



Stabilizing volatile azido in a 3D nitrogen-rich energetic metal–organic framework with excellent energetic performance



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ABSTRACT

The appearance of the nitrogen-rich energetic MOFs provides another opportunity for the new-generation of high energetic explosives. In this work, an insensitive energetic nitrogen-rich ligand, 3-amino-1, 2, 4-triazole (Hatz) was imported into the system of transition-metal azides via the coordination polymerization strategy in the hope to prepare mixed-ligand nitrogen-rich high energetic MOF materials with low sensitivity and finally a solvent-free 3D energetic compacted metal-organic framework (MOF), $\text{Cd}_3(\text{atz})_4(\text{N}_3)_2$ (**1**) was successfully isolated under hydrothermal conditions. Compound **1** was characterized by single crystal X-ray diffraction, IR spectroscopy, elemental analysis (EA), differential scanning calorimetry (DSC), and thermogravimetry analysis (TGA). Topological analysis shows that the 3D framework of **1** can be abstracted into a ten-connected topological network. The volatile azido ion can be viewed as a counter anion to be stabilized in a 3D framework as the connection of Cd(II) ions with two independent atz^- ligands still remains a 3D framework. Compound **1** has a high calculated density (ρ) of 2.517 g cm^{-3} . The standard molar enthalpy of formation ($\Delta_f H^\circ$) of **1** was calculated to be $1330.10 \text{ kJ mol}^{-1}$, which is higher than those of most of the previously 3D energetic MOFs. Sensitivity tests demonstrate that **1** is insensitive to external mechanical stimuli. TGA demonstrates that **1** has an excellent thermostability which can be stable up to 372°C . Compound **1** can be served as a high-energy-density material with a favorable level of safety due to its excellent energetic performances, low sensitivities and excellent thermostability.

1. Introduction

Energetic materials have been studied and used extensively for nearly two centuries since that they can be applied in both military and civilian purposes as propellants, explosives and pyrotechnics, which makes a significant contribution to the development of the world economy. The well-known energetic materials are the metal-based inorganic explosives (e.g., lead azide, lead styphnate or mercury fulminate) which have been most commonly employed as primary explosives because of their high sensitivities toward mechanical stimuli [1,2]. Metal-organic frameworks (MOFs) or coordination polymers (CPs) which can be readily prepared by the self-assembly of metal ions or metal-containing clusters (also known as secondary building units)

with electron-donating organic ligands through coordination bonds between metal center and organic linker [3,4]. Functional CPs usually exhibit wide ranging potential applications such as second-order nonlinear optical materials, ferroelectric materials, luminescent materials, energy storage, heterogeneous catalysis, etc. [5–19]. In recent years, several groups have demonstrated that MOFs can be used as energetic materials by the utilization of multi-dentate nitrogen-rich compounds as coordination ligands [20–26]. Particularly because of their inherent advantages such as reinforced structures, high density, high heats of detonation and thermostability, and most of which exhibit lower sensitivities [27]. The appearance of the energetic MOFs provides a new approach to prepare novel energetic materials with high energy and low sensitivity.

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The exceptional energetic performance of the hitherto several reported MOFs has proved that nitrogen-rich MOFs have the potential to be used as the new-generation of high explosives [20]. For example, recently, professor Lan's group reported a 3D nitrogen-rich MOFs, [Zn(Hdtz)]·DMA ($H_3dtz = 4, 5\text{-di}(1H\text{-tetrazol-5-yl})\text{-2H-1, 2, 3-triazole}$, DMA = N, N'-dimethylacetamide) with the nitrogen content of 47.26% which shows a high heat of detonation and low sensitivity [24]. Pang's group recently described a 3D Cu(II)-based energetic MOF, [Cu(atrz)₃(NO₃)₂]_n (atrz = 4, 4'-azo-1, 2, 4-triazole) with a heat of detonation higher than that of CL-20 (about 1.5 kcal g⁻¹) [28]. In 2016, Shreeve also proposed that nitrogen-rich MOFs can offer another opportunity for safer energetic materials [29]. Despite these advancements, the contradiction between sensitivity and high energy is still obvious. Hence, to harmonize the conflict between sensitivity and energy, more work needs to be done to expand the research of energetic materials in the hope of finding more powerful, stable and less sensitive energetic materials.

The azido ion (N₃⁻) has been attracted considerable attention to prepare energetic materials due to the fact that it possesses 100% nitrogen content, high enthalpy of formation and strong explosive power. While the great disadvantage of the metal-based inorganic azides (such as copper azide, cobalt azide, and cadmium azide) is that they are too sensitive toward external stimuli especially the stimulus of electrostatic discharge and cause terrible explosion accidents, which limits the practical applications for human beings. Modifying the existing transition-metal azides by introducing insensitive materials to reduce the sensitivities of these azides is an effective approach to overcome these limitations. For example, in 2016, Wang's group have used a carbonized MOF as the conductive porous carbon matrix to templated synthesize a composite primary explosive MOF/copper azide with relatively low sensitivities [30]. In 2010, Gogotsi's group have reported that when copper azides are confined inside templated carbon nanotubes the electrical conductivity can be improved thus to reduce the electrostatic discharge sensitivity [31]. However, the heat of detonation (ΔH_{det}) will be inevitably decrease with the introduction of carbon materials. Compared with the previously reported approaches, the more effective approach would be importing an insensitive energetic nitrogen-rich heterocycle ligand to the extremely sensitive transition-metal azides by coordination polymerization to assemble compacted energetic MOF materials, which could reduce the sensitivity of metal azides and at the same time could improve the energetic performances. On the other hand, it is known to us that five-membered nitrogen-rich heterocycles have excellent chemical stability due to the conjugate feature of the aromatic ring, such as imidazole, triazole and tetrazole derivatives [32,33]. These kinds of nitrogen-rich ligands own high enthalpy of formation, which is derived from the powerful energy release of the energetic C–N, N–N, and N=N bonds, to provide the main energy sources of energetic materials [34]. Moreover, these kinds of nitrogen-rich ligands release mainly environmentally friendly N₂ after combustion. As the derivative of triazole, 3-amino-1, 2, 4-triazole (Hatz) with nitrogen content as high as 66.67%, which is inclined to form rigid metal-organic complexes to enhance the structural stability, has been employed extensively to construct functional MOFs [35–41]. Meanwhile, the versatile coordination modes of azido ion can also provide an opportunity to construct high density target energetic MOF materials. Based on the above considerations, in this work, Hatz was imported into the system of transition-metal azides (for example, copper azide, cobalt azide, and cadmium azide) via the coordination polymerization strategy in the hope to prepare mixed-ligand nitrogen rich MOF materials with high energy and low sensitivity. Fortunately, a solvent-free 3D energetic MOF, Cd₃(atz)₄(N₃)₂ (**1**) was successfully synthesized using a simple hydrothermal method. Structural analysis reveals that compound **1** features a 3D high-density structure. Compound **1** shows high thermostability, high value for enthalpy of formation ($\Delta_f H^\circ$), remarkable heat of detonation and acceptable mechanical sensitivity, which are discussed in detail. Additionally, the luminescent property of **1** was also investigated.

2. Experimental section

Caution! The reactive raw material sodium azide and the as-synthesized energetic compound might explode under external stimuli (e.g., friction, impact, electrostatic discharge, or elevated temperatures) and generate high energy output, which should be prepared and handled with care. The target energetic compound should be synthesized and used with small scales. Proper protective measures such as safety glass, leather gloves, a protective apron, a face shield, ear plugs, and earthed equipment should be undertaken during treatments.

2.1. Materials and measurements

All chemicals were purchased from Macklin chemical reagent company, Shanghai, China and used without further purification. The elemental analysis of C, H, and N was measured on an Elementar Vario EL III microanalyzer. Powdered X-ray diffraction (PXRD) pattern was collected on a Rigaku Miniflex 600 diffractometer using Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$). The simulated pattern was derived from the Mercury Version 1.4 software (<http://www.ccdc.cam.ac.uk/products/mercury/>) [42]. The FT-IR spectrum was obtained on a PerkinElmer Spectrum using KBr disks in the range of 4000–400 cm⁻¹. Thermogravimetric analysis (TGA) experiments and differential scanning calorimetry (DSC) measurements were done on METTLER TOLEDO instrument in N₂ with the sample heated in an Al₂O₃ crucible at a heating rate of 5 °C min⁻¹. The combustion heat was measured by oxygen bomb calorimetry (5E-AC8018, Changsha Kaiyuan Instruments Co., LTD, China). Solid-state photoluminescent excitation and emission spectra were performed on an Edinburgh EI920 fluorescence spectrometer equipped with a 450 W Xe lamp and a R928P PMT detector.

2.2. Synthesis of Cd₃(atz)₄(N₃)₂ (**1**)

A mixture of Cd(NO₃)₂·4H₂O (231.4 mg, 0.75 mmol), Hatz (85 mg, 1 mmol) and NaN₃ (32.5 mg, 0.5 mmol) was placed in a 20 mL of Teflon-lined stainless steel vessel with 10 mL of deionized water. The mixture was heated from room temperature to 160 °C in 2 h and kept at this temperature for 3 days. The reaction system was cooled slowly to room temperature during another 2 days. Colorless prismatic crystals of **1** were collected, washed thoroughly with deionized water and ethanol, and dried in air at room temperature (yield: 79 mg, 42% based on Cd(NO₃)₂·4H₂O). The optical image of the crystals of **1** please see Fig. S1. Elemental analysis (%): calcd. for C₈H₁₂N₂₂Cd₃ (Mr = 753.60) C 12.75, H 1.61, N 40.89; found: C 12.52, H 1.72, N 40.76. IR (cm⁻¹, KBr): 3426 cm⁻¹ (s), 3324 cm⁻¹ (s), 2058 cm⁻¹ (vs), 1652 cm⁻¹ (w), 1622 cm⁻¹ (s), 1540 cm⁻¹ (vs), 1503 cm⁻¹ (vs), 1458 cm⁻¹ (w), 1418 cm⁻¹ (w), 1330 cm⁻¹ (m), 1283 cm⁻¹ (m), 1233 cm⁻¹ (s), 1220 cm⁻¹ (m), 1124 cm⁻¹ (w), 1054 cm⁻¹ (s), 1003 cm⁻¹ (w), 902 cm⁻¹ (m), 872 cm⁻¹ (w), 779 cm⁻¹ (w), 737 cm⁻¹ (w), 669 cm⁻¹ (w), 653 cm⁻¹ (m), 461 cm⁻¹ (w), 447 cm⁻¹ (w), 419 cm⁻¹ (w) (Fig. S2).

2.3. Single-crystal X-ray structural determination

Intensity data set of **1** was collected on a Rigaku Mercury CCD diffractometer equipped with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) using an ω scan technique at 293 K. The data set was reduced by CrystalClear programmes [43]. The structure was solved by direct method using the Siemens SHELXTL 2014, package of crystallographic software using the multi-scan absorption corrections [44–46]. The final structure was refined using a full-matrix least-squares refinement on F^2 . All the other non-hydrogen atoms were refined anisotropically. The hydrogen atoms on carbon atoms of **1** were generated geometrically and those of amino groups were located from the difference maps. The detailed crystallographic data and structure refinement parameters for **1** are summarized in Table 1. Selected bond

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