SUPPLEMENTARY INFORMATION

A Chain-of-Dimers Anion in a Novel Hybrid Halometallate $(C_5H_{14}N_2)_3\{Sb_2Br_9\}_2$ Exhibiting Photoluminescence Atypical for One-Dimensional Anions

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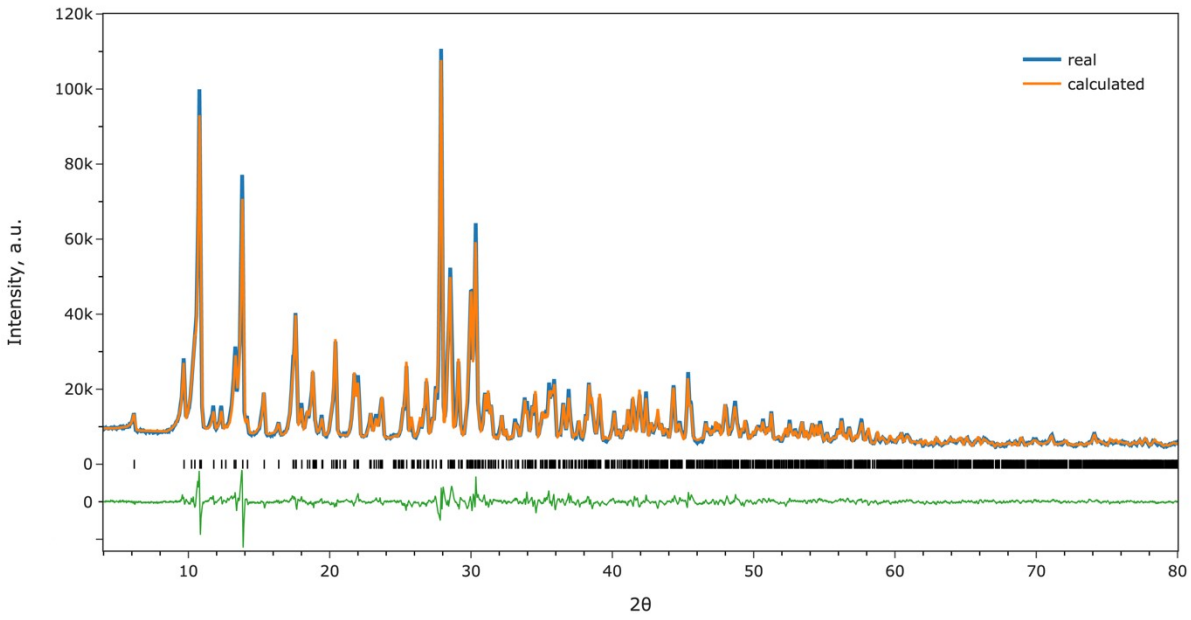

Figure S1. Results of the Rietveld profile analysis: triclinic, a = 9.46110(10) Å, b = 10.18888(12) Å, c = 5.29902(17) Å, α = 95.4714(8)°, β = 105.9850(10)°, γ = 113.1576(9)°, V = 1268.46(3) Å^3, R_p = 0.0482, wR_p = 0.0665.

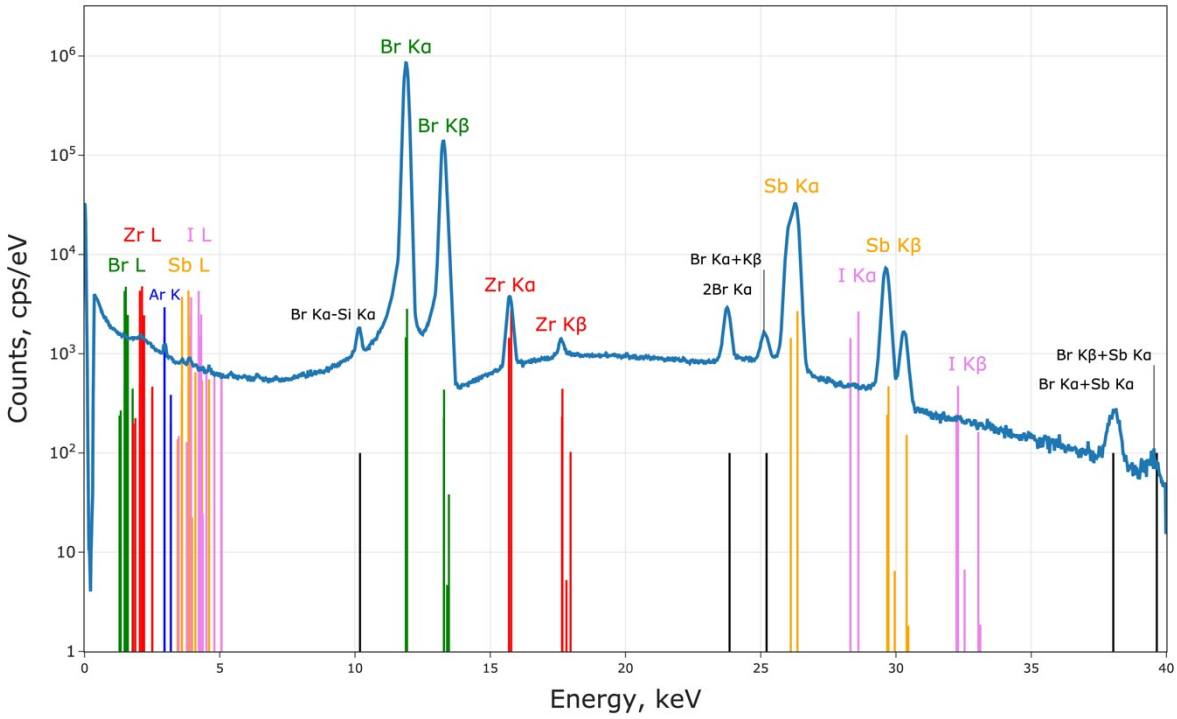

Figure S2. X-ray fluorescence (XRF) spectrum of $(C_5H_{14}N_2)_3\{Sb_2Br_9\}_2$ *and theoretical X-ray fluorescence lines of elements: orange – Sb, green – Br, violet – I, red – Zr, blue – Ar, black – escape and sum peaks. Element analysis demonstrates the presence of Br and Sb and the absence of I in*

the sample. There are Zr lines and Ar lines at the spectra, because zirconium is a casing material of X-ray tube and argon is a part of air, respectively. Also, there are sum peaks at the spectrum: sum of two Br Kα lines, Br Kα + Br Kβ, Br Kα + Sb Kα, and Br Kβ + Sb Kα lines. In addition, the escape peak Br Kα - Si Kα is observed (Si is a detector material).

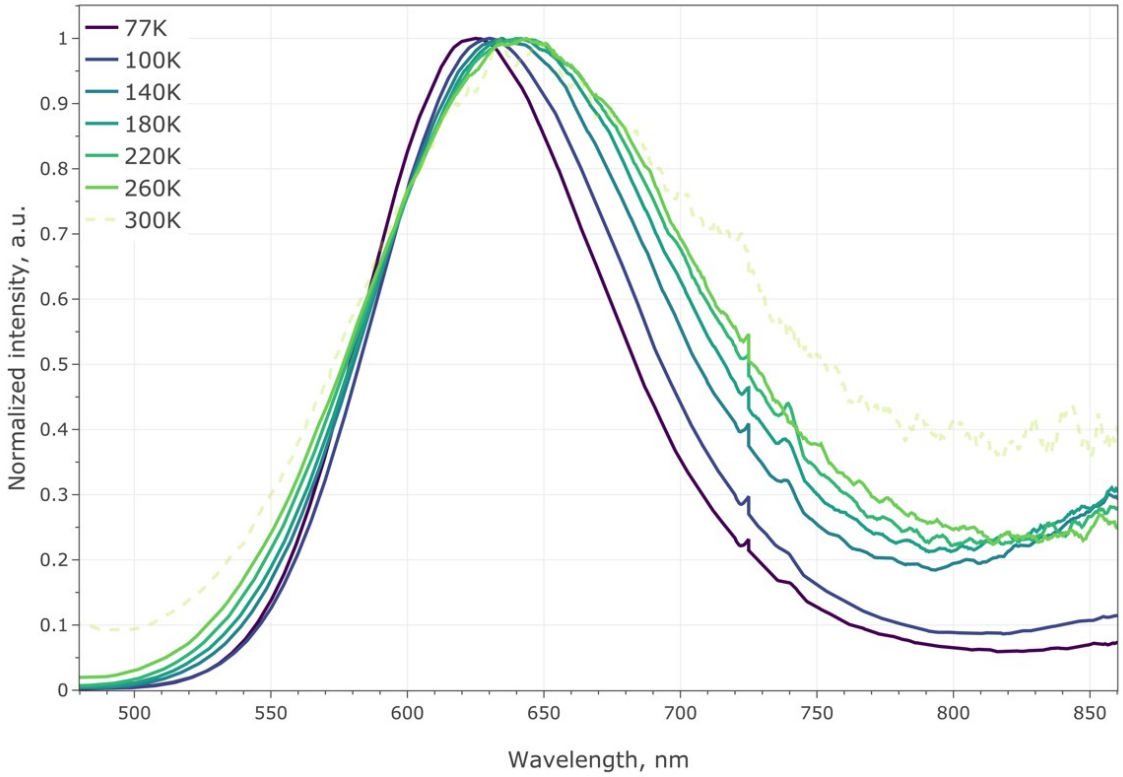

Figure S3. Temperature-dependent PL spectra with normalized intensity for the red emission band.

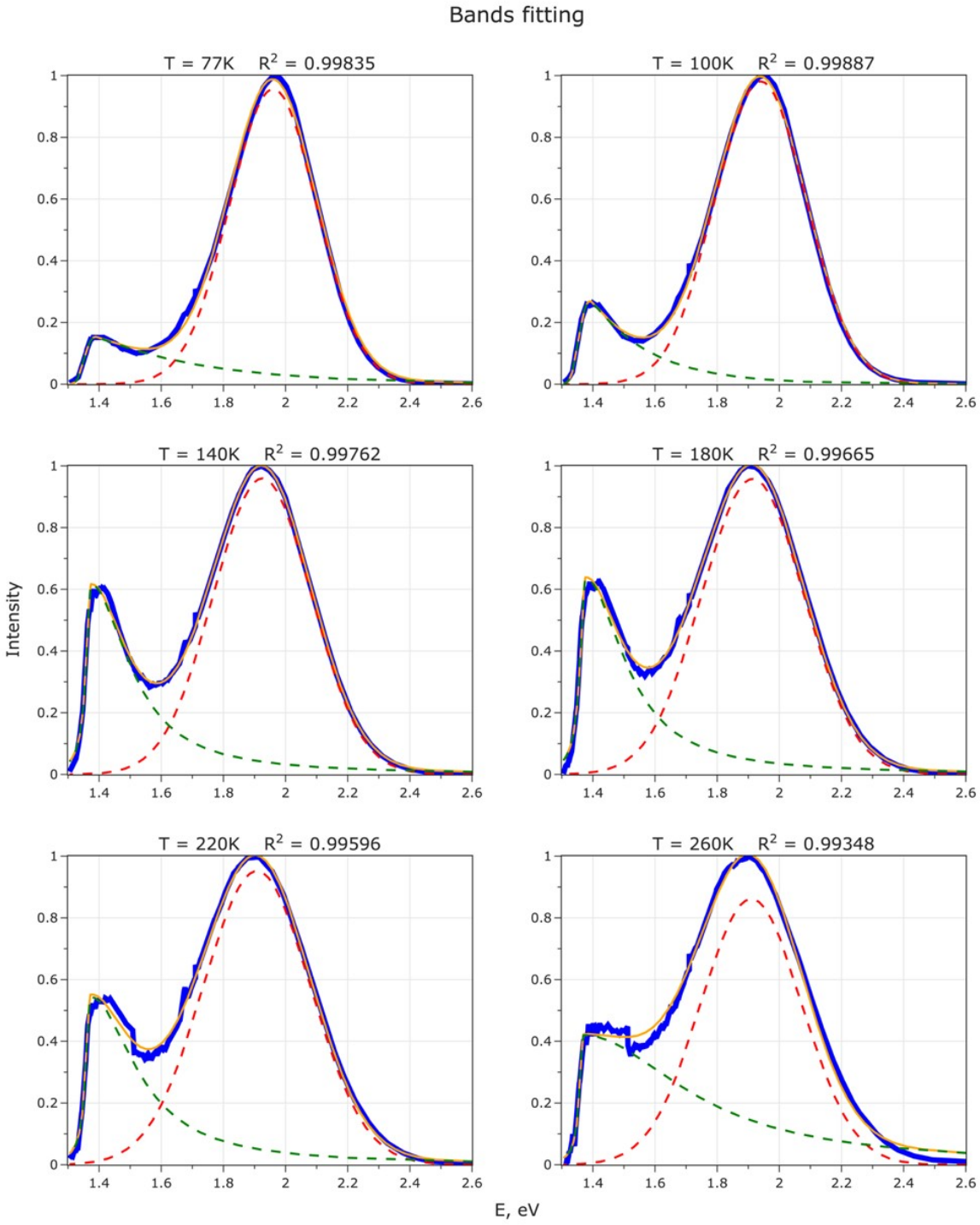

Figure S4. Temperature-depending PL spectra fitting.

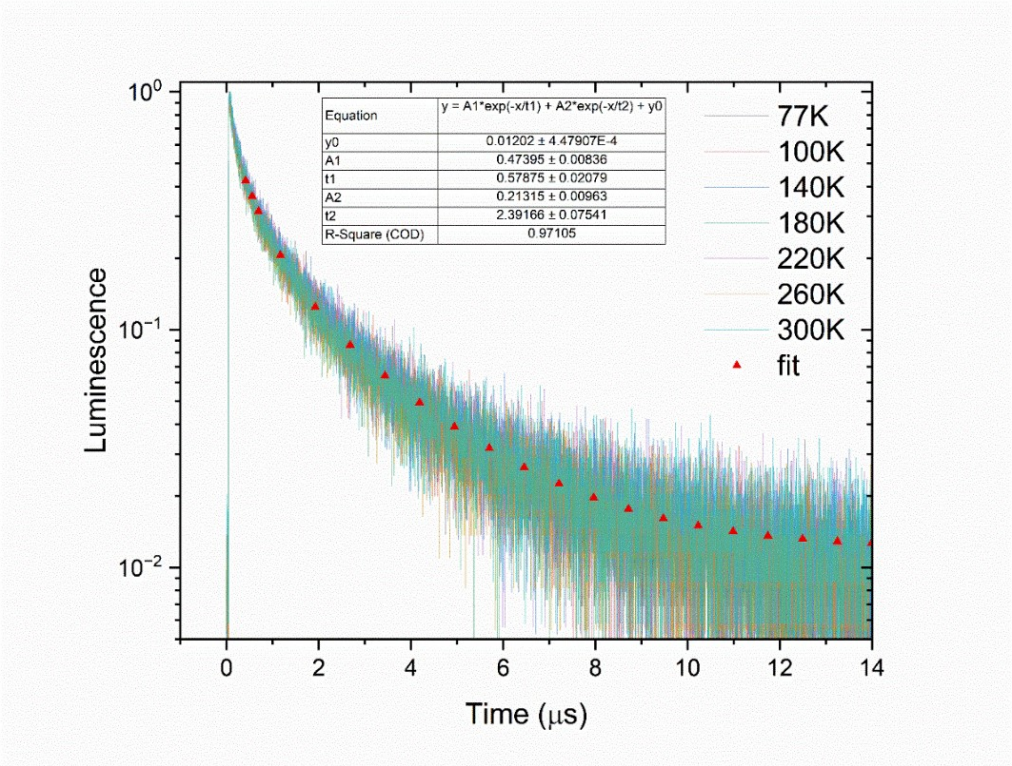

Figure S5. PL lifetime for broad red emission near 625 nm.

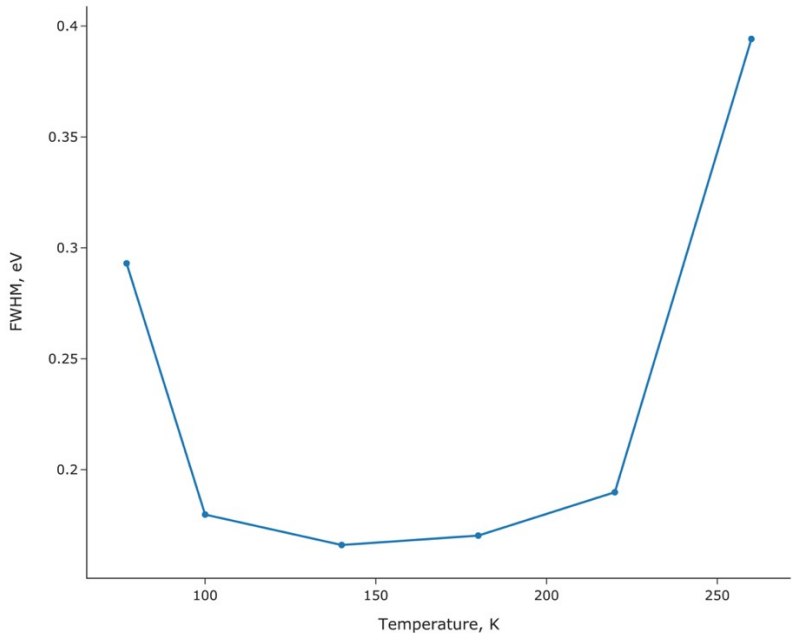

Figure S6. Full width at half maximum (*FWHM*) *vs.* temperature plot for the IR band near 880 nm.

Equation S1. The average lifetime for the double exponential curve:

$$\tau_{av} = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2}$$

Table S1. Selected bond angles for the $\{Sb_2Br_9\}^{3-}$ anion in the crystal structure of $(C_5H_{14}N_2)_3\{Sb_2Br_9\}_2$.

Atoms	Angle, °
Br1—Sb1—Br6	90.23(9)
Br1—Sb1—Br4	176.62(12)
Br4—Sb1—Br5	89.65(11)
Br4—Sb1—Br6	90.61(11)
Br4—Sb1—Br2	94.31(15)
Br4—Sb1—Br3	93.15(13)
Br5—Sb1—Br1	87.00(10)
Br5—Sb1—Br6	95.65(11)
Br2—Sb1—Br1	84.99(12)
Br2—Sb1—Br5	86.65(13)
Br2—Sb1—Br6	174.59(15)
Br2—Sb1—Br3	92.20(15)
Br3—Sb1—Br1	90.19(13)
Br3—Sb1—Br5	177.05(14)
Br3—Sb1—Br6	85.27(12)
Br6—Sb2—Br5	95.72(11)
Br6—Sb2—Br10	86.63(10)
Br7—Sb2—Br5	90.63(11)
Br7—Sb2—Br6	90.02(11)
Br7—Sb2—Br9	94.43(13)
Br7—Sb2—Br10	176.65(12)
Br9—Sb2—Br5	86.04(12)
Br9—Sb2—Br6	175.20(13)
Br9—Sb2—Br10	88.91(12)
Br8—Sb2—Br5	174.64(15)
Br8—Sb2—Br6	86.00(13)
Br8—Sb2—Br7	94.45(14)
Br8—Sb2—Br9	91.85(14)
Br8—Sb2—Br10	85.17(12)
Br10—Sb2—Br5	89.85(10)
Br14—Sb3—Br15	93.08(10)
Br14—Sb3—Br10	97.13(10)
Br13—Sb3—Br14	88.72(11)
Br13—Sb3—Br15	83.36(11)
Br13—Sb3—Br10	170.52(12)
Br12—Sb3—Br14	177.42(14)
Br12—Sb3—Br15	89.46(11)
Br12—Sb3—Br13	91.98(13)
Br12—Sb3—Br10	82.50(11)
Br11—Sb3—Br14	85.22(11)
Br11—Sb3—Br15	177.17(12)
Br11—Sb3—Br13	94.32(13)
Br11—Sb3—Br12	92.25(14)
Br11—Sb3—Br10	93.60(12)
Br10—Sb3—Br15	88.86(10)
Br1^{i}—Sb4—Br14	88.43(9)

Br16—Sb4—Br14	82.97(11)
Br16—Sb4—Br1^{i}	169.88(12)
Br16—Sb4—Br15	88.65(11)
Br15—Sb4—Br14	92.91(10)
Br15—Sb4—Br1^{i}	97.14(10)
Br17—Sb4—Br14	88.82(11)
Br17—Sb4—Br1^{i}	82.24(11)
Br17—Sb4—Br16	92.21(12)
Br17—Sb4—Br15	178.15(14)
Br18—Sb4—Br14	177.07(12)
Br18—Sb4—Br1^{i}	94.16(12)
Br18—Sb4—Br16	94.58(13)
Br18—Sb4—Br15	85.41(12)
Br18—Sb4—Br17	92.88(14)
Sb3—Br14—Sb4	86.99(9)
Sb1—Br1—Sb4^{ii}	174.84(13)
Sb1—Br5—Sb2	84.29(10)
Sb4—Br15—Sb3	87.02(9)
Sb2—Br6—Sb1	84.34(10)
Sb3—Br10—Sb2	174.91(12)

Symmetry code: (i) *x*, *y*, 1 + *z*; (ii) *x*, *y*, –1 + *z*.

Table S2. Length of Br···Br contacts and shortest Sb···Sb distances.

Atoms	**Distance, Å**
Br8···Br11^{i}	3.5875(7)
Br2···Br18^{ii}	3.5922(7)
Br9···Br11^{iii}	3.6811(4)
Br3···Br18^{iv}	3.6835(4)
Sb1···Sb2	4.2148(2)
Sb3···Sb4	4.3968(3)

Symmetry code: (i) *x*, 1 + *y*, *z*; (ii) *x*, –1 + *y*, –1 + *z*; (iii) 1 + *x*, 1 + *y*, *z*; (iv) –1 + *x*, –1 + *y*, –1 + *z*.

Table S3. Results of temperature-dependent PL spectra fitting.

***T*, K**	***E*$_{max}$, eV**	***FWHM*, eV**
77	1.960	0.3309
100	1.940	0.3454
140	1.925	0.3712
180	1.915	0.3883
220	1.908	0.4064
260	1.910	0.4230