

Supporting Information

Highly Soluble Supertetrahedra upon Selective Partial Butylation of Chalcogenido Metalate Clusters in Ionic Liquids

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1. Methods

General synthesis methods. All reactions and measurements were carried out under dry Ar atmosphere using Schlenk technique or a glovebox (type Unilab plus; MBraun). The starting material $K_4[SnS_4] \cdot 4H_2O$ was prepared by solid state reaction of K_2S , Sn and S according to the literature.^[1] Elements were used as received: K lumps (Acros Organics, 98%), Sn powder (Sigma-Aldrich, 99%), and S powder (Alpha Aesar, 99,999%). Water was degassed by application of dynamic vacuum for 30 minutes (2 times). 2,6-Dimethylmorpholine (DMMP; Sigma-Aldrich, 99,8%) was distilled and stored over molecular sieve (3 Å). 2-Methylimidazole (Fisher Scientific GmbH, 99%), 1-bromo-butane (Sigma-Aldrich, 99%), and NaH (60%, dispersion in Paraffin Liquid, Tokyo Chemical Industry Co., Ltd.) were used for the synthesis of **A** as received. THF, pentane, CH_2Cl_2 , CH_3CN , and CH_3CN-d_3 were purified by distillation.

Synthesis and crystallization of $(C_4C_1C_4Im)Br$ (A**).** The ionic liquid **A** was prepared according to a literature method,^[2] yet under air and in larger scale (50 g instead of 2 g). Crystals of **A** form instantly upon mixing a drop of immersion oil (NVH oil Cat.# NVHO-1 from Jena Bioscience GmbH) with a drop of freshly synthesized **A**.

Synthesis and crystallization of $(C_4C_1C_4Im)_{4+x}[Sn_{10}O_4S_{16}(SBu)_4]Br_x$ with $x = 3$ (1a**) and $x = 2$ (**1b**).** 50 mg of $K_4[SnS_4] \cdot 4H_2O$ (0.11 mmol, 1.0 eq.), 500 mg of $(C_4C_1C_4Im)Br$ (**A**), and 100 μ L of DMMP were combined in a borosilicate glass ampoule, which was sealed air-tight thereupon. The ampoule was heated to 180 °C at a heating rate of 30 °C/h, kept at 180 °C for 72 h, and then cooled down to room temperature at a cooling rate of 5 °C/h. Colorless plate-like crystals of **1a** were obtained in approximately 65% yield (based on Sn). Colorless crystals of **1b** were obtained from a solution of single crystals of **1a** in CH_3CN upon evaporation of the solvent. The transformation is quantitative according to all analytical tests that were performed on the crystalline material.

Light microscopy. Visual inspection of crystals of **1a** and **1b** (Figure S1) was performed with a stereo light microscope SteREO Discovery.V8 by Carl Zeiss. The microscope was equipped with a high-intensive cold-light source CL 1500 ECO, an Achromat S 0.63x objective (FWD 107 mm), a PL 10x/21 Br ocular, and an AxioCam MRc 5 camera with a 60N-C 2/3'' 0,63x adapter. The raw photo material was examined by the AxioVision40x64 4.9.1 SP1 software.

Micro-X Ray Fluorescence (μ -XRF) Spectroscopy. μ -XRF data were recorded on a Bruker M4 Tornado, equipped with an Rh-target X-ray tube and a silicon drift detector. The emitted fluorescence photons were detected with an acquisition time of 240 s. Upon deconvolution of the spectra, quantification of the elements was achieved based on the S K, Br K, and Sn L radiation. The spectra are shown in Figures S2 and S3, Tables S1 and S2 summarize the data that confirm the heavy-atom ratio of compounds **1a** and **1b**.

Single-Crystal X-ray Diffraction. Crystals suitable for X-ray diffraction analyses of compounds **A**, **1a**, and **1b** were investigated with a STOE StadiVari diffractometer at 100 K, using Cu $K\alpha$ radiation ($\lambda = 1.54186$) from an X-ray micro source with X-ray optics and a Pilatus 300K Si hybrid pixel array detector. Upon scaling with spherical absorption correction (STOE X-Area Lana), the structure solution was performed by dual space methods, followed by full-matrix-least-squares refinement against F^2 , using SHELXT15, SHELXL15, and OLEX2 software.^[3] Table S3 summarizes the crystallographic data for compounds **A**, **1a**, and **1b**. The structures are illustrated in Figure 1, for supplementary crystal structure figures, see Figures S4–S7.

NMR Spectroscopy. NMR studies of a solution of single crystals of compound **1a** in CH₃CN-d₃ were carried out on a Bruker DPX AV 500 at room temperature. The raw data were examined by means of MestReNova 6.0. ¹H-NMR and ¹¹⁹Sn-NMR spectra are given in Figure 2, Figure S8 shows the ¹³C-NMR spectrum.

Raman Spectroscopy. Raman data were collected on an S&I Mono-Vista CRS+ device. The measurements were performed with a laser wavelength of 532 and 633 nm and a gratings of 300 and 1200 grooves mm⁻¹. The measurement had a duration of 10 s with 10 coadditions and 10 s with 25 coadditions. The Raman spectra of **1a** and **1b** are shown in comparison with the spectrum of (C₄C₁C₁Im)₄[Sn₁₀O₄S₁₆(SMe)₄]^[4] in Figure S9.

Electrospray Ionization Mass Spectrometry (ESI-MS). Mass spectra were recorded on a fresh solution of single crystals of **1b** with attached reaction media in CH₃CN on a Thermo Fisher Scientific Finnigan LTQ-FT hybride mass spectrometer equipped with a linear ion trap (LTQ) and a FT-ICR (FT). Figure S10 shows the overview spectrum and the high-resolution mass peak.

Optical absorption spectroscopy. Optical absorption properties of compounds **1a**, **1b**, and (C₄C₁C₁Im)₄[Sn₁₀O₄S₁₆(SMe)₄] were measured under inert conditions employing a Varian Cary 5000 UV/VIS/NIR spectrometer from Agilent, equipped with a Praying Mantis accessory for the solid state samples. Tauc plots (Figure S11) were generated using the Kubelka-Munk-function $(F(R_{\infty})/hv)^{1/\gamma}$, with $\gamma = 2$ and 0.5 .^[5-7]

Quantum chemical methods. All structures were optimized at the level of density functional theory (DFT) with the PBE functional^[8] employing triple- ζ basis sets^[9] together with suited auxiliary bases^[10] for the density-fitting approximation in the Coulomb part. For Sn, Dirac-Fock effective core potentials^[11] were used. The counter-ions were modeled with the conductor-like screening model (COSMO)^[12] with a dielectric constant of $\epsilon = 13$ (typical for imidazolium-based ionic liquids). The Cartesian coordinates of the optimized structures are provided in Tables S5 – S11. All subsequent calculations (reaction energies, excitation spectra via time-dependent DFT^[13], NMR shifts and coupling constants) were done for these structure parameters with the PBE0 hybrid functional.^[14] NMR data were calculated within the quasirelativistic all-electron exact two-component (X2C) method^[15] in its scalar-relativistic one-component variant^[16], coupling constants with two-component X2C.^[17] For both cases, the finite nucleus model^[18] and the diagonal local approximation for the unitary decoupling transformation (DLU)^[19] were used, and further triple- ζ basis sets^[20] and integration grids optimized for all-electron calculations (size 4a),^[21] together with suited auxiliary bases^[20] for the density-fitting approximation in the Coulomb part. A self-consistent field threshold of 10^{-8} E_h was applied for the energy convergence and the root mean square of the densities was converged to at least 10^{-8} a.u., while a threshold of 10^{-6} a.u. was used for the norm of the residuum in the coupled perturbed Kohn-Sham equations. All calculations were done with the program suite TURBOMOLE V7.5,^[22] except of the coupling constants, which presently are available only in a local version of TURBOMOLE.

2. Light microscopy

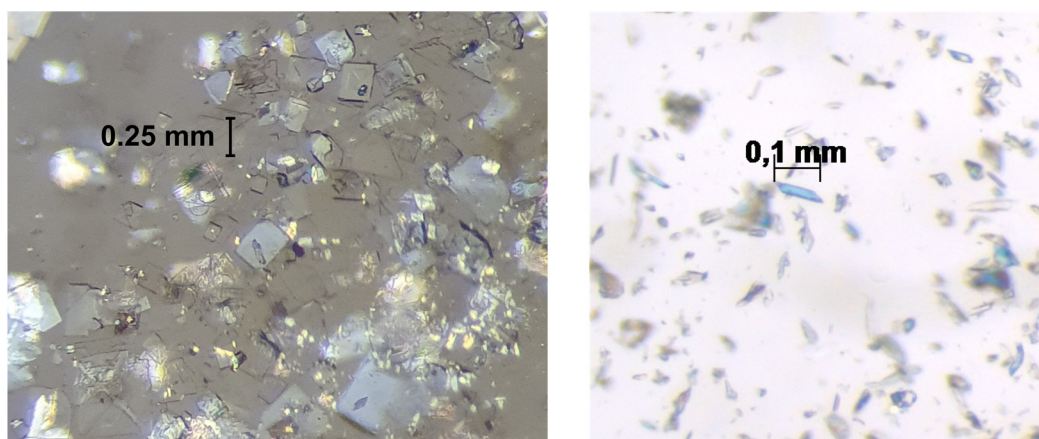


Figure S1. Light-microscopic images of crystals of **1a** (left) and **1b** (right).

3. Micro-X Ray Fluorescence (μ -XRF) Spectroscopy

Elemental analysis was carried out to investigate the heavy-atom ratio of the two compounds and exclude impurities. The bromine concentration could not be determined accurately, because of the low thickness of the sample and the relative high fluorescence energy. Figures S2 and S3 and Tables S1 and S2 display and summarize the results.

Table S1. XRF data of **1a**.

| Element | X-Ray Series | Norm. Cont. (wt.%) | Atom Cont. (at.%) | Atom C. calc. (at.%) | Error (1σ [wt.%]) |
|---------|--------------|--------------------|-------------------|----------------------|---------------------------|
| Sn | L series | 64.78 | 35.53 | 30.30 | 0.08 |
| S | K series | 29.43 | 59.75 | 60.60 | 0.04 |
| Br | K series | 5.79 | 4.72 | 9.38 | 0.00 |

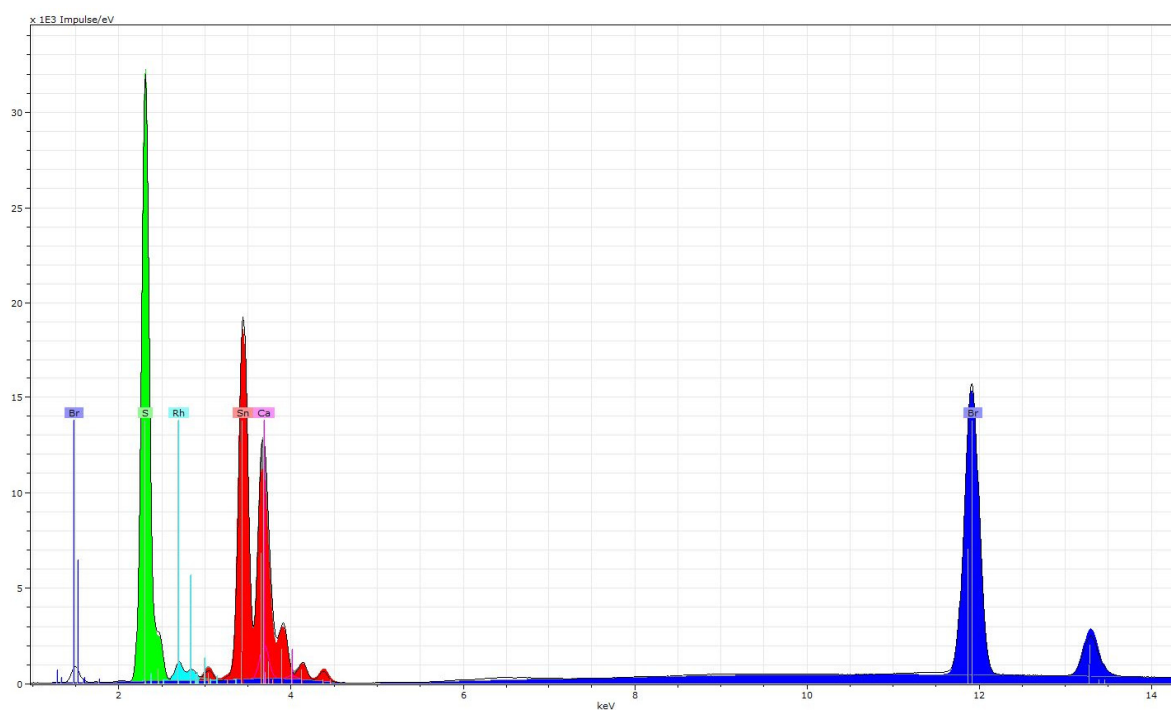


Figure S2. XRF spectrum of **1a** with polynomial integral fit (Br: blue; S: green; Sn: red). Calcium is present because of the device set-up. Therefore, corresponding signals are just deconvoluted, but the calcium concentration is not considered in the calculation of the contents.

Table S2. XRF data of **1b**.

| Element | X-Ray Series | Norm. Cont. (wt.%) | Atom Cont. (at.%) | Atom C. calc (at.%) | Error (1 σ [wt.%]) |
|---------|--------------|--------------------|-------------------|---------------------|---------------------------|
| Sn | L series | 61.49 | 29.82 | 31.25 | 0.19 |
| S | K series | 34.34 | 61.64 | 62.50 | 0.17 |
| Br | K series | 4.17 | 8.54 | 6.25 | 0.00 |

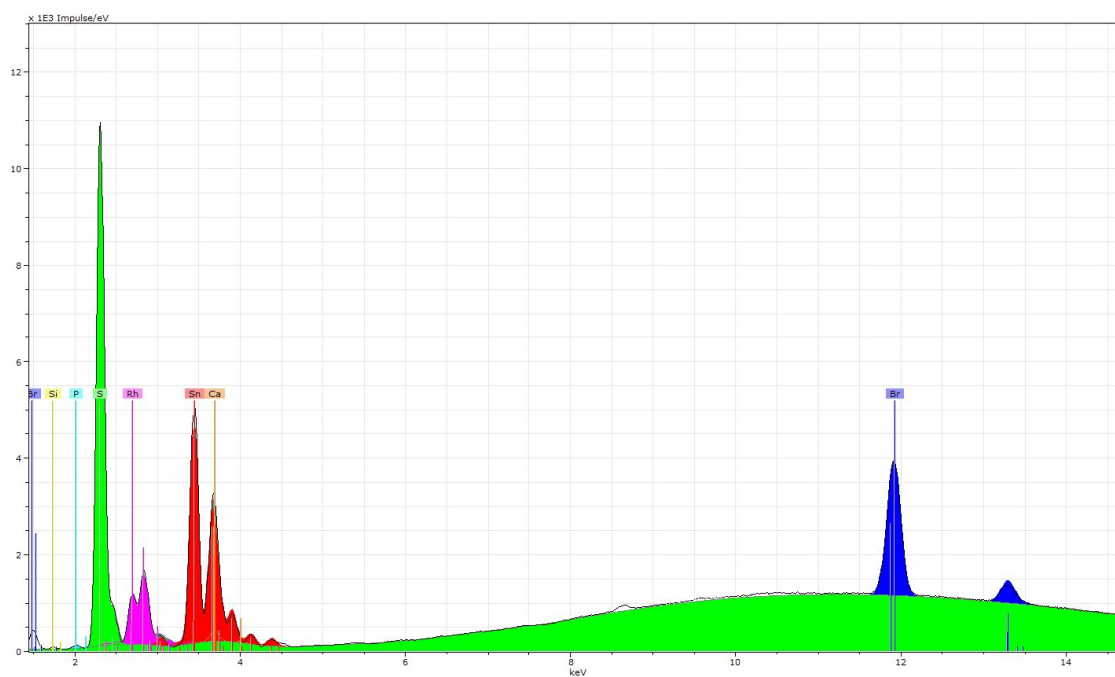


Figure S3. XRF spectrum of **1b** with polynomial integral fit (Br: blue; S: green; Sn: red). Calcium is present because of the device set-up. Therefore, corresponding signals are just deconvoluted, but the calcium concentration is not considered in the calculation of the contents.

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

Table S3. Crystallographic data of **A**, **1a**, and **1b**.

| Compound (CCDC number) | A (2070230) | 1a (2070231) | 1b (2070232) |
|--|---|--|--|
| Empirical formula | C ₁₂ H ₂₃ BrN ₂ | C _{49.88} H ₇₃ Br ₂ N _{9.50} O ₄ S ₂₀ Sn ₁₀ | C ₈₈ H _{159.8} Br ₂ N ₁₂ O ₄ S ₂₀ Sn ₁₀ |
| Formula weight /g·mol ⁻¹ | 275.23 | 2857.59 | 3437.99 |
| Color & shape | colorless needles | colorless plates | colorless blocks |
| Crystal size /mm ³ | 0.038x0.039x0.169 | 0.138x0.223x0.236 | 0.086x0.092x0.101 |
| Crystal system | orthorhombic | triclinic | triclinic |
| Space group | <i>P</i> 2 ₁ 2 ₁ 2 ₁ | <i>P</i> $\bar{1}$ | <i>P</i> $\bar{1}$ |
| <i>a</i> /Å | 10.37880(10) | 23.2642(2) | 15.9784(3) |
| <i>b</i> /Å | 11.1258(2) | 23.2721(2) | 15.9536(2) |
| <i>c</i> /Å | 12.5374(2) | 28.5167(3) | 26.3430(4) |
| α /° | 90 | 83.3330(10) | 97.4140(10) |
| β /° | 90 | 83.4310(10) | 97.4030(10) |
| γ /° | 90 | 80.9970(10) | 89.9570(10) |
| <i>V</i> /Å ³ | 1447.72(4) | 15072.8(2) | 6602.66(18) |
| <i>Z</i> | 4 | 4 | 2 |
| ρ_{calc} /g·cm ⁻³ | 1.263 | 1.259 | 1.729 |
| Radiation (λ /Å) | Cu _{Kα} (1.54186) | Cu _{Kα} (1.54186) | Cu _{Kα} (1.54186) |
| Temperature | 100 K | 100 K | 100 K |
| μ /mm ⁻¹ | 3.658 | 16.358 | 18.79 |
| Min/max transmission | 0.577/0.873 | 0.0001/0.0028 | 0.010/0.087 |
| <i>F</i> (000) | 576 | 5443 | 3388 |
| θ range /° | 5.316–67.686 | 2.924–67.686 | 2.789–67.686 |
| No. measured refl. | 25290 | 311345 | 121129 |
| No. independent refl. | 2803 | 60905 | 25164 |
| No. indep. refl. (<i>I</i> >2 σ (<i>I</i>)) | 2609 | 26906 | 15461 |
| No. of parameters | 140 | 1413 | 1381 |
| No. of restraints | 0 | 0 | 0 |
| <i>R</i> (int) | 0.0453 | 0.0546 | 0.0739 |
| <i>R</i> ₁ (<i>I</i> >2 θ (<i>I</i>)) | 0.0392 | 0.0688 | 0.0487 |
| <i>wR</i> ₂ (all data) | 0.1333 | 0.2197 | 0.1424 |
| <i>S</i> (all data) | 1.109 | 0.845 | 0.940 |
| Flack parameter ^[23] | –1.17(8) | – | – |
| $\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ /e·Å ⁻³ | 0.403/–0.680 | 1.235/–0.903 | 0.907/–1.433 |

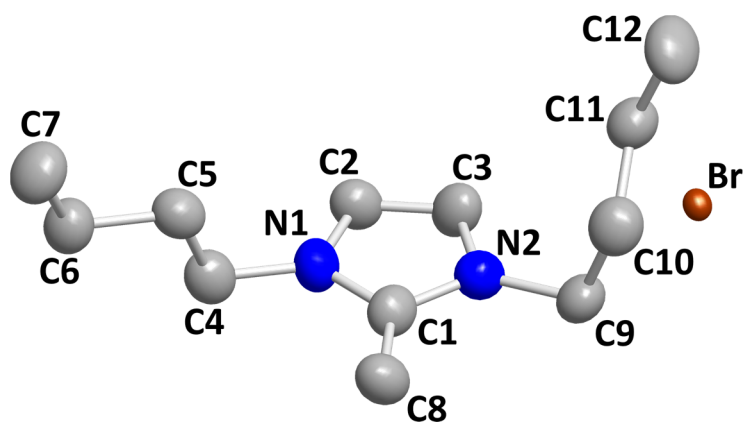


Figure S4. Asymmetric Unit of the crystal structure of **A** (C atoms: grey; N atoms: blue; Br atoms: dark red). Hydrogen atoms are omitted for clarity; displacement ellipsoids are shown at a 50% probability level. Selected interatomic distances [Å]: C2–C3 1.353(17), C1–C8 1.446(16), C1–N1 1.377(15), N1–C4 1.468(16), N2–C9 1.475(14), C–C_{Butyl} 1.446(16) – 1.564(17).

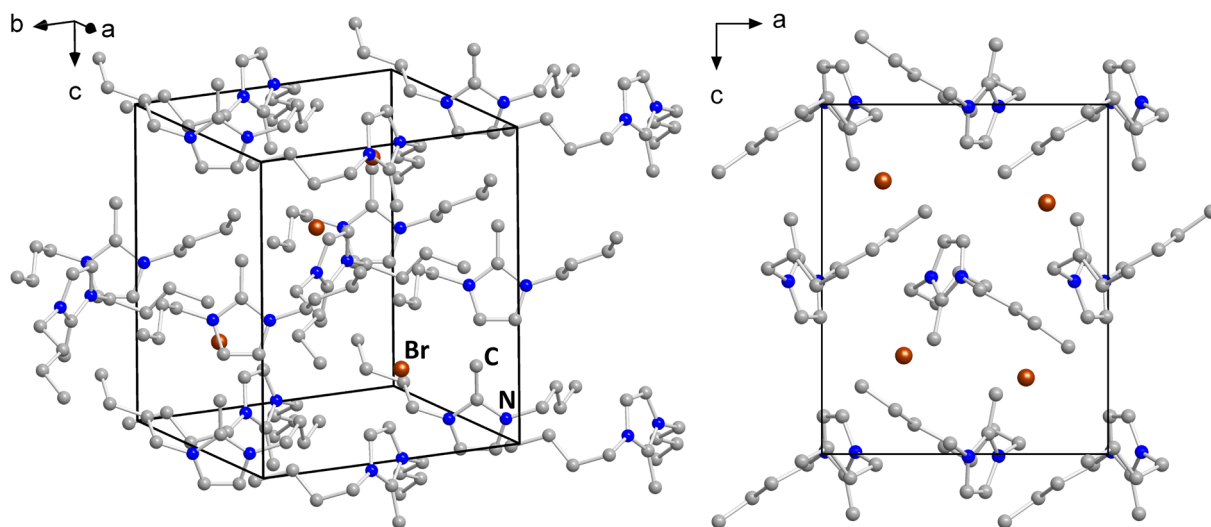


Figure S5. Cut-out of the crystal structure of **A** in two different views (hydrogen atoms are omitted for clarity; atoms are shown in balls-and-sticks model). Color code: grey – C, blue – N, dark red – Br.

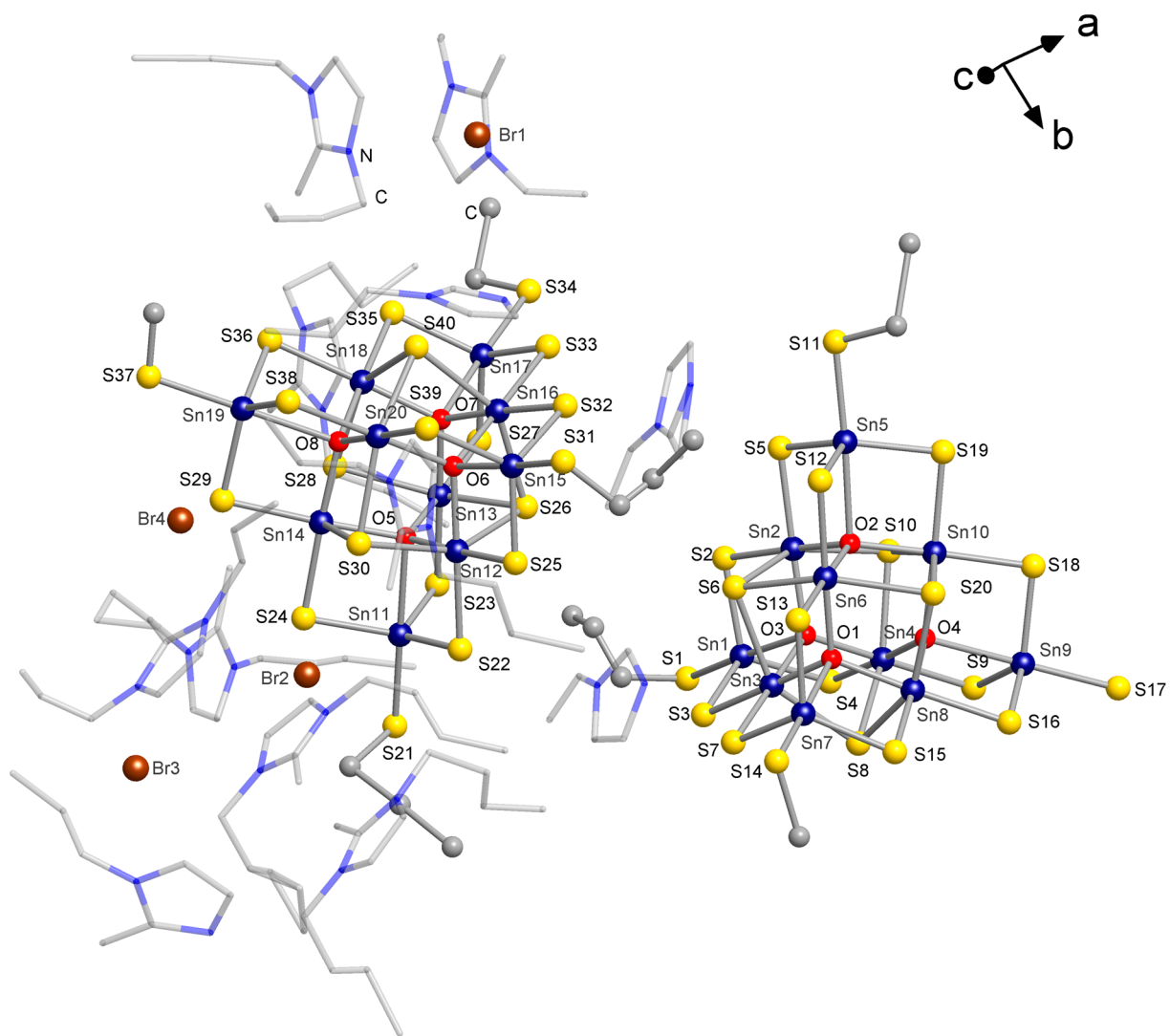


Figure S6. Illustration of the cluster anions in compound **1a** along with all next counterion molecules and bromine anions, along with the labelling scheme for all heavy atoms.

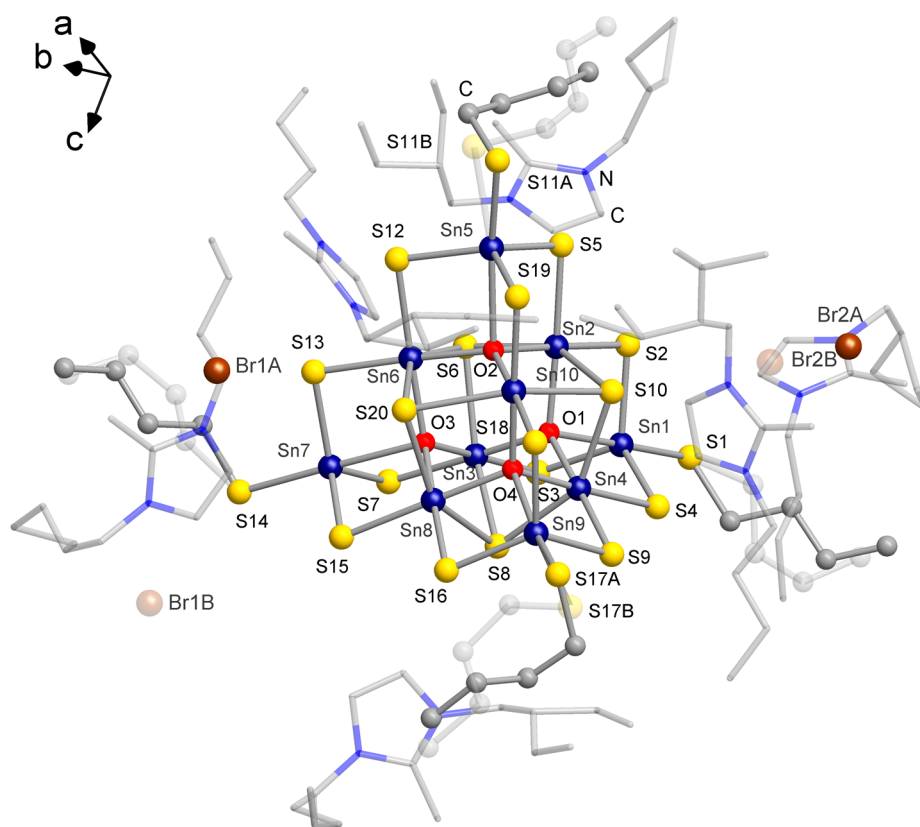


Figure S7. Illustration of the cluster anions in compound **1b** along with all next counterion molecules and bromine anions, along with the labelling scheme for all heavy atoms.

Table S4. Selected interatomic distances [Å] and angles [°] in the cluster molecules in **1a** and **1b**.

| Structural parameter | 1a | 1b |
|--|-------------------------|-------------------------|
| Sn ^A –S ^A | 2.427(3) – 2.450(3) | 2.430(4) – 2.499(7) |
| Sn ^A –S ^B | 2.387(3) – 2.419(3) | 2.399(2) – 2.417(2) |
| Sn ^A –O | 2.477(5) – 2.477(5) | 2.479(4) – 2.550(4) |
| Sn ^B –S ^B | 2.449(3) – 2.472(3) | 2.453(2) – 2.473(2) |
| Sn ^B –S ^C | 2.597(3) – 2.625(2) | 2.600(2) – 2.649(2) |
| Sn ^B –O | 2.077(5) – 2.116(6) | 2.080(5) – 2.111(4) |
| S ^A –C | 1.64(5) – 1.94(2) | 1.78(3) – 1.89(3) |
| S ^A –Sn ^A –S ^B | 94.80(11) – 103.92(10) | 88.3(2) – 110.9(2) |
| Sn ^A –S ^A –C | 99.9(7) – 107.1(17) | 96.7(11) – 107.7(9) |
| S ^A –C–C | 101.9(16) – 115.(2) | 109.(2) – 119.(3) |
| Sn ^A –O–Sn ^B | 99.8(2) – 101.38(18) | 100.05(18) – 102.38(18) |
| Sn ^B –O–Sn ^B | 115.0(2) – 117.8(2) | 115.11(18) – 117.7(2) |
| Sn ^B –S ^C –Sn ^B | 85.63(7) – 86.65(8) | 85.11(5) – 86.60(5) |
| Sn ^A –S ^B –Sn ^B | 93.06(10) – 94.30(9) | 93.47(6) – 95.02(7) |
| S ^B –Sn ^A –S ^B | 113.58(9) – 118.87(9) | 113.27(8) – 118.30(7) |
| S ^B –Sn ^B –S ^B | 95.14(10) – 96.05(9) | 94.85(7) – 95.85(6) |
| S ^B –Sn ^B –S ^C | 99.46(8) – 103.33(8) | 98.54(6) – 102.78(7) |
| S ^C –Sn ^B –S ^C | 146.07(8) – 147.29(7) | 145.95(5) – 147.87(6) |
| S ^A –Sn ^A –O | 175.04(18) – 178.68(15) | 166.5(2) – 178.16(12) |
| S ^B –Sn ^A –O | 78.59(13) – 80.25(16) | 78.01(11) – 79.65(11) |
| S ^B –Sn ^B –O | 84.83(16) – 86.83(17) | 84.88(13) – 86.94(14) |
| S ^B –Sn ^B –O II | 177.35(15) – 179.22(17) | 177.15(13) – 178.95(14) |
| S ^C –Sn ^B –O | 77.32(16) – 79.51(14) | 77.53(12) – 79.51(14) |
| O–Sn ^B –O | 91.3(2) – 92.8(2) | 91.38(17) – 93.20(17) |

5. NMR spectroscopy

4.1. ^1H -NMR spectrum of a solution of **1a** (with traces of attached reaction medium) in $\text{CH}_3\text{CN-d}_3$.

For an image of the ^1H -NMR spectrum, see the main document (Figure 2a and corresponding text).

The following signals can be assigned to $(\text{C}_4\text{C}_1\text{C}_4\text{Im})\text{Br}$:

^1H -NMR (500.2 MHz, $\text{CH}_3\text{CN-d}_3$, 293 K): δ [ppm] = 7.52 (2H, s, C_{imH}); 4.11 (4H, t, $J = 7.5$ Hz, CH_2); 2.58 (3H, s, CH_3); 1.74 (4H, m, CH_2); 1.34 (4H, dq, $J = 7.4$ Hz, $J = 14.9$ Hz, CH_2); 0.91 (6H, t, $J = 7.43$ Hz, CH_3).

The following signals can be assigned to $\text{C}_4\text{C}_1\text{im}$:

^1H -NMR (500.2 MHz, $\text{CH}_3\text{CN-d}_3$, 293 K): δ [ppm] = 7.16 (1H, s, C_{imH}); 6.98 (1H, s, C_{imH}); 3.93 (2H, t, $J = 7.35$ Hz, CH_2); 2.82 (3H, s, CH_3); 1.82 (2H, m, CH_2); 1.4 (2H, m, CH_2); 0.97 (3H, t, $J = 7.36$ Hz, CH_3).

4.2. ^{13}C -NMR spectrum of a solution of **1a** (with traces of attached reaction medium) in $\text{CH}_3\text{CN-d}_3$.

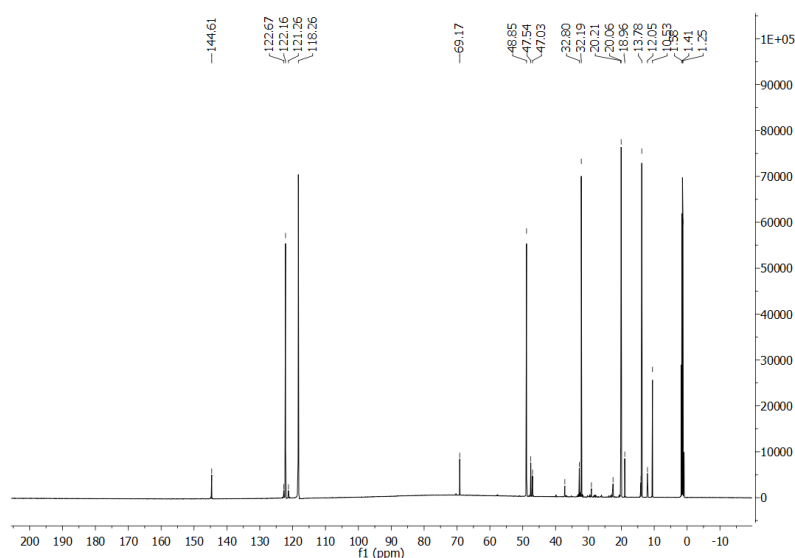


Figure S8. ^{13}C -NMR spectrum of a solution of **1a** (with traces of attached reaction medium) in $\text{CH}_3\text{CN-d}_3$.

The following signals can be assigned to $(\text{C}_4\text{C}_1\text{C}_4\text{Im})\text{Br}$:

^{13}C -NMR (125.8 MHz, $\text{CH}_3\text{CN-d}_3$, 293 K): δ [ppm] = 144.6 (s, C_{im}); 122.2 (s, C_{imH}); 48.9 (s, CH_2); 32.2 (s, CH_3); 20.1 (s, CH_2); 13.8 (s, CH_2); 10.5 (s, CH_3).

The following signals can be assigned to $\text{C}_4\text{C}_1\text{im}$:

^{13}C -NMR (125.8 MHz, $\text{CH}_3\text{CN-d}_3$, 293 K): δ [ppm] = 122.7 (s, C_{imH}); 121.3 (s, C_{imH}); 47.5 (s, CH_2); 32.8 (s, CH_3); 20.2 (s, CH_2); 14 (s, CH_2); 12.1 (s, CH_3).

4.3. ^{119}Sn -NMR spectrum of a solution of **1a** (with traces of attached reaction medium) in $\text{CH}_3\text{CN-d}_3$.

For an image of the ^{119}Sn -NMR spectrum, see the main document (Figure 2b and corresponding text).

The following signals and $^2J_{\text{Sn-O,S-Sn}}$ coupling constants can be assigned to the anion in **1a**:

^{119}Sn -NM (186.5 MHz, $\text{CH}_3\text{CN-d}_3$, 293 K): δ [ppm] = -108.6 (t, $^2J = 125.4$ Hz), -117.2 ($^2J = 245$ Hz; 490 Hz), -290.2 (s); -518.7 (m, -518.1 ... -519.4, $^2J = 144, 245, 376$ Hz).

6. Raman spectroscopy

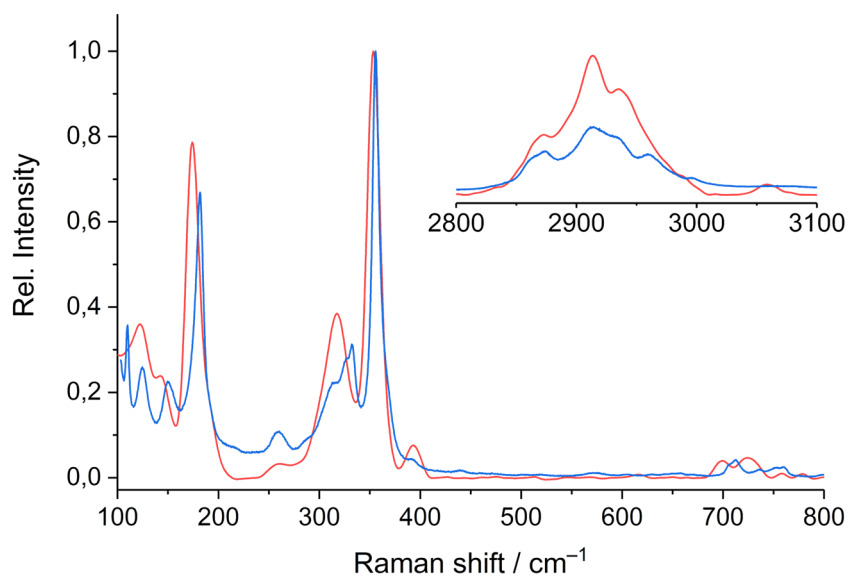
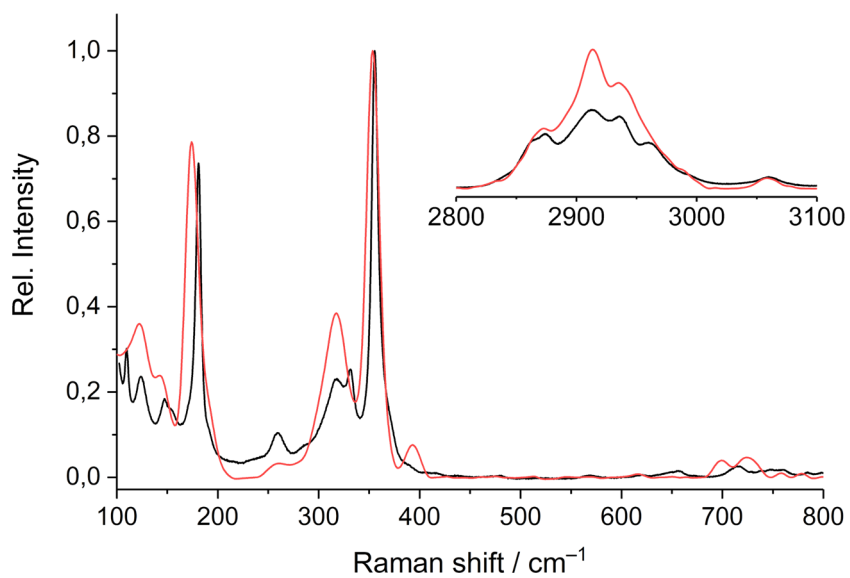
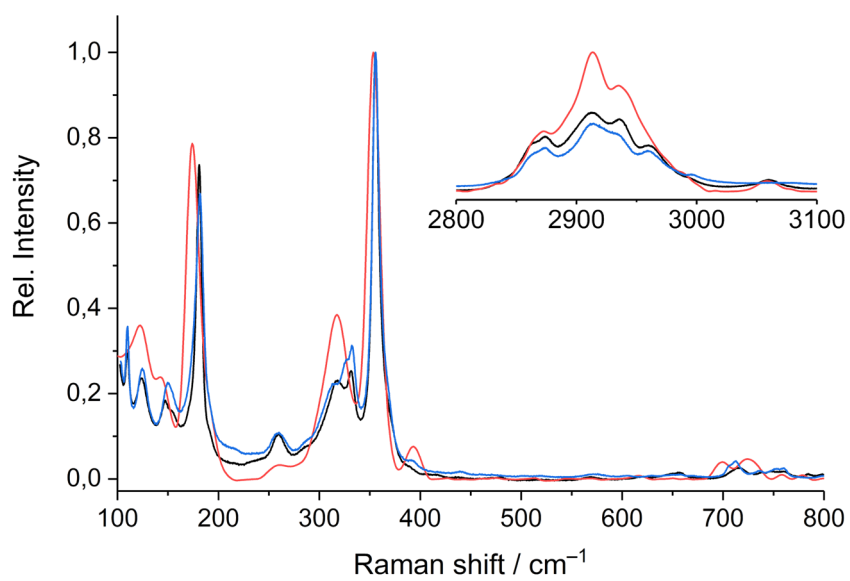


Figure S9. Raman spectra of **1a** (black), **1b** (blue), and $(\text{C}_4\text{C}_1\text{C}_1\text{Im})_4[\text{Sn}_{10}\text{O}_4\text{S}_{16}(\text{SMe})_4]$ (red).^[4]

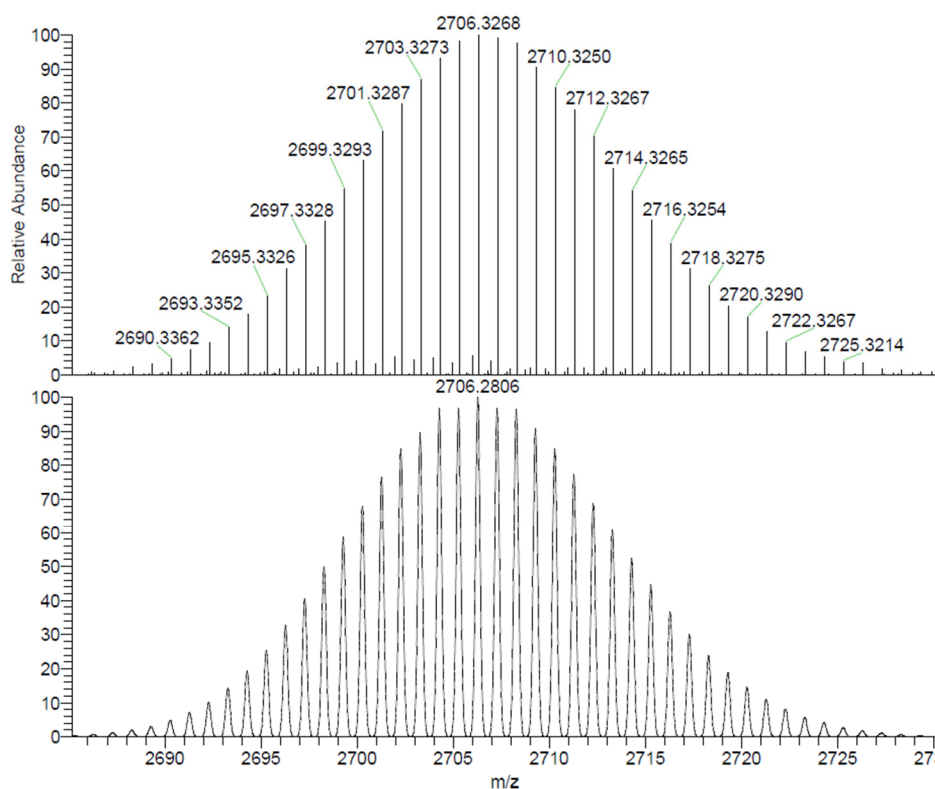
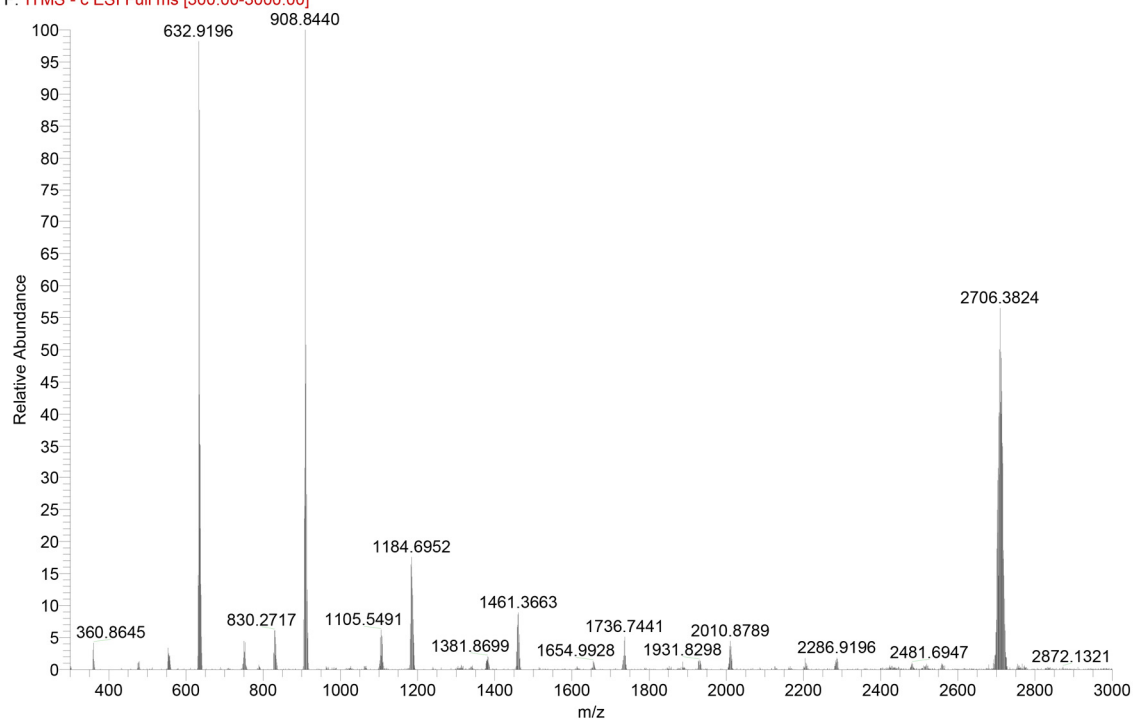
7. Mass Spectrometry

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05/11/2020 09:40:39

201105_SY_691_De_b #16-19 RT: 0.30-0.37 AV: 4 NL: 1.34E4

F: ITMS - c ESI Full ms [300.00-3000.00]



NL:
3.78E4
201105_SY_691_De_b#41-
47 RT: 0.79-1.12 AV: 7 F:
FTMS - c ESI Full ms
[400.00-4000.00]

NL:
1.12E3
C₅₂ H₁₀₅ N₆ O₄ S₂₀ Sn₁₀
C₅₂ H₁₀₅ N₆ O₄ S₂₀ Sn₁₀
p (gss, s/p:40) Chrg 1
R: 10000 Res .Pwr. @FWHM

Figure S10. Top: Overview electro spray-ionization mass spectrum recorded in negative-ion mode, ESI(-), of a fresh solution of single-crystals of compound **1b** with attached reaction media in CH₃CN. Bottom: high-resolution mass peak, detected as the mono-anionic aggregate $\{(C_4C_1C_4Im)_3[Sn_{10}O_4S_{16}(SBU)_4]\}^-$ along with two ionic liquid counterions.

8. Optical Absorption Spectroscopy

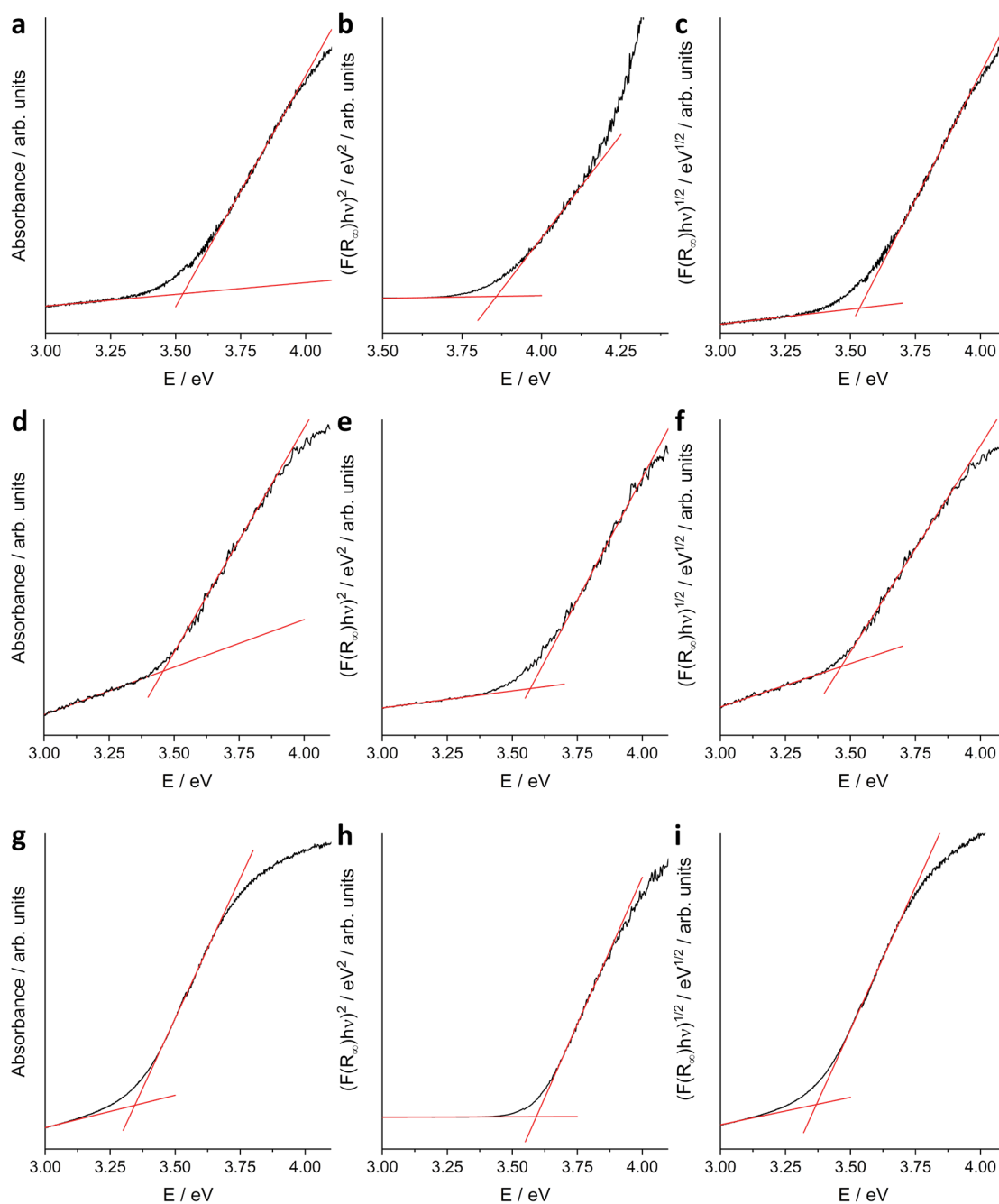


Figure S11. UV-visible absorbance spectra (left hand side) and Tauc plots generated using the Kubelka-Munk-function $(F(R_\infty)h\nu)^{1/\gamma}$ with $\gamma = 0.5$ (center), and $\gamma = 2$ (right hand side) of **1a** (a – c) **1b** (d – f), and $(C_4C_1C_1Im)_4[Sn_{10}O_4S_{16}(SMe)_4]$ (g – i) for comparison.

9. Cartesian Coordinates and Total Energies of Calculated Compounds

Table S5. Total energies E_{tot} and Cartesian coordinates [Å] of $[\text{Sn}_{10}\text{O}_4\text{S}_{20}]^{8-}$ (simultaneous optimization of geometric and electronic structures were done with the PBE functional,^[8] given energies originate from single-point calculations using the PBE0 functional^[14] based on the optimized structures).

| $E_{\text{tot}} = -10407.42534419 \text{ E}_h$ | | | |
|--|------------|------------|------------|
| Atom | x | y | z |
| Sn | 4.1243210 | -0.5577800 | -0.3748783 |
| S | 6.4672801 | -0.8545209 | -0.5845729 |
| S | 3.3653901 | -2.2512591 | 1.2633490 |
| S | 3.1937401 | -0.9329423 | -2.6373161 |
| S | 3.8129661 | 1.7636041 | 0.4245902 |
| O | 1.3754254 | -0.2042960 | -0.1329228 |
| Sn | 0.9037088 | -1.6984116 | 1.2861965 |
| Sn | 0.7524391 | -0.5581454 | -2.1210846 |
| Sn | 1.2914186 | 1.7967423 | 0.5407715 |
| S | 0.2709790 | -3.4681398 | 2.9719726 |
| S | 0.1233818 | -2.8737204 | -0.9715952 |
| S | 0.8925459 | 0.4750013 | 2.8153655 |
| O | -1.1498696 | -1.1976423 | 1.2579677 |
| S | -0.0618573 | -0.9655289 | -4.4756837 |
| S | 0.6769481 | 2.1008652 | -2.0285771 |
| O | -1.2754250 | -0.2269956 | -1.6289128 |
| S | 1.1237004 | 4.1829519 | 1.3493604 |
| O | -0.8181741 | 1.7629612 | 0.6246500 |
| Sn | -2.1618312 | -3.0240845 | 3.0782878 |
| Sn | -2.2239852 | -1.7289336 | -0.4836984 |
| Sn | -1.6878695 | 0.6285547 | 2.1789947 |
| Sn | -2.4830987 | -0.6141647 | -4.1048626 |
| Sn | -1.8393255 | 1.7685942 | -1.2239214 |
| Sn | -1.3390553 | 4.3579375 | 1.5175533 |
| S | -3.0304310 | -4.5860185 | 4.6346618 |
| S | -3.3244582 | -3.4950906 | 0.9441805 |
| S | -2.6983536 | -0.7912270 | 4.0041820 |
| S | -3.4828609 | -2.3013355 | -2.5943749 |
| S | -3.5604235 | 0.4332769 | 0.3029609 |
| S | -2.2912894 | 2.8447804 | 3.2288751 |
| S | -3.5061359 | -0.9390816 | -6.2177445 |
| S | -3.0345237 | 1.7061155 | -3.4463590 |
| S | -2.4637903 | 4.1516120 | -0.6768700 |
| S | -1.7846553 | 6.5599556 | 2.2741091 |

Table S6. Total energies E_{tot} and Cartesian coordinates [Å] of $[\text{Sn}_{10}\text{O}_4\text{S}_{16}(\text{SMe})_4]^{4-}$ (simultaneous optimization of geometric and electronic structures were done with the PBE functional,^[8] given energies originate from single-point calculations using the PBE0 functional^[14] based on the optimized structures).

| $E_{\text{tot}} = -10566.56982606 E_h$ | | | |
|--|------------|------------|------------|
| Atom | x | y | z |
| Sn | 4.7752030 | -0.7495772 | -0.2999687 |
| S | 7.2374733 | -1.1088526 | -0.4664411 |
| S | 4.2709667 | -2.4802426 | 1.3402443 |
| S | 4.0897255 | -1.1654408 | -2.6109084 |
| S | 4.7115979 | 1.5767811 | 0.4533623 |
| O | 2.3201967 | -0.4247874 | -0.0905240 |
| H | 7.4174715 | 1.1922257 | -1.2923875 |
| C | 7.6763986 | 0.1975819 | -1.6765100 |
| Sn | 1.8150818 | -1.9320984 | 1.3467142 |
| Sn | 1.6640186 | -0.7785319 | -2.1009317 |
| Sn | 2.2073768 | 1.6067559 | 0.5887585 |
| H | 7.1731878 | 0.0300403 | -2.6371092 |
| H | 8.7626586 | 0.1429820 | -1.8264009 |
| S | 1.1892764 | -3.6940334 | 3.0259150 |
| S | 1.0111192 | -3.0592631 | -0.9125205 |
| S | 1.7737167 | 0.2603258 | 2.8344213 |
| O | -0.2724932 | -1.4400795 | 1.3349148 |
| S | 0.8598308 | -1.1927463 | -4.4462099 |
| S | 1.5559455 | 1.8675564 | -1.9652757 |
| O | -0.4011844 | -0.4471482 | -1.6292446 |
| S | 2.0421833 | 3.9830310 | 1.3951290 |
| O | 0.0667058 | 1.5986067 | 0.6871902 |
| Sn | -1.1685139 | -3.0789349 | 2.9643220 |
| Sn | -1.3567737 | -1.9593860 | -0.4441845 |
| Sn | -0.8116924 | 0.4238292 | 2.2522579 |
| Sn | -1.4673750 | -0.7942899 | -3.8425572 |
| Sn | -0.9655814 | 1.5777358 | -1.1920063 |
| Sn | -0.3918882 | 3.9135720 | 1.4838673 |
| S | -2.0069878 | -4.7623303 | 4.6008521 |
| S | -2.4492668 | -3.7125682 | 0.9797563 |
| S | -1.8189139 | -0.9928276 | 4.0629377 |
| H | -4.0320211 | -3.4061958 | 4.8671658 |
| S | -2.6019138 | -2.5321371 | -2.5488165 |
| S | -2.6394767 | 0.2162724 | 0.3448961 |
| S | -1.4248467 | 2.6272570 | 3.2885917 |
| S | -2.4612317 | -1.1418411 | -6.1026835 |
| S | -2.1531825 | 1.5118532 | -3.3998969 |
| S | -1.5978855 | 3.9438620 | -0.6428009 |
| S | -0.7751918 | 6.2412565 | 2.2925472 |
| C | -3.8074492 | -4.4248831 | 4.5270565 |
| C | -4.2287079 | -0.8086024 | -5.7475137 |
| C | -2.6069369 | 6.2623392 | 2.3781492 |
| H | -4.2959189 | -5.1433726 | 5.1982632 |
| H | -4.1917259 | -4.5676143 | 3.5091238 |
| H | -4.7725478 | -0.9199206 | -6.6947192 |
| H | -4.3684085 | 0.2134146 | -5.3729849 |
| H | -4.6263874 | -1.5268737 | -5.0195190 |
| H | -2.9000871 | 7.2594540 | 2.7318047 |
| H | -3.0492371 | 6.0892062 | 1.3888408 |
| H | -2.9763071 | 5.5086402 | 3.0850325 |

Table S7. Total energies E_{tot} and Cartesian coordinates [\AA] of $[\text{Sn}_{10}\text{O}_4\text{S}_{16}(\text{SBu})_4]^{4-}$ (simultaneous optimization of geometric and electronic structures were done with the PBE functional,^[8] given energies originate from single-point calculations using the PBE0 functional^[14] based on the optimized structures).

| $E_{\text{tot}} = -11037.90613053 E_h$ | | | |
|--|------------|------------|------------|
| Atom | x | y | z |
| Sn | -1.9182728 | 1.9240037 | -0.0332436 |
| S | -2.4911827 | 0.2270228 | 1.9289466 |
| S | -0.2270113 | 2.5051632 | -1.9988031 |
| S | -4.1205926 | 2.0835666 | -1.2179049 |
| S | -2.0848894 | 4.1255357 | 1.1545301 |
| O | -1.7261022 | 0.0272524 | -1.0220013 |
| O | -0.0202342 | 1.7371876 | 0.9497402 |
| Sn | -1.8971404 | -1.7029077 | 0.2209239 |
| S | -0.2120604 | -2.5539003 | -1.6369388 |
| S | -4.1161403 | -2.0661765 | -0.9168586 |
| S | -2.0677216 | -3.7317116 | 1.6914139 |
| O | -0.0045628 | -1.3777043 | 1.1715293 |
| Sn | 1.7068386 | 1.9167191 | -0.2945910 |
| S | 2.0645512 | 4.1378903 | 0.8431064 |
| S | 2.5670333 | 0.2332020 | 1.5612386 |
| S | 3.7352444 | 2.0957075 | -1.7653719 |
| O | 1.3887822 | 0.0224960 | -1.2455863 |
| Sn | 0.0860326 | 3.8805254 | 2.2523140 |
| S | 0.2025891 | 2.2561539 | 4.0703039 |
| S | 0.0779626 | 5.9499378 | 3.6506118 |
| Sn | -3.8615907 | -0.0829931 | -2.3216900 |
| S | -2.2440294 | -0.1968763 | -4.1444359 |
| S | -5.9285855 | -0.0847510 | -3.7215694 |
| Sn | -0.2765714 | -0.0799072 | -2.5923044 |
| S | 1.4542519 | -0.2083252 | -4.4029233 |
| Sn | 0.0947583 | 0.2877361 | 2.5186125 |
| S | 0.2346660 | -1.4434559 | 4.3286499 |
| Sn | 1.7345587 | -1.7166305 | -0.0375665 |
| S | 2.0950988 | -3.7359968 | 1.4157788 |
| S | 3.7533116 | -2.0705636 | -1.4933317 |
| Sn | 0.0889044 | -3.3021108 | 2.7474616 |
| S | 0.0647768 | -5.2809821 | 4.2682210 |
| Sn | 3.3113045 | -0.0628311 | -2.8202029 |
| S | 5.2926239 | -0.0372960 | -4.3349932 |
| C | 1.2409339 | 7.1112478 | 2.8173960 |
| C | -7.1122164 | -1.1653496 | -2.8124271 |
| C | 5.0104047 | -1.5149997 | -5.4090463 |
| C | 2.5858241 | 7.2214759 | 3.5309285 |
| C | -7.2869066 | -2.5319587 | -3.4683578 |
| C | -8.3207036 | -3.4067352 | -2.7514850 |
| C | 5.0684825 | -0.3087670 | -7.6800290 |
| C | 4.2949457 | -1.2205835 | -6.7269688 |
| C | 4.3065573 | -0.0184945 | -8.9735960 |
| C | 3.4992630 | 8.2850942 | 2.9118269 |
| C | 4.8353394 | 8.4166294 | 3.6454924 |
| C | -8.5256884 | -4.7583460 | -3.4376892 |
| C | 1.4785780 | -4.9445671 | 5.4103166 |
| C | 1.0904383 | -4.2566914 | 6.7186273 |
| C | 0.1900650 | -5.0879504 | 7.6334824 |
| C | -0.1846642 | -4.3545130 | 8.9222212 |
| H | 0.7305433 | 8.0865244 | 2.8005729 |
| H | 1.3774190 | 6.7938044 | 1.7730588 |

Table S7 (continued)

| | | | |
|---|------------|------------|------------|
| H | -8.0680566 | -0.6201520 | -2.7904616 |
| H | -6.7708063 | -1.2735890 | -1.7723987 |
| H | 4.4587039 | -2.2659406 | -4.8263200 |
| H | 6.0139614 | -1.9277872 | -5.5984712 |
| H | 3.0863834 | 6.2391185 | 3.5077251 |
| H | 2.4133755 | 7.4608262 | 4.5945085 |
| H | -6.3126495 | -3.0480016 | -3.4863247 |
| H | -7.5878978 | -2.3926235 | -4.5211522 |
| H | -9.2834409 | -2.8689753 | -2.7005304 |
| H | -8.0002876 | -3.5644345 | -1.7074373 |
| H | 6.0422934 | -0.7740535 | -7.9153759 |
| H | 5.2949295 | 0.6385751 | -7.1628811 |
| H | 3.3062824 | -0.7822051 | -6.5091827 |
| H | 4.1026429 | -2.1886473 | -7.2263382 |
| H | 4.0779079 | -0.9475235 | -9.5195600 |
| H | 4.8846993 | 0.6322038 | -9.6465580 |
| H | 3.3499693 | 0.4845644 | -8.7624316 |
| H | 2.9780068 | 9.2583063 | 2.9172615 |
| H | 3.6797445 | 8.0384238 | 1.8515083 |
| H | 4.6803196 | 8.6879626 | 4.7017864 |
| H | 5.4714764 | 9.1903288 | 3.1903800 |
| H | 5.3934498 | 7.4680250 | 3.6245725 |
| H | -7.5825849 | -5.3244260 | -3.4856228 |
| H | -8.8858951 | -4.6258987 | -4.4701439 |
| H | -9.2616538 | -5.3760044 | -2.9017763 |
| H | 2.2291880 | -4.3531570 | 4.8677081 |
| H | 1.9292162 | -5.9294095 | 5.6113078 |
| H | 0.6040834 | -3.2940836 | 6.4875063 |
| H | 2.0248050 | -4.0105876 | 7.2569249 |
| H | 0.7004149 | -6.0360633 | 7.8798099 |
| H | -0.7258139 | -5.3636295 | 7.0839559 |
| H | -0.8186957 | -4.9769605 | 9.5711246 |
| H | -0.7378487 | -3.4280177 | 8.7022522 |
| H | 0.7118609 | -4.0752637 | 9.4984457 |

Table S8. Total energies E_{tot} and Cartesian coordinates [Å] of $(\text{C}_4\text{C}_1\text{C}_4\text{Im})^+$ (simultaneous optimization of geometric and electronic structures were done with the PBE functional,^[8] given energies originate from single-point calculations using the PBE0 functional^[14] based on the optimized structures).

| $E_{\text{tot}} = -580.0137372402 E_h$ | | | |
|--|------------|------------|------------|
| Atom | x | y | z |
| N | 1.6382657 | 0.5559128 | -0.8993174 |
| C | 2.4053938 | 1.7691580 | -0.5692511 |
| C | 1.2671369 | -0.4114000 | -0.0297499 |
| C | 1.1566261 | 0.2474135 | -2.1578906 |
| H | 2.8548100 | 2.1107212 | -1.5110238 |
| H | 3.2258543 | 1.4751446 | 0.0982569 |
| C | 1.5562662 | 2.8736355 | 0.0612382 |
| N | 0.5610271 | -1.3278125 | -0.7300148 |
| C | 1.5762966 | -0.4624239 | 1.4164502 |
| H | 1.3479122 | 0.8814612 | -3.0150013 |
| C | 0.4806512 | -0.9319234 | -2.0518081 |
| H | 1.1147934 | 2.5097355 | 1.0040355 |
| H | 2.2544625 | 3.6795691 | 0.3407818 |
| C | 0.4612780 | 3.4347716 | -0.8487872 |
| C | -0.0782229 | -2.5324956 | -0.1816587 |
| H | 2.4854811 | 0.1090764 | 1.6371203 |
| H | 1.7365924 | -1.4985107 | 1.7410358 |
| H | 0.7552354 | -0.0415856 | 2.0166450 |
| H | -0.0363444 | -1.5248930 | -2.7966448 |
| C | -0.3144942 | 4.5760590 | -0.1908386 |
| H | -0.2412844 | 2.6323036 | -1.1290116 |
| H | 0.9186847 | 3.7897495 | -1.7881776 |
| H | 0.5797600 | -2.9398766 | 0.5978888 |
| H | -0.1122861 | -3.2667558 | -0.9978583 |
| C | -1.4787307 | -2.2588863 | 0.3662470 |
| H | -1.0953492 | 4.9641529 | -0.8603891 |
| H | 0.3537105 | 5.4115734 | 0.0674184 |
| H | -0.8038390 | 4.2402534 | 0.7363307 |
| C | -2.1330946 | -3.5346062 | 0.9029455 |
| H | -2.1014670 | -1.8266172 | -0.4342782 |
| H | -1.4207267 | -1.5045430 | 1.1689075 |
| H | -2.1788942 | -4.2859480 | 0.0963777 |
| H | -1.4954100 | -3.9663681 | 1.6927059 |
| C | -3.5369005 | -3.2855094 | 1.4544669 |
| H | -4.2037218 | -2.8842582 | 0.6760302 |
| H | -3.5152511 | -2.5611209 | 2.2832339 |
| H | -3.9842209 | -4.2151570 | 1.8335851 |

Table S9. Total energies E_{tot} and Cartesian coordinates [Å] of $(\text{C}_4\text{C}_1\text{C}_1\text{Im})^+$ (simultaneous optimization of geometric and electronic structures were done with the PBE functional,^[8] given energies originate from single-point calculations using the PBE0 functional^[14] based on the optimized structures).

| $E_{\text{tot}} = -462.1772848829 E_h$ | | | |
|--|------------|------------|------------|
| Atom | x | y | z |
| N | -1.7584650 | -1.7685601 | -2.9693008 |
| C | -1.1905912 | -0.5442126 | -2.9121044 |
| C | -1.8115963 | -2.7178558 | -1.8601064 |
| C | -2.2819614 | -1.9747624 | -4.2304713 |
| N | -1.3531578 | 0.0281545 | -4.1253057 |
| C | -0.5154676 | 0.0278342 | -1.7272739 |
| H | -0.7961046 | -2.9567603 | -1.5216739 |
| H | -2.3006810 | -3.6303305 | -2.2128985 |
| H | -2.3888589 | -2.2942056 | -1.0288271 |
| C | -2.0255813 | -0.8490139 | -4.9568060 |
| H | -2.7911668 | -2.8931826 | -4.4966068 |
| C | -0.8473221 | 1.3445020 | -4.5419881 |
| H | -1.1359146 | -0.1035564 | -0.8298374 |
| H | -0.3257190 | 1.0980472 | -1.8611832 |
| H | 0.4485407 | -0.4725817 | -1.5462068 |
| H | -2.2680881 | -0.5939865 | -5.9813811 |
| H | -0.9647154 | 2.0365452 | -3.6971100 |
| H | -1.5128716 | 1.6931465 | -5.3429204 |
| C | 0.6037430 | 1.2939446 | -5.0197687 |
| H | 0.6863929 | 0.5722761 | -5.8491802 |
| H | 1.2468914 | 0.9197103 | -4.2056120 |
| C | 1.0954678 | 2.6699701 | -5.4758801 |
| C | 2.5461694 | 2.6434028 | -5.9577127 |
| H | 0.9937338 | 3.3867679 | -4.6436463 |
| H | 0.4420179 | 3.0392548 | -6.2841566 |
| H | 2.6687193 | 1.9583075 | -6.8104087 |
| H | 3.2239663 | 2.3074915 | -5.1580073 |
| H | 2.8753805 | 3.6416831 | -6.2792858 |

Table S10. Total energies E_{tot} and Cartesian coordinates [Å] of $\text{C}_4\text{C}_1\text{im}$ (simultaneous optimization of geometric and electronic structures were done with the PBE functional,^[8] given energies originate from single-point calculations using the PBE0 functional^[14] based on the optimized structures).

| $E_{\text{tot}} = -422.4499631125 E_h$ | | | |
|--|------------|------------|------------|
| Atom | x | y | z |
| N | -1.8159368 | -1.7745711 | -2.9133790 |
| C | -1.2671261 | -0.5604762 | -2.8863100 |
| C | -2.2481194 | -1.9618667 | -4.2116357 |
| N | -1.3384020 | 0.0374290 | -4.1198978 |
| C | -0.6637954 | 0.0865285 | -1.6869192 |
| C | -1.9600400 | -0.8543284 | -4.9736790 |
| H | -2.7460151 | -2.8770444 | -4.5219372 |
| C | -0.8034059 | 1.3433312 | -4.5001563 |
| H | -0.7621035 | -0.5947245 | -0.8338347 |
| H | -1.1671178 | 1.0325391 | -1.4322055 |
| H | 0.4051010 | 0.3093740 | -1.8285211 |
| H | -2.1396233 | -0.6135973 | -6.0166942 |
| H | -0.8344542 | 1.9928775 | -3.6134886 |
| H | -1.4855845 | 1.7798333 | -5.2445940 |
| C | 0.6193745 | 1.2732645 | -5.0612874 |
| H | 0.6283108 | 0.6006990 | -5.9353826 |
| H | 1.2867871 | 0.8213083 | -4.3080737 |
| C | 1.1504478 | 2.6509545 | -5.4627028 |
| C | 2.5696941 | 2.5972788 | -6.0294045 |
| H | 1.1275352 | 3.3194250 | -4.5850526 |
| H | 0.4711733 | 3.0985724 | -6.2083314 |
| H | 2.6143926 | 1.9610213 | -6.9266615 |
| H | 3.2755548 | 2.1844243 | -5.2922634 |
| H | 2.9261598 | 3.5988719 | -6.3105073 |

Table S11. Total energies E_{tot} and Cartesian coordinates [Å] of C_1C_1im (simultaneous optimization of geometric and electronic structures were done with the PBE functional,^[8] given energies originate from single-point calculations using the PBE0 functional^[14] based on the optimized structures).

| $E_{\text{tot}} = -304.6129365148 E_h$ | | | |
|--|------------|------------|------------|
| Atom | x | y | z |
| N | -1.7572970 | -1.7870523 | -2.9676660 |
| C | -1.2046323 | -0.5322580 | -2.9410775 |
| C | -1.7847854 | -2.7423926 | -1.8697314 |
| C | -2.2902726 | -1.9769813 | -4.2277606 |
| N | -1.3579072 | 0.0804171 | -4.1146092 |
| C | -0.5307797 | 0.0342756 | -1.7399299 |
| H | -0.7646103 | -2.9799267 | -1.5385781 |
| H | -2.2681473 | -3.6630501 | -2.2131439 |
| H | -2.3513071 | -2.3398325 | -1.0185561 |
| C | -2.0335951 | -0.8158368 | -4.9190808 |
| H | -2.7882283 | -2.9015526 | -4.5014891 |
| H | -1.2127565 | 0.0930764 | -0.8770435 |
| H | -0.1781658 | 1.0458091 | -1.9718646 |
| H | 0.3350754 | -0.5729680 | -1.4312539 |
| H | -2.2960101 | -0.5767801 | -5.9465507 |

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