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A Heat-Resistant and Energetic Metal-organic Framework Assembled by Chelating Ligand

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ABSTRACT: Heat-resistant explosives with high performance and insensitivity to external stimulus or thermal are indispensable both in military and civilian especially utilized under harsh conditions. We designed and synthesized a new heat-resistant three-dimensional chelating energetic metal-organic framework (CEMOF-1) by employing 4-amino-4H-1,2,4-triazole-3,5-diol (ATDO) as a ligand. Due to its chelating 3D structural feature, good oxygen balance (-29.58%) and high crystal density (2.234 g cm⁻³), CEMOF-1 demonstrates high decomposition temperature (445 °C), insensitivity to stimulation, excellent detonation velocity (10.05 km s⁻¹) and detonation pressure (49.36 GPa). The advantages of facile synthesis, thermal stability and powerful explosive performance make CEMOF-1 as a promising candidate for heat-resistant explosives in future applications.

KEYWORDS: metal-organic frameworks, energetic materials, heat-resistant, chelating ligand, explosives

Heat-resistant explosives¹⁻³ are a type of energetic materials (EMs) that can detonate dependably and reliably even at high temperatures. These energetic materials are indispensable as deep underground explosives and space rocket propellants where temperature resistance is required. Currently, the most widely used heat-resistant explosives are 1,3,5-triamino-2,4,6-trinitrobenzene (TATB),⁴ hexanitrostilbene (HNS)⁵ and 2,6-diamino-3,5-dinitropyrazine-1-oxide (ANPyO),⁶⁻⁷. Their decomposition temperatures range between 310 and 360 °C, however, the synthesis of these materials involves the use of strong nitration agents and complex synthetic routes costs. Moreover, with the increase of the excavation depth and of the space aircraft speed, the decomposition temperature need to be further improved, otherwise, complex insulation protection shields are required. Therefore, it is urgently desired to seek novel heat-resistant explosives.

Metal-organic frameworks (MOFs) are a new class of hybrid and crystalline solid-state materials that constructed by inorganic metal centers and organic linkers through strong coordination bonds.⁸⁻¹² MOFs with 1D chains, 2D planes or 3D architectures are considered to be promising candidates for the next generation of EMs, owing to their tunable structures, good stability, and high energetic output. In recent years,

many pioneering studies have focused on the synthesis of novel energetic MOFs for a variety of applications in EMs.¹³⁻¹⁶

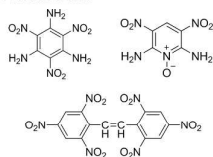
Compared with low-dimensional structures, 3D MOFs with higher structural reinforcement generally provide larger mechanical strength, superior thermo-stability, and improved energy and heat of detonation. However, the decomposition temperatures of the reported energetic MOFs are lower than 400 °C, which limits their potential applications in harsh environment. In addition, many insensitive 3D energetic MOFs, usually composed of N-rich ligands, are rich in carbon and nitrogen but lack oxygen balance. Anchoring N-NO₂ bonds onto the pore-walls of the framework is an efficient way to enhance the oxygen balance but may sacrifice their safety and thermostability. It still remains a challenge to address the contradiction among sensitivity, thermo-stability and explosion power.

To tackle the above obstacles, we intentionally selected 4-amino-4H-1,2,4-triazole-3,5-diol (ATDO) as the ligand to prepare 3D energetic MOFs (Scheme 1). The advantages are summarized as follows: 1) the rigid structure of a five-membered heterocycle may promote structural stability, and the high ratio of N-N and N-C bonds in the heterocycle give rise to an elevated formation enthalpy;¹⁷ 2) unlike the introduction of nitrate ester (-ONO₂) or nitramine (-NHNO₂) groups that usually lead to an increase of sensitivity towards external stimuli such as heat, friction, impact and static electricity, the introduction of the carbonyl oxygen atom in triazole can improve the density and enhance explosive property without sacrificing stability;¹⁸ 3) the introduction of amino groups, according to the literature,¹⁹ has been correlated to enhance the thermal stability of EMs through the formation of multiple hydrogen bonding interactions; 4) ligands that contain both amino groups and the carbonyl oxygen will benefit for the forming of chelating structures, where the extended skeleton can be reinforced by chelating bonds that involves the formation of multiple coordination bonds between a polydentate strut and a single metal ion node.²⁰

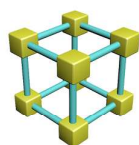
Herein, we reported a facile synthetic method to prepare a chelating energetic metal-organic framework (CEMOF-1) under mild hydrothermal conditions. The structure was confirmed by the single-crystal analysis and we further explored its thermal decomposition properties, non-isothermal kinetics, long-term thermostability, sensitivities, detonation velocities and

detonation pressures. The results indicate that CEMOF-1 exhibits high enthalpy of formation, good detonation performance as well as insensitivity towards external stimulus including electrostatic discharge, friction, and impact. To the best of our knowledge, the CEMOF-1 possesses one of the highest decomposition temperature (445 °C) compared to traditional heat-resistant explosive and energetic MOFs.²¹

(a) Previous work:

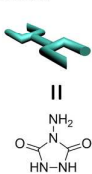


Traditional heat-resistant explosives



MOFs as energetic materials

(b) Our work:



Cd²⁺



3D CEMOFs as heat-resistant explosive

Scheme 1 (a) Traditional heat-resistant explosives and schematic illustration of energetic MOFs; (b) Schematic representation of strategies to prepare heat-resistant energetic MOF by using chelating ligand.

The ligand, ATDO, was prepared through the reaction of diethyl azodicarboxylate (DEAD) with 60% N₂H₄ solution in a mixture of water and ethanol at reflux overnight. CEMOF-1 was then prepared hydrothermally with ATDO and Cd(NO₃)₂ at 75 °C for 1 h. After cooling the mixtures to room temperature, CEMOF-1 precipitated out and was collected by filtration with 90% isolated yields. The structure and purity of CEMOF-1 were confirmed through the use of single crystal X-ray diffraction (SXRD), elemental analyses (EA), Fourier transform infrared spectroscopy (FT-IR), and powder X-ray diffraction (PXRD).

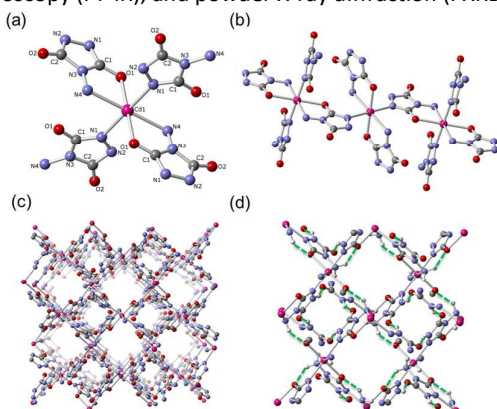


Figure 1 Central cadmium coordinated by four ATDO molecules (a), 1D chains structure formed by metals and ligands (b), packing diagram (c) and hydrogen bonds between ligands (d) of CEMOF-1.

SXRD analyses showed that CEMOF-1 adopts a tetragonal space group *I41/a* and contains mononuclear clusters. In CEMOF-1, Cd(II) ion takes sp^3d^2 hybridization (Figure 1). The lone pair electrons of both N and O from the ATDO can be accommodated within the six empty orbitals from the central

Cd(II) ion. Both the carbonyl and amino groups in the ATDO moiety are capable of acting as electron donors upon coordination to the central metal atom resulting in an elongated, hexa-coordinated octahedron with respect to Cd(II). Each central metal atom coordinates to two N1, two N4 and two O1 atoms. The equatorial plane consists of two nitrogen atoms corresponding to amino groups and two oxygen atoms corresponding to carbonyl group (Cd1–N4 = 2.388 Å and Cd1–O1 = 2.311 Å), forming a cluster with two chelating rings (Figure 1a). The two nitrogen atoms from the other two ATDO moieties coordinate to Cd(II) in the axial position (Cd1–N1 = 2.310 Å). The central Cd (II) ion takes an octahedral configuration with four ATDO molecules and the bond angles of N1–Cd1–N1, O1–Cd1–O1 and N4–Cd1–N4 are 180°. All of the ATDO ligands show a μ_2 -mode coordinating two Cd metal ions. Cadmium atoms and rigid ligands are locked each other alternately and assembled to form 1D chains (Figure 1b). These 1D chains are mutually weaved at regular intervals into a 3D framework structure (Figure 1c). In CEMOF-1, each tetradentate organic ligand (ATDO) acts as a chelating agent and coordinates to two Cd ions with the formation of N–Cd and O–Cd bonds. In addition, there are six types of hydrogen bonds that exist within CEMOF-1, including the intermolecular H-bonds between two ligands and the H-bonds between the ligand and water molecules in the pores. The chelation bonds as well as H-bonds may contribute to their densities and stabilities (Figure 1d and Figure S1). Elemental analysis results indicate that the chemical composition for the crystals of CEMOF-1, in terms of the C, N, H content, are in good agreement with the theoretical values (ESI, section3).

Then the samples were vacuum dried overnight at 100 °C to remove guest water molecules. The PXRD pattern (ESI, Figure S3) of experimental CEMOF-1 are consistent with that of the simulated one, revealing its crystallographic purities. The FT-IR displayed signals at 3281, 3183, 1724 and 1637 cm⁻¹, which can be attributed to the N–H and C=O groups, respectively.

The densities and oxygen balance are critical factors in evaluating the explosion properties of EMs. The crystal density of CEMOF-1 is 2.234 g cm⁻³, which is comparatively higher than traditional heat-resistant explosives (TATB, 1.93 g cm⁻³; HNS, 1.70 g cm⁻³; ANPYO, 1.86 g cm⁻³) as well as that for most of the reported 3D energetic MOFs (ATZ-1, 1.62 g cm⁻³; ATZ-2, 1.68 g cm⁻³; [Cu(Htztr)₂(H₂O)₂]_n, 1.892 g cm⁻³; [Cu(Htztr)]_n, 2.435 g cm⁻³).^{13–14}

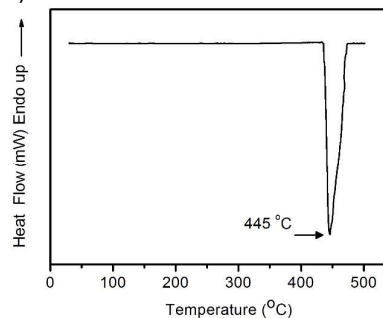


Figure 2 DSC curve of CEMOF-1.

The oxygen balance for CEMOF-1 has a value of -29.58% (-31.11% when fully dried), which is better than commercial heat-resistant explosives and reported 3D energetic MOFs such as ATRZ-1, ATRZ-2 and IFMC-1. The high density and large

oxygen balance, attributed to the two oxygen atoms in the small, rigid ligand as well as the compact chelating structure, lead to beneficial explosive properties.

Thermal stability of heat-resistant explosives is a crucial parameter in terms of performance. Differential scanning calorimetry (DSC) measurements with linear heating rates of 5, 10, 15 and 20 °C were used to analyse the decomposition temperature and apparent activation energy (E_a) of CEMOF-1 (Table 1). The DSC curve of CEMOF-1 has one intense exothermic peak at 445 °C (Figure 2). TG curve (ESI, Figure S4) shows that CEMOF-1 has a single mass-loss event between 400 to 500 °C, considering as the destruction of main framework. According to DSC, TG and PXRD analyses, water molecules have been removed upon activation and the topology of CEMOF-1 could be still retained. These results revealed that the CEMOF-1 without guest water molecules is still stable, attributing to the chelation effect as well as the hydrogen bonds between the ligands.

We utilized both Kissinger's method and Ozawa's method to evaluate the apparent activation energies (E_a) and the rate constants of the initial thermal decomposition process of CEMOF-1. The equations are listed as below:²²⁻²³

$$\frac{d \ln(\beta/T_p^2)}{d(1/T_p)} = -\frac{E_a}{R} \quad \text{Kissinger's method (1)}$$

$$\log \beta + \frac{0.4567 E_a}{RT_p} = C \quad \text{Ozawa's method (2)}$$

where C is a constant; R is the gas constant; T_p is the peak temperature; β is the linear heating rate.

Based on the exothermic peak temperatures measured at different heating rates, the thermo-kinetic parameters (activation energies E_0 and E_k , pre-exponential factor A_k and linear correlation coefficients R_k and R_0) of the exothermal process for CEMOF-1 were calculated and summarized in Table 1. With the increasing of the heating rate, the exothermic peak (T_p) temperature increases. The activation energies of CEMOF-1 are 212.3 kJ mol⁻¹ (E_k) and 209 kJ mol⁻¹ (E_0). Therefore, the Arrhenius equation for CEMOF-1 can be expressed as $\ln(k) = 22.91 - 212.3 \times 10^3/RT$. CEMOF-1 makes an appealing candidate as a heat-resistant explosive with a decomposition temperature larger than 400 °C as well as a high activation energy, implying good thermal stability.

Table 1 Outlines of the exothermic peak temperatures measured at varied heating rates and the thermokinetics parameters for CEMOF-1.

	CEMOF-1	
T_p (°C)	5	445.87
	10	450.72
	15	454.63
	20	456.21
Kissinger's method:		
E_k [kJ·mol ⁻¹]		212.3
$\ln A_k$		22.91
R_k		-0.997
Ozawa's method:		
E_0 [kJ·mol ⁻¹]		209
R_0		-0.9972

Compared with the traditional heat-resistant explosives and some representative reported energetic MOFs, CEMOF-1

shows outstanding thermostability and oxygen balance (Figure 3). The decomposition temperature of this material surpasses that of traditional heat-resistant explosives and is about 50 °C higher than the most thermostable MOFs. Furthermore, the oxygen balance of CEMOF-1 is larger than most 3D MOFs, which may improve the explosive performance for practical applications.

On the basis of the standard BAM Fallhammer techniques (in ESI),²⁴ the safety of CEMOF-1 to mechanical stimulation, including impact and friction, were tested and outlined (Table 2). The results of impact sensitivities (IS) test of CEMOF-1 (>40 J) shows this material is insensitive to impact. Furthermore, the IS value of CEMOF-1 is lower than that of TATB, NHS and TNP₂O under similar test conditions. The friction sensitivity is observed to withstand values of up to 360 N for CEMOF-1, which is comparable to TATB and NHS. In addition, the CEMOF-1 is insensitive to electrostatic discharge and will not combust under electrostatic energy higher than 24.75 J. These results indicate remarkably low sensitivities of CEMOF-1 towards external stimulus. The significantly improved safety of CEMOF-1 can most likely be attributed to the 3D chelating framework structure as well as the hydrogen bonds between the ligands that could strongly rigidify the framework

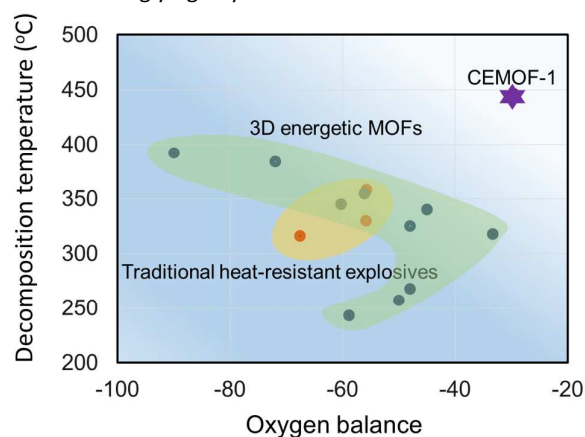


Figure 3 Graphical comparison of the oxygen balance and decomposition temperature of traditional heat-resistant explosives and 3D energetic MOFs.

Working as a heat-resistant explosive, detonation pressure and detonation velocity are critical parameters that affect the explosive performance. Considering the CEMOF-1 as metal-containing explosives, we chose an empirical method, Kamlet-Jacobson (K-J), to predict its detonation pressure and detonation velocity. The equation utilized for this calculation is as follows:²⁵

$$D = 1.01 \Phi^{1/2} (1 + 1.30 \rho) \quad (3)$$

$$P = 1.558 \Phi \rho^2 \quad (4)$$

$$\Phi = 31.68 N(MQ)^{1/2} \quad (5)$$

We firstly obtained the density (ρ), enthalpy of formation (ΔH_f), heat of detonation (Q), moles of detonation gases per gram of explosive (N) and average molecular weight of detonation gases (M), and then used these values to estimate the detonation velocity (D) and detonation pressure (P) of CEMOF-1. The energy of detonation was calculated by using

Density functional theory (DFT) with the presence of water molecules in the host. The ΔH_f for CEMOF-1 was calculated to be 2.94 kcal g⁻¹. The D and P values of CEMOF-1 are 10.07 km s⁻¹ and 49.36 GPa, which is higher than those traditional heat-resistant explosives and most 3D energetic MOFs (Table 2). Though the presence of water molecules contributes to the density and oxygen balance of the MOF, water molecules may affect the explosive performance of the CEMOF-1 due to its low reaction activity.^{14,21} Therefore, the experimental explosive performance of CEMOF-1 without the water may be better than the calculated results taking into considerations of

water molecule. It is also worth emphasizing that advanced heat-resistant explosives should be insensitive to external stimulus and show excellent explosive performance to be considered for use in potential applications. CEMOF-1 can be obtained in high yield and demonstrates attractive properties, making it a promising candidate for heat-resistant explosives. The relatively outstanding explosive performance of CEMOF-1 may be originated from the high-nitrogen containing ligand, high density and good oxygen balance together with the chelating skeletons.

Table 2 Physical properties, decomposition temperatures, calculated detonation parameters and sensitivity performance of heat-resistant explosives and 3D energetic MOFs.

Compounds	ρ^a /g cm ⁻³	Ω^b (%)	T_{dec}^c /°C	D^d /km s ⁻¹	P^e /GPa	IS^f /J	FS^g /N
CEMOF-1	2.234	-29.58	445	10.07	49.36	>40	>360
TATB	1.93	-55.81	330	8.114	-	-	-
HNS	1.70	-67.52	316	7.000	-	-	-
ANPyO	1.86	-55.78	358	-	-	-	-
ATRZ-1 ¹³	1.68	-58.83	243	-	-	22.5	-
ATRZ-2 ¹³	1.62	-49.99	257	-	-	30	-
IFMC-1 ²⁶	1.47	-89.98	392	8.21	26.23	>40	>360
Cu(3,5-DNBA)(N ₃) ₂ ²⁷	2.03	-48.00	268	-	-	23.5	>360
[Cu(Htztr) ₂ (H ₂ O) ₂] _n ¹⁴	1.892	-60.24	345	8.18	30.57	>40	>360
{[Cu(Htztr)]H ₂ O} _n ¹⁴	2.316	-48.00	325	7.92	31.99	>40	>360
[Cu(Htztr)] _n ¹⁴	2.435	-56.09	355	10.40	56.48	32	>360
[Pb(Htztr) ₂ (H ₂ O)] _n ²⁸	2.519	-45.03	340	7.715	31.57	>40	>360
[Pb(H ₂ tztr)(O)] _n ²⁸	3.511	-28.86	318	8.122	40.12	>40	>360
[Cu ₄ Na(Mtta) ₅ (CH ₃ CN)] _n ¹⁵	1.975	-71.97	384	7.225	24.43	36	>360
[Co ₉ (bta) ₁₀ (Hbta) ₂ (H ₂ O) ₁₀ ·(22H ₂ O)] _n ²⁹	1.975	-35.04	300	-	-	>40	>360
[Co ₉ (bta) ₁₀ (Hbta) ₂ (H ₂ O) ₁₀] _n ²⁹	-	-40.54	253	8.657	32.18	27	>360

^aDensities obtained from X-ray measurements (g cm⁻³). ^bOxygen balance. ^cDecomposition temperature. ^dDetonation velocity (km s⁻¹). ^eDetonation pressure (GPa). ^fImpact sensitivity (J). ^gFriction sensitivity (J).

In conclusion, we applied 4-amino-4H-1,2,4-triazole-3,5-diol as a chelating ligand to synthesize a new energetic MOF (CEMOF-1). The rigidity of the 3D chelating structure impart the materials with high decomposition temperature (445 °C) as well as insensitivity to external stimulation, which are crucial for heat-resistant explosives. Compared to both traditional heat-resistant explosives and 3D energetic MOFs, CEMOF-1 has outstanding thermal stability and insensitivity to external stimulus. Taking advantage of good oxygen balance and high density, CEMOF-1 possesses excellent calculated detonation velocity of 10.07 km s⁻¹ and detonation pressure of 49.36 GPa. Our results demonstrate that CEMOF-1 is an attractive energetic material. The design strategy as well as facile synthetic method may provide a way to obtain high-performance heat-resistant explosives that may use in harsh conditions such as in deep well mining or aerospace technology.

Associate Content

The Supporting Information is available free of charge on the ACS Publications website

Synthetic procedures of ATDO and CEMOF-1, Sensitivities tests of CEMOF-1, Hydrogen bonds between ligand and water molecules

of CEMOF-1 in the crystal structure, Ligand structures of reported energetic MOFs, X-ray crystallography data of ATDO and CEMOF-1, PXRD pattern and TG profile of CEMOF-1, Calculation method of enthalpy of formation.

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Notes

The authors declare no competing financial interest.

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