Supporting Information

A 3D solvent-free energetic metal-organic framework (EMOF) achieved by removing inclusion molecules from a new coordination polymer

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Table S1 Elemental analyses of **1** by ICP-AES method.

	Expt. (ω/%)	RSD (%)	Calc. (ω/%)
Cu	29.867	1.11	29.86
Na	3.572	0.95	3.58
molar ratio (Cu/Na)	3:1		2.997:1

Table S2. Selected bond lengths (Å) and bond angles (°) for **1**.

Cu(1)-N(2)	1.998(9)	Cu(1)-N(2)#3	1.998(9)
Cu(1)-N(2)#1	1.998(9)	Cu(2)-N(3)#4	1.874(7)
Cu(1)-N(2)#2	1.998(9)	Cu(2)-N(3)	1.874(7)
Na(1)-O(1)	2.266(7)	Na(1)-O(1)#7	2.266(7)
Na(1)-O(1)#5	2.266(7)	Na(1)-O(1)#6	2.266(7)
N(2)-Cu(1)-N(2)#1	104.4(2)	N(3)-N(2)-Cu(1)	126.1(6)
N(2)#1-Cu(1)-N(2)#2	120.2(5)	C(2)-N(2)-Cu(1)	126.4(8)
N(2)-Cu(1)-N(2)#2	104.4(2)	N(2)-N(3)-Cu(2)	125.1(6)
N(2)#1-Cu(1)-N(2)#3	104.4(2)	C(1)-N(3)-Cu(2)	126.3(7)
N(2)#2-Cu(1)-N(2)#3	104.4(2)	N(3)#4-Cu(2)-N(3)	180.0
N(2)-Cu(1)-N(2)#3	120.2(5)	O(1)-Na(1)-O(1)#6	94.2(3)
O(1)#5-Na(1)-O(1)#6	117.58(19)	O(1)-Na(1)-O(1)#7	117.58(19)
O(1)-Na(1)-O(1)#5	117.58(19)	O(1)#7-Na(1)-O(1)#6	117.58(19)
O(1)#5-Na(1)-O(1)#7	94.2(3)	C(1)-O(1)-Na(1)	133.2(6)

Symmetry transformations used to generate equivalent atoms: #1 5/4-Y,1/4+X,3/4-Z; #2 -1/4+Y,5/4-X,3/4-Z; #3 1-X,3/2-Y,+Z; #4 1-X,1-Y,1-Z; #5 3/4-Y,-1/4+X,1/4-Z; #6 1-X,1/2-Y,+Z; #7 1/4+Y,3/4-X,1/4-Z.

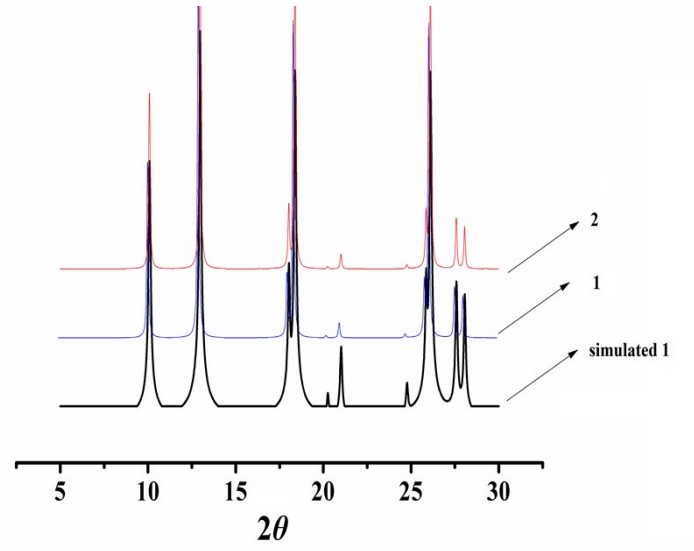
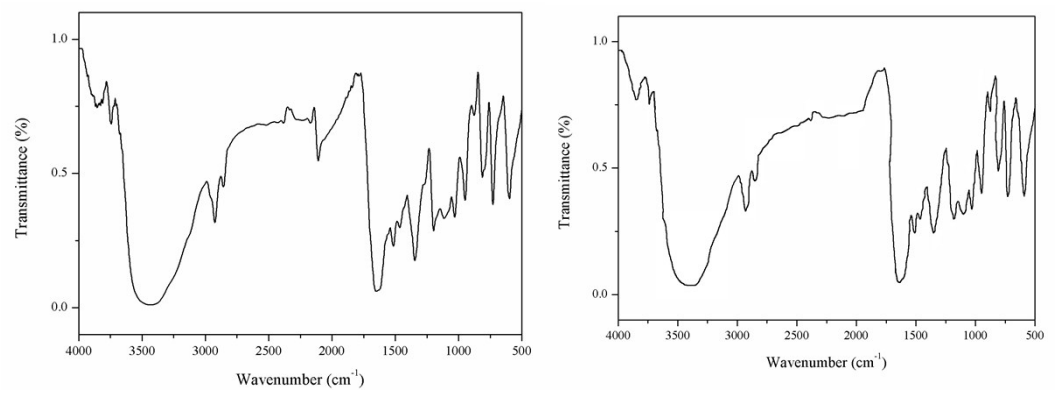


Figure S1. X-ray powder diffraction patterns of **1** and **2**.



a **b**

Figure S2. IR spectras of **1** (a) and **2** (b).

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# SQUEEZE RESULTS (Version = 150216)
# Note: Data are Listed for all Voids in the P1 Unit Cell
# i.e. Centre of Gravity, Solvent Accessible Volume,
# Recovered number of Electrons in the Void and
# Details about the Squeezed Material
loop_
_platon_squeeze_void_nr
_platon_squeeze_void_average_x
_platon_squeeze_void_average_y
_platon_squeeze_void_average_z
_platon_squeeze_void_volume
_platon_squeeze_void_count_electrons
_platon_squeeze_void_content
1   0.250   0.000  -0.015        153        86 ''
2   0.250   0.500  -0.017        153        86 ''
3   0.750   0.000  -0.015        153        86 ''
4   0.750   0.500  -0.015        153        86 ''
_platon_squeeze_void_probe_radius                  1.20
```

Figure S3. The SQUEEZE details of **1**. (Z = 4; so the Formula unit is 1/4 of the unit cell, this then is consistent with 1/4 of the SQUEEZED-OUT electrons (= 86/4 = 21.5) being associated with the solvent part of the Formulas unit. As a CH_3CN molecule has 22 electrons, this then is consistent with the one CH_3CN (22 electrons) molecule in **1**.

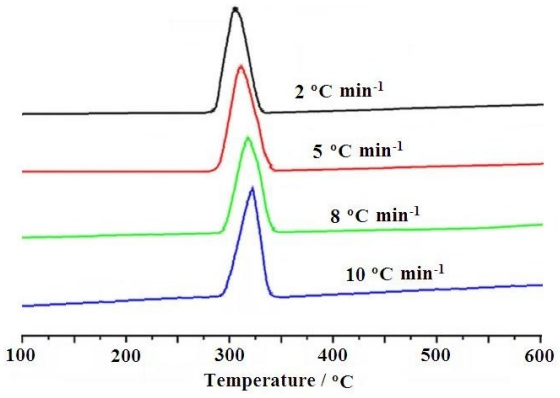

Figure S4 DSC curves of **2** under different heating rates

1. Oxygen bomb calorimetry

The constant-volume combustion energies of **1** and **2** were investigated by a precise rotating-oxygen bomb calorimeter (RBC-type II).[1] Approximately 10 mg of the samples were pressed with a well-define amount of benzoic acid (Calcd. 30 mg) to form a tablet to ensure better combustion. The recorded data are the average of six single measurements. The calorimeter was calibrated by the combustion of certified benzoic acid (Standard Reference Material, 39i, NIST) in an oxygen atmosphere at a pressure of 30.5 bar. The experimental values of the constant volume combustion energies ($\Delta_c U$) for **1** and **2** were (-12553.83 ± 7.15) J g^{-1} and (-14038.42 ± 4.74), respectively. Then the enthalpies of combustion ($\Delta_c H^\theta_m$) was calculated as (-7555.52 ± 4.30) kJ mol^{-1} for **1** (-9025.30 ± 3.05) kJ mol^{-1} for **2** on the basis of the formula $\Delta_c H^\theta_m = \Delta_c U^\theta_m + \Delta nRT$, $\Delta n = n_g$(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). Subsequently, according to combustion reaction equation (3,4), Hess's law in thermochemical equation (5,6) and the known enthalpies of formation of the combustion products[2,3] CuO (s), $\Delta_c H^\theta_m$ (CuO, s) = (-156) kJ mol^{-1}, Na_2O (s), $\Delta_c H^\theta_m$ (Na_2O, s) = (-416) kJ mol^{-1}, CO_2 (g), $\Delta_c H^\theta_m$ (CO_2, g) = (-393) kJ mol^{-1}, H_2O (l), $\Delta_c H^\theta_m$ (H_2O, l) = (-242) kJ mol^{-1}, the standard enthalpies of formation for **1** ($\Delta_f H^\theta_m$) and **2** ($\Delta_f H^\theta_m$) are obtained as (3147.63 ± 4.30) kJ mol^{-1} and (3396.26 ± 3.05) kJ mol^{-1}, respectively, evidencing that N-N and N=N bonds in structure make a decisive contribution to the enthalpy of formation of **1** and **2**.

$$Cu_3NaC_{10}H_7N_{17}O_{4(s)} + \frac{23}{2}O_{2(g)} \rightarrow 3CuO_{(s)} + \frac{1}{2}Na_2O_{(s)} + 10CO_{2(g)} + \frac{7}{2}H_2O_{(l)} + \frac{17}{2}N_{2(g)} \quad (3)$$

$$Cu_3NaC_8H_4N_{16}O_{4(s)} + \frac{17}{4}O_{2(g)} \rightarrow 3CuO_{(s)} + \frac{1}{2}Na_2O_{(s)} + 8CO_{2(g)} + 2H_2O_{(l)} + 8N_{2(g)} \quad (4)$$

$$\Delta_f H^\theta_{m(s)} = 3\Delta_f H^\theta_m(CuO,s) + \frac{1}{2}\Delta_f H^\theta_m(Na_2O,s) + 10\Delta_f H^\theta_m(CO_2,g) + \frac{7}{2}\Delta_f H^\theta_m(H_2O,l) - \Delta_c H^\theta_m(\mathbf{1},s) \quad (5)$$

$$\Delta_f H^\theta_{m(s)} = 3\Delta_f H^\theta_m(CuO,s) + \frac{1}{2}\Delta_f H^\theta_m(Na_2O,s) + 8\Delta_f H^\theta_m(CO_2,g) + 2\Delta_f H^\theta_m(H_2O,l) - \Delta_c H^\theta_m(\mathbf{2},s) \quad (6)$$

2. The detonation properties of compounds 1 and 2

$$Cu_3NaC_{10}H_7N_{17}O_4 \rightarrow 3Cu + \frac{1}{2}Na_2O + \frac{7}{2}H_2O + 10C + \frac{17}{2}N_2 \quad (7)$$

$$Cu_3NaC_8H_4N_{16}O_4 \rightarrow 3Cu + \frac{1}{2}Na_2O + 2H_2O + \frac{3}{4}CO_2 + \frac{29}{4}C + 8N_2 \quad (8)$$

$$D = 1.01\Phi^{1/2}(1 + 1.30\rho) \quad (9)$$

$$P = 1.558\Phi\rho^2 \quad (10)$$

$$\Phi = 31.68N(MQ)^{1/2} \quad (11)$$

$$Q = \frac{-[\Delta H_f(\text{detonation products}) - \Delta H_f(\text{explosive})]}{\text{formula weight of explosive}} \quad (12)$$

Where D represents detonation velocity (km s^{-1}), P is detonation pressure (GPa), ρ is the density of explosive (g cm^{-3}), N is the moles of detonation gases per gram of explosive (mol g^{-1}), M is the average molecular weight of these gases (g mol^{-1}), Q is the heat of detonation (kcal g^{-1}) and Φ is a characteristic parameter of an explosive. Additionally, to further verify the calculated results, the commercial program EXPLO5 v6.0116[4] was employed to evaluate the detonation properties of compounds **1** and **2**, which further demonstrated the accuracy of the new method.

Table S3 The physicochemical properties of some energetic materials

Explosive	ρ [a] (g cm^{-3})	N [b] (%)	Ω [c] (%)	T_{dec} [d] (°C)	Q [e] (kcal g^{-1})	D [f] (km s^{-1})	P [g] (GPa)
ATRZ-1[5]	1.680	53.35	−58.83	243	3.618	9.160	35.68
ATRZ-2[5]	2.160	43.76	−49.99	257	1.381	7.773	29.70
TNT[6]	1.654	18.50	−74.00	244	1.22	7. 178	20.50

RDX[6]	1.806	37.80	−21.60	210	1.44	8.600	33.92
HMX[7]	1.950	37.80	−21.60	287	1.320	8.900	38.39
CHP[8a]	1.948	14.71	−11.48	194	1.25	8.225	31.73
NHP[8a]	1.983	33.49	−11.48	220	1.37	9.184	39.69
CHHP[8b]	2.000	23.58	−13.05	231	0.75	6.205	17.96
ZnHHP[8b]	2.117	23.61	−49.99	293	0.7	7.016	23.58
$[Cu(Htztr)]_n$[9]	2.435	49.08	−56.09	355	3.9582	10.40	56.48

[a] Density from X-ray diffraction. [b] Nitrogen content. [c] Oxygen balance. [d] Decomposition temperature. [e] The heat of detonation. [f] Detonation velocity. [g] Detonation pressure. ATRZ = 4,4'-azo-1,2,4-triazole; HMX = octogen; RDX= cyclotrimethylenetrinitramine; TNT = trinitrotoluene; CHP = cobalt hydrazine perchlorate; NHP = nickel hydrazine perchlorate; CHHP = cobalt hydrazine hydrazinecarboxylate perchlorate; ZnHHP = zinc hydrazine hydrazinecarboxylate perchlorate; H_2tztr = 3-(1*H*-tetrazol-5-yl)-1*H*-triazole.

3. References

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