

Electronic Supporting Information

Competitive coordination and lewis-base interactions of amines in supertetrahedral clusters based materials by controllable naked T3-InS precursor method: from isolated clusters with various substituted ligands, chain to 3-D open framework

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Experimental Section:

Chemicals and Materials

Indium powder (In, 99.99%), sulfur powder (S, $\geq 99.5\%$), (1,5-diazabicyclo [4.3.0]-5-nonene) ($C_7H_{12}N_2$, 98%), and methanol absolute all used without any further purification.

Synthesis of $(HDBN)_3(C_7H_{10}N)_3 [In_{10}S_{16}(SH)_4] (H_2O)_2$ (**T3-0**)

A mixture of $InCl_3 \cdot 4H_2O$ (80 mg, 0.27 mmol), sulfur powder (48.0 mg, 1.5 mmol), 1,5-diazabicyclo [4.3.0]-5-nonene (DBN) 1.0 mL, 3,5-dimethylpyridine 1.0 mL, H_2O 0.5 mL and MeOH 0.5 mL was prepared and stirred in a 23-mL Teflon-lined stainless steel autoclave for half an hour. The vessel was sealed and heated at 180 °C for 8 days, and then the autoclave was cooled to room temperature naturally without any other operations. Colourless polyhedron crystal was obtained with a few impurities. The raw products were washed three times with ethanol, then filtered off, and further purified by hand with a yield of 72.4 mg (11.2% based on indium). Elem anal. (Calcd.) (*wt %*): C (19.97) 19.72; N (4.99) 5.11; H (2.95) 3.12; S (25.38) 25.73.

Synthesis of $(HDBN)_{4.5}(C_7H_{10}N)_{0.5} [In_{10}S_{16}(SH)_3(DBN)]$ (**T3-1**)

A mixture of **T3-0** 10 mg, DBN 1.0 mL and MeOH 0.5 mL was prepared and stirred in a 23-mL Teflon-lined stainless steel autoclave for half an hour. The vessel was sealed and heated at 120 °C for 5 days, and then the autoclave was cooled to room temperature naturally without any other operations. Colourless block-like crystal was obtained, and the raw products were washed three times with ethanol. Then filtered off with a yield of 6.56 mg (63% based on indium). Elem anal. (Calcd.) (*wt %*): C (20.16) 20.32; N (6.44) 6.58; H (3.16) 3.12; S (24.35) 24.49.

Synthesis of $(HDBN)_4 [In_{10}S_{16}(SH)_2(DBN)_2]$ (**T3-2**)

The synthesis process is the same as that of compound **T3-1**, except that it is heated to 140 °C for 5 days. Colourless block-like crystal was obtained with a yield of 6.98 mg (67.2% based on indium). Elem anal. (Calcd.) (*wt %*): C (20.37) 20.42; N (6.79) 6.89; H (3.17) 3.10; S (23.30) 23.39.

Synthesis of $(HDBN)_6 [In_{20}S_{33}(DBN)_6]$ (**T3-3**)

The synthesis process is the same as that of compound **T3-1**, except that it is heated to 180 °C for 5 days. Colourless block-like crystal was obtained with a yield of 7.33 mg (71.7% based on indium). Elem anal. (Calcd.) (*wt %*): C (20.80) 20.62; N (6.93) 7.11; H (3.12) 3.21; S (21.81) 21.68.

It is worth noting that by controlling a single variable of synthesis conditions, we raised the reaction temperature to 200 °C and reacted for 8 days, and the reaction products did not change.

Synthesis of (HDBN)₂(CH₃NH₃)₂ [In₁₀S₁₇(DBN)₂] (**T3-4**)

A mixture of **T3-0** 10 mg, DBN 0.5 mL, CH₃NH₂ 1.5 mL and MeOH 0.5 mL was prepared and stirred in a 23-mL Teflon-lined stainless steel autoclave for half an hour. The vessel was sealed and heated at 180 °C for 5 days, and then the autoclave was cooled to room temperature naturally without any other operations. Colourless block-like crystal was obtained, and the raw products were washed three times with ethanol. Then filtered off with a yield of 6.34 mg (66.5% based on indium). Elem anal. (Calcd.) (*wt %*): C (15.97) 15.72; N (6.21) 6.31; H (2.77) 2.84; S (24.16) 24.33.

Synthesis of (HDBN)_{1.5}(C₂H₈NO)_{4.5} [In₁₀S₁₈] (**T3-5**)

A mixture of **T3-0** 10 mg and CH₃CH₂NH₂OH 1.0 mL was prepared and stirred in a 23-mL Teflon-lined stainless steel autoclave for half an hour. The vessel was sealed and heated at 180 °C for 5 days, and then the autoclave was cooled to room temperature naturally without any other operations. Colourless block-like crystal was obtained, and the raw products were washed three times with ethanol. Then filtered off with a yield of 7.16 mg (77.8% based on indium). Elem anal. (Calcd.) (*wt %*): C (10.68) 10.72; N (4.79) 4.93; H (2.55) 2.37; S (26.32) 26.38.

X-ray Crystallography

Data collection for **T3-0—T3-5** was carried out on an Agilent Technologies SuperNova Single Crystal Diffractometer using Cu K α radiation ($\lambda = 1.54184$ Å) at 150 K or 293 K. Absorption corrections were applied by using the program CrysAlis (multi-scan). The structure was solved and refined using Full-matrix least-squares based on F^2 with program SHELXS-97 and SHELXL-97 within OLEX2. The six

structures of **T3-0**—**T3-5** contain large solvent accessible voids, in which counterions and solvent molecules can not be recognized and simulated because of the disorder. Thus, the contribution of corresponding electron density was removed by the SQUEEZE routine in PLATON.

Powder X-Ray Diffraction

Powder X-ray diffraction (PXRD) of the compound was obtained using a Bruker Model D8Avance powder diffractometer at room temperature with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The patterns of **T3-0**—**T3-5** were recorded at 5–60° (2 θ) with a scanning step width of 0.02°, and the patterns of cluster **A** was recorded at 5–60° (2 θ) with a scanning step width of 0.0194834°.

Elemental Analysis

Energy dispersive spectroscopy (EDS) analysis was performed on scanning electron microscope (SEM) equipped with EDS detector. An accelerating voltage of 25 kV and 40 s accumulation time were applied. EDS results clearly confirmed the presence of In and S elements. Elemental analysis of C, H, N and S was performed on VARIDEL III elemental analyzer.

Thermogravimetric Measurement

A Shimadzu TGA-50 thermal analyzer measured the TG curve by heating the sample from room temperature to 800 °C with heating rate of 10 °C/min under N₂ flow.

Fourier-Transform Infrared Absorption

Fourier transform-Infrared spectral analysis was performed on a Thermo Nicolet Avatar 6700 FT-IR spectrometer with Potassium bromide optics allowing the instrument to observe from 500-4000 cm⁻¹.

High resolution mass spectrum

Weigh 15 mg of compound **T3-0**—**T3-5** to 10 mL beakers, respectively, then add five drops of concentrated HCl to dissolve the sample until the solution is clear and transparent. Subsequently, adjust the pH of the solutions to 3~4 and test them after filtration.

Theoretical Calculations.

ADF2016 software is used to carry out the first principle calculation based on density functional theory (DFT) for a series of cluster models. The series of electronic energy calculations are based on the single crystal structure data of compounds **T3-0**—**T3-5**. PBE/TZP basis sets are used for C, N, H, In and S atoms.

Table S1. Crystal data and structure refinement parameters for compounds **T3-0**—**T3-1**.

	T3-0	T3-1
Formula	C ₄₂ H ₇₇ N ₉ O ₂ In ₁₀ S ₂₀	C ₄₂ H _{78.5} In ₁₀ N _{11.5} S ₁₉
Mr	2529.52	2502.00
Temp (K)	150(10)	150(10)
Wavelength (Å)	1.54184	1.54184
Cryst syst	Cubic	Triclinic
Space group	<i>Fd-3m</i>	<i>P-1</i>
a/Å	27.3492(4)	15.6957(6)
b/Å	27.3492(4)	15.7514(5)
c/Å	27.3492(4)	20.2475(7)
α/°	90	67.203(3)
β/°	90	71.383(3)
γ/°	90	75.454(3)
V (Å ³)	20456.6(9)	4326.5(3)
Z	8	2
ρ (g cm ⁻³)	1.165	1.444
μ (mm ⁻¹)	21.486	25.213
F(000)	6512.0	1724.0
Collected reflns	7729	17298
Completeness	99.7%	99.1%
GOF on F ²	1.135	0.943
R ₁ ^a /wR ₂ ^b [I > 2(I)]	0.0434/0.1704	0.0839/0.2537
R ₁ ^a /wR ₂ ^b (all data)	0.0481/0.1807	0.1121/0.2759

^aR₁ = Σ||F_o| - |F_c||/Σ|F_o|. ^bwR₂ = {Σ[w(F_o² - F_c²)²]/Σ[w(F_o²)²]}^{1/2}

Table S2. Crystal data and structure refinement parameters for compounds **T3-2**—**T3-3**.

	T3-2	T3-3
Formula	C ₄₂ H ₇₈ In ₁₀ N ₁₂ S ₁₈	C ₈₄ H ₁₅₀ In ₂₀ N ₂₄ S ₃₃
Mr	2476.44	4850.65
Temp (K)	293(2)	150(10)
Wavelength (Å)	1.54184	1.54184
Cryst syst	Monoclinic	Trigonal
Space group	<i>I2/m</i>	<i>R-3c</i>
a/Å	20.1028(16)	19.92330(10)
b/Å	19.975(2)	19.92330(10)
c/Å	24.2769(17)	69.6002(3)
α/°	90	90
β/°	112.012(9)	90
γ/°	90	120
V (Å ³)	9037.9(15)	23925.6(3)
Z	4	6
ρ (g cm ⁻³)	1.450	1.677
μ (mm ⁻¹)	2.927	26.830
F(000)	3656.0	11065
Collected reflns	33801	186075
Completeness	99.9%	99.7
GOF on F ²	0.953	1.045
R ₁ ^a /wR ₂ ^b [I > 2(I)]	0.0706/0.2014	0.0388/0.1058
R ₁ ^a /wR ₂ ^b (all data)	0.1206/0.2371	0.0393/0.1063

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

Table S3. Crystal data and structure refinement parameters for compounds **T3-4**—**T3-5**.

	T3-4	T3-5
Formula	C ₃₀ H ₆₂ N ₁₀ In ₁₀ S ₁₇	C _{19.5} H _{55.5} N _{7.5} O _{4.5} In ₁₀ S ₁₈
Mr	2256.11	2192.49
Temp (K)	150(2)	293(2)
Wavelength (Å)	0.71073	1.54184
Cryst syst	Monoclinic	Tetragonal
Space group	<i>I2/a</i>	<i>I4₁/acd</i>
a/Å	21.4044(6)	20.1739(6)
b/Å	27.2254(8)	20.1739(6)
c/Å	25.6704(7)	31.9031(13)
α /°	90	90
β /°	102.398(3)	90
γ /°	90	90
<i>V</i> (Å ³)	14610.4(7)	12984.1(9)
<i>Z</i>	8	8
ρ (g cm ⁻³)	1.992	1.765
μ (mm ⁻¹)	3.606	33.238
<i>F</i> (000)	8280.0	6224.0
Collected reflns	13837	11314
Completeness	99.9%	99.8%
GOF on <i>F</i> ²	1.161	1.112
<i>R</i> ₁ ^a / <i>wR</i> ₂ ^b [<i>I</i> > 2(<i>I</i>)]	0.0839/0.2183	0.0609/0.1990
<i>R</i> ₁ ^a / <i>wR</i> ₂ ^b (all data)	0.1116/0.2372	0.0917/0.2223

$$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|. \quad ^b wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$$

Table S4. Time regulation of cluster transformation.

Entry	Synthetic conditions	Time (day)	Product
1	T3-0 10 mg, DBN 1.0 mL, MeOH 0.5 mL, 180 °C	1-2	T3-1, T3-3
2	T3-0 10 mg, DBN 1.0 mL, MeOH 0.5 mL, 180 °C	2-3	T3-2, T3-3
3	T3-0 10 mg, DBN 1.0 mL, MeOH 0.5 mL, 180 °C	5	T3-3
4	T3-0 10 mg, DBN 1.0 mL, MeOH 0.5 mL, 180 °C	12	T3-3

Table S5. Temperature regulation of cluster transformation.

Entry	Synthetic conditions	Temp. (°C)	Product
1	T3-0 10 mg, DBN 1.0 mL, MeOH 0.5 mL, 5 d	100	T3-0
2	T3-0 10 mg, DBN 1.0 mL, MeOH 0.5 mL, 5 d	120	T3-1
3	T3-0 10 mg, DBN 1.0 mL, MeOH 0.5 mL, 5 d	140	T3-2
4	T3-0 10 mg, DBN 1.0 mL, MeOH 0.5 mL, 5 d	160	T3-2
5	T3-0 10 mg, DBN 1.0 mL, MeOH 0.5 mL, 5 d	180	T3-3
6	T3-0 10 mg, DBN 1.0 mL, MeOH 0.5 mL, 5 d	200	T3-3

Table S6. Amine regulation of cluster transformation.

Entry	Synthetic conditions	Temp. (°C)	Product
1	T3-0 10 mg, DBN 1 mL, CH₃NH₂ 0.5 mL , MeOH 0.5 mL, 5 d	180	T3-3
2	T3-0 10 mg, DBN 0.5 mL, CH₃NH₂ 1.5 mL , MeOH 0.5 mL, 5 d	180	T3-4
3	T3-0 10 mg, ethanolamine 1.0 mL, 5 d	180	T3-5

Table S7. Electronic energy of series molecular clusters, [HDBN]⁺ and H₂S.

Compound	Binding energy (eV)	Compound	Binding energy (eV)
T3-0	-120.64046784	T3-1	-241.41470328
T3-2	-361.40762895	T3-3	-942.27361721
B	-481.87267018	C	-599.07784543
[HDBN] ⁺	-121.72363508	H ₂ S	-11.05568324

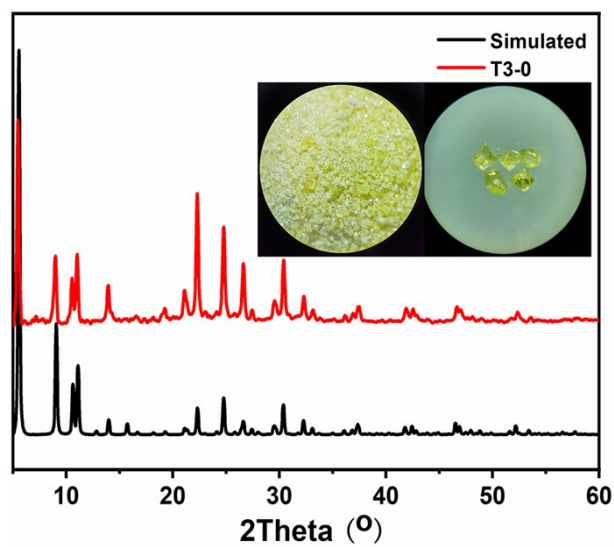


Figure S1. Crystal photograph and PXRD pattern of compound T3-0.

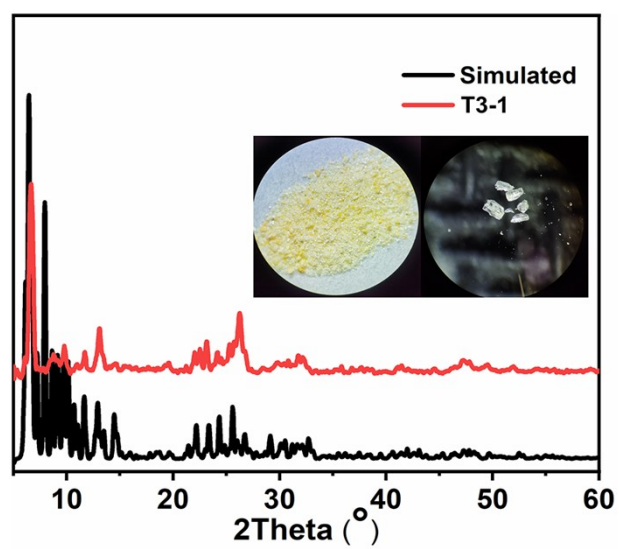


Figure S2. Crystal photograph and PXRD pattern of compound T3-1.

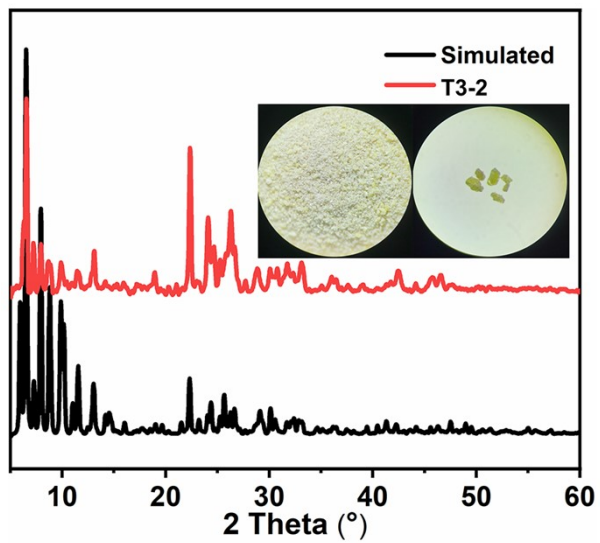


Figure S3. Crystal photograph and PXRD pattern of compound T3-2.

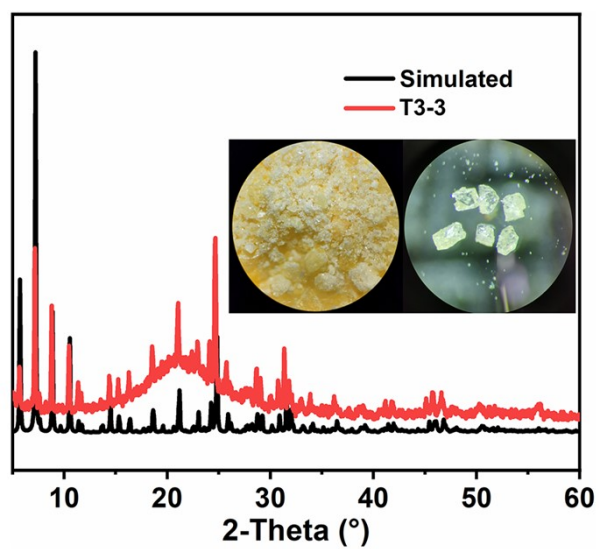


Figure S4. Crystal photograph and PXRD pattern of compound T3-3.

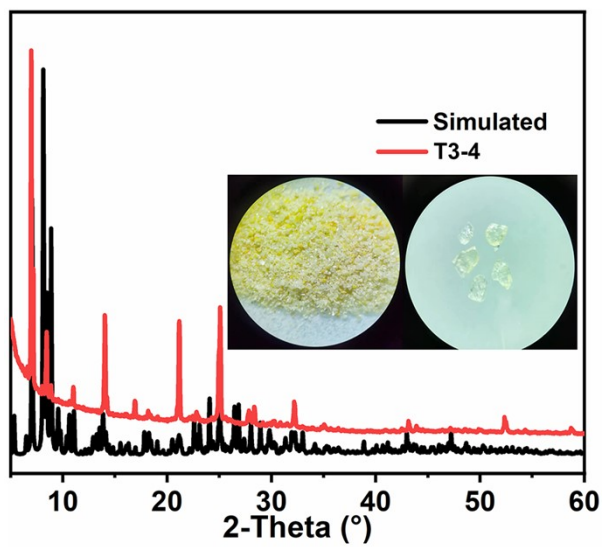


Figure S5. Crystal photograph and PXRD pattern of compound T3-4.

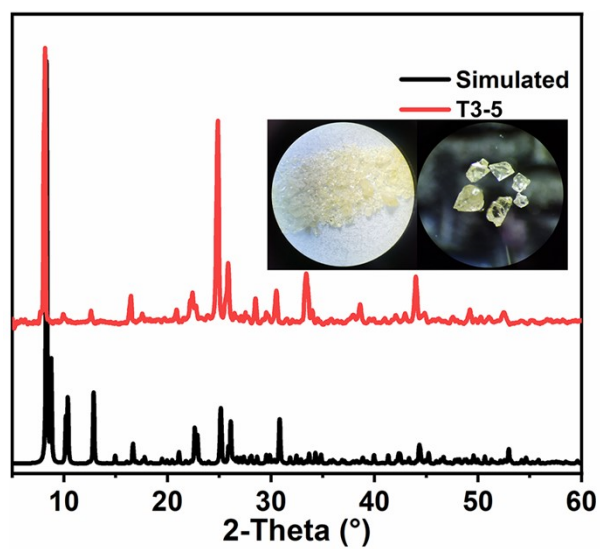


Figure S6. Crystal photograph and PXRD pattern of compound T3-5.

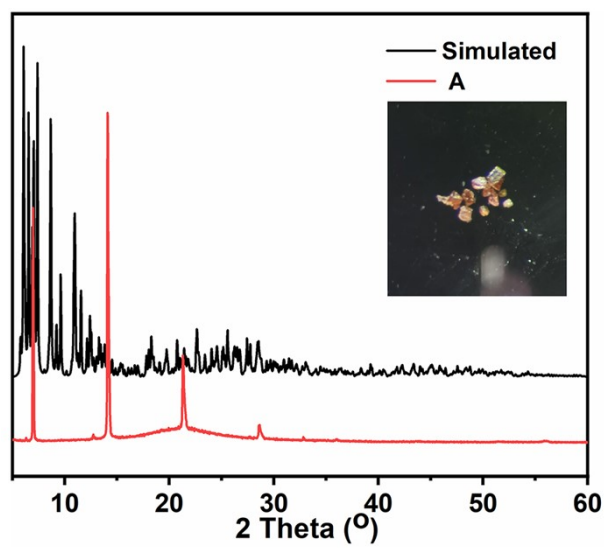


Figure S7. Crystal photograph and PXRD pattern of cluster A.

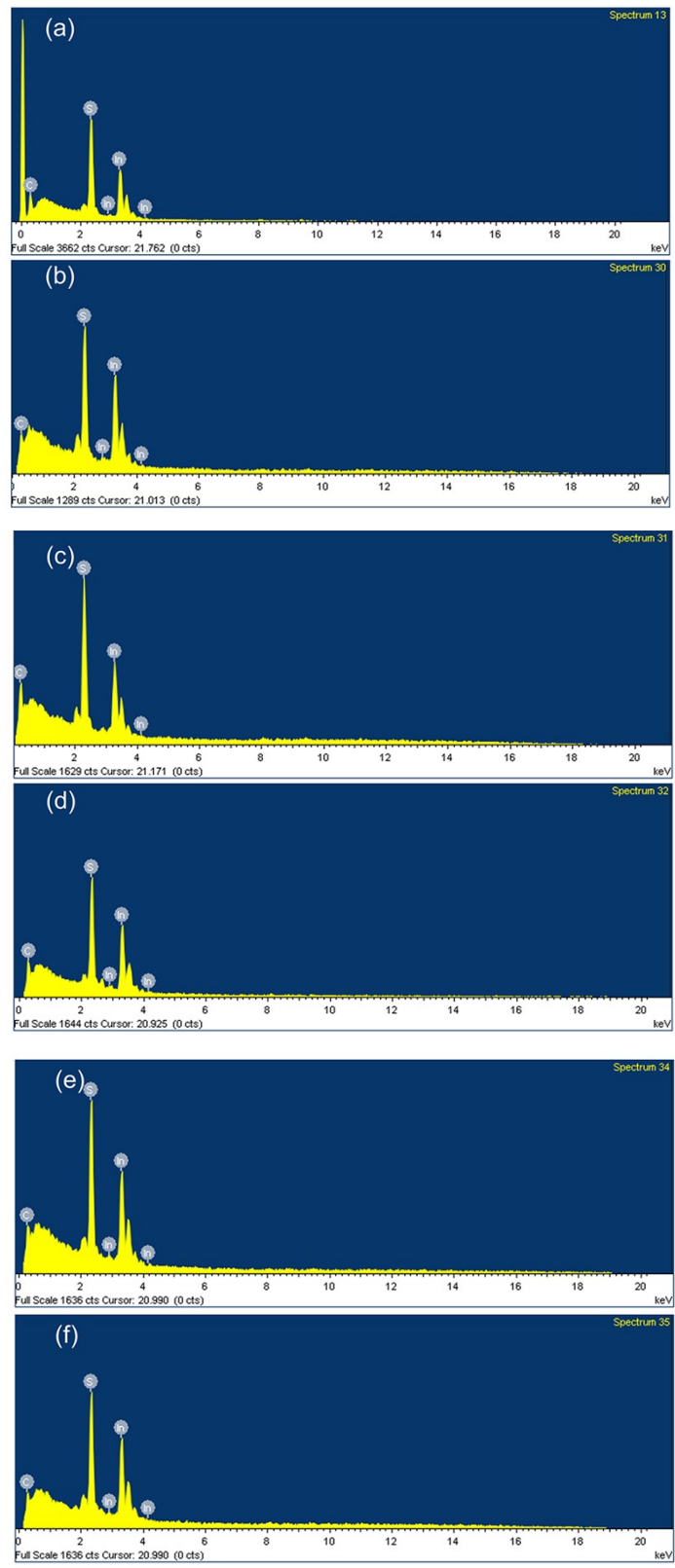


Figure S8. Energy dispersive X-ray spectra (EDS) for T3-0 (a), T3-1 (b), T3-2 (c), T3-3 (d), T3-4 (e) and T3-5 (f).

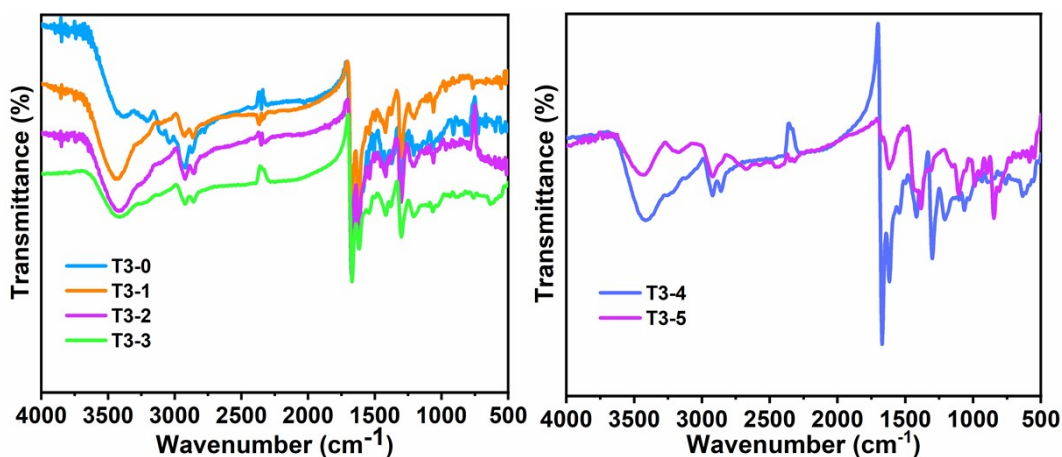


Figure S9. FTIR spectra of compounds **T3-0**—**T3-5**.

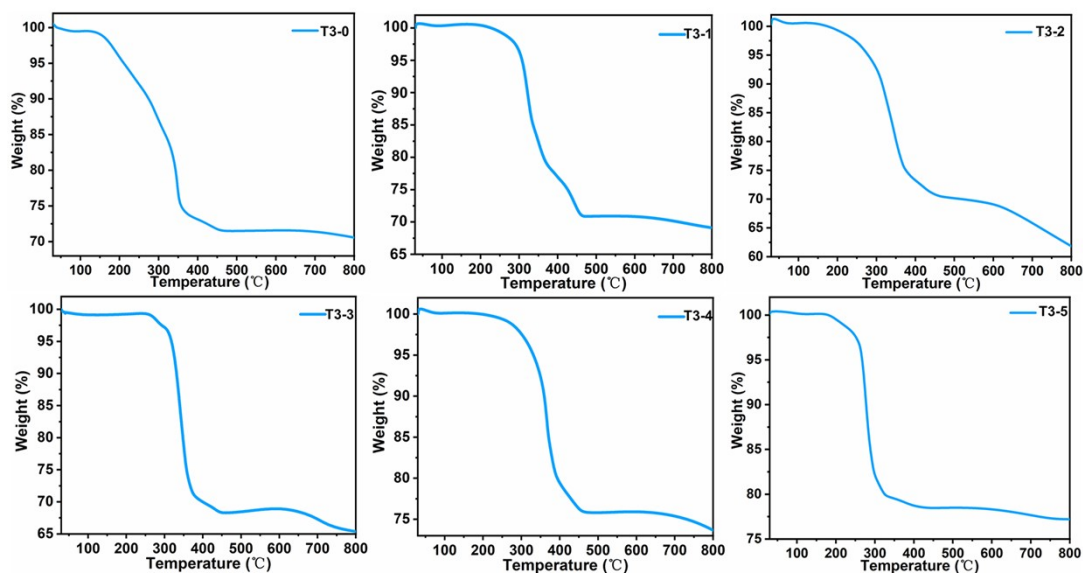


Figure S10. TGA curves of compounds **T3-0**—**T3-5**.

Note: Thermogravimetric analysis shows that the weight of counterions lost by **T3-0**—**T3-5** at high temperature is 27.96%, 29.33%, 29.96%, 30.93%, 24.54% and 21.58%, respectively. For compounds with two counterions, the proportion of counterions can be calculated by a system of linear equations in two unknowns in combination with the information provided by HRMS, EA and TGA.

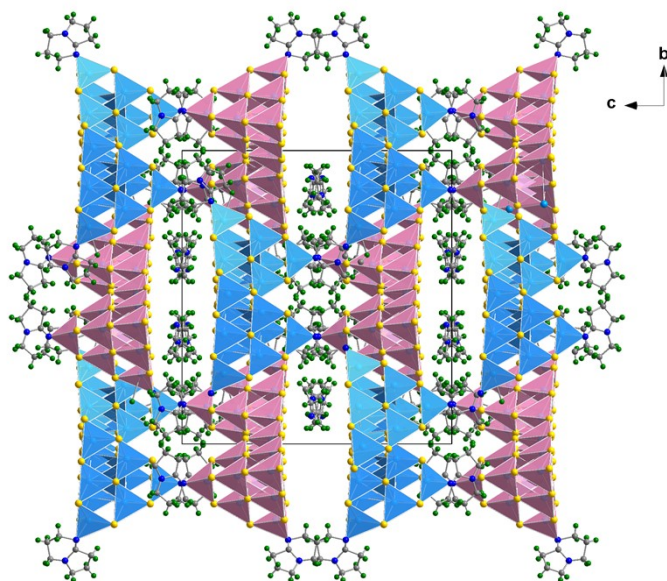


Figure S11. The spatial arrangement of polyhedron diagram of 1D chain structure in compound **T3-4** along the *a*-axis (for clear display, adjacent 1D chains are displayed in blue and purple respectively).

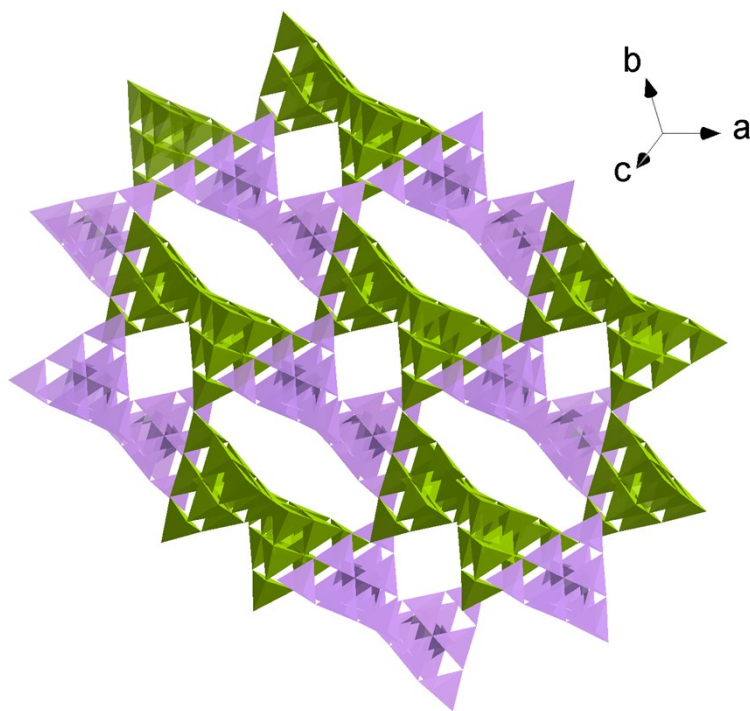


Figure S12. The interpenetration of frameworks of **T3-5**.