Electronic Supplementary Material (ESI) for Dalton Transactions.
This journal is © The Royal Society of Chemistry 2017

Electronic Supplementary Information

Self-assembled energetic 3D metal-organic framework $[Na_8(N_5)_8(H_2O)_3]_n$ based on *cyclo*-N_5^-

Yuangang Xu,[a] Pengcheng Wang,*[a] Qiuhan Lin,[a] Xuefeng Mei,[b] Ming Lu*[a]

[a] School of Chemical Engineering, Nanjing University of Science and Technology, Xiaolingwei 200, Nanjing 210094, Jiangsu, China

[b] Pharmaceutical Analytical & Solid-State Chemistry Research Center, Shanghai Institute of Materia Medica, Chinese Academy of Sciences, Shanghai 201203, China

E-mail: *alexwpch@njust.edu.cn (P. W.); luming@njust.edu.cn (M. L.)*

Table of Contents

1. Experimental Procedures

General Methods. All reagents and solvents were purchased from Sigma-Aldrich, Aladdin, and Energy Chemical as analytical grade and were used as received. DSC plots were acquired on a differential scanning calorimeter (Mettler Toledo DSC-1) at a scan rate of 5 °C min^{-1} in perforated stainless steel containers under a nitrogen flow of 50 mL min^{-1}. TG analysis was also performed at a heating rate of 5 °C min^{-1} on a Mettler Toledo TGA/SDTA851e instrument. IR spectra were recorded on a Thermo Nicolet IS10 instrument. Raman spectra were collected using a Horiba-Jobin Yvon Labram HR800 Raman spectrometer with a 514.532 nm Ar^+ laser. A 50× objective was used to focus the laser beam. Elemental analyses were carried out on a vario EL III CHNOS elemental analyzer. The morphologies of complex **2** were analyzed by the HIROX KH-7700 digital microscope system and scanning electron microscope (Hitachi S4800, Hitachi TM3000).

Caution: Although we have not experienced any difficulties in synthesizing and handing the complex, it is a potentially dangerous explosive. Proper protective precautions must be used.

Complex **1** was prepared according to our previously reported methods.[1]

Complex **2**: 1.0 mmol of $[Na(H_2O)(N_5)]\cdot 2H_2O$ (147 mg) was added to 10 ml of ammonia, 2M in methanol. Single crystals of **2** were obtained by maintaining the solutions at ambient temperature for several days. Colorless crystals; yield: 85%; T_d = 129 °C; IR (KBr): $\tilde{\nu}$ = 3626, 3407, 2036, 1615, 1393, 1361, 1231, 1032, 587 cm^{-1}; Raman (514.532 nm, 25 °C): 1178, 117 cm^{-1}; Elemental analysis calcd (%) for $Na_8N_{40}H_6O_3$ (798.24): H 0.76, N 70.19; found: H 0.82, N 70.11.

Fig. S1 3D digital microscope image of crystal **2**.

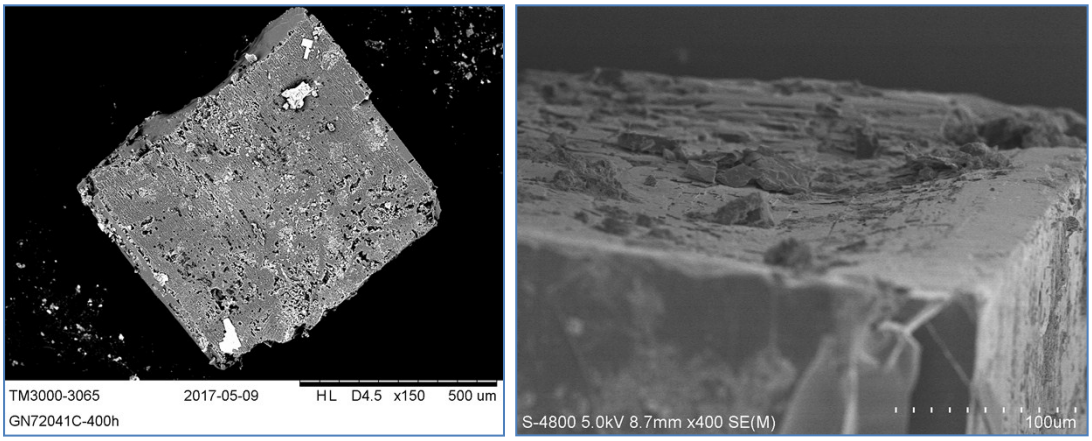

Fig. S2 Scanning electron microscope images of crystal **2**.

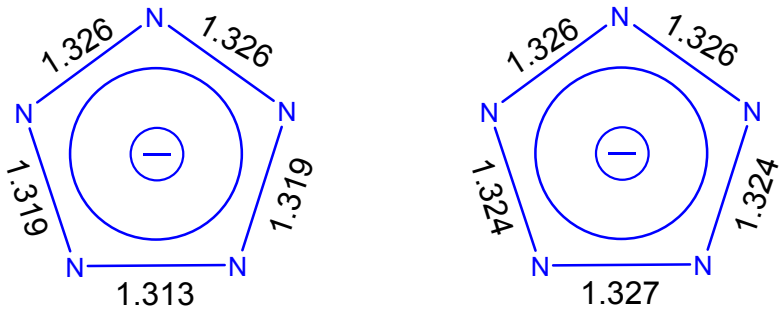

Fig. S3 The two forms of N_5^- rings. Bond lengths in Å.

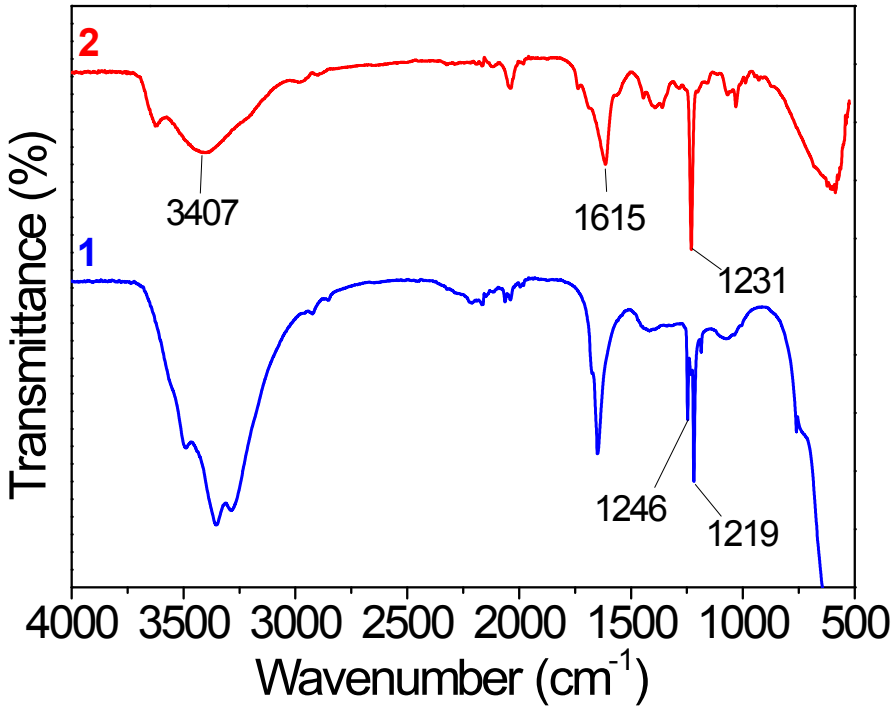

Fig. S4 The IR spectra of crystal **1** and **2**.

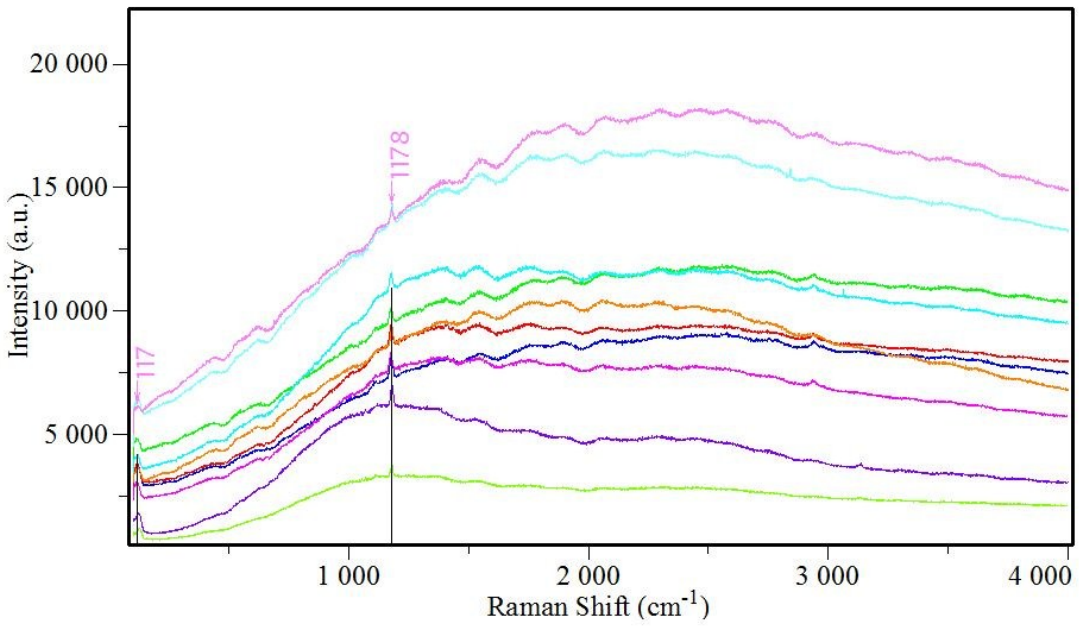

Fig. S5 The Raman spectra of crystal **2**.

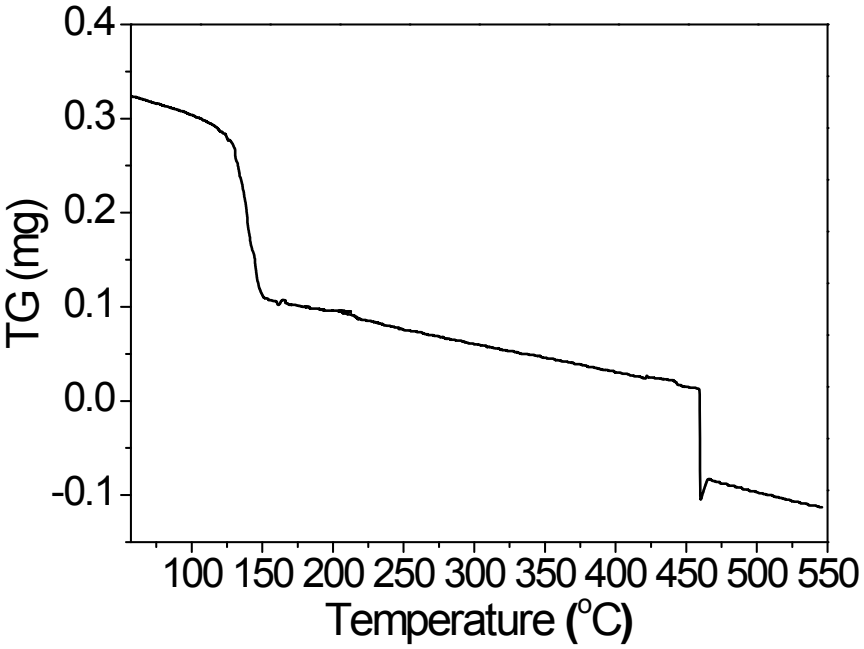

Fig. S6 The TG curve of crystal **2**.

2. Single-crystal X-ray Diffraction Analysis

The single crystal X-ray diffraction measurements for **2** were conducted on a Bruker Smart Apex II diffractometer using Mo-Kα radiation (λ = 0.71073 Å) with a graphite monochromator at 100 K. An Oxford Cobra low-temperature device was used to maintain the low temperature. Integration and scaling of intensity data was 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 O-H 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]. The highly disordered guest molecules in **2**, which led to high *R* and w*R* values, were removed by the SQUEEZE routine[5] in *PLATON*.

Table S1 Crystal data and structure refinement details of complex **2**.

CCDC	1544793
Empirical formula	$Na_8N_{40}H_6O_3$
Temperature / K	100.0
Crystal system	cubic
Space group	*P*m-3n
a / Å	18.238(10)
b / Å	18.238(10)
c / Å	18.238(10)
α /°	90
β /°	90
γ /°	90
Volume / Å^3	6067(10)
Z	6
ρ_{calc} / g cm^{-3}	1.301
μ / mm^{-1}	0.179
F(000)	2352.0
Crystal size / mm^3	0.28 × 0.15 × 0.12
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.466 to 54.968
Index ranges	$-23 \le h \le 8$, $-9 \le k \le 22$, $-21 \le l \le 23$
Reflections collected	14408
Independent reflections	1279 [R_{int} = 0.0717, R_{sigma} = 0.0329]
Data / restraints / parameters	1279 / 0 / 70
Goodness-of-fit on F^2	1.078
Final *R* indexes [$I >= 2\sigma(I)$]	R_1 = 0.0606, wR_2 = 0.1803
Final *R* indexes [all data]	R_1 = 0.0784, wR_2 = 0.2027
Largest diff. peak / hole / e Å^{-3}	1.10 / -0.51

Table S2 Bond lengths of complex **2**.

parameter	bond length (Å)	parameter	bond length (Å)
N6 N5	1.329(3)	Na2 $N5^{5}$	2.475(3)
N6 $N5^{1}$	1.329(3)	Na2 $N5^{8}$	2.475(3)
N6 Na3	2.402(3)	Na2 $N1^{9}$	2.530(4)
Na1 $Na1^{2}$	4.116(4)	Na2 N3	2.465(3)
Na1 Na2	4.188(2)	Na2 $N3^{7}$	2.465(3)
Na1 $Na2^{3}$	4.188(2)	Na2 O2	2.578(7)
Na1 $Na2^{4}$	4.188(2)	Na2 O1	2.671(6)
Na1 $N4^{3}$	2.470(3)	N4 $N4^{1}$	1.315(4)
Na1 N4	2.470(3)	N2 N3	1.321(3)
Na1 $N4^{5}$	2.470(3)	N3 $N3^{6}$	1.327(4)
Na1 $N2^{3}$	2.455(3)	O2 $Na3^{10}$	2.863(9)
Na1 N2	2.455(3)	O1 $Na2^{6}$	2.671(6)
Na1 $N2^{5}$	2.455(3)	Na3 $N6^{11}$	2.402(3)
N5 $Na2^{3}$	2.475(3)	Na3 $N6^{12}$	2.402(3)
N5 N4	1.317(3)	Na3 $N6^{13}$	2.402(3)
N1 $Na2^{4}$	2.530(4)	Na3 $O2^{14}$	2.863(9)
N1 N2	1.325(3)	Na3 $O2^{15}$	2.863(9)
N1 $N2^{6}$	1.325(3)	Na3 $O2^{16}$	2.863(9)
Na2 $Na1^{7}$	4.188(2)	Na3 $O2^{3}$	2.863(9)

Table S3 Bond angles of complex **2**.

parameter	bond angle (°)	parameter	bond angle (°)
N5 N6 $N5^{1}$	108.4(3)	$N5^{8}$ Na2 O1	109.96(13)
N5 N6 Na3	125.83(14)	$N1^{9}$ Na2 Na1	53.627(18)
$N5^{1}$ N6 Na3	125.82(14)	$N1^{9}$ Na2 $Na1^{7}$	53.627(18)
$Na1^{2}$ Na1 $Na2^{3}$	109.06(3)	$N1^{9}$ Na2 O2	156.6(2)
$Na1^{2}$ Na1 Na2	109.06(3)	$N1^{9}$ Na2 O1	155.29(19)
$Na1^{2}$ Na1 $Na2^{4}$	109.06(3)	N3 Na2 $Na1^{7}$	123.60(8)
$Na2^{3}$ Na1 Na2	109.88(3)	N3 Na2 Na1	54.91(5)
$Na2^{4}$ Na1 $Na2^{3}$	109.88(3)	$N3^{7}$ Na2 Na1	123.60(8)
$Na2^{4}$ Na1 Na2	109.88(3)	$N3^{7}$ Na2 $Na1^{7}$	54.91(5)
N4 Na1 $Na1^{2}$	55.08(6)	N3 Na2 $N5^{5}$	91.20(8)
$N4^{5}$ Na1 $Na1^{2}$	55.08(6)	$N3^{7}$ Na2 $N5^{5}$	177.61(10)
$N4^{4}$ Na1 $Na1^{2}$	55.08(6)	$N3^{7}$ Na2 $N5^{8}$	91.20(8)
$N4^{5}$ Na1 $Na2^{4}$	122.44(6)	N3 Na2 $N5^{8}$	177.61(10)
$N4^{5}$ Na1 Na2	54.07(5)	N3 Na2 $N1^{9}$	90.30(9)
$N4^{4}$ Na1 $Na2^{4}$	127.68(6)	$N3^{7}$ Na2 $N1^{9}$	90.30(9)

N4	Na1	Na2	127.68(6)	N3^{7}	Na2	N3	88.99(11)
N4	Na1	Na2^{4}	54.07(5)	N3	Na2	O2	106.17(15)
N4	Na1	Na2^{3}	122.44(6)	N3^{7}	Na2	O2	106.17(15)
N4^{5}	Na1	Na2^{3}	127.68(6)	N3	Na2	O1	72.36(13)
N4^{4}	Na1	Na2	122.44(6)	N3^{7}	Na2	O1	72.36(13)
N4^{4}	Na1	Na2^{3}	54.07(5)	O2	Na2	Na1^{7}	123.51(6)
N4^{5}	Na1	N4	90.48(8)	O2	Na2	Na1	123.51(6)
N4^{5}	Na1	N4^{4}	90.48(8)	O2	Na2	O1	48.1(3)
N4^{4}	Na1	N4	90.48(8)	O1	Na2	Na1	122.05(6)
N2^{5}	Na1	Na1^{2}	123.87(7)	O1	Na2	Na1^{7}	122.05(6)
N2	Na1	Na1^{2}	123.87(7)	N5	N4	Na1	126.86(16)
N2^{4}	Na1	Na1^{2}	123.87(7)	N4^{1}	N4	Na1	123.32(8)
N2^{5}	Na1	Na2^{3}	53.74(6)	N4^{1}	N4	N5	108.59(13)
N2^{4}	Na1	Na2^{3}	127.05(8)	N1	N2	Na1	123.49(18)
N2	Na1	Na2^{3}	56.15(6)	N3	N2	Na1	127.77(16)
N2^{5}	Na1	Na2^{4}	56.15(6)	N3	N2	N1	108.7(2)
N2^{4}	Na1	Na2	56.15(6)	N2	N3	Na2	123.35(16)
N2^{4}	Na1	Na2^{4}	53.74(6)	N2	N3	N3^{6}	107.75(13)
N2	Na1	Na2^{4}	127.05(8)	N3^{6}	N3	Na2	128.20(6)
N2^{5}	Na1	Na2	127.05(8)	Na2	O2	Na3^{10}	103.6(2)
N2	Na1	Na2	53.74(6)	Na2^{6}	O1	Na2	110.0(3)
N2^{5}	Na1	N4	87.76(7)	N6^{11}	Na3	N6	180.00(14)
N2	Na1	N4	178.22(8)	N6^{11}	Na3	N6^{12}	90.0
N2^{4}	Na1	N4	89.82(8)	N6^{13}	Na3	N6	90.0
N2	Na1	N4^{5}	89.81(8)	N6^{11}	Na3	N6^{13}	90.0
N2^{4}	Na1	N4^{4}	178.22(8)	N6^{12}	Na3	N6^{13}	180.00(14)
N2^{5}	Na1	N4^{5}	178.22(8)	N6^{12}	Na3	N6	90.0
N2	Na1	N4^{4}	87.76(7)	N6^{11}	Na3	O2^{14}	75.66(8)
N2^{4}	Na1	N4^{5}	87.76(7)	N6^{12}	Na3	O2^{4}	75.66(8)
N2^{5}	Na1	N4^{4}	89.81(8)	N6^{12}	Na3	O2^{14}	75.66(8)
N2^{5}	Na1	N2	91.95(10)	N6^{11}	Na3	O2^{15}	75.66(8)
N2^{5}	Na1	N2^{4}	91.95(10)	N6	Na3	O2^{4}	75.66(8)
N2^{4}	Na1	N2	91.95(10)	N6^{12}	Na3	O2^{16}	104.34(8)
N6	N5	Na2^{4}	128.46(16)	N6	Na3	O2^{15}	104.34(8)
N4	N5	N6	107.2(2)	N6^{13}	Na3	O2^{16}	75.66(8)
N4	N5	Na2^{4}	123.99(16)	N6^{13}	Na3	O2^{14}	104.34(8)
N2^{6}	N1	Na2^{3}	126.16(15)	N6^{13}	Na3	O2^{4}	104.34(8)
N2	N1	Na2^{3}	126.17(15)	N6^{11}	Na3	O2^{16}	104.34(8)
N2^{6}	N1	N2	107.1(3)	N6^{12}	Na3	O2^{15}	104.34(8)
Na1	Na2	Na1^{7}	107.21(4)	N6^{11}	Na3	O2^{4}	104.34(8)

$N5^{8}$	Na2	$Na1^{7}$	54.86(5)	N6	Na3	$O2^{16}$	75.66(8)
$N5^{8}$	Na2	Na1	123.22(8)	N6	Na3	$O2^{14}$	104.34(8)
$N5^{5}$	Na2	Na1	54.86(5)	$N6^{13}$	Na3	$O2^{15}$	75.66(8)
$N5^{5}$	Na2	$Na1^{7}$	123.22(8)	$O2^{15}$	Na3	$O2^{16}$	151.33(17)
$N5^{5}$	Na2	$N5^{8}$	88.51(13)	$O2^{4}$	Na3	$O2^{15}$	41.0(2)
$N5^{5}$	Na2	$N1^{9}$	87.32(9)	$O2^{4}$	Na3	$O2^{16}$	151.33(17)
$N5^{8}$	Na2	$N1^{9}$	87.32(9)	$O2^{14}$	Na3	$O2^{4}$	151.33(17)
$N5^{8}$	Na2	O2	76.06(15)	$O2^{14}$	Na3	$O2^{16}$	41.0(2)
$N5^{5}$	Na2	O2	76.06(15)	$O2^{14}$	Na3	$O2^{15}$	151.33(17)
$N5^{5}$	Na2	O1	109.96(13)				

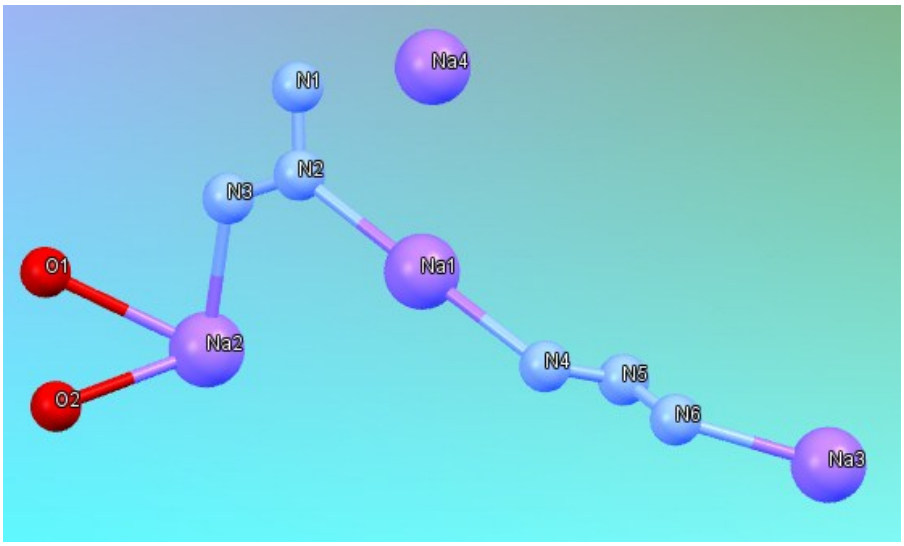

Fig. S7 The asymmetric unit of crystal **2**.

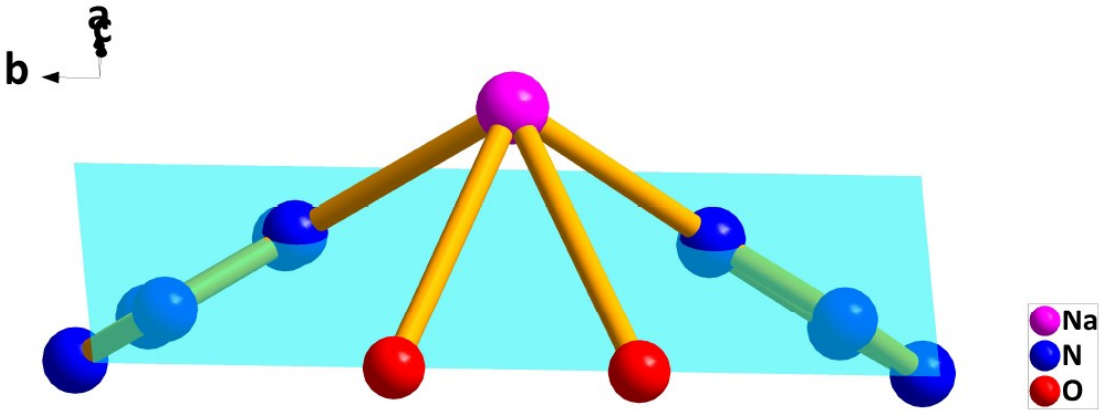

Fig. S8 Coordination environment of Na3 in crystal **2**.

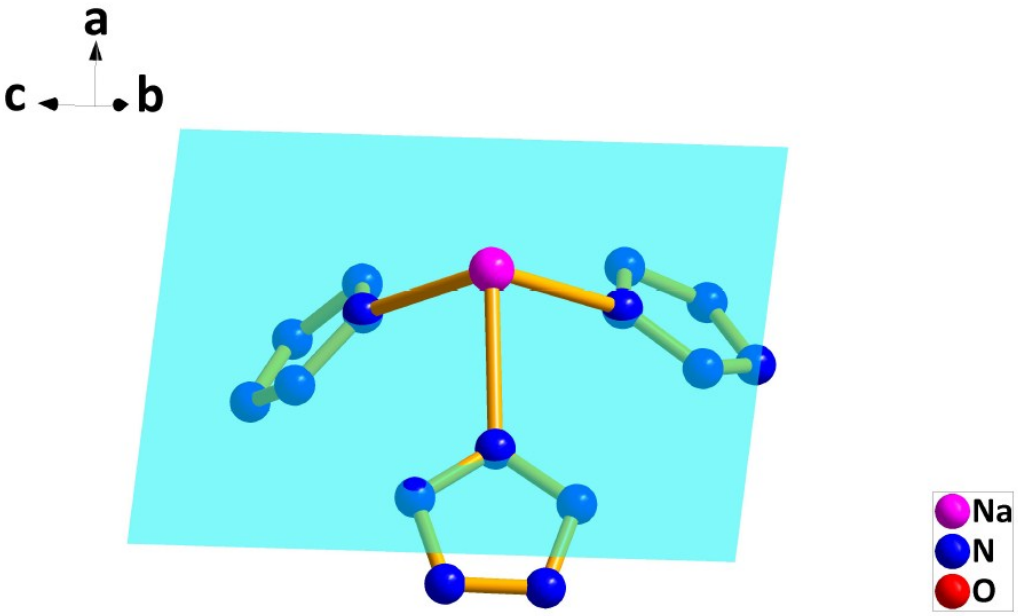

Fig. S9 Coordination environment of Na1 in crystal **2**.

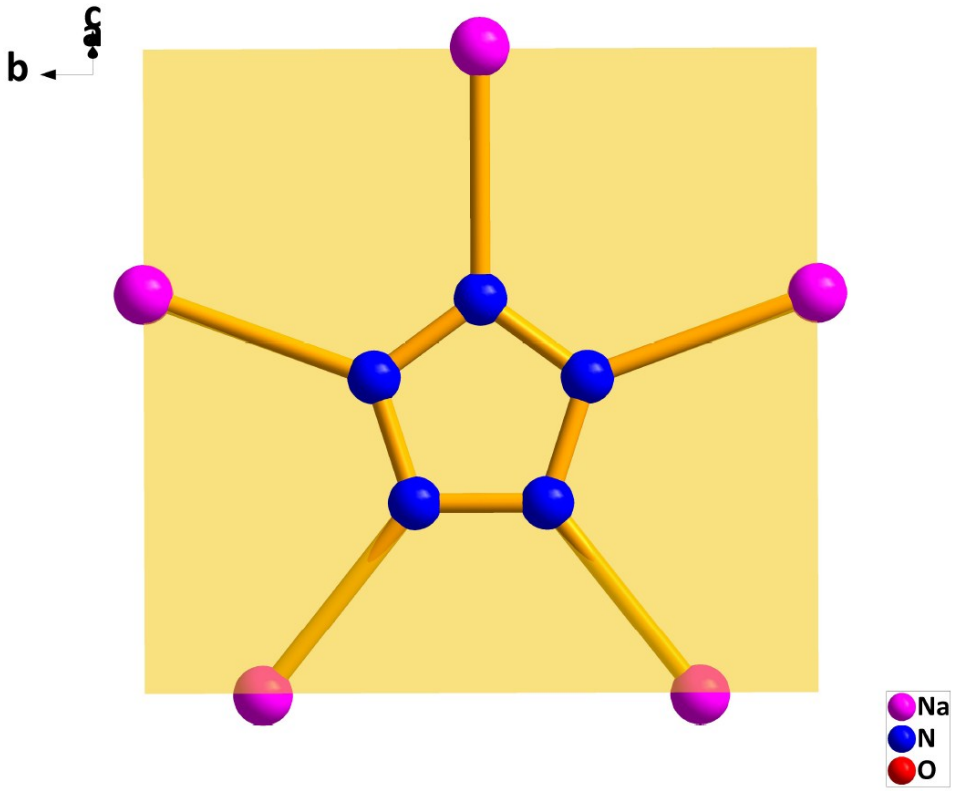

Fig. S10 Coordination model of *cyclo*-N_5^- in crystal **2**.

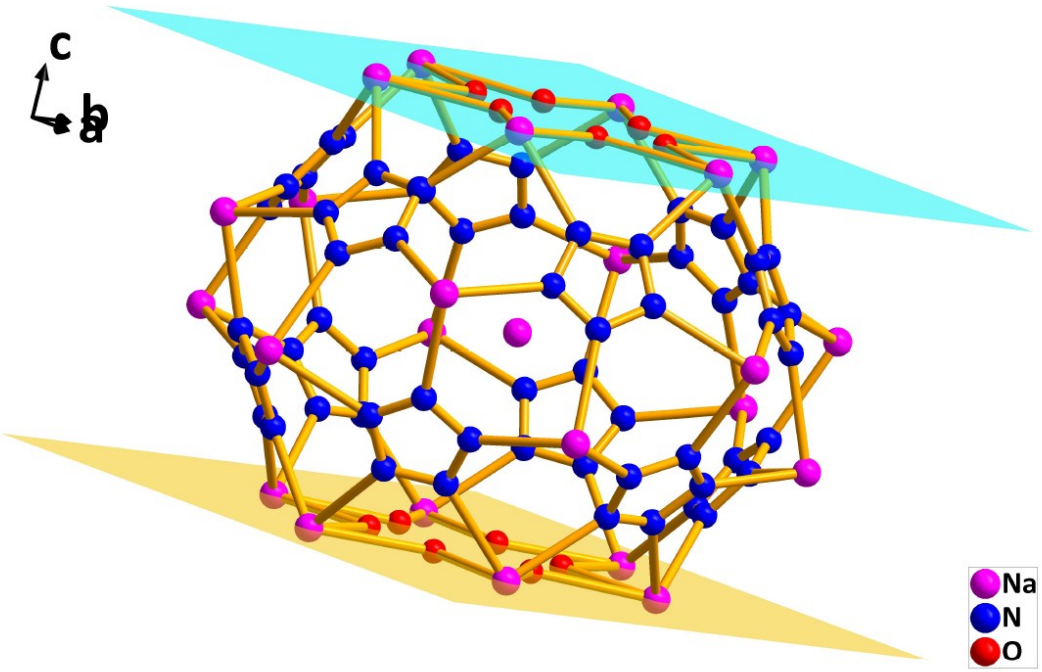

Fig. S11 Selected one cage in crystal **2**.

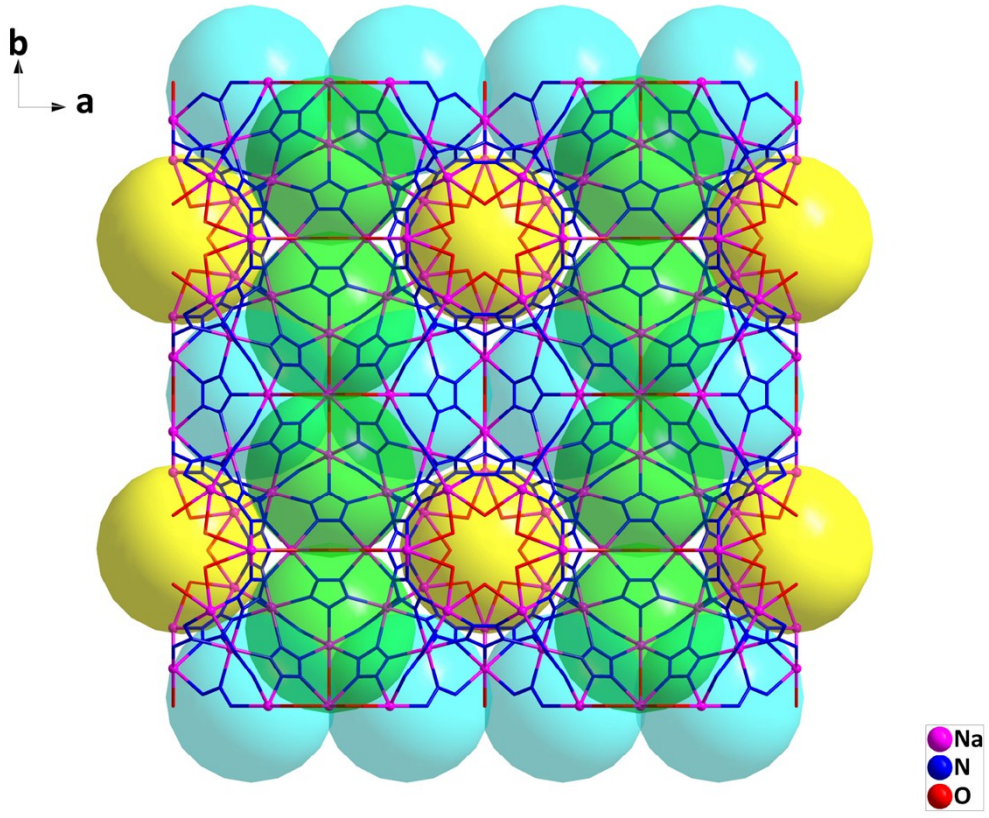

Fig. S12 3D framework of **2** view along c axis.

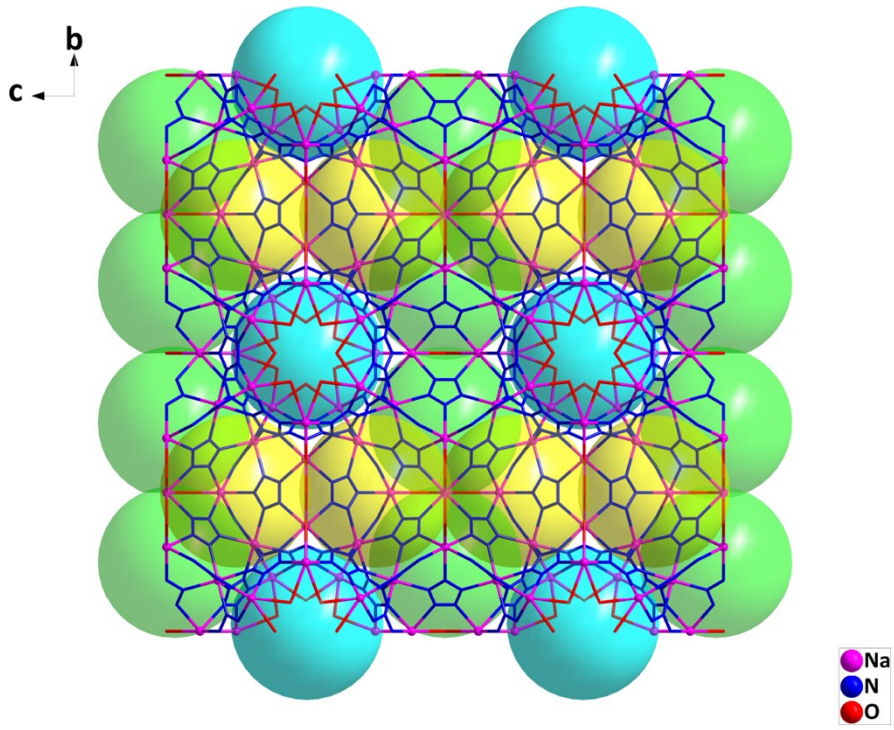

Fig. S13 3D framework of **2** view along a axis.

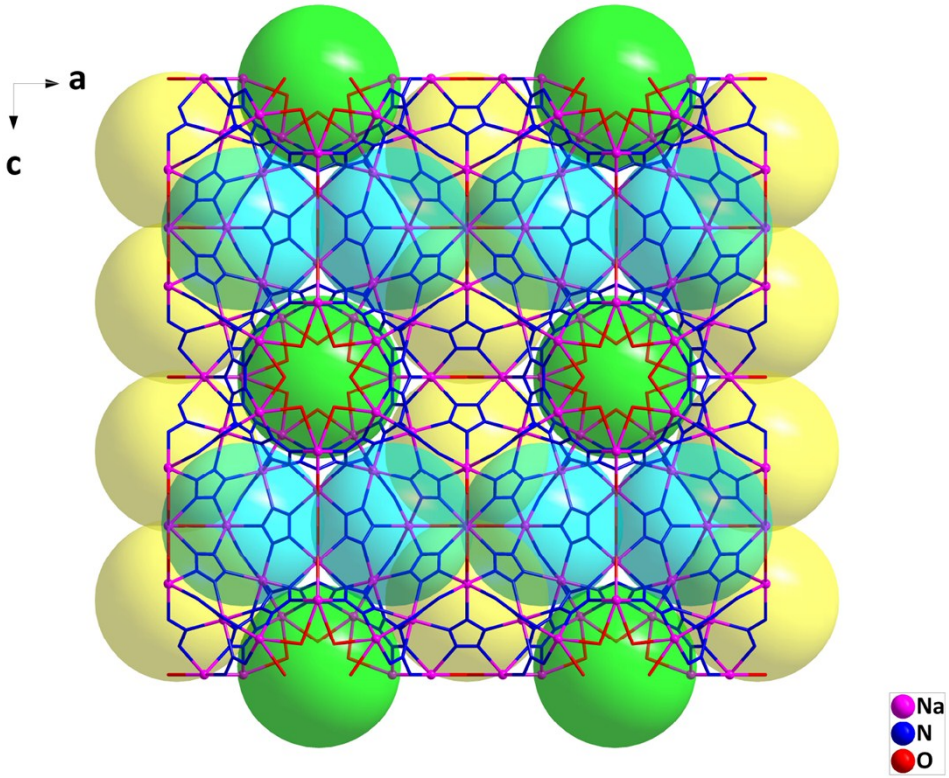

Fig. S14 3D framework of **2** view along b axis.

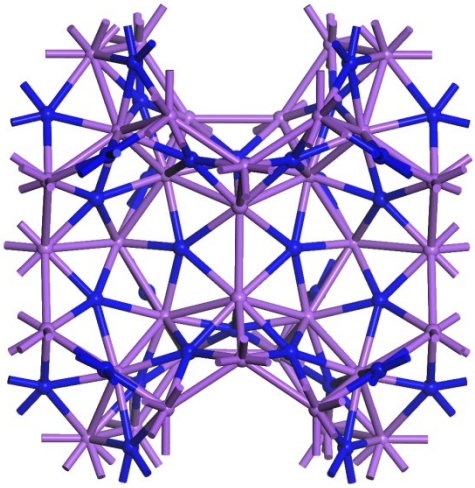

Fig. S15 A schematic representation of the topology, in which the *cyclo*-N_5^- ligands are represented by blue spheres and the Na ions are represented by purple spheres.

3. Computational Details

The experimental result for the constant volume combustion energy ($\Delta_c U$) of **2** is -4784.74 J g^{-1}. According to the formula $\Delta_c H_m^\theta = \Delta_c U_m^\theta + \Delta nRT, \Delta n = n_g(products) - n_g(reactants)$, ($n_g$ is the total molar amount of gases in the products or reactants, R = 8.314 J mol^{-1} K^{-1}, and T = 298.15 K), the enthalpy of combustion $(\Delta_c H_m^\theta)$ can be derived to be -3779.71 kJ mol^{-1} for eqn (1). The combustion reaction equation is listed as follows:

$$Na_8N_{40}H_6O_3(s) + 4\ O_2(g) \rightarrow 4\ Na_2O_2(s) + 3\ H_2O(l) + 20\ N_2(g) \quad (1)$$

$$\Delta_f H_m^\theta(2,s) = 4\ \Delta_f H_m^\theta(Na_2O_2, s) + 3\ \Delta_f H_m^\theta(H_2O, l) - \Delta_c H_m^\theta(1, s) \quad (2)$$

Based on the calculated enthalpy of combustion and the known enthalpy of formation of the combustion products[6] determined experimentally, Na_2O_2(s), $\Delta_c H_m^\theta$(Na_2O_2, s) = -510.9 kJ mol^{-1}, H_2O (l), $\Delta_c H_m^\theta$(H_2O, l) = -285.830 kJ mol^{-1}, the standard enthalpy of formation of **2**, $\Delta_c H_m^\theta$, was back-calculated from the combustion equation. On the basis of Hess's law in thermochemical eqn (2), the standard enthalpy of formation ($\Delta_f H_m^\theta$) of **2** is calculated to be 878.62 kJ mol^{-1}.

On the basis of the largest exothermic principle proposed by Kamlet-Jacobs (K-J),[7] We employed a widely used empirical method[8-10] which employed the hypothesis of BKW equation and arbitrary theory of the Kamlet-Jacobs method to investigate the detonation properties of metal-containing explosives. For systems with metals, the most stable products of detonation reaction were assumed under the constraints of stoichiometrically available oxygen.[11] The detonation reaction of **2** is described by equation (3), and the detonation properties are calculated by
K-J equations as follows:

$$Na_8N_{40}H_6O_3(s) \rightarrow 3\ Na_2O(s) + 2\ Na(s) + 2\ NH_3(g) + 19\ N_2(g) \quad (3)$$

$$D = 1.01\varphi^{\frac{1}{2}}(1 + 1.30\rho)$$
$$P = 1.558\varphi\rho^2$$
$$\varphi = 31.68N(MQ)^{1/2}$$
$$Q = \frac{-[\Delta_f H_m^\theta(detonation\ products) - \Delta_f H_m^\theta(explosive)]}{formula\ weight\ of\ explosive}$$

where: D is detonation velocity (km s^{-1}), 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 the chemical energy of detonation (kcal g^{-1}) and ρ is the density of explosive (g

cm^{-3}). According to the known enthalpies of formation, including NH_3(g) (-46 kJ mol^{-1}), Na_2O(s) (-416 kJ mol^{-1}) and the $\Delta_f H_m^\theta$ of **2**, the *Q* for **2** is 0.664 kcal·g^{-1}. Utilizing the above equation (3), and the known values of *N*, *M* and *Q*, the *D* and *P* can be obtained.

References

1 Y. Xu, Q. Wang, C. Shen, Q. Lin, P. Wang and M. Lu, *Nature*, 2017, **549**, 78-81.
2 *SAINT v7.68A* Bruker AXS Inc.: Madison, WI, 2009.
3 G. M. Sheldrick, *SHELXL-2014/7*, University of Göttingen, Germany, 2014.
4 *SADABS v2008/1* Bruker AXS Inc.: Madison, WI, 2008.
5 (*a*) A. L. Spek, *Acta Cryst. D*, 2009, **65**, 148-155. (*b*) A. L. Spek, *Acta Cryst. C*, 2015, **71**, 9-18.
6 J. D. Cox, D. D. Wagman and V. A. Medvedev, *CODATA Key Values for Thermodynamics*, Hemisphere Publishing Corp, New York, 1989.
7 M. J. Kamlet and S. Jacobs, *J. Chem. Phys*., 1968, **48**, 23-35.
8 Y. Wang, J. Zhang, H. Su, S. Li, S. Zhang and S. Pang, *J. Phys. Chem. A*, 2014, **118**, 4575-4581.
9 Y. Zhang, S. Zhang, L. Sun, Q. Yang, J. Han, Q. Wei, G. Xie, S. Chen and S. Gao, *Chem. Commun.*, 2017, **53**, 3034-3037.
10 X. Qu, S. Zhang, B. Wang, Q. Yang, J. Han, Q. Wei, G. Xie and S. Chen, *Dalton Trans.*, 2016, **45**, 6968-6973.
11 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.