Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

In-Situ Synthesized 3D Heterometallic Metal-Organic Framework (MOF) as High-Energy-Density Materials Shows High Heat of denotation, Good Thermostability and Insensitivity

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Table S1 Elemental Analyses by ICP-AES Method

	Expt. (ω / %)	RSD (%)	Calc. (ω / %)
Cu	34.644	1.18	34.65
Na	3.118	0.93	3.13
molar ratio (Cu/Na)	4 : 1		3.978 : 1

Table S2 Crystal data and structure refinement for **1**.

	1
CCDC	
empirical formula	Cu4 Na C12 N21 H18
formula weight	733.62
crystal system	*Triclinic*
space group	*P* -1
Temperature (K)	296(2) K
a (Å)	8.7330(8)
b (Å)	8.9376(8)
c (Å)	16.4561(14)
V (Å3)	1233.48(19)
Dc (Mg/cm^3)	1.975
Z	2
F(000)	728
μ (mm^{-1})	3.469
no. of reflections collected	6152
no. of unique reflections	4284
R(int)	0.0207
goodness of fit on *F*2	1.077
R_1 [I > 2σ(I)]	0.0379
wR_2 (all data)	0.1150

Table S3 Selected bond lengths (Å) and bond angles (°) for **1**.

N(20)-Cu(1)#1	2.097(4)	N(4)-Cu(3)-N(6)	96.70(15)
Cu(1)-N(13)	2.003(4)	N(14)#2-Cu(3)-N(6)	102.83(14)
Cu(1)-N(8)	2.006(4)	N(21)#5-Cu(3)-N(6)	111.53(15)
Cu(1)-N(18)	2.096(4)	N(6)-N(7)-Cu(2)	127.8(3)
Cu(1)-N(20)#1	2.097(4)	N(8)-N(7)-Cu(2)	123.2(3)
Cu(2)-N(12)	2.011(4)	C(8)-N(12)-Cu(2)	131.9(3)
Cu(2)-N(19)	2.052(4)	N(11)-N(12)-Cu(2)	122.3(3)
Cu(2)-N(7)	2.061(4)	N(7)-N(6)-Cu(3)	127.5(3)
Cu(2)-N(15)#2	2.115(4)	N(5)-N(6)-Cu(3)	119.5(3)
Cu(4)-N(5)	2.005(4)	N(15)-N(14)-Cu(3)#6	126.5(3)
Cu(4)-N(16)#3	2.019(4)	N(13)-N(14)-Cu(3)#6	123.9(3)
Cu(4)-N(3)	2.077(4)	N(14)-N(15)-Cu(2)#6	128.2(3)
Cu(4)-N(11)#4	2.088(4)	N(16)-N(15)-Cu(2)#6	121.0(3)
Cu(3)-N(4)	2.016(4)	N(20)-N(18)-Cu(1)	126.1(3)
Cu(3)-N(14)#2	2.079(4)	N(19)-N(18)-Cu(1)	123.8(3)
Cu(3)-N(21)#5	2.103(4)	C(11)-N(19)-Cu(2)	131.8(3)
Cu(3)-N(6)	2.147(4)	N(18)-N(19)-Cu(2)	121.0(3)
N(14)-Cu(3)#6	2.079(4)	C(11)-N(21)-Cu(3)#5	129.7(3)
N(15)-Cu(2)#6	2.115(4)	N(20)-N(21)-Cu(3)#5	120.7(3)
N(21)-Cu(3)#5	2.103(4)	C(4)-N(5)-Cu(4)	129.2(3)
N(11)-Cu(4)#7	2.088(4)	N(6)-N(5)-Cu(4)	121.8(3)
N(16)-Cu(4)#8	2.019(4)	N(10)-N(11)-Cu(4)#7	125.9(3)
N(10)-Na(1)#9	2.438(4)	N(12)-N(11)-Cu(4)#7	124.9(3)
N(9)-Na(1)	2.519(5)	C(4)-N(8)-Cu(1)	130.0(3)
N(2)-Na(1)#10	2.688(5)	N(7)-N(8)-Cu(1)	122.4(3)
N(1)-Na(1)#3	2.454(5)	C(2)-N(4)-Cu(3)	133.7(4)
N(17)-Na(1)	2.516(7)	N(3)-N(4)-Cu(3)	120.9(3)

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Na(1)-N(2)#10	2.688(5)	C(6)-N(13)-Cu(1)	130.1(3)
N(18)-N(20)-Cu(1)#1	123.9(3)	N(14)-N(13)-Cu(1)	121.8(3)
N(21)-N(20)-Cu(1)#1	124.9(3)	N(2)-N(3)-Cu(4)	123.0(3)
N(13)-Cu(1)-N(8)	130.48(17)	N(4)-N(3)-Cu(4)	126.4(3)
N(13)-Cu(1)-N(18)	112.55(16)	N(11)-N(10)-Na(1)#9	121.0(3)
N(8)-Cu(1)-N(18)	95.80(15)	N(9)-N(10)-Na(1)#9	126.4(3)
N(13)-Cu(1)-N(20)#1	95.01(16)	C(8)-N(9)-Na(1)	123.9(3)
N(8)-Cu(1)-N(20)#1	112.87(16)	N(10)-N(9)-Na(1)	126.5(3)
N(18)-Cu(1)-N(20)#1	110.03(14)	N(3)-N(2)-Na(1)#10	101.0(3)
N(12)-Cu(2)-N(19)	126.92(16)	N(1)-N(2)-Na(1)#10	116.4(3)
N(12)-Cu(2)-N(7)	121.80(16)	C(2)-N(1)-Na(1)#3	139.4(4)
N(19)-Cu(2)-N(7)	94.38(16)	N(2)-N(1)-Na(1)#3	111.2(3)
N(12)-Cu(2)-N(15)#2	96.39(15)	C(10)-N(17)-Na(1)	166.0(7)
N(19)-Cu(2)-N(15)#2	112.74(15)	N(10)#9-Na(1)-N(1)#8	117.03(18)
N(7)-Cu(2)-N(15)#2	103.22(14)	N(10)#9-Na(1)-N(17)	120.0(2)
N(5)-Cu(4)-N(16)#3	132.69(16)	N(1)#8-Na(1)-N(17)	122.5(2)
N(5)-Cu(4)-N(3)	99.61(16)	N(10)#9-Na(1)-N(9)	96.45(15)
N(16)#3-Cu(4)-N(3)	105.74(16)	N(1)#8-Na(1)-N(9)	85.93(18)
N(5)-Cu(4)-N(11)#4	106.42(15)	N(17)-Na(1)-N(9)	94.5(2)
N(16)#3-Cu(4)-N(11)#4	100.57(16)	N(10)#9-Na(1)-N(2)#10	96.03(15)
N(3)-Cu(4)-N(11)#4	111.40(16)	N(1)#8-Na(1)-N(2)#10	86.86(16)
N(4)-Cu(3)-N(14)#2	126.83(15)	N(17)-Na(1)-N(2)#10	80.7(2)
N(4)-Cu(3)-N(21)#5	125.97(16)	N(9)-Na(1)-N(2)#10	167.40(16)
N(14)#2-Cu(3)-N(21)#5	91.45(16)		
N(20)-Cu(1)#1	2.097(4)	N(14)#2-Cu(3)-N(21)#5	91.45(16)
Cu(1)-N(13)	2.003(4)	N(4)-Cu(3)-N(6)	96.70(15)
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Cu(1)-N(20)#1	2.097(4)	N(6)-N(7)-Cu(2)	127.8(3)
Cu(2)-N(12)	2.011(4)	N(8)-N(7)-Cu(2)	123.2(3)
Cu(2)-N(19)	2.052(4)	C(8)-N(12)-Cu(2)	131.9(3)
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Cu(4)-N(5)	2.005(4)	N(5)-N(6)-Cu(3)	119.5(3)
Cu(4)-N(16)#3	2.019(4)	N(15)-N(14)-Cu(3)#6	126.5(3)
Cu(4)-N(3)	2.077(4)	N(13)-N(14)-Cu(3)#6	123.9(3)
Cu(4)-N(11)#4	2.088(4)	N(14)-N(15)-Cu(2)#6	128.2(3)
Cu(3)-N(4)	2.016(4)	N(16)-N(15)-Cu(2)#6	121.0(3)
Cu(3)-N(14)#2	2.079(4)	N(20)-N(18)-Cu(1)	126.1(3)
Cu(3)-N(21)#5	2.103(4)	N(19)-N(18)-Cu(1)	123.8(3)
Cu(3)-N(6)	2.147(4)	C(11)-N(19)-Cu(2)	131.8(3)
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N(15)-Cu(2)#6	2.115(4)	C(11)-N(21)-Cu(3)#5	129.7(3)
N(21)-Cu(3)#5	2.103(4)	N(20)-N(21)-Cu(3)#5	120.7(3)
N(11)-Cu(4)#7	2.088(4)	C(4)-N(5)-Cu(4)	129.2(3)
N(16)-Cu(4)#8	2.019(4)	N(6)-N(5)-Cu(4)	121.8(3)
N(10)-Na(1)#9	2.438(4)	N(10)-N(11)-Cu(4)#7	125.9(3)
N(9)-Na(1)	2.519(5)	N(12)-N(11)-Cu(4)#7	124.9(3)
N(2)-Na(1)#10	2.688(5)	C(4)-N(8)-Cu(1)	130.0(3)
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N(18)-N(20)-Cu(1)#1	123.9(3)	N(14)-N(13)-Cu(1)	121.8(3)
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N(13)-Cu(1)-N(8)	130.48(17)	N(4)-N(3)-Cu(4)	126.4(3)
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N(19)-Cu(2)-N(7)	94.38(16)	N(2)-N(1)-Na(1)#3	111.2(3)
N(12)-Cu(2)-N(15)#2	96.39(15)	C(10)-N(17)-Na(1)	166.0(7)
N(19)-Cu(2)-N(15)#2	112.74(15)	N(10)#9-Na(1)-N(1)#8	117.03(18)
N(7)-Cu(2)-N(15)#2	103.22(14)	N(10)#9-Na(1)-N(17)	120.0(2)
N(5)-Cu(4)-N(16)#3	132.69(16)	N(1)#8-Na(1)-N(17)	122.5(2)
N(5)-Cu(4)-N(3)	99.61(16)	N(10)#9-Na(1)-N(9)	96.45(15)
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N(5)-Cu(4)-N(11)#4	106.42(15)	N(17)-Na(1)-N(9)	94.5(2)
N(16)#3-Cu(4)-N(11)#4	100.57(16)	N(10)#9-Na(1)-N(2)#10	96.03(15)
N(3)-Cu(4)-N(11)#4	111.40(16)	N(1)#8-Na(1)-N(2)#10	86.86(16)
N(4)-Cu(3)-N(14)#2	126.83(15)	N(17)-Na(1)-N(2)#10	80.7(2)
N(4)-Cu(3)-N(21)#5	125.97(16)	N(9)-Na(1)-N(2)#10	167.40(16)
C(2)-N(4)-Cu(3)	133.7(4)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z; #2 x+1,y,z; #3 x+1,y-1,z; #4 x,y-1,z; #5 -x+2,-y,-z; #6 x-1,y,z

#7 x,y+1,z; #8 x-1,y+1,z; #9 -x+1,-y+1,-z+1; #10 -x+1,-y,-z+1

1. FTIR spectra

The infrared spectra of compound **1** displays strong and sharp peaks at approximately 2942 cm^{-1}, which represent the C-H(CH_3) stretching vibrations. The peak at 2251 cm^{-1} corresponds to the stretching vibrations of C≡N. Moreover, the characteristic absorption bands at approximately 1622

cm^{-1} indicative of the presence of C=N stretching vibrations in corresponding metal compound. The peak at 1493 cm^{-1} corresponds to the stretching vibrations of the C-C, and 1379 cm^{-1} corresponding to the stretching vibrations of the C-N. Consequently, the infrared spectrum is found to be in good consistent with the structural features of the compound.

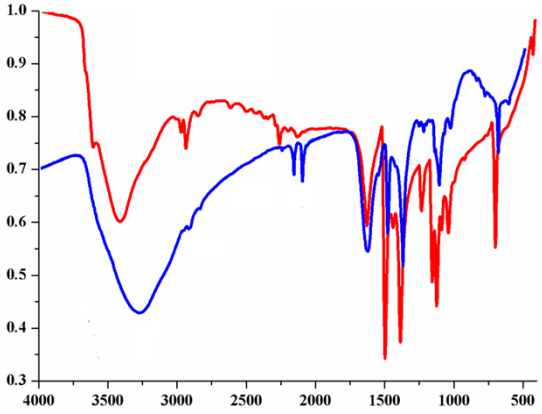

Fig. S1 FTIR spectra of **1** (red) and **1a** (blue).

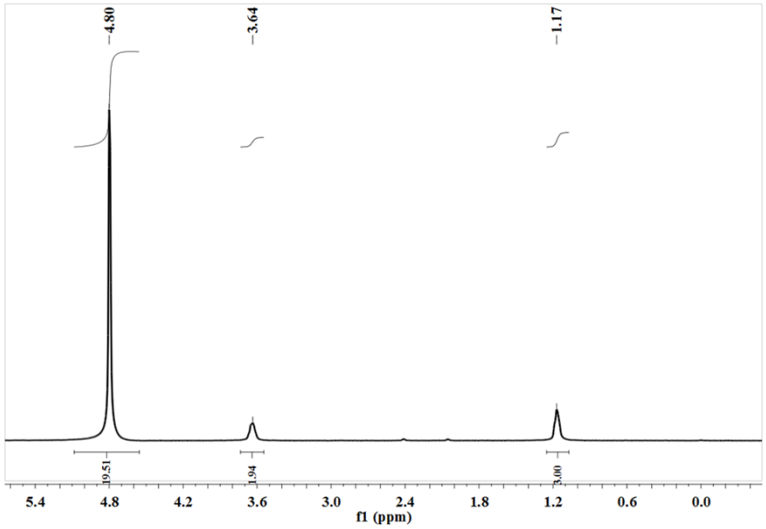

Fig. S2 1H NMR of **1**.

2. ICP-AES

The content of Cu and Na for as-synthesized compound **1** were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) on a J-A1100 (Jarrell-Ash, USA) ICP spectrometer. The experimental conditions are listed in Table S2. ICP-AES analysis of **1** reveals that the molar ratio of Cu to Na is 4:1.

3. Heat of detonation

Density functional theory (DFT) is applied to calculate the energy of detonation (ΔE_{det}), from which heat of detonation (ΔH_{det}) is calculated by a linear correlation equation ($\Delta H_{det} = 1.127\Delta E_{det} + 0.046$, $r = 0.968$). The values of ΔE_{det} and ΔH_{det} are listed in Table S4.

Table S4 Calculated parameters used in the detonation reactions.

	Compound (hartree)	Na (hartree)	Cu (hartree)	N_2 (hartree)	C (hartre)	NH_3 (hartree)	ΔE_{det} (hartee)	ΔE_{det} (kcal·g^{-1})	ΔH_{det} (kcal·g^{-1})	ΔH_{det} (kcal·cm^{-3})
1	-2561.8746	-162.279911	-196.1132	-109.447	-37.738	-56.5045	2.406	2.058	2.366	4.672