Supporting Information

Access to primary explosives via constructing energetic coordination polymers based on bis-tetrazole oxide and non-lead metals

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1.1. Chemicals and Equipments

All reagents were purchased commercially and used without further purification. TG and DSC analysis was conducted on a Mettler Toledo TGA/DSC 2 instrument with the linear heating rate of 5 °C min^{-1} under N_2 atmosphere. Single crystal X-ray diffraction data were tested in a Rigaku supernova Single X-ray Diffractometer area detector (Mo *K*α, 0.71073 Å).Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 ADVANCE X-ray powder diffractometer (Cu *K*α, 1.5418 Å). The sensitivity to impact stimuli was determined by the standard staircase method applying fall hammer apparatus of BAM DFH-10 with a 5 kg drop weight.[1] The friction sensitivity was determined on a BAM FSKM-10 apparatus by following the BAM method.[2] The constantvolume combustion energy of the compound was determined with an IKA C 5003 control calorimeter.[3] Modified Koenen test was recorded with high speed camera Olympus i-Speed 3.

1.2. PXRD curves of compounds 1 and 5

The powder X-ray diffraction(PXRD) measurements of compounds **1** and **5** support their stability in air and high phase purity (compared with their SXRD results), as is shown in **Fig. S1** and **S2**.

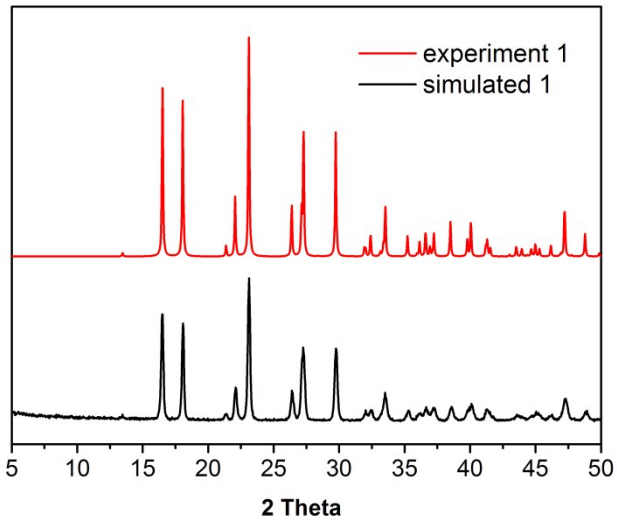

Fig. S1 PXRD and SXRD curves of compound **1**.

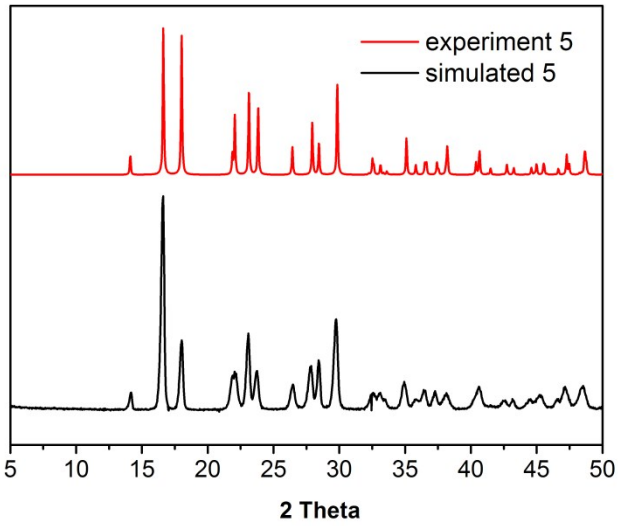

Fig. S2 PXRD and SXRD curves of compound **5**.

1.3. X-ray crystallography

Suitable crystals were chosen and placed in a Rigaku supernova Single X-ray Diffractometer area detector using graphite monochromated Mo *K*α radiation (λ= 0.71073 Å) at 298(2) K. Its structures were solved by direct methods and successive Fourier difference syntheses using the SHELXTL software suite. Hydrogen atoms attached to oxygen were placed from difference Fourier maps and were refined using riding model. Data collection parameters and refinement statistics are given in **Table S1**.

Table S1 Crystallographic data for compounds **1** and **5**.

Empirical formula	$MnC_2H_4O_4N_8$(**1**)	$ZnC_2H_4O_4N_8$(**5**)
Formula weight (g/mol)	259.07	269.50
Crystal system	monoclinic	monoclinic
Space group	P 21/c	P 21/c
a/Å	6.5782(4)	6.2940(3)
b/Å	10.7299(7)	10.6563(7)
c/Å	5.5290(3)	5.5677(4)
α(°)	90	90
β(°)	93.119(5)	95.069(5)
γ(°)	90	90
V(Å^3)	389.68(4)	371.97(4)
Z	2	2
Dc/g cm^{-3}	2.207	2.406
F(000)	258	268
R1 (all data)	0.0550	0.0533
wR2 (all data)	0.0923	0.1183

1.4. Sensitivity test

Impact sensitivities were determined by fall hammer apparatus of BAM DFH-10. about twenty milligrams of tested compounds were shifted into a iron cap, and were hit by 5 kg drop hammer, and the calculated values of *h*50 represent the drop height of 50% initiation probability.

Friction sensitivities of six compounds were measured by applying BAM FSKM-10 using about 20 mg sample.

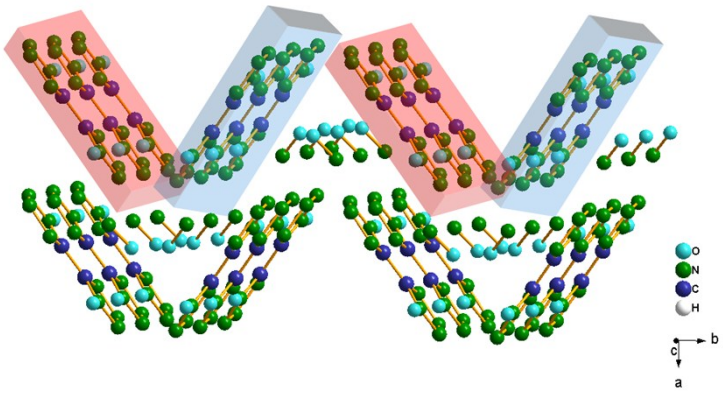

Fig. S3 V-type arrangement of BTO2- ions in TKX-50 crystal structure.

1.5. Oxygen bomb calorimetry

The constant-volume combustion energies of six compounds was investigated by a precise oxygen bomb calorimeter (IKA C 5003 control).[3] Approximately 200 mg of the samples were pressed with a well-define amount of benzoic acid (Calcd. 800 mg) to form a tablet to ensure better combustion. The recorded data are the average of five single measurements. The calorimeter was calibrated by the combustion of certified benzoic acid (Standard Reference Material, GBW(E)130035) in an oxygen atmosphere. The experimental constant volume combustion energies ($\Delta_c U$) of compounds can be converted to the standard molar combustion enthalpy ($\Delta_c H^\theta_m$) based on equation (1). Their combustion reaction equation is listed as equation (2-6):

$$\Delta_c H_m^\theta = \Delta_c U + \Delta nRT \qquad (1)$$

where $\Delta n = n_g$(products)-n_g(reactants), (n_g is the total molar amount of gases in the products or reactants, R = 8.314 J mol^{-1} K^{-1}, T = 298.15 K). Thus the $\Delta_c H^\theta_m$ value of compounds **1** to **5** is (-1535.05 ± 4.34), (-1509.73 ± 5.22), (-1368.01 ± 3.89), (-1488.76 ± 5.35) and (-1549.76 ± 4.28) kJ mol^{-1}, respectively.

Compound **1**

$MnC_2H_4N_8O_4+2O_2(g)=MnO_2(s)+2CO_2(g)+2H_2O(l)+4N_2(g)$ (2)

Compound **2**

$CoC_2H_4N_8O_4+3/2O_2(g)=CoO(s)+2CO_2(g)+2H_2O(l)+4N_2(g)$ (3)

Compound **3**

$NiC_2H_4N_8O_4+3/2O_2(g)=NiO(s)+2CO_2(g)+2H_2O(l)+4N_2(g)$ (4)

Compound **4**

$CuC_2H_4N_8O_4+3/2O_2(g)=CuO(s)+2CO_2(g)+2H_2O(l)+4N_2(g)$ (5)

Compound **5**

$ZnC_2H_4N_8O_4+3/2O_2(g)=ZnO(s)+2CO_2(g)+2H_2O(l)+4N_2(g)$ (6)

$$\Delta_f H_m^\theta(compound) = \sum \Delta_f H_m^\theta(products) - \Delta_c H_m^\theta(compound) \quad (7)$$

Based on the calculated enthalpies of combustion and known enthalpies of formation of the combustion products[4] determined experimentally, $MnO_2(s)$, $\Delta_f H^\theta_m(MnO_2, S)$=(-520) kJ mol^{-1}, $CoO(s)$, $\Delta_f H^\theta_m(CoO, S)$=(-237.9) kJ mol^{-1}, $NiO(s)$, $\Delta_f H^\theta_m(NiO, S)$=(-244.3) kJ mol^{-1}, CuO, $\Delta_f H^\theta_m(CuO, S)$=(-157.3) kJ mol^{-1}, $ZnO(s)$, $\Delta_f H^\theta_m(ZnO, S)$=(-350.5) kJ mol^{-1}, $CO_2(g)$, $\Delta_f H^\theta_m(CO_2, g)$=(-393.5) kJ mol^{-1}, $H_2O(l)$, $\Delta_f H^\theta_m(H_2O, l)$=(-285.8) kJ mol^{-1}. $\Delta_f H^\theta_m$ was back calculated from the thermochemical equations (7) of Hess's law, the standard enthalpy of formation ($\Delta_f H^\theta_m$) of compounds **1** to **5** is calculated as -343.55, -86.77, -234.89, -27.14 and -159.34 kJ mol^{-1}, respectively.

1.6. Modified Koenen test

The modified Koenen test of five compounds were burn tested within a fume hood on top of a heat proof mat which had a small enclosure mounted on top of it to minimise the effects of the airflow on the burn test. Approximately 10 mg of sample was placed into an sealed aluminum DSC crucible. The crucible was then transferred onto a heat proof tile and ignited using a blow torch. The test was recorded with high speed camera Olympus i-Speed 3(exposure 1/3000 sec).

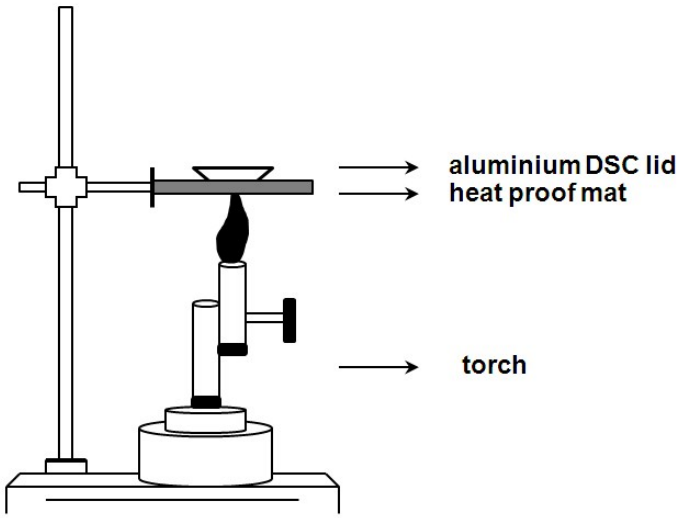

Fig. S4 The device model of modified Koenen test.

Fig. S5 The remainder of TKX-50 after experiment.

References

[1] R. Meyer, J. Kohler, Eds. *Explosives*. 4th edn.; VCH Publishers, New York, 1993, pp 149–150.

[2] R. Meyer, J. Kohler, Eds. *Explosives*. 4th edn.; VCH Publishers, New York, 1993, pp 197–199.

[3] X.-Y. Liu, Q. Yang, Z.-Y. Su, S.-P. Chen, G. Xie, Q. Wei, S.-L. Gao, *RSC Adv*. **2014**, *4*, 16087-16093.

[4] J.-D. Cox, D.-D. Wagman, V.-A. Medvedev, *CODATA Key Values for Thermodynamics*; Hemisphere Publishing Corp: New York, 1989.