Electronic Supplementary Information

Refinement of the sensitive azides *via in situ* generated azole-based metal−organic frameworks towards stable 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.

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: 16 °C (temperature); 42 % (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** and **2** are > 40 and 32 J, respectively by dozens of experiments.

Friction sensitivity. The friction sensitivity was determined using a FSKM-10 BAM friction apparatus produced by OZM Research on the basis of STANAG 4487. The friction sensitivities of **1** and **2** are > 360 and 324 N, respectively. Compound **1** belongs to insensitive explosives while compound **2** belongs to sensitive explosives.

2. Tables

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

Compound **1**			
Zn(1)−N(1)	2.011(4)	Zn(1)−N(4)#2	2.014(4)
Zn(1)−N(7)#1	2.063(4)	Zn(1)−Br(1)	2.3554(8)
N(1)−Zn(1)−N(7)#1	100.18(15)	N(7)#1−Zn(1)−Br(1)	105.79(11)
N(1)−Zn(1)−N(4)#2	108.92(16)	N(4)#2−Zn(1)−N(7)#1	99.64(15)
N(1)−Zn(1)−Br(1)	123.58(12)	N(4)#2−Zn(1)−Br(1)	114.67(12)
Compound **2**			
Cd(1)−N(7)#1	2.382(4)	Cd(1)−N(4)#4	2.370(4)
Cd(1)−N(7)#2	2.382(4)	Cd(1)−N(2)	2.363(4)
Cd(1)−N(4)#3	2.370(4)	Cd(1)−N(2)#5	2.363(4)
N(7)#1−Cd(1)−N(7)#2	180.0	N(2)#5−Cd(1)−N(7)#2	88.88(14)
N(4)#3−Cd(1)−N(7)#1	94.05(14)	N(2)−Cd(1)−N(7)#1	88.88(14)
N(4)#3−Cd(1)−N(7)#2	85.95(14)	N(2)−Cd(1)−N(7)#2	91.12(14)
N(4)#4−Cd(1)−N(7)#2	94.05(14)	N(2)#5−Cd(1)−N(4)#4	86.01(14)
N(4)#4−Cd(1)−N(7)#1	85.95(14)	N(2)5−Cd(1)−N(4)#3	93.99(14)
N(4)#3−Cd(1)−N(4)#4	180.0	N(2)−Cd(1)−N(4)#4	93.99(14)
N(2)#5−Cd(1)−N(7)#1	91.12(14)	N(2)−Cd(1)−N(4)#3	86.01(14)
N(2)−Cd(1)−N(2)#5	180.00(18)		

Symmetry codes for **1**: #1 1 − *x*, 1 − *y*, 1 − *z*; #2 1/2 − *x*, − 1/2 + *y*, 3/2 − *z*; #3 1/2 − *x*, 1/2 + *y*, 3/2 – *z*; For **2**: #1 1 − *x*, − 1/2 + *y*, 3/2 − *z*; #2 *x*,1/2 − *y*, − 1/2 + *z*; #3 3/2 − *x*, − 1/2 + *y*, *z*; #4 − 1/2 + *x*, 1/2 − *y*, 1 − *z*; #5 1 − *x*, − *y*, 1 − *z*; #6 1 − *x*, 1/2 + *y*, 3/2 − *z*; #7 1/2 + *x*, 1/2 − *y*, 1 – *z*.

3. Graphics

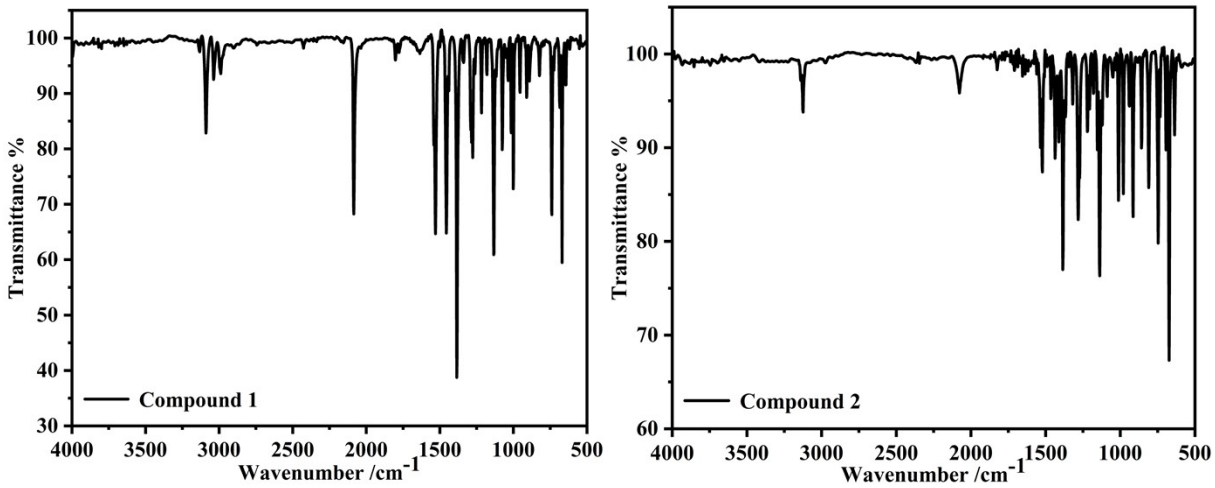

Figure S1 The FT-IR spectra of **1** and **2**.

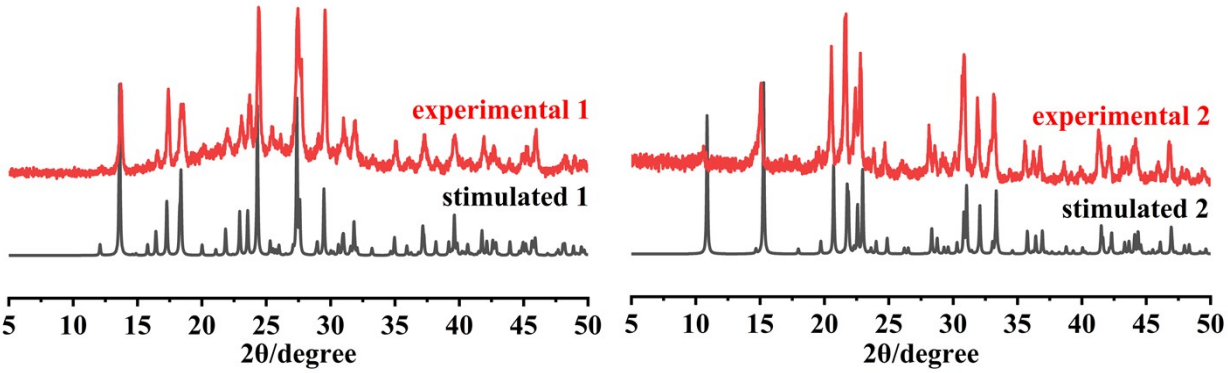

Figure S2 Powdered *X*-ray diffraction (PXRD) patterns of **1** and **2**.

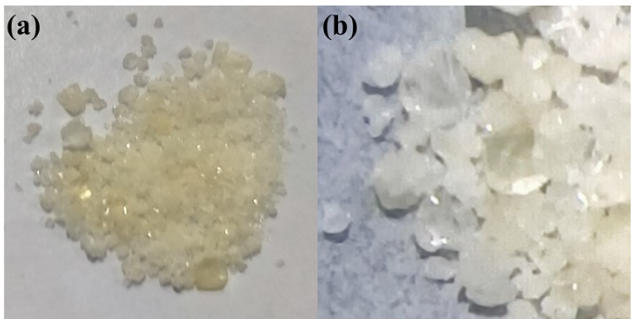

Figure S3 Crystal morphologies of (a) compound **1** and (b) compound **2**.

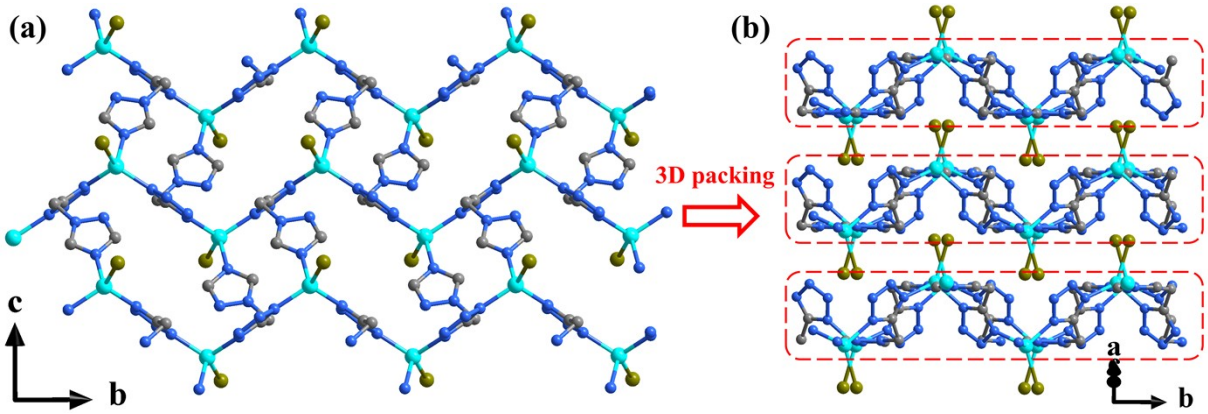

Figure S4 (a) The 2D planar layers of compound **1** parallel to the *bc* plane and (b) stacking modes of 2D layers.

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.