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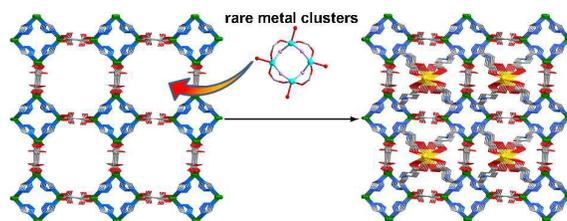
Graphical Abstract

An enhanced extended hook method to realize tetranuclear metal clusters embedded in energetic metal–organic framework channels

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The rare tetranuclear Zn clusters were successfully embedded into energetic 3D metal-organic framework channels by an extended bifunctional tetrazolate-carboxylate hook ligand.



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The rare tetranuclear Zn clusters were successfully embedded into 3D energetic metal-organic frameworks channels by an enhanced extended hook method. The obtained metal-organic framework owns not only high enthalpies of combustion and low sensitivity but also strong green fluorescence.

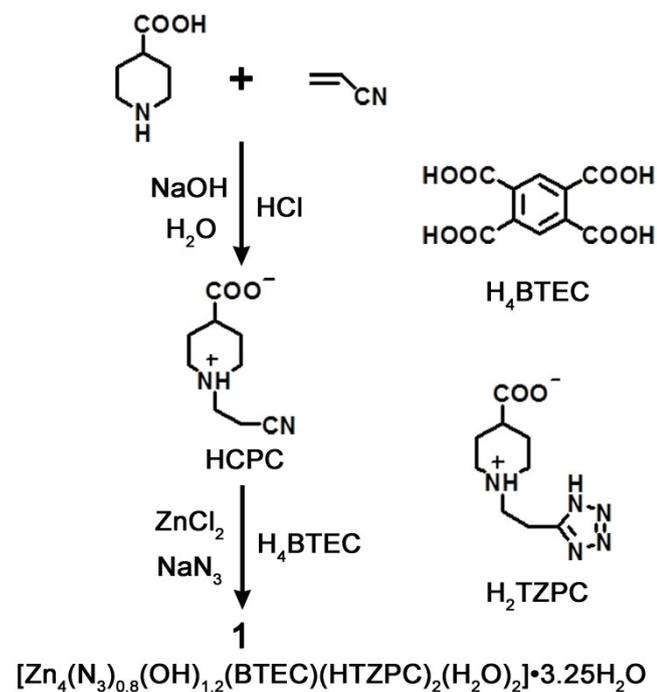
Metal-organic frameworks (MOFs) have extensively attracted attention for their intriguing topological structures and potential applications in gas separation, catalysis, sensing, luminescence, ionic conductivity and nonlinear optics¹. The fast development of MOFs is ascribed to the ingenious design and usage of rich inorganic and organic building blocks to establish infinite frameworks. At the level of materials design, lots of endeavours have been made to functional MOFs, such as introducing functional groups or open metal sites, employing multiple metal or ligands building block, postsynthetic modification or postsynthetic building block replacement². However, it still remains a challenge in some extent to construct multi-functional MOFs with desired structures and characterizations. The metal-centered guest entrapment could enrich and widen the MOFs materials with diverse functional properties from luminescence to catalysis³, providing an alternative platform to realize materials functionalization. The method to actualize the guest molecules incorporating into the space of the MOFs mainly contains impregnation, chemical vapour deposition, ion exchange and so on⁴. It is annoying that the definite window size of the MOFs frequently leads to inaccessibility for larger sized molecules and possible leaching for smaller sized molecules. Recently, Bu and his co-workers developed a feasible approach of embedding metal clusters in MOFs channels by extended hooks originating from second multidentate ligands through

covalent interactions (called the extended hook method)⁵. This access not only overcomes the above-mentioned space-constrained disadvantages but also likely holds great promise for realizing structure design and performance adjustment through selecting proper guest metal clusters and organic ligand. Nevertheless, the existence of open metal sites in the host framework is a prerequisite and the length of the hook with the radius of cages or channels in MOFs should match well, which remains a difficult task in crystal engineering. In this communication, we describe a new approach, an improved extended hook method, through designing a flexible bifunctional ligand, in which one group takes part in building a 3D host framework while another group grabs the metal clusters. Thus, it not only avoids the need for the open metal sites but also can realize regulation of the pole size of 3D host framework by selecting different length ligand.

Azide and tetrazolate derivatives, a family of nitrogen-rich energetic compounds, possess high heats of formation, propulsive power, specific impulse and environmentally compatible characteristics⁶, and are widely used as bridging and/or terminal ligands in the reported energetic compounds⁷. Azide- and tetrazolate-based compounds are considered to be potential green replacements of traditional energetic materials, such as 2,4,6-trinitrotoluene (TNT), 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) and 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX)⁸. Meanwhile, 1, 2, 4, 5-benzenetetracarboxylic acid (H₄BTEC), a well-known excellent organic ligand, has been employed in constructing porous and luminescent MOFs⁹. To illustrate our strategy, we innovatively combine these components into a new 3D MOF [Zn₄(N₃)_{0.8}(OH)_{1.2}(BTEC)(HTZPC)₂(H₂O)₂]·3.25H₂O **1** (H₂TZPC = 1-(2-(1*H*-tetrazol-5-yl)ethyl)piperidine-4-carboxylic acid) and implement encapsulation rare tetranuclear Zn clusters [Zn₄(μ_{1,1}-N₃)_{1.6}(μ₂-OH)_{2.4}(CO₂)₄(H₂O)₄] into framework channels of **1** by an extended tetrazolate-carboxylate ligand hook. Notably, compound **1** exhibits high enthalpies of combustion and low sensitivity, and strong green fluorescence.

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^b University of Chinese Academy of Sciences, Beijing 100039, P. R. China. Electronic Supplementary Information (ESI) available: IR, PXRD, TGA-DSC, luminescence spectra, experimental section, crystallographic information. CCDC 1471950. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x



Scheme 1. Syntheses of 1

The cyano-carboxylate precursor of 1-(2-cyanoethyl) piperidine-4-carboxylic acid (HCPC) was synthesized by the literature method (Scheme 1)¹⁰ and characterized by elemental analyses, ¹H and ¹³C NMR and mass spectra (ESI). Orange block crystals of 1 were obtained by hydrothermal reaction of HCPC, ZnCl₂, H₄BTEC and NaN₃ at 90°C for 3 days (Scheme 1, ESI). The new tetrazolate-carboxylate ligand (H₂TZPC) was generated through the in-situ [2+3] cycloaddition reaction of HCPC and NaN₃, which is clearly confirmed by the absence of cyano group peak in the 2254 cm⁻¹ and the appearance of the tetrazolate group peaks at ca. 1497 and 1434 cm⁻¹ in the IR spectra of HCPC and 1 (Fig. S1). The measured powdered X-ray diffraction (PXRD) pattern matches well with the simulated one based on the single-crystal X-ray data, indicating the pure phase of 1 (Fig. S2).

Single-crystal X-ray diffraction analyses reveal that compound 1 crystallizes in the acentric space group *P*-4. The hydroxyl O and terminal azido N atoms locate at the same position, labelled as X atom, in which the μ₂-OH⁻/μ_{1,1}-N₃⁻ occupancy rate is 6:4. The asymmetric unit of 1 contains two independent Zn(II) atoms, half a molecule of BTEC⁴⁻, one HTZPC⁻ ligand, one coordinate water molecule, one X atom, five eighths lattice water molecules (Fig. 1). The coordination environments of Zn1 and Zn2 are remarkably different. The Zn1 atom adopts a trigonal pyramid geometry (τ₄ = 0.81)¹¹ by two nitrogen atoms (N14/N11B) from two different HTZPC⁻ ligands and two oxygen atoms (O22/O23A) from two different BTEC⁴⁻ ligands. The bond lengths of Zn1–N/O are in the normal range of 2.027(6) to 2.076(7) Å. The Zn2 atom possesses a distorted square pyramid configuration (τ₅ = 0.30)¹² by two oxygen atoms (O11/O12C) from two independent HTZPC⁻ ligands, one water molecule and one symmetry-related XC atom in the equatorial plane, as well as one X atom lying at the

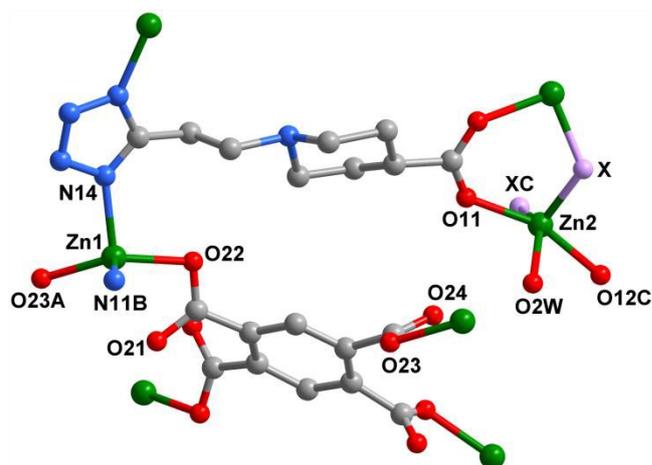


Fig. 1 The coordination environments around the Zn(II) ion, TZPC and BTEC ligands in 1. X = 0.4N₃⁻ + 0.6OH⁻. Symmetry codes: (A) *x*, *y*, *z* + 1; (B) *y*, -*x*, -*z* + 2; (C) -*y* + 1, *x*, -*z*.

axial position with the axial angles varying from 95.5(7)° to 118.0(18)°. Each HTZPC⁻ ligand coordinates to four Zn(II) atoms through carboxylate oxygen atoms (O11 and O12) and tetrazolate nitrogen atoms (N11 and N14). The BTEC⁴⁻ ligand possesses a symmetry center and bridges four Zn1 atoms through individual monodentate coordination modes of carboxylate group.

A prominent structure feature in 1 is that the rare tetranuclear Zn2 clusters ([Zn₄(μ_{1,1}-N₃)_{1.6}(μ₂-OH)_{2.4}(CO₂)₄(H₂O)₄]) are captured in the center of 8-ring channel of the framework built by Zn1, tetrazolate group and BTEC⁴⁻ ligand (Fig. 2). Insight into the formation of the complex 3D framework, 1 can be gained by starting from its multiple inorganic and organic building blocks. There are two types of inorganic building blocks: trigonal pyramid Zn1 node [ZnN₂O₂], and hydroxyl and azido ions-bridged plane-symmetry tetranuclear clusters [Zn₄(μ_{1,1}-N₃)_{1.6}(μ₂-OH)_{2.4}(CO₂)₄(H₂O)₄] (Fig. 2). There are another two kinds of organic ligands: the BTEC⁴⁻ ligand symmetrically binding four Zn1 nodes, and the HTZPC⁻ ligand coordinating two Zn1 nodes and one tetranuclear cluster. As a consequence, the structure of 1 can be described from outside to inside as follow: firstly, the Zn1 nodes are linked by BTEC⁴⁻

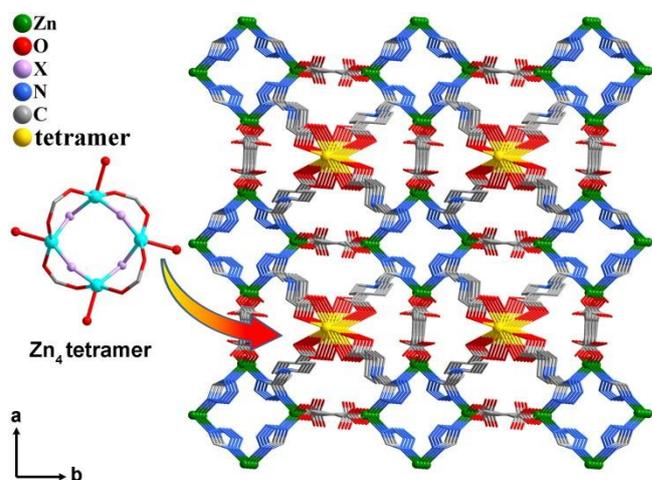


Fig. 2 View of the 3D structure of 1 along the *c* axis. The Zn₄ tetramer represents [Zn₄(μ_{1,1}-N₃)_{1.6}(μ₂-OH)_{2.4}(CO₂)₄(H₂O)₄].

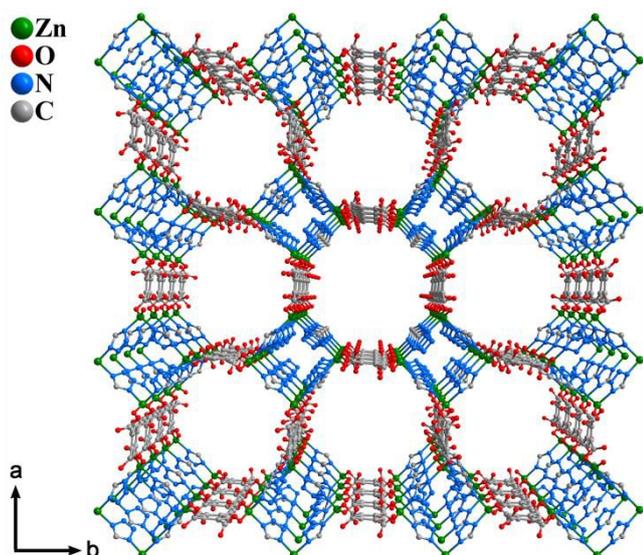


Fig. 3 The 3D framework consist of Zn1 atom, tetrazolate group and BTEC ligand, with the TZPC ligand omitted except the tetrazolate group.

ligand to form 1D chain along the *c* axis (Fig. S3), and then the tetrazolate group adopts a μ_2 -bridge fashion to link these 1D chains to produce a 3D host framework with 1D octolateral channels along the *c* axis (Fig. 3). The host framework can be described as a *mot-e* topology found in MOF112 (Fig. S4)¹³. Then, the HTZPC⁻ ligands are anchored onto the 3D host framework through the N ends of tetrazolate group, while the carboxylate ends stretch toward the centers of channels to grab Zn₂ tetranuclear clusters to generate an encapsulated framework. As a result, the pore of the final framework disappears because the large size tetranuclear clusters occupy the space. The above analyses show that the HTZPC⁻ ligand has a vital effect on the initial porous 3D framework, and captures metal clusters. Replacement of the HTZPC⁻ ligand with a series of different length tetrazolate-carboxylate ligands provides a feasible route to realizing the pore size of 3D host framework more manageable and creating new functional materials. It's well known that *d*¹⁰ metal coordination compounds are a class of excellent light emitting materials¹⁴. The solid-state photoluminescence of **1** was investigated at room temperature. As shown in Fig. S5, compound **1** exhibits a strong green fluorescent broad emission band centered at 487 nm with the lifetime of 6.67 ns and the total quantum yield Φ of 4.5% when excited at 410 nm. To understand more thoroughly the emission nature, the theoretical calculation on the structure of **1** by the method of the density of states (DOS) has been done, which was performed with the CASTEP code based on the density functional theory using a plane-wave expansion of the wave functions. The calculation result (Fig. S6) shows that the top of the valence bands (VBs) between energy -2.0 and 0 eV is dominated by a mixture of $p-\pi$ orbitals of HTZPC⁻ and BTEC⁴⁻ ligands, while the bottom of conduction bands (CBs) is almost contributed by the $4s$ orbital of Zn²⁺. Accordingly, the emission peak at 487 nm can be mainly ascribed to the ligand-to-metal charge transfer.

As the thermal behavior and the enthalpy of combustion are two significant parameters to evaluate the performance of energetic materials, we tested the differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and combustion enthalpy of **1** (Fig. S7). The DSC curve reveals two main successive endothermic processes, with peaks locating at 100 and 190 °C, respectively. The TGA curve shows a mass loss of 11.8% (calc. 11.6%) from 25 to 210 °C, which corresponds to the loss of azide, coordinated and lattice water molecules. Upon further heating, exothermic stages occur in the range of 280–370 °C, caused by the decomposition of the framework. The decomposition temperature of **1** is 280 °C, which is comparable to that of HMX (287 °C), one of the energetic materials commonly employed¹⁵, and is higher than the criterion of 200 °C for “green” metal energetic materials^{7b, 16}. The relatively high thermal stability is presumably caused by the strong structural reinforcement in 3D frameworks. To study the energy of combustion enthalpy of **1**, the measured constant-volume combustion heats ($\Delta_c U$) is 14.118 kJ/g. The enthalpy of combustion ($\Delta_c H$) was calculated from $\Delta_c U$ with a gas volume correction: $\Delta_c H = \Delta_c U + \Delta nRT$, where Δn depends on the change about the number of gas constituents in the reaction process. The calculated $\Delta_c H$ values is -14.111 kJ/g, which is lower than that of TNT ($\Delta_c H = -16.27$ kJ/g), but larger than those of commercially used RDX ($\Delta_c H = -9.61$ kJ/g) and HMX ($\Delta_c H = -9.60$ kJ/g)¹⁷. It is also much higher than those of 1D Zn(II) coordination polymer $[\text{Zn}(\text{N}_2\text{H}_4)_2(\text{N}_3)_2]_n$, 3D Cu(II) MOF $[\text{Cu}_3(\text{MA})_2(\text{N}_3)_3]$ (MA = melamine) and our previously reported aminotetrazolate-based MOF $[\text{Zn}(\text{tzeg})]_n$, $[\text{Cd}(\text{tzeg})(\text{H}_2\text{O})]_n$ and $[\text{Cu}(\text{tzeg})(\text{H}_2\text{O})]_n$ ($\text{H}_2\text{tzeg} = \text{N}-[2-(1H\text{-tetrazol-5-yl})\text{ethyl}]\text{glycine}$)^{8d, 18}. Based on the U.N. recommendations on the transport of dangerous goods, the impact and friction sensitivities (FSSs) of **1** were also investigated with standard BAM drop hammer and friction tester techniques¹⁹. The impact sensitivity of **1** is >40 J, classified as “insensitive”. Furthermore, no friction sensitivity is observed up to 36 kg (360 N) for **1**. This indicates that **1** is insensitive to the external stimulus, which may be potential energetic materials due to the higher enthalpy of combustion and lower sensitivity.

In summary, we have illustrated a new synthetic approach for the encapsulation of rare tetranuclear metal clusters into an energetic 3D MOF. The usage of flexible bifunctional ligands in entrapment of metal clusters in MOF channels represents a general versatile route to modulate the pore size of the 3D host framework and realize structural diversity for various applications. Ongoing work in our laboratory includes exploring the influence of different length hook ligand between two functional groups on the structures and performances of 3D MOFs.

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- 19 Impact: insensitive > 40 J, less sensitive ≥ 35 J, sensitive ≥ 4 J, very sensitive ≤ 3 J; Friction: insensitive > 360 N, less sensitive = 360 N, sensitive < 360 N > 80 N, very sensitive ≤ 80 N, extreme sensitive ≤ 10 N. According to the U.N. Recommendations on the Transport of Dangerous Goods.