Electronic Supplementary Material (ESI) for Chemical Science.

Ionic liquid cations as methylation agent for extremely weak chalcogenido metalate nucleophiles

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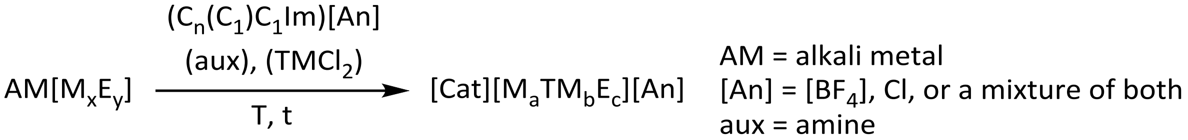
SUPPORTING INFORMATION

Content:

1. Syntheses

General. All reactions were performed in borosilicate glass ampoules. All reactants were treated under argon atmosphere by using standard *Schlenk* technique and gloveboxes. Ionic liquids of the type $(C_m(C_n)C_1Im)[BF_4]$ and $(C_m(C_n)C_1Im)Cl$ were purchased from Sigma Aldrich; in the formulae, $(C_m(C_n)C_oIm)^+$ denote tri(/di)-alkylated imidazolium cations, with *n*, *m* and *o* specifying the chain lengths of the alkyl substituents in the respective 1, 2 and 3 positions of the imidazole ring. Chalcogenidostannate salts were prepared according to the quoted literature procedures. Amines ethane-1,2-diamine (*en*) or 2,6-dimethylmorpholine (DMMP) were dried and freshly distilled prior to use. Products of the ionothermal reactions were analyzed by X-ray powder diffraction, single-crystal X-ray diffraction, micro X-ray fluorescence spectroscopy (µ-XFS), and Raman spectroscopy.



$$AM[M_xE_y] \xrightarrow[T,\ t]{(C_n(C_1)C_1Im)[An]\ (aux),\ (TMCl_2)} [Cat][M_aTM_bE_c][An]$$

AM = alkali metal
$[An] = [BF_4]$, Cl, or a mixture of both
aux = amine

Scheme S1: General ionothermal synthesis of chalcogenido metalates with different ionic liquids, auxiliaries (Aux) and transition metal chlorides ($TMCl_2$) as additives at different temperatures (T) with different reaction durations (t).

Synthesis of $(C_4C_1C_1Im)_5[Sn_{10}S_{16}O_4(S{-}Me)_4][BF_4]$ (1a). Compound **1a** was obtained by the reaction of $Li_4SnS_4{\cdot}13H_2O$[S1] in a mixture of $(C_4C_1C_1Im)[BF_4]$ and $(C_4C_1C_1Im)Cl$ in a 3:2 ratio. As an auxiliary, 50 µL of *en* were added. The reaction mixture was heated at 150°C for 4 d. After a few weeks, compound **1a** crystallizes as colorless bars.

Synthesis of $(C_4C_1C_1Im)_4[Sn_{10}S_{16}O_4(S{-}Me)_4]$ (1b). Compound **1b** was obtained by the reaction of $Na_4SnS_4{\cdot}14H_2O$[S2] in a mixture of $(C_4C_1C_1Im)[BF_4]$ and $(C_4C_1C_1Im)Cl$ in a 1:1 ratio. As an auxiliary, 50 µL of *en* were added and as an additive, 11 mg of $MnCl_2$ were added. The reaction mixture was heated at 180°C for 4 d. After a few weeks, compound **1b** crystallizes as colorless bars.

Synthesis of $[Cat]_x[Sn_{10}S_{16}O_4(S{-}Me)_4][An]_y$ (1c). Compound **1c** was obtained by the reaction of $Na_4SnS_4{\cdot}14H_2O$[S2] in a mixture of $(C_4C_1C_1Im)[BF_4]$ and $(C_4C_1C_1Im)Cl$ in a 3:2 ratio. As an auxiliary, 75 µL of DMMP were added. The reaction mixture was heated at 180°C for 4 d. After a few weeks, compound **1c** crystallizes as colorless trigonal prisms or octahedral blocks.

Synthesis of $[Cat]_x[Sn_{10}S_{16}O_4(S{-}Me)_4][An]_y$ (1d). Compound **1d** was obtained by the reaction of $Li_4SnS_4{\cdot}13H_2O$[S1] in a mixture of $(C_4C_1C_1Im)[BF_4]$ and $(C_4C_1C_1Im)Cl$ in a 4:1 ratio. As an auxiliary, 100 µL of *en* were added. The reaction mixture was heated at 150°C for 4 d. After a few weeks **1d** crystallizes in colorless octahedral blocks.

Synthesis of $(C_4C_1C_1Im)_4[Sn_{10}S_{16}O_4(S–Me)_4]$ (1e and 1f). Compound **1e** and **1f** were obtained by the reaction of $Na_4SnS_4·14H_2O$[S2] in a mixture of $(C_4C_1C_1Im)[BF_4]$ and $(C_4C_1C_1Im)Cl$ in a 3:2 ratio. As an additive, 11 mg of $MnCl_2$ were added. The reaction mixture was heated at 150°C for 4 d. After a few days, compounds **1e** and **1f** crystallize as colorless blocks.

Synthesis of $(dmmpH)_6[Mn_4Sn_4Se_{13}(Se–Me)_4]$ (2). Compound **2** was obtained by the reaction of 60 mg of $K_2[Sn_2Se_5]$[S3] and 20 mg of $MnCl_2$ in the presence of 50 µL of DMMP in 0.5 mL of $(C_4C_1Im)[BF_4]$. Upon heating of the reaction mixture at 120 °C for 96 h, compound **2** crystallized as orange blocks.

Synthesis of $(C_6C_1Im)_6[Hg_6Te_{10}(Te–Me)_2]$ (3a) and $(C_8C_1Im)_6[Hg_6Te_{10}(Te–Me)_2]$ (3b). Compounds **3a** und **3b** were synthesized in the reaction of 50 mg of $Na_2[HgTe_2]$[S4] in 250 µL of $(C_6C_1Im)[BF_4]$ or $(C_8C_1Im)[BF_4]$, respectively. The mixture was heated at 60 °C overnight. Red plates of **3a** and **3b** were obtained in nearly quantitative crystalline yield upon cooling to room temperature.

2. Single-crystal X-ray Diffraction Studies, Data Collection, Refinement and Crystallographic Details

Crystals suitable for X-ray diffraction analyses were investigated with a STOE IPDS-II (**1d**), IPDS-2T (**2**), StadiVari (**1b**, **1e**, **1f**) or a Bruker D8 Quest (**1a**, **1c**, **3a**, **3b**) diffractometer at 100 K using. On the STOE IPDS-II and IPDS-2T diffractometers, diffraction experiments were run with Mo-*K*α radiation and a graphite monochromator (λ = 0.71073 Å). The STOE StadiVari diffractometer used Cu Kα radiation (λ = 1.54186) from an X-ray micro source with X-ray optics and a Pilatus 300K Si hybrid pixel array detector. On the Bruker D8 Quest diffractometer, Mo-Kα radiation from an X-ray micro source tube with X-ray optics and a Photon 100 charge-integrating pixel array detector were used. Upon numerical absorption correction (STOE X-AREA; **1d**, **2**), scaling with spherical absorption correction (STOE X-Area LANA; **1b**, **1e**, **1f**) or scaling with multiscan absorption correction (Bruker SADABS; **1a, 1c, 3a, 3b**), respectively, the structure solution was performed by direct methods, followed by full-matrix-least-squares refinement against *F*2, using SHELXT15, SHELXL15, and OLEX2 software.[S5] Table S1 summarizes the crystallographic data for **1a** – **3b**.

Table S1. Crystallographic data of **1a** – **3b**.

Compound (CCDC number)	**1a**	**1b**	**1c**	**1d**	**1e**	**1f**	**2**	**3a**	**3b**
CCDC number	1902904	1902905	1902906	1902968	1902973	1902969	1902970	1902971	1902972
Empirical formula	$BC_{36.5}F_4H_{63.5}N_{9.5}O_4S_{20}Sn_{10}$	$C_{32.}79H_{59.71}N8$ O4S20Sn10	$O_4S_{20}Sn_{10}$	$O_4S_{20}Sn_{10}$	$C_5H_{9.33}N_{1.33}O_4S_{20}Sn_{10}$	$C_3H_9O_4S_{20}Sn_{10}$	$C_{40}H_{96}Mn_4N_6O_6Se_{17}Sn_4$	$C_{62}H_{120}Hg_6N_{12}Te_{12}$	$C_{74}H_{144}Hg_6N_{12}Te_{12}$
Formula weight /g·mol^{-1}	2611.37	2458.2	1892.1	1892.1	1980.24	1937.20	2794.06	3768.43	3936.74
Color & shape	colorless rods	colorless needles	colorless, blocks	colorless blocks	colorless blocks	colorless blocks	orange block	red plate	red plate
Crystal size /mm³	0.07x0.14x0.35	0.05x0.13x0.19	0.116x0.137x 0.174	0.05x0.05x0.08	0.1x0.139x0.157	0.069x0.093x 0.141	0.15x0.14x 0.14	0.11x0.09x 0.01	0.27x0.15x 0.01
Crystal system & space group	orthorhombic *Pbcm*	triclinic $P\bar{1}$	cubic $Fd\bar{3}m$	cubic $Fd\bar{3}m$	tetragonal $I\bar{4}c2$	hexagonal $P6_3/mmc$	trigonal $R\bar{3}$	triclinic $P\bar{1}$	triclinic $P\bar{1}$
a /Å	17.727(4)	13.1046(5)	73.6160(17)	27.248(3)	29.1874(4)	18.9995(7)	16.4857(3)	10.0647(14)	10.0664(8)
b /Å	35.611(7)	21.8727(10)	73.6160(17)	27.248(3)	29.1874(4)	18.9995(7)	16.4857(3)	11.591(2)	11.5576(9)
c /Å	31.733(6)	27.9377(12)	73.6160(17)	27.248(3)	57.5222(14)	31.8469(13)	54.2335(15)	21.309(3)	24.550(2)
α /°	90	79.966(4)	90	90	90	90	90	78.961(5)	89.172(3)
β /°	90	79.823(3)	90	90	90	90	90	83.155(4)	85.585(3)
γ /°	90	84.995(3)	90	90	90	120	120	83.555(5)	83.936(2)
V /Å³	20032(7)	7748.1(6)	398948(28)	20230(7)	49003.4(18)	9955.9(8)	12764.8(6)	2385.5(7)	2831.7(4)
Z	8	4	136	8	24	4	6	1	1
ρ_{calc} /g·cm^{-3}	1.732	2.107	1.071	1.242	1.610	1.292	2.181	2.623	2.309
Radiation (λ /Å)	$Mo_{K\alpha}$ (0.71073)	$Cu_{K\alpha}$ (1.54186)	$Cu_{K\alpha}$ (1.54186)	$Mo_{K\alpha}$ (0.71073)	$Cu_{K\alpha}$ 1.54186)	$Cu_{K\alpha}$ (1.54186)	$Mo_{K\alpha}$ (0.71073)	$Mo_{K\alpha}$ (0.71073)	$Mo_{K\alpha}$ (0.71073)
Temperature	100K	100K	100K	100K	100K	100K	100 K	100 K	100 K
µ /mm^{-1}	2.904	30.511	19.998	2.842	28.762	23.580	9.035	13.253	11.170
Min/max transmission	0.4361/ 0.8333	0.0001/ 0.0227	0.0013/ 0.0163	0.6250/ 0.7667	0.0547/ 0.1595	0.136/ 0.293	0.3342/ 0.3997	0.0050/ 0.0249	0.0074/ 0.0277
F(000)	9924.0	4658.0	115872.0	6816.0	21616	3516	7824	1680	1776
θ range /°	1.283–25.242	2.406–67.679	7.612–64.986	2.114–17.977	2.635–39.990	8.260–67.686	2.471–26.853	2.186–27.500	2.261–27.998
No. measured refl.	152311	73246	171427	2622	44492	18008	42399	52343	88604
No. independent refl.	20058	28890	15027	368	7341	3419	5975	10898	13672
No. indep. refl. (I>2σ(I))	5781	21424	4134	213	6030	1257	4152	8587	9797
No. of parameters	640	1028	261	21	505	73	249	729	632
No. of restraints	4	6	0	0	0	0	9	1416	2296
R(int)	0.1020	0.0895	0.1740	0.1198	0.1785	0.0556	0.0954	0.0494	0.0602
R_1 (I>2θ(I))	0.0500	0.1157	0.0353	0.0543	0.0650	0.0632	0.0551	0.0599	0.0499
wR_2 (all data)	0.1463	0.3620	0.0609	0.1205	0.1776	0.2127	0.1578	0.1451	0.1292
S (all data)	0.645	1.403	0.643	1.036	1.000	0.833	1.038	1.110	1.067
Δ*ρmax*, Δ*ρmin* /e·Å^{-3}	1.749/-0.881	3.069/-2.558	0.491/-0.470	0.550/-1.456	0.880/-692	0.644/-970	3.27/-1.46	4.14/-2.33	2.10/-1.53

3. Details of the Crystals Structures

Comparison of the anion in **1b** with the purely inorganic cluster $[Sn_{10}O_4S_{20}]^{10-}$:[S6]

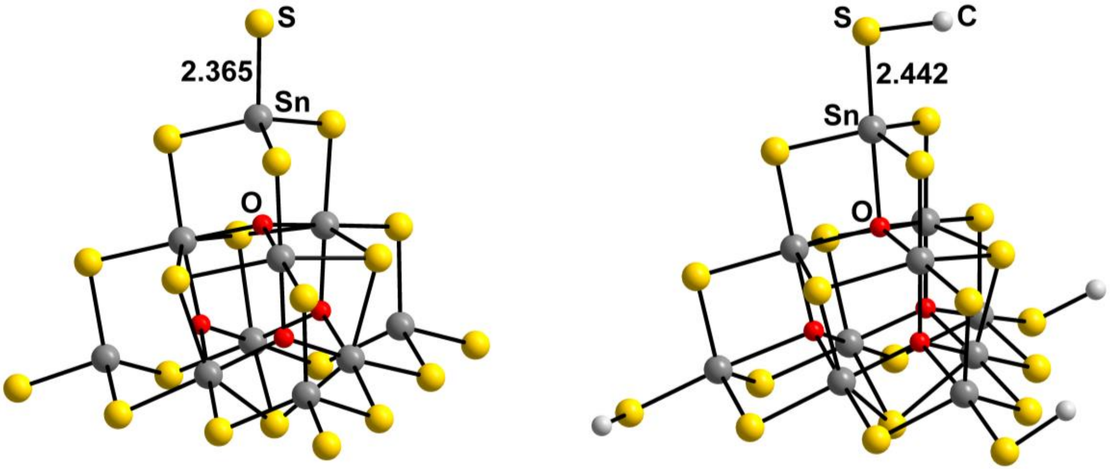


Figure S1: Comparison of the molecular structure of the cluster anions in in $[Li_8(H_2O)_{29}][Sn_{10}O_4S_{20}]$ (left) and **1b** (right) with specification of the bond lengths to the (former) terminal S atoms.[S6] The atoms are drawn as balls and sticks with arbitrary atomic radii, H atoms are omitted. Color code: grey – Sn, yellow – S, red – O, light grey – C.

Comparison of the anion in **2** with the purely inorganic cluster $[Mn_4Sn_4Se_{17}]^{10-}$:[S7]

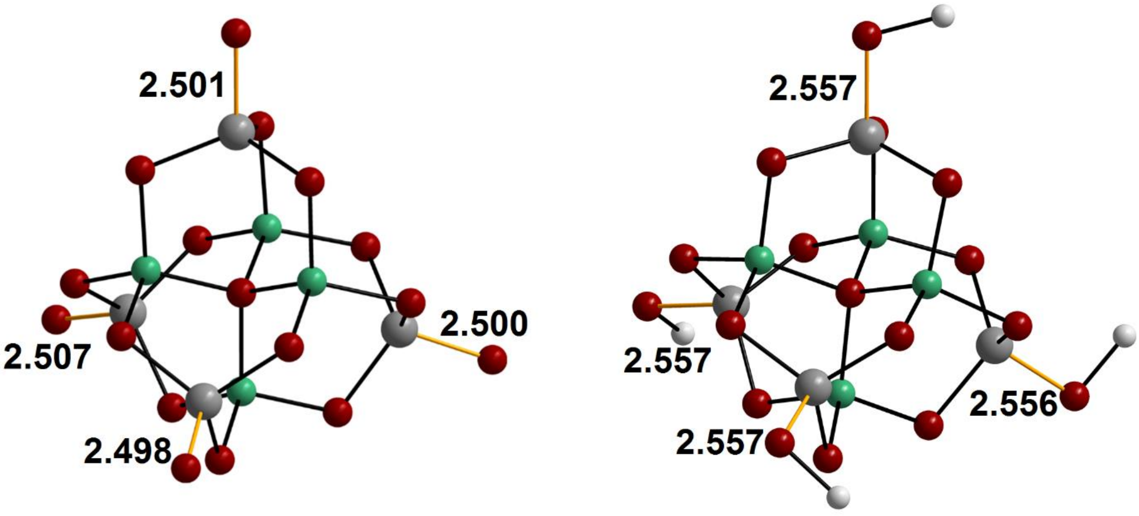


Figure S2: Comparison of the molecular structure of the cluster anions in $[Cs_{10}(H_2O)_{15.5}][Mn_4Sn_4Se_{17}]$ (left) and **2** (right) with specification of the bond lengths to the (former) terminal Se atoms.[S7] The atoms are drawn as balls and sticks with arbitrary atomic radii, H atoms are omitted. Color code: grey – Sn, dark red – Se, teal – Mn, light grey – C.

Hydrogen bonding situation in the crystal structure of **2**:

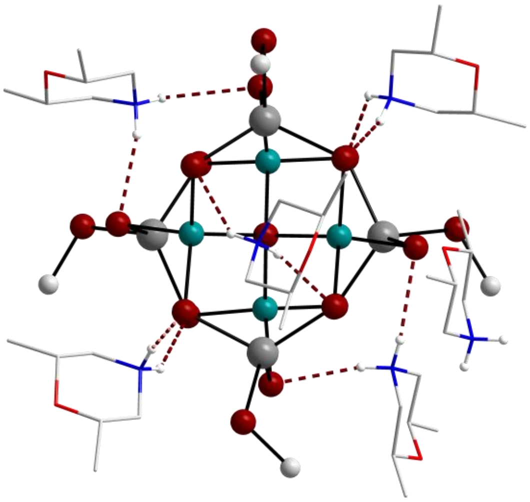


Figure S3: Section of the crystal structure of **2** showing the anion and the six closest (dmmpH)$^+$ cations. Hydrogen bonds between the nitrogen bonded H atoms of the cations and Se atoms of the cluster are represented as dashed red lines. The anion is drawn as balls and sticks with arbitrary atomic radii and the cations as wireframes. All H atoms except for the nitrogen bonded ones are omitted. Color code: grey – Sn, dark red – Se, teal – Mn, red – O, blue – N, light grey – C, light blue – H.

Comparison of the anions in **3a** and **3b** with related tellurido mercurates.

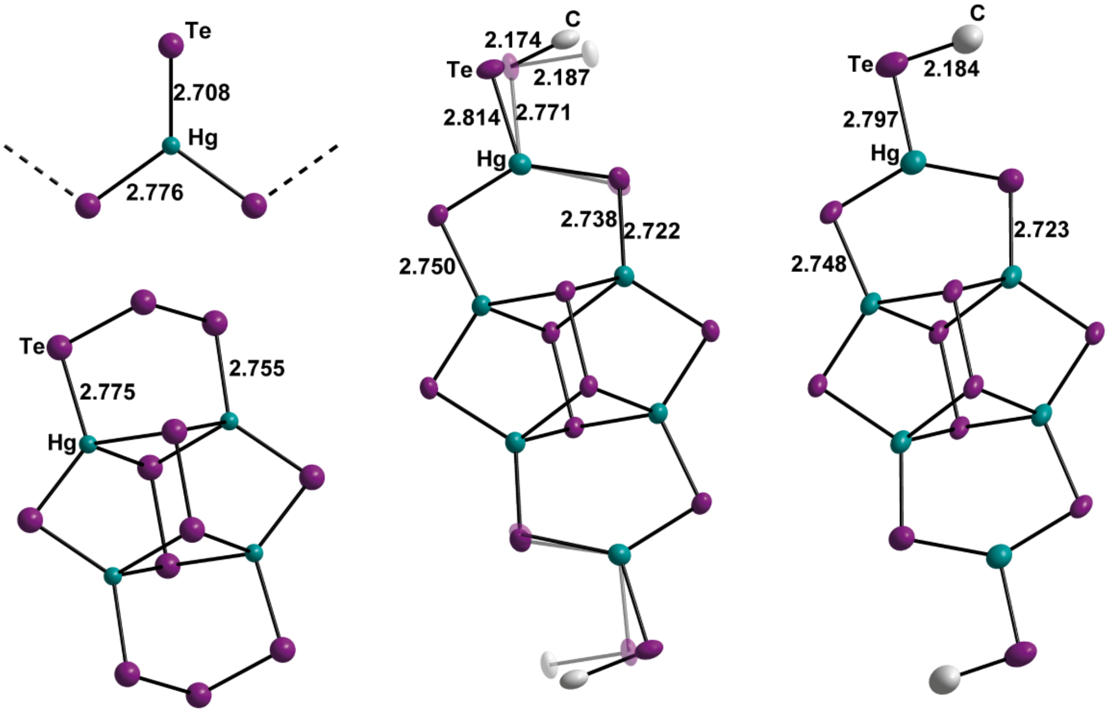


Figure S4: Molecular structure of the $[Hg_6Te_{10}(Te–Me)_2]^{6–}$ anions in **3a** (center) and **3b** (right), compared to the molecular structure of the anions in $Na_2[HgTe_2]$ (top left) and $\{N(C_4H10)_4\}_4[Hg_4Te_{12}]$ (bottom left).[S4,S8] The atoms are shown as balls with arbitrary diameter the literature-known compounds and as thermal ellipsoids at the 50 % probability level for **3a** and **3b**. H atoms are omitted and disordered parts with minor occupancy are represented semi-transparent. Lengths of specific Hg–Te bonds are shown to illustrate the effect of the methylation. Color code: teal – Hg, violet – Te, light grey – C.

4. Vibrational Spectroscopy Data of 1a – 1f

Raman spectroscopy: A commercially available Renishaw inVia Raman microscope was used for the Raman measurements of **1a** – **1f**. The spectra were measured using a 532 nm laser (10 mW) as excitation source and were recorded in a backscattering geometry at room temperature. The excitation laser was focused with a 50 × objective onto the sample surface. The same objective was used to collect the scattered light, which was then dispersed by a spectrometer with a focal length of 250 mm and finally detected by a charge-coupled device (CCD) camera with a spectral resolution of about 1 cm^{-1}.

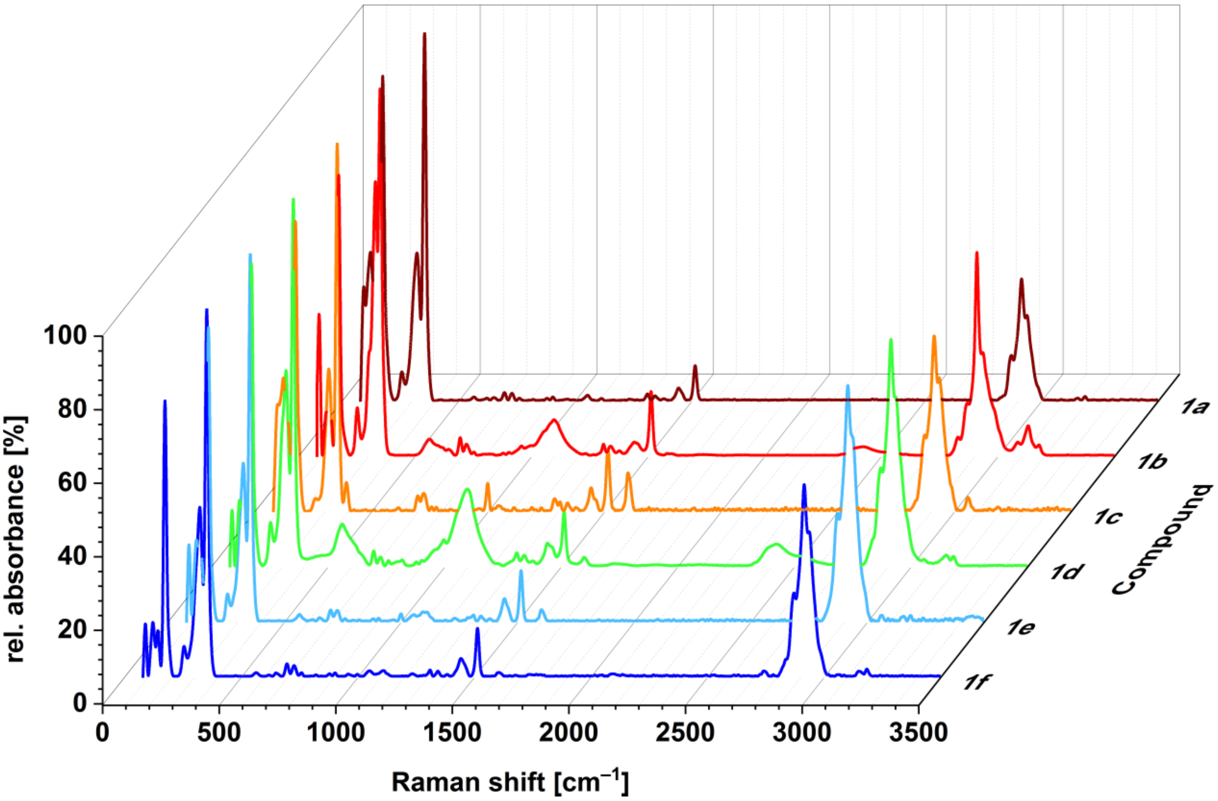


Figure S5: Raman spectra of **1a** (brown), **1b** (red), **1c** (orange), **1d** (green), **1e** (light blue) and **1f** (blue). The broad signals at approximately 560 cm^{-1}, 1100 cm^{-1} 2350 cm^{-1} were caused by Paratone oil or unidentified decomposition products, respectively.

5. Optical Absorption Spectroscopy of 2

Optical absorption measurements: The optical absorption properties of **2** were analyzed using diffuse reflection of powdered crystalline samples. The measurements were performed with a Varian Cary 5000 dual-beam spectrometer and a Praying Mantis sample holder from Harrick.

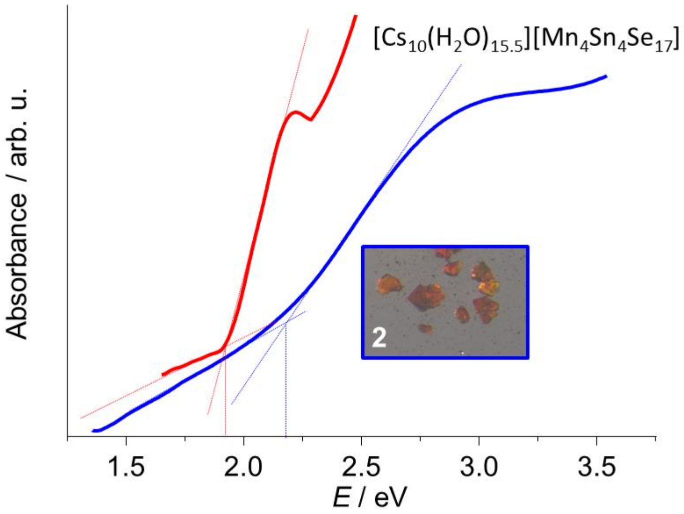


Figure S6: Optical absorption spectra of **2** and $[Cs_{10}(H_2O)_{15.5}][Mn_4Sn_4Se_{17}]$.[S7]

6. References for the Supporting Information

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