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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Supporting Information

1. FT-IR and Raman spectra

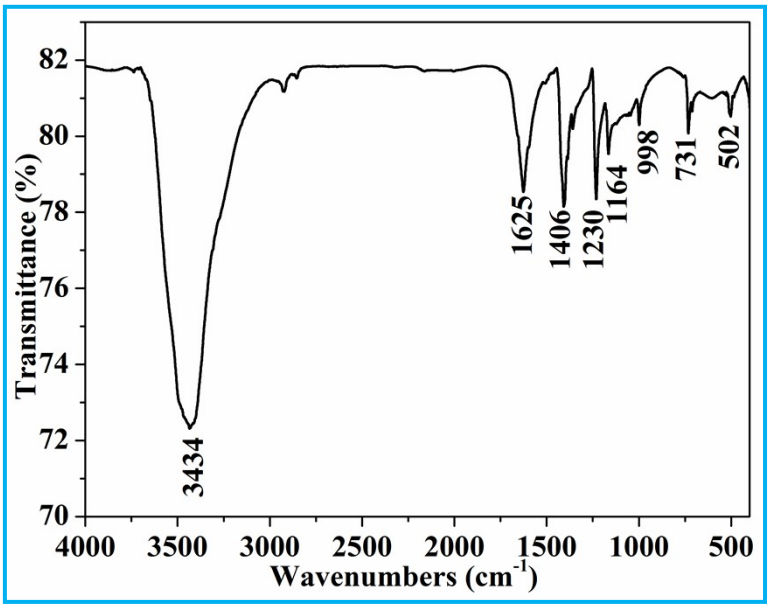

Figure S1. FT-IR spectrum of $[Pb(BTO)(H_2O)]_n$.

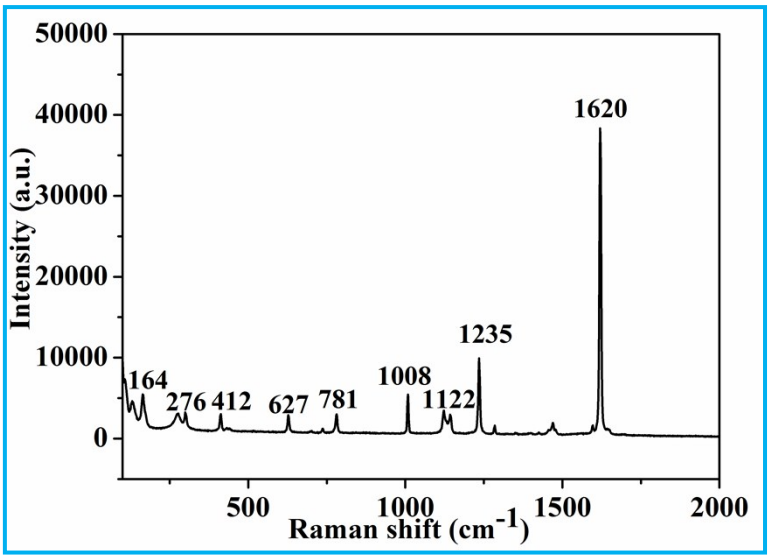

Figure S2. Raman spectrum of $[Pb(BTO)(H_2O)]_n$.

2. DTA and TG-DTG curves

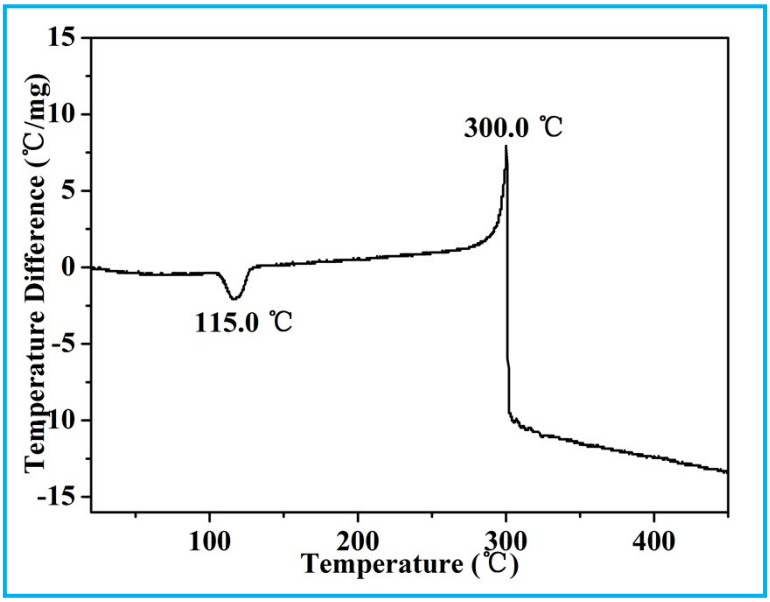

Figure S3. DTA curve of $[Pb(BTO)(H_2O)]_n$ (1.02 mg) under the linear heating rate of 5 °C/min in air atmosphere.

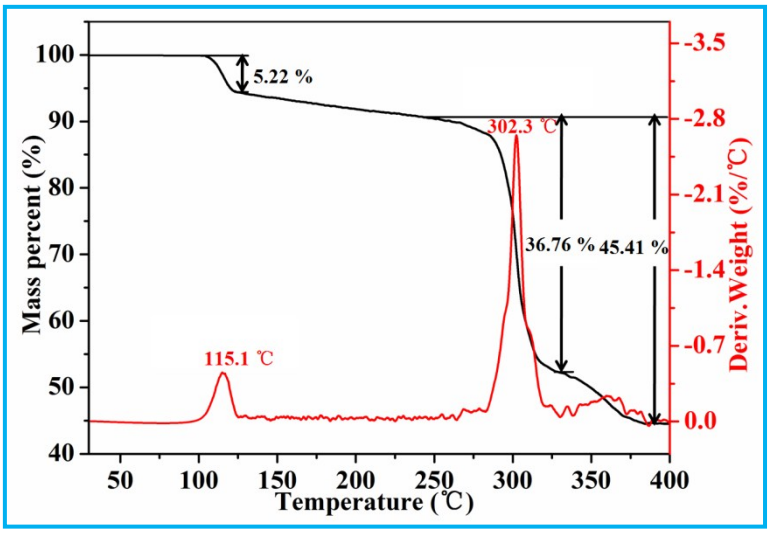

Figure S4. TG-DTG curves of $[Pb(BTO)(H_2O)]_n$ (0.32 mg) under the linear heating rate of 5 °C/min in flowing high-purity nitrogen

3. Heat of detonation

Density functional theory (DFT) is used to calculate the energy of detonation (ΔE_{det}), from which ΔH_{det} is estimated by using a linear correlation equation (ΔH_{det} = 1.127 ΔE_{det} + 0.046, r=0.968). As in ref.[1], the DFT calculations for $[Pb(BTO)(H_2O)]_n$ was performed with the code DMOl3[2] under 3D periodic boundary conditions employing the Monkhorst–Pack multiple K-point sampling of the Brillouin zone[3] and the Perdew–Becke–Ezerhoff (PBE) exchange-correlation function.[4] The complete detonation reactions are described by Equations (1).

$$PbC_2H_2O_3N_8 \longrightarrow PbO + H_2O + 1/2\ CO_2 + 3/2\ C + 4\ N_2 \quad (1)$$

Table S1. Calculated parameters used in the detonation reactions.

$PbC_2H_2O_3N_8$ (hartree)	PbO (hartree)	H_2O (hartree)	CO_2 (hartree)	C (hartree)	N_2 (hartree)	ΔE_{det} (hartree)	ΔE_{det} (kcal/g)	ΔH_{det} (kcal/g)	ΔH_{det} (kcal/cm^3)
-20268.3	-19602.9015	-76.3776	-188.1896	37.738	-109.447	0.5311	0.8473	1.0010	3.8267

4. Detonation performances

The essential step for the development of new energetic compounds is to accurately predict their detonation properties, which often play an important role in energy levels and potential applications. The *D* and *P* of the compound were calculated using Kamlet–Jacbos equations[5] as follows, which were usually applied to the energetic MOFs reported previously:

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

$$P = 1.558\,\Phi\rho^2 \quad (3)$$

$$\Phi = 31.68\,N(MQ)^{1/2} \quad (4)$$

where *D* is detonation velocity (km/s). *P* is detonation pressure (GPa). *N* is moles of detonation gases per gram of explosive. *M* is average molecular weight of the gases. *Q* is chemical energy of detonation (kcal/g). ρ is density of explosive (g/cm^3). The *D* and *P* of $[Pb(BTO)(H_2O)]_n$ are calculated to be 9.204 km/s and 53.06 GPa.

5. Sensitivity

For initial safety testing, the impact sensitivity of the compound were determined using the fall hammer test with approximately 30 mg samples (10 kg drop hammer). The data collected is summarized in Table 1. the impact sensitivity of the title complex is 7.5 J, classifying it as impact sensitive energetic materials.

6. X-ray crystallographic data

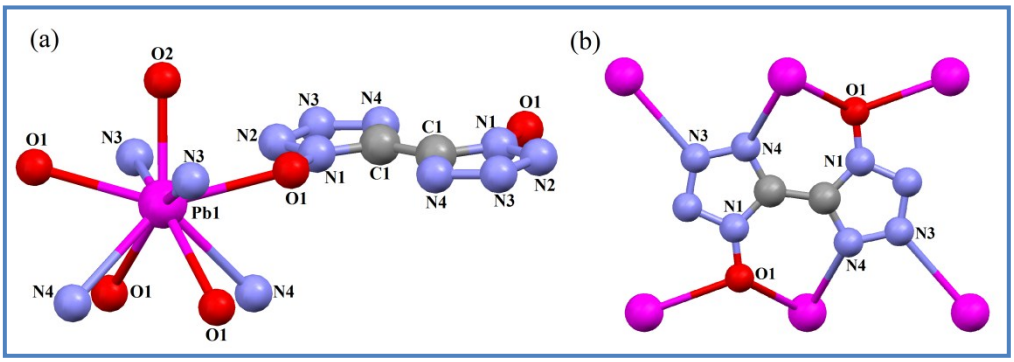

Figure S5. (a) Coordination environment of Pb(II) ions and (b) Coordination mode of BTO ligand in the target complex (Hydrogen atoms are omitted for clarity).

Table S2. Bond Lengths [Å] and angles [°] for $[Pb(BTO)(H_2O)]_n$.

bond	Length/Å	bond	Angle/°
Pb(1)-O(1W)	2.518(11)	O(1W)-Pb(1)-O(1)#2	74.77(13)
Pb(1)-O(1)#2	2.728(7)	O(1W)-Pb(1)-O(1)	74.77(13)
Pb(1)-O(1)	2.728(7)	O(1)-Pb(1)-O(1)#2	149.5(3)
O(1)-N(1)	1.330(12)	N(1)-O(1)-Pb(1)	106.1(6)
O(1W)-H(1)	0.8596	Pb(1)-O(1W)-H(1)	114.2
N(1)-C(1)	1.339(13)	O(1)-N(1)-C(1)	130.5(9)
N(1)-N(2)	1.345(12)	O(1)-N(1)-N(2)	120.2(9)
N(2)-N(3)	1.321(13)	C(1)-N(1)-N(2)	109.3(8)
N(3)-N(4)	1.343(12)	N(3)-N(2)-N(1)	105.5(8)
C(1)-N(4)	1.344(13)	N(2)-N(3)-N(4)	111.3(8)
C(1)-C(1)#1	1.430(19)	N(3)-N(4)-C(1)	105.7(8)
		N(1)-C(1)-N(4)	108.0(8)
		N(4)-C(1)-C(1)#1	126.2(11)
		N(1)-C(1)-C(1)#1	125.8(11)

Symmetry transformations used to generate equivalent atoms: #1 –x+1/2,-y+1/2,-z; #2 -x,y,-z+1/2

Table S3. Torsion Angles for $[Pb(BTO)(H_2O)]_n$.

A-B-C-D	Angle/°	A-B-C-D	Angle/°
O(1W)-Pb(1)-O(1)-N(1)	83.9(5)	N(2)-N(3)-N(4)-C(1)	-1.1(10)
O(1)#2-Pb(1)-O(1)-N(1)	83.9(5)	N(1)-C(1)-N(4)-N(3)	2.0(10)
Pb(1)-O(1)-N(1)-C(1)	166.5(9)	C(1)#1-C(1)-N(4)-N(3)	-177.2(12)
Pb(1)-O(1)-N(1)-N(2)	-14.0(9)	N(4)-C(1)-N(1)-O(1)	177.2(8)
O(1)-N(1)-N(2)-N(3)	-178.1(8)	N(4)-C(1)-N(1)-N(2)	-2.2(10)
C(1)-N(1)-N(2)-N(3)	1.5(10)	C(1)#1-C(1)-N(1)-O(1)	-3.5(19)
N(1)-N(2)-N(3)-N(4)	-0.2(10)	C(1)#1-C(1)-N(4)-N(3)	-177.2(12)

Symmetry transformations used to generate equivalent atoms: #1 –x+1/2,-y+1/2,-z; #2 -x,y,-z+1/2

Table S4. Hydrogen bonds for $[Pb(BTO)(H_2O)]_n$.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA
O(1W)-H(1)...O(1)#3	0.860	2.133	2.879	144.97

Symmetry transformations used to generate equivalent atoms: #3 -x, -y+1, -z

[1] O. S. Bushuyev, P. Brown, A. Maiti, R. H. Gee, G. R. Peterson, B. L. Weeks and L. J. Hope-Weeks, *J. Am. Chem. Soc.*, 2012, **134**, 1422-1425.

[2] B. Delley, *Chem. Phys.*, 1990, **92**, 508-517.

[3] H. J. Monkhorst and J. D. Pack, *Phys. Rev. B*, 1976, **13**, 5188.

[4] J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.

[5] M. J. Kamlet and H. Hurwitz, *J. Chem. Phys.*, 1968, **48**, 3685-3692.