

Synthesis, characterization, and photoluminescence of isostructural Mn, Co, and Zn MOFs having a diamondoid structure with large tetrahedral cages and high thermal stability†

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Three novel Mn, Co, and Zn MOFs containing large tetrahedral cages have been prepared and are stable up to 400 °C; X-ray diffraction revealed the frameworks are isostructural having a diamondoid structure of “hourglass” subunits connected by triangular carboxylate ligands.

Metal–organic frameworks (MOFs) have become a burgeoning field of research in recent years due to their potential applications in heterogeneous catalysis, non-linear optics, magnetism, and gas-storage.^{1,2} They have also been designed with photoluminescence properties.³ Careful selection of organic ligands and secondary building units (SBUs) allows the construction of MOFs with desired properties and structural-types.^{4,5} In the last decade, one of the most frequently used ligands in MOF studies was the anion of benzenetricarboxylic acid (H₃BTC, Fig. 1).⁶ The expansion of BTC to benzenetribenzoate (BTB, Fig. 1) by Yaghi and coworkers recently resulted in new structural types with significantly increased porosity.⁷

One of the main concerns in MOF materials is their thermal stability. By introducing a triazine ring into a TATB ligand (the anion of 4,4',4''-s-triazine-2,4,6-triyl-tribenzoic acid, H₃TATB, Fig. 1), we hope to improve the thermal stability of the resulting MOFs because H₃TATB was used as a monomer for the preparation of high-temperature-resistant polymers.⁸ Repulsions between the C–H bonds on the central ring and those on the peripheral rings play a key role in controlling the conformation of BTB; the TATB ligand with no C–H bonds on the central ring is not subject to such repulsions. Therefore, TATB is expected to be flatter than BTB, and thus should produce new structural types in MOF studies. In addition, the triazine ring is better suited for π – π stacking than the central ring in BTB due to the increased

quadrupole moment. TATB should strengthen the resulting MOFs even more.

In this communication, we report three novel, isostructural MOFs having a diamondoid structure with large tetrahedral cages, namely, Co₆O(TATB)₄·(H⁺)₂·(H₂O)₂·(Py) (Py = pyridine) (**1**), Mn₆O(TATB)₄·(H⁺)₂·(H₂O)₈·(DMF)₂ (DMF = dimethylformamide) (**2**), and Zn₆O(TATB)₄·(H⁺)₂·(H₂O)₅·(DMSO)₄ (DMSO = dimethylsulfoxide) (**3**). The protons in the formulae were added to balance the overall charge of the MOFs (*vide infra*). The TATB ligand, which has never been used as a ligand before our work, was prepared using a modified literature method (see supporting information†).

The hydro- or solvo-thermal reactions between H₃TATB and Co(NO₃)₂·6H₂O, Mn(NO₃)₂ and Zn(NO₃)₂·6H₂O resulted in the formation of complexes **1**, **2**, and **3** respectively.‡

Single-crystal diffraction analysis§ revealed that **1**, **2**, and **3** are isostructural. The following discussions on structural aspects will mainly focus on **3**.

IR spectroscopic studies showed that the carboxyl groups of H₃TATB are deprotonated during the reaction. Each carboxylate adopts a bidentate bridging coordination mode connecting a four-coordinate Zn (*T_r*-Zn) and a six-coordinate Zn (*O_h*-Zn) in a *syn-anti* configuration (Fig. 2a).

Every six carboxylate groups from six TATB ligands bridge two *T_r*-Zn atoms and one *O_h*-Zn to form an “hourglass” structural subunit. This unique hourglass arrangement can be attributed to

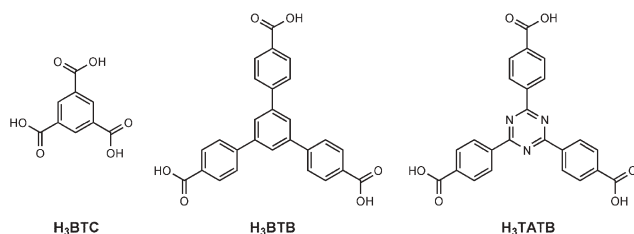


Fig. 1 Triangular carboxylate ligands.

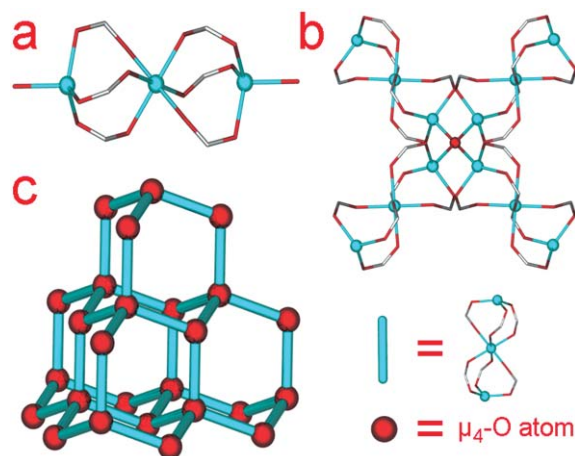


Fig. 2 View of (a) an hourglass subunit (colour scheme: aqua, Zn; red, O; and grey, C), (b) μ₄-O atom connecting four hourglass subunits in a tetrahedral geometry, and (c) a diamondoid network.

† Electronic supplementary information (ESI) available: details of the synthesis of the ligand, drawings of TGA and XRD. See <http://www.rsc.org/suppdata/cc/b5/b502007g>
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the fact that the octahedral ligand field stabilization energies for Mn^{2+} (high spin d^5), Co^{2+} (high spin d^7) and Zn^{2+} (d^{10}) are very small, so there is little energy difference between tetrahedral and octahedral ligand fields. There are examples in the literature in which Zn,⁹ Mn and Co¹⁰ are arranged in such an hourglass arrangement.

There are no discrete SBUs in the structure. Every hourglass subunit binds two $\mu_4\text{-O}$ atoms and every $\mu_4\text{-O}$ atom connects four hourglass subunits (Zn-O : 2.067(1) Å, Fig. 2b), forming an infinite diamondoid network throughout the lattice (Fig. 2c).

As expected, the TATB ligand is almost planar in the three coordination networks. For example, the average dihedral angle between the central and peripheral rings is only 4.7° in **3**. By comparison, the average dihedral angle is 37.1° in MOF-14 in which the BTB ligand was used.^{7a} The TATB ligands appear in pairs by forming $\pi\text{-}\pi$ stacking in a staggered arrangement (Fig. 3). The two triazine rings are stacked in such a way that the negatively charged nitrogen atoms are aligned with the positively charged carbon atoms from the other ring to maximize $\pi\text{-}\pi$ stacking, similar to those in compounds based on tripyridyltriazine.¹¹ In fact, the $\pi\text{-}\pi$ stacking found in **2** is probably the strongest that has ever been found, the distance between the centres of the two triazine rings being only 3.14 Å.¹² By comparison, typical $\pi\text{-}\pi$ stacking interactions between two phenyl rings were found at distances around 3.5 Å.¹³ The pair of ligands cover each adamantane window in the diamond net (Fig. 4a), and every two adamantanes shares the pair. Each ligand in the pair acts as the face of a tetrahedral cage, in which every 12 Zn ions are connected by four TATB ligands and four $\mu_4\text{-O}$ atoms, while the $\mu_4\text{-O}$ atom acts as the vertex. The cage has an edge length of 18.218 Å ($\text{O}\cdots\text{O}$ distance) and a volume of 715 Å³, in which free solvent molecules reside. Every face of the tetrahedron is covered by another tetrahedron (Fig. 4b) to form a “super-tetrahedral cage.” This super-cage is different from the T_2 super-tetrahedron consisting of four tetrahedra.³ The centre of the super-tetrahedron in **3** contains a fifth tetrahedron surrounded by four tetrahedra.

Thermal gravimetric analysis (TGA) showed that complexes **1**, **2** and **3** can be stable up to 400 °C. For complex **1**, a weight loss of 5.08% from 50 to 340 °C corresponds to the loss of pyridine and water molecules in the lattice (calcd.: 5.23%). Complex **1** is stable up to 420 °C, and decomposes at higher temperatures. For complex **2**, the gradual weight loss of 13.32% from 50 to 260 °C is consistent with the loss of all guest molecules in the lattice (calcd.: 12.41%). There is no weight loss between 260 and 395 °C, and complex **2** decomposes above 395 °C. For complex **3**, there is a weight loss of 15.66% from 50 to 300 °C, corresponding to the loss of all solvent molecules in the lattice (calcd.: 15.77%). There is

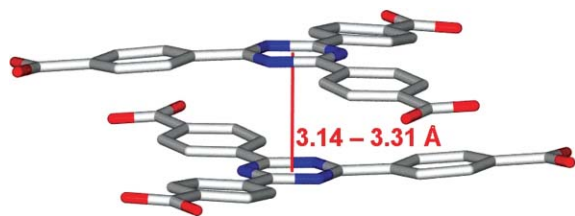


Fig. 3 $\pi\text{-}\pi$ Stacking of two triazine rings: the negatively charged nitrogen atoms (in blue) are aligned with the positively charged carbon atoms (in grey) in the other ring.

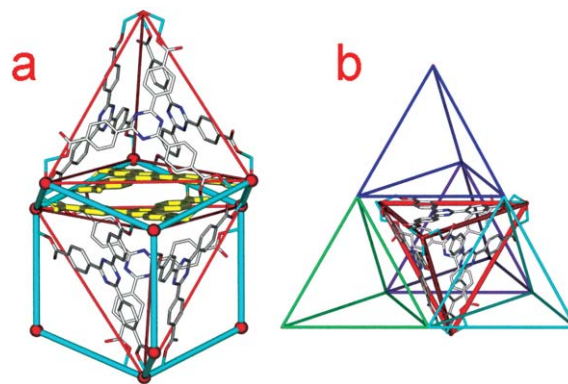


Fig. 4 View of (a) a pair of TATB ligands (gold) covers the window of the adamantane and connects two tetrahedral cages, and (b) every face of a tetrahedral cage capped by another tetrahedral cage.

no weight loss from 300 to 440 °C, and **3** decomposes at higher temperatures. For complexes **1** and **3**, X-ray powder diffraction patterns were measured to validate stability. The samples were heated to 100, 200, 300, and 405 °C, respectively. XRD patterns of both samples fit well with the simulated data, although slight shifts of some peaks are observed at 300 or 405 °C (see supporting information†). The thermal stability of all three MOFs from this work is comparable to that of high-thermal-stability (430 °C) MOFs in the literature.¹⁴ By comparison, MOF-177, also a Zn MOF but with the BTB ligand, has a reported decomposition temperature of 350 °C, although its high porosity may partially account for the lesser thermal stability.^{7b}

The three MOFs in this report have been formulated based on crystallographic studies and elemental analyses. In the formula of **3**, the addition of two protons is the only way to balance the overall charge of the MOF since **3** contains only Zn^{2+} , which has no other stable oxidation state. The oxidation states of Co and Mn in **1** and **2** have been temporarily assigned based on crystallographically determined M–O distances (Table 1). For **1** the distances are consistent with the +2 oxidation state for both four and six coordinate Co atoms.¹⁰ However, for **2**, although the $T_r\text{-Mn-O}$ distances are consistent with the +2 oxidation state, the $O_r\text{-Mn-O}$ distances are slightly shorter than those found in other molecular compounds.¹⁰ This may imply a partial oxidation of the central Mn atoms. Nevertheless, **2** can still be formulated as containing only Mn^{2+} ions. The hourglass arrangement in **2** also favours the d^5 electron configuration and the Mn^{2+} oxidation state assignment (*vide supra*).

Photoluminescence studies of **3** showed that the excitation of the solid samples of H_3TATB and **3** at 268 nm produces the same two luminescence peaks at 422 nm and 484 nm. These intense blue luminescence signals may result from ligand-based $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.¹⁵

Table 1 Selected bond distances (Å) in complexes **1–3**

	$T_r\text{-M}$		$O_r\text{-M}$ M–O
	M–O	M– $\mu_4\text{-O}$	
1	1.958(8)	2.073(3)	2.067(7)
2	2.00(2)	2.124(6)	2.06(2)
3	1.954(4)	2.067(1)	2.068(4)

In conclusion, we have prepared three isostructural Mn, Co and Zn MOFs with diamondoid networks containing large tetrahedral cages using the unexplored TATB ligand. The introduction of triazine rings into MOFs enhances the thermal stability significantly. One of the reasons for the improved stability is due to the exceptionally strong π - π stacking between every two adjacent triazine rings. The introduction of flat nitrogen-containing triangular ligands can be used as a general strategy to design new MOF structural types with increased thermal stability.

The syntheses of MOFs using TATB ligands and other transition metals are currently underway.

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Notes and references

† *Synthesis of 1*: A hydrothermal reaction of H₃TATB (0.01 g, 2.27×10^{-5} mol), Co(NO₃)₂·6H₂O (0.025 g, 8.59×10^{-5} mol) and 0.01 mL pyridine in 12 mL H₂O at 180 °C for 4 days resulted in the formation of deep-blue crystals of **1** (yield: 28%). Anal. calcd. for **1** (%): C 54.20, H 2.57, N 8.14; found: C 54.40, H 2.51, N 8.03.

Synthesis of 2: A mixture of H₃TATB (0.01 g, 2.27×10^{-5} mol), Mn(NO₃)₂ (0.05 mL) and 0.025 mL pyridine in 1.5 mL *N,N*-dimethylformamide was sealed in a Pyrex tube and heated to 110 °C for 3 days, then cooled to room temperature. The resultant light-yellow octahedral crystals were washed with DMF to give **2** (yield: 35%). Anal. calcd. for **2** (%): C 52.01, H 3.25, N 8.33; found: C 51.54, H 3.34, N 8.03.

Synthesis of 3: A solvothermal reaction of H₃TATB (0.005 g, 1.13×10^{-5} mol), Zn(NO₃)₂·6H₂O (0.020 g, 6.72×10^{-5} mol), 1.5 mL dimethylsulfoxide (DMSO), and 5 drops H₂O₂ (30% aq. solution) was sealed in a Pyrex tube and heated to 90 °C, held for 12 h, and then heated to 120 °C for 3 days (cooled to rt at a rate of 0.1 °C min⁻¹). The resultant pale-yellow octahedral crystals were washed with DMSO to give the pure sample (yield: 50%). Anal. calcd. for **3** (%): C, 48.67, H, 3.30, N, 6.55; found: C, 48.39, H, 3.24, N, 6.49.

§ *Crystal data for 1*: C₉₆H₅₃Co₆N₁₂O_{26.5}, *M* = 2152.08, cubic, space group *Fd* $\bar{3}$, *a* = 25.7202 (5) Å, *V* = 17014.6(6) Å³, *Z* = 8, *D*_c = 1.680 g cm⁻³, μ = 1.236 mm⁻¹, *F*(000) = 8696, 15971 reflections measured, 759 unique (*R*_{int} = 0.0702) which were used in all calculations. Final residuals (for 106 parameters) were *R*1 = 0.0753, *wR*2 = 0.2336. CCDC 262518.

Crystal data for 2: C₉₆H₅₃Mn₆N₁₂O_{27.5}, *M* = 2146.16, cubic, space group *Fd* $\bar{3}$, *a* = 25.764 (6) Å, *V* = 17102(7) Å³, *Z* = 8, *D*_c = 1.667 g cm⁻³, μ = 0.954 mm⁻¹, *F*(000) = 8680, 6561 reflections measured, 443 unique (*R*_{int} = 0.0936) which were used in all calculations. Final residuals (for 109 parameters) were *R*1 = 0.0937, *wR*2 = 0.2425. CCDC 262519.

Crystal data for 3: C₉₆H₅₄N₁₂O₂₇Zn₆, *M* = 2199.73, cubic, space group *Fd* $\bar{3}$, *a* = 25.6887 (3) Å, *V* = 16952.2(3) Å³, *Z* = 8, *D*_c = 1.724 g cm⁻³, μ = 1.765 mm⁻¹, *F*(000) = 8880, 18078 reflections measured, 964 unique (*R*_{int} = 0.0508) which were used in all calculations. Final residuals (for 109 parameters) were *R*1 = 0.0399, *wR*2 = 0.1224. CCDC 262520. See <http://www.rsc.org/suppdata/cc/b5/b502007g/> for crystallographic data in CIF or other electronic format.

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