metal clusters as the SBUs. Here compound 1 is taken as the example to present and discuss their structures in detail. As shown in Fig. 1a, six $Co(\pi)$ ions in a SBU are linked via twelve carboxylate groups from twelve ligands, in which the adjacent $Co(\pi)$ ions are triplebridged through one carboxylate group *via* $\eta^1:\eta^1:\mu_2$ -mode, another carboxylate group *via* $\eta^1:\eta^2:\mu_3$ -mode and one oxygen atom from the third carboxylate group with $\eta^1:\eta^2:\mu_3$ -mode. The triple-bridge mode is repeated among the six Co(II) ions, resulting in the formation of a [24-MC-6] metallacrown SBU consisting of a [Co-O-C-O] repeating unit with a nonbonding Co--Co distance of 3.459 Å. Each Co(II) ion is coordinated by five carboxylic oxygen atoms and one phenolic oxygen atom from



Fig. 1 (a) [24-MC-6] metallacrown SBU for compound 1. (b) Simplified view of the {Co₆} chair structure. (c) Coordination modes of HipO²⁻ ligands. Color scheme: black for C, red for O, and purple for Co.

 $HipO^{2-}$ ligands, to form a distorted octahedral geometry with the Co-O bond distances in the range of 2.021(3)-2.166(3) Å and the O-Co-O angles ranging from 79.31(10)° to 97.18(10)° and 170.62(11)° to 174.74(10)°. Similar to other [24-MC-6]based MOF reported previously, six Co(II) ions in the SBU of compound 1 presents a chair-like conformation (Fig. 1b).^{9c} All HipO²⁻ ligands adopt $\eta^1:\eta^1:\eta^2:\eta^1:\mu_5$ coordination mode (Fig. 1c), which is very different from those found in the reported complexes where the phenolic oxygen atom of the ipO^{3-} ligand bridges two metal ions in a η^2 -mode to form a planar dinuclear core of $[M_2(ipO)_2]^{2-}$ (M = V^{II}, Cu^{II}).¹⁶ As a result, the μ_5 -briding HipO²⁻ ligands in compound 1 help to construct the [24-MC-6] metallacrown SBUs, as well as to link them along the crystallographic a-, b- and c-axes (Fig. 2) into the final 3D [24-MC-6]-based MOF without auxiliary ligands (Fig. 3). Among the reported [24-MC-6]-based MOFs, only one heterometallic example was constructed without any auxiliary ligand,^{9f} while others were constructed with formate groups as auxiliary ligands in their SBU skeletons.9a-e Compared with these examples with auxiliary ligands, the successful construction of the [24-MC-6]-based MOFs without auxiliary ligands in this work was attributed to the carboxylate groups of the



Fig. 2 Portion view of the coordination details of compound **1** showing twelve ligands around each [24-MC-6] metallacrown SBU, ligands with green, blue and yellow ochre benzene ring expand in crystallographic *a-, b-* and *c*-axes, respectively.



Fig. 3 3D framework of compound 1 viewed from the *a*-axis direction.

 H_3 ipO ligands playing the role of the auxiliary ligand of formate. Because of this, the arrangements of the [24-MC-6] metallacrown SBUs in the crystal cell of compound 1 show a regular change indicated by the orientation of their symmetry axes. As shown in Fig. 4, the symmetry axes of the two SBUs locating in the diagonal vertices of cubic crystal cell show the same orientation, which are different from those of the other six SBUs. It results in a novel arrangement mode of the SBUs different from those in the other [24-MC-6]-based MOFs reported in the literature. From the viewpoint of structural topology, if the [24-MC-6] metallacrown SBU is viewed as a 6-connected node which is linked to six nearest neighbours, the



Fig. 4 The packing mode of [24-MC-6] metallacrown SBUs in a cubic crystal cell of compound 1.



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Fig. 5 Schematic representation of the (4,6)-connected network of compound 1.

whole 3D framework of compound **1** could be rationalized as a uninodal (4,6)-connected pcu topology net with the Schläfli symbol of $\{4^{12} \cdot 6^3\}$ as shown in Fig. 5.

Thermal analysis and PXRD

Thermogravimetric analysis (TGA) was carried out to examine the thermal stability of compounds 1-4 (Fig. S2 in the ESI[†]). The crushed single-crystal sample was heated up to 850 °C in N_2 at a heating rate of 10 °C min⁻¹. The TGA studies reveal that the first weight loss of 6.5% between 40 and 160 °C for compound 1 corresponds to the loss of free lattice water (calc. 7.0%). The pyrolysis of ligands occurs at 350 °C and ends at 600 °C with the final residue probably being CoO (found, 28.3%; calc., 29.4%). Compounds 2 and 3 undergo a weight loss of 6.9% (calc. 7.1%) in the temperature region of 40-170 °C and 6.1% (calc. 6.0%) in the region of 40-250 °C, respectively, corresponding to the loss of their free lattice water molecules. For compound 4, the free lattice water molecules lost in the temperature range of 40-350 °C with a weight loss of 6.5% (calc. 7.9%). The followed decomposition of the frameworks occurs above 310 °C for compounds 2 and 3, and 350 °C for compound 4 with a complicated course of weight losses which is not complete even when the temperature reached 850 °C. The above thermal behaviours are attributed to the structural features and the TGA results of compounds 1-4 agree well with their formula, respectively. Furthermore, the PXRD experimental and computer-simulated patterns of the corresponding complexes are shown in Fig. S3 in the ESI.† The PXRD patterns of the bulk samples match their simulated patterns from the single-crystal structures, demonstrating the phase purity.

Magnetic properties

The variable-temperature magnetic susceptibility of compounds 1 and 2 were measured in a temperature range from 300 to 2 K under 1 kOe applied field. As shown in Fig. 6, the $\chi_m T$ value of compound 1 at room temperature is 29.74 cm³ K mol⁻¹, which is much higher than that expected for six noninteracting Co(II) ions with octahedral coordination geometry ($\chi_m T = 11.25$ cm³ mol⁻¹ K, S = 3/2 ions and g = 2) due to the spin–orbital coupling of Co(II) ions.¹⁷ Upon cooling, the $\chi_m T$



Fig. 6 $\chi_m, \chi_m T$ vs. T curves for compound 1 recorded under a 1000 Oe applied field.

value decreases gradually and reaches a minimum of 15.62 cm³ mol⁻¹ K at 10 K, then abruptly increases to a peak of 16.56 cm³ mol⁻¹ K at 4.0 K followed by a drop down to 15.59 cm³ mol⁻¹ K at 2 K. In the higher temperature range of 50-300 K, the reciprocal molar magnetic susceptibility data obey the Curie–Weiss law with the Weiss constant θ = -51.99 K and the Curie constant $C = 34.42 \text{ cm}^3 \text{ K mol}^{-1}$ (Fig. S4 in the ESI[†]), suggesting dominant antiferromagnetic interactions between Co(II) ions, while the contribution of spin-orbital coupling and zero splitting should not be ignored.¹⁸ The type of magnetic behavior suggested by the steep increase of $\chi_m T$ below 10 K should be related to the ferromagnetic interactions between the effective spins S'_i of Co(II) ions, which overcomes the effect of spin-orbital coupling and compensates the decrease of $\chi_m T$.¹⁹ The magnetization curve (*M*-*H*) is shown in Fig. 7, at 2 K, the magnetization value increases rapidly from the very beginning, then reaches a maximum value of $15.29N\beta$ at the highest field (5 kOe), which is approaching the expected saturation value of $18.0N\beta$ for six "isolated" Co(II) ions with S = 3/2 ions and g = 2. To determine whether the magnetic ordering occurs at low temperature, the temperature dependencies of field-cooled (FC) and zero-field cooled (ZFC) magnetization were performed under a field of 20 Oe (Fig. S5 in the ESI⁺). No divergence between the FC and ZFC data was observed,



Fig. 7 The field-dependent magnetization plots ($M/N\beta$ vs. H) plots of compound 1.



Fig. 8 $\chi_m, \chi_m T$ vs. T curves for compound 2 recorded under a 1000 Oe applied field.

indicating the absence of any long-range magnetic ordering in compound **1**. The AC susceptibility was further performed under the DC field $H_{\rm DC} = 0$ Oe and the AC field $H_{\rm AC} = 2.5$ Oe from 2 to 8 K (Fig. S6 in the ESI†). The in-phase signal (χ') is frequency-independent and a peak appears at 2.2 K, whereas the out-of-phase signal (χ'') is not observed.

For compound 2, the $\chi_m T$ value at room temperature is 16.68 cm^3 K mol⁻¹, which is smaller than the spin-only value expected for six non-interacting Mn (II) ions with octahedral coordination geometry ($\chi_m T = 26.25 \text{ cm}^3 \text{ K mol}^{-1}$, S = 5/2 ions and g = 2). Upon lowering of the temperature, the $\chi_m T$ value decreases gradually to 13.63 cm³ mol⁻¹ K at 100 K and then monotonously decreases to attain a value of 0.41 cm³ mol⁻¹ K at 2 K (Fig. 8). The fit of the $\chi_{\rm m}^{-1}$ versus T curve agrees with the Curie-Weiss law in the temperature range of 60-300 K with a Weiss temperature θ = -38.21 K and a Curie constant C = 18.82 cm^3 K mol⁻¹ (Fig. S4 in the ESI[†]). The negative Weiss constant value reveals the existence of antiferromagnetic coupling between the $Mn(\pi)$ ions of compound 2. This magnetic behaviour of compound 2 is similar to that of compound 1 in the high temperature range, but is different from that of compound 1 in the low temperature range where ferromagnetic interactions between the Co(II) ions are observed. This dissimilarity arises probably from the difference of the spin-orbital coupling and magnetic anisotropy of Co(II) and Mn(II) ions with different electronic structures.

Considering its higher metal/ligand ratio and magnetic density stemming from the special dense packing mode of [24-MC-6] metallacrown SBUs, the MCE of compound 1 was investigated. The isothermal magnetic entropy changes $-\Delta S_{\rm m}$ can be described as Maxwell relations by integrating over the magnetic field change, $\Delta S_{\rm m} = \int [\partial M(T,H)/\partial T]_H dH$.²⁰ As shown in Fig. 9, the maximum value of $-\Delta S_{\rm m}$ of compound 1 is 15.20 J kg⁻¹ K⁻¹ for $\Delta H = 50$ kG at 6 K. To the best of our knowledge, the MCE investigation on cobalt-based MOFs is extremely rare. There were only two examples of cobalt-based MOFs where their MCE were studied. One shows a $-\Delta S_{\rm m}$ value of 13.23 J kg⁻¹ K⁻¹ for $\Delta H = 80$ kG at 4 K,^{13a} and the other has a $-\Delta S_{\rm m}$ value of 2.4 J kg⁻¹ K⁻¹ and a $\Delta T_{\rm ad}$ value of 1.5 K for $\mu_0 \Delta H = 50$ kG.^{13b} Compared with these two examples, compound 1



Fig. 9 Experimental $-\Delta S_m$ obtained from the magnetization data of compound 1 at various fields and temperatures.

shows the highest value of $-\Delta S_{\rm m}$ for cobalt-based MOFs reported so far.

Luminescence properties

The luminescence properties of compounds 3 and 4 were investigated in the solid state at room temperature. The emission spectra of compounds 3, 4 and the ligand (H_3 ipO) are depicted in Fig. 10. Upon excitation at 335 nm and 336 nm, compounds 3 and 4 exhibit strong photoluminescene at room temperature with maximum emission peaks at 406 and 402 nm, respectively. The maximum emission peak of the free ligand (H₃ipO) is at 447 nm, which is excited at 347 nm. Considering the d¹⁰ closed shell electronic configuration of Zn(II) and Cd(II) ions, the emissions of both compounds 3 and 4 are neither the metal-to-ligand charge transfer (MLCT) nor the ligand-to-metal charge transfer (LMCT).²¹ The emission peaks for compounds 3 and 4 could be originated from the intraligand $\pi \rightarrow \pi^*$ transitions.²² Compared with the maximum emission peak at 447 nm of the free ligand, those of compounds 3 and 4 show a blue shift. It is presumably attributed to the coordination of ligands to metal centers,²² which effectively increases the rigidity and asymmetry of the ligands and the thus reduced the loss of energy by radiationless decay.²³



Fig. 10 Emission spectra of compounds 3 and 4 in the solid state at room temperature.

Conclusions

In summary, we have successfully synthesized and characterized four novel isostructural 3D [24-MC-6]-based MOFs with a (4,6)-connected net. These MOFs were constructed without any auxiliary ligand and exhibit a dense packing mode which is different from the other [24-MC-6]-based MOFs reported in the literature. Magnetic studies reveal that compound 1 shows dominant antiferromagnetic interactions (in 300-50 K) and ferromagnetic-like behaviors (at lower temperatures), while antiferromagnetic exchanges between the Mn(II) ions are observed in compound 2. Compound 1 also exhibits a MCE with the highest $-\Delta S_{\rm m}$ value among the cobalt-based MOFs reported so far. Both 3 and 4 exhibit photoluminescence in the solid state at room temperature which can be ascribed to intraligand $\pi \rightarrow \pi^*$ transitions. This work provides not only new examples of metallacrown cluster-based MOFs with novel structures and properties, but also new insights into the design of molecule-based magnetic cryocooling materials from transition metal-based MOFs.

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Notes and references

- (a) N. Stock and S. Biswas, *Chem. Rev.*, 2012, **112**, 933;
 (b) J. P. Zhang, Y. B. Zhang, J. B. Lin and X. M. Chen, *Chem. Rev.*, 2012, **112**, 1001;
 (c) Y. F. Zeng, X. Hu, F. C. Liu and X. H. Bu, *Chem. Soc. Rev.*, 2009, **38**, 469.
- 2 (a) M. O'Keeffe and O. M. Yaghi, *Chem. Rev.*, 2012, 112, 675; (b) S. M. Cohen, *Chem. Rev.*, 2012, 112, 970; (c) T. R. Cook, Y. R. Zheng and P. J. Stang, *Chem. Rev.*, 2013, 113, 734.
- 3 (a) X. J. Li, F. L. Jiang, M. Y. Wu, L. Chen, J. J. Qian, K. Zhou, D. Q. Yuan and M. C. Hong, *Inorg. Chem.*, 2014, 53, 1032; (b) E. C. Yang, Y. Y. Zhang, Z. Y. Liu and X. J. Zhao, *Inorg. Chem.*, 2014, 53, 327.
- 4 (a) Y. Q. Lan, S. L. Li, H. L. Jiang and Q. Xu, Chem. Eur. J., 2012, 18, 8076; (b) S. D. Han, J. P. Zhao, Y. Q. Chen, S. J. Liu, X. H. Miao, T. L. Hu and X. H. Bu, Cryst. Growth Des., 2014, 14, 2.
- 5 (a) D. S. Li, J. Zhao, Y. P. Wu, B. Liu, L. Bai, K. Zou and M. Du, *Inorg. Chem.*, 2013, 52, 8091; (b) Y. W. Li, J. R. Li, L. F. Wang, B. Y. Zhou, Q. Chen and X. H. Bu, *J. Mater. Chem. A*, 2013, 1, 495.
- 6 G. Mezei, C. M. Zaleski and V. L. Pecoraro, *Chem. Rev.*, 2007, **107**, 4933.

- 7 (a) V. L. Pecoraro, *Inorg. Chim. Acta*, 1989, 155, 171;
 (b) M. S. Lah and V. L. Pecoraro, *J. Am. Chem. Soc.*, 1989, 111, 7258.
- 8 (a) J. J. Bodwin and V. L. Pecoraro, *Inorg. Chem.*, 2000, 39, 3434; (b) M. Moon, I. Kim and M. S. Lah, *Inorg. Chem.*, 2000, 39, 2710; (c) D. Moon, J. Song, B. J. Kim, B. J. Suh and M. S. Lah, *Inorg. Chem.*, 2004, 43, 8230; (d) D. Moon and M. S. Lah, *Inorg. Chem.*, 2005, 44, 1934; (e) R. H. Wang, M. C. Hong, J. H. Luo, R. Cao and J. B. Weng, *Chem. Commun.*, 2003, 1018.
- 9 (a) J. H. He, Y. T. Zhang, Q. H. Pan, J. H. Yu and R. R. Xu, Microporous Mesoporous Mater., 2006, 90, 145; (b) Y. Fu, J. Su, S. H. Yang, G. B. Li, F. H. Liao, M. Xiong and J. H. Lin, Inorg. Chim. Acta, 2010, 363, 645; (c) T. Z. Zhang, Z. M. Zhang, Y. Lu and E. B. Wang, J. Coord. Chem., 2012, 65, 48; (d) L. Han, L. Qin, X. Z. Yan, L. P. Xu, J. L. Sun, L. Yu, H. B. Chen and X. D. Zou, Cryst. Growth Des., 2013, 13, 1807; (e) J. P. Zhao, W. C. Song, R. Zhao, Q. Yang, B. W. Hu and X. H. Bu, Cryst. Growth Des., 2013, 13, 2858; (f) X. Meng, X. Z. Song, S. Y. Song, G. C. Yang, M. Zhu, Z. M. Hao, S. N. Zhao and H. J. Zhang, Chem. Commun., 2013, 49, 8483.
- 10 (a) M. Evangelisti and E. K. Brechin, Dalton Trans., 2010,
 39, 4672; (b) Y. Z. Zheng, G. J. Zhou, Z. P. Zheng and R. E. P. Winpenny, Chem. Soc. Rev., 2014, 43, 1462;
 (c) T. N. Hooper, J. Schnack, S. Piligkos, M. Evangelisti and E. K. Brechin, Angew. Chem., Int. Ed., 2012, 51, 4633;
 (d) Y. Z. Zheng, M. Evangelisti, F. Tuna and R. E. P. Winpenny, J. Am. Chem. Soc., 2012, 134, 1057;
 (e) E. Cremades, S. Gomez-Coca, D. Aravena, S. Alvarez and E. Ruiz, J. Am. Chem. Soc., 2012, 134, 10532;
 (f) J. W. Sharples and D. Collison, Polyhedron, 2013, 54, 91.
- 11 D. M. Low, L. F. Jones, A. Bell, E. K. Brechin, T. Mallah, E. Rivière, S. J. Teat and E. J. L. McInnes, *Angew. Chem., Int. Ed.*, 2003, 42, 3781.
- 12 (a) P. F. Shi, Y. Z. Zheng, X. Q. Zhao, G. Xiong, B. Zhao, F. F. Wam and P. Cheng, *Chem. Eur. J.*, 2012, 18, 15086;
 (b) M. Wu, F. Jiang, X. Kong, D. Yuan, L. Long, S. A. Al-Thabaiti and M. Hong, *Chem. Sci.*, 2013, 4, 3104;
 (c) Y. C. Chen, F. S. Guo, Y. Z. Zheng, J. L. Liu, J. D. Leng, R. Tarasenko, M. Orendáč, J. Prokleška, V. Sechovský and M. L. Tong, *Chem. Eur. J.*, 2013, 19, 14876.
- 13 (a) C. B. Tian, Z. J. Lin and S. W. Du, Cryst. Growth Des.,
 2013, 13, 3746; (b) R. Sibille, T. Mazet, B. Malaman,

T. Gaudisson and M. François, *Inorg. Chem.*, 2012, **51**, 2885; (c) C. B. Tian, R. P. Chen, C. He, W. J. Li, Q. Wei, X. D. Zhang and S. W. Du, *Chem. Commun.*, 2014, **50**, 1915.

- 14 (a) G. M. Sheldrick, Acta Crystallogr., Sect. A: Fundam. Crystallogr., 2008, 64, 112; (b) O. V. Dolomanov, L. J. Bourthis, R. L. Gildea, J. A. K. Howard and H. J. Puschmann, Appl. Crystallogr., 2009, 42, 339.
- 15 J. Zhu, X. Z. Wang, Y. Q. Chen, X. K. Jiang, X. Z. Chen and Z. T. Li, *J. Org. Chem.*, 2004, **69**, 6221.
- 16 (a) E. Solari, A. Klose and C. Floriani, *Polyhedron*, 1996, 15, 4103; (b) Y. Z. Zheng, M. L. Tong and X. M. Chen, *New J. Chem.*, 2004, 28, 1412; (c) S. Y. Yang, L. S. Long, R. B. Huang, L. S. Zheng and S. W. Ng, *Inorg. Chim. Acta*, 2005, 358, 1882; (d) Z. B. Han, Y. K. He, C. H. Ge, J. Ribas and L. Xu, *Dalton Trans.*, 2007, 3020; (e) Y. Z. Zheng, Y. B. Zhang, M. L. Tong, W. Xue and X. M. Chen, *Dalton Trans.*, 2009, 1396; (f) M. A. Nadeem, A. W. Thornton, M. R. Hill and J. A. Stride, *Dalton Trans.*, 2011, 40, 3398.
- 17 (a) F. Luo, Y. X. Che and J. M. Zheng, *Cryst. Growth Des.*, 2009, 9, 1066; (b) Y. G. Huang, D. Q. Yuan, L. Pan, F. L. Jiang, M. Y. Wu, X. D. Zhang, W. Wei, Q. Gao, J. Y. Lee, J. Li and M. C. Hong, *Inorg. Chem.*, 2007, 46, 9609; (c) O. Kahn, *Molecular Magnetism*, Wiley-VCH, New York, 1993.
- 18 (a) H. P. Jia, W. Li, Z. F. Ju and J. Zhang, *Chem. Commun.*, 2008, 371; (b) J. Li, B. Li, P. Huang, H. Y. Shi, R. B. Huang, L. S. Zheng and J. Tao, *Inorg. Chem.*, 2013, 52, 11573; (c) J. Y. Zou, W. Shi, N. Xu, L. L. Li, J. K. Tang, H. L. Gao, J. Z. Cui and P. Cheng, *Chem. Commun.*, 2013, 49, 8226.
- 19 Q. Li, J. Qian, C. Tian, P. Lin, Z. He, N. Wang, J. Shen, H. Zhang, T. Chu, D. Yuan, Y. Yang, L. Xue and S. W. Du, *Dalton Trans.*, 2014, **43**, 3238.
- 20 (a) R. Sessoli, Angew. Chem., Int. Ed., 2012, 51, 43;
 (b) M. Evangelisti, F. Luis, L. J. deJongh and M. J. Affronte, J. Mater. Chem., 2006, 16, 2534.
- 21 A. Barbieri, G. Accorsi and N. Armaroli, *Chem. Commun.*, 2008, 2185.
- 22 (a) C. S. Liu, J. J. Wang, Z. Chang, L. F. Yan and X. H. Bu, *CrystEngComm*, 2010, 12, 1833; (b) X. L. Wang, C. Qin, E. B. Wang and Z. M. Su, *Chem. – Eur. J.*, 2006, 12, 2680.
- 23 (a) S. L. Zheng, J. H. Yang, X. L. Yu, X. M. Chen and W. T. Wong, *Inorg. Chem.*, 2004, 43, 830; (b) S. Sanda, S. Parshamoni, A. Adhikary and S. Konar, *Cryst. Growth Des.*, 2013, 13, 5442.