Supporting Information

for

Self-assembly of sliver(I)-based high-energy metal-organic frameworks (HE-MOFs) at ambient

temperature and pressure: synthesis, structure and superior explosive performance

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EXPERIMENTAL SECTION

Caution

Caution: Title compound is dangerous materials, explosions of which may occur in certain conditions. Although we had no difficulties on synthesizing and handing the compounds, proper safety precautions such as safety glasses, plastic spatulas and face shields must be used, especially when the experiments on a large scale.

Materials and General Methods

K_2DNMAF was synthesized according to a previously reported method[1]. Other commercially available reagents were used without further purification. The melting and decomposition (onset) points were measured on a differential scanning calorimeter (DSC, Mettler Toledo DSC823e) at a scan rate of 5 °C min^{-1} in closed Al containers with a nitrogen flow of 50 mL min^{-1}. In addition, thermogravimetric analysis (TGA) was carried out at a heating rate of 5 °C min^{-1} on a Mettler Toledo TGA/SDTA851e instrument. The infrared (IR) spectra of solids were recorded using KBr pellets on a Thermo Nicolet iS10 spectrometer. Elemental analyses were carried out on a Vario EL III CHNOS elemental analyzer. The constant-volume combustion energies ($\Delta_c U$) of compounds 1 and 2 were measured using a precise rotating-oxygen bomb calorimeter (Parr 6400, Parr Instrument Company, Moline Illinois, USA). Approximately 50 mg of the sample were pressed with a well-define amount of benzoic acid (calculated 250 mg, NIST Thermo chemical Standard 39j) to form a tablet to ensure better combustion. The procedure for a standardization test is exactly same as for testing an EMOF sample. The recorded data are the average of five single measurements.

Synthesis of $\{Ag_2(DNMAF) \cdot (H_2O)_2\}_n$ (Compound 1). K_2DNMAF (0.0080 g, 0.0178 mmol) was dissolved in 3ml ions-free water, then $AgNO_3$ (0.018 g, 0.1068 mmol) was added at the room temperature and kept it in a 5 ml sealed glass vial. Yellow crystals (0.00786 g, 0.0126 mmol) were obtained after 24 hours (yield: 71%, based on K_2DNMAF).

Synthesis of $\{Ag_2(DNMAF)\}_n$ (Compound 2). K_2DNMAF (0.0080 g, 0.0178 mmol) was dissolved in 3ml ions-free water, then added aqueous $AgNO_3$ (0.018 g, 0.1068 mmol) dropwise at 90 ℃. The solution was kept at the 90 ℃ in 5 ml sealed glass vial. Yellow crystals (0.00788 g, 0.0134 mmol) were observed after 24 hours (yield: 75%, based on K_2DNMAF).

X-ray crystallographic study

An orange plate crystal 1 of dimensions 0.26 × 0.14 × 0.13 mm³, an orange plate crystal 2 of dimensions 0.24 × 0.13 × 0.12 mm³ were performed on a Bruker Smart Apex II diffractometer with graphite-monochromated Mo Kα radiation (λ= 0.71073 Å) at 205 K and 173 K, respectively. Integration and scaling of intensity data were accomplished using the SAINT program[2]. The structures were solved by intrinsic using SHELXT2014 and refinement was carried out by a full-matrix least-squares technique using SHELXT2014[3]. The hydrogen atoms were refined isotropically, and the heavy atoms were refined anisotropically. N-H and OH hydrogens were located from different electron density maps, and C-H hydrogens were placed in calculated positions and refined with a riding model. Data were corrected for the effects of absorption using SADABS[4] Relevant crystal data and refinement results are summarized in Table 1.

Table S1 Crystal data and structure refinement for 1 and 2.

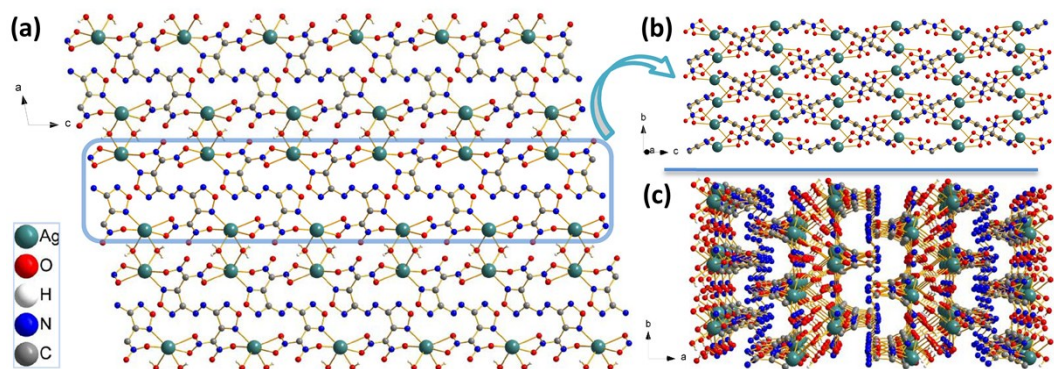| Compound	1	2
CCDC	1544883	1548958
Empirical formula	C3H2AgN5O6	C3AgN5O5
Formula weight	311.97	293.95
Crystal system	monoclinic	monoclinic
Space group	P2$_1$/c	P2$_1$/c
a	10.346(2)	10.1571(8)
b	5.3225(11)	4.9006(4)
c	14.977(3)	14.4249(11)
α	90	90
β	101.245(3)	103.473(2)
γ	90	90
V	808.93(3)	698.25(10)
Z	4	4
Dc(g/cm3)	2.545	2.796
T(K)	205	173
μ(mm-1)	2.516	2.896
F(000)	592.0	560.0
GOF on F	1.099	1.034
R1[I>2σ(I)]	0.0333	0.0251
wR2(I>2σ(I))	0.1089	0.0594
R1[all data]	0.0373	0.0297
wR2(all data)	0.1142	0.0623

Figure S1 Compound 1: (a) 3-D frameworks seen along the b- axes; (b) a top perspective view of the 2D layers; (b) 2D layer in 2, and (c) The 3D network extended based on the chains along the c- axe
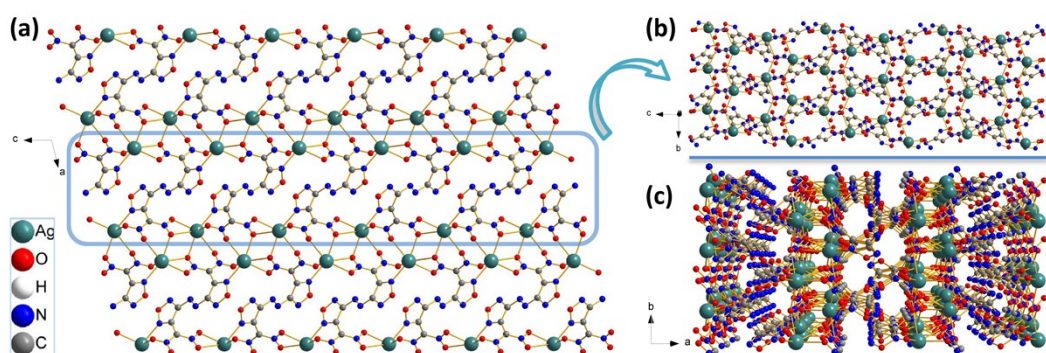

Figure S2 Compound 2: (a) 3-D frameworks seen along the b- axes; (b) a top perspective view of the 2D layers; (b) 2D layer in 2, and (c) The 3D network extended based on the chains along the c- axe
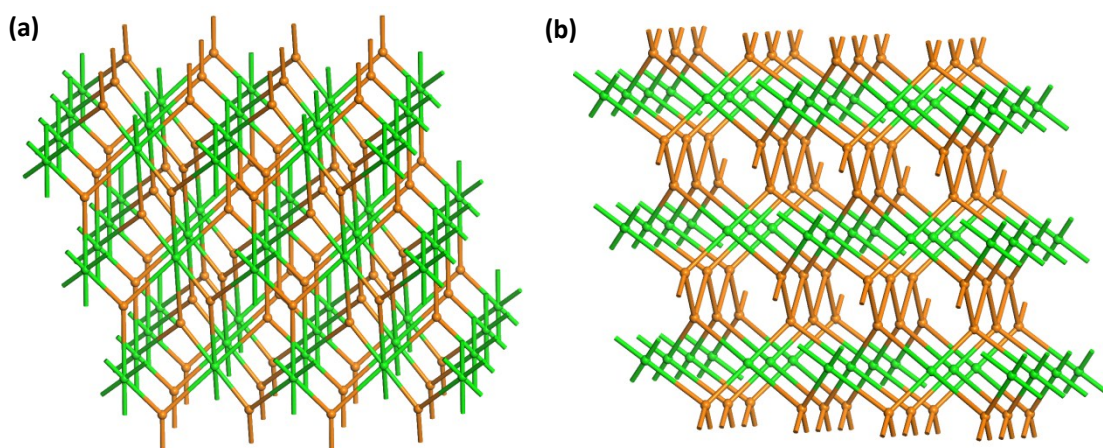

Figure S3 (a) the **bbf** topology of compound 1; (b) the **flu** topology of compound 2

Table S2 Bond lengths [Å] and angles [°] for compound 1

Ag1 - O1	2.411(2)	O1 - Ag1 - O1	87.85(5)
Ag1 - O1	2.491(2)	O1 - Ag1 - O5	78.57(6)
Ag1 - O5	2.593(2)	O1 - Ag1 - O5	84.58(7)
Ag1 - O6	2.539(2)	O1 - Ag1 - O6	128.42(7)
Ag1 - N1	2.357(2)	O1 - Ag1 - O6	85.38(7)
O1 - Ag1	2.491(2)	O6 - Ag1 - O5	49.91(6)
O1 - H1A	0.8218	N1 - Ag1 - O1	156.50(8)
O1 - H1B	0.8868	N1 - Ag1 - O1	93.74(8)
O2 - N1	1.388(3)	N1 - Ag1 - O5	118.73(8)
O2 - N2	1.362(3)	N1 - Ag1 - O6	111.29(7)
O3 - N4	1.255(3)	Ag1 - O1 - Ag1	128.75(9)
O4 - N4	1.237(3)	Ag1 - O1 - H1A	107.1
O5 - Ag1	2.593(2)	Ag1 - O1 - H1A	106.3
O5 - N5	1.241(3)	Ag1 - O1 - H1B	108.9
O6 - Ag1	2.539(2)	Ag1 - O1 - H1B	98
O6 - N5	1.258(3)	H1A - O1 - H1B	105.9
N1 - C2	1.300(3)	N2 - O2 - N1	111.19(19)
N2 - C1	1.305(3)	N5 - O5 - Ag1	93.90(16)
N3 - N3	1.259(4)	N5 - O6 - Ag1	96.08(15)
N3 - C1	1.391(4)	O2 - N1 - Ag1	123.41(15)
N4 - C3	1.374(3)	C2 - N1 - Ag1	126.03(19)
N5 - C3	1.371(3)	C2 - N1 - O2	106.0(2)
C1 - C2	1.431(4)	C1 - N2 - O2	105.2(2)
C2 - C3	1.450(3)	N3 - N3 - C1	112.1(3)
		O3 - N4 - C3	116.3(2)
		O4 - N4 - O3	120.8(2)
		O4 - N4 - C3	122.9(2)
		O5 - N5 - O6	120.1(2)
		O5 - N5 - C3	123.9(2)
		O6 - N5 - C3	116.0(2)
		N2 - C1 - N3	117.9(2)
		N2 - C1 - C2	109.7(2)
		N3 - C1 - C2	132.2(2)
		N1 - C2 - C1	107.7(2)
		N1 - C2 - C3	124.2(3)
		C1 - C2 - C3	128.1(2)
		N4 - C3 - C2	120.6(2)
		N5 - C3 - N4	122.2(2)
		N5 - C3 - C2	116.8(2)

Table S3 Bond lengths [Å] and angles [°] for compound 2

|			
Ag1 - O2	2.420(2)	O2 - Ag1 - O3	95.25(7)
Ag1 - O3	2.471(2)	N1 - Ag1 - O2	105.02(8)
Ag1 - N1	2.383(2)	N1 - Ag1 - O3	158.56(9)
O5 - N5	1.258(3)	N2 - O1 - N1	110.5(2)
O1 - N1	1.397(3)	N4 - O2 - Ag1	102.66(16)
O1 - N2	1.366(3)	N4 - O3 - Ag1	116.00(17)
O4 - N5	1.242(3)	N3 - N3 - C3	111.9(3)
O2 - Ag1	2.420(2)	O2 - N4 - O3	120.4(2)
O2 - N4	1.251(3)	O2 - N4 - C1	116.0(2)
O3 - Ag1	2.471(2)	O3 - N4 - C1	123.5(3)
O3 - N4	1.253(3)	O5 - N5 - C1	117.1(2)
N3 - N3	1.255(5)	O4 - N5 - O5	121.1(2)
N3 - C3	1.412(4)	O4 - N5 - C1	121.7(2)
N4 - C1	1.379(3)	O1 - N1 - Ag1	124.46(17)
N5 - C1	1.385(3)	C2 - N1 - Ag1	128.7(2)
N1 - C2	1.288(4)	C2 - N1 - O1	106.8(2)
N2 - C3	1.303(4)	C3 - N2 - O1	105.4(2)
C2 - C1	1.454(4)	N1 - C2 - C1	123.3(3)
C2 - C3	1.442(4)	N1 - C2 - C3	107.3(2)
		C3 - C2 - C1	129.4(3)
		N4 - C1 - N5	121.2(2)
		N4 - C1 - C2	117.3(2)
		N5 - C1 - C2	121.2(2)
		N3 - C3 - C2	133.1(3)
		N2 - C3 - N3	116.9(2)
		N2 - C3 - C2	109.9(3)

Thermal decomposition
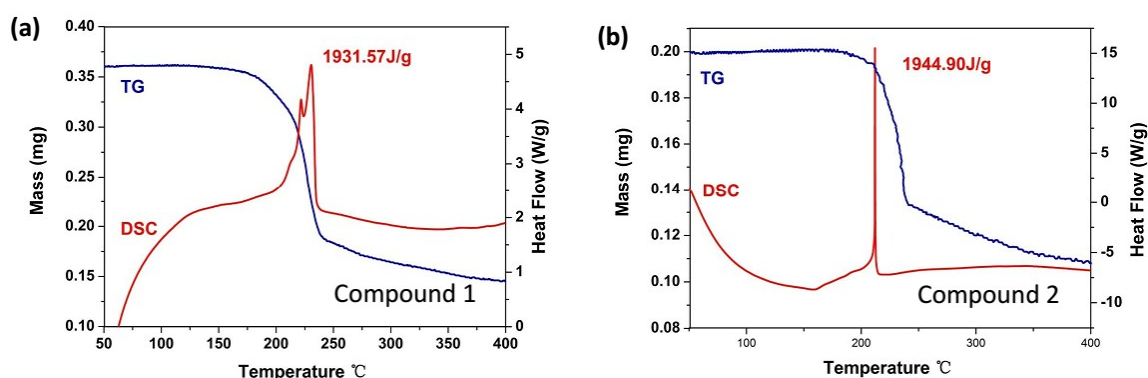
Figure S4 (a) DSC and TG curves of 1, (b) DSC and TG curves of 2.

The differential scanning calorimetry (DSC) and thermogravimetry (TG) curves were carried out to characterize the thermal stabilities of compound 1 and 2 with a linear heating rate of 5 °C·min⁻¹ in a nitrogen atmosphere (Fig. S4).

For compound 1, the DSC curve indicates that an intense exothermic process occurs at 218 °C, and ends at 235 °C with a peak temperature of 230 °C and the corresponding decomposition enthalpy of 1931.57 J·g⁻¹. For compound 2, the DSC curve indicates that a more intense exothermic process occurs at 211 °C, and ends at 212 °C with the corresponding decomposition enthalpy of 1944.90 J·g⁻¹. As shown in Fig. S4 (b), the sharp peak suggests that the process is very rapid owing to solvent-free MOF.

Vibration spectroscopy

In the IR spectra (Fig. S5), it is cleared that there are coordinated water molecules in the compound 1, while, the compound 2 is solvent-free MOF.
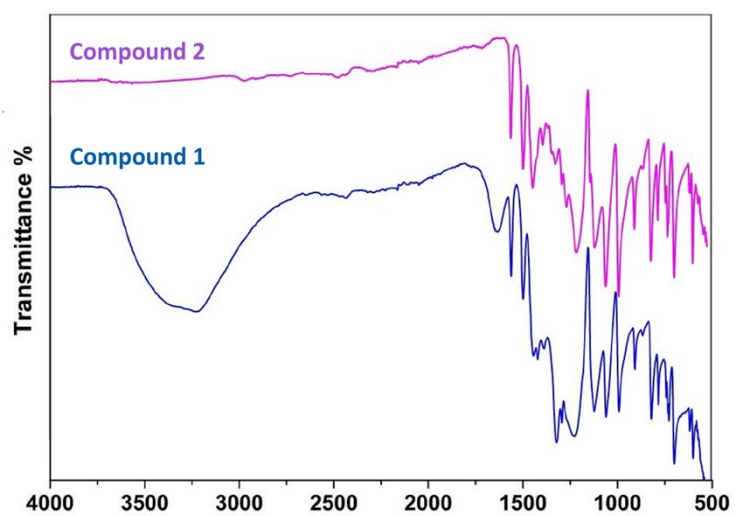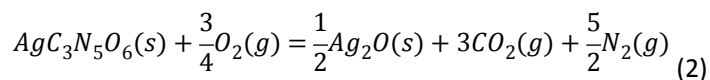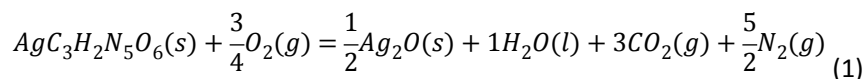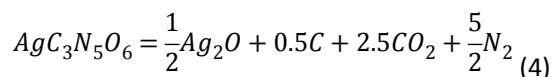

Figure S5 the IR curves of compound 1 (blue line) and 2 (purple line).

Calculation of Detonation Properties

$$AgC_3H_2N_5O_6(s) + \frac{3}{4}O_2(g) = \frac{1}{2}Ag_2O(s) + 1H_2O(l) + 3CO_2(g) + \frac{5}{2}N_2(g) \quad (1)$$

$$AgC_3N_5O_6(s) + \frac{3}{4}O_2(g) = \frac{1}{2}Ag_2O(s) + 3CO_2(g) + \frac{5}{2}N_2(g) \quad (2)$$

The combustion reaction of the complex 1 and 2 is equation (1) and (2), respectively.

The complete detonation reaction considered is described by equation (3) and (4), and the detonation properties are calculated by Kamlet-Jacobs equations[5] (5-7) as follows:

$$C_3H_2N_5O_6 = \frac{1}{2}Ag_2O + 0.5C + 1H_2O + 2.5CO_2 + \frac{5}{2}N_2 \quad (3)$$

$$AgC_3N_5O_6 = \frac{1}{2}Ag_2O + 0.5C + 2.5CO_2 + \frac{5}{2}N_2 \quad (4)$$
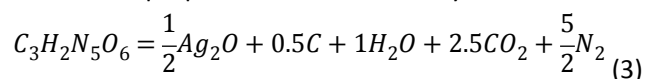
$$AgD = 1.01(N\bar{M}^{1/2}Q^{1/2})(1 + 1.30\rho) \quad (5)$$

$$P = 1.55\rho^2 N\bar{M}^{1/2}Q^{1/2} \quad (6)$$

$$Q = \frac{-\left[\Delta H_f(detonation\ products) - \Delta H_f(explosive)\right]}{Mw} \quad (7)$$

Where D is detonation velocity, P is detonation pressure, Q is heat of detonation, N is the number of moles of the gas generated per gram, $\bar{M}$ is the average molecular weight of gaseous product, and ρ is crystal density.
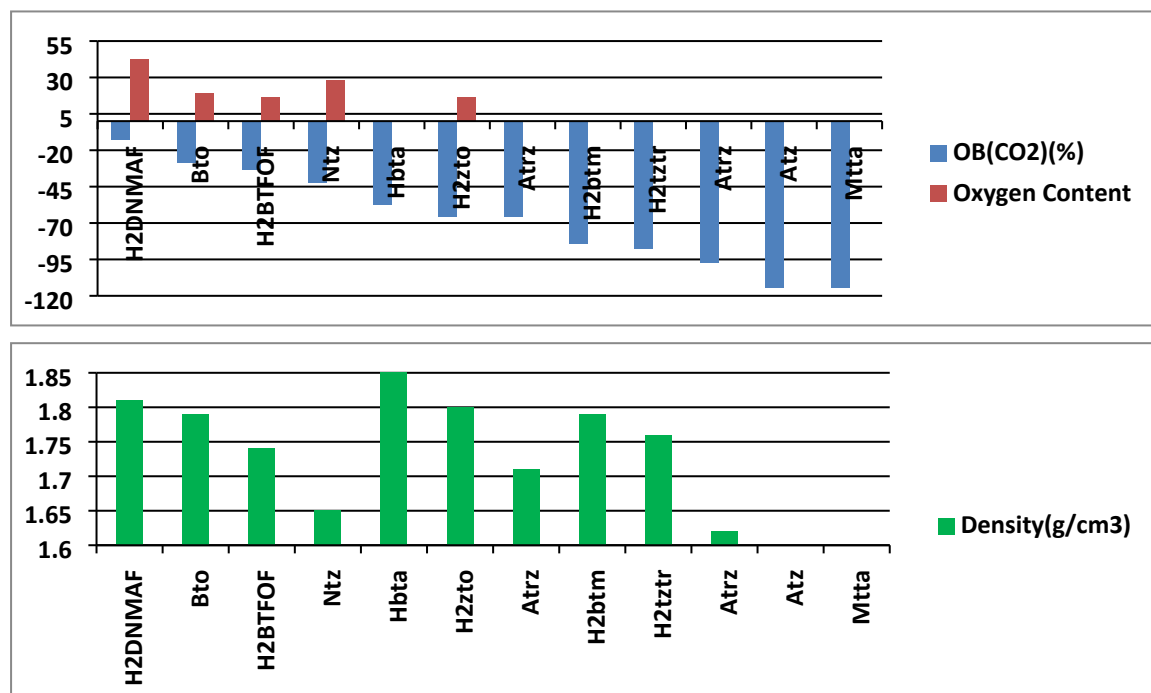

Figure S6 OB(CO2), oxygen content, and density of several ligands.

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