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Hydrothermal synthesis of a novel thermally stable three-dimensional ytterbium–organic framework†

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We describe the hydrothermal synthesis and structural characterization of a novel three-dimensional ytterbium–organic framework, thermally stable up to 550 °C.

Crystal engineering of metal–organic frameworks (MOFs) has attracted much interest in view of the potential applications[1] and unusual topologies[2] of these novel materials. d-Block elements are usually preferred over f-block elements for the construction of MOFs, since the latter have high and variable coordination numbers and a wide variety of coordination environments. While this may create obstacles to the design of MOFs, it may also lead to unusual molecular architectures. Lanthanide centres also have unique properties stemming from their *f*–*f* electronic transitions. A careful selection of appropriate organic ligands which can act as light collectors ("antennae") and transfer absorbed energy to the coordinated lanthanide ion (emitters), can thus lead to the formation of luminescent MOF devices.

We report a novel three-dimensional (3D) Yb^{3+}–organic framework in which metal centres are coordinated to 2,6-naphthalenedicarboxylate (NDC^{2-}) ligands. As with other MOFs we have reported,[3] this compound has been synthesized hydrothermally under optimised conditions, in order to obtain a highly crystalline product. H_2NDC seems a promising organic ligand, since this rigid molecule is able to establish bridges between several metal centres, while its low solubility in aqueous media, caused by the presence of conjugated aromatic rings, can be minimized by using hydrothermal methods. A search in the Cambridge Structural Database (CCDC)[4] reveals that only a very few MOFs with NDC^{2-} have been reported, all containing Zn^{2+}.[5] Yb^{3+} is one of the smallest lanthanide ions, (with an effective ionic radius in a eight coordination mode of 0.99 Å), thus offering good prospects for minimizing the problems stemming from high coordination numbers.[6] This metal centre has been virtually unexplored, with only a few reports being found in the literature.[7]

Hydrothermal reaction of $YbCl_3{\cdot}6H_2O$ with H_2NDC and triethylamine (at 145 °C for a period of 4 h),‡ led to the formation of colourless crystals formulated by single-crystal X-ray diffraction as $[Yb_2(NDC)_3(H_2O){\cdot}(H_2O)_2]_n$ (CUmof-9).§ Phase purity and bulk homogeneity were confirmed by powder X-ray diffraction (see ESI) and elemental analysis. The structure contains two crystallographically unique metal centres which appear in both hexa- [Yb(2)] and hepta-coordinated [Yb(1)] environments, showing octahedral and pentagonal-bipyramidal coordination geometries, respectively (Fig. 1a). An interesting and useful feature of CUmof-9, which does not occur in other Yb^{3+} structures,[7] is that only one solvent molecule is directly connected to the framework, in this case to Yb(1) [O(11) atom]. This can be explained by considering that each centre is coordinated to six O atoms from six different NDC^{2-} ligands (Figs. 1b and 2), with the inherent steric hindrance preventing the formation of further coordinative bonds to solvent molecules. The carboxylate groups adopt the bidentate *syn*,*syn*-bridging coordination fashion, establishing bridges between consecutive metal centres [Yb(1)···Yb(2) 4.6351(2) Å] and leading to the formation of a pseudo-bimetallic paddlewheel motif (Fig. 1b), which repeats itself along the *c* direction to form zig-zag metallic chains (Fig. 2).

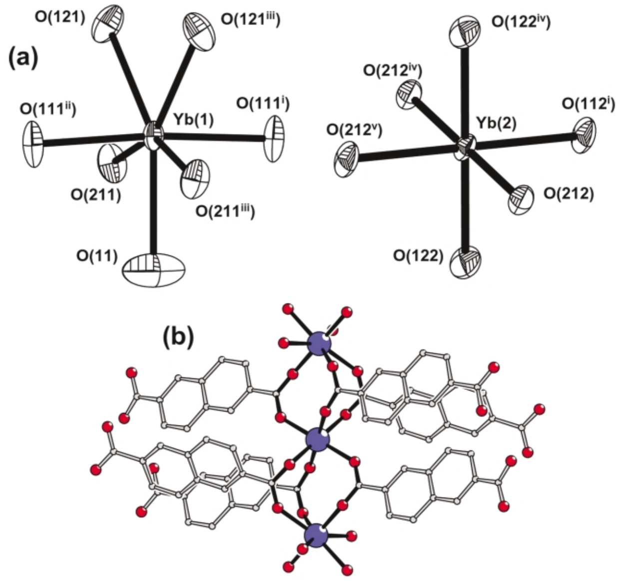

Fig. 1 **(a)** Coordination environments for the two crystallographically unique Yb^{3+} metal centres in CUmof-9. **(b)** Pseudo-bimetallic paddlewheel motif formed by the bridging carboxylate groups. Thermal displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (in Å): Yb(1)–O(111) 2.169(3); Yb(1)–O(121) 2.273(4); Yb(1)–O(11) 2.303(6); Yb(1)–O(211) 2.338(3); Yb(2)–O(122) 2.198(3); Yb(2)–O(212) 2.200(3); Yb(2)–O(112) 2.216(3). Symmetry transformations used to generate equivalent atoms: (i) $x + \frac{1}{2}, y - \frac{1}{2}, z$; (ii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iii) $1 - x, y, \frac{1}{2} - z$; (iv) $1 - x, -y, -z$; (v) $\frac{1}{2} - x, \frac{1}{2} - y, -z$.

As often happens in MOFs synthesized by hydrothermal methods and/or in the absence of large included molecules or ions, the structure of CUmof-9 does not contain significant voids (Fig. 3). However, there are small residual channels running parallel to the metallic chains and containing disordered water molecules, involved in hydrogen-bonding with the

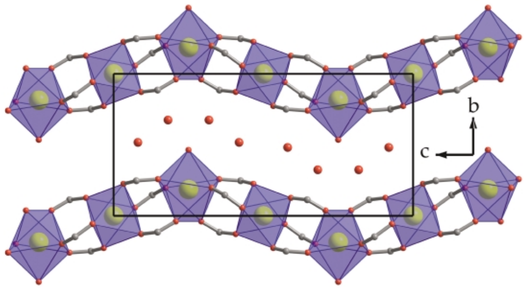

Fig. 2 Yb^{3+} chains formed by parallel linking of the paddlewheel motif. Coordinated water molecules are oriented towards small channels which contain disordered water molecules.

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† Electronic supplementary information (ESI) available: SEM images, experimental and simulated PXRD patterns, thermal analysis plots and FT-IR spectra for CUmof-9. See http://www.rsc.org/suppdata/cc/b3/b302140h/

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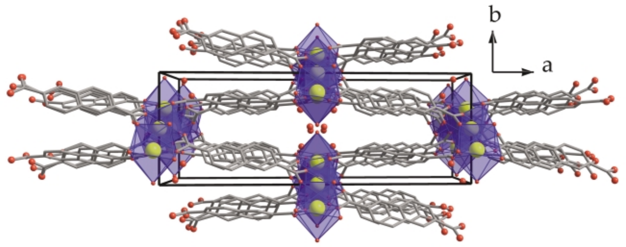

Fig. 3 Perspective view of CUmof-9 along the *c* axis.

coordinated water molecules and carboxylate groups (Fig. 2). Water molecules can be removed below *ca.* 200 °C, with the dehydrated CUmof-9 showing thermal stability up to 550 °C (when complete oxidation of the framework begins). Interestingly, dehydration is reversible, and the framework regenerates CUmof-9 after absorption of water (see ESI).

Topologically, the framework is assembled by 4- (bridging NDC^{2-}) and 6-connected nodes (Yb^{3+} centres). However, if we consider nodes located in the geometric centre of each pseudo-bimetallic paddlewheel motif, CUmof-9 can be seen as a pseudo-5-connected 3D framework with a $4^4 5^5$ topology (Fig. 4).[7] The incomplete Schläfli symbol (one ring fewer around each node), when compared to the notation of a true 5-connected framework,[8] reflects the simplification.

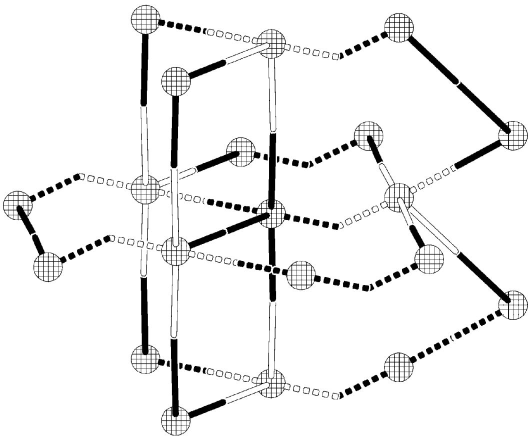

Fig. 4 Topological representation of CUmof-9 as a pseudo-5-connected framework: grey circles are the nodes of the network; dashed lines correspond to the Yb-node bridges and full (black or white) lines are NDC^{2-} bridges.

In conclusion, elimination of coordination sites by using multitopic ligands leads to highly crystalline and thermally stable lanthanide–organic frameworks containing only few OH oscillators directly connected to the emitter. We are currently applying the synthetic strategies reported here to other lanthanide centres, such as Eu^{3+} and Tb^{3+}, with the aim to produce functional luminescent materials.

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Notes and references

‡ *Synthesis* of CUmof-9: To a solution of $YbCl_3 \cdot 6H_2O$ (1.080 g, Aldrich) in distilled water (6.13 g), 2,6-naphthalenedicarboxylic acid (H_2NDC, 0.103 g, Aldrich) and triethylamine (TEA, 0.081 g, Avocado) were added, and the mixture was stirred thoroughly for 5 minutes at ambient temperature. The suspension, with a molar composition of 5.85 Yb^{3+} : 1.00 NDC : 1.68 TEA : 714 H_2O, was transferred to a Parr Teflon-lined stainless steel vessel (21 cm^3) and placed for 4 h at 145 °C in a preheated oven. The reaction vessel was allowed to cool slowly to ambient temperature at a rate of 10 °C h^{-1}, yielding colourless crystals of CUmof-9 which were manually harvested and preserved in a portion of the mother liquor. The remaining microcrystalline product was washed with absolute ethanol and air-dried at 70 °C. CUmof-9 is air- and light-stable, and insoluble in water and common organic solvents such as methanol, ethanol, acetone, dichloromethane, toluene and chloroform. Calculated elemental composition (based on single-crystal data): C 41.47, H 2.32. Found: C 40.80, H 2.35%.

§ *Crystal data* for CUmof-9: $C_{36}H_{24}O_{15}Yb_2$ (including the 6 H-atoms for the water molecules), M = 1042.63, monoclinic, space group $C2/c$, Z = 4, a = 23.2842(7), b = 8.2568(2), c = 17.5010(6) Å, β = 97.836(1)°, V = 3333.20(17) $Å^3$, μ(Mo-Kα) = 5.654 mm^{-1}, D_c = 2.078 g cm^{-3}, T = 180(2) K. Data were collected on a Nonius KappaCCD diffractometer. Of a total of 9531 reflections collected, 3811 were independent (R_{int} = 0.0511). The structure was solved by direct methods and refined by full-matrix least squares on F^2. Final $R1$ = 0.0340 [$I > 2\sigma(I)$] and $wR2$ = 0.0792 (all data), and goodness-of-fit on F^2 S = 1.075. The uncoordinated water molecule was disordered over two sites, and was modelled with 50% occupancy in each. CCDC reference number 205337. See http://www.rsc.org/suppdata/cc/b3/b302140h/ for crystallographic data in CIF or other electronic format.

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