Electronic Supplementary Information

Nitrate anions embedded in rigid and cationic 3D energetic MOFs constructed by the chelating ligand towards insensitive energetic materials

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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, China). Firstly, we adopt the certified benzoic acid (about 1.0 g, pellet), which has an isothermal heat of combustion of (−26434 ± 3) $J \cdot g^{-1}$ at 298.15 K, by the combustion in an oxygen atmosphere to calibrate the calorimeter. Then, 150 mg of the samples were prepared and mixed with certified benzoic acid, which were pressed to form a pellet to ensure better combustion. Finally, the pellet was placed in combustion pots, which were subsequently burned in an atmosphere of pure oxygen.

$$Q = -[\Delta_f H^o \text{ (denotation products)} - \Delta_f H^o \text{ (explosive)}] \text{ / formula weight of explosive}$$

Q is the heat of detonation ($kcal \cdot g^{-1}$).

For **1**

$\rho = 2.293\ g \cdot cm^{-3}$

$Q = \Delta H_{det} = 2253.903\ kJ \cdot mol^{-1} = 1.270\ kcal \cdot g^{-1}$

Sensitivities Test. The mechanical 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'.[2] Test conditions: 29°C (temperature); 36 % (relative humidity).

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. A weight was dropped from a set height onto a 10 mg sample placed on a copper cap. Each subsequent test was made at the next lower height if explosion occurred and at the next

higher height if no explosion happened until the value of 50% probability of the explosion is obtained. The values of **1** is > 40 J by dozens of experiments.

Friction sensitivity. The friction sensitivity was determined using a FSKM-10 BAM friction apparatus produced by OZM Research based on STANAG 4487. The friction sensitivity of **1** is greater than 360 N. Compound **1** is an insensitive energetic material.

2. Table

Table S1. Selected bond distances (Å) and bond angles (°).

Compound **1**			
Zn(2)–O(5)	1.938(3)	Zn(1)–O(5)	1.958(3)
Zn(2)–O(1W)	2.343(4)	Zn(1)–N(11)	1.963(3)
Zn(2)–N(21)	2.220(4)	Zn(1)–N(22)	1.982(4)
Zn(2)–N(14)#1	1.989(4)	Zn(1)–N(12)#3	1.981(4)
Zn(2)–N(24)#2	1.996(4)		
O(5)–Zn(2)–O(1W)	85.93(14)	C(11)–N(12)–N(11)	106.1(3)
O(5)–Zn(2)–N(21)	90.00(14)	N(22)–N(21)–Zn(2)	114.1(3)
O(5)–Zn(2)–N(14)#1	109.73(15)	C(22)–N(21)–Zn(2)	133.7(3)
O(5)–Zn(2)–N(24)#2	124.36(15)	C(22)–N(21)–N(22)	104.9(3)
N(21)–Zn(2)–O(1W)	175.87(14)	C(11)–N(14)–Zn(2)#4	126.4(3)
N(14)#1–Zn(2)–O(1W)	84.55(14)	C(12)–N(14)–Zn(2)#4	129.1(3)
N(14)#1–Zn(2)–N(21)	97.51(14)	C(12)–N(14)–C(11)	103.6(3)
N(14)#1–Zn(2)–N(24)#2	124.19(15)	C(22)–N(24)–Zn(2)#5	129.2(3)
N(24)#2–Zn(2)–O(1W)	86.41(15)	C(21)–N(24)–Zn(2)#5	125.0(3)
N(24)#2–Zn(2)–N(21)	95.33(15)	C(21)–N(24)–C(22)	103.0(4)
O(5)–Zn(1)–N(11)	114.23(15)	O(3)–N(1)–O(2)	119.2(5)
O(5)–Zn(1)–N(22)	94.92(14)	O(3)–N(1)–O(4)	120.2(5)
O(5)–Zn(1)–N(12)#3	103.55(14)	O(4)–N(1)–O(2)	120.6(4)
N(11)–Zn(1)–N(22)	117.26(15)	N(12)–C(11)–N(13)	125.3(4)
N(11)–Zn(1)–N(12)#3	112.77(15)	N(12)–C(11)–N(14)	112.1(4)
N(12)#3–Zn(1)–N(22)	112.04(15)	N(13)–C(11)–N(14)	122.5(4)
Zn(2)–O(5)–Zn(1)	118.19(17)	N(21)–C(22)–N(25)	125.3(4)
N(12)–N(11)–Zn(1)	120.7(3)	N(21)–C(22) –N(24)	113.0(4)
C(12)–N(11)–Zn(1)	131.7(3)	N(24)–C(22)–N(25)	121.6(4)
C(12)–N(11)–N(12)	106.0(3)	N(11)–C(12)–N(14)	112.1(4)

N(12)–N(22)–Zn(1)	116.8(3)	N(11)–C(12)–N(15)	126.0(4)
C(21)–N(22)–Zn(1)	137.0(3)	N(14)–C(12)–N(15)	121.8(4)
C(21)–N(22)–N(21)	106.2(3)	N(22)–C(21)–N(24)	112.8(4)
N(11)–N(12)–Zn(1)#3	120.9(3)	N(22)–C(21)–N(23)	124.4(4)
C(11)–N(12)–Zn(1)#3	131.1(3)	N(24)–C(21)–N(23)	122.8(4)

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

3. Graphics

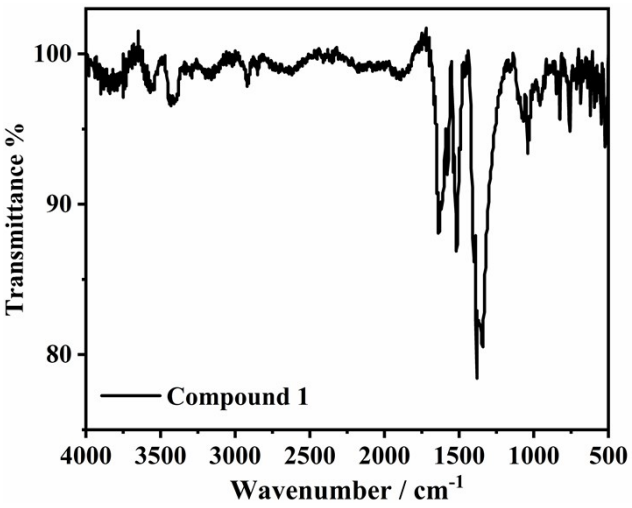

Figure S1. The IR spectra of **1**.

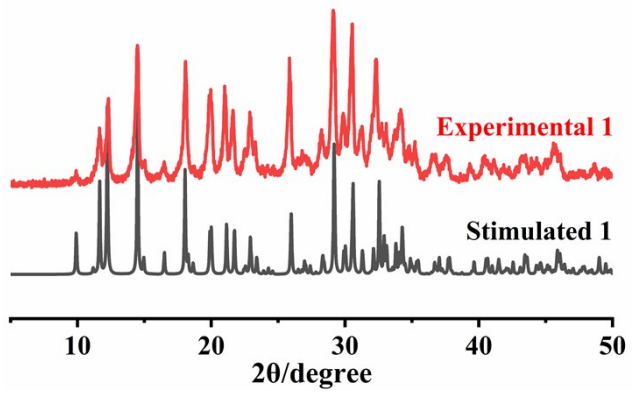

Figure S2. Powdered *X*-ray diffraction (PXRD) patterns of **1**.

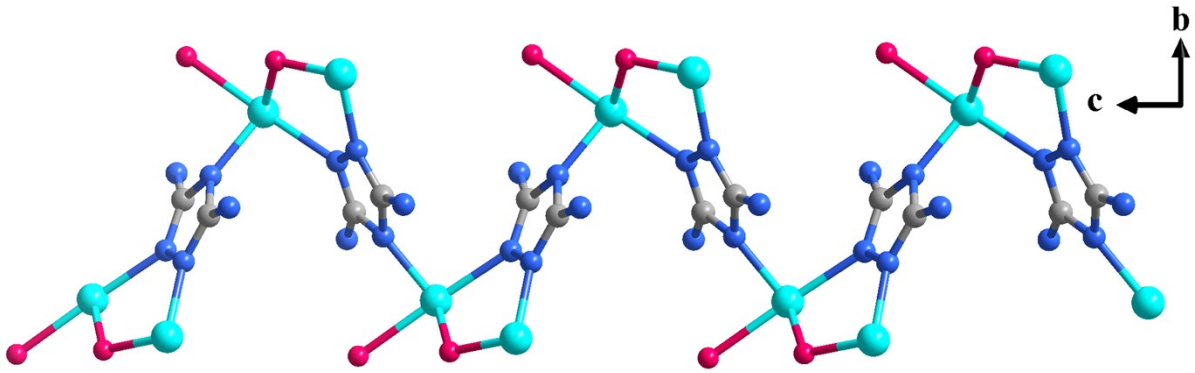

Figure S3. The 1D structure of compound **1** along the *c* axle.

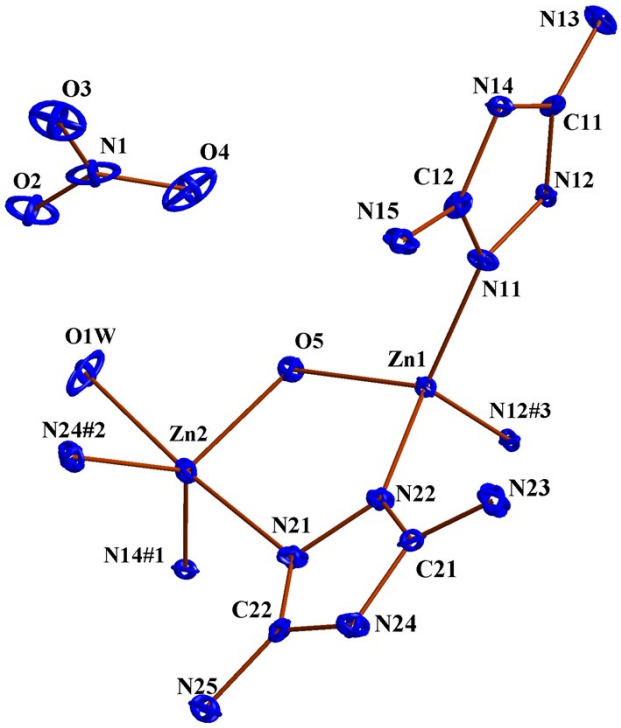

Figure S4. Schematic diagram of ADP in compound **1**.

4. References

[1] Y. Wang, J.-C. Zhang, H. Su, S.-H. Li, S.-W. Zhang, and S.-P. Pang, J. Phys. Chem. A, 2014, **118**, 4575–4581.

[2] Impact: insensitive > 40 J, less sensitive ≥ 35 J, sensitive ≥ 4 J, very sensitive ≤ 3 J; Friction: insensitive > 360 N, less sensitive = 360 N, 80 N < sensitive < 360 N, very sensitive ≤ 80 N, extremely sensitive ≤ 10 N.