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COMMUNICATION

Anionic Metal-Organic Frameworks Lead the Way to Eco-Friendly High-Energy-Density Materials

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To develop environmentally friendly high-energy-density materials with outstanding detonation performances, anionic metal-organic frameworks (anionic MOFs) are introduced into the area of energetic materials. In this work, two anionic complexes, $[(AG)_3(Co(btm)_3)]$ (1) and $\{[(AG)_2(Cu(btm)_2)]\}_n$ (2) (H2btm=bis(tetrazole)methane, AG=aminoguanidinium), have been prepared and characterized by single-crystal X-ray diffraction analysis. Theoretical analysis predict that these two anionic energetic MOFs should show extensive hydrogen bonding with remarkably high nitrogen contents, good thermal stabilities, favorable insensitivities, and excellent detonation performances, and this has been confirmed by experimental results. Notably, the heats of detonation of 1 (4.75 kcal g⁻¹) and 2 (5.41 kcal g⁻¹) are far superior to those of all hitherto reported MOF-based high-energy-density materials.

The development of high-energy-density materials (HEDMs), including propellants, explosives, and pyrotechnic agents, is crucial to meet the growing needs of a variety of military and civilian applications.¹ In the quest for more powerful, stable, and insensitive HEDMs, much attention has been paid to environmental issues and minimizing polluting combustion products generated during the preparation and utilization of such materials.²⁻⁵ Nitrogen-rich compounds mainly produce eco-friendly N₂ gas during the process of decomposition and release enormous energy on account of the huge gap in the average bond energies of N-N (160 kJ mol⁻¹) and N=N (418 kJ mol⁻¹) of explosives compared to that of N≡N (954 kJ mol⁻¹) of detonation products, and so are central to research in the area

of green HEDMs.⁶ To achieve advanced HEDMs, pioneering scientists such as Klapötke, Shreeve, and many others have contributed considerable research on nitrogen-rich compounds.⁷⁻¹² However, it is often difficult to achieve a good balance between high energy and low sensitivity. Recently, nitrogen-rich MOFs with favorable thermal stability and low sensitivity have attracted much attention by virtue of their strong structural reinforcement and complicated coordination architectures.¹³⁻¹⁸ In addition, these high-nitrogen MOFs exhibit excellent detonation performances and high heats of detonation, which make them very promising candidates for high-performance HEDMs.¹³⁻¹⁸ These MOFs are constructed by joining metal ions with nitrogen-rich linkers and are termed energetic MOFs or high-energy MOFs (HE-MOFs). According to S. Chen, some 37 HE-MOFs have been reported during the past few years.¹⁹ Among them, [Cu(3-(1H-tetrazol-5-yl)-1H-triazole)]_n (TRTR-3)¹⁷ and [Cu(4,4'-azo-1,2,4-triazole)₃(NO₃)₂]_n (ATRZ-1)¹⁵ exhibit the most outstanding detonation performances. Specifically, TRTR-3 exhibits an unprecedented detonation velocity of 10.40 km s⁻¹ and a detonation pressure of 56.48 GPa, coupled with amazing thermal stability and suitable sensitivity.¹⁷ In 2014, Shreeve highlighted that these compounds with predictable energetic performance hold great promise for developing new-generation green high explosives.²⁰

To date, all of the reported energetic MOFs can generally be classified into two types: cationic HE-MOFs (counter ions (Cl) typically NO₃⁻ and ClO₄⁻) and neutral HE-MOFs (no Cl), both of which display excellent energetic properties. However, there has been a conspicuous paucity of research on anionic HE-MOFs, even though they could prove to be the most important type. This incompleteness may be related to the fact that the procedures for assembling anionic MOFs are challenging as they mostly lead to the formation of either cationic MOFs or are difficult to control.²¹ Ghosh admitted that it is often serendipitous to build up an anionic framework.²¹

However, their potentially appealing properties are of great interest to our group and so they are a focus of our current research. As is known, high nitrogen content generally means

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high energy, and azoles (triazoles and tetrazoles) with high nitrogen content and multiple N-coordination sites are desirable linkers for assembling various high-performance HEDMs.²²⁻²⁷ However, materials with high energy are usually inherently unstable.¹³ Fortunately, cations such as NH_2NH_3^+ , NH_3OH^+ , NH_4^+ , and so on, are rich in both nitrogen and hydrogen donors, making them not only conducive to improving nitrogen content but also for forming multiple hydrogen bonds (H-bonds). These H-bonds can greatly increase the stability and insensitivity of the target materials.²⁸⁻²⁹ Beyond these, transition metals (TM) are considered to be green ions (although researchers should bear in mind that metal ions should be used as little as possible) compared with heavy metal ions (Pb^{2+} or Hg^{2+}), and so TM-based HEDMs are excellent candidates for replacing common primary explosives, such as mercury fulminate, lead azide, and lead styphnate.^{17,22} Anionic MOFs constructed from Cu (or Co), azole ligands, and nitrogen-rich cations may be expected to show several advantageous features, making them superior to cationic and neutral HE-MOFs for developing eco-friendly HEDMs (see Figure 1).

Based on the above considerations, we have synthesized two anionic HE-MOFs: $[(\text{AG})_3(\text{Co}(\text{btm})_3)]$ (**1**) and $\{[(\text{AG})_2(\text{Cu}(\text{btm})_2)]_n\}$ (**2**) (H2btm=bis(tetrazole)methane, AG=aminoguanidinium). Here, btm^{2-} (N%=74.7) and AG^+ (N%=74.6%) were used as ligand and counter ion, respectively. The reasons why we choose AG^+ as counterion are as follow: (a) Compared with AG^+ , there are smaller number of hydrogen bonds in NH_4^+ and NH_3OH^+ . (b) The attempt of using NH_2NH_3^+ as counterion during our experiments always leads to the formation of spongelike material, which absorbs all of the solvents. It may have significant application in some other fields but not in the field of energetic materials. (c) AG^+ is rich in H-donors and nitrogen. It is easy to result in stoichiometric crystal products containing no crystal water and coordinated

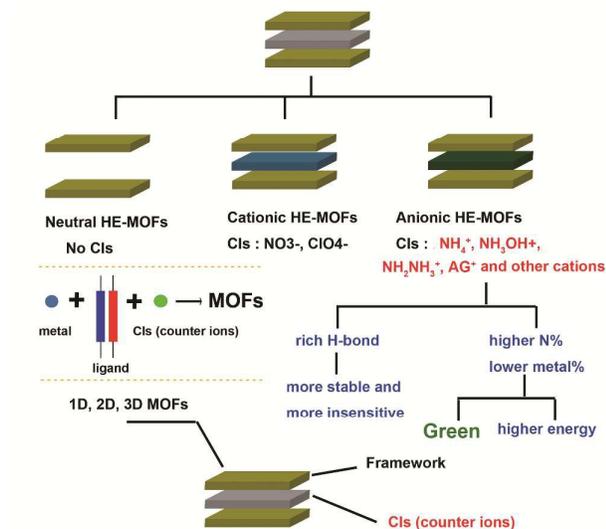


Figure 1. Advantages of anionic HE-MOFs compared with previous HE-MOFs (cationic and neutral HE-MOFs)

water when AG^+ is combined with anionic frameworks. Crystals of **1** and **2** suitable for single-crystal X-ray diffraction analysis were obtained by slow crystallization from water. Both compounds crystallize in the monoclinic P_{21}/c space group. The phase purities of the two materials were confirmed by X-ray powder diffraction (see Figure S1). The two MOFs display excellent physicochemical properties and outstanding energetic performances. In particular, these complexes show the greatest heats of detonation and have the highest nitrogen contents among known HE-MOFs.

Complex **1** exists as a mononuclear molecule. As shown in Figure 2 (a), the central Co^{III} is hexa-coordinated by six nitrogen atoms (N1, N8, N9, N16, N17, and N24) from three btm anions in a regular octahedral arrangement. The nitrogen atoms in the btm anion coordinate to one Co^{III} ion in chelating mode (see Figure 2 (b)). The Co-N bond lengths are in the range 1.911-1.936 Å (see Table S2), and are much shorter than those in $[\text{Co}_5(3\text{-amino-1H-1,2,4-triazole})_7(\text{N}_3)_3]$ (3-aTRZ) (1.986-2.208 Å)¹⁶, indicating strong interactions between Co^{III} ions and N atoms through electrostatic forces and chelation. Each $(\text{Co}(\text{btm})_3)^{3-}$ anion is connected to several AG^+ cations through hydrogen bonds, by which the hydrogen bonded three-dimensional (3D) framework is assembled (see Figure 2(c, d)). It is worth pointing out that compound **1** has a remarkable 29 kinds of hydrogen bonds, which will greatly enhance the stability of the material (see Table S3).

Compound **2** shows a layer-like structure. The asymmetric unit of compound **2** consists of one divalent Cu^{II} ion, two btm dianions, and two aminoguanidinium cations. In Figure 3(a), it can be seen that the central Cu^{II} displays a regular octahedral configuration, involving coordination by six nitrogen atoms (N1, N1', N4, N4', N5, and N5') from four btm ligands. Each btm ligand exhibits a tridentate coordination mode (see Figure 3(b)), as opposed to the bidentate mode in **1**. N1 (N1') and N5 (N5') in btm coordinate to Cu^{II} in chelating mode, whereas N4 (N4') coordinates to another Cu^{II} in a bridging mode. The layered structure is thereby constructed with infinite expansion (see Figure 3(c, d)). The AG^+ cations reside between

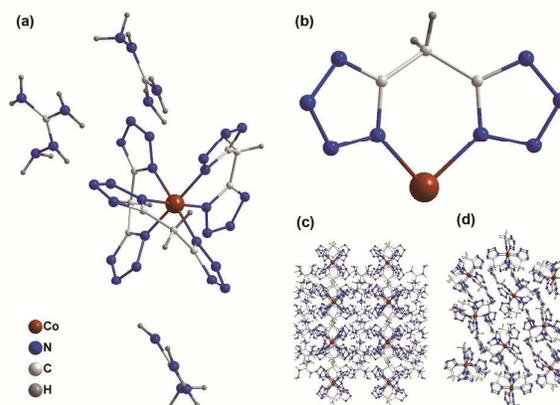


Figure 2. (a) Coordination environment of $\text{Co}(\text{III})$ ions in **1**, (b) coordination sites of btm, (c) 3D supramolecular network in **1** (a-axis), (d) 3D supramolecular network in **1** (b-axis).

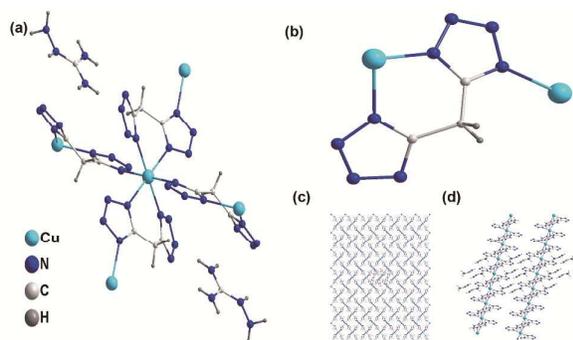


Figure 3. (a) Coordination environment of Cu(II) ions in **2**, (b) coordination sites of btm in **2**, (c) 3D supramolecular network in **2** (a-axis), (d) 3D supramolecular network in **2** (b-axis).

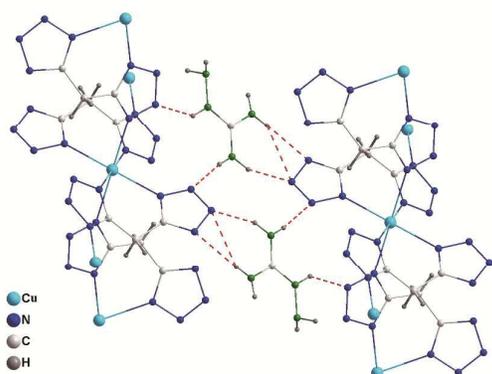


Figure 4. Extensive hydrogen bonding in **2**. The aminoguanidinium nitrogen atoms are shown in green for ease of identification. Red dashed lines represent hydrogen bonds

adjacent layers. They lead to the formation of a large number of hydrogen bonds, by which the 2D coordination polymer further form a 3D network (see Figure 4). There are twelve different hydrogen bonds, with lengths in the range 2.06–2.62 Å (see Table S3). These hydrogen bonds, along with ring strain, chelation, bridging action, and the electrostatic force, are conducive to improving thermal stability and insensitivity.

Nitrogen content is important for the detonation performances of energetic materials. High nitrogen content will lead to high energetic performance and environmental benignity. Low metal content will permit environmental benignity. Being based on azole ligands and nitrogen-rich cations, the two MOFs have very high nitrogen contents and low metal contents. The nitrogen contents in complexes **1** and **2** are 68.65% and 65.41%, respectively. These values are higher than those of known MOF-based energetic materials (see Figure 5), including ATRZ-1 (53.35%),¹⁵ TRTR-3 (49.10%),¹⁷ and 3-atrz (51.68%).¹⁶ This illustrates that nitrogen contents are increased sharply by adopting the anionic MOF strategy. Additionally, the low metal contents of the title complexes (< 12.6%) are much lower than those of most previously reported HE-MOFs. Indeed, the metal content of compound **1** is only 8%, which is the lowest value among HE-MOFs prepared to

date. This verifies that the anionic MOF strategy permits great reduction in the use of metal ions. Last, but not least, the density of **1** is 1.684 g cm⁻³, which is slightly higher than that of ATRZ-1 (1.678 g cm⁻³).¹⁵ Meanwhile, the favorable density of compound **2** (1.826 g cm⁻³) is nearly equal to that of one of the most excellent HE-MOFs, 3-atrz (1.834 g cm⁻³).¹⁶

The thermal stabilities of **1** and **2** were investigated by means of differential scanning calorimetry (DSC) and thermogravimetric analysis (TG). Thermal decomposition temperatures of green energetic materials must be higher than 200 °C to meet the requirements of a variety of applications.^{2, 30–31} As shown in Figure 6, the decomposition temperatures (T_d) of the two compounds measured from their TG curves are 268.1 and 212.5 °C, respectively, exceeding the threshold value of 200 °C, indicating that they have good thermal stability. The suitable stabilities of **1** and **2** were also clarified by their DSC curves, which show that their first intense exothermic processes appear at 268.1 and 212.5 °C, respectively (see Figure S4). Apparent activation energies (E_a), determined by Kissinger's method³² and Ozawa's method³³, are 190.8 and 202.4 kJ mol⁻¹, respectively (see Table S4), which further illustrate the thermo-kinetic inertness of the two complexes.

Of particular note is that the decomposition residue amounts to only 12.69% for **2**, much lower than that of the green HE-MOF, TRTR-3 (50.09%)¹⁷, and is almost equal to its own Cu content (12.37%). This indicates that all nonmetallic substances are transformed into gaseous products, despite the low oxygen balance level, which always leads to nonmetallic solid products in traditional HEDMs. It was thus confirmed experimentally that Cu-based energetic MOFs decompose completely, highlighting their superiority as green HEDMs.

The safeties of compounds **1** and **2** to mechanical stimulation, including impact, friction, and electrostatic discharge, were tested according to the corresponding standard methods (see Supporting Information) and are partly

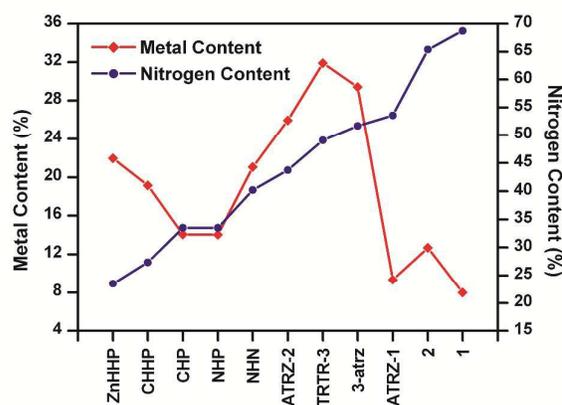


Figure 5. Comparison of the nitrogen and metal contents of nine reported HE-MOFs, **1**, and **2**. ZnHHP: $[(Zn_2(N_2H_4)_3(N_2H_3CO_3)_2)(ClO_4)_2 \cdot H_2O]_n$,¹⁴ CHHP: $[(Co_2(N_2H_4)_4(N_2H_3CO_3)_2)(ClO_4)_2 \cdot H_2O]_n$,¹⁴ CHP: $[Co(NH_2NH_2)_5(ClO_4)_2]_n$,¹³ NHP: $[Ni(NH_2NH_2)_5(ClO_4)_2]_n$,¹³ NHN: $[Ni(N_2H_4)_3(NO_3)_2]_n$,¹³ ATRZ-2: $[Ag(atrz)_{1.5}(NO_3)]_n$,¹⁵ TRTR-3: $[Cu(3-(1H-tetrazol-5-yl)-1H-triazole)]_n$,¹⁷ 3-atrz: $[Co_5(3-amino-1H-1,2,4-triazole)_7(N_3)_3]$,¹⁶ ATRZ-1: $[Cu(4,4'-azo-1,2,4-triazole)_3(NO_3)_2]_n$,¹⁵

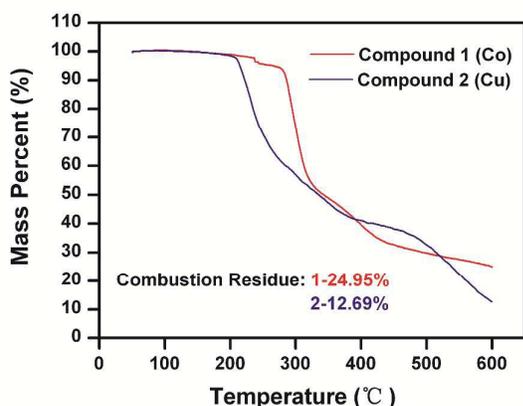


Figure 6. TG traces of 1 and 2.

listed in Table 1. The impact, friction, and electrostatic sensitivities of the two compounds are higher than 40 J, 360 N, and 20 J, respectively, classifying them as “insensitive”.¹⁵ With respect to impact sensitivity; the values of the two compounds (> 40 J) exceed ATRZ-1 (22.5 J) and TRTR-3 (32 J).

Table 1. Physicochemical and energetic properties of 1, 2, and some known HE-MOFs

Item	ρ^a	N% ^b	T _d ^c	D ^d	P ^e	IS ^f	FS ^g
1	1.684	68.7	268.1	10.21	44.45	>40	>360
2	1.826	65.4	212.5	10.97	53.92	>40	>360
ATRZ-1	1.68	53.6	243	9.16	35.68	22.5	>360
3-atrz	1.83	51.7	285	8.75	34.32	>40	>360
TRTR-3	2.44	49.1	355	10.40	56.50	32	>360
NHP	1.98	33.5	220	9.18	39.69		
CHHP	2.00	27.3	231	6.21	17.96	7.5	
ZnHHP	2.12	23.5	293	7.02	23.58		
CHP	1.95	33.5	194	8.23	31.73	5	

^a Density of compounds (g cm⁻³); ^b nitrogen content (%); ^c decomposition temperature (°C); ^d detonation velocity (km s⁻¹); ^e detonation pressure (GPa); ^f impact sensitivity (J); ^g friction sensitivity (N); ATRZ-1: [Cu(4,4'-azo-1,2,4-triazole)₃(NO₃)₂]_n,¹⁵ 3-atrz: [Co₅(3-amino-1H-1,2,4-triazole)₇(N₃)₃];¹⁶ TRTR-3: [Cu(3-(1H-tetrazol-5-yl)-1H-triazole)]_n,¹⁷ NHP: [Ni(NH₂NH₂)₃(ClO₄)₂]_n,¹³ CHHP: [(Co₂(N₂H₄)₄(N₂H₃CO₃)₂)(ClO₄)₂·H₂O]_n,¹⁴ ZnHHP: [(Zn₂(N₂H₄)₃(N₂H₃CO₃)₂)(ClO₄)₂·H₂O]_n,¹⁴ CHP: [Co(NH₂NH₂)₃(ClO₄)₂]_n.¹³

Heats of formation, important parameters to assess the energetic properties of the target compounds, were obtained according to the specified method (see the Supporting Information), and are listed in Table S6. The favourable heats of formation of **1** and **2** are 519.7 and 783.9 kJ mol⁻¹, respectively, higher than those of most energetic materials, and prompted us to consider the detonation performances of the two compounds.

Heats of detonation (ΔH_{det}) of **1** and **2** were calculated based on density functional theory and an empirical equation to assess detonation performances (see the Supporting Information). Heat of detonation is a critical parameter, on which detonation performance parameters, including detonation velocity (D) and detonation pressure (P), are

strongly dependent. To the best of our knowledge, TRTR-3 (3.96 kcal g⁻¹) and ATRZ-1 (3.62 kcal g⁻¹) show the highest ΔH_{det} values among the reported neutral and cationic HE-MOFs, respectively. The heat of detonation of compound **1** was calculated as 4.75 kcal g⁻¹. Remarkably, compound **2** was calculated to have a higher heat of detonation (5.41 kcal g⁻¹) than complex **1**. These ΔH_{det} values of the two anionic HE-MOFs are clearly superior to those of existing HE-MOFs (see Figure 7). The superior performances of **1** and **2** can be attributed to their nitrogen-rich compositions, high strain energies, and novel MOF structures.

With heats of detonation in hand, detonation velocity (D) and detonation pressure (P) were estimated using the Kamlet-Jacobs equation (see the Supporting Information).³⁴ The D and P of **1** were evaluated as 10.21 km s⁻¹ and 44.45 GPa, respectively. The D value of **1** greatly exceeds those of most energetic MOFs and is comparable to the highest value reported for an HE-MOF, that is, 10.40 km s⁻¹ for TRTR-3. Most gratifyingly, P and D calculated for **2** are 53.92 GPa and 10.97 km s⁻¹, respectively, which exceed those of all hitherto reported HE-MOFs.

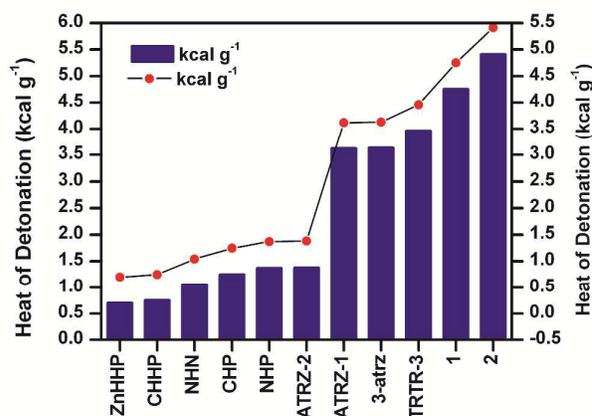


Figure 7. Bar chart representation of previously reported ΔH_{det} values for nine MOF-based HEDMs, namely ZnHHP, CHHP, NHN, CHP, NHP, ATRZ-2, ATRZ-1, 3-atrz, and TRTR-3, along with the predicted ΔH_{det} values for 1 and 2.

Conclusions

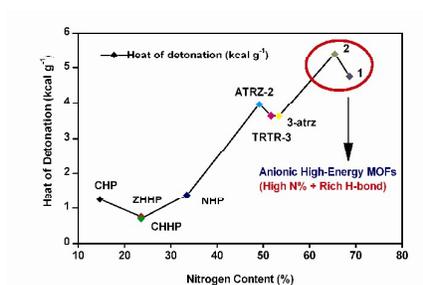
In conclusion, two eco-friendly HEDMs, **1** and **2**, have been synthesized based on an anionic MOF strategy. They show unique structures, very high nitrogen contents, good thermal stabilities, favorable insensitivities, and remarkable detonation performances. In particular, by combining azole ligands and nitrogen-rich cations, complexes **1** and **2** show heats of detonation exceeding those of all hitherto reported HE-MOFs. In view of its comprehensively excellent properties, compound **2** is highly promising as a new-generation green HEDM

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Table of Content



Abstract: Eco-friendly high-energy materials with remarkably high nitrogen and heat of detonation are achieved based on anionic MOFs strategy. Meanwhile, their stabilities and insensitivities are well improved by hydrogen bonds.