Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

$Na_{10}Zn(NO_3)_4(SO_3S)_4$: a nonlinear optical crystal combining inorganic π-conjugated and non-π-conjugated heteroanion groups

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Raman Spectra.

The Raman spectra of $Na_{10}Zn(NO_3)_4(SO_3S)_4$ was obtained using the CCD detector of the LABRAM HR evolution spectrometer with 532 nm radiation.[1] Approximately 0.01 g $Na_{10}Zn(NO_3)_4(SO_3S)_4$ powders were placed on a slide and exposed to laser irradiation with a wavelength of 532 nm.[2] The Raman spectra of $Na_{10}Zn(NO_3)_4(SO_3S)_4$ were recorded in the 4000−100 cm^{-1} region (2.5−100 μm)[1] and shown in Figure S2.

Thermal Stability.

The thermal stability was investigated by the thermogravimetry (TG) on a simultaneous NETZSCH STA 449C thermal analyzer in an atmosphere of flowing N_2. Approximately 10.3 mg $Na_{10}Zn(NO_3)_4(SO_3S)_4$ powders were placed into an Al_2O_3 crucible, heated at a rate of 15 K min^{-1} from room temperature to 1073 K.[3]

Table S1. Crystal data and structure refinement for $Na_{10}Zn(NO_3)_4(SO_3S)_4$.

Empirical formula	**$Na_{10}Zn(NO_3)_4(SO_3S)_4$**
Formula weight	991.79
Wavelength (Å)	1.54056
Temperature (K)	293
Crystal system, space group	tetragonal, $P\bar{4}$
a, b, c (Å)	11.2790(2), 11.2790(2), 5.3919(2)
α, β, γ (°)	90, 90, 90
Volume (Å^3)	685.94(4)
Z, Calculated density (g/cm^3)	1, 2.401
Absorption coefficient (mm^{-1})	9.540
F(000)	488.0
Crystal size (mm)	0.08 × 0.03 × 0.03
2Θ range for data collection (deg.)	7.84 to 153.14
Limiting indices	-14 ≤ h ≤ 14, -14 ≤ k ≤ 13, -4 ≤ l ≤ 6
Reflections collected / unique	6360
Independent reflections	1422 [R_{int} = 0.0385, R_{sigma} = 0.0289]
Data / restraints / parameters	1422/0/108
Goodness-of-fit on F^2	1.061
Final R indices [I>2sigma(I)]	R_1 = 0.0207, wR_2 = 0530
R indices (all data)	R_1 = 0.0213, wR_2 = 0.0534
Largest diff. peak and hole (e.A^{-3})	0.23/-0.33
Flack parameter	0.0 (2)

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$.

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for $Na_{10}Zn(NO_3)_4(SO_3S)_4$. *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	*X*	*Y*	*Z*	*U*(eq)
Zn1	3725.2(14)	3373.5(15)	3650.3(16)	8.8(3)
Zn1	5027(5)	7455(7)	3113(6)	16.9(13)
S1	7445.7(11)	4605.6(18)	3570.2(12)	6.8(3)
S2	4991.9(11)	9606.0(19)	3674.0(13)	9.1(3)
O1	5346.5(16)	5881(3)	3512(2)	10.8(5)
O2	2027.8(16)	5879(3)	3497.1(19)	10.6(5)
O3	2903(4)	3238(5)	6304(4)	71.1(12)
O4	1026(5)	5305(8)	3158(7)	20.9(15)
O5	4924(4)	7078(6)	6295(4)	73.0(12)
O6	5882(2)	2026(3)	6494(3)	41.5(7)
N1	8007.8(15)	4137(2)	6513.3(18)	8.3(4)
Na1	2004(5)	7456(7)	3023(6)	15.2(13)
Na2	4481(5)	4853(8)	3122(7)	22.7(16)
Na3	2571(5)	4821(7)	3078(6)	17.6(14)

Table S3. Selected bond lengths (Å) for $Na_{10}Zn(NO_3)_4(SO_3S)_4$.

Atom Atom	lengths (Å)	Atom Atom	lengths (Å)
Zn1-S1	2.3590(6)	O4-Na2	2.444(2)
Zn1-S1^{1}	2.3590(6)	Na1-O5^{4}	2.5009(17)
Zn1-S1^{2}	2.3590(6)	Na1-O2^{6}	2.3201(18)
Zn1-S1^{3}	2.3590(6)	Na1-O2^{10}	2.3201(18)
S2-S1	2.0274(7)	Na1-O1^{4}	2.3465(18)
S2-O3	1.4576(16)	Na1-Na3^{10}	3.9829(14)
S2-O2	1.4573(17)	Na1-Na3	3.6102(13)
S2-O1	1.4746(17)	Na1-Na3^{6}	3.9829(14)
S2-Na3^{4}	3.3321(10)	Na1-Na3^{4}	3.6102(13)
S2-Na2^{3}	3.3700(11)	Na1-Na2^{5}	3.4262(10)
S2-Na2^{5}	3.3859(11)	Na1-Na2^{8}	3.4262(10)
S1-Na2^{5}	3.0259(13)	Na3-S2^{4}	3.3321(10)
O6-N1	1.248(3)	Na3-O6^{8}	2.503(2)
O6-Na3^{6}	2.498(2)	Na3-O6^{9}	2.498(2)
O6-Na3^{7}	2.503(2)	Na3-O5^{9}	2.584(2)
O6-Na2^{6}	2.761(2)	Na3-O1^{4}	2.3528(19)
O3-Na3	2.4729(18)	Na3-N1^{8}	2.965(2)
O3-Na2	2.2791(18)	Na3-N1^{9}	2.927(2)
O5-N1	1.253(3)	Na3-O4^{8}	2.653(2)
O5-Na1	2.5009(17)	Na3-Na1^{9}	3.9829(14)
O5-Na3^{6}	2.584(2)	Na3-Na2^{11}	3.9814(15)
O5-Na3	2.848(2)	Na3-Na2^{8}	3.7152(14)
O5-Na2^{8}	2.981(2)	Na3-Na2	3.3541(14)
O2-Na1^{9}	2.3201(18)	Na2-S2^{12}	3.3858(11)
O2-Na2^{3}	2.286(2)	Na2-S1^{1}	3.3700(11)
O1-Na1	2.3465(18)	Na2-S1^{12}	3.0259(13)
O1-Na3^{4}	2.3528(19)	Na2-O6^{9}	2.761(2)
O1-Na25	2.4859(19)	Na2-O5^{7}	2.981(2)
N1-O4	1.249(3)	Na2-O2^{1}	2.286(2)
N1-Na3^{7}	2.965(2)	Na2-O1^{12}	2.4859(19)
N1-Na3	3.053(2)	Na2-Na1^{12}	3.4262(10)

N1-Na3[6]	2.927(2)	Na2-Na3[7]	3.7152(14)
O4-Na3[7]	2.653(2)	Na2-Na3[13]	3.9814(15)
O4-Na3	2.491(2)		

Symmetry transformations used to generate equivalent atoms:

[1]-1/2+X,1/2-Y,-1/2+Z; [2]+X,1-Y,-1/2+Z; [3]1/2+X,1/2-Y,-1/2+Z; [4]1/2+X,1/2+Y,+Z; [5]1/2+X,-1/2+Y,+Z; [6]+X,1+Y,+Z; [7]+X,2-Y,-1/2+Z; [8]-1/2+X,1/2+Y,+Z; [9]-1/2+X,3/2-Y,-1/2+Z; [10]1/2+X,1/2-Y,1/2+Z; [11]+X,-1+Y,+Z; [12]+X,1-Y,1/2+Z; [13]1/2+X,3/2-Y,1/2+Z; [14]-1/2+X,1/2-Y,1/2+Z; [15]-1/2+X,-1/2+Y,+Z

Table S4. Selected angles (°) for $Na_{10}Zn(NO_3)_4(SO_3S)_4$.

Atom Atom Atom	Angles (°)	Atom Atom Atom	Angles (°)
S1 Zn1 S1	105.22(3)	O6 N1 O5	119.4(2)
S1 Zn1 S1^{2}	111.637(16)	O6 N1 O4	119.92(18)
S1^{3} Zn1 S1^{2}	105.22(3)	O4 N1 O5	120.7(2)
S1^{1} Zn1 S1^{3}	111.637(16)	O2 S2 S1	109.66(8)
S1 Zn1 S1^{3}	111.637(16)	O2 S2 O3	111.37(11)
S1^{1} Zn1 S1^{2}	111.637(16)	O2 S2 O1	110.43(11)
S2 S1 Zn1	111.98(3)	O1 S2 S1	102.87(7)
O3 S2 O1	110.32(10)	O3 S2 O1	111.88(7)

Symmetry transformations used to generate equivalent atoms:

^{1}-1/2+X,1/2-Y,-1/2+Z; ^{2}+X,1-Y,-1/2+Z; ^{3}1/2+X,1/2-Y,-1/2+Z; ^{4}1/2+X,1/2+Y,+Z; ^{5}1/2+X,-1/2+Y,+Z; ^{6}+X,1+Y,+Z; ^{7}+X,2-Y,-1/2+Z; ^{8}-1/2+X,1/2+Y,+Z; ^{9}-1/2+X,3/2-Y,-1/2+Z; ^{10}1/2+X,1/2-Y,1/2+Z; ^{11}+X,-1+Y,+Z; ^{12}+X,1-Y,1/2+Z; ^{13}1/2+X,3/2-Y,1/2+Z; ^{14}-1/2+X,1/2-Y,1/2+Z; ^{15}-1/2+X,-1/2+Y,+Z

Table S5. Anisotropic displacement parameters (Å2×103) for $Na_{10}Zn(NO_3)_4(SO_3S)_4$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zn1	14.58(18)	14.58(18)	32.0(3)	0	0	0
S1	12.8(2)	30.5(3)	38.2(3)	-14.0(3)	-2.7(2)	3.8(2)
S2	11.5(2)	14.7(2)	17.3(2)	0.99(19)	0.06(18)	0.29(17)
O1	15.6(8)	24.0(8)	26.8(8)	-3.3(6)	-6.1(6)	-2.1(6)
O2	28.9(9)	31.0(9)	22.3(8)	6.5(7)	7.6(7)	5.9(7)
O3	23.4(8)	16.3(7)	37.8(9)	2.7(7)	3.6(8)	1.0(6)
O4	33.8(10)	35.2(10)	23.0(8)	-3.5(8)	-6.2(7)	-2.1(8)
O5	28.6(9)	23.4(8)	40.9(10)	3.1(8)	0.4(9)	-9.8(6)
O6	38.6(11)	31.3(9)	25.6(9)	5.5(8)	1.4(7)	-11.2(9)
N1	21.5(9)	19.7(9)	19.8(9)	1.4(7)	-1.1(8)	-2.3(7)
Na1	25.2(6)	26.2(7)	21.8(6)	0	0	9.0(5)
Na2	28.1(5)	39.9(6)	30.2(5)	4.6(5)	-5.0(4)	-15.2(4)
Na3	20.2(4)	26.7(5)	29.3(5)	-4.8(4)	-1.6(4)	0.0(3)

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

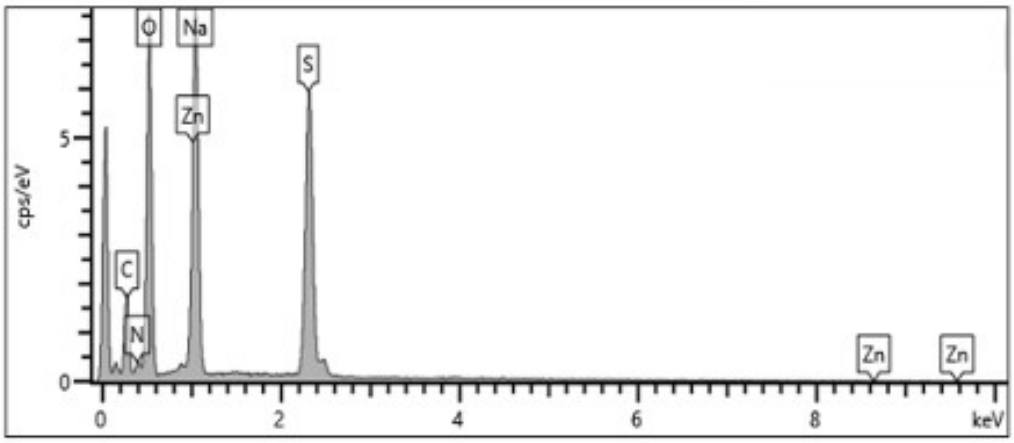

Figure S1. Energy dispersive X-ray spectroscopy result for $Na_{10}Zn(NO_3)_4(SO_3S)_4$.

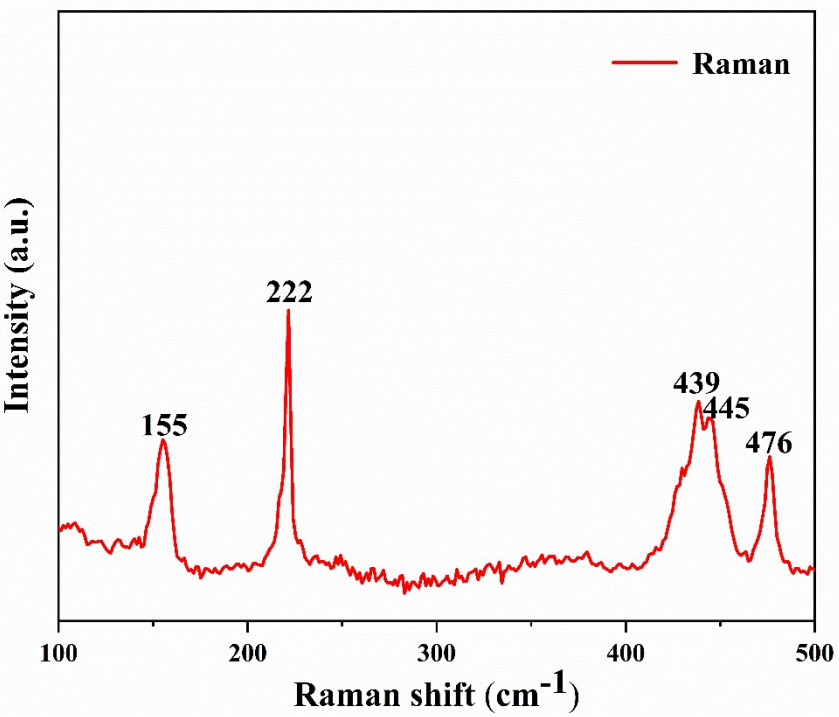

Figure S2. Raman spectra of $Na_{10}Zn(NO_3)_4(SO_3S)_4$.

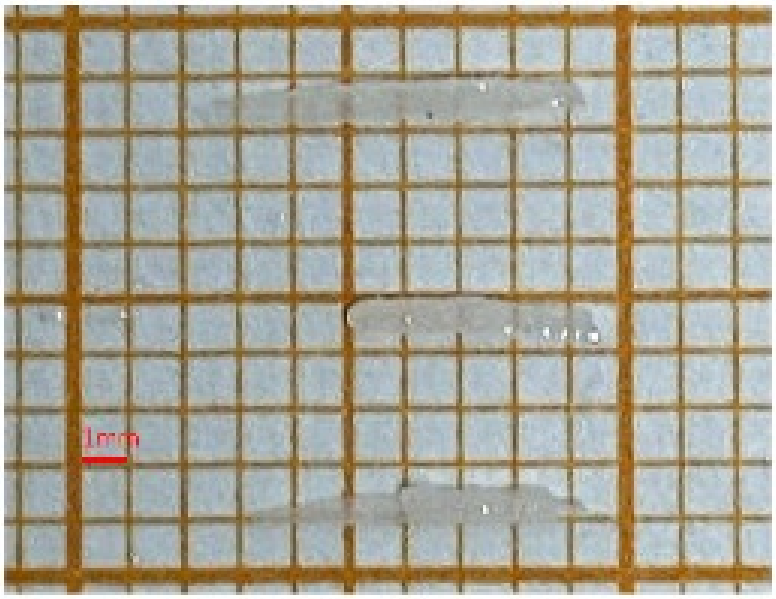

Figure S3. The crystal photograph of $Na_{10}Zn(NO_3)_4(SO_3S)_4$.

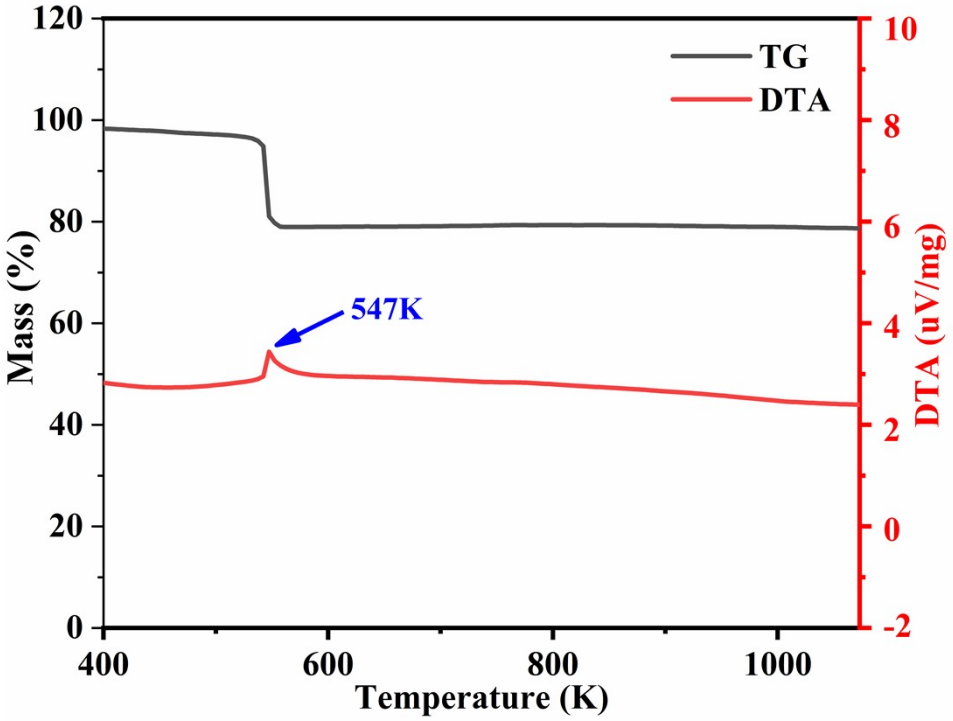

Figure S4. TG and TGA curves for $Na_{10}Zn(NO_3)_4(SO_3S)_4$.

The thermogravimetry (TG) and differential thermal analysis (DTA) curves reveal that $Na_{10}Zn(NO_3)_4(SO_3S)_4$ could be stable up to 547 K (Figure S4). This result indicates that $Na_{10}Zn(NO_3)_4(SO_3S)_4$ possesses a good thermal stability.

Figure S5. The thickness of $Na_{10}Zn(NO_3)_4(SO_3S)_4$.

References.

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