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A Novel 3D energetic MOF of high energy content: synthesis and superior explosive performance of Pb(II) compound with 5,5'-bistetrazole-1,1'-diolate

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Abstract: The development of high-performance insensitive energetic materials is important because of the increasing demands for these materials in military and civilian applications. A novel 3D energetic metal–organic framework (MOF) of exceptionally high energy content, [Pb(BTO)(H₂O)]_n, was synthesized and structurally characterized by single crystal X-ray diffraction, featuring a three-dimensional parallelogram porous framework, where BTO represents 5,5'-bistetrazole-1,1'-diolate. The thermal stability and energetic properties were determined, exhibiting that good thermostability ($T_d = 309.0$ °C), excellent detonation pressure (P) of 53.06 GPa and a detonation velocity (D) of 9.204 km/s, and acceptable sensitivity to confirmed impact ($IS = 7.5$ J). Notably, the complex possesses unprecedented superior density than the reported energetic MOFs. Results highlight this new MOF as potential energetic materials.

Introduction

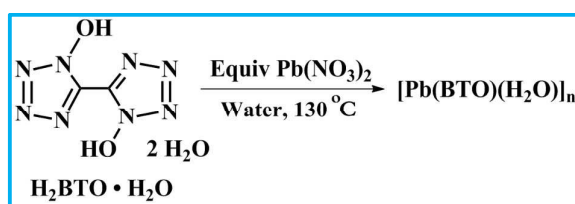
The synthesis and design of high-energy density materials that can release a large amount of energy on demand have been widely investigated for civilian and military applications.^[1] However, insensitivity and high energy usually generate contradictory effects, which make the requirement of high stability with high energetic performance a major challenge.^[2] Given the requirements of high energy, insensitivity, and stability for energetic materials, many energetic salts and co-crystals were synthesized through weak intermolecular interactions^[3] by several scholars, including Klapötke,^[4] Shreeve,^[1a,5] and others.^[6]

In addition to energetic salts and co-crystals, another powerful and straightforward route is through the formation of energetic metal organic frameworks. The investigation of MOFs has attracted considerable interest because of their intriguing structures and unique properties.^[7] Moreover, their potential applications have been explored in various fields, such as gas storage,^[8] catalysis,^[9] molecular sensing,^[10] separation,^[11] and drug delivery materials.^[12] In the past few years, as potential energetic materials, MOF-based compounds exhibit high density and heat of detonation; such compounds with high mechanical strengths and complicated frameworks are conducive to improving thermal stability and insensitivity, whereas the energetic characteristics of MOFs are rarely explored. During the past two years, Hope-Weeks and coworkers recently reported four 1D and 2D energetic MOFs with good detonation performance and heat of detonation.^[13] However, these coordination polymers were highly sensitive to the impact derived from the low-rigidity characteristics of such linear polymeric structures, which makes them infeasible for practical use. Compared with the 1D linear and 2D layered structures, 3D frameworks possess more complicated connection modes, which could further enhance structural reinforcement and improve the stabilities and energetic properties.^[14] In recent years, the use of 3D energetic metal–organic frameworks as new-generation high explosives have attracted intense research interest in the field of chemical c from participating scientists, such as Chen,^[15] Pang,^[14b,16] Shreeve,^[14a,17] and others.^[18] For example, in 2013, Pang et al.^[16c] first reported two 3D, highly energetic MOFs exhibiting the simultaneous requirements of high thermal stability and high heat of detonation.

Notably, the aforementioned energetic MOFs are all constructed with nitrogen-rich ligands because of their various coordination modes, inherently energetic N–N, N=N, C–N, and C=N bonds, and structural stability. The focus has recently shifted to compounds possessing good thermal stability and high nitrogen content, such as 5,5'-bistetrazole-1,1'-diolate (BTO), to obtain highly energetic materials with high nitrogen content and low sensitivity. As a triazole derivative, BTO is a promising green energetic material with a high nitrogen content ($N\% = 66.7\%$).^[4d] Numerous energetic ionic salts based on BTO have been investigated by Klapötke and coworkers.^[3a, 3b, 4c–e] However, related energetic MOFs containing BTO ligands are less well-developed despite the high nitrogen contents and potential applications in energetic materials.

In our continuous search for highly energetic compounds, we explore the preparation of halogen-free energetic 3D energetic MOF, for which one polymer $[\text{Pb}(\text{BTO})(\text{H}_2\text{O})]_n$ (**1**) is designed. Herein, we select BTO as our research object for the following reasons: (1) The rigid structure of BTO would significantly promote the structural stability of MOFs. (2) The high nitrogen content ($N\% = 66.7\%$) of BTO is conducive to forming high-energy compounds. (3) Compared with other ligands, such as hydrazine, hydrazine carboxylate, and 4,4'-azo-1,2,4-triazole, BTO contains more than 10 potential coordination N and O atoms and could be selectively coordinated to central ions, facilitating the formation of multidimensional energetic MOFs. (4) BTO containing N–O building blocks can effectively combine the benefits of each of the fragments and improve energetic performance. Owing to the excellent physical and chemical performances of Pb(II) compounds, investigations on these substances remain considerably important before other substitutes are developed, although the application of these metals may lead to toxic metal pollution. We select Pb(II) as a metal center to construct energetic MOFs on the basis of the following considerations: (1) lead(II) shows good catalytic performances for propellants, which may exhibit the potential application as additives in pyrotechnics and propellants;^[15a] (2) As a heavy p-block metal ion, lead(II), with its large radius, flexible coordination environment, and variable stereochemical activity, provides unique opportunities for formation of unusual network topologies with interesting properties.^[15a, 19] As anticipated, the target 3D energetic MOF with exceptionally high energy content are obtained and exhibit good thermostability, excellent detonation properties, and acceptable sensitivity to confirmed impact, indicating the potential applications of such energetic materials. Notably, the complex possesses unprecedented superior density than the reported energetic MOFs.

The target complex was synthesized by a simple and one-step hydrothermal reaction of lead dinitrate with $\text{H}_2\text{BTO} \cdot \text{H}_2\text{O}$ in water (Scheme 1). The reaction system was cooled slowly to room temperature over a further 3 days. Colorless plates single-crystals suitable for X-ray diffraction were obtained.



Scheme 1. Synthesis of energetic 3D MOFs $[\text{Pb}(\text{BTO})(\text{H}_2\text{O})]_n$.

Results and discussion

Vibrational Spectroscopy

In the IR spectra (Figure S1), the intense broad band at 3434 cm^{-1} corresponds to $\nu(\text{O-H})$. The low value reveals that the OH group is involved in intermolecular hydrogen bonding. The peak at 1625 cm^{-1} corresponds to the stretching vibrations of the C=N, and 1406 cm^{-1} corresponds to the stretching vibrations of the N=N. Moreover, the characteristic absorption band at approximately 1230 cm^{-1} indicative of the presence of N-O stretching vibrations.^[4d] In the Raman spectra (Figure S2), the intensity characteristic absorption band absorption at 1620 cm^{-1} [$\nu_{\text{sym}}(\text{C}=\text{N})$] can be observed,^[4f] whereas the IR spectrum exhibits a signal at 1625 cm^{-1} , which

corresponds to the stretching vibrations of the C=N. Furthermore, the peak at 1235 cm⁻¹ corresponds to the stretching of the N-O.^[4f] Consequently, the vibrational spectroscopy is found to be in good consistent with the structural features of the compound.

Structural description

Single-crystal analysis reveals that the complex crystallizes in the monoclinic space group *c2/c* with *Z* = 4. Table 1 shows the selected data and parameters for X-ray diffraction. The asymmetric unit is crystallographically independent with one Pb(II) ion, one BTO ligand, and one coordination water molecule. Figure S5a shows that each Pb(II) ion is coordinated in a slightly distorted mono-capped antiprismatic coordination environment in which the bottom quadrilateral is formed by two N atoms and two O atoms from two different BTO ligands [Pb(1)–O(1) = 2.786 Å, Pb(1)–N(4) = 2.862 Å]; the top quadrilateral is formed by two N atoms and two O atoms from four different BTO ligands [Pb(1)–O(1) = 2.728 Å, Pb(1)–N(3) = 2.892 Å]; and the capping atom O2 is from the coordination water molecule [Pb(1)–O(1W) = 2.518 Å]. All Pb(II) ions have the same coordination environment with a slightly distorted mono-capped antiprismatic geometry. The adjacent Pb(II) ions along the *b*-axis are bridged by two oxygens from the two different ligands in an antiparallel manner with a Pb...Pb separation distance of 4.416 Å and Pb–O–Pb angle of 106.41° (Figure 1a). Figure S5b shows that atoms N4 and O1 in the BTO ligand adopt chelating modes to connect to one Pb(II) ion, whereas atom N3 adopts monodentate bridging modes to link with three Pb(II) ions. In this manner, each BTO serves as a hexadentate bridge connecting six Pb(II) ions to form a 3D parallelogram porous framework along the *c*-axis with the approximate dimensionality of 45.91 Å², of which pores are filled with coordinated water molecules (Figure 1b). One kind of hydrogen bonding interactions [O(1W)–H(1)...O(1)^{3#} = 2.133 Å; 3# = -*x*, -*y*+1, -*z* symmetry transformation] (Supporting Information) in the parallelogram porous framework, which could further enhance structural reinforcement. The complex [Pb(BTO)(H₂O)]_n represents a good example of a symmetrical, ordered 3D energetic coordination polymer.

Table 1. Crystal data and structure refinement of [Pb(BTO)(H₂O)]_n.

Empirical formula	C ₂ H ₂ N ₈ O ₃ Pb
Formula weight	393.31
CCDC number	1444740
Crystal size [mm ³]	0.21 x 0.20 x 0.19
Crystal system	Monoclinic
Space group	<i>c2/c</i>
<i>a</i> [Å]	14.342(3)
<i>b</i> [Å]	6.5757(12)
<i>c</i> [Å]	8.4715(16)
α [°]	90
β [°]	121.21(3)
γ [°]	90
<i>V</i> [Å ³]	683.3(2)
<i>Z</i>	4
ρ_{calcd} [g cm ⁻³]	3.823
<i>T</i> [K]	293(2)
<i>F</i> (000)	704
<i>R</i> _{int}	0.0247
Data	671
Restraints	0
parameters	65
GOF ^[a] on <i>F</i> ²	1.055
<i>R</i> ₁ ^[b] (<i>I</i> > 2σ(<i>I</i>))	0.0553
ωR_2 (<i>I</i> > 2σ(<i>I</i>))	0.1257
<i>R</i> ₁ (all data)	0.0553
ωR_2 ^[c] (all data)	0.1257

$$^{[a]} \text{GOF} = \text{Goodness of Fit. } ^{[b]} R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}. \quad ^{[c]} \omega R_2 = \left[\frac{\omega (F_o^2 - F_c^2)^2}{\omega (F_o^2)^2} \right]^{1/2}.$$

Density is a highly important physical property of energetic materials. The crystal density of $[\text{Pb}(\text{BTO})(\text{H}_2\text{O})]_n$ is 3.823 g/cm^3 , and the density based on gas-pycnometer measurement is 3.812 g/cm^3 at $25 \text{ }^\circ\text{C}$. To the best of our knowledge, this value is superior to the reported energetic MOFs, such as ATRZ-1 ($\rho = 1.680 \text{ g/cm}^3$), $[\text{Pb}(\text{Htztr})_2(\text{H}_2\text{O})]_n$ ($\rho = 2.519 \text{ g/cm}^3$), and $[\text{Pb}(\text{Htztr})(\text{O})]_n$ ($\rho = 3.511 \text{ g/cm}^3$).^[15a] The superior density of the target complex is probably due to incorporation of heavy metal Pb or the rigid structural framework.

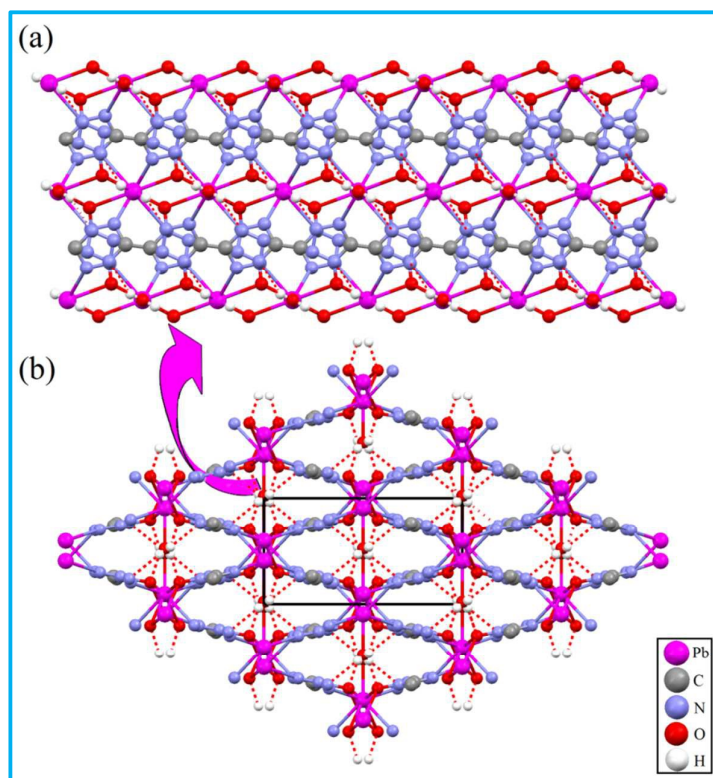


Figure 1. (a) The 3D MOF of the target complex depicted along the crystallographic b axis. (b) along the crystallographic c axis.

Thermal decomposition

Thermal stability is our first concern because an unacceptably low decomposition temperature will strictly limit the application of energetic materials. In this work, thermal analyses of the crystal presented considerable practical challenges. In a first attempt to acquire a differential thermal analysis (DTA) trace for $[\text{Pb}(\text{BTO})(\text{H}_2\text{O})]_n$, 1.02 mg detonates at $300.0 \text{ }^\circ\text{C}$ in an open crucible made of Al_2O_3 . In this case, complete detonation is accompanied by bang and destroys the crucible and pallet (Figure 2). DTA of $[\text{Pb}(\text{BTO})(\text{H}_2\text{O})]_n$ revealed a violent reaction at $300.0 \text{ }^\circ\text{C}$ followed by explosion, leading to an abnormal curve (Figure S3). These data are collected at a ramp rate of $10 \text{ }^\circ\text{C/min}$ under atmosphere. Thereafter, small samples of $[\text{Pb}(\text{BTO})(\text{H}_2\text{O})]_n$ (approximately 0.09 mg) are used in differential scanning calorimetry (DSC) experiments at a heating rate of $5 \text{ }^\circ\text{C/min}$ in flowing high-purity nitrogen. Figure 3 shows a typical result. The DSC curve shows that one intense exothermic process occurs at $281.7 \text{ }^\circ\text{C}$ and ends at $325.2 \text{ }^\circ\text{C}$ with a peak temperature of $309.0 \text{ }^\circ\text{C}$ and corresponding decomposition enthalpy of $2,207 \text{ J/g}$. The thermal stability of $[\text{Pb}(\text{BTO})(\text{H}_2\text{O})]_n$ is higher than that of HMX ($287.0 \text{ }^\circ\text{C}$),^[13b] which is a highly energetic material commonly employed,^[20] and higher than those of 1D MOFs (CHP, $194.0 \text{ }^\circ\text{C}$)^[15b] and 2D MOFs (CHHP, $231.0 \text{ }^\circ\text{C}$).^[13a] Furthermore, the thermal stability of $[\text{Pb}(\text{BTO})(\text{H}_2\text{O})]_n$ (approximately 0.32 mg) was investigated by thermogravimetric analysis (TGA) experiments at a heating rate of $5 \text{ }^\circ\text{C/min}$ in flowing high-purity nitrogen. The typical TG-DTG curves (Figure S4)

show that it undergoes three mass loss stages. The first weight loss stage starts at 104.7 °C, ends at 120.6 °C, accompanied by about 5.22% weight loss, and the corresponding DTG peak temperature appears at 115.1 °C (endothermic), which is attributed to the loss of one coordinated water molecule (4.57%). Second step have 36.76% mass loss due to the collapse of the main framework. The onset temperature is 270.7 °C and peak temperature is 302.3 °C (exothermic). Afterwards, it continues losing weight but on a slower velocity from 326.3 to 383.2 °C. The mass of the final residue was 44.6% of initial. 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.

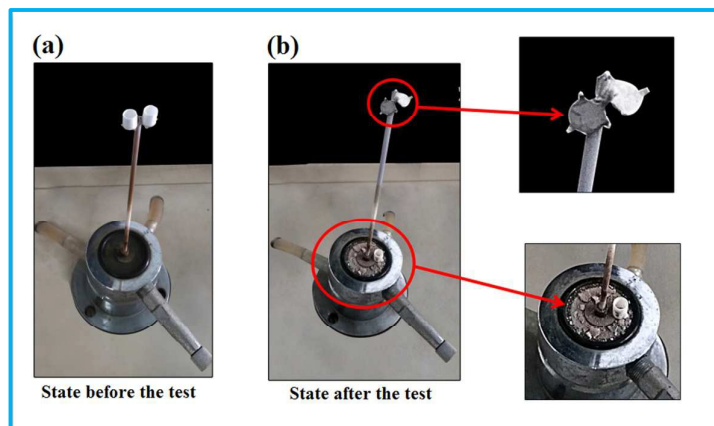


Figure 2. DTA test of the target complex (about 1.02 mg sample) on a WCR-1B analyzer at a heating rate of 10 °C /min, atmosphere, and the reference α -Al₂O₃. (a) state before the test; (b) the destroy crucible and pallet after the test.

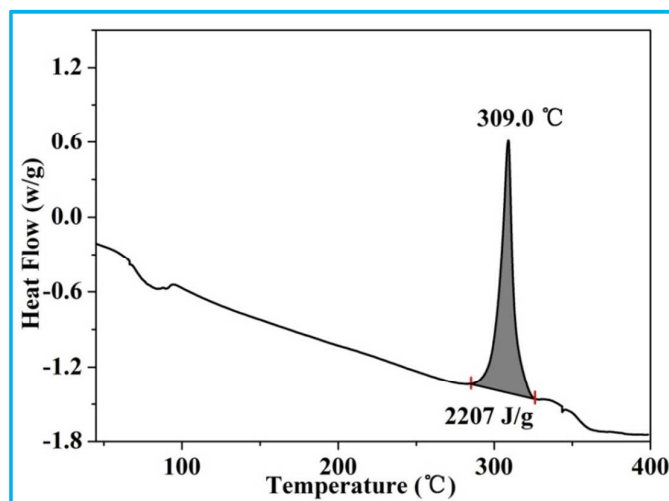


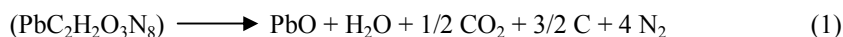
Figure 3. Differential Scanning Calorimetry thermogram of [Pb(BTO)(H₂O)]_n (0.09 mg) with a aluminum pan, ramp rate of 5 °C/min under nitrogen flow.

Detonation properties

For initial safety testing, the impact sensitivity of the compound is determined (Supporting Information). Table 2 summarizes the data collected. The impact sensitivity of [Pb(BTO)(H₂O)]_n is 7.5 J. Thus, [Pb(BTO)(H₂O)]_n can be classified as an impact-sensitive energetic material. However, compared with the reported energetic coordination polymers, such as 1D MOFs (CHP, IS = 0.5 J)^[13b] and 2D MOFs (ZnHHP, IS = 2.5 J; CHHP, IS = 0.8 J)^[13a], the 3D MOFs exhibit significantly lower sensitivities that are also comparable to those of HMX (IS = 7.4 J)^[13b] and RDX (IS = 7.4 J)^[13b].

The drastic process of decomposition demonstrates the potential detonation properties of the complex; this process is necessary to estimate the heat of detonation (ΔH_{det}) of $[\text{Pb}(\text{BTO})(\text{H}_2\text{O})]_n$, which is compared with that of 1D, 2D, and 3D MOFs and common energetic materials. Then, we adopted the same methodology recently employed for NHP and CHP.^[13b] Density functional theory is used to calculate the energy of detonation (ΔE_{det}), from which ΔH_{det} is estimated by using a linear correlation equation ($\Delta H_{\text{det}} = 1.127 \Delta E_{\text{det}} + 0.046$, $r = 0.968$) developed from known ΔH_{det} data for 10 commonly used high explosives (Table S1).

For the complex, water, nitrogen, carbon, and carbon dioxide are assumed to be the final products of decomposition of the organic part of the framework, and the formation of metal oxides is assumed to be governed by oxygen deficiency. The complete detonation reaction is expressed in Equation (1), as follows:



The heat of detonation (ΔH_{det}) is calculated to be 1.001 kcal/g (3.827 kcal/cm³). Such value is higher than those of 1D MOFs ZnHHP (0.750 kcal/g) and CHHP (0.700 kcal/g) but lower than those of RDX (1.386 kcal/g) and HMX (1.320 kcal/g) (see in Table 2). The relatively low ΔH_{det} values may be probably due to the existing coordination water. Figure 4 shows that despite the lack of advantage of the ΔH_{det} of the per gram complex, the ΔH_{det} of per cm³ (3.827 kcal/cm³) is higher than that of traditional explosives and energetic MOFs, except for ATRZ-1 because of its high density.

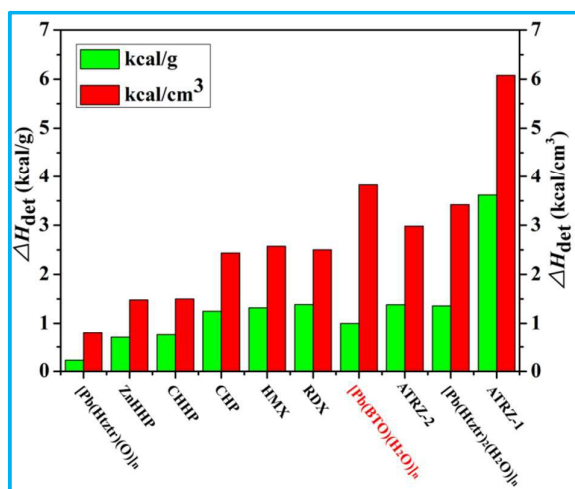


Figure 4. Bar chart representation of ΔH_{det} values in literature for common explosive materials and previously reported values for energetic MOFs along with the predicted ΔH_{det} value for $[\text{Pb}(\text{BTO})(\text{H}_2\text{O})]_n$. The error bars correspond to the 96% statistical-confidence level for these values.

Table 2. Physicochemical properties of $[\text{Pb}(\text{BTO})(\text{H}_2\text{O})]_n$.

	$T_d^{[a]}$	$\rho^{[b]}$	$N^{[c]}$	$\Delta H_{\text{det}}^{[d]}$	$D^{[e]}$	$P^{[f]}$	$IS^{[g]}$
$[\text{Pb}(\text{BTO})(\text{H}_2\text{O})]_n$	309	3.823	28.5	1.001	9.204	53.06	7.5
CHP ^[13b]	194	1.948	14.71	1.250	8.225	31.73	0.5
CHHP ^[13a]	231	2.000	28.25	0.750	6.205	17.96	0.8
ZnHHP ^[13a]	293	2.117	23.61	0.700	7.016	23.58	2.5
ATRZ-1 ^[14b]	243	1.680	53.35	3.618	9.160	35.68	22.5
ATRZ-2 ^[14b]	257	2.160	43.76	1.381	7.773	29.70	30.0
$[\text{Pb}(\text{Htztr})_2(\text{H}_2\text{O})]_n^{[15a]}$	340	2.519	39.40	1.359	7.715	31.57	>40.0
$[\text{Pb}(\text{Htztr})(\text{O})]_n^{[15a]}$	318	3.511	27.20	0.225	8.122	40.12	>40.0
HMX ^[13b]	287	1.950	37.84	1.320	8.900	38.39	7.4
RDX ^[13b]	210	1.806	37.80	1.386	8.600	33.92	7.4

[a] Decomposition temperature (DSC, °C). [b] Density from X-ray diffraction analysis (g/cm³). [c] Nitrogen content (%). [d] The heat of detonation (kcal/g). [e] Detonation velocity (km/s). [f] Detonation pressure (Gpa). [g] Impact sensitivity (J). CHP = cobalt hydrazine perchlorate; CHHP = cobalt hydrazine hydrazinecarboxylate perchlorate; ZnHHP = zinc hydrazine hydrazinecarboxylate perchlorate; ATRZ = 4,4'-azo-1,2,4-triazole; Htztr = 3-(tetrazol-5-yl)triazole.

The detonation velocity (D) and detonation pressure (P) of the complex are calculated by the Kamlet–Jacobs^[21] equations, which are usually applied to the energetic MOFs reported previously (Supporting Information), to analyze the detonation characteristics. Table 2 lists the comparison of the physicochemical properties of several energetic materials and the complex. D and P of the complex are calculated to be 9.204 km/s and 53.06 GPa, respectively, which indicate its absolute advantage over the known energetic MOFs, except for [Cu(Htztr)]_n.^[15d]

Conclusions

In conclusion, A 3D energetic MOF with exceptionally high energy content are obtained in a simple and straightforward manner. Compared with 1D, 2D, and common energetic materials, the 3D MOF exhibit excellent physical and detonation properties, such as high thermal stabilities, excellent detonation properties, and acceptable sensitivity to confirmed impact. Specifically, the complex exhibits the unprecedented superior density than the reported energetic MOFs. The finding examples the potential application and advances the integrated performance of the MOF-based high-energy-density materials.

Experimental

Safety Precautions! Although we experienced no difficulties in the synthesis of the material, small-scale syntheses are strongly encouraged. The compounds should be handled with extreme care, and eye protection and gloves must be worn at all times. Especially, the energetic MOF, [Pb(BTO)(H₂O)]_n, owing to such unpredictability with its tremendous power makes this an exceptionally hazardous material. Even small quantities (< 1 mg, e.g., a small single crystal) can cause severe physical damage to their surroundings.

General methods

5,5'-bistetrazole-1,1'-diolate (BTO) was synthesized according to ref.[4d]. All other materials were commercially available and used without further purification. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet-5700 FTIR spectrometer by using pressed KBr pellets to evaluate the chemical bonding of the samples from 4000 cm⁻¹ to 400 cm⁻¹. Raman spectra was measured by InVia Raman spectrometer with an excitation wavelength of 514 nm. DSC was performed by a Q200 DSC instrument (TA Instruments, United States) at a heating rate of 5 °C/min in flowing high-purity nitrogen. About 0.09 mg sample was sealed in aluminum pans in the temperature range of 40-400 °C for DSC experiments. Differential thermal analysis (DTA) curve was recorded on a WCR-1B analyzer at a heating rate of 10 °C/min, atmosphere, and the reference α -Al₂O₃. TGA was performed with an SDT Q600 TGA instrument (TA Instruments, United States) at a heating rate of 5 °C/min in flowing high-purity nitrogen. The sensitivity to impact stimuli was determined by fall hammer apparatus applying standard staircase method using a 10 kg drop weight and the results were reported in terms of height for 50% probability of explosion ($h_{50\%}$).

X-ray crystallography

The single-crystal X-ray experiments were performed on a Smart Apex CCD diffractometer (Bruker) equipped with graphite monochromatized Mo K α radiation ($\lambda = 0.71073$ Å) using the ω and ϕ scan mode. The structure was solved by direct methods using SHELXS-97^[22] and refined by means of full-matrix least-squares procedures on F^2 with the SHELXL-97 program^[23]. All non-H atoms were located using subsequent Fourier-difference methods and refined anisotropically. In all cases, hydrogen atoms were placed in their calculated positions and thereafter allowed to ride on their parent atoms. Other details of crystal data, data collection

parameters, and refinement statistics are given in Table 1. The selected bond lengths, angles and torsion angles data are presented in Tables S2 and S3 (ESI†).

Synthetic procedures

[Pb(BTO)(H₂O)]_n: A mixture of 1*H*,1'*H*-5,5'-bistetrazole-1,1'-diolate dihydrate (41.2 mg, 0.20 mmol) and Pb(NO₃)₂ (66.2 mg, 0.20 mmol) were dissolved in 6 mL of water and stirring at room temperature. The mixture was put into a 10 mL Teflon liner, heated to 130 °C over 4 h and kept at this temperature for 3 days. The reaction system was cooled slowly to room temperature over a further 3 days. colorless plates single-crystals suitable for X-ray diffraction were obtained, yield 53.5 mg (0.14 mmol, 68 %). DSC (5 °C/min): 309.0 (dec.). IR (cm⁻¹, KBr): 3434 (s), 1625 (m), 1406 (m), 1358 (w), 1230 (m), 1164 (w), 998 (w), 731 (w), 502 (w). Raman (514 nm, 1.7 mw, 25 □): 1620, 1235, 1122, 1008, 781, 627, 412, 276, 164 cm⁻¹. Anal. Calcd. For PbC₂H₂N₈O₃ (393.32): C, 6.10; H, 0.51; N, 28.48%. Found: C, 5.96; H, 0.61; N, 28.56%.

Acknowledgements

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