Electronic Supplementary Information

$[Na_4(N_5)_4(H_2O)_2]\cdot H_2O\cdot 2MeOH$: a honeycomb-like sodium-pentazolate-framework with helical chains

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1. Single-crystal X-ray diffraction analysis of framework **1**

Table S1. Crystal data, data collection, and refinement for framework **1**

$H_2N_{10}Na_2O{\cdot}0.5(H_2O){\cdot}CH_4O$	D_x = 1.614 Mg m^{-3}
M_r = 245.15	Mo $K\alpha$ radiation, λ = 0.71073 Å
Trigonal, $P3_221$	Cell parameters from 9535 reflections
a = 9.6556 (6) Å	θ = 2.7–27.5°
c = 18.7426 (9) Å	μ = 0.21 mm^{-1}
V = 1513.3 (2) Å^3	T = 100 K
Z = 6	Needle, colourless
F(000) = 750	0.08 × 0.05 × 0.04 mm
Bruker APEX-II CCD diffractometer	2143 reflections with $I > 2\sigma(I)$
ϕ and ω scans	R_{int} = 0.081
Absorption correction: multi-scan *SADABS2016*/2 (Bruker,2016/2) was used for absorption correction. wR2(int) was 0.1717 before and 0.1205 after correction. The Ratio of minimum to maximum transmission is 0.8579. The λ/2 correction factor is Not present.	θ_{max} = 27.5°, θ_{min} = 2.7°
T_{min} = 0.549, T_{max} = 0.640	h = -12→12
12964 measured reflections	k = -12→12
2285 independent reflections	l = -24→22
Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.055	$w = 1/[\sigma^2(F_o^2) + (0.097P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.144	$(\Delta/\sigma)_{max} < 0.001$
S = 1.05	$\Delta\rangle_{max}$ = 0.55 e Å^{-3}
2285 reflections	$\Delta\rangle_{min}$ = -0.38 e Å^{-3}
147 parameters	Absolute structure: Flack x determined using 793 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
4 restraints	Absolute structure parameter: -0.2 (2)
Primary atom site location: dual	

Table S2. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for framework **1**

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Na2	0.2518 (2)	0.4756 (2)	0.78806 (10)	0.0083 (4)	

Na1	0.2012 (2)	0.7469 (2)	0.62081 (11)	0.0093 (4)	
N3	-0.2473 (5)	0.3349 (6)	0.7082 (3)	0.0130 (8)	
N2	-0.1516 (5)	0.3222 (5)	0.7551 (2)	0.0127 (9)	
N10	0.4649 (5)	1.1450 (5)	0.5869 (2)	0.0120 (9)	
N9	0.5777 (5)	1.2356 (5)	0.5416 (3)	0.0136 (8)	
N5	-0.0076 (5)	0.5107 (5)	0.6823 (2)	0.0120 (9)	
N4	-0.1574 (5)	0.4516 (5)	0.6627 (2)	0.0119 (8)	
N7	0.4907 (6)	0.9918 (5)	0.5127 (2)	0.0119 (9)	
O1	0.1970 (5)	0.2031 (5)	0.7668 (2)	0.0178 (7)	
H1A	0.175721	0.131776	0.798675	0.021*	
H1B	0.114791	0.167106	0.737155	0.021*	
O3	-0.3215 (6)	0.000000	0.666667	0.0323 (14)	
H3A	-0.422032	-0.075946	0.671768	0.049*	0.5
H3B	-0.310868	0.073601	0.695990	0.049*	0.5
N8	0.5956 (5)	1.1418 (5)	0.4949 (2)	0.0114 (8)	
N1	-0.0024 (5)	0.4311 (5)	0.7390 (2)	0.0110 (9)	
N6	0.4099 (5)	0.9930 (5)	0.5694 (2)	0.0125 (9)	
O2	-0.1306 (6)	-0.0538 (6)	0.7606 (2)	0.0335 (11)	
H2	-0.211088	-0.053055	0.743972	0.050*	
C1	-0.1420 (12)	-0.2014 (9)	0.7459 (4)	0.0433 (19)	
H1C	-0.192614	-0.274037	0.786261	0.065*	
H1D	-0.034691	-0.185860	0.738264	0.065*	
H1E	-0.206600	-0.247706	0.702853	0.065*	

Table S3. Atomic displacement parameters (Å^2) for framework **1**

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Na2	0.0085 (9)	0.0106 (9)	0.0070 (7)	0.0058 (7)	0.0003 (7)	0.0006 (7)
Na1	0.0086 (9)	0.0073 (9)	0.0089 (8)	0.0018 (8)	0.0010 (8)	0.0000 (7)
N3	0.0091 (18)	0.014 (2)	0.0119 (18)	0.0029 (17)	-0.0024 (19)	0.0053 (18)
N2	0.010 (2)	0.012 (2)	0.012 (2)	0.0025 (17)	0.0015 (17)	0.0048 (17)
N10	0.014 (2)	0.0092 (19)	0.011 (2)	0.0050 (17)	0.0020 (18)	-0.0020 (17)
N9	0.015 (2)	0.0099 (18)	0.0124 (18)	0.0039 (17)	0.006 (2)	0.002 (2)
N5	0.0098 (18)	0.011 (2)	0.012 (2)	0.0029 (17)	-0.0023 (16)	0.0010 (17)
N4	0.0082 (19)	0.0134 (19)	0.0105 (19)	0.0028 (17)	-0.0013 (15)	0.0031 (17)
N7	0.017 (2)	0.0057 (17)	0.011 (2)	0.0042 (16)	0.0039 (16)	0.0024 (16)
O1	0.0147 (17)	0.0112 (17)	0.0250 (14)	0.0045 (15)	0.0000 (16)	0.0017 (16)
O3	0.028 (2)	0.023 (3)	0.044 (3)	0.0115 (16)	-0.0055 (15)	-0.011 (3)
N8	0.013 (2)	0.0075 (18)	0.0101 (19)	0.0029 (16)	0.0039 (17)	0.0015 (14)

N1	0.0081 (19)	0.012 (2)	0.0103 (18)	0.0035 (17)	-0.0011 (17)	0.0029 (16)
N6	0.011 (2)	0.0094 (19)	0.014 (2)	0.0032 (17)	0.0019 (16)	0.0018 (18)
O2	0.030 (2)	0.038 (3)	0.033 (2)	0.016 (2)	-0.0006 (19)	-0.004 (2)
C1	0.056 (5)	0.034 (4)	0.030 (4)	0.016 (4)	-0.003 (3)	-0.008 (3)

Table S4. Geometric parameters (Å, º) for framework **1**

Na2—Na1^{i}	3.827 (3)	N10—N6	1.328 (6)
Na2—N2^{ii}	2.505 (5)	N9—N8	1.332 (6)
Na2—N9^{iii}	2.471 (5)	N5—N4	1.315 (6)
Na2—N4^{i}	2.489 (5)	N5—N1	1.326 (6)
Na2—N7^{iv}	2.509 (5)	N7—N8	1.331 (6)
Na2—O1	2.443 (4)	N7—N6	1.321 (6)
Na2—N1	2.449 (5)	O1—H1A	0.8551
Na1—N3^{i}	2.580 (5)	O1—H1B	0.8856
Na1—N10^{iii}	2.598 (5)	O3—H3A	0.8815
Na1—N5	2.448 (5)	O3—H3A^{vii}	0.88 (16)
Na1—O1^{v}	2.498 (4)	O3—H3B^{vii}	0.86 (6)
Na1—N8^{vi}	2.515 (5)	O3—H3B	0.8629
Na1—N6	2.419 (5)	O2—H2	0.8400
N3—N2	1.326 (6)	O2—C1	1.402 (10)
N3—N4	1.332 (6)	C1—H1C	0.9800
N2—N1	1.326 (6)	C1—H1D	0.9800
N10—N9	1.311 (6)	C1—H1E	0.9800
N2^{ii}—Na2—Na1^{i}	129.92 (12)	N3—N2—N1	107.8 (4)
N2^{ii}—Na2—N7^{iv}	86.72 (15)	N1—N2—Na2^{ii}	124.9 (3)
N9^{iii}—Na2—Na1^{i}	130.75 (14)	N9—N10—Na1^{iii}	120.3 (3)
N9^{iii}—Na2—N2^{ii}	84.24 (16)	N9—N10—N6	108.4 (4)
N9^{iii}—Na2—N4^{i}	82.53 (16)	N6—N10—Na1^{iii}	126.5 (3)
N9^{iii}—Na2—N7^{iv}	93.87 (16)	N10—N9—Na2^{iii}	130.7 (3)
N4^{i}—Na2—Na1^{i}	58.41 (11)	N10—N9—N8	108.6 (4)
N4^{i}—Na2—N2^{ii}	166.10 (17)	N8—N9—Na2^{iii}	119.6 (3)
N4^{i}—Na2—N7^{iv}	89.93 (15)	N4—N5—Na1	119.1 (3)
N7^{iv}—Na2—Na1^{i}	60.45 (11)	N4—N5—N1	109.0 (4)
O1—Na2—Na1^{i}	39.77 (10)	N1—N5—Na1	131.7 (3)
O1—Na2—N2^{ii}	105.53 (16)	N3—N4—Na2^{v}	130.9 (3)
O1—Na2—N9^{iii}	169.68 (18)	N5—N4—Na2^{v}	120.5 (3)
O1—Na2—N4^{i}	87.47 (14)	N5—N4—N3	107.3 (4)

O1—Na2—N7^{iv}	83.53 (15)	N8—N7—Na2^{viii}	116.8 (3)
O1—Na2—N1	95.24 (15)	N6—N7—Na2^{viii}	132.7 (3)
N1—Na2—Na1^{i}	120.72 (12)	N6—N7—N8	108.9 (4)
N1—Na2—N2^{ii}	89.79 (15)	Na2—O1—Na1^{i}	101.49 (16)
N1—Na2—N9^{iii}	88.03 (15)	Na2—O1—H1A	126.1
N1—Na2—N4^{i}	93.99 (15)	Na2—O1—H1B	101.2
N1—Na2—N7^{iv}	175.84 (16)	Na1^{i}—O1—H1A	104.8
N3^{i}—Na1—Na2^{v}	130.22 (13)	Na1^{i}—O1—H1B	115.4
N3^{i}—Na1—N10^{iii}	80.32 (16)	H1A—O1—H1B	108.4
N10^{iii}—Na1—Na2^{v}	134.01 (12)	H3A—O3—H3A^{vii}	93.5
N5—Na1—Na2^{v}	59.94 (11)	H3A—O3—H3B	104.1
N5—Na1—N3^{i}	96.65 (16)	H3A^{vii}—O3—H3B^{vii}	104.1
N5—Na1—N10^{iii}	86.56 (14)	H3A—O3—H3B^{vii}	49.8
N5—Na1—O1^{v}	90.35 (15)	H3B—O3—H3A^{vii}	49.8
N5—Na1—N8^{vi}	91.31 (15)	H3B—O3—H3B^{vii}	146.0
O1^{v}—Na1—Na2^{v}	38.74 (10)	N9—N8—Na1^{ix}	132.1 (3)
O1^{v}—Na1—N3^{i}	157.28 (17)	N7—N8—Na1^{ix}	120.3 (3)
O1^{v}—Na1—N10^{iii}	121.79 (15)	N7—N8—N9	106.7 (4)
O1^{v}—Na1—N8^{vi}	77.83 (14)	N2—N1—Na2	130.5 (3)
N8^{vi}—Na1—Na2^{v}	59.08 (11)	N2—N1—N5	107.5 (4)
N8^{vi}—Na1—N3^{i}	80.42 (16)	N5—N1—Na2	121.6 (3)
N8^{vi}—Na1—N10^{iii}	160.24 (16)	N10—N6—Na1	131.5 (3)
N6—Na1—Na2^{v}	122.49 (12)	N7—N6—Na1	121.1 (3)
N6—Na1—N3^{i}	84.74 (15)	N7—N6—N10	107.3 (4)
N6—Na1—N10^{iii}	89.01 (15)	C1—O2—H2	109.5
N6—Na1—N5	175.06 (17)	O2—C1—H1C	109.5
N6—Na1—O1^{v}	90.13 (14)	O2—C1—H1D	109.5
N6—Na1—N8^{vi}	93.60 (15)	O2—C1—H1E	109.5
N2—N3—Na1^{v}	132.4 (3)	H1C—C1—H1D	109.5
N2—N3—N4	108.3 (4)	H1C—C1—H1E	109.5
N4—N3—Na1^{v}	115.8 (3)	H1D—C1—H1E	109.5
N3—N2—Na2^{ii}	119.5 (3)		
Na2^{ii}—N2—N1—Na2	38.4 (6)	N3—N2—N1—Na2	-172.7 (3)
Na2^{ii}—N2—N1—N5	-148.6 (3)	N3—N2—N1—N5	0.3 (5)
Na2^{iii}—N9—N8—Na1^{ix}	-21.9 (6)	N2—N3—N4—Na2^{v}	166.2 (3)
Na2^{iii}—N9—N8—N7	169.3 (3)	N2—N3—N4—N5	-0.6 (6)
Na2^{viii}—N7—N8—Na1^{ix}	22.4 (5)	N10—N9—N8—Na1^{ix}	168.9 (4)
Na2^{viii}—N7—N8—N9	-167.3 (3)	N10—N9—N8—N7	0.2 (6)

Na2^{viii}—N7—N6—Na1	-16.7 (6)	N9—N10—N6—Na1	-178.7 (3)
Na2^{viii}—N7—N6—N10	164.3 (4)	N9—N10—N6—N7	0.1 (6)
Na1^{v}—N3—N2—Na2^{ii}	-6.3 (6)	N4—N3—N2—Na2^{ii}	151.0 (3)
Na1^{v}—N3—N2—N1	-157.1 (4)	N4—N3—N2—N1	0.2 (6)
Na1^{v}—N3—N4—Na2^{v}	-32.2 (6)	N4—N5—N1—Na2	173.1 (3)
Na1^{v}—N3—N4—N5	160.9 (3)	N4—N5—N1—N2	-0.7 (5)
Na1^{iii}—N10—N9—Na2^{iii}	-10.6 (6)	N8—N7—N6—Na1	179.0 (3)
Na1^{iii}—N10—N9—N8	156.9 (3)	N8—N7—N6—N10	0.0 (5)
Na1^{iii}—N10—N6—Na1	26.0 (6)	N1—N5—N4—Na2^{v}	-167.6 (3)
Na1^{iii}—N10—N6—N7	-155.3 (3)	N1—N5—N4—N3	0.9 (6)
Na1—N5—N4—Na2^{v}	17.3 (5)	N6—N10—N9—Na2^{iii}	-167.7 (3)
Na1—N5—N4—N3	-174.2 (3)	N6—N10—N9—N8	-0.2 (6)
Na1—N5—N1—Na2	-12.7 (6)	N6—N7—N8—Na1^{ix}	-170.5 (3)
Na1—N5—N1—N2	173.5 (4)	N6—N7—N8—N9	-0.1 (6)

Symmetry codes: (i) *x*-*y*+1, -*y*+1, -*z*+4/3; (ii) -*x*, -*x*+*y*, -*z*+5/3; (iii) *x*-*y*+1, -*y*+2, -*z*+4/3; (iv) -*x*+*y*, -*x*+1, *z*+1/3; (v) *x*-*y*, -*y*+1, -*z*+4/3; (vi) *y*-1, *x*, -*z*+1; (vii) *x*-*y*, -*y*, -*z*+4/3; (viii) -*y*+1, *x*-*y*+1, *z*-1/3; (ix) *y*, *x*+1, -*z*+1.

Table S5. Hydrogen bonds (Å, º) for framework **1**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···O2^{ii}	0.86	2.07	2.816 (6)	145
O1—H1*B*···O2	0.89	2.30	2.885 (6)	123
O2—H2···O3	0.84	2.01	2.779 (7)	152
O3—H3*A*···N3	0.88	2.35	3.043(6)	135
O3—H3*B*···N2	0.86	2.38	3.164(4)	151
O3—H3*B*···N3	0.86	2.29	3.043(5)	146

Symmetry code: (ii) -*x*, -*x*+*y*, -*z*+5/3.

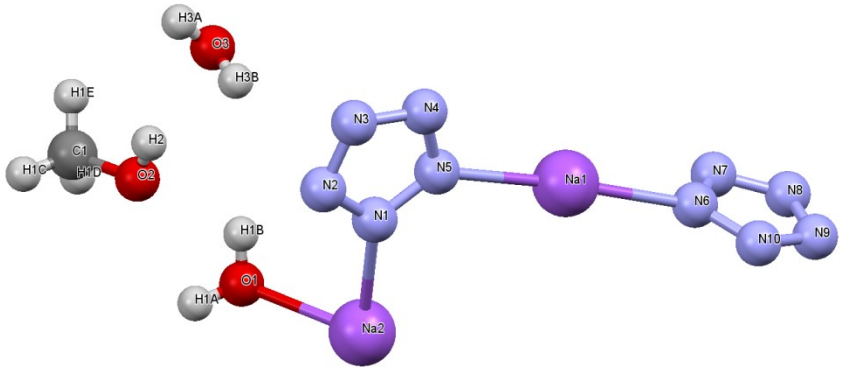


Fig. S1 The asymmetric unit of framework **1**.

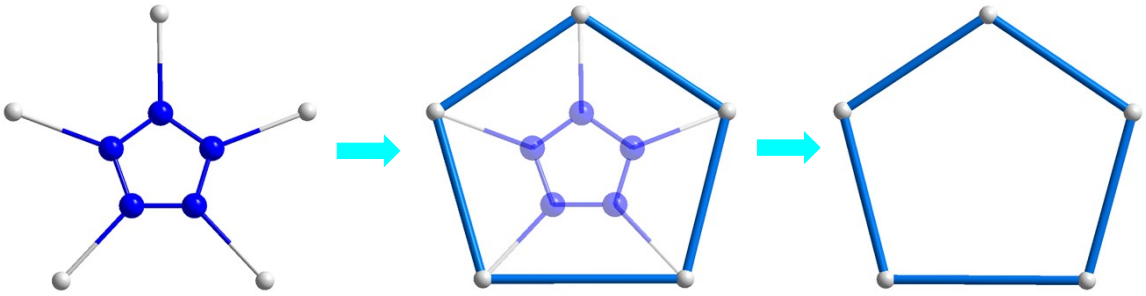


Fig. S2 Simplify the Na_5N_5 building unit into an enlarged pentagon.

2. IR spectra

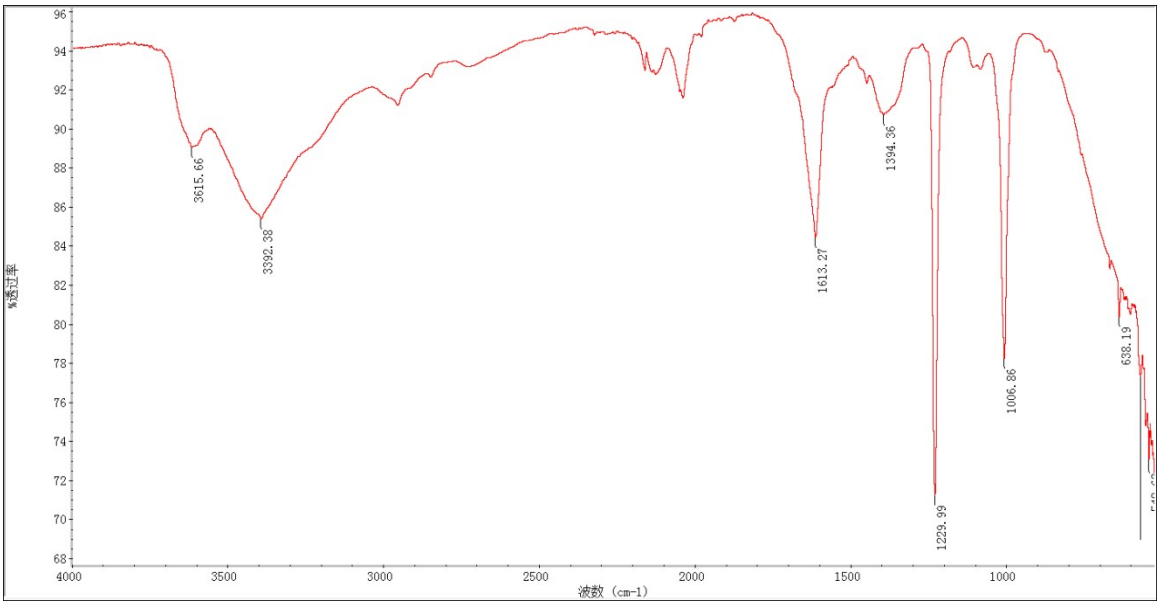


Fig. S3 The IR spectrum of framework **1**.

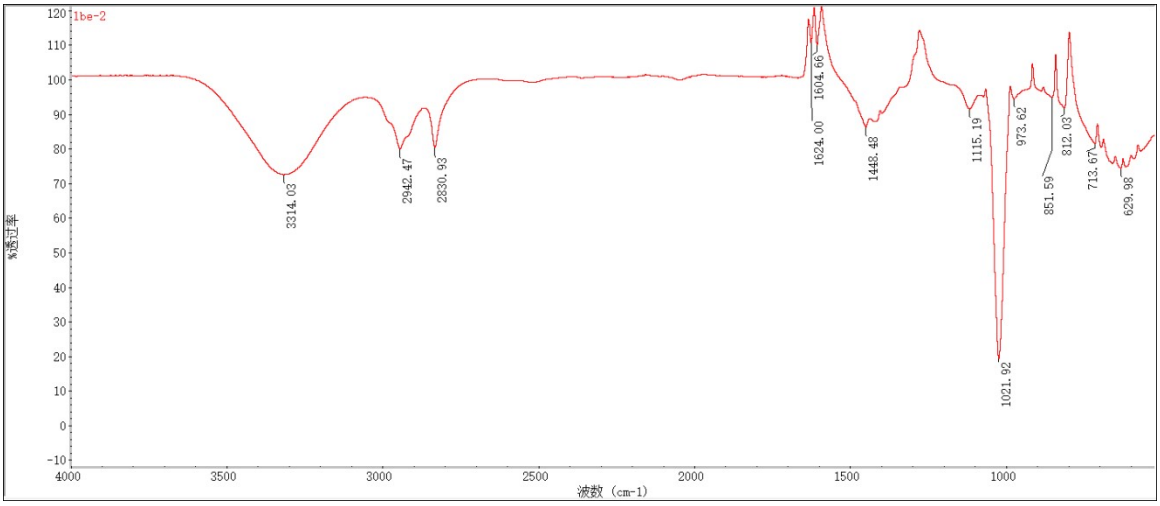


Fig. S4 The IR spectrum of MeOH.

3. PXRD patterns of framework **1**

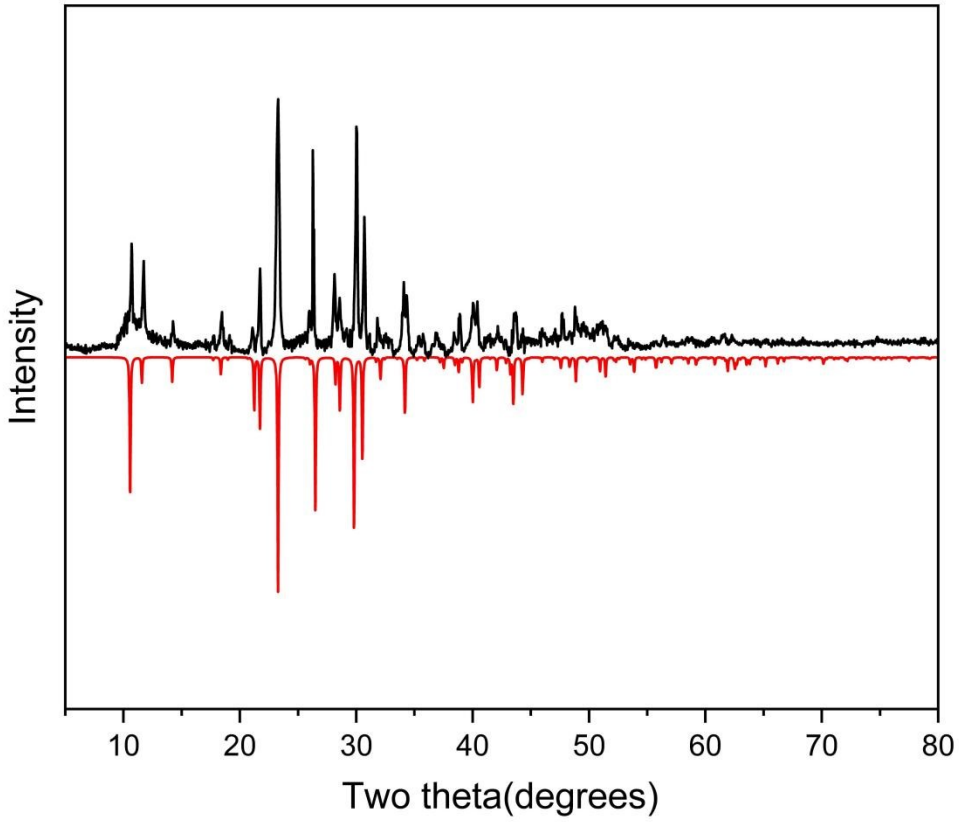


Fig. S5 The PXRD pattern (in black) of framework **1** and the calculated pattern (in red) from its single-crystal structure

4. Experimental section

4.1 Caution

Although no explosion or hazards were observed during the preparation and handling of these energetic compounds, all the materials investigated are potentially energetic materials. Small-scale syntheses are strongly encouraged. Manipulations must be carried out in a hood behind a safety shield. Eye protection and leather gloves must be worn at all times.

4.2 General methods

All reagents were purchased from Energy chemical in analytical grade and were used as supplied, if not stated otherwise. The decomposition (onset) points were obtained on a differential scanning calorimeter (NETZSCH DSC 204 F1 Phoenix) at a scan rate of 5 ^{o}C min^{-1} in closed Al containers with a high-purity nitrogen flow of 50 mL min^{-1}. IR spectra were recorded on a Thermo Nicolet iS10 spectrometer equipped with a Thermo Scientific Smart iTR diamond ATR accessory. Elemental analyses were carried out on a vario EL

III CHNOS elemental analyzer. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer using Cu Kα (λ = 1.5406 Å) radiation.

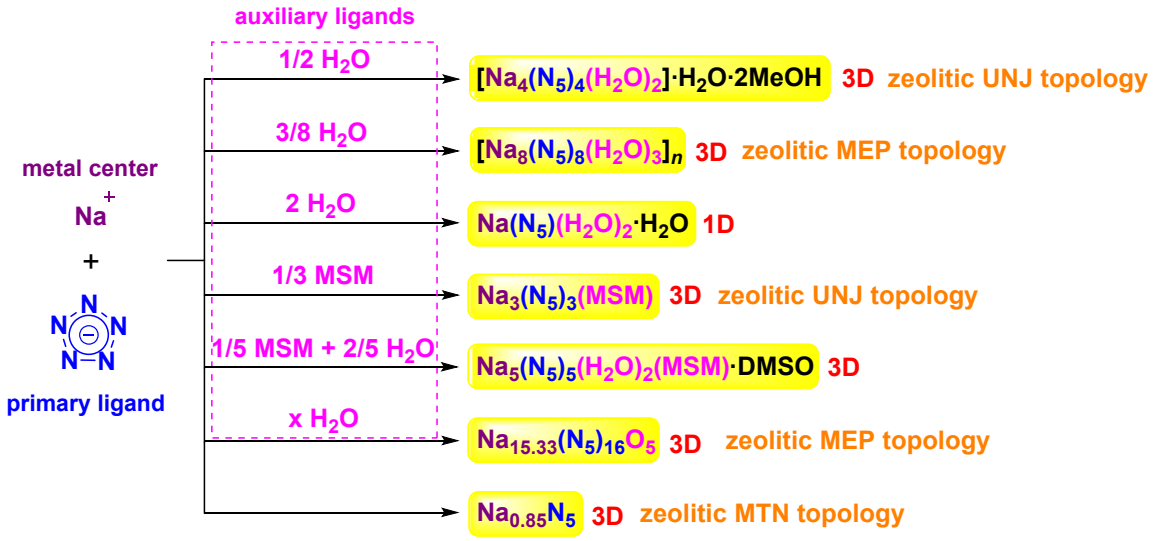
4.3 X-ray crystallography

A colourless needle crystal of dimensions 0.08 × 0.05 × 0.04 mm^3 was mounted 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[1]. The structures were solved by intrinsic using SHELXT2015[2] and refinement was carried out by a full-matrix least-squares technique using SHELXL2014[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. Data were corrected for the effects of absorption using SADABS[4] Relevant crystal data and refinement results are summarized in Table S1.

4.4 Synthesis procedures

NaN_5 was synthesized according to our previously published procedures.[5]

$[Na_4(N_5)_4(H_2O)_2]\cdot H_2O\cdot 2MeOH$: 100 mg (1 mmol) NaN_5 was dissolved into the mixture of ammonia (2 M) in MeOH (5 mL) and H_2O (3 mL) under ultrasonic. The mixture was then placed in the dark at ambient temperature for several days to obtain colorless crystals of $[Na_4(N_5)_4(H_2O)_2]\cdot H_2O\cdot 2MeOH$. Yield: 97.5 mg, 74 %. IR (ATR): 3616, 3392, 1613, 1394, 1230, 1007, 638 cm^{-1}. Elem anal. Calcd (%) for $C_2H_{14}Na_4N_{20}O_5$ (MW = 490.228): C 4.90, N 57.14, H 2.88; Found: C 4.82, N 57.20, H 2.81.



Scheme S1 Syntheses of sodium-pentazolate-frameworks. MSM = (methylsufonyl)methane; DMSO = dimethyl sulfoxide.

5. The theoretical simulation of the porosity of framework **1**

The accessible surface area (Sacc) and total free volume (Vfree) were calculated through the probes with a diameter of 0.364 nm and 0 nm, respectively (Fig. S6). The calculated BET surface area and the pore volume of framework **1** are 614.3 m^2 g^{-1} and 0.28 cm^3 g^{-1}, respectively. In addition, the pore total accessible volume of framework **1** is about 34.1% as calculated by *PLATON* program (see *ref. ActaCrystallogr., Sect. A: Found. Crystallogr.*, 1990, 46, C34).

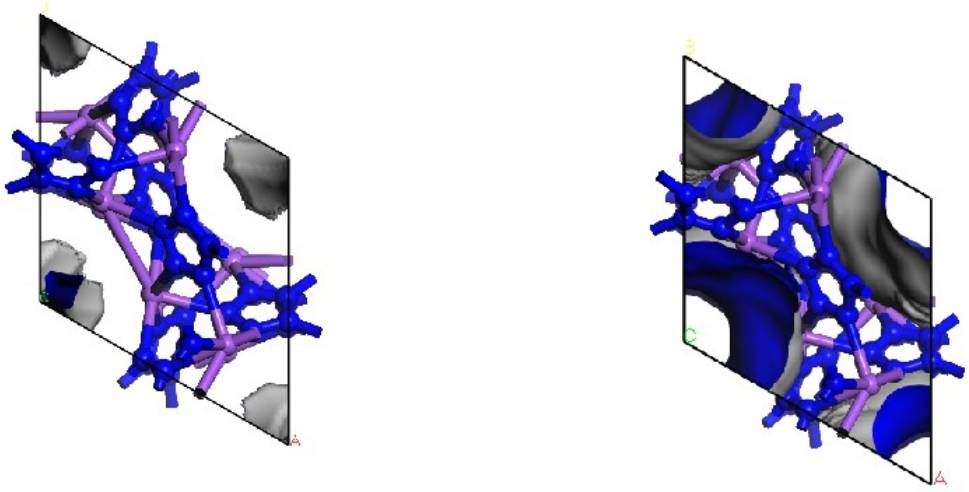


Fig. S6 Visualization pores in framework **1** by probes of diameter 0.364 nm (left) and 0 nm (right). Computational results obtained using software programs from Dassault Systèmes BIOVIA. The accessible surface area and total free volume of each calculation was performed with the Atoms Volume & Surfaces, and graphical displays generated with BIOVIA Materials Studio (2017).

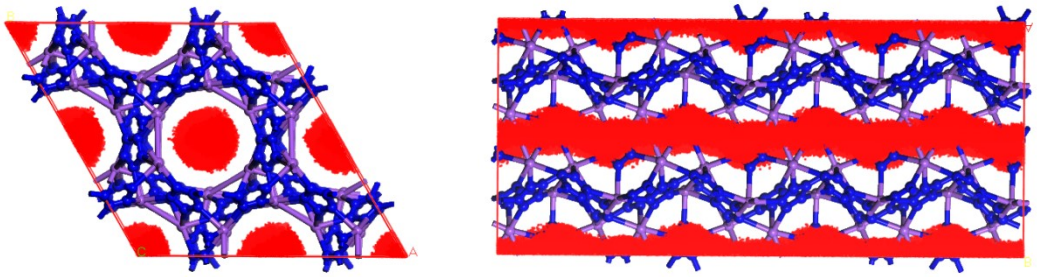


Fig. S7 The calculated N_2 absorption diagram of $[Na_4(N_5)_4(H_2O)_2]\cdot H_2O\cdot 2MeOH$ (the water molecules and methanol molecule were removed) at 1 atm and 273 K (2.58 mmol g^{-1}). The adsorption of N_2 onto $[Na_4(N_5)_4(H_2O)_2]\cdot H_2O\cdot 2MeOH$ (the water molecules and methanol molecule were removed) was based on the Metropolis Monte Carlo method（N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, E. Teller, J. Chem. Phys. 21 (1953) 1087–1092.）and was simulated using Sorption Module of Material Studio packages (2017). The graphical displays generated with BIOVIA Materials Studio (2017).

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