A pcu-type metal–organic framework with spindle $[Zn_7(OH)_8]^{6+}$ cluster as secondary building units†

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The *in situ* solvothermal reaction of 9,10-dicyanoanthracene and $ZnCl_2/NaN_3$ gave the complex, $\{[Zn_7(OH)_8(DTA)_3]\cdot H_2O\}_n$ (1) (DTA^{2-} = 9,10-ditetrazolateanthracene), which presents a pcu-type topological framework formed by DTA^{2-} bridging unprecedented heptanuclear spindle $[Zn_7(OH)_8]^{6+}$ clusters as SBUs, and exhibits strong luminescent emission with long lifetime.

The rational design of metal–organic frameworks (MOFs) has attracted considerable attention in supramolecular and materials chemistry due to their enormous variety of interesting structural topologies and wide potential applications as functional materials.[1] The major task of the synthesis for such MOFs is to choose appropriate metal-connecting nodes and/or organic bridging ligands to control the formation of these complexes with required structures and properties. In this case, metal cluster entities as secondary building units (SBUs) have been proved as an effective and powerful synthetic strategy in constructing new MOFs,[2] in which neutral zinc carboxylate clusters are most commonly used, usually comprising of two, three or four zinc centers. Further, some novel MOFs with penta-, hexa-, octa-, undeca-nuclear (and even higher) SBUs have also been constructed in recent years.[3,4] Depending on their architecture, MOFs based on polynuclear metallic units offer potential for unique properties, such as luminescence, magnetism and catalysis. Moreover, with expansion of such cluster SBUs, it is also believed that new MOFs might exhibit characteristics (such as optoelectronic property) similar to those of nanosized metal oxide semiconducting materials.[4] The synthetic challenge is to increase and control the degree of nuclearity of the inorganic "clusters" that are mainly responsible for the physical properties.

On the other hand, in such reported MOF materials, most organic bridging moieties are di- or multi-carboxylate ligands. As the analog of carboxylic acid, although a few tetrazolate-based coordination solids have been reported,[5] the coordination chemistry of multidentate tetrazolate-based ligands remains largely unexplored. Recently, Long *et al.* have synthesized several microporous MOF materials by using 1,4-ditetrazolatebenzene (DTB^{2-}) as an organic linkage, some of which exhibit good hydrogen storage properties.[5j] Herein, we report a novel MOF architecture, $\{[Zn_7(OH)_8(DTA)_3]\cdot H_2O\}_n$ (**1**) with a **pcu**-type (primitive cubic lattice net) topology,[6] constructed by 9,10-ditetrazolateanthracene (DTA^{2-}, an analog of DTB^{2-}, Chart 1S, ESI†) bridging unprecedented heptanuclear spindle $[Zn_7(OH)_8]^{6+}$ cationic clusters. We selected H_2DTA as the ligand, in view of its bulky skeleton spacer (anthracene ring) and the rich coordination chemistry of tetrazolates, attempting to construct MOFs with unique structure types and associated properties. It is worth noting that many MOFs are constructed from tetrahedral, square, triangular, octahedral, or trigonal-prismatic building blocks, however, to the best of our knowledge, MOFs based on the assembly of such a spindle heptanuclear building units have not been reported.

Maple prism crystals of **1** were obtained by the *in situ* solvothermal reaction of 9,10-dicyanoanthracene (DCA) with $ZnCl_2$ and NaN_3 (Fig. 1(a)),‡ which has high thermal stability (decomp. *ca.* 380 °C, Fig. 3S, ESI†). Its purity was further confirmed by XRPD (Fig. 1S, ESI†). It should be pointed out that in the solvothermal process the two nitriles of DCA have been converted to tetrazolate groups, giving the ligand DTA^{2-}, which has been observed several times previously.[7]

X-Ray crystal structure analysis§ revealed that **1** crystallizes in the trigonal space group $R\bar{3}c$, and shows a structure in which nanosized heptanuclear spindle cationic $[Zn_7(OH)_8]^{6+}$ clusters (Fig. 1(b) and (d)) are linked *via* DTA^{2-} ligands to produce a neutral three-dimensional (3D) framework. All of the Zn^{II} ions in the cluster have a tetrahedral coordination geometry, but lie in three types of coordination environments: each of two Zn^{II} ions (Zn1), located on a three-fold axis and related to each other by the

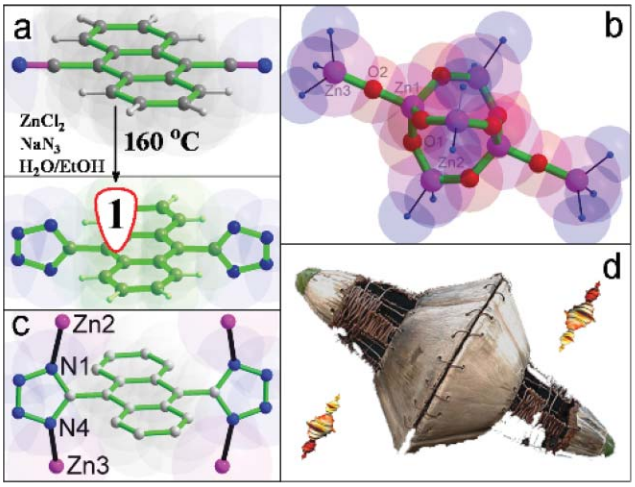

Fig. 1 (a) Preparation of **1**. (b) The spindle $[Zn_7(OH)_8]^{6+}$ clusters showing the local coordination environments of Zn^{II}. (c) The coordination mode of the ligand DTA^{2-}. Zn^{II} are shown in purple, O in red, N in blue, and C in grey. (d) Artistic spindles (from www.mixedmediasculpture.com).

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symmetry operation '$y - 1/3$, $x + 1/3$, $-z - 1/6$', is tetrahedrally coordinated by four hydroxy O atoms (Zn1–O1 1.959(4), Zn1–O2 1.927(7) Å); the Zn2 atom lies on a two-fold axis and three such equatorial Zn^{II} ions are related to each other by the symmetry operations '$1 - y$, $1 + x - y$, z' and '$y - x$, $1 - x$, z', with each coordinating to two hydroxy O (Zn2–O1 1.925(4) Å) and two tetrazolate N atoms (Zn2–N1 2.035(4) Å). The remaining two axial Zn^{II} (Zn3) ions are also on a three-fold axis and are related to each other by the symmetry operation 'y, x, $-z - 1/2$', and each Zn3 ion is coordinated to one hydroxy O (Zn3–O2 1.886(7) Å) and three tetrazolate N atoms (Zn3–N4 2.005(4) Å). Eight hydroxyl groups also perform two types of bridging modes with different Zn–O–Zn angles and Zn–Zn distances: six bent (O1, on a normal position, 133.7(2)° and 3.569(3) Å) and two quasi-linear (O2, on a three-fold axis, ~180° and 3.813(2) Å). The former is normal, but for the latter, the flat disk-like thermal ellipsoid of the O2 atom with large U_{eq} [101(4) nm^2], along with the largest diff. peak nearby reveals the bent characteristic of Zn–O2–Zn. The thermal ellipsoid has its long axes (U_{11} and U_{22}) perpendicular, while the short one (U_{33}) is parallel to the Zn–Zn vector (ratio U_{11}/U_{33} *ca.* 8.4 (CIF file of ESI†)). This indicates that the bent Zn–O–Zn is located randomly or rotates around the Zn–Zn vector. A similar situation has been observed in a reported complex.[8] Thus, eight OH^- bond seven Zn^{II} atoms to form a spindle cationic cluster with higher symmetry, different from any previously reported Zn_7 cluster.[9] To the best of our knowledge, this unusual heptanuclear cluster has never been observed either in the solid state or in coordination chemistry. The cluster is 11.8 Å in length and 5.6 Å in width at the spindle collar. Furthermore, each Zn_7 cluster is contacted to six DTA^{2-} ligands by twelve Zn–N bonds, with each ligand coordinating one equatorial (Zn2) and one axial Zn^{II} (Zn3) atoms through its two tetrazolate groups. The Zn_7 cluster thus resides in the trigonal-bipyramid capsule formed by the six DTA^{2-} ligands (Fig. 2(a)). Each DTA^{2-} ligand lies in an inversion center with the dihedral angle between the tetrazolate plane and anthracene ring being 78.6°, and coordinates to two Zn_7 clusters using its four N donors from two tetrazolate groups in a side-*trans* bridging fashion. Notably, each tetrazolate ring is attached to two Zn^{II} ions *via* its N1 and N4 atoms (Fig. 1(c)), in an uncommon "opposite-on" coordination mode, although observed in some complexes.[5g,h] This type of ligand usually adopts a N2 and N3 bridging mode in its metal complexes. The unusual coordination mode in **1** is probably due to the bulky anthracene group between two tetrazolate groups. This explanation is also likely in other tetrazolate systems adopting this coordination mode, in which the 5-substituents are always bulky.[5g,h] Such a bridging coordination mode of DTA^{2-} in **1** is different from those in related DTB^{2-} complexes,[5d,j] obviously owing to the different size of spacer groups.

These heptanuclear clusters, which behave as SBUs, are interconnected through the tetrazolate groups of DTA^{2-} cations to generate an extended 3D framework (Fig. 2(b), (c)). A better insight into the structure of **1** can be obtained by the standard procedure of reducing multidimensional structures to simple node-and-linker reference nets, known as the topological approach.[10] Herein, each heptanuclear SBU in **1** is connected to six adjacent SBUs through six DTA^{2-} moieties along six directions (Fig. 2(a)), therefore, each SBU can be defined as a six-connected node. As DTA^{2-} only acts as a bridging ligand (*viz.* double bridge), there is no need to consider it in the topological analysis, only as a linker. On the basis of this simplification, the structure of **1** can be described as a six-connected 3D network with a **pcu**-type (or strictly, decorated **pcu**-type) topology (Fig. 2(d) and 3).[6] From a geometric stacking point of view, the coordinated Zn_7 cluster has a trigonal-biyramid configuration with the six DTA^{2-} as edges (Fig. 3). Thus, such trigonal-biyramid blocks accumulate by sharing six edges with each other to form the 3D structure.

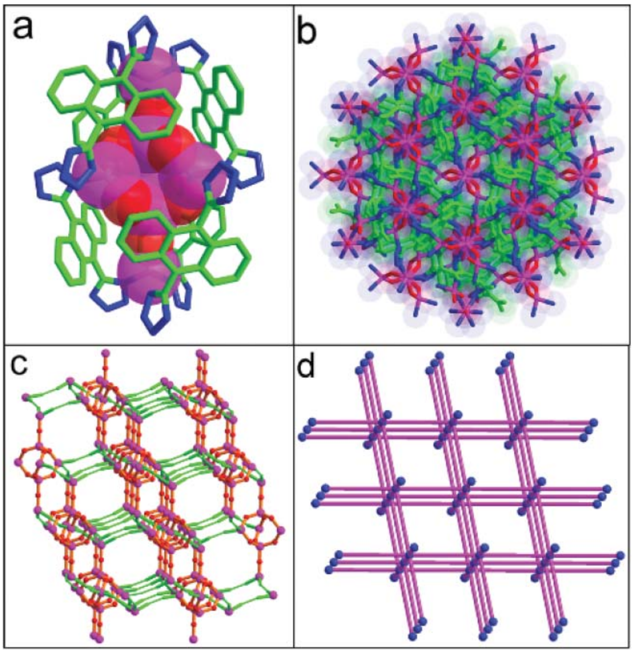

Fig. 2 (a) The capsule formed by six ligands bonding one $[Zn_7(OH)_8]^{6+}$. (b) 3D structure of **1** viewing from the *c* direction. (c) 3D framework structure with the anthracene groups omitted and each tetrazolate shown as a green stick, Zn^{II} is shown as purple, O as red. (d) Schematic representation of the **pcu** network in **1** with ligands represented by purple sticks and $[Zn_7(OH)_8]^{6+}$ by blue spheres.

Encouraged by the single-crystal diffraction result, which reveals the presence of heptanuclear OH-bridging Zn^{II} clusters, being further linked by bulky conjugated aromatic organic moieties in the framework, optical diffuse reflectance, absorption and photoluminescence spectra of **1** in the solid state were measured at room temperature, to investigate its electric and optical properties. The reflectance result shows the presence of an optical gap, $E_g \approx 2.9$ eV (Fig. 4S, ESI†), which suggests that **1** may have semiconductor property. However, no semicircles, but rather scattered data points were observed in impedance spectra measured between −20 and 220 °C, indicating that **1** is actually an insulator with extremely large resistance ($>10^9$ ohm at r.t.)

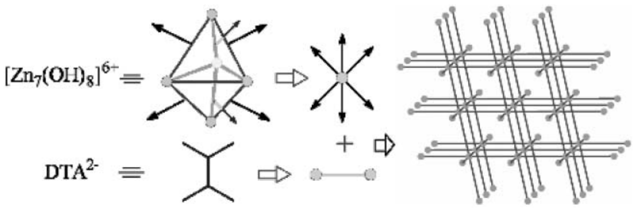

Fig. 3 Schematic representation for the formation of the **pcu** net in **1**.

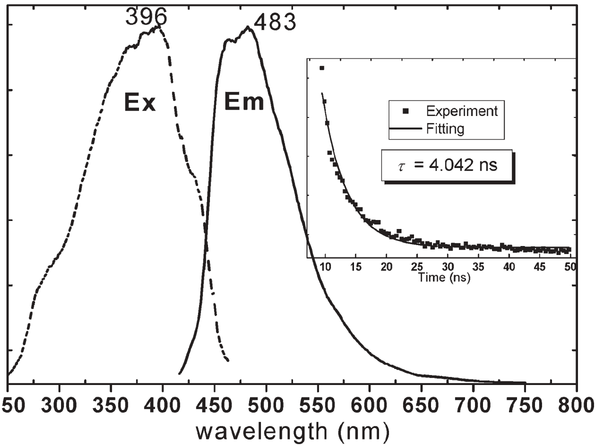

Fig. 4 Solid-state photoluminescent spectra of **1** (inset, lifetime).

(Fig. 5S, ESI†). In the absorption spectra of **1**, there are two clear absorption peaks centered at 236 and 372 nm, corresponding to the K- and B-band, respectively, which essentially matched the absorptions of DCA (Fig. 6S, ESI†), although narrowed. Thus, the characteristic B-band absorption of **1** should be assigned as the intra-ligand $\pi \rightarrow \pi^*$ transition in the anthracene ring of the ligand DTA^{2-}. In addition, **1** exhibits intense blue photoluminescence with an emission maximum at 483 nm upon excitation at 396 nm (Fig. 4), which is different (and stronger) from that of DCA in emission position (Fig. 7S, ESI†). This emission is assignable as a $\pi_L^* \rightarrow \pi_L$ transition since the heteroatoms of the heterocyclic aromatic ligand will have decreased π and π* orbital energies (the HOMO and LUMO, as well as orbitals with energies close to these, may not be significantly contributed by the d^{10} metal atoms, so that LMCT can be excluded from consideration[11]). The enhancement of luminescence may be attributed to the ligand chelation to the metal center, which effectively increases the rigidity and asymmetry of the ligand and reduces the loss of energy by radiationless decay. The lifetime of the 483 nm peak was measured as 4.042 ns (Fig. 4), suggesting that this compound may be an excellent candidate for potential photoactive materials.

In summary, we have obtained a 3D Zn^{II} complex by using a di-tetrazolate ligand with a bulky spacer. It shows a **pcu**-type network topology with an unprecedented heptanuclear spindle $[Zn_7(OH)_8]^{6+}$ cluster as secondary building units, and has strong luminescent emission with long lifetime. Further work is being focused on using other tetrazole ligands to construct MOFs.

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Notes and references

‡ *Synthesis* of $\{[Zn_7(OH)_8(DTA)_3]\cdot H_2O\}_n$ (**1**): A mixture of DCA (23 mg, 0.1 mmol), NaN_3 (26 mg, 0.4 mmol) and $ZnCl_2$ (55 mg, 0.4 mmol) in 10 mL of H_2O–EtOH (2 : 1) was sealed in a Teflon-lined stainless autoclave and heated to 160 °C for 12 h, held at this temperature for 36 h, and then cooled to room temp. over 24 h. Maple crystals were collected and washed with water and acetone. Yield: ~20% based on DCA. Anal. Calc. for $C_{48}H_{34}Zn_7N_{24}O_9$ (1548.58): C 37.23, H 2.21, N 21.71%; found: C 37.51, H 2.02, N 21.95%.

§ *Crystal data* for **1**: $C_{48}H_{34}Zn_7N_{24}O_9$, $M_r = 1548.58$; trigonal; space group $R\bar{3}c$; $a = b = 13.934(2)$, $c = 48.052(10)$ Å; $V = 8080(2)$ Å^3; $Z = 6$; $D_c = 1.910$ g cm^{-3}; $T = 293$ K; reflections collected/unique = 24129/2065; $R1 = 0.0507$, $wR2 = 0.1109$ ($I > 2\sigma(I)$); $R1 = 0.0785$, $wR2 = 0.1231$ (all data) and GOF = 1.044. CCDC 625275. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b615675d

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