Supporting Information

The structure modulation by cationic modification with planar groups in sulfates

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Table S1. Crystal data and structure refinement

Empirical formula	$Zn[CS(NH_2)_2]_3SO_4$
Formula weight (g/mol)	389.80
Temperature (K)	292.99(10)
Crystal system	orthorhombic
Space group	$Pna2_1$
a (Å)	11.1636(2)
b (Å)	7.79590(10)
c (Å)	15.5296(3)
α (°)	90
β (°)	90
γ (°)	90
Volume ($Å^3$)	1351.55(4)
Z	4
ρ(calcd) (g/cm^3)	1.916
μ (mm^{-1})	5.617
F(000)	792.0
Crystal size (mm^3)	0.303 × 0.298 × 0.113
Radiation	Ga Kα (λ = 1.3405 Å)
2θ range for data collection (°)	9.864 to 111.588
Index ranges	$-13 \le h \le 11$, $-8 \le k \le 9$, $-19 \le l \le 17$
Reflections collected	5730
Independent reflections	2166 [R_{int} = 0.0343, R_{sigma} = 0.0278]
Data/restraints/parameters	2166/1/163
Goodness-of-fit on F^2	1.119
Final R indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0352, wR_2 = 0.0877
Final R indexes [all data]	R_1 = 0.0354, wR_2 = 0.0878
Largest diff. peak/hole ($eÅ^{-3}$)	0.43/-0.88
Flack parameter	-0.02(3)

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$ and $wR_2 = [\sum[w(F_o^2-F_c^2)^2]/[\sum[w(F_o^2)^2]]^{1/2}$ for $F_o^2 > 2\sigma(F_c^2)$

Table S2. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$)

Atom	*x*	*y*	*z*	*U*(eq)
C1	3619(4)	586(6)	4444(3)	26.8(9)
C2	6145(4)	6003(6)	3507(3)	24.9(9)
C3	4922(4)	6624(5)	6294(4)	24.1(9)
N1	6646(4)	6425(6)	2767(3)	46.1(13)
N2	5015(4)	6352(6)	3634(4)	43.1(12)
N3	3504(4)	377(6)	5275(3)	39.7(11)
N4	2802(4)	-69(6)	3917(4)	43.8(12)
N5	4312(4)	7450(6)	6883(3)	33.3(9)
N6	6041(4)	7084(5)	6136(4)	38.9(11)
O1	6545(3)	1861(4)	5799(2)	29.9(7)
O2	6632(3)	3045(4)	7230(3)	32.6(8)
O3	6961(3)	29(4)	6993(2)	27.3(8)
O4	4972(3)	1220(4)	6819(3)	31.2(7)
S1	6266.6(9)	1547.5(11)	6738.7(7)	19.3(2)
S2	7038.9(9)	5018.1(13)	4273.3(8)	25.6(3)
S3	4192.9(9)	5024.5(13)	5741.8(8)	25.9(3)
S4	4786.8(11)	1684.8(14)	3979.7(8)	27.9(3)
Zn1	5636.8(5)	3411.8(7)	5040.2(4)	21.0(2)

[a]U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table S3. Anisotropic displacement parameters ($Å^2 \times 10^3$)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	24(2)	26(2)	30(3)	-4.3(19)	-1.8(18)	-6.0(17)
C2	25(2)	26(2)	23(2)	5.2(18)	-4.5(16)	-3.7(17)
C3	23(2)	21(2)	29(3)	-0.1(15)	-4.7(19)	5.5(15)
N1	34(2)	74(3)	31(3)	26(2)	-2(2)	2(2)
N2	29(2)	55(3)	46(3)	26(2)	-5(2)	6.9(19)
N3	39(2)	51(2)	29(3)	5.5(19)	2.7(18)	-23(2)
N4	39(3)	60(3)	32(2)	-4(2)	-1(2)	-30(2)
N5	35(2)	32(2)	33(2)	-12.6(19)	0.9(16)	2.0(15)
N6	27(2)	33(2)	56(3)	-19(2)	6(2)	-5.4(17)
O1	33.1(18)	36.8(17)	19.7(17)	6.0(13)	8.6(13)	13.9(13)
O2	32.1(19)	29.6(16)	36(2)	-13.0(16)	2.8(14)	-5.0(14)
O3	30.8(18)	25.3(17)	25.8(19)	3.7(11)	-3.6(14)	5.2(12)
O4	18.0(16)	38.3(17)	37.4(19)	-2.1(17)	6.1(14)	-3.3(13)
S1	18.7(5)	20.3(5)	19.0(5)	-1.2(4)	1.5(4)	0.1(3)
S2	15.6(5)	34.8(6)	26.4(5)	10.5(4)	-1.4(4)	-1.5(3)
S3	17.2(5)	29.5(5)	31.0(6)	-10.1(4)	0.2(4)	0.3(3)
S4	27.3(6)	33.6(6)	22.8(6)	-4.5(4)	6.0(5)	-11.7(4)
Zn1	20.6(3)	19.7(3)	22.6(4)	0.7(2)	1.7(2)	0.04(19)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Table S4. Selected bond distances (Å) and angles (deg.)

C1—N3	1.308(6)	S1—O1—Zn1	124.83(19)
C1—N4	1.327(6)	O2—S1—O1	108.6(2)
C1—S4	1.719(4)	O2—S1—O3	111.0(2)
C2—N1	1.320(7)	O2—S1—O4	111.7(2)
C2—N2	1.305(7)	O3—S1—O1	106.3(2)
C2—S2	1.733(5)	O3—S1—O4	110.83(19)
C3—N5	1.310(7)	O4—S1—O1	108.1(2)
C3—N6	1.322(7)	C2—S2—Zn1	101.67(15)
C3—S3	1.718(5)	C3—S3—Zn1	107.39(16)
O1—S1	1.511(4)	C1—S4—Zn1	107.49(17)
O1—Zn1	1.970(3)	O1—Zn1—S2	106.86(10)
O2—S1	1.452(3)	O1—Zn1—S3	114.19(11)
O3—S1	1.469(3)	O1—Zn1—S4	106.14(11)
O4—S1	1.473(3)	S3—Zn1—S2	114.57(4)
S2—Zn1	2.3317(12)	S3—Zn1—S4	111.27(5)
S3—Zn1	2.3165(12)	S4—Zn1—S2	102.87(5)
S4—Zn1	2.3293(13)	N1—C2—S2—Zn1	-152.5(4)
N3—C1—N4	119.6(4)	N2—C2—S2—Zn1	28.1(5)
N3—C1—S4	123.4(3)	N3—C1—S4—Zn1	-19.3(5)
N4—C1—S4	117.0(4)	N4—C1—S4—Zn1	160.7(4)
N1—C2—S2	117.7(4)	N5—C3—S3—Zn1	-165.2(4)
N2—C2—N1	119.3(4)	N6—C3—S3—Zn1	16.7(5)
N2—C2—S2	123.0(4)	Zn1—O1—S1—O2	-73.8(3)
N5—C3—N6	119.2(4)	Zn1—O1—S1—O3	166.7(2)
N5—C3—S3	117.3(4)	Zn1—O1—S1—O4	47.6(3)
N6—C3—S3	123.5(4)		

Table S5. Hydrogen atom coordinates ($Å \times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$)

Atom	x	y	z	U(eq)
H1A	6227.85	6924.12	2374.71	55
H1B	7389.38	6201.59	2676.84	55
H2A	4605.88	6850.83	3237.29	52
H2B	4680.59	6082.22	4113.79	52
H3A	2902.54	-182.68	5477.25	48
H3B	4030.02	798.82	5619.87	48
H4A	2202.76	-627.64	4122.38	53
H4B	2872.99	64.46	3369.26	53
H5A	4639.3	8278.76	7162.56	40
H5B	3583.11	7162.04	6991.42	40
H6A	6359.23	7914.89	6419.63	47
H6B	6450.39	6551.28	5750.94	47

Table S6. The HOMO-LUMO gap, polarizability anisotropy and hyperpolarizability of each group

Groups	HOMO-LUMO Gap (eV)	Polarizability Anisotropy	Hyperpolarizability
$[C(1)S(NH_2)_2]$	5.48	40	273.7
$[C(2)S(NH_2)_2]$	5.41	40.1	283.7
$[C(3)S(NH_2)_2]$	5.42	39.9	273.7
$[SO_4]$	9.56	0.68	11.2
$[ZnS_3O]$	3.77	30.9	513.1

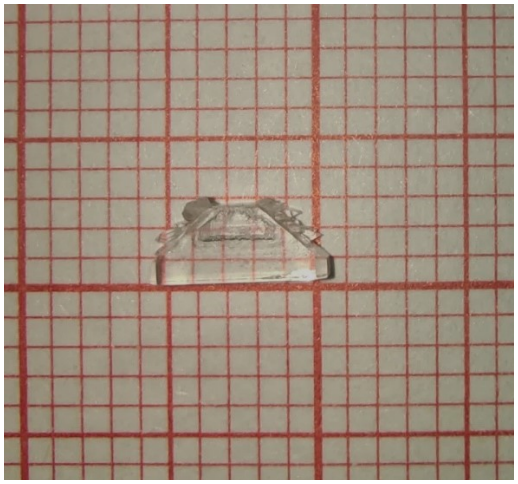

Figure S1. As-grown ZTS crystals

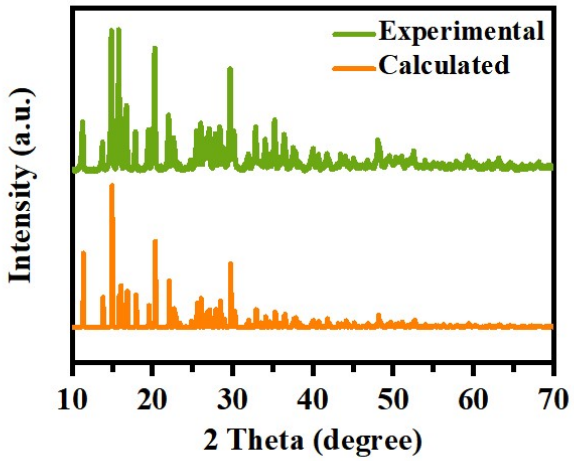

Figure S2. The powder X-ray diffraction patterns

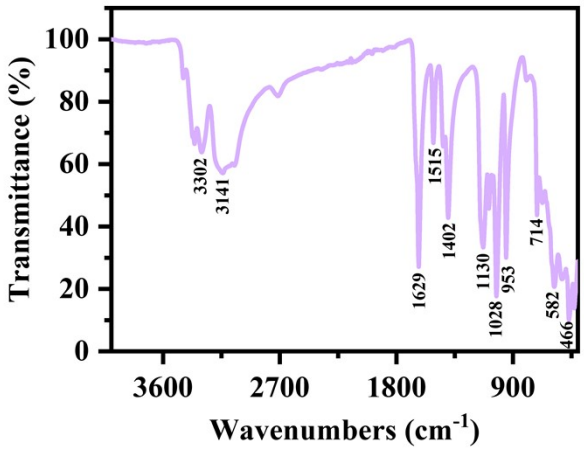

Figure S3. The Fourier transform infrared spectrum

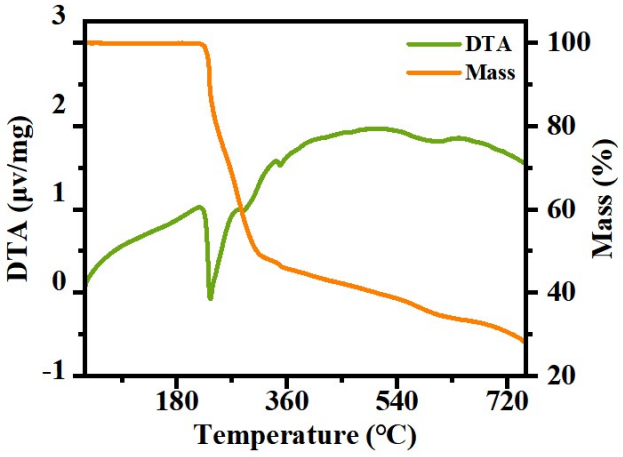

Figure S4. TGA and DTA curves of ZTS.

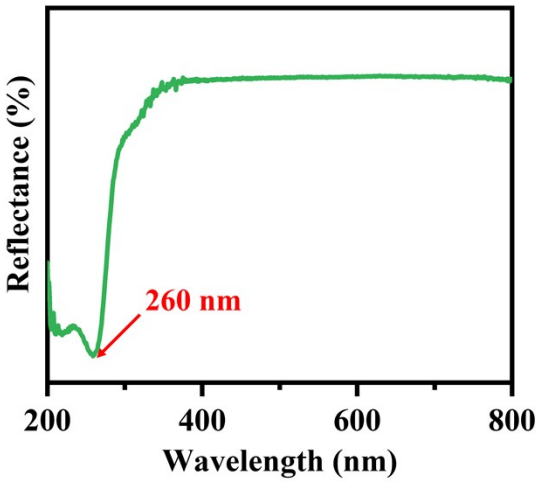

Figure S5 The UV-vis-NIR diffuse reflectance spectrum

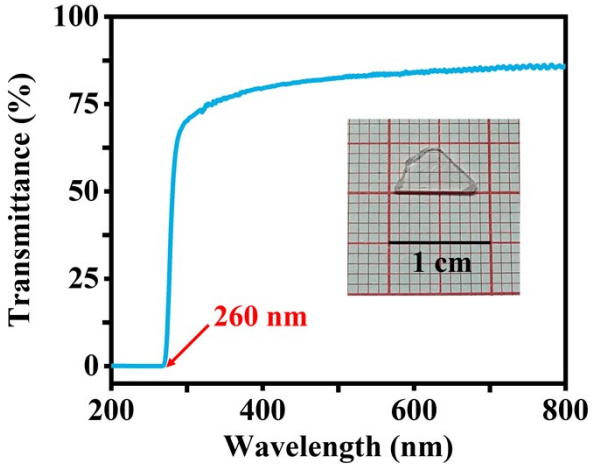

Figure S6 the UV-vis-NIR transmittance spectrum with the inset of one as-grown crystal

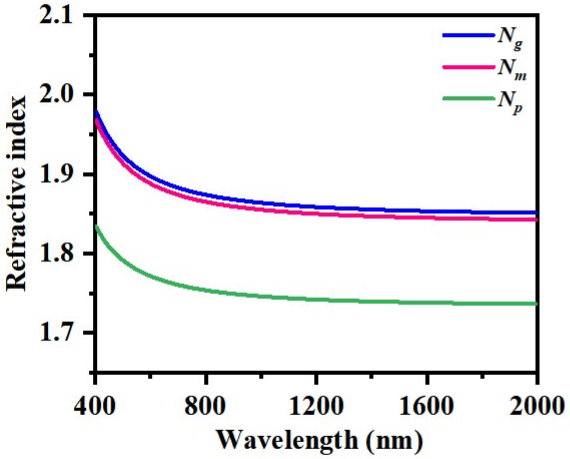

Figure S7 Calculated refractive indices

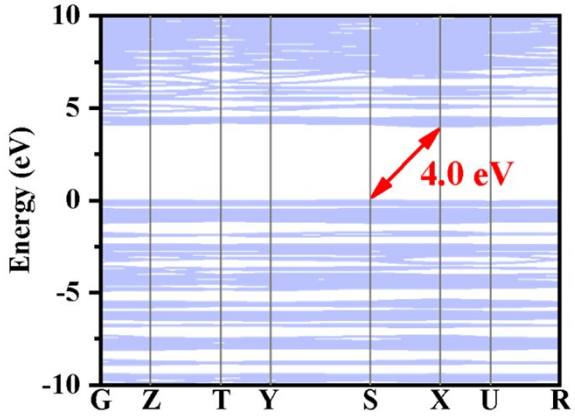

Figure S8 The electronic band structure