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Environmentally-friendly high-energy MOFs: crystal structure, thermostability, insensitivity and remarkable detonation performance

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Abstract: It is an alternative method to prepare new-generation green high-energy-density materials with excellent performance on the basis of coordination chemistry strategy. In the present work, hydrothermal reaction of Cu(II)/Cu(I) with a rigidly nitrogen-rich ligand, 3-(1*H*-tetrazol-5-yl)-1*H*-triazole (H_2tztr), lead to three high-energy metal-organic frameworks (MOFs), $[Cu(Htztr)_2(H_2O)_2]_n$ (**1**), $\{[Cu(tztr)]\cdot H_2O\}_n$ (**2**) and $[Cu(Htztr)]_n$ (**3**). Referred to the coordination geometry configuration of Cu(II)/Cu(I) and flexible coordination fashion of the ligand, the energies of the complexes **1-3** are gradually improved when they are structurally transformed from **1** of a mononuclear structure to **2** of a 3D porous MOF incorporated with guest water molecules to **3** of well-isolated layer structure. The title complexes show outstanding thermostability (T_{dec} = 345 °C for **1**, 325 °C for **2** and 355 °C for **3**) and low sensitivity confirmed by experimental and theoretical characterization. Noteworthily, complex **3** features superior detonation property in the known energetic MOFs.

Keywords: green high-energy-density materials · metal-organic frameworks · detonation characteristic · insensitivity

High energy density materials (HEDMs) encompassing all propellants, explosives and pyrotechnics have attracted intense research interest in the chemical sciences, with participating scientists including Klapötke,[1–8] Shreeve,[9–16] and so on.[17-19] Nowadays, environmental concerns have been pushing the development towards new-generation green energetic materials which not only perform good thermal stability, mechanical insensitivity and better performances to meet the conflicts of high energy and safety,[20-25] but also have environmentally-friendly synthesis and detonation processes to fulfill the issues of the growing environmental pollution.[26] As a consequence, it is an urgent and appealing subject for constructing energetic materials with excellent property and environmentally-friendly characteristic simultaneously. As potential energetic materials, MOF-based compounds exhibit high density and heat of detonation, of which the good mechanical strengths and complicated frameworks are conducive to improve the thermal stability and insensitivity,[27-37] while the energetic characteristics of MOFs are rarely explored. During the past two years, four 1D and 2D energetic MOFs with good detonation performance and heat of detonation have been reported by Hope-Weeks and co-workers.[38,39] As shown, these energetic MOFs are sensitive to impact that makes them infeasible practical use. In 2013,[40] two 3D energetic MOFs, $[Cu(atrz)_3(NO_3)_2]_n$ (ATRZ-**1**) and $[Ag(atrz)_{1.5}(NO_3)]_n$ (ATRZ-**2**) were synthesized with a flexible ligand, 4,4'-azo-1,2,4-triazole (atrz), exhibiting high density (1.68 and 2.16 g cm^{-3}) and good thermostability (decomposition temperatures of 243 and 257 ^{o}C) due to their strong structural reinforcements and extensive coordination networks. More importantly, the two MOF-based energetic materials exhibit much lower sensitivity and higher heat of detonation than the conventional explosives[41] and the energetic MOFs reported previously.[38,39] Recently, we obtained two 2D energetic lead(II)-MOFs of which the insensitivity and thermal stability are prompted by the formations of structural framework.[42] Suffice it to say, compared with the traditional energetic materials and primary explosives, it is an advanced strategy to obtain high-performance HEDMs[43-46] on the basic of constructing energetic MOFs by using high-energy organic linkers to bridge non-toxic metal ions.

As is really known, pentacyclic nitrogen-rich heterocycles with potential N-coordination site are considered to be suitable candidates to construct energetic MOFs since their relatively small volume which reduces steric hindrance and increases the density,[1] and high heats of formation which depend on an enormous energy release of the average bond energies of N–N (160 kJ mol^{-1}), N=N (418 kJ mol^{-1}), and N≡N (954 kJ mol^{-1}).[47,48] Significantly, the combustion products of nitrogen-rich heterocycles are halogen free, low smoking and friendly to environment.[49,50] As the integration of triazole and tetrazole, 3-(tetrazol-5-yl)triazole (H_2tztr) with high nitrogen content (N% = 71%) is quite a desirable ligand for assembling various energetic MOFs because of the unique advantages: i) H_2tztr with the decomposition temperature up to 300 °C possesses rigid structural framework, which would improve the insensitivity and thermostability of the anticipated coordination compounds. ii) H_2tztr ligand forebode abundant coordination modes such as multidentate or bridging building block as shown in Scheme S1, offering the possibility for constructing unpredictable and fascinating MOFs. Moreover, Cu(II)/Cu(I) ions exhibit good coordination ability with N atoms in ligands,[51,52] and more importantly, are environmentally-friendly ions compared with the heavy metal ions such as lead or mercury.[53,54] To date, numerous copper-nitrogen MOFs have been synthesized and characterized in the literature.[55] Of particular interest is that copper-based MOFs with nitrogen-rich ligands would be used as green HEDMs to substitute for poisonous and polluting primary explosives like lead azide ($Pb(N_3)_2$)[56-59], lead styphnate (2,4,6-trinitroresorcinate)[60,61] or mercury fulminate ($Hg(CNO)_2$).[62-63] Based on the consideration above, three green energetic MOFs, $[Cu(Htztr)_2(H_2O)_2]_n$ (**1**), $\{[Cu(tztr)]\cdot H_2O\}_n$ (**2**) and $[Cu(Htztr)]_n$ (**3**), were obtained by hydrothermal method, which present mononuclear structure, 3D porous framework and 2D layer-like structure, respectively. Three energetic complexes display excellent thermostability, low sensitivity and environmental friendly. Especially, complex **3** possesses the record heat of detonation among the reported energetic MOFs.[38-40]

The ligand, 3-(1*H*-tetrazol-5-yl)-1*H*-triazole, was synthesized through the procedure developed by Sharpless and coworkers (see Supporting Information).[64-67] **1** and **2** were synthesized by one-step hydrothermal reaction of $CuCl_2$ with H_2tztr in water while pH was adjusted to about 4.5 and 7.0 with ammonia solution, respectively. Blue flaky and green prism-shaped crystals were manually selected for X-ray structure determination. Referred to the coordination geometry configuration of Cu(I) and deprotonation degree of the ligand, complex **3** was obtained as colorless flaky crystal by one-step hydrothermal reaction of CuCN with H_2tztr in water while pH equals to 5.5 with ammonia solution.

Complex **1** crystallizes in triclinic space group $P\bar{1}$ and exists as a mononuclear molecule. As shown in Figure 1, Cu(II) ion is hexa-coordinated by four nitrogen atoms and two oxygen atoms in a stretched octahedron of which the equatorial plan is defined by four nitrogen atoms (N1, N2, N1a and N2a) from two H_2tztr ligands (Cu1-N1 = 2.003 Å, Cu1-N2 = 1.982 Å, Cu1-N1a = 2.003Å and Cu1-N2a = 1.982 Å) and the axial position is occupied by two oxygen atoms (O1 and O1a) from two coordination water molecules (Cu1-O1 = 2.583 Å and Cu1-O1a = 2.583Å). The average of N-Cu-N bond angles is in the range 81.14-98.86^{o}. The mononuclear structure as described is further extended into a 3D superamolecular framework *via* hydrogen-bonding, from which O1 and N7 atoms act as two hydrogen-bonding donors, interacting with the acceptors of N4, N5, N6 and O1 atoms from the adjacent molecule, with 2.955 Å for O(1)-H(3)···N(4), 2.901 Å for O(1)-H(3)···N(5), 2.897 Å for O(1)-H(4)···N(6), 2.865 Å for N(7)-H(1)···O(1), 3.016 Å for N(7)-H(1)···N(4) (Figure S4). The ligand H_2tztr adopts the bidentate chelating modes in **1** (Mode I in Scheme S1).

Figure 1.

Complex **2** crystallizes in the monoclinic *P*2(1)/*n* space group with a 3D porous metal-organic framework. The asymmetry unit is made up of one Cu(II) ion, one H_2tztr ligand and one free water (Figure S5a). The Cu(II) ion is penta-coordinated by five nitrogen atoms from four H_2tztr ligands (Cu-N = 1.987-2.222 Å and ∠N-Cu-N = 80.64-164.64^{o}) in a distorted square pyramid. The basal plane is formed by one Cu(II) ion in the center and four nitrogen atoms in four vertexes, while the apical position is occupied by one nitrogen atom. As shown in Figure S5b, the N1, N2 atoms in H_2tztr ligand adopt chelating modes to connect to one Cu(II) ion, while the N3, N4, N5 atoms adopt monodentate bridging modes to link with three Cu(II) ions, respectively (Mode V in Scheme S1). The porous 3D structural framework is obtained by the combination between Cu(II) ions and H_2tztr ligands, of which pores are filled with lattice water molecules (Figure 2).

Figure 2.

Complex **3** crystallizes in the monoclinic space group *P*2(1)/*n*, in which only one crystallographically independent copper atom is found (Figure 3a). The Cu(I) ion exhibits a distorted tetrahedral configuration, which is coordinated by four nitrogen atoms [Cu(1)-N(1a) = 2.078 Å, Cu(1)-N(2b) = 2.025 Å, Cu(1)-N(3c) = 2.005 Å and Cu(1)-N(5) = 2.101 Å] from four different H_2tztr ligands. Among the common coordination geometries of Cu(I) ion, the tetrahedral geometry is most stable.[68] The N-Cu-N bond angles fall into the range of 99.895 to 115.290°. As shown in Figure 3b, the N1, N2, N3, N5 atoms in H_2tztr ligand adopt monodentate bridging modes to connect to four Cu(I) ions, respectively (Mode IV). In this way, the 2D layer-like structure is constructed by the interlinkage between Cu(I) ions and H_2tztr ligands. The adjacent layers are correlated by hydrogen-bonding (N(6)-H(6A)···N(7) = 2.831Å), yielding a stable 3D supramolecular network (Figure 3c).

Figure 3.

The phase purity of the bulk materials are confirmed by X-ray powder diffraction (XRPD) (Figure S1-S3). The densities are indentified as 1.892 $g\cdot cm^{-3}$ for **1**, 2.316 $g\cdot cm^{-3}$ for **2** and 2.435$g\cdot cm^{-3}$ for **3** on the basic of experimental method by using Automatic Density Analyzer. Compared with the known energetic MOFs,[38-40] the nitrogen contents of three title complexes (52.72% for **1**, 45.23% for **2**, 49.08% for **3**) only slightly lower than ATRZ-**1** (53.35%).[40]

The thermostabilities of **1-3** were investigated using thermogravimetric analysis. As shown in Figure 4, the decomposition temperatures of main frameworks in complexes **1-3** were measured to be 345 ^{o}C, 325 ^{o}C and 355 ^{o}C, respectively, which are higher than HMX (287 ^{o}C), one of the most energetic materials commonly employed,[69,70] and those of known energetic MOFs.[38-40] The abrupt curves of weight loss demonstrate the rapid release of energy, before that, **1** and **2** undergo continuous dehydration processes. Moreover, the thermal behaviors of three complexes were investigated by differential scanning calorimetric test (see the Supporting Information).

Figure 4.

The drastic processes of decomposition demonstrate the potential detonation properties of three complexes, it is necessary to estimate the heat of detonation (ΔH_{det}) of **1-3**, and compared with the values of energetic MOFs and classical energetic materials. We selected the identical method for $(Co(NH_2NH_2)_5(ClO_4)_2)_n$ (CHP) and $(Ni(NH_2NH_2)_5(ClO_4)_2)_n$ (NHP) reported in Ref. 38. Density functional theory (DFT) was used to calculate the energy of detonation (ΔE_{det}) (Table S4), from which ΔH_{det} was estimated by using a linear correlation equation developed from known ΔH_{det} data of eleven common high explosives.

For three complexes, water, nitrogen, carbon, and ammonia were indentified as the decomposition products of the organic component of the frameworks by using thermogravimetry-infrared (TG-IR) coupled technology, and the formations of copper oxide or elementary copper were supposed to attribute to the insufficiency of oxygen. All nonmetal-containing products, including water, are treated as a gas. The detonation reactions considered for three complexes are described by Equations (1), (2) and (3):

$$CuC_6H_8N_{14}O_2 \rightarrow CuO + 6\ C + 2\ NH_3 + 6\ N_2 + H_2O \qquad (1)$$

$$CuC_3H_3N_7O \rightarrow Cu + 3\ C + 1/3\ NH_3 + 10/3\ N_2 + H_2O \qquad (2)$$

$$CuC_3H_2N_7 \rightarrow Cu + 3\ C + 2/3\ NH_3 + 19/6\ N_2 \qquad (3)$$

The heat of detonation (ΔH_{det}) of **1-3** are calculated as 2.1281, 1.3220 and 3.9582 $kcal \cdot g^{-1}$, respectively. To the best of our knowledge, the ΔH_{det} value of **3** is unprecedentedly superior than the reported energetic MOFs, and much higher than those of hexanitrohexaa-zaisowutzitane (CL-20; about 1.5 $kcal \cdot g^{-1}$)[71] and octanitrocubane (ONC; about 1.8 $kcal \cdot g^{-1}$),[72] the most intense organic explosives known (Figure 5). The brilliant ΔH_{det} of **3** probably attributes to the high nitrogen contents and the rigid structural framework, while the relatively low values of **1** and **2** are affected by lattice water.

Figure 5.

To study the detonation characteristics, the detonation velocity (D) and detonation pressure (P) of three complexes were calculated by Kamlet-Jacbos[73] equations which were usually applied to the energetic MOFs reported previously (see the Supporting Information). The comparison of physicochemical properties between some energetic materials and three complexes are listed in

Table 1. The *D* and *P* of complex **3** are calculated to be 10.40 km·s^{-1} and 56.48 GPa, which have an absolutely advantage over the known energetic MOFs including ATRZ-**1**. For **1** and **2**, the continuously dehydration process with the collapse of main frameworks show that water molecules largely influence on the detonation properties, owing to the emergence of vast vapor pressure.

For safety testing, the impact, friction and electrostatic sensitivities of three complexes were investigated (see the Supporting Information). The collected data are summarized in Table 1. The impact sensitivities of **1-3** are of 40 J, 40 J and 32 J, respectively, whereas the impact sensitivity for TNT is 15 J under the same test condition. Evidently, the impact sensitivities of **1-3** are lower than that of TNT and the known energetic MOFs such as ATRZ-1 (IS = 22.5J). No friction sensitivities are observed up to 36 kg (360 N) for the complexes. In addition, three complexes are most likely to be less sensitive to electrostatic discharge than both HMX and TNT. Compared with the energetic MOFs reported previously, the complexes **1-3** are insensitive to the external stimulus. It is probable that the tight integration between the rigid ligands and metal ions would generate stable and insensitive structural framework. Additionally, water molecules occur in complexes **1** and **2**, resulting in low sensitivity.

Non-isothermal kinetics analyses of three complexes were determined by differential scanning calorimetric tests. As shown in Table S5, the apparent activation energies E_k and E_o, pre-exponential factor *A*, linear correlation coefficients R_k and R_o for three complexes were calculated by Kissinger's method[77] and Ozawa–Doyle's method.[78,79] The E_a values derived from the averages of the E_k and E_o are calculated as 194.22 kJ·mol^{-1}, 202.52 kJ·mol^{-1}, 246.28 kJ·mol^{-1} for **1-3**, which reveal that three complexes show thermo-kinetically inert.

Table 1

In conclusion, three environmentally-friendly energetic MOFs have been synthesized based on the H_2tztr ligand with rigid structure and high nitrogen content. The structural characterizations of complexes **1-3** have been carried out using elemental analysis, FT-IR spectrum, thermal analysis, and single-crystal X-ray diffraction. **1** exhibits a mononuclear structure, **2** adopts a 3D porous framework with the guest water molecules, while **3** performs 2D layer-like structure. As high-performance HEDMs, the title complexes exhibit excellent physicochemical properties, such as high thermostabilities, low sensitivities. Specifically, complex **3** provides the unprecedented thermostability and heat of detonation. The finding examples the potential application and advances the integrated performance of the MOF-based HEDMs.

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Appendix A. Supplementary data

The CIF files give crystallographic data for compounds. Figs. S1-S6 and Tables S1-S5. CCDC 1000293, 1000294 and 1000295.

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Figure Captions:

Figure 1. Coordination environment of Cu(II) ions in **1**. (Hydrogen atoms are omitted for clarity)

Figure 2. 3D porous structure of **2**. (Hydrogen atoms are omitted for clarity)

Figure 3. (a) Coordination environment of Cu(I) ions, (b) coordination model of ligand, and (c) 3D supramolecular network formed by several 2D layers in **3.** (Hydrogen atoms are omitted for clarity)

Figure 4. TG curves of **1**, **2** and **3**.

Figure 5. Bar chart representation of the literature ΔH_{det} values for the common explosive materials, including CL-20 and ONC. Previously reported values for energetic MOFs $(((Zn_2(N_2H_4)_3(N_2H_3CO_2)_2)(ClO_4)_2\cdot H_2O)n$ (ZnHHP), $((Co_2(N_2H_4)_4(N_2H_3CO_2)_2)(ClO_4)_2\cdot H_2O)n$ (CHHP), CHP, NHP, ATRZ-**1**, and ATRZ-**2**), along with the predicted ΔH_{det} value for **1**, **2** and **3** are also shown.

Table 1: Physicochemical properties of **1-3** and some energetic materials.

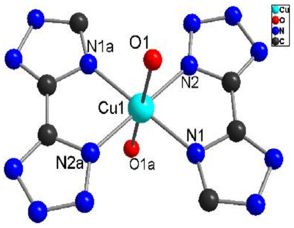

Figure 1.

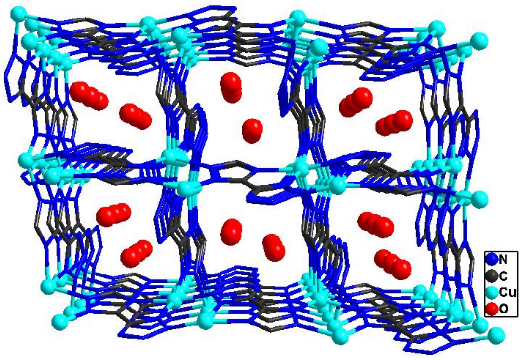

Figure 2.

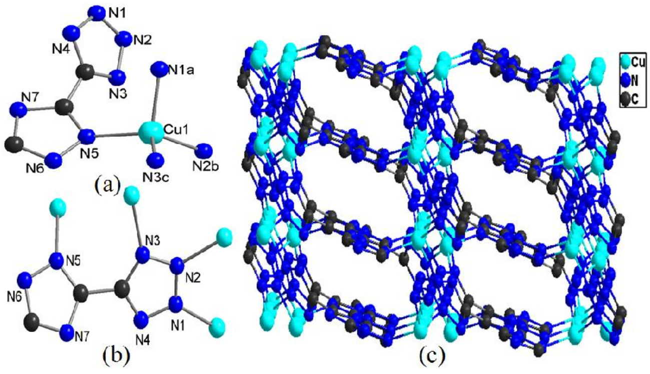

Figure 3.

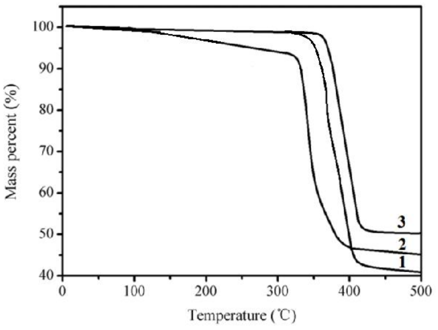

Figure 4.

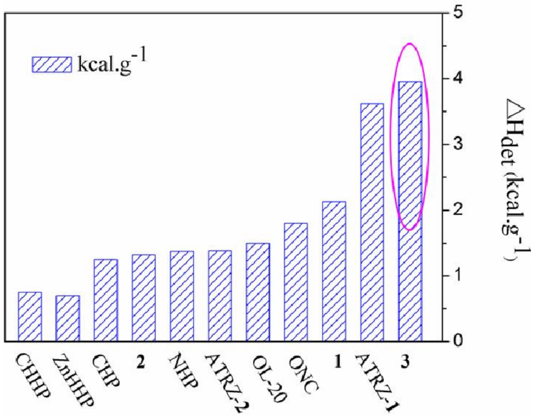

Figure 5.

Table 1

Compound	ρ (g·cm^{-3})[a]	N (%)[b]	Ω (%)[c]	T_{dec} (°C)[d]	D (km·s^{-1})[e]	P (GPa)[f]	IS (J)[g]	FS (N)[h]	ESD (J)[i]
1	1.892 (1.885)[j]	52.72	-60.24	345	8.18	30.57	>40	>360	>24.75
2	2.316 (2.308)[j]	45.23	-48.00	325	7.92	31.99	>40	>360	>24.75
3	2.435 (2.419)[j]	49.08	-56.09	355	10.40	56.48	32	>360	>24.75
HMX[38,74]	1.950	37.80	-21.60	287	8.900	38.39	7.4	-	0.2
RDX[38]	1.806	37.80	-21.60	210	8.600	33.92	7.5	120	0.15[75,76]
TNT[38]	1.654	18.50	-74.00	244	7.178	20.50	15	353	0.57[75,76]
ATRZ-**1**[40]	1.680	53.35	-58.83	243	9.160	35.68	22.5	-	24.75
ATRZ-**2**[40]	2.16	43.76	-49.99	257	7.773	29.70	30	-	>24.75
CHP[38]	1.948	14.71	-11.48	194	8.225	31.73	0.5	-	-
NHP[38]	1.983	33.49	-11.48	220	9.184	39.69	-	-	-
CHHP[39]	2.000	23.58	-13.05	231	6.205	17.96	0.8	-	-
ZnHHP[39]	2.117	23.61	-49.99	293	7.016	23.58	-	-	-

[a] From X-ray diffraction. [b] Nitrogen content. [c] Oxygen balance. [d] Decomposition temperature. [e] Detonation velocity. [f] Detonation pressure. [g] Impact sensitivity. [h] Friction sensitivity. [i] Electrostatic sensitivity. [j] Density measured by gas pycnometer (25 °C).

Graphical abstract

Synopsis

- Three environmentally-friendly MOF-based HEDMs with high-nitrogen ligand present superior detonation property, thermostability and insensitivity.

Graphic