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## Three-dimensional homochiral manganese–lanthanide frameworks based on chiral camphorates with multi-coordination modes<sup>†</sup>

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A series of 3D homochiral manganese–lanthanide frameworks have been synthesized based on chiral camphoric acid. In the heterometallic features, D-camphoric acids are unprecedentedly embedded in three coordination modes.

The chemistry of hybrid solid metal-organic frameworks (MOFs) constructed from organic multitopic linkers and metal nodes has received much attention, owing to the highly desired properties resulting from judicious choice of the building blocks.<sup>1-5</sup> Chirality has been of great reputation as "a signature of nature", which is intimately involved in the high level of functioning exhibited by natural systems, from the growth of plants and animals, the helical structure of DNA and the design of drugs to the  $\beta$  decay of radioactive elements.<sup>6-8</sup> Chiral MOFs are of particular interest showing promise in not only the intriguing variety of architectures and topologies, but also their applications such as in nonlinear optics, enantiomerically selective catalysis and separation.9-11 Homochirality is a ubiquitous feature in almost every aspect of science and life. The origin of homochirality and questions of control and amplification of homochirality are indistinct. Two strategies have been applied in the synthesis of homochiral MOFs: the incorporation of enantiopure organic ligands and specific orientation of achiral linkers. Compared with the latter, individual crystals obtained through the former strategy can prevent the tendency to racemize and be homochiral without a chiral resolution process.<sup>12,13</sup> To develop species of homochiral MOFs, it can be advantageous to utilize p-camphoric acid as an enantiopure ditopic organic linker to induce a given handedness, as it is commercially available, relatively inexpensive, has comparatively small volume, versatile coordination behaviour and what is more important, it is unlikely to undergo racemization originating from the cleavage of strong C-C bonds.14

Heteronuclear metal-organic frameworks are currently of widespread interest owing to not only their fascinating aesthetically pleasing molecular structures, but also the amazing properties and envisioned technological applications such as magnetism, adsorption, gas storage, ion-exchange, catalysis.<sup>15-19</sup> Sparked by the structural diversity and interesting properties found in and proposed for 3d-4f complexes, interest in rational syntheses has been increasing rapidly. However, the preparation is still a huge challenge because of the variable and versatile coordination behavior of lanthanide ions and other factors. The previous strategy for synthesizing heterometallic MOFs was most concentrated on "two-step selfassembly", whereas one-pot assembly can provide more flexible coordination modes in a multicomponent system. According to the hard-soft acid-base theory, lanthanide ions are hard acids preferring oxygen to nitrogen atoms, while the Mn transition ion is a borderline acid which has a strong tendency to coordinate to N as well as O-donors.<sup>20,21</sup> Therefore, in our one-pot synthetic strategy, we use p-camphoric acid, which serves as a bridge for heterometallic centres and a chiral source to form multidimensional MOFs. Although MOFs comprising of monometal with camphoric acid were much reported,<sup>22,23</sup> heterometallic MOFs were never documented. Owing to the steric hindrance, the entity charge balance and coordination mode of the metal ions, neutral bipyridine ligands as secondary ligands can provide chelating N-donors to cater for hard-soft acid-base theory in order to achieve one-pot assembly. Simultaneously, the conjugated  $\pi$  systems containing aromatic rings are currently of interest in the development of fluorescent materials.

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Here we present four 3D isostructural homochiral manganeselanthanide frameworks {MnLn(D-cam)<sub>2</sub>(D-Hcam)(2,2'-bpy)}<sub>n</sub> (Ln = Nd **1**, Dy **2**, Eu **3** and La **4**) obtained by the reaction of Ln(NO<sub>3</sub>)<sub>3</sub>. 6H<sub>2</sub>O, D-camphoric acid, MnCl<sub>2</sub>·4H<sub>2</sub>O and 2,2'-bipy.<sup>‡</sup> The charming aspect of these homochiral frameworks is that they are the first 3d–4f heterometallic features in the system of chiral camphoric acids. And also, there are six reported coordination modes of cam acid but just at most two coordination modes in one structure,<sup>24–26</sup> herein the D-camphoric acids unprecedentedly provide three coordination modes with appropriate degree in one structure.

In 1, the Mn(II) site is located in six-coordinated distorted octahedral coordination geometry with an  $N_2O_4$  set from one

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2,2'-bipy molecule and three D-cam acids. Considering weak interaction, the coordination geometry of Mn(II) is a heavily distorted pentagonal bipyramid. The other metal centre, the eightcoordinated Nd(III) ion, adopts a distorted dicapped trigonalprismatic coordination mode, which bonds to eight oxygen donors from six D-cam ligands (Fig. S2, ESI<sup>†</sup>). The Nd(III)–O bond lengths vary from 2.382(4) Å to 2.513(4) Å. All of the Ln(III)–O separations are in the ranges compatible with the values of the previously published series of lanthanide complexes with organic carboxylic acids as bridging ligands.<sup>27</sup> The average Ln–O separations, La–O > Nd–O > Eu–O > Dy–O, result from lanthanide contraction.

Heterometallic centres are linked by Mn-O-Nd rods and Mn-O-C-O-Nd rods with the Mn...Nd distance of 3.760(2) Å to form  $\{MnNdO_{11}C_7N_2\}$  as the secondary building unit (SBU). Each SBU is interconnected with six SBUs along multi-direction through the modes of SBU-Cam-SBU (Fig. 1). In the asymmetric unit of **1**, D-cam acids serve as  $\mu_2$ - $\kappa^1$ ,  $\kappa^1$ ,  $\kappa^1$ ,  $\kappa^1$  (cam-1),  $\mu_5$ - $\kappa^2$ ,  $\kappa^1$ ,  $\kappa^1$ ,  $\kappa^1$ (cam-2) and  $\mu_4$ - $\kappa^1$ ,  $\kappa^2$ ,  $\kappa^1$  (cam-3) bridging ligands, respectively. Two carboxyls of cam-1 chelate with Nd1 and Nd1A and connect these two Nd centres with the separation of Nd1···Nd1A of 10.412(3) Å. Cam-1 is one of SBUs' linkers (SBU-cam-1-SBU), which enables infinite prolongation of SBUs in the form of 21 right-handed helical chains along b orientation with the pitch length of 13.054(4) Å. In cam-2, O5 and O6 are coordinated to Nd1B forming a bidentate chelate structure, besides, O6 is also bound to the Mn1B centre. The two oxygen donors O7 and O8 of the other carboxyl are bound to two different metal centres Mn1 and Nd1, respectively. The distances of the above metal centres bridged by two carboxyls are 10.340(3) Å for Nd1B···Nd1, 9.475(3) Å for Mn1B···Mn1,



**Fig. 1** (a) View of three kinds of p-cam in SBU. (b) Crystallographic coordination modes of the p-cam ligands observed in **1**. (c) View of  $2_1$  helical chains in **1**. A represents the *ac* layer; B1 and B2 represent different connection modes prolongation along *b* orientation. Symmetry codes: A,  $-x_r$ , -1/2 + y, 1/2 - z; B, -1/2 + x, 3/2 - y,  $-z_r$ ; C,  $1 - x_r$ , 1/2 + y, 1/2 - z. Colour codes: cam-1 = green; cam-2 = blue; cam-3 = pink.

10.371(3) Å for Mn1···Nd1B and 8.356(2) Å for Mn1B···Nd1. The SBUs are in turn connected to two adjacent cam-2 acids to generate a  $2_1$  left-handed helical chain propagating along the *a* axis. The helical pitch, given by one full rotation around the  $2_1$  helical axis, was 12.590(4) Å. Cam-3 is partly deprotonated and the coordination mode of the deprotonated carboxyl constructed by O9 and O10 is similar to the one of O5 and O6. The other carboxyl is not deprotonated and is bound to the Nd1C centre only using the O12 atom. The separation of bridged Nd1…Nd1C is 10.143(2) Å and that of Mn1…Nd1C is 10.381(3) Å. Likewise cam-3 connects two adjacent SBUs in a continuous winding fashion to constitute a helical cycle also along *b*-axis orientation with the pitch length equalling the length of the *b* axis, consequently the chain has *P* helicity. There is another type of helix along the *c* axis originating from cam-2 and cam-3 each with two SBUs, respectively, bridged by cam-2 and cam-3 where the SBU-cam-2-SBU-cam-3-SBU-cam2 unit constitutes a left-hand screw cycle. The helical pitch is 24.189(8) Å (the length of the crystallographic c axis). Thus it can be seen that the four kinds of helices are joined together with the ratio 1:1:1:1. Simultaneously, cam-1 and cam-3 interlink SBUs into undulating (4,4) ac layers, which are further pillared by cam-2 into a 3D structure with cam-2 joining SBUs between the layers. Therefore, the resulting three-dimensional framework is formed by stretching the helices and it is homochiral owing to the presence of the enantiopure building block.<sup>24</sup> Circular dichroism spectra of 1-4 exhibit an obvious positive Cotton effect at similar wavelengths suggesting the optical activity of the bulk samples (Fig. S17, ESI<sup>+</sup>).<sup>28</sup>

Topologically, if considering the SBU as a node, the overall framework can be represented as a six-connected net with a vertex symbol of  $4.4.4^2.4.4.4.4^2.4^2.6^4.6^4.6^4.6^4.6^4.6^4$  and a short Schläfli symbol of  $4^9.6^{6.29}$  As shown in Fig. 2, this net consists of wavelike (4,4) sheets cross-linked by zigzag chains. It is different from other reported six-connected nets that tend to contain rather planar (4, 4) sheets. Seen from the orientation of the *a*-axis, an amazing hexagonal 3D topological structure is taken on (Fig. S7, ESI†). More analysis indicates that the Mn( $\pi$ ) ion has no obvious contribution in the construction of the 3D framework. Hence, if



**Fig. 2** (a) The topological structure of **1** viewed along *b* orientation. (b) Each heterometallic centre unit can be considered as a node, connected to six others through six cam ligands along multi-direction. (c) View of the (4,4) layer constructed by cam-1 and cam-3.

regarding Nd as a node, it exhibits a similar topologic structure (Fig. S8, ESI<sup>†</sup>). In addition, multiple hydrogen bonds are found in the network cooperatively stabilizing the helical structure.

The X-ray powder diffraction (XRPD) patterns of **1–4** indicate that the bulk products are all pure phase. The thermogravimetric (TG) studies show that **1–4** display similar thermal behaviour. The TG curves give a thermo-stability sequence of 2 > 3 > 1 > 4, which may be due to the comparable Ln–O bond lengths.

The solid-state luminescent properties of **1–4** were investigated at room temperature (Fig. S7, ESI<sup>†</sup>).<sup>30–34</sup> The broad emission peak at 400 nm of **1** is comparable to that of the ligands.<sup>35,36</sup> The enhancement and red-shift of the emission bands at 468 and 545 nm may be attributed to intraligand charge transfer or/and the charge transfer between ligands and metal ions. The broad emission spectra for **2** similar to those of **1** are centred at 480, 545 and 575 nm and no obvious emission band of Ln(m) can be observed because of the quenching action of the single electron of the Mn( $\pi$ ) ion.<sup>27,37</sup> The emission peaks of **3** appeared at 534, 592, 617 and 690 nm, and only the band (although broad) at around 617 nm probably can be assigned to  ${}^{5}D_{0}{}^{-7}F_{2}$  transitions. Polymer **4** shows an identical spectrum to that of **1** with peaks at 407, 475 and 545 nm. These results have been commonly observed.<sup>32</sup>

The magnetic susceptibility measurements of **1–4** show that the  $\chi_m$  value increases continuously with decreasing temperature and no maximum is observed, respectively. The plots of  $\chi_m^{-1}$  vs. *T* over the whole temperature range obey the Curie–Weiss law with negative  $\theta$  values, but considering crystal field splitting and spin–orbit coupling of Ln(m), it results in the possible spin re-orientation or multiple magnetic transitions. The  $\chi_m T$  product decreases continuously as the temperature is lowered, because of the depopulation of the Stark levels. A more detailed analysis of chiral 3d–4f polymers is a rather difficult issue considering (i) the number of magnetic pathways for exchange between spin carriers in such molecular aggregates; (ii) lanthanide ions cannot be easily modelled; (iii) the intracomplex magnetic interactions remain weak between Mn(m) and Ln(m) ions and (iv) the occurrence of Dzyaloshinsky–Moriya or the antisymmetric interaction.

In conclusion, four 3D homochiral manganese-lanthanide frameworks have been successfully obtained based on p-camphoric acid by one-pot assembly. The results present the first examples of heterometallic homochiral camphoric acid features. Notably, it is a breakthrough that D-cam acids unfold three coordination modes in one structure. Polymers have been designed to form structurally defined heterometallic helices. Luminescent and magnetic properties reveal potential multifunctional ploymers with special chiral photoactive or magnetic applications. Furthermore, we have demonstrated an effective strategy to yield homochiral heterometallic frameworks in which chiral ligands, especially camphoric acids, are introduced into heteronuclear systems. In the future, we envisage utilizing this method for synthesis of high-nuclearity heterometallic frameworks, which subsequently give access to design such compounds into photo- and magnetic physical functionalities.

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#### Notes and references

 $\ddagger$  Syntheses of 1–4. A mixture of Ln(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.3 mmol) (Ln = Nd, Dy, Eu and La), p-camphoric acid (0.9 mmol), KOH (1.8 mmol), MnCl<sub>2</sub>·4H<sub>2</sub>O (2.5 mmol), 2,2'-bipy (0.8 mmol) and distilled water (15 mL) was stirred for 1 h. The mixture was then transferred to a 25 mL Teflon-lined steel autoclave and kept at 160 °C for 5 days under autogenous pressure. After the mixture had been slowly cooled down to room temperature, yellow block crystals of 1–4 were obtained and washed with distilled water.

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