

3D Energetic Metal–Organic Frameworks: Synthesis and Properties of High Energy Materials**

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Metal–organic frameworks (MOFs) have attracted great attention because of their intriguing molecular topologies and potential applications in chemical separation,^[1] gas storage,^[2] drug delivery,^[3] catalysis^[4] and chemical sensor technology.^[5] Particularly, MOFs could also be potential energetic materials because of their high densities and high heats of detonation. For example, Hope-Weeks and co-workers recently reported two hydrazine-perchlorate 1D MOFs [(Ni(NH₂NH₂)₃(ClO₄)₂)_n (NHP), and (Co(NH₂NH₂)₃(ClO₄)₂)_n (CHP)] with linear polymeric structures,^[6] which were regarded as possibly the most powerful metal-based energetic materials known to date, with heats of detonation comparable with that of hexanitrohexaazaisowutzitane (CL-20; about 1.5 kcal g^{−1}). Unfortunately, these coordination polymers were highly sensitive to impact deriving from their low rigidity characteristic of such linear polymeric structures, which makes practical use infeasible. In order to decrease the sensitivities, the same authors also used a hydrazine derivative (hydrazine-carboxylate) as the ligand to construct MOFs with 2D sheet structures [((Co₂(N₂H₄)₄(N₂H₃CO₂)₂)(ClO₄)₂·H₂O)_n (CHHP) and ((Zn₂(N₂H₄)₃(N₂H₃CO₂)₂)(ClO₄)₂·H₂O)_n (ZnHHP)], which showed a considerable reduction to the sensitivity, however, concomitantly their heats of detonation decreased (Figure 1).^[7]

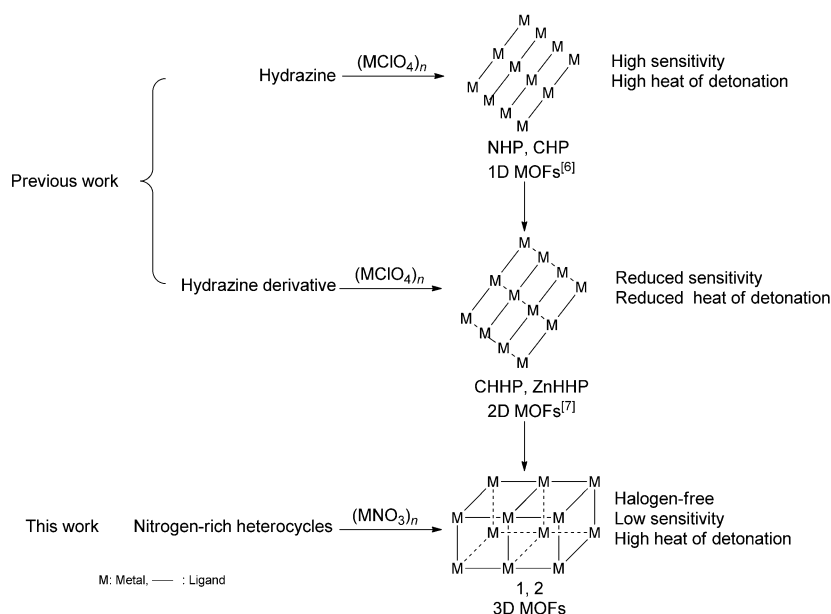


Figure 1. Energetic MOFs with different topologies.

Despite these advances, current coordination frameworks are only limited to be a 1D or 2D structure. Compared with 1D linear and 2D layered structures, three-dimensional (3D) frameworks possess more complicated connection modes, which could further enhance structural reinforcement, hence improve the stabilities and energetic properties. A lot of 3D MOFs have been synthesized with interesting magnetic,^[8] catalytic,^[9] and luminescent properties,^[10] some of them incorporate a variety of energetic moieties such as nitrate anions (NO₃[−]),^[8b] perchlorate anions (ClO₄[−])^[8c] into the 3D frameworks. However, their potential applications as energetic materials have not been disclosed or discussed; relevant data about energetic properties are also missing in the literature. Additionally, both reported 1D and 2D energetic MOFs based on the perchlorate anions, have been scrutinized by the US Environmental Protection Agency (EPA) because they promote thyroid dysfunction and are teratogenic.^[11]

Continuing our interest in finding new highly energetic, eco-friendly energetic materials, we explore the preparation of halogen-free energetic 3D MOFs, for which two polymers [Cu(atrz)₃(NO₃)₂]_n (**1**) and [Ag(atrz)_{1.5}(NO₃)₂]_n (**2**) were designed by replacing the hydrazine ligand with 4,4'-azo-1,2,4-triazole (atrz).^[12] Here, we chose to use atrz as a ligand for the following reasons: 1) as a nitrogen-rich heterocyclic backbone,^[13] atrz possesses a high nitrogen content (N % =

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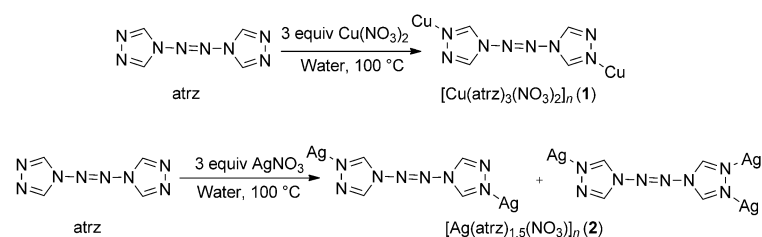
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68.3), high heat of formation (878 kJ mol^{-1}), and good thermal stability with a decomposition temperature of up to 313°C , which could improve the energetic performances of the target polymers; 2) compared with hydrazine, atrz as a ligand has more than six potentially coordinated N atoms in a molecule, which may show more bridging modes, meeting the geometric needs of a 3D structure;^[14] 3) its decomposition results predominantly in the generation of environmentally benign nitrogen gas. Recent modeling and testing have shown that the presence of high concentrations of nitrogen species in the combustion products of propellants can reduce gun barrel erosion by promoting the formation of iron nitride rather than iron carbide on the interior surface of the barrel.^[15] In addition, the perchlorate anion was also replaced by the nitrate anion for environmental concerns. As anticipated, the target 3D energetic MOFs were obtained, and they exhibit potentially significant physical and energetic properties.

The copper complex **1** was synthesized by a simple and one-step hydrothermal reaction of copper dinitrate pentahydrate with atrz^[12] in water (Scheme 1). Dark-blue needles, suitable for X-ray structure determination, of complex **1** crystallized from a clear green solution after several days. Using an analogous route, the silver complex **2** was obtained



Scheme 1. Synthesis, coordination mode, and formulae for 3D energetic MOFs.

as colorless plates. Coordination polymers **1** and **2** are air-stable with the maintenance of their crystallinities for at least several weeks and are insoluble in common organic solvents, such as dimethyl sulfoxide (DMSO), chloroform, methanol, ethanol, and acetone.

Complex **1** crystallizes in the monoclinic $P2_1/n$ space group, with a 3D porous metal–organic framework. As depicted in Figure 2, the asymmetry unit is made up of one Cu^{II} atom, three atrz ligands and two nitrate anions. The Cu^{II} atom is six-coordinated by six atrz nitrogen atoms in a regular octahedron with Cu–N bond lengths from 2.010 to 2.030 Å, which are much shorter than that of its analogous polymer $[\text{Cu}(4,4'\text{-bis-1,2,4-triazole})_2(\text{NO}_3)_2]_n$ (2.310 Å),^[8b] implying that the nitrogen atoms of atrz have stronger coordination interactions with the Cu^{II} atoms. The equatorial plane is formed by the coordination of four nitrogen atoms (N1', N5, N6, and N7) and one copper atom (Cu1). The axial positions are occupied by N8 and N9 atoms, with a N8–Cu1–N9 bond angle of 180° . All Cu^{II} atoms have the same coordination environment with an octahedral geometry. The adjacent Cu...Cu distance (Cu1–Cu2) is 11.790 Å and is longer than that of $[\text{Cu}(4,4'\text{-bis-1,2,4-triazole})_2(\text{NO}_3)_2]_n$ (4.086 Å). It indicates that the ligand atrz is very similar to that of 4,4'-bis-

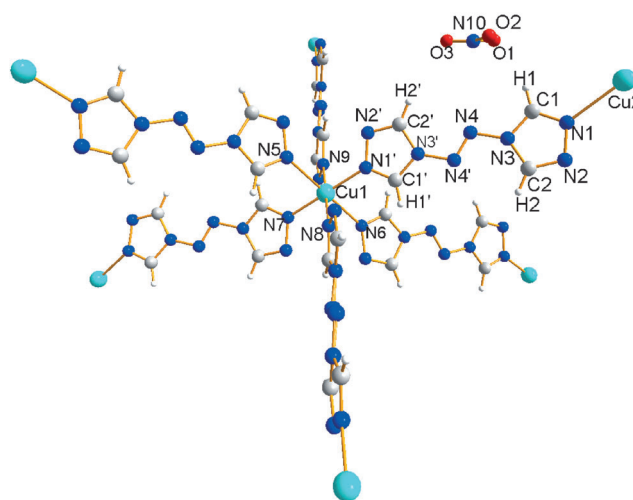


Figure 2. Coordination structure of **1**. Selected bond lengths and angles: N1'–Cu1 2.010(2), N6–Cu1 2.031(2), N7–Cu1 2.031(2), N8–Cu1 2.010(2); N1'–Cu1–N7 $180.00(65)^\circ$; N1'–Cu1–N6 $87.971(63)^\circ$; N1'–Cu1–N8 $89.651(60)^\circ$; N6–Cu1–N8 $90.937(65)^\circ$; N8–Cu1–N9 $180.000(65)^\circ$. More nitrate anions are omitted for clarity.

1,2,4-triazole, however, with a larger dimension and more rigid conformation.

In the three-dimensional structure, each atrz serves as a bidentate bridge connecting two Cu^{II} centers to form a 3D equilateral triangle porous framework with the approximate dimensionalities of $69.50 \text{ \AA}^2$ (Figure 3), whereas $[\text{Cu}(4,4'\text{-bis-1,2,4-triazole})_2(\text{NO}_3)_2]_n$ features a CsCl-like cubic topology. In the 3D architecture of **1**, the pores along the a axis are filled with the nitrate anions. Complex **1** represents a good example of symmetrical, ordered 3D energetic coordination polymer.

Complex **2** is a 3D irregular porous coordination polymer. The asymmetric unit contains one silver atom, one and half atrz ligands, and one free nitrate anion. The silver atom is four-coordinated by four atrz nitrogen atoms, forming a tetrahedral geometry (see Figure S2 in the Supporting Informa-

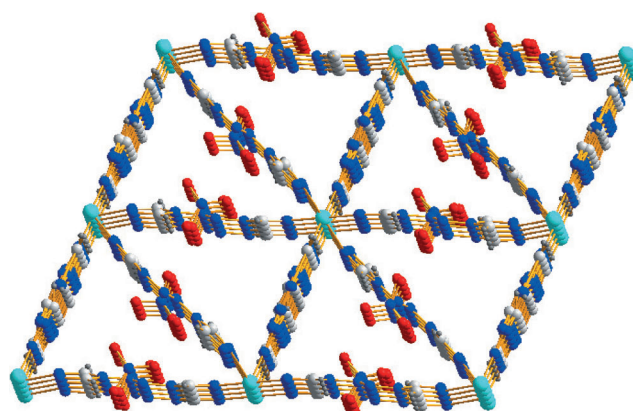


Figure 3. The 3D porous MOF of **1** depicted along the crystallographic a axis.

tion). For example, Ag2 is four-coordinated by four nitrogen atoms (N2', N6, N7, and N8). Among them, three nitrogen atoms (N2', N6, and N8) are coplanar, and the Ag2-N7 bond is at the axial site with the N7-Ag2-N8 bond angle of 92.20(8)°. The Ag-N bond distances vary from 2.241(2) Å to 2.473(2) Å, but all Ag-N bond distances found in **2** are within the normal range observed in N-containing heterocyclic Ag complexes.^[16] Interestingly, there is a binuclear hexagon metallacycle Ag₂N₄, which is formed by two crystallographically independent silver atoms (Ag2 and Ag3) and four nitrogen atoms (N1', N2', N5, and N6). In the metallacycle, the Ag...Ag (Ag2-Ag3) contact is 4.005(1) Å, and the two silver atoms are not coplanar with the dihedral angle of 21.47(3)° (Ag2-N6-N5-Ag3).

In complex **2**, it is worth pointing out that the atrz ligand exhibits two different coordination modes binding to silver atoms, versus only one mode for complex **1**. The first mode is that atrz adopts a bidentate coordination mode which is very similar to that for complex **1**, bridging Ag2 and Ag4 through two terminal triazole groups. Another is that atrz acts as a tridentate bridge to link three Ag atoms (Ag1, Ag2 and Ag3). These connection modes result in the formation of a 3D irregular porous MOFs. In the 3D structure, two types of pores (A and B) are formed parallel to the crystallographic *a* axis and the bigger pores (A) host the NO₃⁻ anions, similar to that observed in **1** (Figure 4).

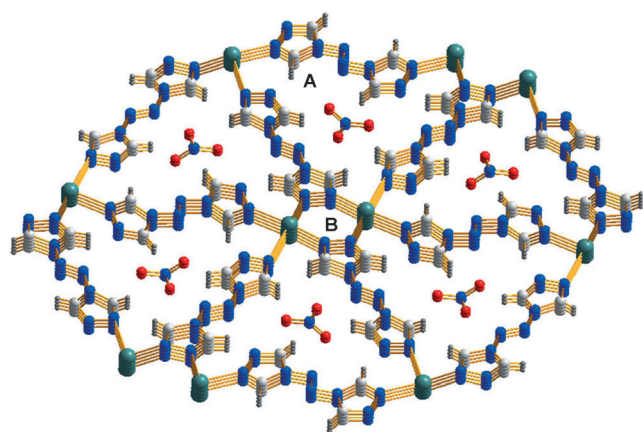


Figure 4. The 3D porous MOF of **2** depicted along the crystallographic *a* axis.

The densities of **1** and **2** are 1.68 and 2.16 g cm⁻³, respectively, which are higher than that of the free ligand (1.62 g cm⁻³). It confirms that the densities of energetic MOFs could be clearly increased by pairing with the right metal. Additionally, these complexes have remarkably high nitrogen content. Among them, the nitrogen content of **1** is reaching as high as 53.35%, which would be twice more than that of 2D CHHP (23.58%).

The thermal behavior of these crystals have been investigated using differential scanning calorimetry. Melting points are not observed in the DSC plots of **1** and **2**. The decomposition of **1** occurs with an onset peak at 243°C, whereas the silver complex **2** decomposes at 257°C (see Figure S1). Their thermal stabilities are nearly comparable to

HMX (287°C), one of the most energetic materials commonly employed,^[17] and all higher than those of 1D MOFs (CHP, 194°C) and 2D MOFs (CHHP, 231°C). Their relatively high thermal stabilities are presumably caused by the strong structural reinforcement in 3D frameworks, and the extensive network may act as an energy sink to suppress decomposition. The decomposition temperatures of **1** and **2** are higher than the criterion of 200°C for “green” metal energetic materials.^[18]

For initial safety testing, the impact, friction, and electrostatic discharge sensitivities of **1** and **2** were investigated (see the Supporting Information). The data collected are summarized in Table 1. The impact sensitivities of **1** and **2** are 22.5 and

Table 1: Physicochemical properties of **1** and **2**.

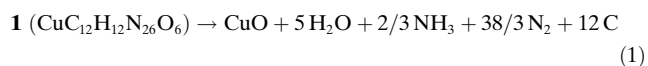
Entry	<i>T</i> _d ^[a]	<i>d</i> _c ^[b]	N % ^[c]	IS [J] ^[d]	FS ^[e]	ESD [J] ^[f]
atrz	313	1.62	68.27	14	92%	> 10.12
1	243	1.68	53.35	22.5	0%	24.75
2	257	2.16	43.76	30	0%	> 24.75
CHP	194	1.95	14.71	0.5	–	–
CHHP	231	2.00	23.58	0.8	–	–

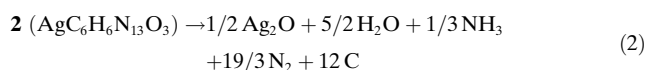
[a] Decomposition temperature (DSC, °C). [b] Density from X-ray diffraction analysis (g cm⁻³). [c] Nitrogen content. [d] Impact sensitivity. [e] Friction sensitivity. [f] Electrostatic sensitivity.

30 J, respectively, classifying them as “sensitive”.^[19] When compared to the impact sensitivity of the free ligand (14 J), the ability of metal–organic frameworks to desensitize energetic compounds is also illustrated. In addition, both complexes are also sensitive to neither friction (0%) nor electrostatic discharge (≥ 24.75 J), while the electrostatic sensitivity of HMX is only 0.2 J. Therefore, compared with those reported energetic coordination polymers such as 1D MOFs (CHP, IS = 0.5 J) and 2D MOFs (ZnHHP, IS = 2.5 J; CHHP, IS = 0.8 J), these 3D MOFs exhibit significantly lower sensitivities. It is probable that the 3D framework structures in **1** and **2** could facilitate the molecules more rigid than that of 1D or 2D structures. Additionally, the sensitive NO₃⁻ anions and metal ions have all been encapsulated inside the 3D structure, resulting in lower sensitivity.

To estimate the heat of detonation of these two new explosives and see how they compared with the heat of detonation (Δ*H*_{det}) values for 1D MOFs, 2D MOFs, and common energetic materials, we adopted the same methodology recently employed for NHP and CHP.^[6] In this method we also use density functional theory (DFT) to compute the energy of detonation (Δ*E*_{det}), from which Δ*H*_{det} is estimated by using a linear correlation developed from known Δ*H*_{det} data for eleven commonly used high explosives (Table S1).

For both complexes **1** and **2**, water, nitrogen, carbon, and ammonia were assumed to be the final products of decomposition of the organic part of the framework and the formation of metal oxides was assumed to be governed by the deficiency of oxygen. The complete detonation reactions are described by Equations (1) and (2).





Both complexes possess remarkably high heats of detonation (ΔH_{det}) and their heats of detonation are superior to all of the previously reported energetic MOFs (e.g. CHP, NHP, and CHHP). Among them, the heat of detonation of complex **1** is 3.62 kcal g^{-1} ($6.08 \text{ kcal cm}^{-3}$), which is even higher than those of CL-20 (about 1.5 kcal g^{-1})^[20] and octanitrocubane (ONC; about 1.8 kcal g^{-1}),^[21] the most powerful organic explosives known (Figure 5). The relatively high heat of detonation

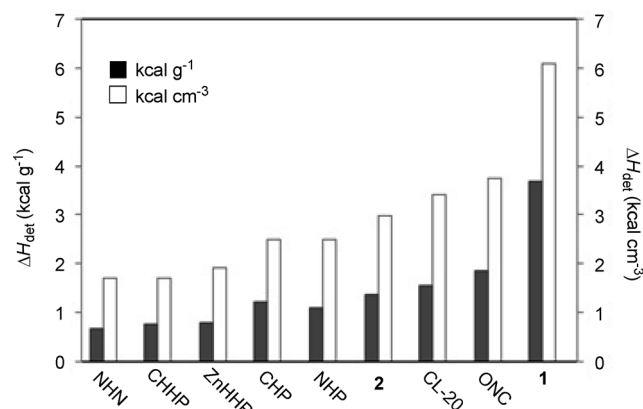


Figure 5. Bar chart representation of the literature ΔH_{det} values for the common explosive materials including hexanitrohexaazaisowurtzite (CL-20), and octanitrocubane (ONC). Previously reported values for energetic MOFs (NHN, CHHP, ZnHHP, CHP, and NHP), along with the predicted ΔH_{det} values for **1** and **2** are also shown. Error bars correspond to the 95% statistical-confidence level for these values.

could result from the nitrogen-rich heterocyclic ligand and the fascinating structure motifs, like CL-20 and its derivatives,^[22] these 3D cage compounds have high strain energies locked in the molecules, and it is released as an additional energy on detonation. To the best of our knowledge, complex **1** exhibits the highest heat of detonation among the reported metal-based energetic compounds, while retaining good stability, which makes it a competitive highly energetic material.

In summary, two novel energetic MOFs were synthesized in a simple and straightforward manner. These MOFs represent a novel type of molecular architecture for energetic compounds, featuring 3D metal–organic framework structure with channels incorporating sensitive anions. Compared to 1D and 2D MOFs, they exhibit excellent physical and detonation properties, such as high thermal stabilities, low sensitivities, and high heats of detonation. Specifically, **1** exhibits the unprecedented heat of detonation, which is the highest value known for metal-based energetic compounds, and even higher than those of CL-20, ONC, and NHP. The results highlight these new MOFs as potential energetic materials. The present study provides a new insight in the design and synthesis of MOF-based energetic materials, and we anticipate the methodology described herein can be extended to produce a new family of 3D metal–organic explosives.

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