

Supplementary Information

Cation-intercalated copper azide breaks the safety–energy Trade-off in primary explosives

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1. Tables

Table S1. Selected synthetic conditions for CA-based primary explosives with superior initiating efficiency to LA.

Compounds	Main raw material	Temperature	Time	Note
MOFT-CA	HUKST-1 (customized, literature-based), HN_3	400 °C (carbonization)	1260 min	Ref 1
CA@C Shell	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 3-amino-1,2,4-triazole-5-carboxylic acid, 1,3,5-benzenetricarboxylate, 1,3,5-benzenetri-carbaldehyde, tris(4-aminophenyl)benzene, HN_3	150 °C (synthesis of precursor Cu-MOF- NH_2), 80 °C (synthesis of precursor Cu-MOF@COF), 600 °C (carbonized)	10395 min	Ref 2
Cu-MTZ	1-methyl-5H-tetrazole (customized, literature-based), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, NaN_3	RT	16 min	Ref 3
CAA-1	4-amino-1,2,4-triazole, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, NaN_3	80 °C	35 min	Ref 4
CMA	5-amino-2-methyl-tetrazole,	80 °C	35 min	Ref 4

	Cu(NO ₃) ₂ ·3H ₂ O, NaN ₃			
Cu-1-BMTTZ	1,3-bis(1-methyltetrazol-5-yl)triaz-1-ene (customized, literature-based), Cu(ClO ₄) ₂ ·6H ₂ O, NaN ₃	140 °C	4320 min	Ref 5
Cu-2-BMTTZ	1,3-bis(2-methyltetrazol-5-yl)triaz-1-ene (customized, literature-based), Cu(NO ₃) ₂ ·3H ₂ O, NaN ₃	140 °C	480 min	Ref 6
CMA-1	1-methyl-5-aminotetrazole, CuCl ₂ ·2H ₂ O, NaN ₃	70 °C	40 min	Ref 7
CMA-2	1-methyl-5-aminotetrazole, CuCl ₂ ·2H ₂ O, NaN ₃	70 °C	40 min	Ref 7
ICA-1	Tetraethylammonium chloride, Cu(NO ₃) ₂ , NaN ₃	RT	< 10 min	This work

1 **Table S2. Crystallographic data and structure refinements for ICA-1.**

Compound	ICA-1
Formula	C ₁₆ H ₄₀ N ₅₆ Cu ₈
Formula weight	1525.36
<i>T</i> /K	100.0(1)
λ /Å	1.54184
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁
<i>a</i> /Å	8.6582(1)
<i>b</i> /Å	24.7519(3)
<i>c</i> /Å	11.8844(1)
α /°	90
β /°	91.136(1)
γ /°	90
<i>V</i> /Å ³	2546.41(5)
<i>Z</i>	2
<i>D_c</i> /g cm ⁻³	1.989
reflns coll.	13883
unique reflns	8122
<i>R</i> _{int}	0.0235
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)] ^[a]	0.0253
<i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] ^[b]	0.0674
<i>R</i> ₁ (all data)	0.0254
<i>wR</i> ₂ (all data)	0.0675
GOF on <i>F</i> ²	1.067
BASF	0.42(2)
Completeness	0.985
CCDC number	2558505

2 ^[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; ^[b] $wR_2 = \{\Sigma w[(F_o)^2 - (F_c)^2]^2/\Sigma w[(F_o)^2]^2\}^{1/2}$

1 **Table S3. Selected bond distances (Å) for ICA-1.**

ICA-1			
Cu1–N31	2.015(3)	Cu7–N101	2.014(3)
Cu1–N41	2.011(3)	Cu7–N151	1.990(3)
Cu1–N61B	2.362(3)	Cu7–N141	2.394(3)
Cu1–N201	2.016(3)	Cu7–N161	2.025(3)
Cu1–N121J	2.001(3)	Cu7–N111	2.008(3)
Cu2–N41	2.040(3)	Cu6–N131	2.015(3)
Cu2–N51	1.975(3)	Cu6–N101	2.012(3)
Cu2–N201	2.000(3)	Cu6–N141	1.983(3)
Cu2–N191	2.013(3)	Cu6–N93	1.992(3)
Cu2–N143D	2.438(3)	Cu5–N81	1.998(3)
Cu8–N131A	2.030(3)	Cu5–N161	2.011(3)
Cu8–N151	2.010(3)	Cu5–N171	2.023(3)
Cu8–N93A	2.330(3)	Cu5–N191A	2.369(3)
Cu8–N121	2.016(3)	Cu5–N71	2.007(3)
Cu8–N111	2.001(3)	Cu4–N91	2.469(4)
Cu3–N81B	2.028(3)	Cu4–N181	1.991(3)
Cu3–N31A	2.023(3)	Cu4–N171	2.040(3)
Cu3–N51	2.011(3)	Cu4–N61	2.011(3)
Cu3–N181	2.009(3)	Cu4–N71	1.995(3)

2 Symmetry codes: A) $x - 1, y, z$; B) $x + 1, y, z$; C) $x - 1, y, z + 1$; D) $x + 1, y, z - 1$; E) $x, y, z - 1$; F)
3 $-x, y + 1/2, -z + 1$; G) $-x + 1, y + 1/2, -z + 1$; H) $-x + 2, y + 1/2, -z + 1$; I) $x, y, z + 1$; J) $x + 2, y, z$
4 $- 1$; K) $x - 2, y, z + 1$.

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1 **Table S4. Selected unbonded N⋯N distances (Å) for ICA-1.**

N⋯N	distances (Å)
N111B⋯N151B	2.5518
N121B⋯N131	2.7283
N131⋯N93	2.7358
N131⋯N141	2.9526
N141⋯N101	2.7133
N93⋯N101	2.9057
N101⋯N161	2.7494
N81B⋯N181	2.8811
N51⋯N31A	2.8345
N181⋯N61	2.6828
N31A⋯N61	2.9452
N171⋯N71	2.5595
N31A⋯N121D	2.9141
N201A⋯N41A	2.5771
N161⋯N81	2.8985
N191A⋯N81	2.9744
N191A⋯N51A	2.6609

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1 **Table S5. Nonclassical weak hydrogen-bond geometries (Å, °) for ICA-1.**

D–H···A	$d_{(D-H)}/\text{\AA}$	$d_{(H\cdots A)}/\text{\AA}$	$d_{(D\cdots A)}/\text{\AA}$	D–H···A/°
C11–H11B···N153	0.99	2.55	3.294(6)	132
C13–H13A···N113	0.99	2.52	3.420(6)	151
C13–H13B···N53	0.99	2.56	3.340(6)	136
C21–H21B···N163	0.99	2.57	3.415(5)	144
C23–H23B···N63	0.99	2.55	3.481(5)	157
C25–H25B···N193	0.99	2.56	3.538(5)	168
C27–H27B···N103	0.99	2.53	3.300(5)	135

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Table S6. The results of the long-term thermal stability test of ICA-1.

Two grams of **ICA-1** were heated under vacuum at 75 °C for 48 h. The weight difference of the sample before and after treatment was recorded, and the long-term thermal stability of **ICA-1** was evaluated based on the corresponding mass loss fraction.

Item	No. 1	No. 2	Average
mass loss of the sample [mg]	0.70	0.60	0.65
mass fraction of the sample loss [%]	0.035	0.030	0.032

1 **Table S7. Independent elastic constants C_{ij} (GPa) of LA, CA, and ICA-1.** LA and CA:
2 orthorhombic $Pnma$ (#62, 9 independent constants); **ICA-1:** monoclinic $P2_1$ (#4, 13 independent
3 constants). Entries marked — are symmetry-forbidden (identically zero).

C_{ij}	LA	CA	ICA-1
C_{11}	67.7	52.8	41.8
C_{22}	69.6	82.2	26.5
C_{33}	28.3	44.8	26.3
C_{12}	26.1	16.7	5.6
C_{13}	19.8	28.3	9.7
C_{23}	21.2	7.1	8.8
C_{44}	14.7	5.0	5.4
C_{55}	16.6	26.0	9.0
C_{66}	15.1	9.6	5.5
C_{15}	—	—	−4.2
C_{25}	—	—	1.1
C_{35}	—	—	−2.5
C_{46}	—	—	−0.04

Table S8. Polycrystalline VRH moduli and anisotropy indices of LA, CA, and ICA-1.

Property	LA	CA	ICA-1
B_H (GPa)	30.3	31.7	15.5
G_V (GPa)	15.9	16.6	8.7
G_R (GPa)	14.4	10.6	7.3
G_H (GPa)	15.1	13.6	8.0
E (GPa)	38.9	35.8	20.5
ν	0.286	0.312	0.280
B/G_H	2.00	2.33	1.94
A^U	0.72	2.83	0.97

Table S9. Cauchy pressures (GPa) of LA, CA, and ICA-1.

Component	LA	CA	ICA-1
$C_{12} - C_{66}$	+11.0	+7.1	+0.1
$C_{13} - C_{55}$	+3.2	+2.3	+0.8
$C_{23} - C_{44}$	+6.5	+2.1	+3.4
Mean	+6.9	+3.8	+1.4

Table S10. Input ignition energy evaluation tests for LA.

Charging voltage (V)	Ignition delay time (ms)
2	×
2.5	19.07
3	11.43

The result is recorded as “×” for “not responding”.

Table S11. Input ignition energy evaluation tests for ICA-1.

Charging voltage (V)	Ignition delay time (ms)
2	20.97
2.5	11.59
3	8.41

The result is recorded as “×” for “not responding”.

2. Graphics

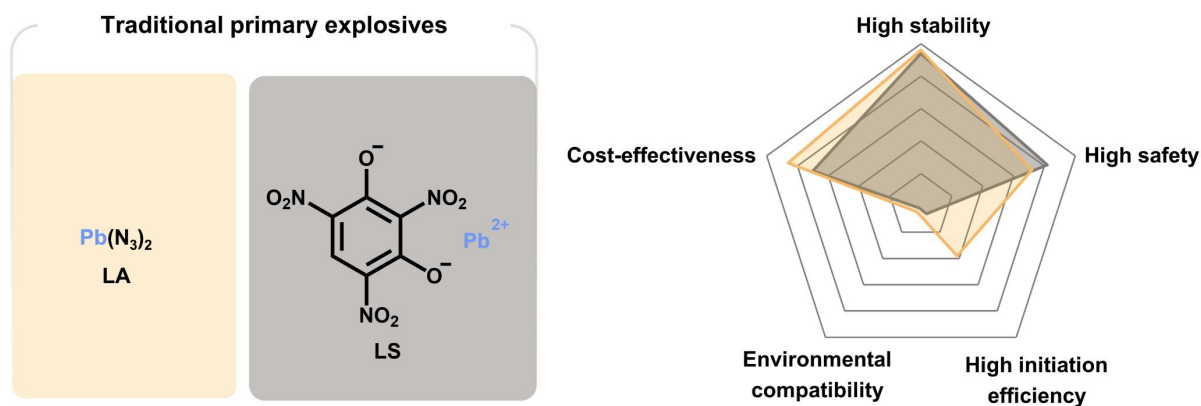


Fig. S1. Traditional lead-based primary explosives, such as $\text{Pb}(\text{N}_3)_2$ (LA) and lead styphnate (LS).

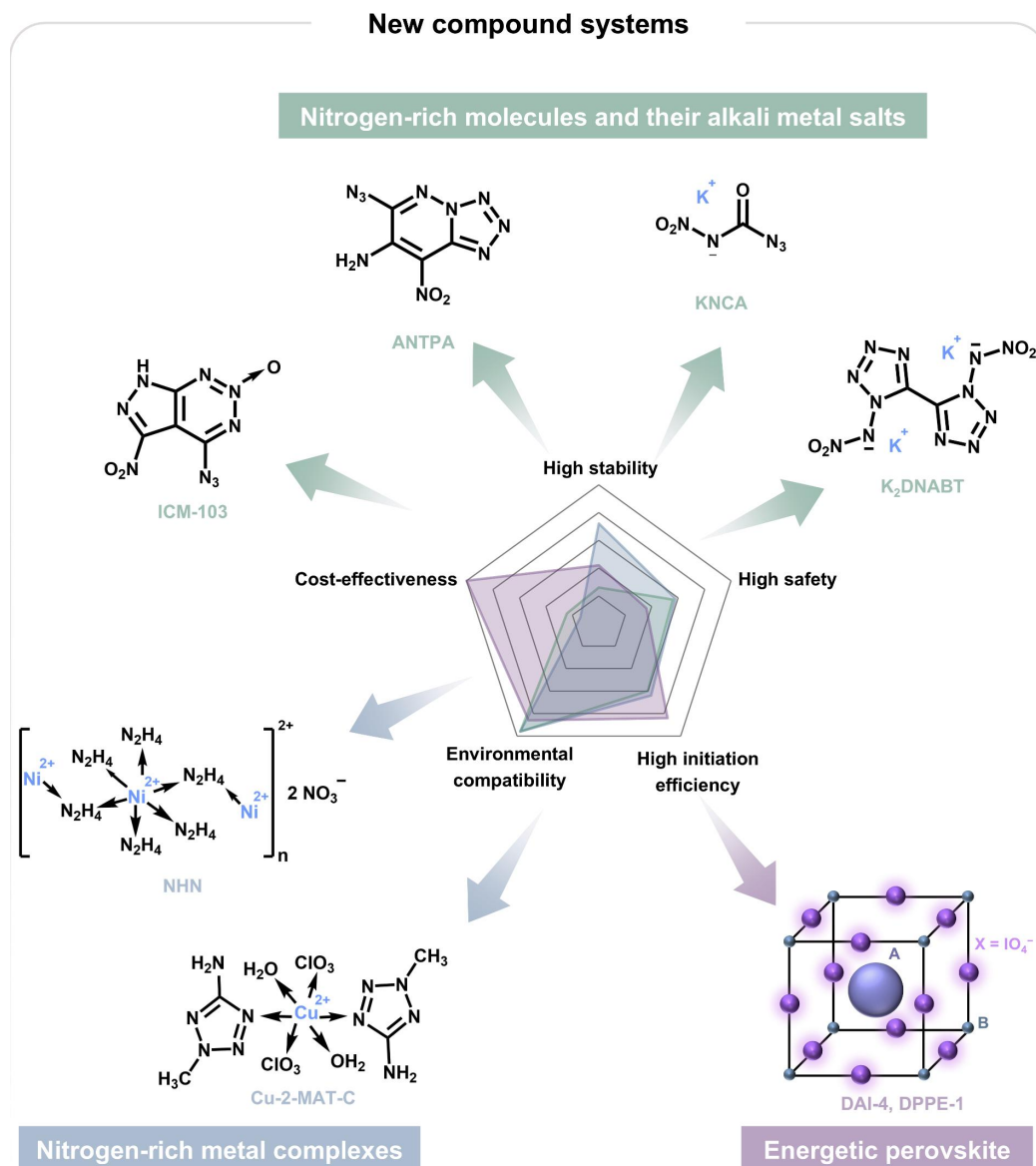


Fig. S2. New energetic compounds. Nitrogen-rich molecules and their alkali metal salts, such as 6-nitro-7-azido-pyrazol[3,4-d][1,2,3]triazine-2 oxide (**ICM-103**), 6-azido-8-nitro-tetrazolo[1,5-b]pyridazine-7-amine (**ANTPA**), potassium nitrocarbamoyl azide (**KNCA**), and dipotassium 1,1'-dinitramino-5,5'-bistetrazolate (**K₂DNABT**); Nitrogen-rich metal complexes, such as [Ni(N₂H₄)₃](NO₃)₂ (**NHN**, N₂H₄ = hydrazine) and [Cu(H₂O)₂(2-MAT)₂(ClO₃)₂] (**Cu-2-MAT-C**, 2-MAT = 2-methyl-5-aminotetrazole); Energetic perovskites, such as (H₂dabco)(NH₄)(IO₄)₃ (**DAI-4**, H₂dabco²⁺ is 1,4-diazabicyclo[2.2.2]octane-1,4-diium cation) and (H₂dabco)₂Na(NH₄)(IO₄)₆ (**DPPE-1**).

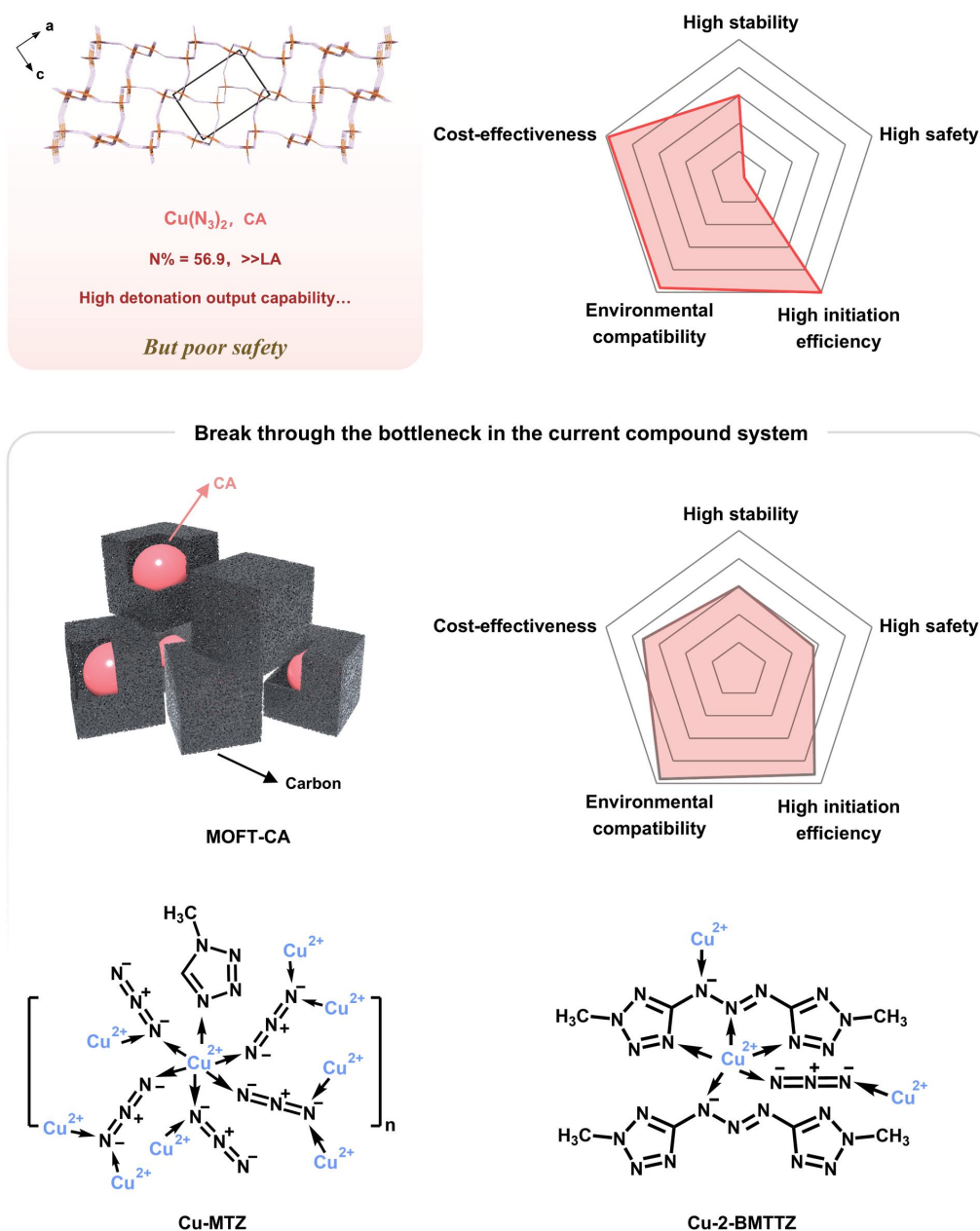


Fig. S3. Different strategies for breaking through the bottleneck in the copper azide system.

Copper azide is composited with inert materials to enhance its safety, for instance, copper azide@carbon (**MOFT-CA**); Through the competitive coordination of nitrogen-rich ligands to enhance safety, such as $[\text{Cu}(\text{N}_3)_2(\text{MTZ})]$ (**Cu-MTZ**, MTZ = 1-methyl-5H-tetrazole) and $[\text{Cu}(\text{N}_3)(2\text{-BMTTZ})]$ (**Cu-2-BMTTZ**, H(2-BMTTZ) = 1,3-bis(2-methyltetrazol-5-yl)triaz-1-ene).

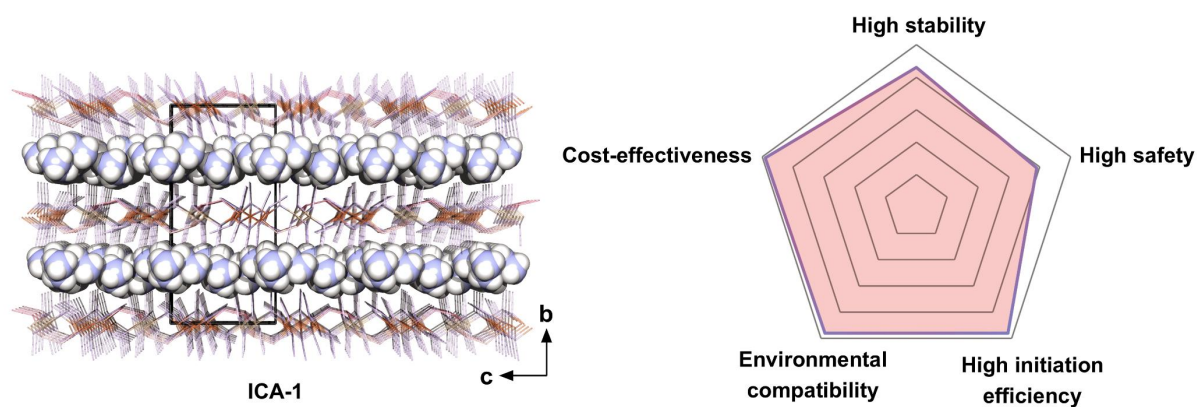


Fig. S4. This work proposes a strategy of cation-intercalated copper azide layers by employing disc-shaped spacer cations as intercalants to a deeply passive and high-energy CA derivative.

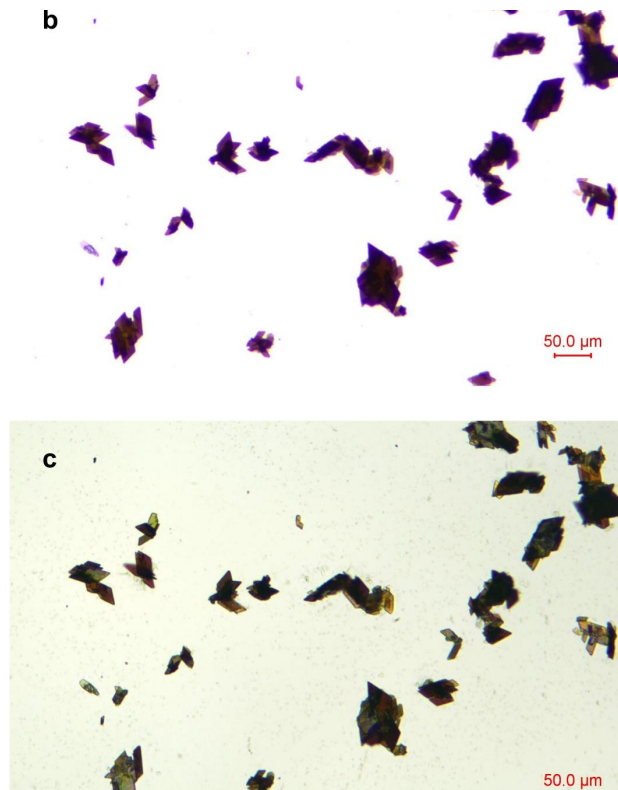
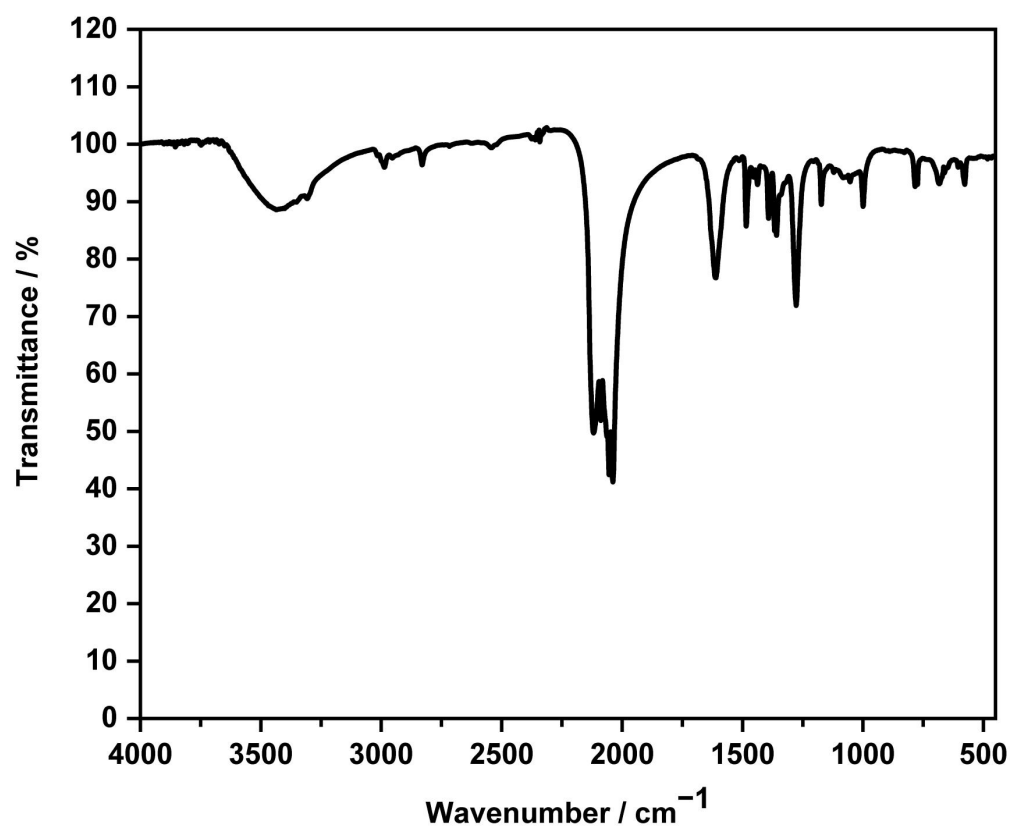


Fig. S5. Optical images of ICA-1. a, Gram-scale synthesis of ICA-1 *via* a single batch reaction. b, Optical micrograph of ICA-1. c, Polarized optical micrograph of ICA-1.



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2 Fig. S6. IR spectrum of ICA-1.

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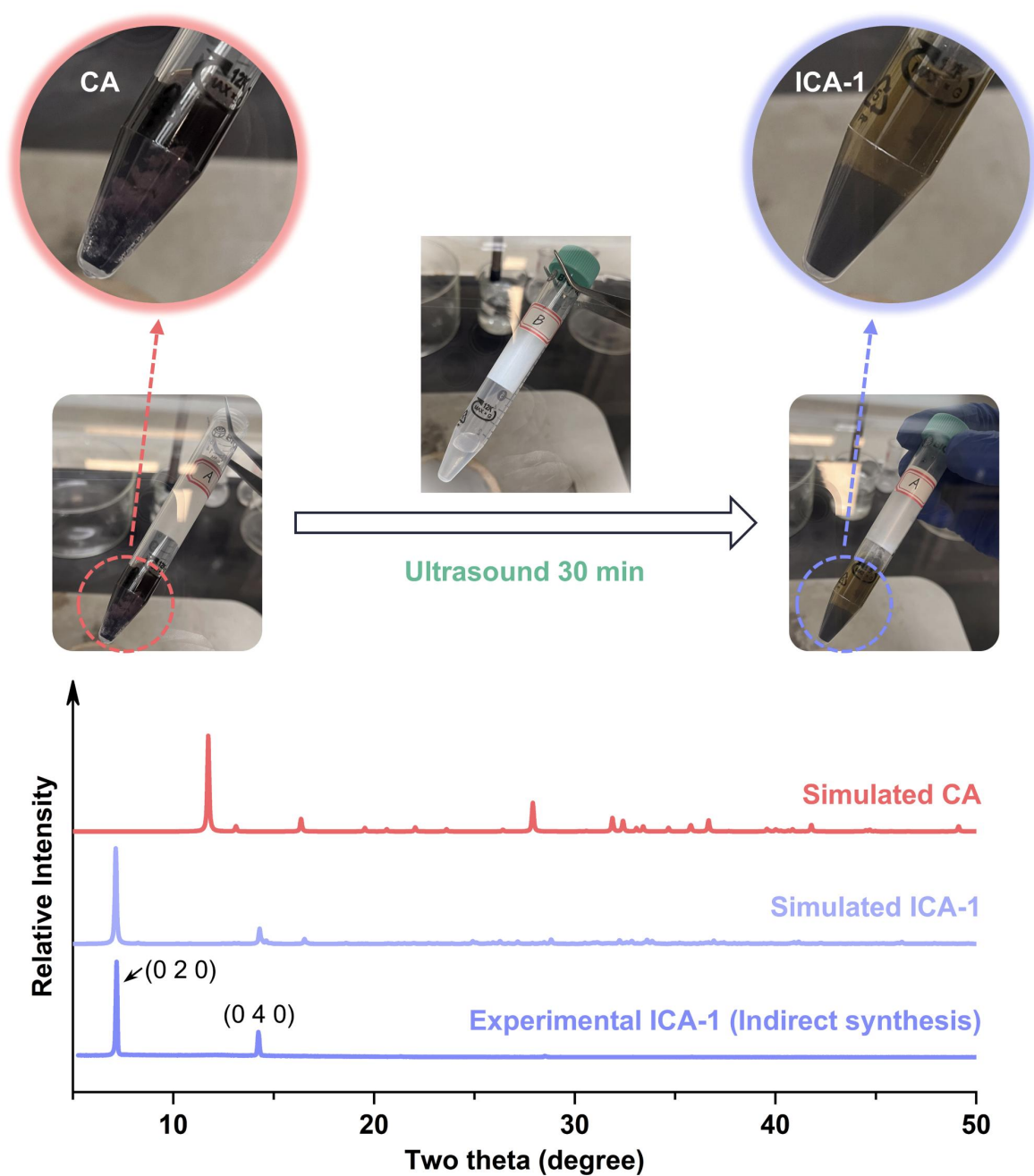


Fig. S7. Facile transformation of CA to ICA-1 at room temperature *via* Et₄N⁺ cation intercalation and N₃⁻ ions supplementation.

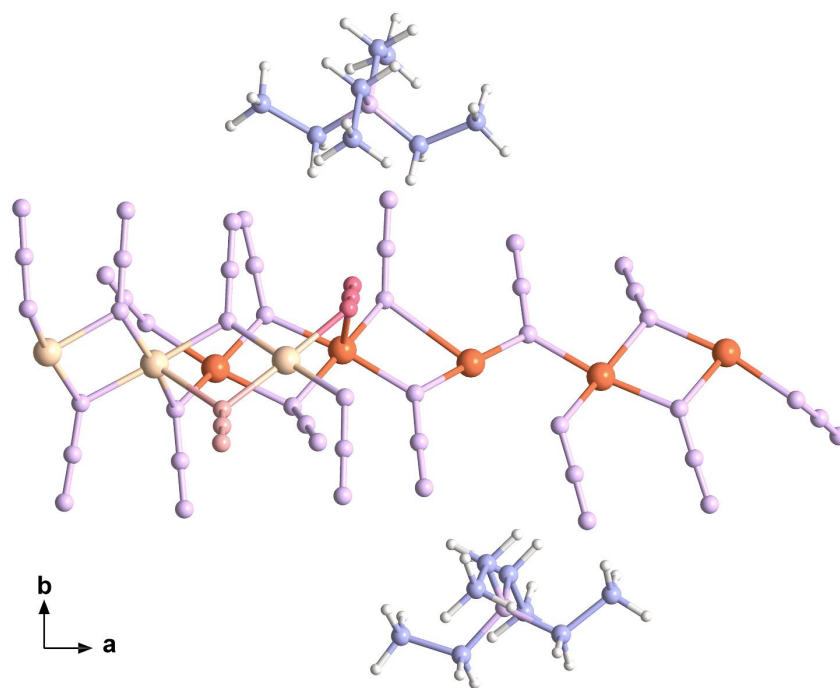
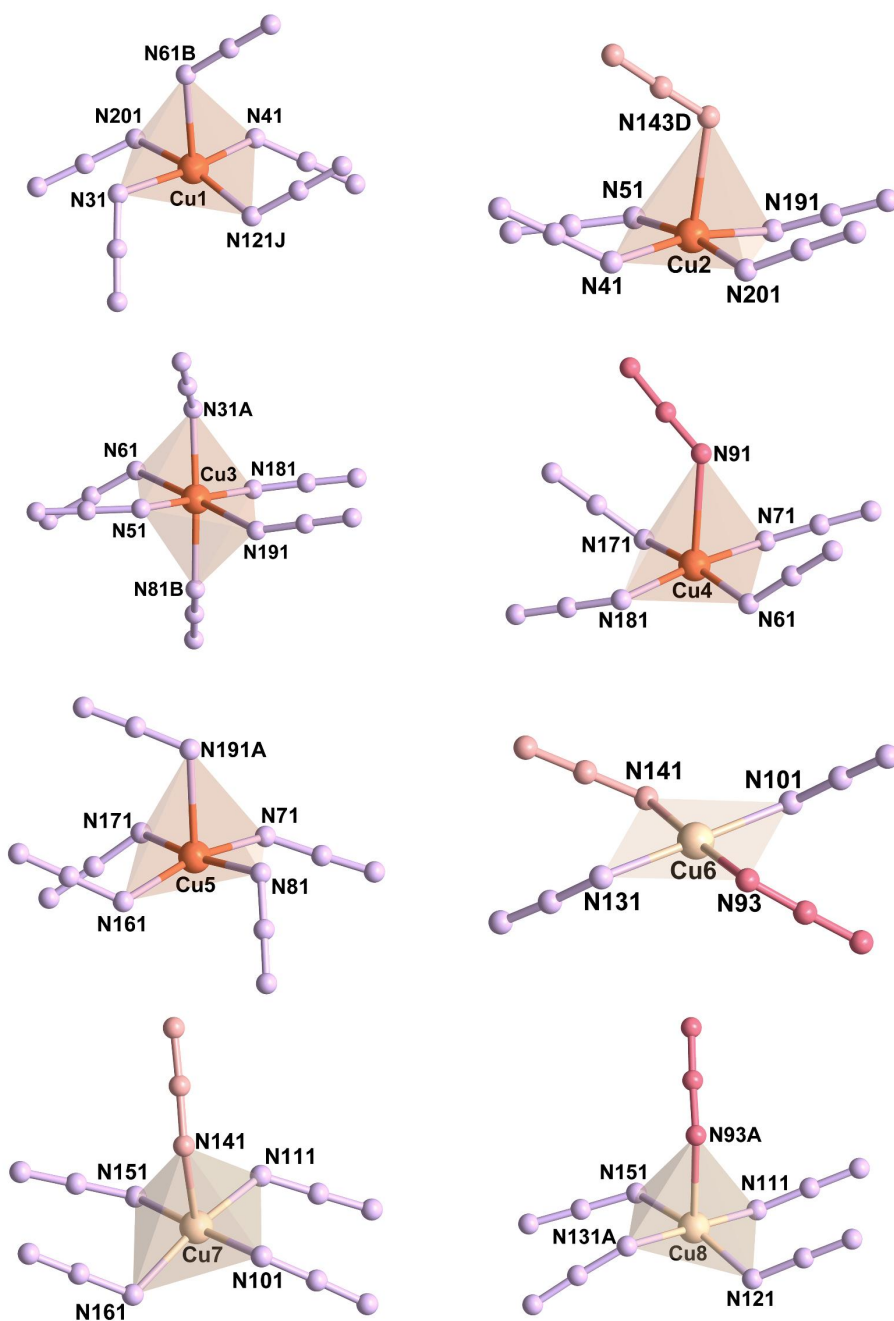


Fig. S8. Structure of the asymmetric unit of ICA-1.



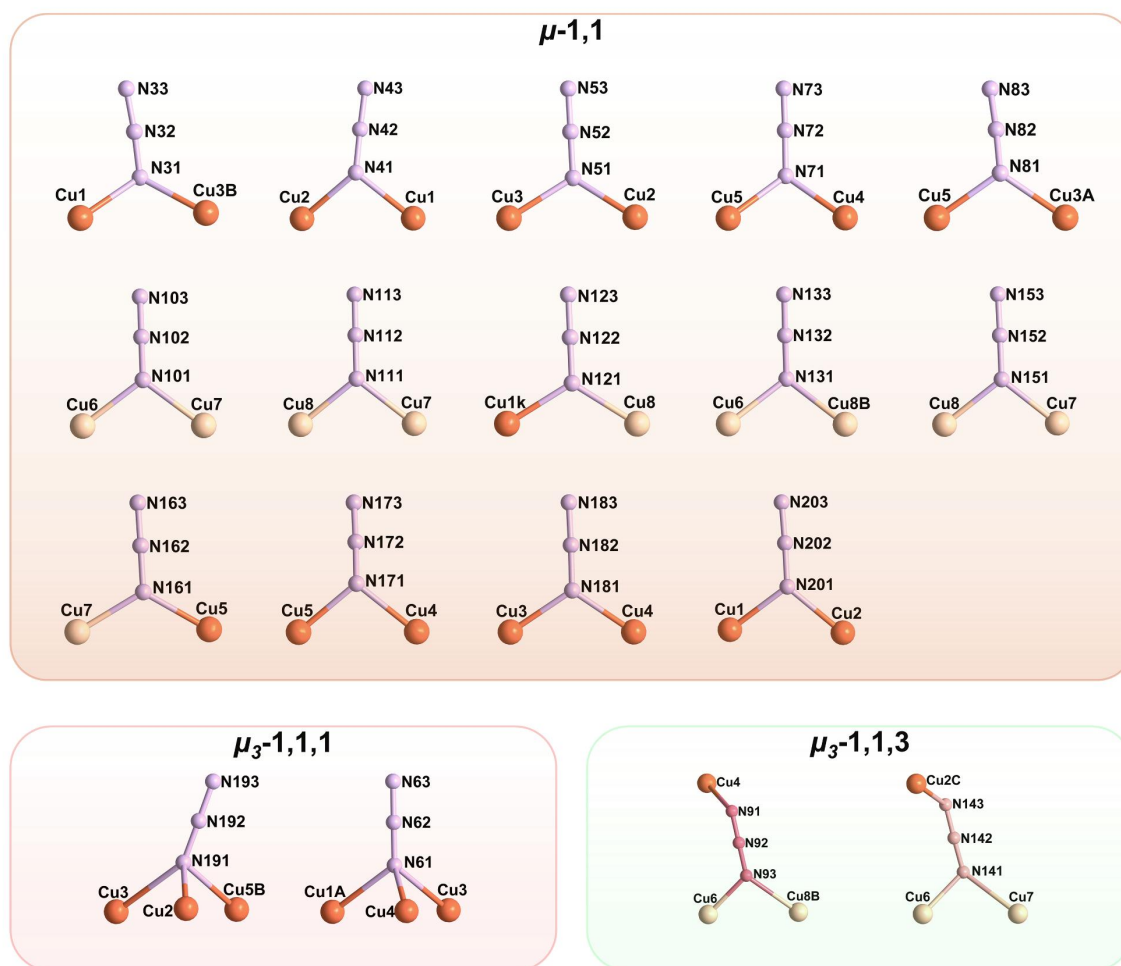
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2 **Fig. S9. Coordination modes of crystallographically independent Cu(II) atoms in ICA-1.** Cu1,

3 Cu2, Cu4, Cu5, Cu7 and Cu8 adopt five-coordinate distorted square-pyramidal geometries. Cu3 is

4 six-coordinate with a distorted octahedral environment and Cu6 is four-coordinate in a distorted

5 square-planar arrangement.



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2 **Fig. S10. Bridging modes of all N_3^- ions in ICA-1.**

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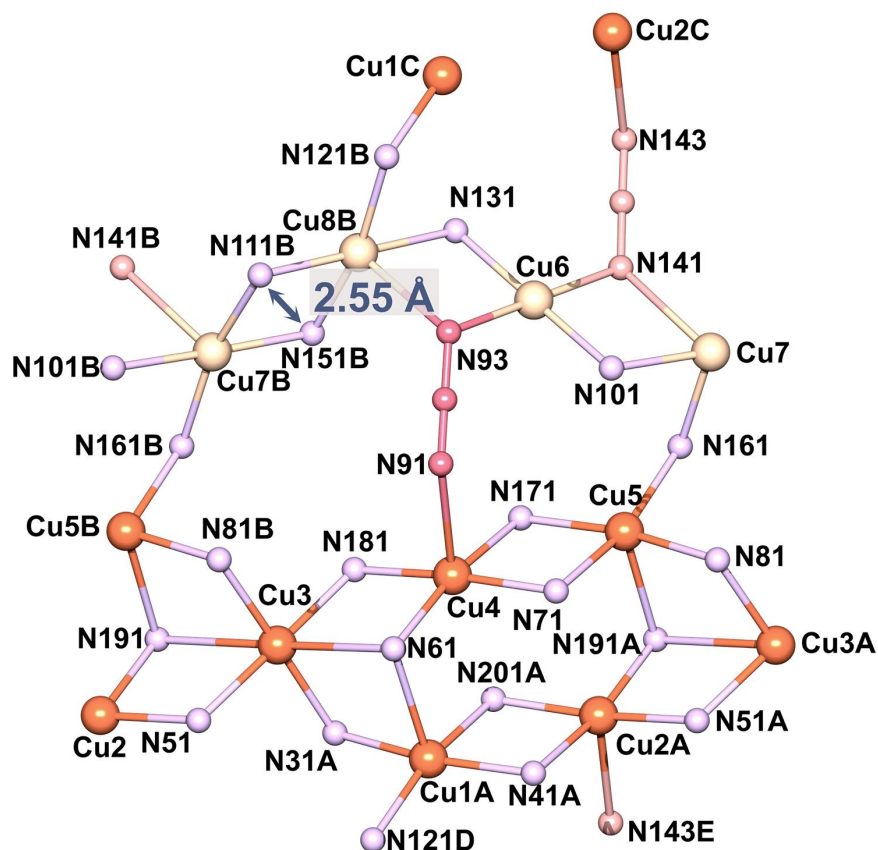


Fig. S11. Coordination modes of Cu(II) ions and N₃⁻ anions in one single layer of ICA-1 within the unit cell. (Atom colour codes: Cu1, Cu2, Cu3, Cu4, and Cu5, orange; Cu6, Cu7, and Cu8, yellow; N91, N92, and N93, rose red; N141, N142, and N143, light pink; The remaining nitrogen atoms, bluish violet. For the N₃⁻ anions acting in the μ -1,1 (end-on) bridge mode, only the coordinated nitrogen atoms are shown, while the rest of the atoms are omitted for clarity. Carbon atoms and hydrogen atoms are rendered in bluish-violet and white, respectively. Symmetry codes: A) $x - 1, y, z$; B) $x + 1, y, z$; C) $x - 1, y, z + 1$; D) $x + 1, y, z - 1$; E) $x, y, z - 1$; F) $-x, y + 1/2, -z + 1$; G) $-x + 1, y + 1/2, -z + 1$; H) $-x + 2, y + 1/2, -z + 1$; I) $x, y, z + 1$; j) $x + 2, y, z - 1$; k) $x - 2, y, z + 1$.

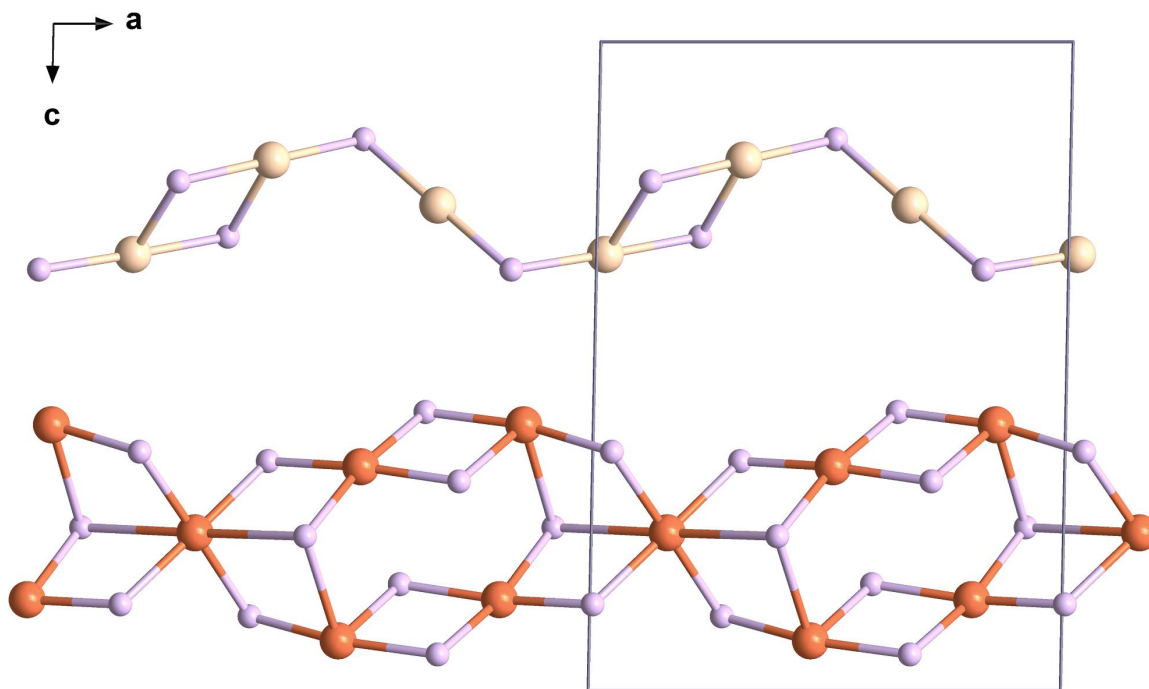
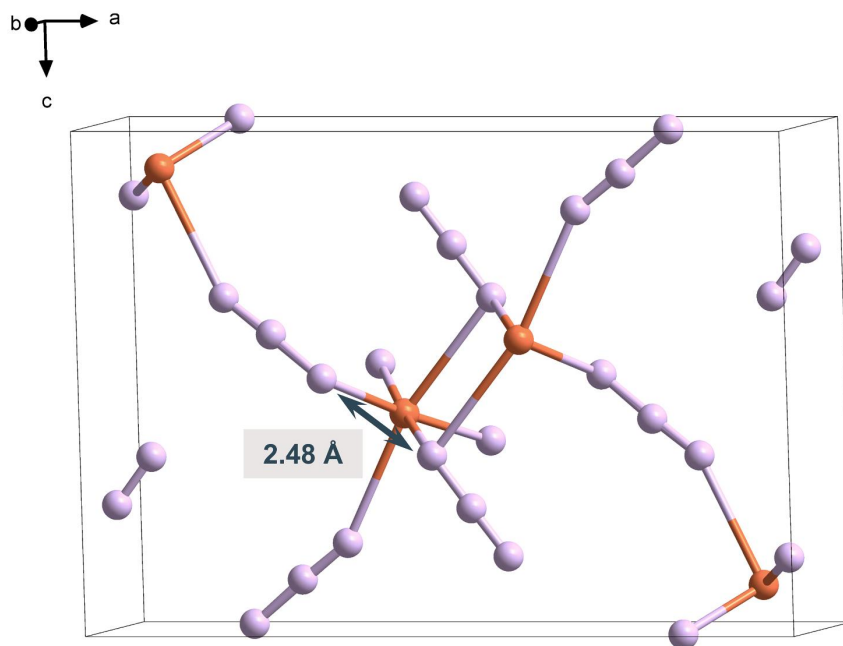


Fig. S12. Structure of two distinct types of infinite 1D chains extending along the a axis.



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2 **Fig. S13. The shortest non-bonding N···N contact distance in CA.**

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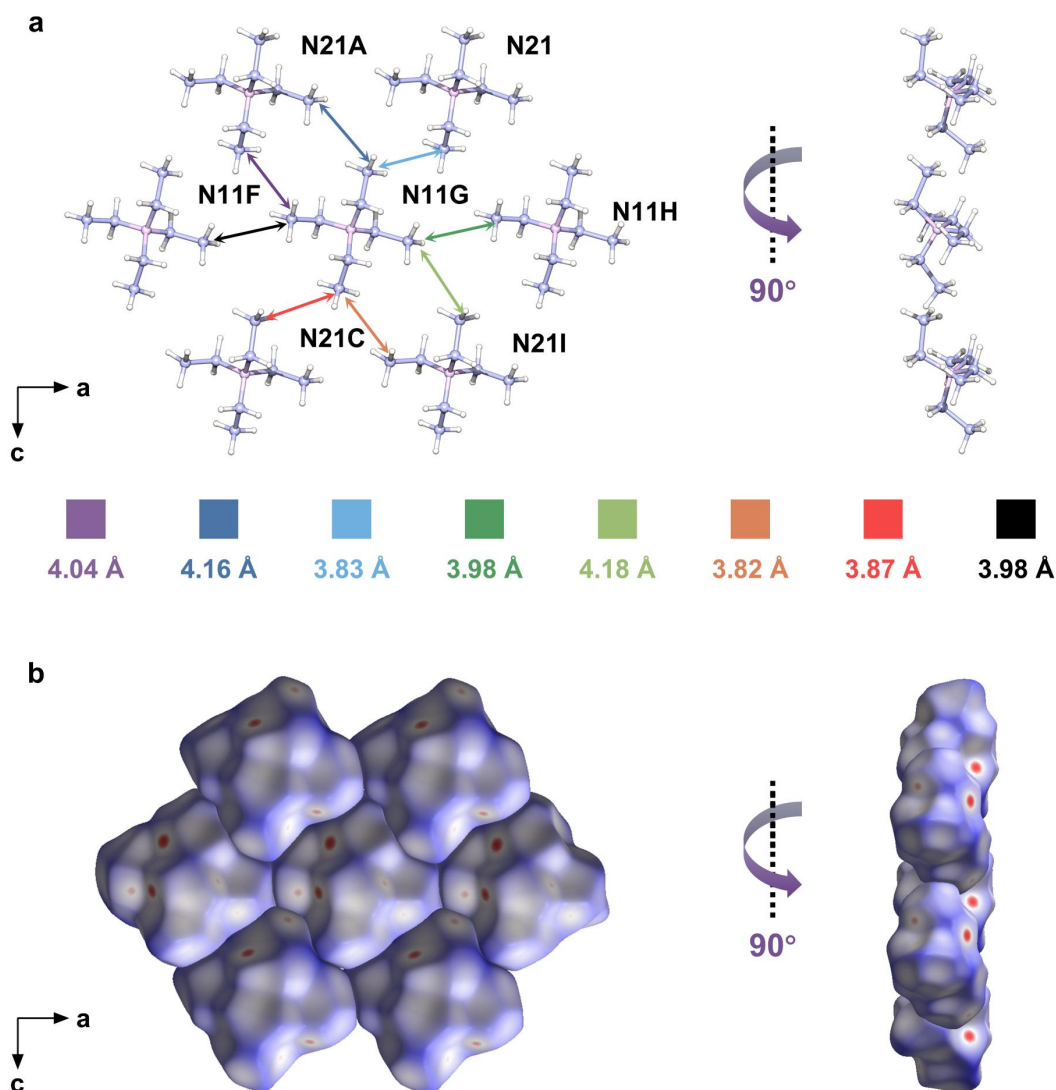
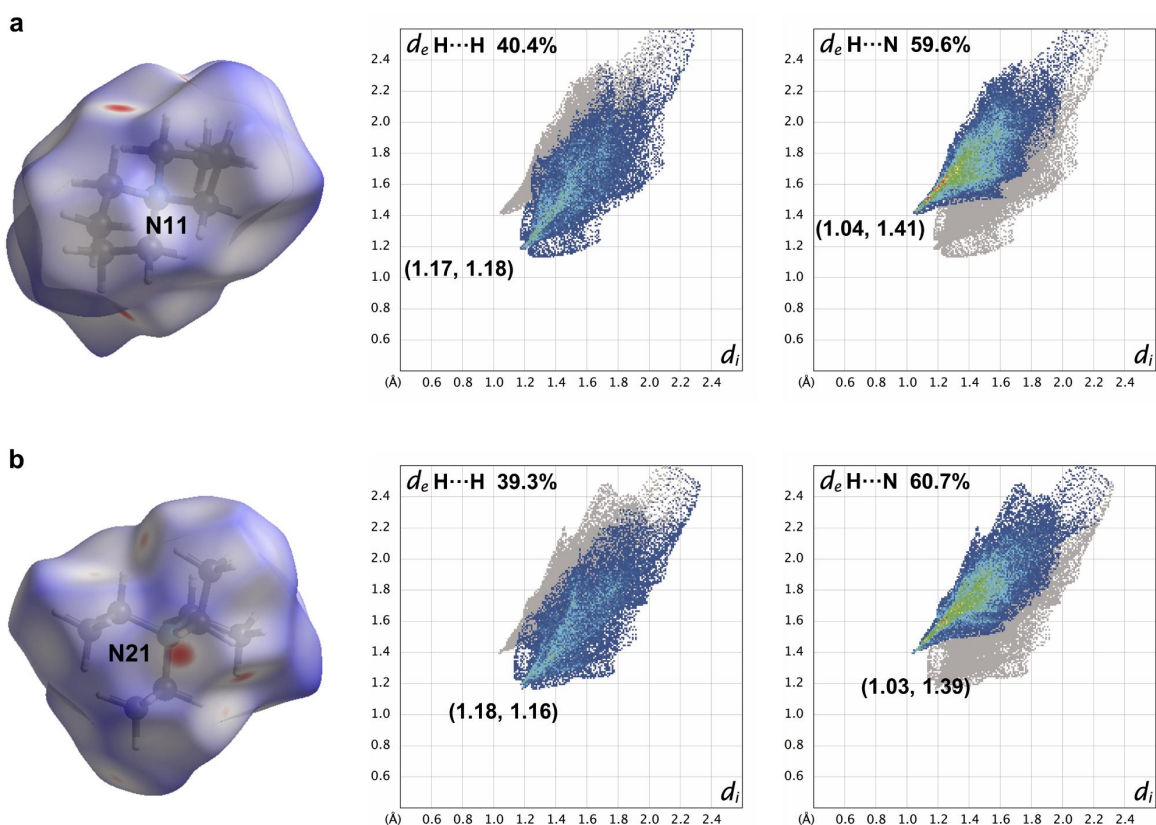


Fig. S14. Packing mode of Et_4N^+ cations. **a**, Two crystallographic independent Et_4N^+ cations are respectively arranged along the a axis and then alternately assembled to form a plane perpendicular to the b axis. **b**, the close contact between Et_4N^+ cations can be intuitively proved by the calculation results of Hirshfeld surface analysis. Symmetry codes: A) $x - 1, y, z$; B) $x + 1, y, z$; C) $x - 1, y, z + 1$; D) $x + 1, y, z - 1$; E) $x, y, z - 1$; F) $-x, y + 1/2, -z + 1$; G) $-x + 1, y + 1/2, -z + 1$; H) $-x + 2, y + 1/2, -z + 1$; I) $x, y, z + 1$. It shows that Et_4N^+ cations are arranged in a closely packed manner. This feature is preserved even at 90° rotation.

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3 **Fig. S15. The non-covalent interactions of Et_4N^+ cations.** **a**, The fingerprint plots for the
 4 crystallographically independent Et_4N^+ cations, in which the only nitrogen atom is marked as N11.
 5 **b**, The fingerprint plots for the crystallographically independent Et_4N^+ cations, in which the only
 6 nitrogen atom is marked as N21. Red regions on the Hirshfeld surface correspond to weak
 7 interactions between methyl groups, as well as between methyl groups and N_3^- ions. Notably, the
 8 $\text{H}\cdots\text{H}$ interaction peak in the fingerprint plot is broader than the $\text{H}\cdots\text{N}$ peak. This pattern indicates
 9 more uniform $\text{Et}_4\text{N}^+\cdots\text{Et}_4\text{N}^+$ interactions and stronger local $\text{Et}_4\text{N}^+\cdots\text{N}_3^-$ interactions. Fingerprint
 10 plots indicate the shortest contact between N11 and surrounding Et_4N^+ cations occurs at $(d_i, d_e) =$
 11 $(1.17, 1.18)$ Å, while contacts with N_3^- ions appear at $(d_i, d_e) = (1.04, 1.41)$ Å, where d_i and d_e

1 denote the spatial distances from a point on the Hirshfeld surface to the nearest internal and external
2 nucleus, respectively. For N21, the shortest (d_i , d_e) pair for $\text{Et}_4\text{N}^+ \cdots \text{Et}_4\text{N}^+$ interaction is (1.18, 1.16)
3 Å. The shortest $\text{Et}_4\text{N}^+ \cdots \text{N}_3^-$ contact is (1.03, 1.39) Å. These results indicate that Et_4N^+ cations
4 experience predominantly electrostatic repulsion, with short contacts arising merely from packing
5 effects. Meanwhile, short contacts exist between Et_4N^+ cations and N_3^- ions, whose distances and
6 angles fall within the range characteristic of potential weak non-classical hydrogen-bonding
7 interactions. Nevertheless, the carbon-bound hydrogen atoms were modelled using riding
8 coordinates, and such interactions are inherently weak. Accordingly, interactions between the
9 organic and inorganic layers are dominated by Coulombic attraction.

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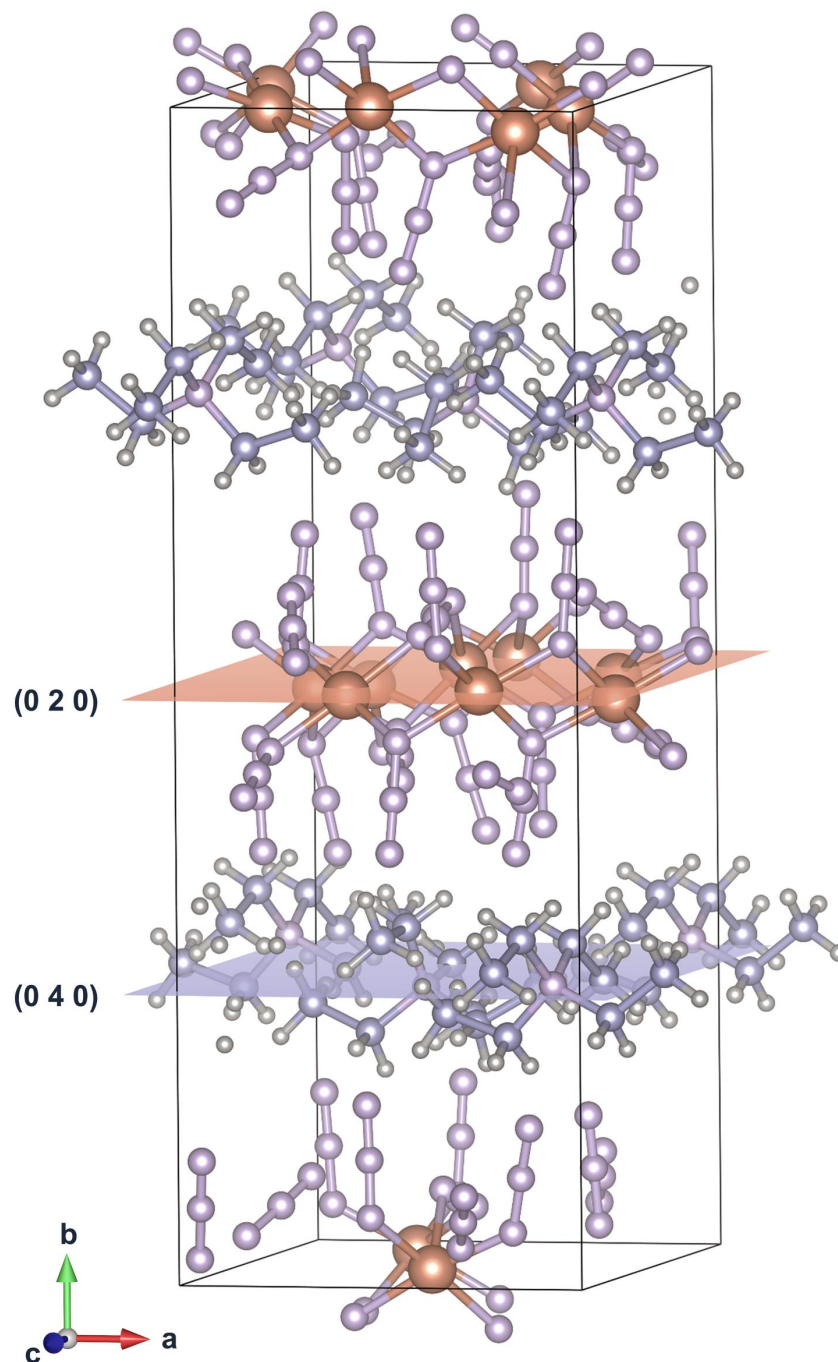
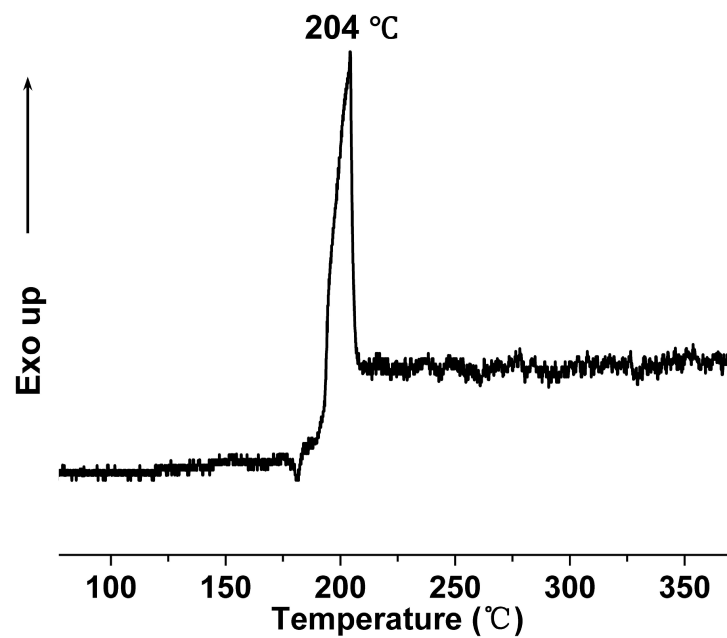


Fig. S16. The (0 2 0) and (0 4 0) lattice planes in the crystal structure of ICA-1, as determined using VESTA.



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2 **Fig. S17. DTA curve of ICA-1 with a heating rate of 5 °C·min⁻¹.**

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2 **Fig. S18. Quartz tube shattered during a DTA test.**

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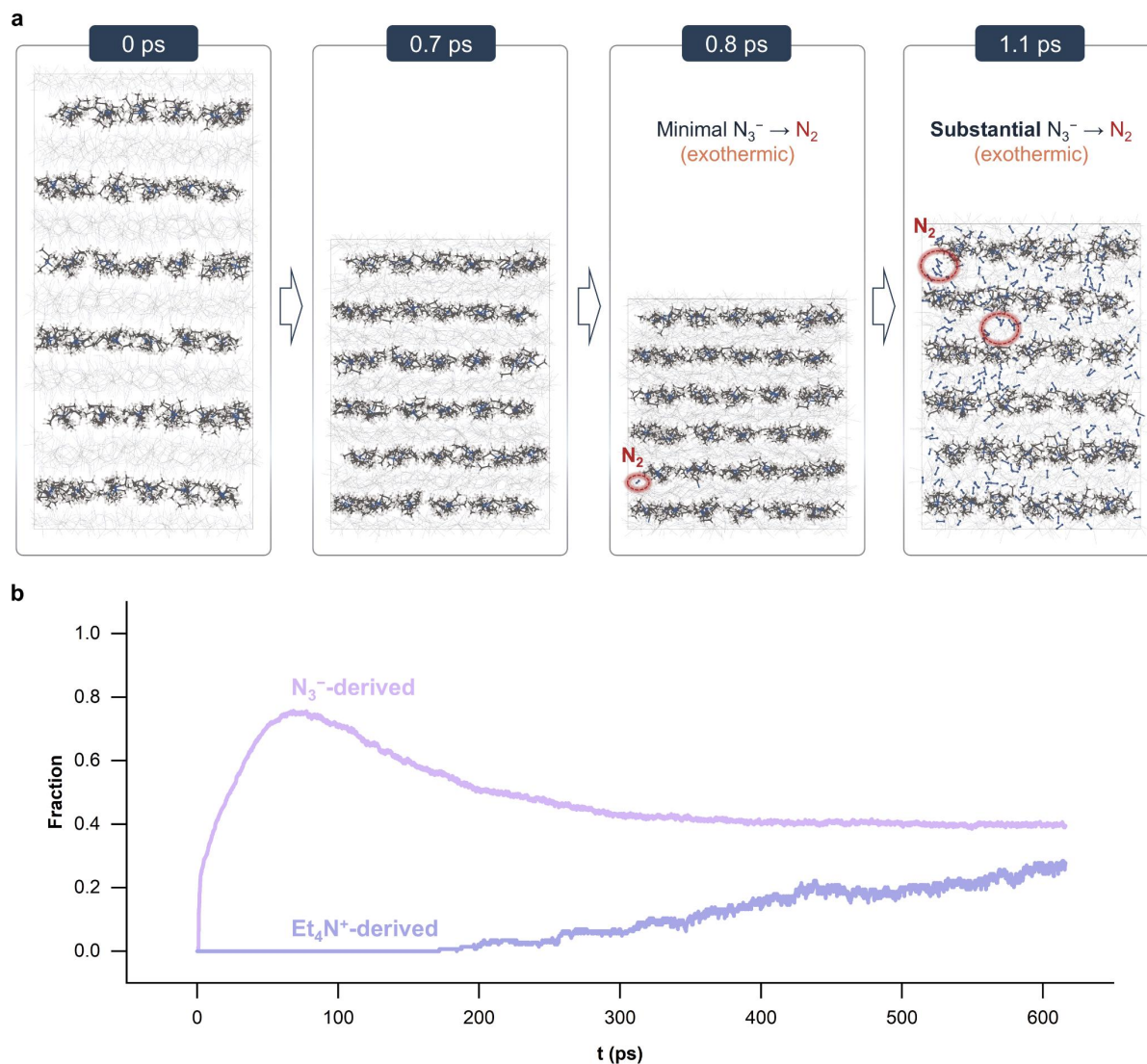
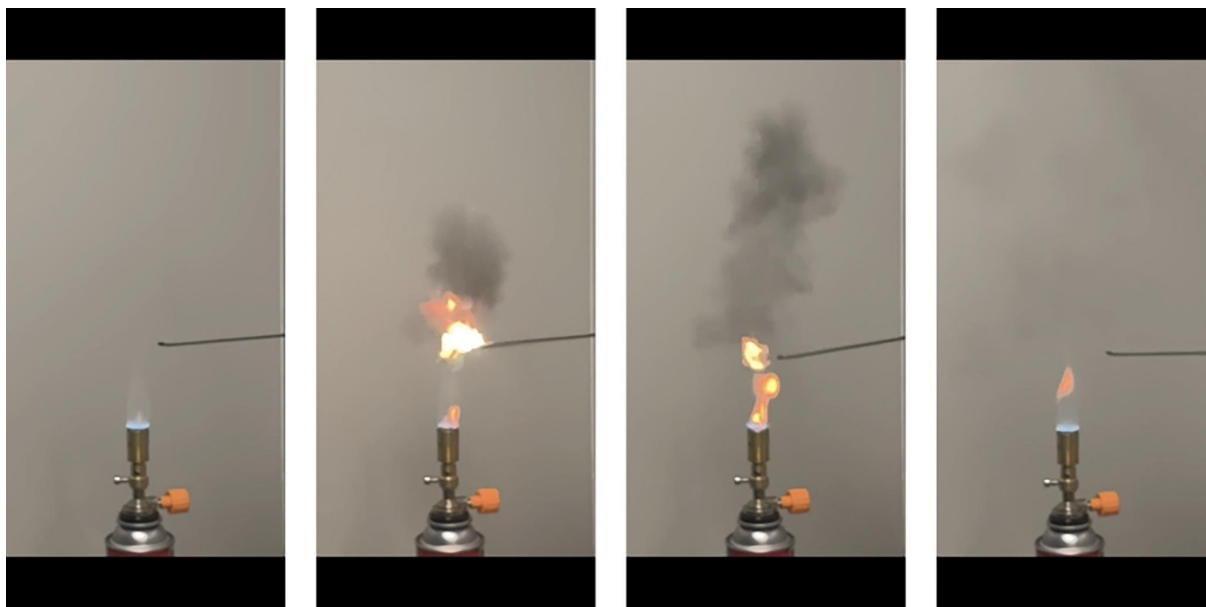


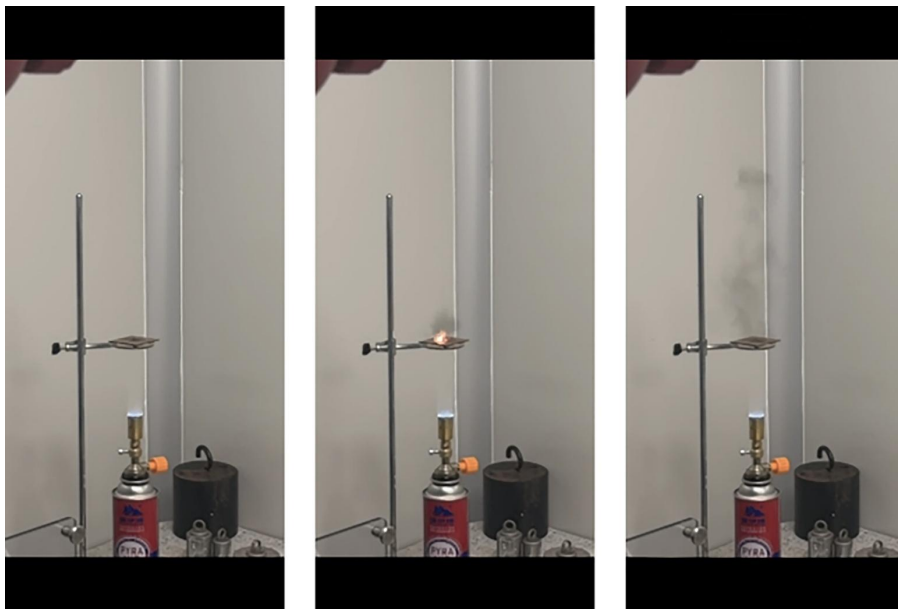
Fig. S19. Dynamic simulations of ICA-1 under shock loading at $6.8 \text{ km}\cdot\text{s}^{-1}$. **a**, under shock loading, lattice compression occurs first, followed by the gradual formation of N_2 . **b**, Fraction of initial nitrogen atoms from assigned sources converted into N_2 molecules as a function of time.



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2 **Fig. S20. Flame test of ICA-1.**

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2 **Fig. S21. Hot plate test of ICA-1.**

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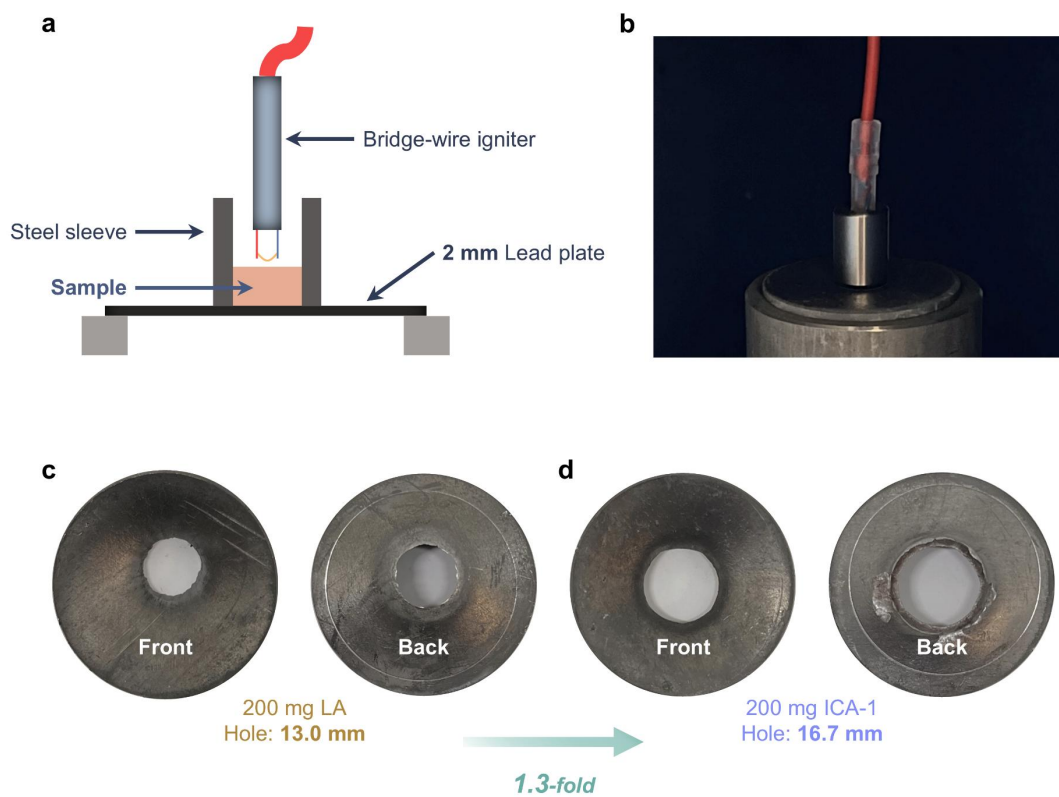


Fig. S22. Evaluation of the detonation output capability. **a**, Schematic of detonation output capability test apparatus. **b**, Photograph of the test setup test apparatus. **c**, **d**, Damage to the 2 mm-thick lead plate caused by the explosions of **LA** and **ICA-1**.



Fig. S23. Detonation process for MPC determination captured by conventional camera.

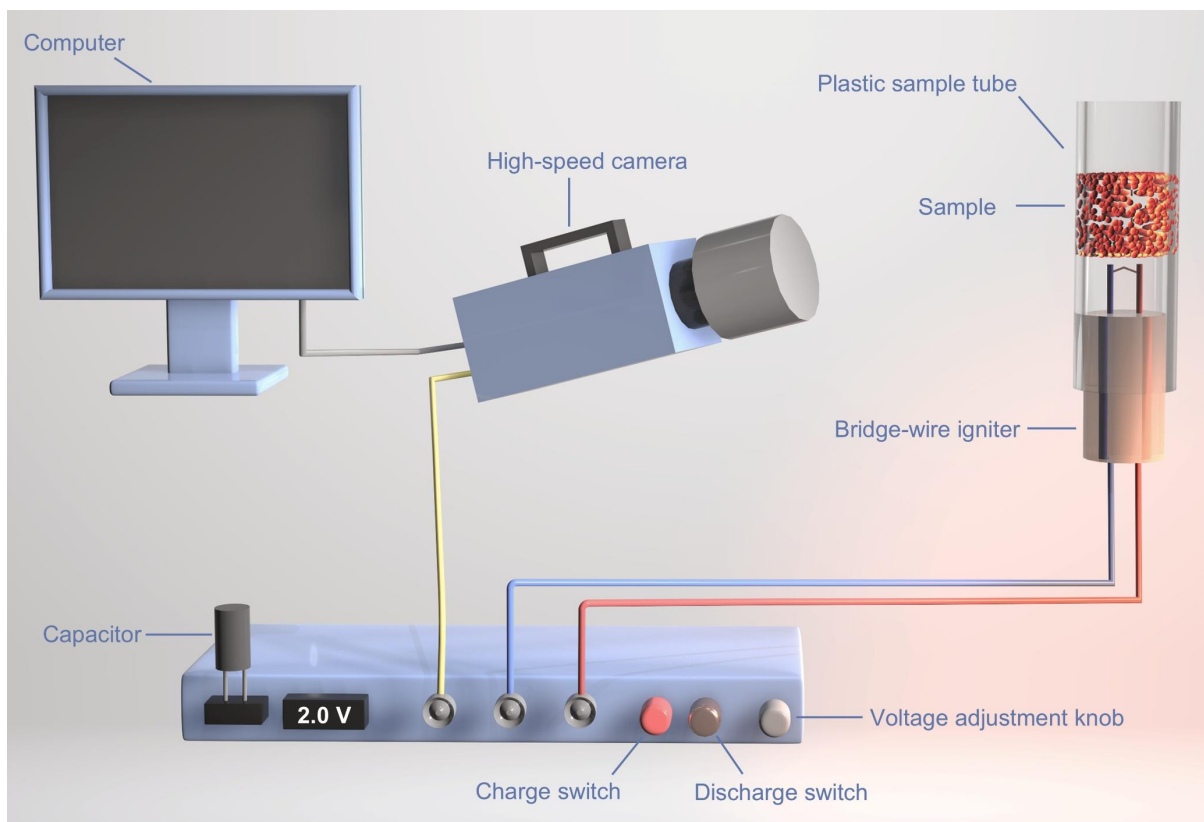


Fig. S24. Schematic of the experimental setup for input ignition energy evaluation.

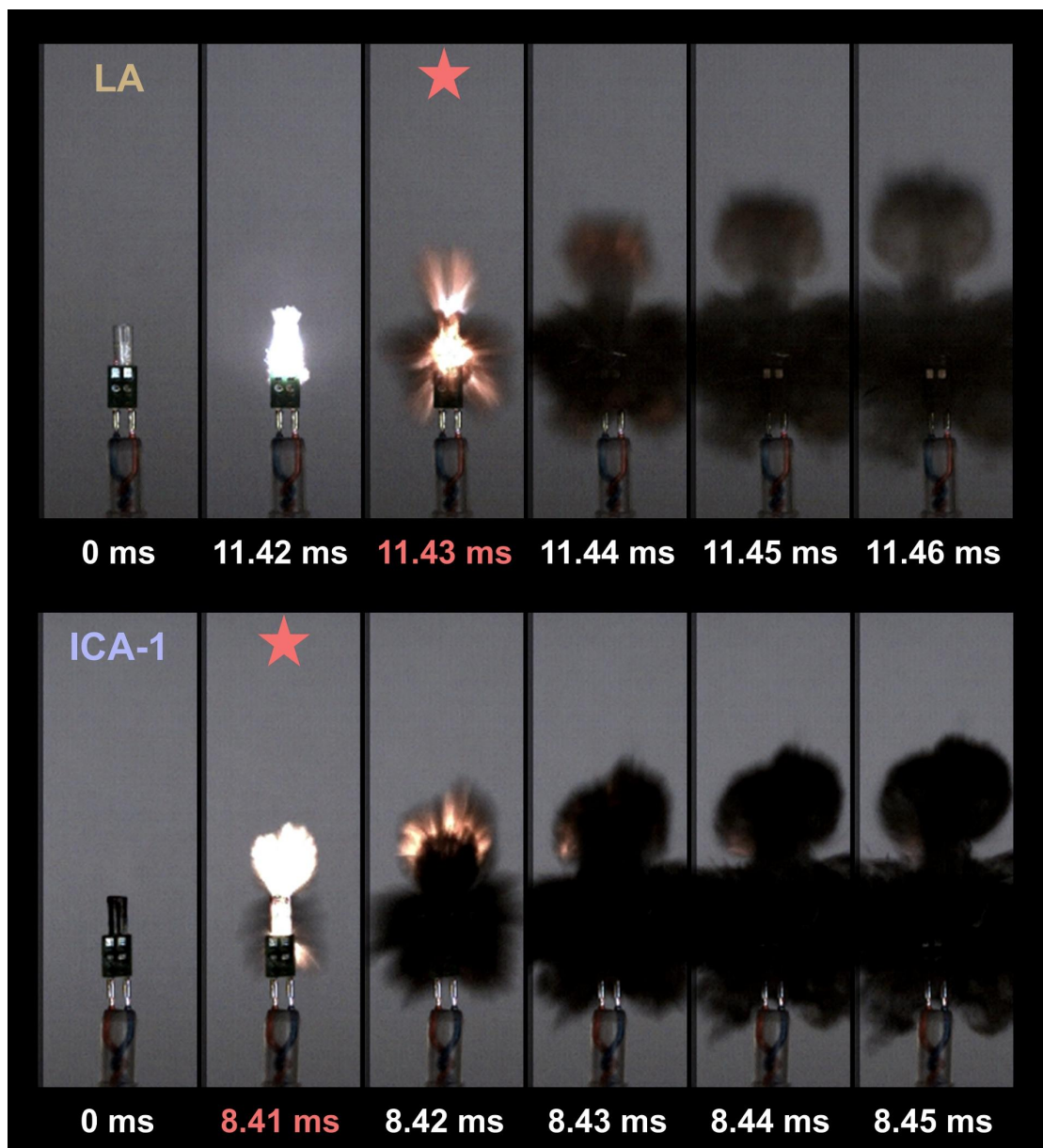
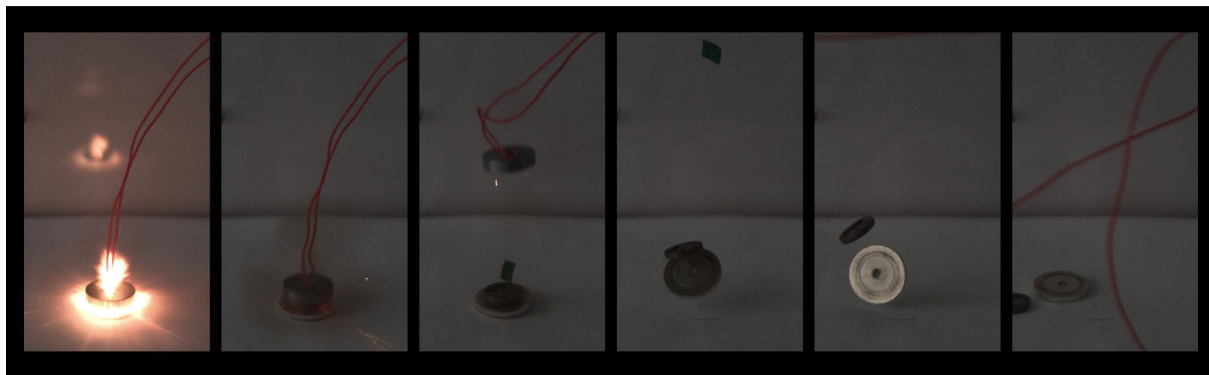


Fig. S25. Ignition events captured in input ignition energy evaluation tests (charging voltage: 3 V).



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2 **Fig. S26. Snapshots of the detonation process of ICA-1 as a primary charge in energetic chip.**

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3. References

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