

Electronic Supplementary Information

A highly stable and tightly packed 3D energetic coordination polymer assembled by nitrogen-rich tetrazole derivative

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Index:

1. Experimental details	S3
2. Scheme	S6
3. Table	S7
4. Graphics	S9
5. References	S11

1. Experimental details

Heat of combustion. The constant-volume combustion energies of the compounds were determined by a precise oxygen bomb calorimetry (5E-AC8018, Changsha Kaiyuan Instruments Co., LTD, China). The correct value of the heat exchange was calculated according to the Linio-Pyfengdelel-Wsava equation.^[1]

Firstly, we adopted the certified benzoic acid (about 1000 mg, pellet) by the combustion of in an oxygen atmosphere at a pressure of 2.30 MPa to calibrate the calorimeter. In the second place, 150 mg of the samples were prepared and well mixed with certified benzoic acid (calculated: 600 mg), which were pressed to form a pellet to ensure better combustion. Finally, the pellet was placed in combustion pots, which were subsequently burned in a 2.30 MPa atmosphere of pure oxygen.

Friction and Impact Sensitivity Test. The sensitivities of the compounds were determined according to the BAM (German: Bundesanstalt für Materialforschung und Prüfung) standard for friction and impact. The classification of the tested compounds results from the “UN Recommendations on the Transport of Dangerous Goods”.

Impact sensitivity: The impact sensitivity was tested on a BAM fall hammer BFH-12 produced by OZM Research. Impact sensitivity tests were carried out according to STANAG 4489. The calculated value of h_{50} represents the drop height of 50% initiation probability. A 5 kg weight was dropped from a set height onto a 20 mg sample placed on a copper cap. The test results show that no explosion happens at the point of 80 cm, which corresponds to an impact energy of 40 J. The sensitivity tests reveal that compound **1** is insensitive to impact.

Friction sensitivity: The friction sensitivity was determined using a FSKM-10 BAM friction apparatus produced by OZM Research on the basis of STANAG 4487. No friction sensitivity was observed up to 360 N to illustrate that compound **1** is insensitive to friction.

Detonation properties for compound 1.

Detonation performance of the related energetic materials **1** here was evaluated by the empirical Kamlet formula, as

$$D = 1.01 \Phi^{1/2} (1 + 1.30\rho)$$

$$P = 1.558 \Phi \rho^2$$

$$\Phi = 31.68 N(MQ)^{1/2}$$

$$Q = -[\Delta H_f(\text{detonation products}) - \Delta H_f(\text{explosive})]/\text{formula weight of explosive}$$

where D represents detonation velocity ($\text{km}\cdot\text{s}^{-1}$) and P is detonation pressure (GPa), ρ is the density of explosive ($\text{g}\cdot\text{cm}^{-3}$). Φ , N , M and Q are characteristic parameters of an explosive. N is the moles of detonation gases per gram of explosive, M is the average molecular weight of these gases and Q is the heat of detonation ($\text{kcal}\cdot\text{g}^{-1}$).

When the K-J (Kamlet-Jacobs) equation is employed, the overall calculation process can be described as follows: for the explosives composed of C, H, N, and O elements, all N atoms are converted to N_2 ; O atoms form H_2O with H atoms first and then form CO_2 with C atoms; the remaining C atoms are retained in the solid state; if there are O atoms left, they will form O_2 . To preserve Kamlet's method, the developed theory is employed to determine the detonation products from metal-containing explosives. In most cases, metal atoms are converted to their oxidation states, emitting more heat after detonation. Otherwise, metal atoms can be treated as their reduction states, if the heat of formation (HOF) of metallic oxides is higher than that of H_2O , or there is no O atom in the molecule. Besides, O atoms form H_2O with H atoms first and the remaining ones then form CO_2 with C atoms. However, if the amount of O atoms is not sufficient to oxidize all H atoms, the remaining H atoms can produce NH_3 with N atoms, and the rest of the N atoms are released as N_2 gas. On the other hand, the remaining C atoms are retained in the solid state if they are not completely oxidized by O atoms. If there are redundant O atoms, however, they can be expelled as O_2 . For systems with metals, the most stable products were assumed under the constraints of stoichiometrically available oxygen, i.e., $\text{CdO}(\text{s})$ for **1**. The complete detonation reactions are described by equations 1.



For **1**

$$\rho = 2.709 \text{ g}\cdot\text{cm}^{-3}$$

$$Q = \Delta H_{det} = 1830 \text{ J}\cdot\text{g}^{-1} = 0.438 \text{ kcal}\cdot\text{g}^{-1}$$

$$N = 5/281.54 = 0.0178 \text{ mol}\cdot\text{g}^{-1}$$

$$M = (17.03 \times 1 + 28.01 \times 4)/5 = 25.81 \text{ g}\cdot\text{mol}^{-1}$$

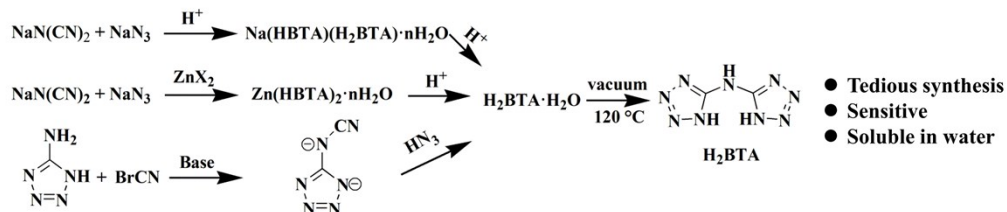
$$P = 1.558 \times (2.709)^2 \times [0.0178 \times (25.81 \times 438)^{1/2}] = 1.558 \times (2.709)^2 \times 3.81 = 21.64 \text{ GPa}$$

$$D = 1.01 \times (1.893)^{1/2} \times (1 + 1.30 \times 2.709) = 6.283 \text{ km}\cdot\text{s}^{-1}$$

2. Scheme

Scheme S1. Various Strategies for the BTA²⁻-Based Energetic Materials

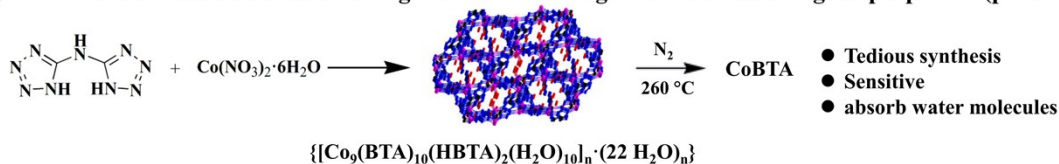
a) Multi-steps to synthesis the sensitive H₂BTA increasing the safety risk (previous work)^[2]



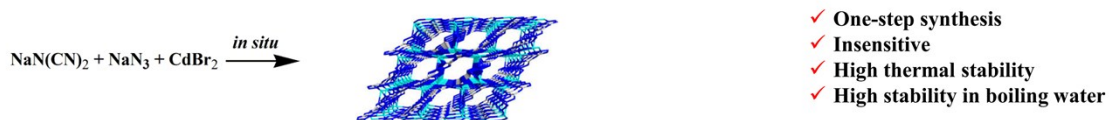
b) BTA²⁻-based energetic salts with low thermal stability and low energy density (previous work)^[3]



c) Porous channels of the sensitive energetic MOF with negative effects to energetic properties (previous work)^[4]



d) One step to synthesis the tight 3D energetic CP with high stabilities and high energy density (this work)



3. Table

Table S1. Crystal data and structure refinement for **1**.

Compound	1
CCDC	1527239
Empirical formula	C ₂ H ₃ N ₉ OCd
<i>M_r</i> (g mol ⁻¹)	281.53
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>Z</i>	4
<i>a</i> /Å	6.5352(19)
<i>b</i> /Å	9.853(3)
<i>c</i> /Å	10.779(3)
<i>α</i> ^o	90
<i>β</i> ^o	95.922(4)
<i>γ</i> ^o	90
<i>V</i> /Å ³	690.4(3)
<i>D_c</i> /g cm ⁻³	2.709
Temperature (K)	293(2)
<i>F</i> (000)	536
<i>Reflns</i>	1577
<i>Params</i>	125
<i>S</i> on <i>F</i> ²	1.053
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>)) ^a	0.0122
<i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>)) ^b	0.0306
<i>R</i> ₁ (all data)	0.0136
<i>wR</i> ₂ (all data)	0.0310

^a $R_1 = \sum(F_o - F_c)/\sum F_o$; ^b $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table S2. Selected bond distances (Å) and bond angles (°).

Compound 1			
Cd(1)–O(1W)	2.3279(16)	Cd(1)–N(16)#1	2.3609(15)
Cd(1)–N(11)	2.3288(15)	Cd(1)–N(18)#2	2.3811(16)
Cd(1)–N(19)	2.3501(15)	Cd(1)–N(13)#3	2.4062(16)
O(1W)–Cd(1)–N(11)	112.11(5)	N(16)#1–Cd(1)–N(13)#3	98.85(6)
O(1W)–Cd(1)–N(19)	85.53(6)	N(18)#2–Cd(1)–N(13)#3	75.52(6)
N(11)–Cd(1)–N(19)	76.98(5)	C(12)–N(19)–Cd(1)	128.71(11)
O(1W)–Cd(1)–N(16)#1	82.11(6)	N(18)–N(19)–Cd(1)	126.72(10)
N(11)–Cd(1)–N(16)#1	86.09(5)	C(12)–N(16)–Cd(1)#4	137.84(11)
N(19)–Cd(1)–N(16)#1	153.49(5)	N(17)–N(16)–Cd(1)#4	115.74(10)
O(1W)–Cd(1)–N(18)#2	80.96(5)	N(17)–N(18)–Cd(1)#2	117.74(11)
N(11)–Cd(1)–N(18)#2	166.43(5)	N(19)–N(18)–Cd(1)#2	131.84(11)
N(19)–Cd(1)–N(18)#2	101.28(5)	N(12)–N(13)–Cd(1)#5	122.71(12)
N(16)#1–Cd(1)–N(18)#2	99.81(5)	N(14)–N(13)–Cd(1)#5	116.88(11)
O(1W)–Cd(1)–N(13)#3	156.29(6)	C(11)–N(11)–Cd(1)	129.69(11)
N(11)–Cd(1)–N(13)#3	91.56(6)	N(12)–N(11)–Cd(1)	125.61(11)
N(19)–Cd(1)–N(13)#3	101.82(6)		

Symmetry codes for compound 1. #1 $x + 1/2, -y + 1/2, z - 1/2$. #2 $-x + 1, -y, -z + 2$. #3 $-x + 1/2, y - 1/2, -z + 3/2$. #4 $x - 1/2, -y + 1/2, z + 1/2$. #5 $-x + 1/2, y + 1/2, -z + 3/2$.

5. Graphics

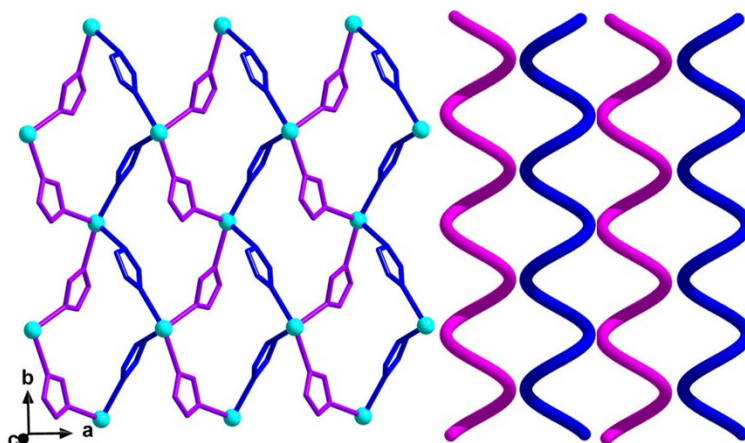


Figure S1. Plots of the left-handed and right-handed chiral layers constructed by the two types of helical chains in **1**.

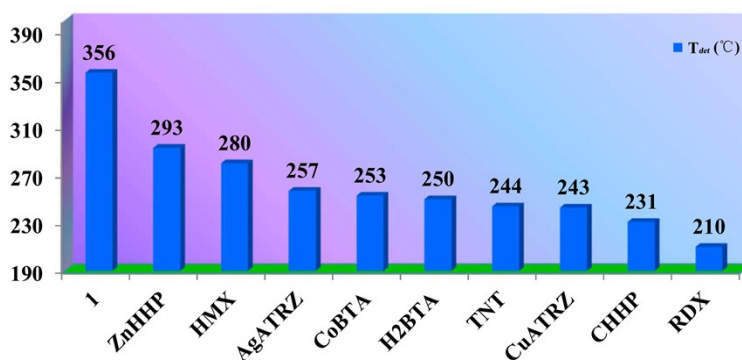


Figure S2. Comparison of the thermal decomposition temperature of the ligand H₂BTA, traditional explosives TNT, HMX, RDX and some reported energetic MOFs with **1**.

Note: $\text{ZnHHP}^{[5]} = \text{Zn}_2(\text{N}_2\text{H}_4)_3(\text{N}_2\text{H}_3\text{CO}_2)_2(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}]_n$; $\text{CHHP}^{[5]} = [\text{Co}_2(\text{N}_2\text{H}_4)_4(\text{N}_2\text{H}_3\text{CO}_2)_2(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}]_n$

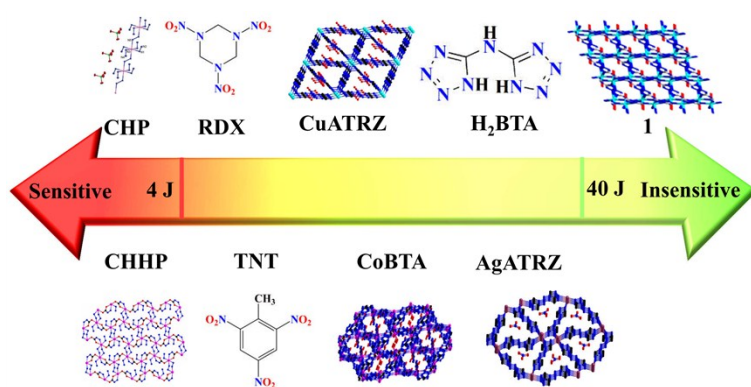


Figure S3. Comparison of the impact sensitivity of the ligand H₂BTA, traditional explosives TNT, RDX and some reported energetic MOFs with **1**.

Note: CHP^[6] = [Co(N₂H₄)₅(ClO₄)₂]_n

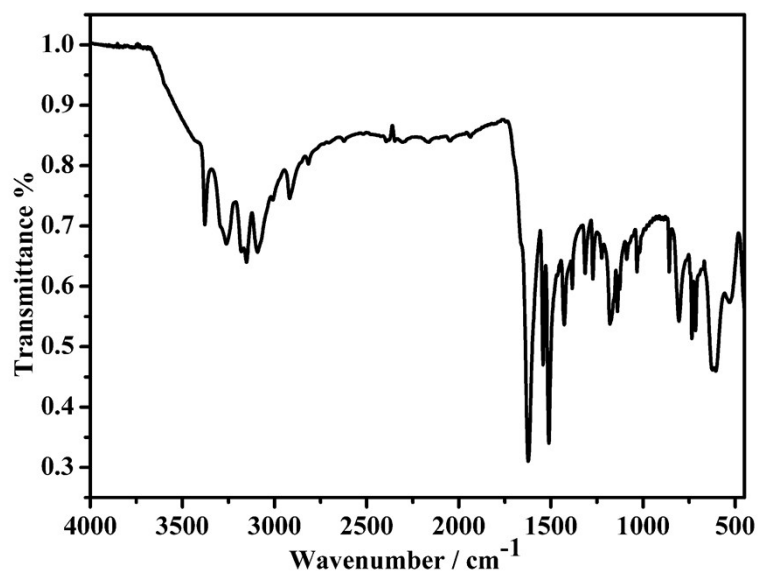


Figure S4. The IR spectra of **1**.

6. References:

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- [2] T. M. Klapötke, P. Mayer, J. Stierstorfer, J. J. Weigand, *J. Mater. Chem.*, 2008, **18**, 5248–5258.
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