

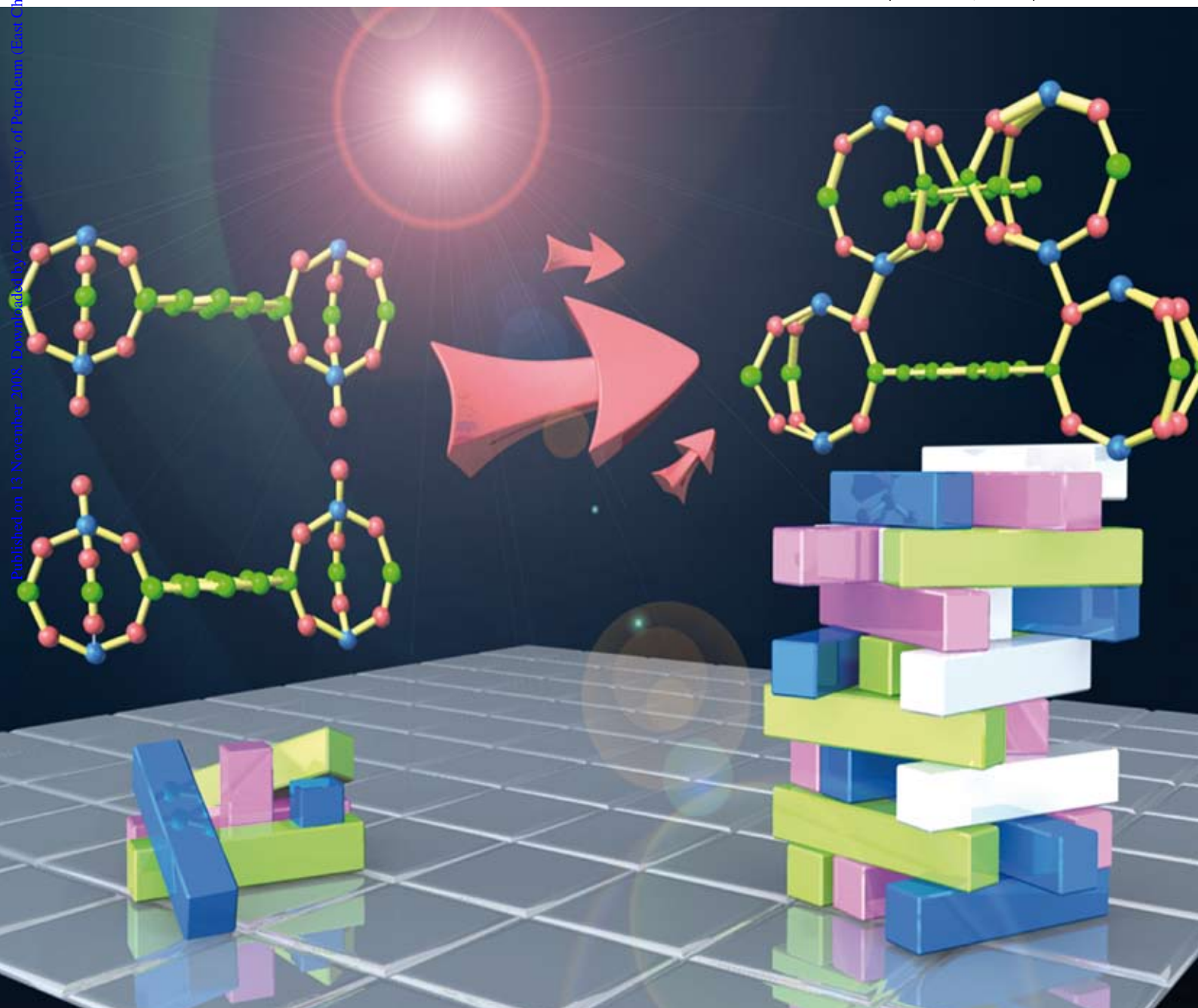
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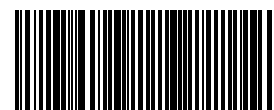
A new luminescent 3D metal–organic framework possessing a rare (3,5)-connected net which can be transformed from a 2D double layer

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A new luminescent 3D metal–organic framework possessing a rare (3,5)-connected net which can be transformed from a 2D double layer†

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Applying a nonplanar dicarboxylate ligand, a new 3D metal–organic framework, $\text{Zn}(\text{TBDC}^1)_{1/2}(\text{TBDC}^2)_{1/2}$ (**1**), possessing a rare (3,5)-connected net has been synthesized and characterized; complex **1** can be formed from a 2D double layer by thermally liberating the coordinated water and dmf molecules, simultaneous with luminescence-increased changes.

Recently, much attention has been focused on design and synthesis of metal–organic frameworks (MOFs) due to their interesting topologies and potential applications such as in luminescence and gas storage.^{1,2} In the past decades, through predigesting the metal ions or clusters as single nodes and organic ligands as the simple linkers,³ many metal–organic frameworks possessing mineral topologies, such as NbO , Pt_3O_4 , and PtS have been synthesized and reported.⁴ Normally, highly connected coordination polymers can be achieved by two routes: applying metal clusters or high-coordination-number lanthanide ions as the nodes.⁵ By applying this strategy, a large number of MOFs with 3-, 4-, 5-, 6-, 7-, 8-, and even 12-connected nets have been documented.⁶ Among the reported topologies, (3,5)-connected nets are somewhat rare,⁷ although several (3,4)- and (3,6)-connected nets have been reported in the literature.^{8,9} In general, the 3-connected example can be achieved by selecting a trigonal organic ligand as a 3-connected node, which proves to be an effective strategy.¹⁰ However, a linear organic ligand can also act as a 3-connected node on the basis of its linking mode. In this communication, we report a new luminescent 3D metal–organic framework, $\text{Zn}(\text{TBDC}^1)_{1/2}(\text{TBDC}^2)_{1/2}$ ($\text{H}_2\text{TBDC} = 2,3,5,6\text{-tetramethyl-1,4-benzenedicarboxylate}$) (**1**), with a rare (3,5)-connected net based on a dinuclear secondary building unit (SBU) and a linear nonplanar dicarboxylate ligand.

As is well known, 2D coordination layers can transform to 3D metal–organic frameworks through thermally liberating coordinated water molecules at the central metal ions (so-called single-crystal-to-single-crystal transformation), which has been studied in recent years.¹¹ In general, the transformation from 2D layer to 3D framework usually results in changes in properties. However, studies on this subject are quite rare. Complex **1** can be transformed from a known 2D double layer, MOF-47,¹² through thermally liberating coordinated water molecules. The changes in luminescence have also been studied.

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† Electronic supplementary information (ESI) available: Figures for complex **1** and TGA for MOF-47 and complex **1**. CCDC reference number 701919. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b815935a

Solvothermal reaction of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and H_2TBDC in H_2O and ethanol at 140 °C for 3 days resulted in the formation of a large amount of colorless plate crystals of **1**.[‡] The formula of $\text{Zn}(\text{TBDC}^1)_{1/2}(\text{TBDC}^2)_{1/2}$ was further confirmed by elemental analysis and thermal gravimetric analysis (TGA).

Single-crystal X-ray diffraction§ reveals that complex **1** is a 3D metal–organic framework. The asymmetric unit of **1** consists of one zinc ion and two half TBDC ligands. The central zinc ion is coordinated by four carboxyl oxygen atoms from different TBDC ligands with the average Zn–O distance of 1.935 Å in a distorted tetrahedral geometry. The basic building unit of **1** is a trigonal dinuclear zinc SBU, which is generated by three carboxylate groups bridging two zinc ions, as shown in Fig. 1a. Two types of TBDC ligands are presented in **1**, TBDC^1 and TBDC^2 , although they adopt similar coordination mode. Both carboxylate groups of TBDC^1 and TBDC^2 adopt bidentate bridging coordination modes to connect two zinc ions, however, each TBDC^1 links two dinuclear zinc SBUs, while each TBDC^2 attaches to three, as shown in Fig. 1b and 1c. Every dinuclear zinc SBU is made up of two TBDC^1 ligands and one TBDC^2 ligand, and the axial positions of the zinc ion in the SBU are occupied by the carboxyl oxygen atoms of TBDC^2 . Due to the space hindrance between the carboxylate groups and the methyl groups in benzene ring, both carboxylate groups of TBDC^1 and TBDC^2 do not locate in a plane with the central benzene ring, with an average dihedral angle between the carboxylate group and the benzene ring of 86.0 and 87.45° for TBDC^1 and TBDC^2 , respectively.

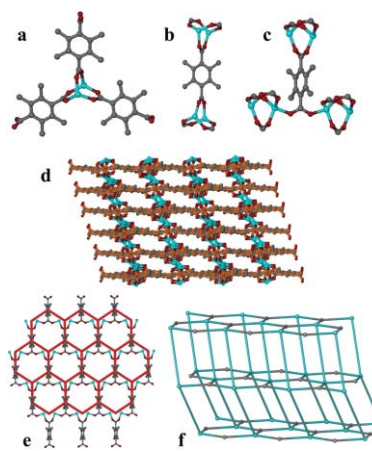


Fig. 1 (a) The dinuclear zinc SBU formed by two TBDC^1 and one TBDC^2 ligands; (b) TBDC^1 ligand linking two SBUs as a linear linker; (c) TBDC^2 ligand linking three SBUs as a trigonal linker; (d) the 3D dense framework of **1**; (e) the (6,3) net formed by TBDC^2 and (f) the (3,5)-connected net of **1**.

Thus, the dinuclear zinc SBUs are first connected by TBDC¹ to generate 1D zigzag chains with the separation between the SBUs of 10.597 Å (see ESI†). One carboxylate group of TBDC² takes part in the formation the 1D zigzag chain. The 1D zigzag chains are further connected by the remaining carboxylate group of TBDC² from the axial positions of the SBUs to generate a 3D dense metal-organic framework (Fig. 1d) containing infinite Zn(COO) chains (see ESI†).

Topologically, each dinuclear SBU is attached to five TBDC ligands (two TBDC¹ and three TBDC²), which can be considered as a 5-connected node; each TBDC¹ ligand connects two dinuclear SBUs and each TBDC² ligand connects three dinuclear SBUs, thus, TBDC¹ can be considered as a linear linker between two SBUs, while TBDC² can be defined as a 3-connected node. On the basis of this simplification, complex **1** possesses a (3,5)-connected net, as shown in Fig. 1f. The net can also be viewed as hexagonal (6,3) honeycomb (Fig. 1e) connected by TBDC¹ ligands. To the best of our knowledge, MOFs possessing (3,5)-connected net are rare, to date, only a few examples have been reported in literature. Most reported (3,5)-connected nets result from the organic ligands,^{7b,7c} which act as 3- or 5-connected nodes. Examples such as found in **1** where the metal clusters act as 5-connected nodes and the organic ligands act as both 3-connected nodes and linear linker are quite rare.

In the past decades, many metal-organic frameworks constructed from 1,4-benzenedicarboxylic acid (BDC) have been reported,^{13,14} however, reports on 2,3,5,6-tetramethyl-terephthalic acid (H₂TBDC) are quite rare. So far, only six examples constructed from TBDC have been reported from CCDC.¹⁵ Recently, Yaghi *et al.* reported a zinc compound, MOF-47, possessing a double layer motif,¹² in which a similar dinuclear zinc SBU as found in **1** is presented. There are two crystallographically independent zinc ions and TBDC ligands in MOF-47. In contrast to complex **1**, there is one coordinated water and one dmf molecule associated with one zinc ion in the SBU, preventing the SBU from extending further. Both carboxylate groups of one TBDC ligand adopt a bidentate bridging mode to connect two zinc ions as in TBDC¹, while two carboxylate groups of the other TBDC ligand are each bound to zinc ion in both bidentate and monodentate bridging coordination mode. The strong hydrogen bonding interactions (2.591 Å) between the coordinated water molecule in one layer and the uncoordinated carboxyl oxygen atom in another layer connect the 2D double layer into a 3D supramolecular architecture with the nearest distance between the Zn and the uncoordinated carboxyl oxygen atom in different layers of 4.018 Å (Fig. 2).

TGA of MOF-47 and **1** was performed under N₂ atmosphere. The thermal behavior of MOF-47 is identical to that of **1** at temperature higher than 120 °C, at which all the coordinated and uncoordinated solvates were lost in MOF-47 (see ESI†).

It has been reported that the structure transformation from 2D layer to 3D framework can occur simultaneously with the dehydration treatment.¹¹ MOF-47 may transform to complex **1** after liberating the coordinated water and dmf molecules through the uncoordinated carboxyl oxygen atom coordinating to the zinc ion in adjacent layer. To confirm this, X-ray powder diffraction was measured for MOF-47. Although diffraction intensity variations and position shifts of the Bragg peaks were observed, the as-synthesised crystals of MOF-47 possess similar peaks to those

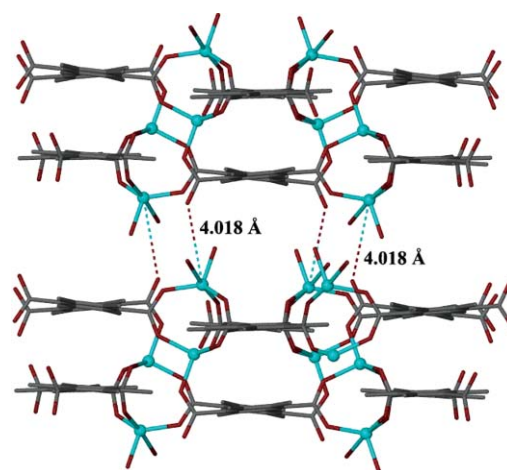


Fig. 2 Projections of the 2D double layers of MOF-47 showing the nearest Zn...O distance between the layers.

simulated from single-crystal X-ray diffraction data, which indicates the purity of the sample. However, after heating the crystals of MOF-47 at 120 °C for one hour, the pattern changed entirely, similar to that simulated from single-crystal X-ray diffraction data of complex **1** (Fig. 3), indicating that MOF-47 was completely transformed to complex **1**. Unfortunately, attempts to collect the crystal data were unsuccessful, although the unit cell similar to complex **1** was obtained.¹⁶

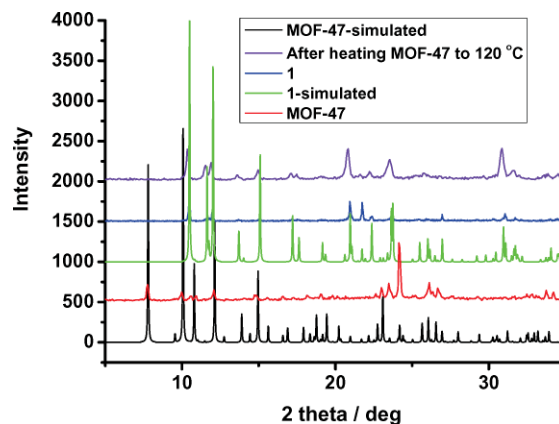


Fig. 3 XRD patterns of MOF-47 and **1**.

The transformation from MOF-47 to complex **1** can also be testified from the luminescent changes. Photoluminescence measurements of H₂TBDC, MOF-47 and **1** in the solid state at room temperature show that H₂TBDC exhibits strong luminescence at $\lambda_{\text{max}} = 359$ nm, upon excitation at 294 nm, and MOF-47 exhibits very weak luminescence at $\lambda_{\text{max}} = 400$ nm, upon excitation at 332 nm, 41 nm red-shift compared to H₂TBDC ligand observed, while **1** exhibits strong luminescence at $\lambda_{\text{max}} = 425$ nm, upon excitation at 352 nm (Fig. 4). These emissions of **1** and MOF-47 can be assigned to the ligand-to-metal charge transfer (LMCT) and/or metal-to-ligand charge transfer (MLCT).¹⁷ However, when MOF-47 was heated to 120 °C for one hour, photoluminescence measurement shows that it exhibits strong luminescence at $\lambda_{\text{max}} = 422$ nm, upon excitation at 352 nm, 22 nm red-shift and almost 10 times intensity compared to MOF-47 is observed. These

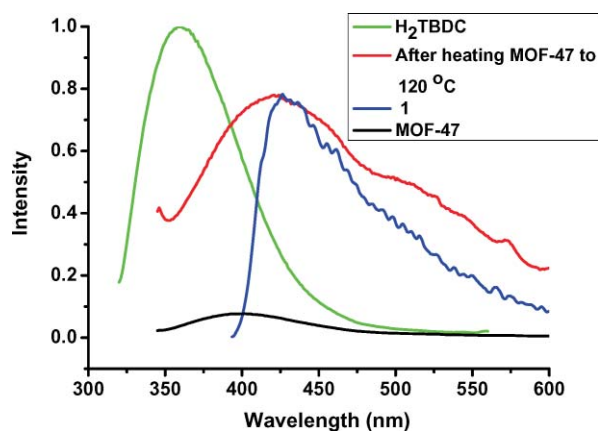


Fig. 4 Solid-state emission spectra of free H₂TBDC, MOF-47, complex **1** and after heating MOF-47 to 120 °C for one hour.

changes in luminescence may derive from the transformation from 2D layer to 3D framework increasing the rigidity of the ligand and reducing the nonradiative decay of the intraligand excited state.¹⁸

In summary, a new 3D metal–organic framework constructed from a nonplanar dicarboxylate ligand, has been synthesized and characterized. Complex **1** possesses a rare (3,5)-connected net, in which TBDC ligands act as 3-connected nodes and the dinuclear zinc SBUs act as 5-connected nodes. Complex **1** can be transformed from a previously reported 2D double layer by liberating the coordinated water and dmf molecules, which was confirmed by X-ray powder diffraction. The luminescence-increased changes were observed simultaneous with the transformation, which indicate that structure transformation can result in a change in properties and a new functional material can be constructed.

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Notes and references

‡ Preparation of MOF-47: A different method was used for preparation of MOF-47. Zn(NO₃)₂·6H₂O (20 mg, 0.07 mmol) and H₂TBDC (10 mg, 0.045 mmol) were suspended in a mixed solvent of DMF (2 ml) and EtOH (1 ml), and heated in an unsealed glass bottle at 75 °C for 2 days. The colorless crystals of MOF-47 were collected, washed with EtOH and dried in the air. Yield: 56%. Preparation of Zn(TBDC¹)_{1/2}(TBDC²)_{1/2} (**1**): Zn(NO₃)₂·6H₂O (20 mg, 0.07 mmol) and H₂TBDC (10 mg, 0.045 mmol) were suspended in a mixed solvent of H₂O (8 ml) and EtOH (8 ml), and heated in a teflon-lined steel bomb at 140 °C for 3 days. The colorless crystalline plate that formed was collected, washed with water and dried in the air. Yield: 54%. Calc. for C₁₂H₁₂O₄Zn: C 50.47, H 4.23%; Found: C 49.95, H 4.36%.

§ Crystallographic data for **1** were collected on a Bruker APEXII CCD diffractometer with Mo-Kα(λ = 0.71073 Å) at room temperature. All structures were solved by the direct method using the SHELXS program of the SHELXTL package and refined by the full-matrix least-squares method with SHELXL.¹⁹ The metal atoms in each complex were located from the *E*-maps, and other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on *F*². The organic hydrogen atoms were generated geometrically (C–H 0.96 Å). Crystal data for **1**: C₁₂H₁₂O₄Zn, monoclinic, space group *C*2/*c*, *a* = 8.8130(10), *b* = 16.3419(18), *c* = 17.301(2) Å, β = 103.185(2)°, *U* = 2426.0(5) Å³, *T* = 298 K, *Z* = 8, *D*_c = 1.564 g cm⁻³, λ = 0.71073 Å. Refinement of 6612 reflections (2481 parameters) with *I* > 1.5σ(*I*) converged at final *R*₁ = 0.0358, *wR*₂ = 0.0935, *gof* = 1.052.

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