Supporting Information

A Three-Dimensional Energetic Coordination Compound (BLG-1) with Super Initiating Ability for Lead-free Primary Explosive

Guorong Lei, Wenchuan Cheng, Zujia Lu, Tonglai Zhang, Zhimin Li* and Jianguo Zhang*

State Key Laboratory of Explosion Science and Technology

Beijing Institute of Technology, Beijing 100081, China

**Corresponding Authors: lizm@bit.edu.cn; zjgbit@bit.edu.cn*

Table S1. Crystal data and structure refinement details of BLG-1.

Compound	BLG-1
Empirical formula	$C_4H_4Br_2CuN_8O_6$
Formula weight	483.51
Temperature / K	298K
Crystal system	monoclinic
Space group	$P2_1/c$
a / Å	9.3556(9)
b / Å	6.8168(7)
c / Å	9.3773(8)
β/ degree	93.497(2)
Volume / Å^3	596.93(10)
Z	2
ρ_{calc} / mg mm^{-3}	2.690
μ / mm^{-1}	0.857
F(000)	462
Crystal size / mm3	0.18 × 0.11 × 0.07
2θ range for data collection	2.18 to 25.01°
Limiting indices	-10<=h<=11, -8<=k<=7, -8<=l<=11
Reflections collected	2734
Independent reflections	1055[R(int) = 0.0628]
Completeness to theta = 25.01	99.9 %
Data/restraints/parameters	1055/0/98
Goodness-of-fit on F^2	1.030
Final R indexes [I>2σ (I)]	R1 = 0.0402, wR2 = 0.0969
Final R indexes [all data]	R1 = 0.0428, wR2 = 0.0984

Table S2. Selected bond lengths (Å) of BLG-1.

Bond	Length/Å	Bond	Length/Å
Cu1-N1	1.980(4)	N2-C1	1.297(6)
Cu1-N11	1.980(4)	N3-C2	1.366(6)
Cu1-O1	2.025(3)	N3-C1	1.378(6)
Cu1-O11	2.025(3)	N3-N41	1.382(5)
Cu1-O2	2.333(3)	N4-N41	1.253(7)
Cu1-O21	2.3333)	O2-Cu1	0.9300
Br1-O3	1.633(3)	C1-H1	0.9300
Br1-O1	1.646(3)	N3-N41	1.382(5)
Br1-O2	1.691(3)	N4-N41	1.253(7)
N1-C2	1.297(6)	O2-Cu1	0.9300
N1-N2	1.402(5)	C1-H1	0.9300

Table S3. Selected angles (°) of BLG-1.

Bond Angle	Angle/°	Bond Angle	Angle/°
N1-Cu1-N11	180	O1-Br1-O2	100.53(16)
N1-Cu1-O21	91.57(14)	C2-N1-N2	109.4(3)
N1#1-Cu1-O21	88.43(14)	C2-N1-Cu1	129.2(3)
N1-Cu1-O21	88.43(14)	N2-N1-Cu1	121.3(3)
N11-Cu1-O21	91.57(14)	C1-N2-N1	106.3(4)
O21-Cu1-O21	180	C2-N3-C1	106.5(4)
N1-Cu1-O1	90.35(15)	C2-N3-N4	122.2(4)
N11-Cu1-O1	89.65(15)	C1-N3-N4	130.8(4)
O21-Cu1-O1	92.77(11)	N41-N4-N3	110.2(5)
O21-Cu1-O1	87.23(11)	Br1-O1-Cu1	112.73(16)
N1-Cu1-O11	89.65(15)	Br1-O2-Cu11	120.52(17)
N11-Cu1-O11	90.35(15)	N2-C1-N3	109.7(4)
O21-Cu1-O11	87.23(11)	N2-C1-H1	125.2
O23-Cu1-O11	92.77(11)	N3-C1-H1	125.2
O1-Cu1-O11	180	N1-C2-N3	108.1(4)
O3-Br1-O1	106.31(17)	N1-C2-H2	126
O3-Br1-O2	105.12(18)	N3-C2-H2	126

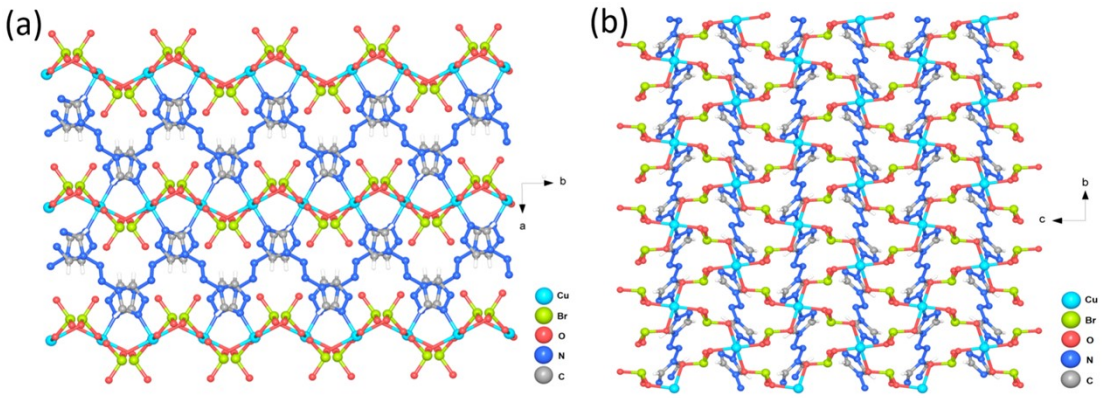

Figure S1. The crystal stacking structure of BLG-1 viewed from (a) *a*-axis and (b) *c*-axis.

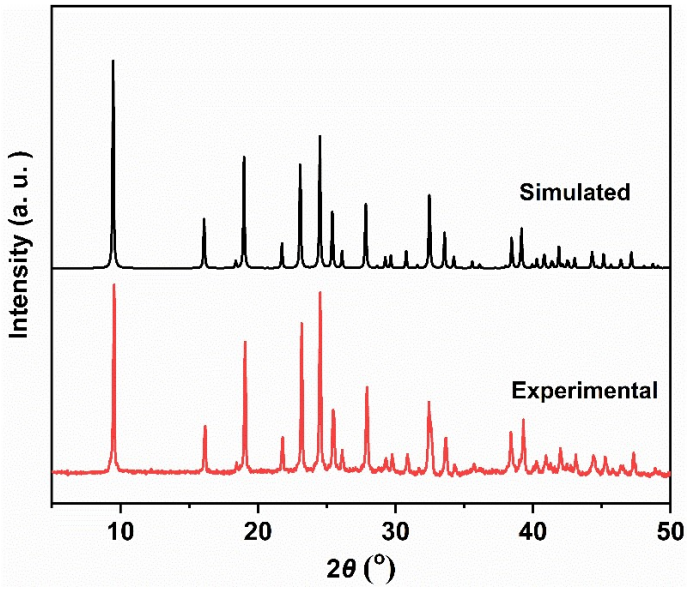

Figure S2. The simulated and experimental XRD patterns of BLG-1.

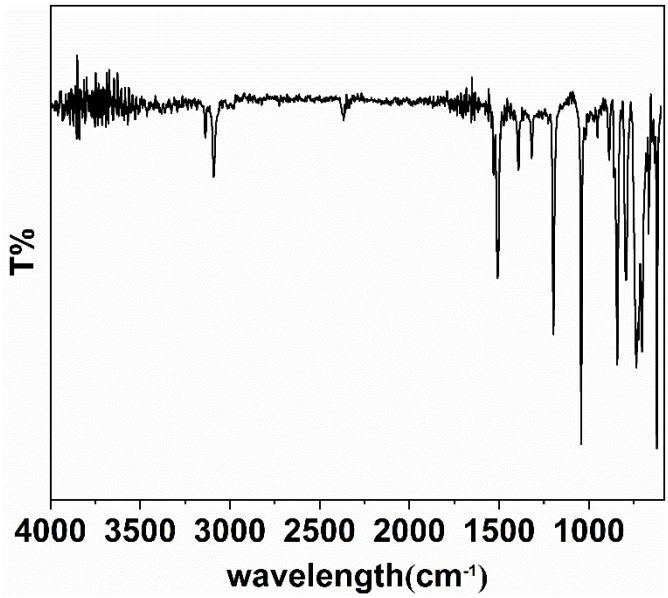

Figure S3. The FT-IR spectrum of BLG-1.

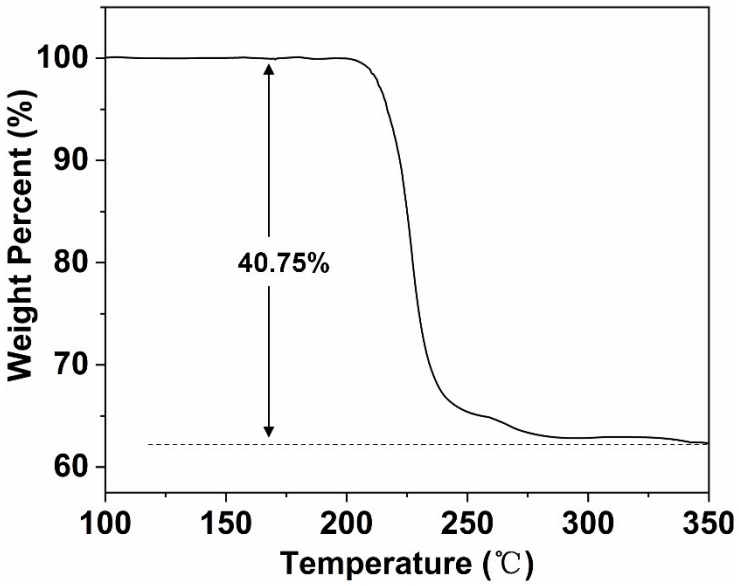

Figure S4. The TG curve of BLG-1 with a heating rate of 5 ^{o}C min^{-1}.

Non-isothermal kinetics

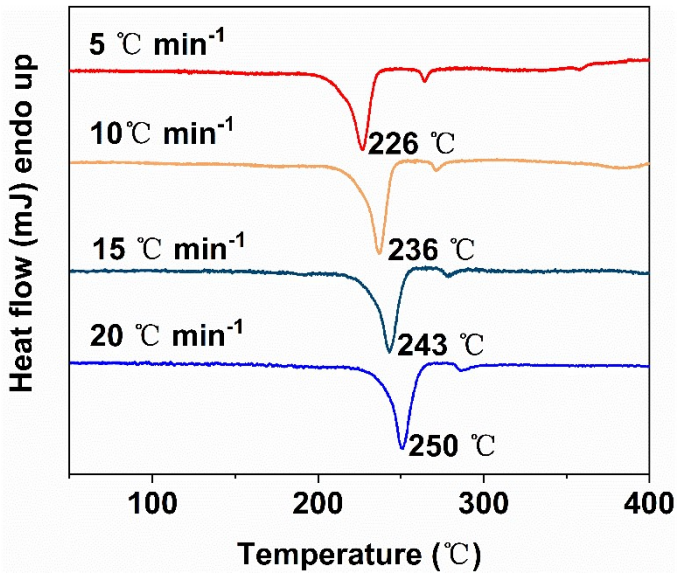

Figure S5. The DSC curve of BLG-1 at different heating rates.

The thermodynamic parameters of BLG-1 were calculated using the Kissinger equation presented below.

$$\ln\left(\frac{\beta}{T_{\mathrm{p}}^2}\right) = \ln\frac{AR}{E_a} - \frac{E_a}{R}\frac{1}{T_{\mathrm{p}}}$$

In the equation, E_a, T_p, β, and R correspond to the activation energy (kJ mol^{-1}), decomposition temperature peak (K), heating rate (K min^{-1}), and ideal gas constant (8.314 J mol^{-1} K^{-1}), respectively. The calculated E_a is 118.2 kJ mol^{-1} for BLG-1.

Formation enthalpy

The constant-volume combustion energy ($\Delta_c U$=-2842.98 kJ mol^{-1}) for BLG-1 was obtained using an oxygen bomb calorimeter calibrated with standard sample benzoic acid. The standard molar combustion enthalpy ($\Delta_c H_m^\theta$) and standard heat of formation enthalpy ($\Delta_f H_m^\theta$) were calculated based on equations (1) and (2), respectively. The $\Delta_f H_m^\theta$ for copper(II) bromide, carbon dioxide, and water are $\Delta_f H_m^\theta(CuBr_2, s)$ =143 kJ mol^{-1}, $\Delta_f H_m^\theta(CO_2, g)$ = -393.51 kJ mol^{-1}, $\Delta_f H_m^\theta(H_2O, l)$ = -285.83 kJ mol^{-1}.

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

$$\Delta n = n_g(\text{products}) - n_g(\text{reactants})$$

$$C_4H_4N_8O_6Br_2Cu(s) + 2O_2 \rightarrow 4CO_2(g) + 2H_2O(l) + 4N_2(g) + CuBr_2(s)$$

$$\Delta_f H^\theta m(\text{compound}) = \sum \Delta_f H^\theta m(\text{products}) - \Delta_c H^\theta m(\text{compound}) \qquad (2)$$

The calculation results:

$$\Delta n = 4 + 4 - 2 = 6$$

$$\Delta_c H^\theta m(\text{BLG-1}) = -2842.98 + 6 \times 8.314 \times 298.15 \times 10^{-3} = -2828.11 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\theta m(\text{BLG-1}) = 4 \times (-393.51) + 2 \times (-285.83) + (-143) - (-2828.11) = 539.41 \text{ kJ mol}^{-1}$$

The laser ignition test

In the test, a single-pulse semiconductor laser device was used as a laser source, and energy (*E*, mJ), delay time (*t*, ms), and output power (*P*, W) were used as evaluation indicators. 20mg of BLG-1 was pressed into the percussion cap with a static pressure of 49 MPa. The results showed that BLG-1 can be detonated under the conditions of *t*=1ms and *P*=13W.

Figure S6. The detonation of BLG-1 with a laser irradiation (*P*=13W, *t*=1ms, *E*=13mJ).

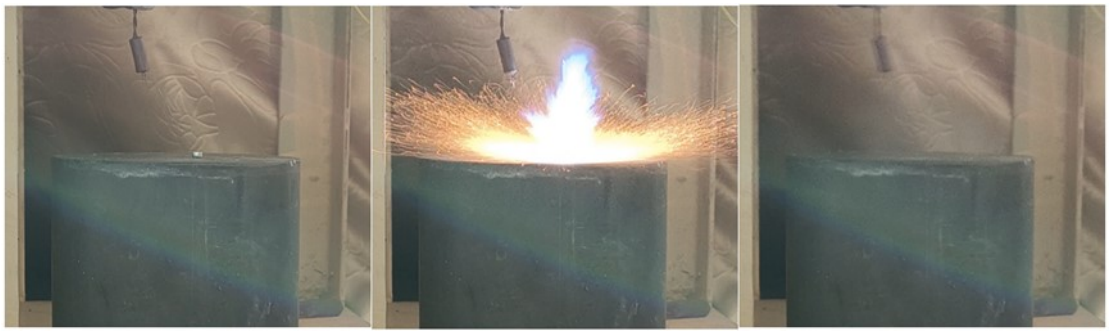

Figure S7. The detonation of 10 mg of BLG-1 in an aluminum crucible.

The initiation test for single charge of BLG-1

In order to evaluate the feasibility of BLG-1 as a single charge of detonator, the initiating ability of the single charge of BLG-1 was tested. In the test, a certain amount of BLG-1 was pressed into the detonator cap with a static pressure of 49 MPa. The results showed that 70mg of BLG-1 could reliably blast out the lead plate with a bore diameter of 7.5mm. When the charge amount was reduced to 40mg, the bore diameter of the hole was reduced to 5.7mm. When the charge amount was reduced to 30mg, BLG-1 failed to blast out the lead plate.

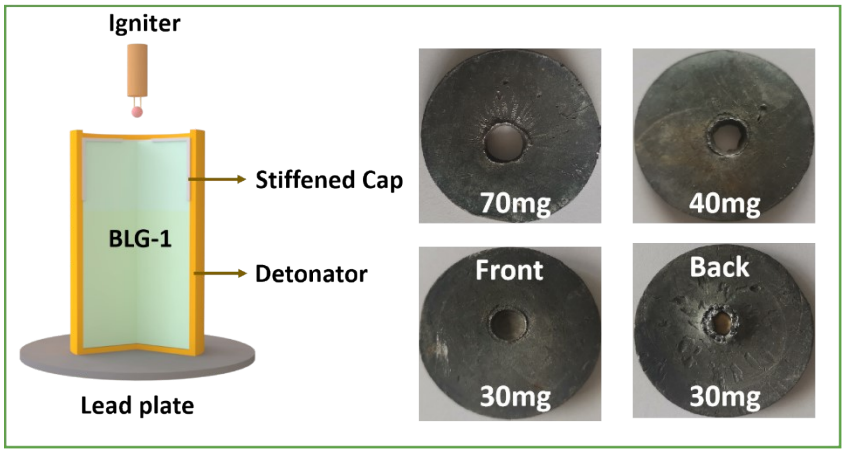

Figure S8. The initiation ability test setup and results.

Table S4. The initiating ability and crystal density of BLG-1 and current reported primary explosives.

Compound	Density (g cm^{-3})	MPC (mg)	$V_{(MPC)}$ ($1x10^{-3}$ cm^3)	Ref.
BLG-1	**2.69**	**3**	**1.12**	**This work**
K_2DNABT	2.17	40	18.4	[1]
DBX-1	2.58	20	7.74	[2]
LA	4.8	20	4.17	[2]
CMA-2	2.07	10	4.83	[3]
CAM	2.02	5	2.48	[4]
ICM-103	1.86	60	32.28	[5]
ANTP	1.82	40	21.96	[6]
BDTT	1.76	60	34.08	[7]
CMA	2.10	15	7.13	[8]
CIA	2.09	50	23.9	[8]
NH_4CuNT	2	25	12.5	[9]
NH_4FeNT	2.2	25	11.35	[9]

Reference

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