Supporting Information

Solvent-Coordinated Tin Halide Complexes as Purified Precursors for Tin-based Perovskites

Masashi Ozaki,[†] Yukie Katsuki,[†] Jiewei Liu,[†] Taketo Handa,[†] Ryosuke Nishikubo,[‡] Shinya Yakumaru,[†] Yoshifumi Hashikawa,[†] Yasujiro Murata,[†] Takashi Saito,[†] Yuichi Shimakawa,[†] Yoshihiko Kanemitsu,[†] Akinori Saeki,[‡] and Atsushi Wakamiya[*,†]*

[†]Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan
[‡]Department of Applied Chemistry, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 566-0871, Japan

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General.

Thermogravimetric analysis (TGA) was performed on a Shimadzu TGA-50 apparatus (Shimadzu Co.,). Karl Fisher titration was performed on a MKH-700 equipped with a high temperature evaporator ADP-512S (Kyoto Electronics Manufacturing Co., Ltd.). ^{119}Sn MAS NMR measurement was performed on a Bruker Avance III 800US Plus instrument. The NMR chemical shifts were reported in ppm with reference to the signal of $SnMe_4$ (δ 0.00 ppm) as an external standard. APCI mass spectra (direct injection method) were measured on a Bruker micrOTOF-Q II (Bruker Co.,). Single X-ray structure analysis was performed on a Bruker Single Crystal CCD X-ray Diffractometer SMART APEX II with Mo Kα radiation (λ = 0.71073 Å) and graphite monochromater. X-ray diffraction (XRD) measurement was performed on a Rigaku RINT 2500 (Rigaku Co.,).

Photo yield spectroscopy (PYS) measurements were carried out using a Bunko Keiki BIP-KV201 (accuracy: ± 0.02 eV, extraction voltage = 10 V) in a vacuum ($<10^{-2}$ Pa). In a N_2-filled glove box, powder samples were placed on a conductive carbon tape on a glass, which was contacted through an aluminum tape and an Au-coated electrode.

The steady-state absorption spectra were measured under air atmosphere using a UV-Vis-NIR spectrophotometer and an integrating sphere system (V-670 and ISN-723, JASCO). Before the measurements the samples were kept in a nitrogen-filled acryl box. For the photoluminescence (PL) measurements, the samples were excited by a femtosecond pulsed laser with a wavelength of 550 nm using a wavelength-tunable Yb:KGW-based femtosecond laser system with an optical parametric amplifier (Light Conversion, pulse duration: 300 fs, repetition rate: 200 kHz). The diameter of the excitation spot was about 0.1 mm and the excitation intensities were set to be 0.5-1.5 μJ/cm^2. To record the PL spectra, liquid-nitrogen-cooled CCD and InGaAs detectors with a monochromater (Roper Scientific) were used for $FASnI_3$ and $MASnI_3$, respectively. In the detection path, long pass filters were put to suppress the scattered excitation light, and only the PL emission from the samples was detected. The PL spectra in the main text were obtained from samples that were protected against degradation in air by using the nitrogen-filled acryl box.

Methylammonium iodide (MAI), formamidinium iodide (FAI) were purchased from Tokyo

Chemical Industry Co., Ltd. (TCI). SnF_2 was purchased from Sigma-Aldrich Co., Ltd. (Aldrich). These materials were used as received. Dehydrated dimethylsulfoxide (DMSO, super dehydrated), *N,N*-dimethylformamide (DMF, super dehydrated), and ethanol (super dehydrated) were purchased from Wako Pure Chemical Industries, Ltd. Toluene (super dehydrated) and dichloromethane (CH_2Cl_2, super dehydrated) were purchased from Kanto Chemical. Co., Inc. All of these solvents were degassed by Ar gas bubbling for 1h and further dried over molecular sieves in an Ar-filled glove box (O_2 ~10 ppm) before use. SnI_2 (99.9%, trace metal basis) was purchased from Kojundo Chemical Laboratory Co., Ltd. $SnBr_2$ (99.8%, Br based) and SnF_2 (99%) were purchased from Aldrich. $SnCl_2$ (97%) was purchased from Wako Pure Chemical Industries, Ltd.

Sublimation of SnI_2

SnI_2 (10.7 g; 99.9% trace metal basis) was placed in a sublimation apparatus (Figure S1), which was heated to 150 °C in a mantle heater for 10 h under reduced pressure of 100 Pa. After cooling down to room temperature, the apparatus was filled with Ar gas. The sublimed SnI_4 was obtained as orange crystals (2.1 g, 3.4 mmol; 1st sublimate). Further heating at 330 °C under pressure of 100 Pa for 1 day. After cooling down to room temperature, the apparatus was refilled with Ar gas. The sublimed SnI_2 was collected in an Ar-filled glove box as red crystals (7.1 g, 19.1 mmol; 2nd sublimate). As residue, 0.85 g of brown solids containing SnO_2 were obtained.

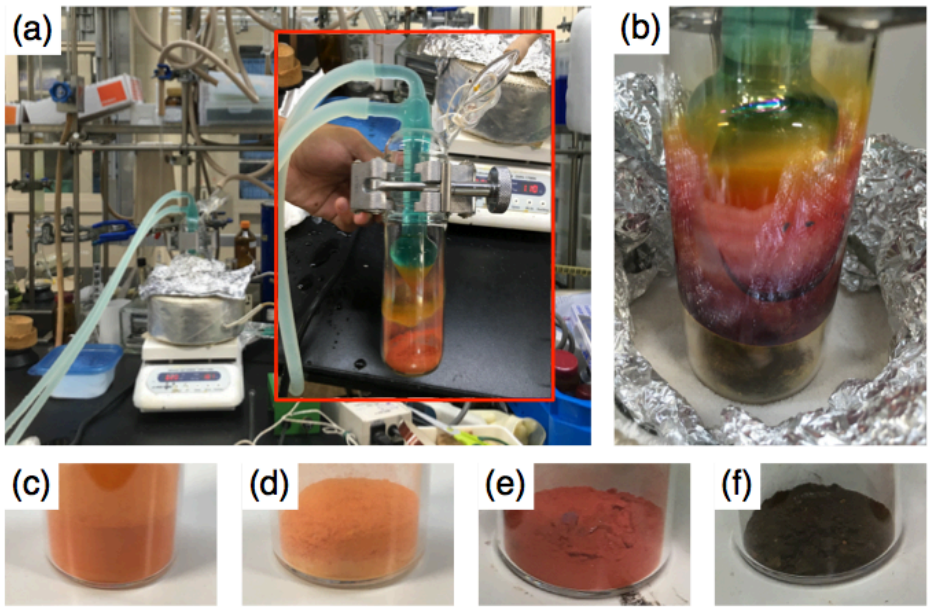

Figure S1. (a) Photos of apparatus for SnI_2 purification by sublimation. (b) After heating at 330 °C under pressure of 100 Pa for 1 day. Collected compounds of (c) commercially available SnI_2 (99.9% trace metal basis), (d) SnI_4 (1st sublimate), (e) SnI_2 (2nd sublimate), and (f) SnO_2 containing residue.

APCI Mass Spectra of SnO_2

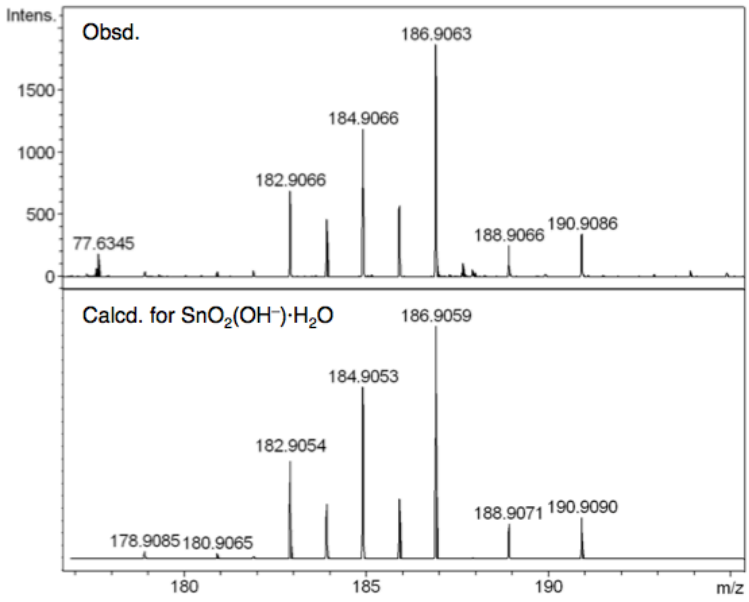

Figure S2. APCI mass spectra (negative ion mode) of residual dark brown solids in sublimation of commercially available sample of SnI_2.

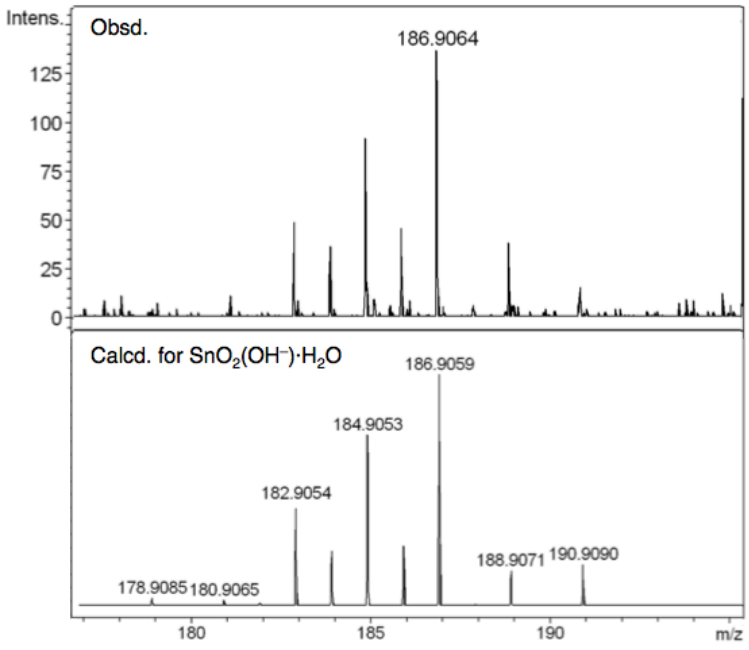

Figure S3. APCI mass spectra (negative ion mode) of insoluble small brown particles in solution of the sublimed SnI_2 in DMF.

Preparation of [SnI_2(dmf)]

In a glove box filled with an inert gas (Ar), SnI_2 (4470 mg, 12.0 mmol; purified by sublimation) was dissolved in dehydrated and degassed DMF (3.0 mL). After stirring at 50 °C for 1 h, the resulting yellow suspension was filtered with a PTFE membrane filter (pore size 0.45 μm) to remove the insoluble solids. Then, toluene (ca. 15 mL) as anti-solvent was slowly added into the solution. After standing at room temperature for 2 days, 3876 mg (8.7 mmol, 72% yield) of [SnI_2(dmf)] was obtained as colorless needle-like crystals by filtration.

^{119}Sn MAS NMR (298 MHz): δ –391.08. Elemental analysis calcd (%) for $C_3H_7I_2NOSn$: C 8.09, H 1.58, N 3.14; found: C 7.92, H 1.58, N 3.07.

Preparation of [Sn_3I_6(dmf)$_2$]

In a glove box filled with an inert gas (Ar), SnI_2 (4.3 g, 11.7 mmol; purified by sublimation) was dissolved in dehydrated and degassed DMF (2.9 mL). After stirring at 50 °C for 1 h, the resulting yellow suspension was filtered with a PTFE membrane filter (pore size 0.45 μm) to remove the insoluble solids. Then, CH_2Cl_2 (ca. 15 mL) as anti-solvent was slowly added into the solution. After standing at room temperature for 2 days, 1.2 g (0.9 mmol, 30% yield) of [$(SnI_2)_3$(dmf)$_2$] was obtained as orange needle-like crystals by filtration.

^{119}Sn MAS NMR (298 MHz): δ –341.33.

Preparation of [SnI_2(dmso)]

In a glove box filled with an inert gas (Ar), SnI_2 (429 mg, 1.2 mmol; purified by sublimation) was dissolved in dehydrated and degassed DMSO (0.58 mL). After stirring at 55 °C for 2 h, the resulting yellow suspension was filtered with a PTFE membrane filter (pore size 0.45 μm) to remove the insoluble solids. Then, CH_2Cl_2 (ca. 10 mL) as anti-solvent was slowly added into the solution. After standing at room temperature for 2 days, 235 mg (0.5 mmol, 45% yield) of [SnI_2(dmso)] was obtained as colorless crystals by filtration.

^{119}Sn MAS NMR (298 MHz): δ –596.89. Elemental analysis calcd (%) for $C_2H_6I_2OSSn$: C 5.32, H 1.33, N 0.00; found: C 5.33, H 1.34, N 0.00.

Preparation of [$SnI_2(dmso)_2$]

In a glove box filled with an inert gas (Ar), SnI_2 (5015 mg, 13.5 mmol; purified by sublimation) was dissolved in dehydrated and degassed DMSO (8.0 mL. After stirring at 90 °C for 30 min, the resulting yellow suspension was filtered with a PTFE membrane filter (pore size 0.45 μm) to remove the insoluble solids. Then, toluene (ca. 40 mL) as anti-solvent was slowly added into the solution. After standing at room temperature for 1 day, 6194 mg (11.7 mmol, 87% yield) of [$SnI_2(dmso)_2$] was obtained as colorless crystals by filtration.

^{119}Sn MAS NMR (298 MHz): δ –150.59. Elemental analysis calcd (%) for $C_4H_{12}I_2O_2S_2Sn$: C 9.09, H 2.29, N 0.00; found: C 9.18, H 2.22, N 0.00.

Preparation of [$SnBr_2(dmf)$]

In a glove box filled with an inert gas (Ar), $SnBr_2$ (1670 mg, 6.0 mmol, 99.8%, Br based) was dissolved in dehydrated and degassed DMF (1.5 mL). After stirring at 50 °C for 30 min, the resulting colorless solution was filtered with a PTFE membrane filter (pore size 0.45 μm). Then, toluene (ca. 15 mL) as anti-solvent was slowly added into the solution. After standing at room temperature for 1 day, 597 mg (1.7 mmol, 28% yield) of [$SnBr_2(dmf)$] was obtained as colorless crystals by filtration.

^{119}Sn MAS NMR (298 MHz): δ –365.02. Elemental analysis calcd (%) for $C_3H_7Br_2NOSn$: C 10.25, H 2.01, N 3.98; found: C 10.22, H 1.94, N 3.98.

Preparation of [$SnBr_2(dmso)_2$]

In a glove box filled with an inert gas (Ar), $SnBr_2$ (4987 mg, 17.9 mmol, 99.8%, Br based) was dissolved in dehydrated and degassed DMSO (8.0 mL). After stirring at 50 °C for 30 min, the resulting colorless solution was filtered with a PTFE membrane filter (pore size 0.45 μm). Then, toluene or CH_2Cl_2 (ca. 40 mL) as anti-solvent was slowly added into the solution. After standing at room temperature for 1 day, 6163 mg (14.2 mmol. 79% yield) of [$SnBr_2(dmso)_2$] was obtained as colorless crystals by filtration.

^{119}Sn MAS NMR (298 MHz): δ –503.69. Elemental analysis calcd (%) for $C_4H_{12}Br_2O_2S_2Sn$: C 11.05, H 2.78, N 0.00.; found: C 11.04, H 2.76, N 0.00.

Preparation of [$Sn_2F_4(dmso)_2$]

In a glove box filled with an inert gas (Ar), SnF_2 (940 mg, 6.0 mmol, 99%) was dissolved in dehydrated and degassed DMSO (2.0 mL). After stirring at 50 °C for 30 min, the resulting colorless solution was filtered with a PTFE filter. Then CH_2Cl_2 (ca. 10 mL) as anti-solvent was slowly added in to the solution. After standing at room temperature for 1 day, 368 mg (1.6 mmol, 26% yield) of [$Sn_2F_4(dmso)_2$] was obtained as colorless needle-like crystals by filtration.

^{119}Sn MAS NMR (298 MHz): δ –493.48.

Preparation of [$SnCl_2(dmf)$]

In a glove box filled with an inert gas (Ar), $SnCl_2$ (3.99 g, 21.0 mmol, 97%) was dissolved in dehydrated and degassed DMF (3 mL). After stirring at 80 °C for 30 min, the resulting colorless solution was filtered with a PTFE filter. Then toluene (ca. 10 mL) as anti-solvent was slowly added into the solution. After standing at room temperature for 1 day, 2.71 g (10.3 mmol, 49% yield) of [$SnCl_2(dmf)$] was obtained as colorless needle-like crystals by filtration.

^{119}Sn MAS NMR (298 MHz): δ –329.87. Elemental analysis calcd (%) for $C_3H_7Cl_2NOSn$: C 13.72, H 2.69, N 5.53; found: C 13.74, H 2.68, N 5.35.

Single Crystal X-Ray Structure Analysis

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication number CCDC-1558255 ([SnI_2(dmf)]), CCDC-1558256 ([$Sn_3I_6(dmf)_2$]), CCDC-1558257 ([SnI_2(dmso)]), CCDC-1558258 ([$SnI_2(dmso)_2$]), CCDC-1558259 ([$SnBr_2$(dmf)]), CCDC-1558260 ([$SnBr_2(dmso)_2$]), CCDC-1558261 ([$Sn_2F_4(dmso)_2$], CCDC-1558262 (SnI_2), and CCDC-1568223 ([$SnCl_2$(dmf)]). Data files can be obtained free of charge from the CCDC *via* www.ccdc.cam.ac.uk/data_request/cif.

SnI_2

Single crystals of SnI_2 suitable for X-ray diffraction analysis were obtained from sublimation of SnI_2. Intensity data were collected at 100 K on a Bruker Single Crystal CCD X-ray Diffractometer (SMART APEX II ULTRA) with Mo Kα radiation (λ = 0.71073 Å) and graphite monochromater. A total of 1245 reflections were measured with a maximum 2θ angle of 51.0°, of which 671 were independent reflections (R_{int} = 0.0111). The structure was solved by direct methods (SHELXS-97[1]) and refined by the full-matrix least-squares on F^2 (SHELXL-97[1]). All non-hydrogen atoms were refined anisotropically. The crystal data are as follows: I_2Sn; FW = 372.52, crystal size 0.11 × 0.11 × 0.09 mm, Monoclinic, *C*2/m, a = 14.184(5) Å, b = 4.4598(17) Å, c = 10.853(4) Å, β = 92.392(4)° , V = 685.9(4) Å^3, Z = 8, D_c = 5.411 g/cm^3. The refinement converged to R_1 = 0.0264, wR_2 = 0.0731 (I>2σ (I)), GOF = 1.148.

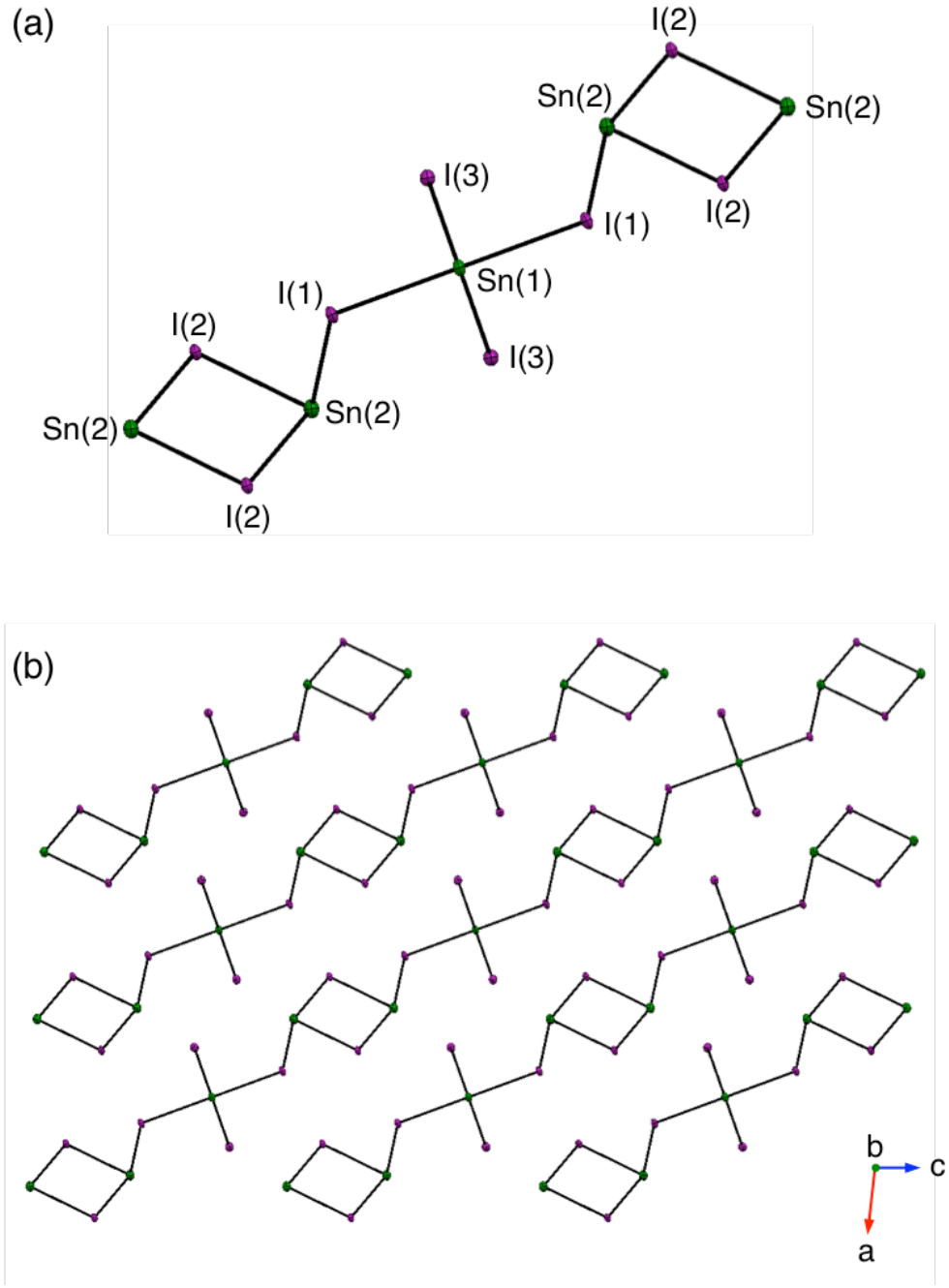

Figure S4. X-ray crystal structure of SnI_2: (a) molecular structure and (b) packing structure along with *b* axis. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å): Sn(1)–I(1) 3.1829(12); Sn(1)–I(3) 3.1548(9); Sn(2)–I(1) 3.1715(10); Sn(2)–I(2) 3.00224(13).

[SnI_2(dmf)]

Single crystals of [SnI_2(dmf)] suitable for X-ray diffraction analysis were obtained by diffusion of toluene into a solution of SnI_2 in DMF at room temperature. Intensity data were collected at 100 K on a Bruker Single Crystal CCD X-ray Diffractometer (SMART APEX II ULTRA) with Mo Kα radiation (λ = 0.71073 Å) and graphite monochromater. A total of 4523 reflections were measured with a maximum 2θ angle of 51.0°, of which 1696 were independent reflections (R_{int} = 0.0229). The structure was solved by direct methods (SHELXS-97[1]) and refined by the full-matrix least-squares on F^2 (SHELXL-97[1]). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $C_3H_7I_2NOSn$; FW = 445.59, crystal size 0.11 × 0.11 × 0.09 mm, Monoclinic, $P2_1/c$, a = 4.4957(4) Å, b = 16.2298(14) Å, c = 12.5040(11) Å, β = 95.2852(11)° , V = 908.47(14) Å^3, Z = 4, D_c = 3.258 g/cm^3. The refinement converged to R_1 = 0.0165, wR_2 = 0.0375 ($I > 2\sigma(I)$), GOF = 1.085.

[$Sn_3I_6(dmf)_2$]

Single crystals of [$Sn_3I_6(dmf)_2$] suitable for X-ray diffraction analysis were obtained by diffusion of CH_2Cl_2 into a solution of SnI_2 in DMF at room temperature. Intensity data were collected at 100 K on a Bruker Single Crystal CCD X-ray Diffractometer (SMART APEX II ULTRA) with Mo Kα radiation (λ = 0.71073 Å) and graphite monochromater. A total of 10751 reflections were measured with a maximum 2θ angle of 51.0˚, of which 2181 were independent reflections (R_{int} = 0.0323). The structure was solved by direct methods (SHELXS-97[1]) and refined by the full-matrix least-squares on F^2 (SHELXL-97[1]). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $C_6H_{14}I_6N_2O_2Sn_3$; FW = 1263.52, crystal size 0.02 × 0.06 × 0.08 mm, Orthorhombic, *P*nma, a = 9.1107(11) Å, b = 27.437(3) Å, c = 9.1779(11) Å, V = 2294.2(5) $Å^3$, Z = 8, D_c = 3.653 g/cm^3. The refinement converged to R_1 = 0.0145, wR_2 = 0.0278 ($I > 2\sigma(I)$), GOF = 1.120.

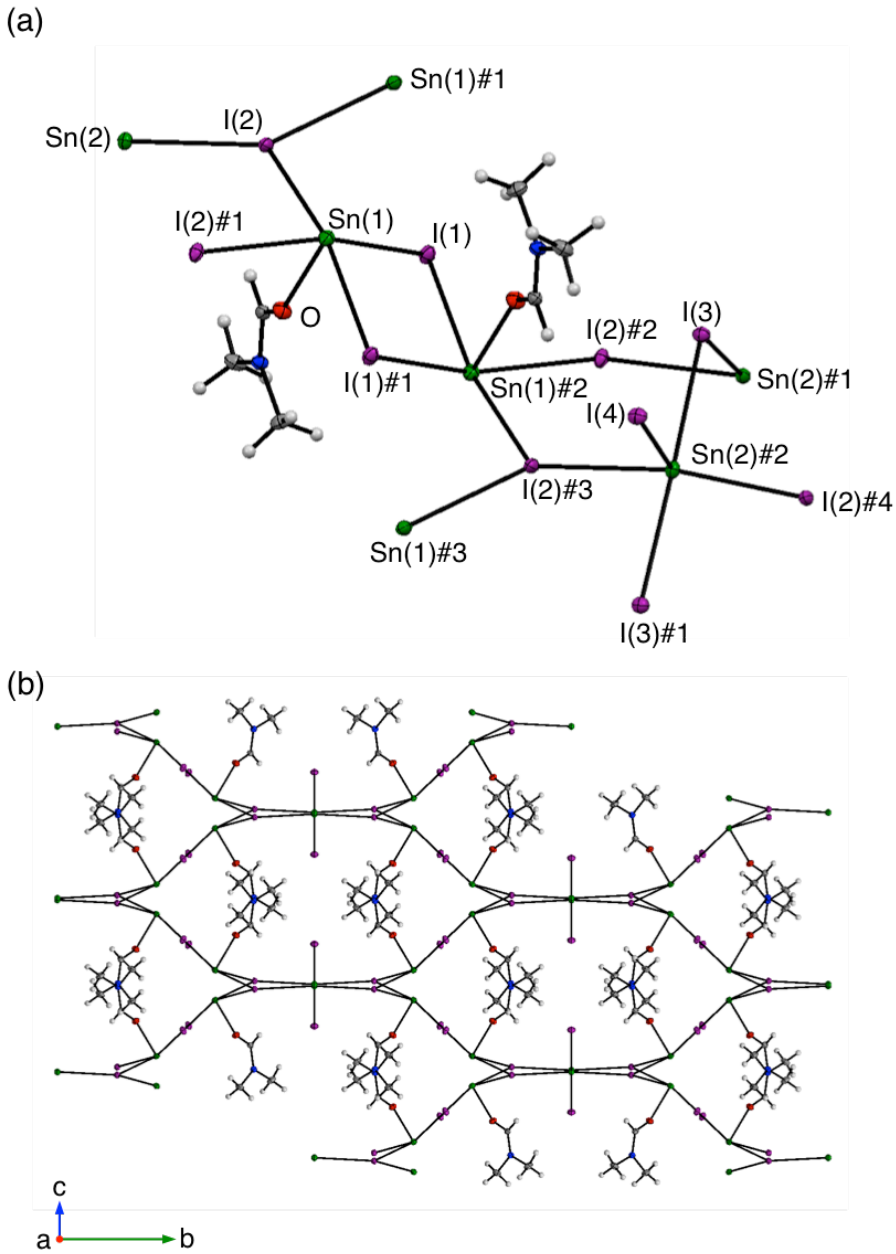

Figure S5. X-ray crystal structure of $[Sn_3I_6(dmf)_2]$: (a) molecular structure and (b) packing structure along with *a* axis. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å): Sn(1)–O 2.179(3); Sn(1)#1–O 2.179(3); Sn(1)–I(1) 3.0691(5); Sn(1)–I(1)#1 3.1853(4); Sn(1)–I(2) 3.1328(5); Sn(1)–I(2)#1 3.2947(5); Sn(1)#1–I(2) 3.2947(5); Sn(1)#2–I(1) 3.1853(4); Sn(1)#2–I(1)#1 3.0690(5); Sn(1)#2–I(2)#2 3.2947(5); Sn(1)#2–I(2)#3 3.1328(4); Sn(1)#3–I(2)#3 3.2947(5); Sn(2)#1–I(2)#2 3.2116(6); Sn(2)#1–I(3) 3.1242(6); Sn(2)#2–I(2)#3 3.2076(5); Sn(2)#2–I(2)#4 3.2076(5); Sn(2)#2–I(3) 3.1242(6); Sn(2)#2–I(3)#1 3.2116(6); Sn(2)#2–I(4) 2.9693(6).

[SnI_2(dmso)]

Single crystals of [SnI_2(dmso)] suitable for X-ray diffraction analysis were obtained by diffusion of CH_2Cl_2 into a solution of SnI_2 in DMSO at room temperature. Intensity data were collected at 100 K on a Bruker Single Crystal CCD X-ray Diffractometer (SMART APEX II ULTRA) with Mo Kα radiation (λ = 0.71073 Å) and graphite monochromater. A total of 4444 reflections were measured with a maximum 2θ angle of 51.0˚, of which 1672 were independent reflections (R_{int} = 0.0262). The structure was solved by direct methods (SHELXS-97[1]) and refined by the full-matrix least-squares on F^2 (SHELXL-97[1]). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $C_2H_6I_2OSSn$; FW = 450.62, crystal size 0.18 × 0.08 × 0.05 mm, Monoclinic, $P2_1/c$, a = 4.4931(7) Å, b = 16.364(3) Å, c = 12.2211(19) Å, β = 94.7866(18)°, V = 895.4(2) Å^3, Z = 4, D_c = 3.343 g/cm^3. The refinement converged to R_1 = 0.0184, wR_2 = 0.0322 ($I > 2\sigma(I)$), GOF = 1.016.

[$SnI_2(dmso)_2$]

Single crystals of [$SnI_2(dmso)_2$] suitable for X-ray diffraction analysis were obtained by diffusion of toluene into a solution of SnI_2 in DMSO at room temperature. Intensity data were collected at 100 K on a Bruker Single Crystal CCD X-ray Diffractometer (SMART APEX II ULTRA) with Mo Kα radiation (λ = 0.71073 Å) and graphite monochromater. A total of 2981 reflections were measured with a maximum 2θ angle of 51.0˚, of which 1101 were independent reflections (R_{int} = 0.0494). The structure was solved by direct methods (SHELXS-97[1]) and refined by the full-matrix least-squares on F^2 (SHELXL-97[1]). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $C_4H_{12}I_2O_2S_2Sn$; FW = 528.74, crystal size 0.12 × 0.09 × 0.06 mm, Monoclinic, $P2_1/c$, a = 14.0668(12) Å, b = 8.3350(7) Å, c = 10.8991(9) Å, β = 91.5950(10)°, V = 1277.39(19) Å^3, Z = 8, D_c = 2.749 g/cm^3. The refinement converged to R_1 = 0.0198, wR_2 = 0.0486 ($I > 2\sigma(I)$), GOF = 1.042.

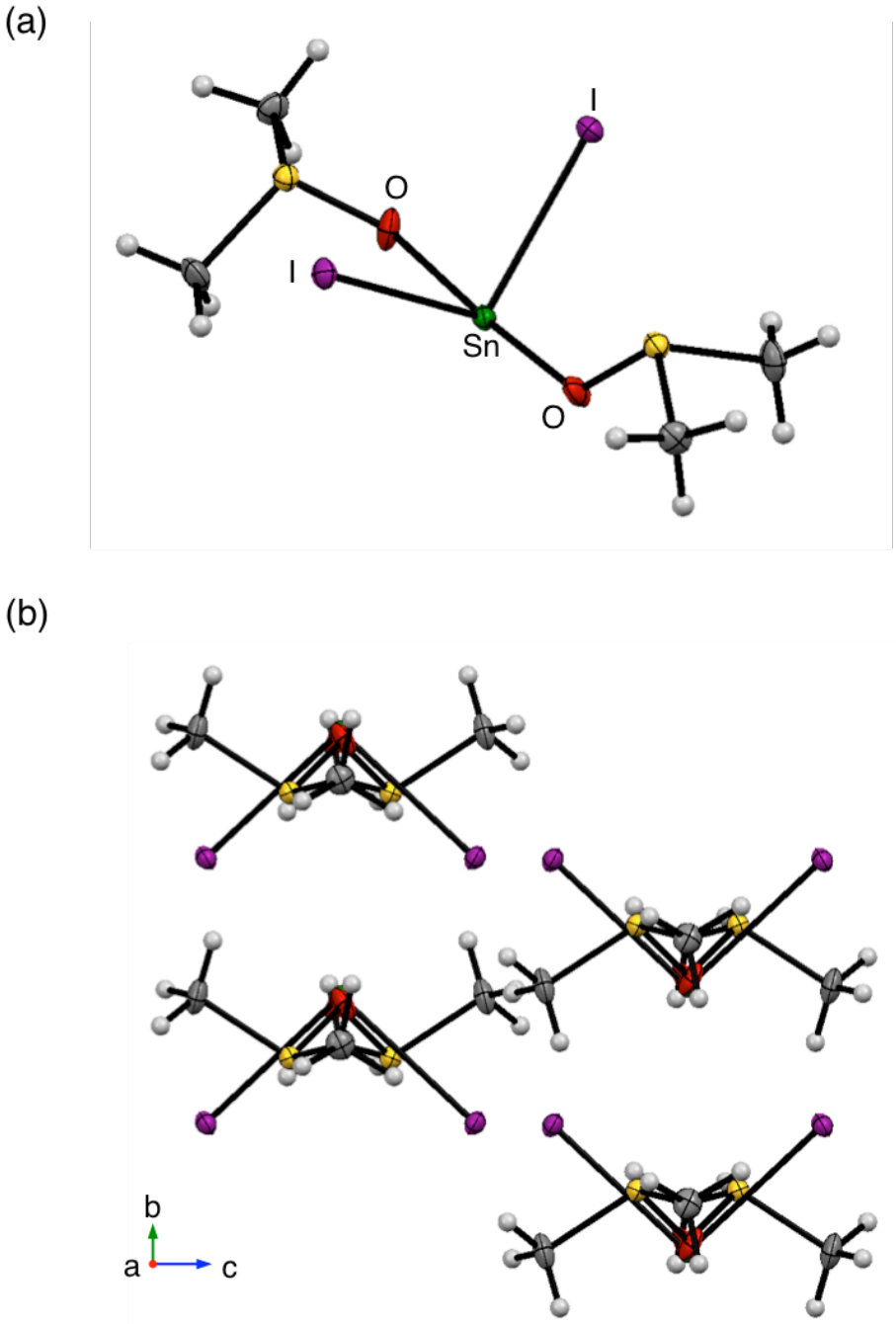

Figure S6. X-ray crystal structure of $[SnI_2(dmso)_2]$: (a) molecular structure and (b) packing structure along with *a* axis. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å): Sn–O 2.394(3); Sn–I 2.9021(4).

[$SnBr_2$(dmf)]

Single crystals of [$SnBr_2$(dmf)] suitable for X-ray diffraction analysis were obtained by diffusion of toluene into a solution of $SnBr_2$ in DMF at room temperature. Intensity data were collected at 100 K on a Bruker Single Crystal CCD X-ray Diffractometer (SMART APEX II ULTRA) with Mo Kα radiation (λ = 0.71073 Å) and graphite monochromater. A total of 4080 reflections were measured with a maximum 2θ angle of 51.0˚, of which 1555 were independent reflections (R_{int} = 0.0206). The structure was solved by direct methods (SHELXS-97[1]) and refined by the full-matrix least-squares on F^2 (SHELXL-97[1]). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $C_3H_7Br_2NOSn$; FW = 351.61, crystal size 0.14 × 0.08 × 0.05 mm, Monoclinic, $P2_1/c$, a = 4.3126(11) Å, b = 16.772(4) Å, c = 11.735(3) Å, β = 98.548(3)°, V = 839.4(4)Å^3, Z = 4, D_c = 2.782 g/cm^3. The refinement converged to R_1 = 0.0176, wR_2 = 0.0358 ($I > 2\sigma(I)$), GOF = 1.003.

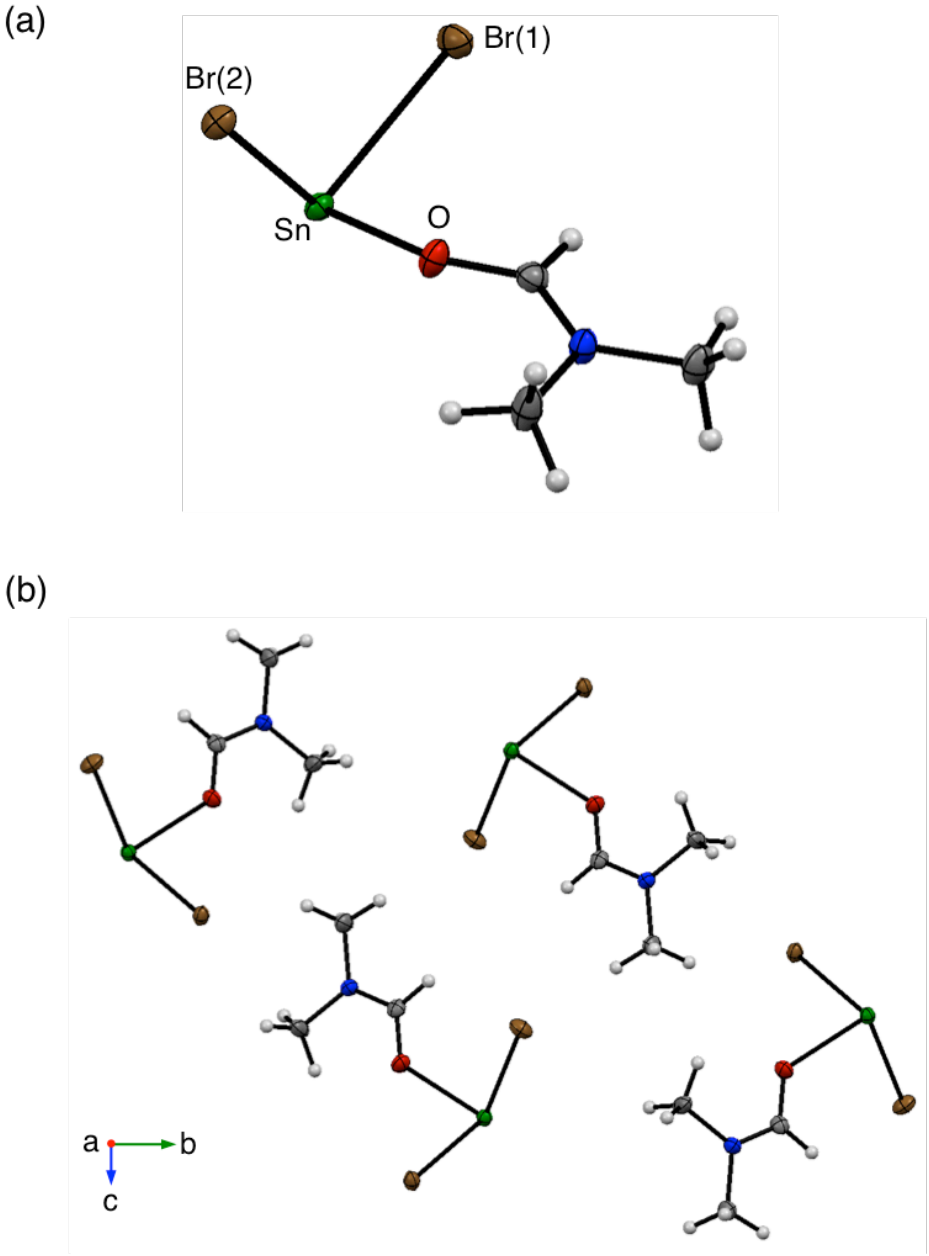

Figure S7. X-ray crystal structure of [$SnBr_2$(dmf)]: (a) molecular structure and (b) packing structure along with *a* axis. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å): Sn–O 2.196(2); Sn–Br(1) 2.7214(6); Sn–Br(2) 2.7226(5).

[$SnBr_2(dmso)_2$]

Single crystals of [$SnBr_2(dmso)_2$] suitable for X-ray diffraction analysis were obtained by diffusion of toluene into a solution of $SnBr_2$ in DMSO at room temperature. Intensity data were collected at 100 K on a Bruker Single Crystal CCD X-ray Diffractometer (SMART APEX II ULTRA) with Mo Kα radiation (λ = 0.71073 Å) and graphite monochromater. A total of 2793 reflections were measured with a maximum 2θ angle of 51.0˚, of which 898 were independent reflections (R_{int} = 0.0222). The structure was solved by direct methods (SHELXS-97[1]) and refined by the full-matrix least-squares on F^2 (SHELXL-97[1]). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $C_4H_{12}Br_2O_2S_2Sn$; FW = 434.76, crystal size 0.10 × 0.04 × 0.04 mm, Orthorhombic, *A*ba2, a = 10.666(2) Å, b = 13.535(3) Å, c = 8.1116(17) Å, V = 1171.0(4) Å^3, Z = 8, D_c = 2.466 g/cm^3. The refinement converged to R_1 = 0.0152, wR_2 = 0.0314 ($I > 2\sigma(I)$), GOF = 0.860.

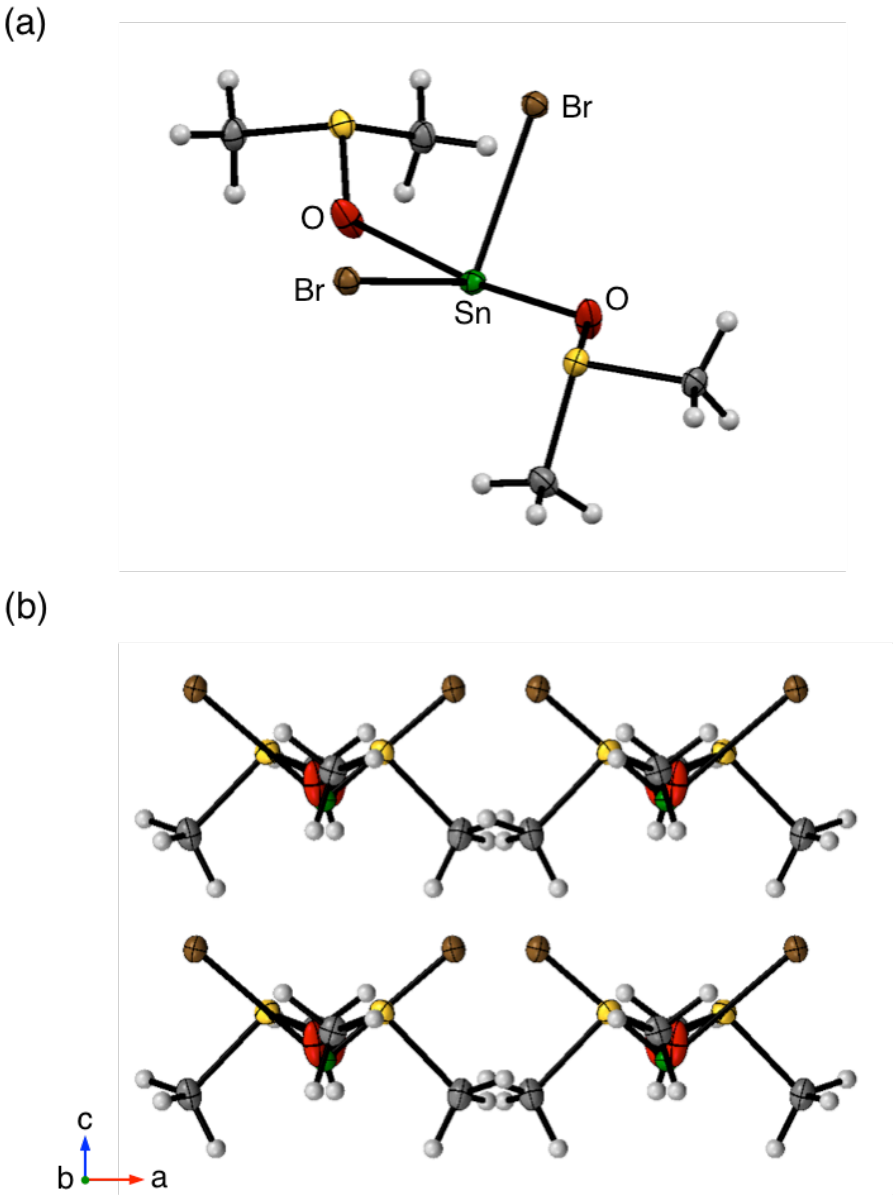

Figure S8. X-ray crystal structure of [$SnBr_2(dmso)_2$]: (a) molecular structure and (b) packing structure along with *b* axis. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å): Sn–O 2.382(2); Sn–Br 2.6553(6).

[$Sn_2F_4(dmso)_2$]

Single crystals of [$Sn_2F_4(dmso)_2$] suitable for X-ray diffraction analysis were obtained by diffusion of CH_2Cl_2 into a solution of SnF_2 in DMSO at room temperature. Intensity data were collected at 100 K on a Bruker Single Crystal CCD X-ray Diffractometer (SMART APEX II ULTRA) with Mo Kα radiation (λ = 0.71073 Å) and graphite monochromater. A total of 3235 reflections were measured with a maximum 2θ angle of 51.0˚, of which 1177 were independent reflections (R_{int} = 0.0164). The structure was solved by direct methods (SHELXS-97[1]) and refined by the full-matrix least-squares on F^2 (SHELXL-97[1]). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $C_2H_6F_2OSSn$; FW = 234.82, crystal size 0.13 × 0.11 × 0.08 mm, Triclinic, *P*-1, a = 5.7373(19) Å, b = 7.827(3) Å, c = 7.981(3) Å, α = 71.162(3)°, β = 72.939(3)°, γ = 74.821(3)°, V = 318.69(18) Å^3, Z = 2, D_c = 2.447 g/cm^3. The refinement converged to R_1 = 0.0144, wR_2 = 0.0368 ($I > 2\sigma(I)$), GOF = 1.168.

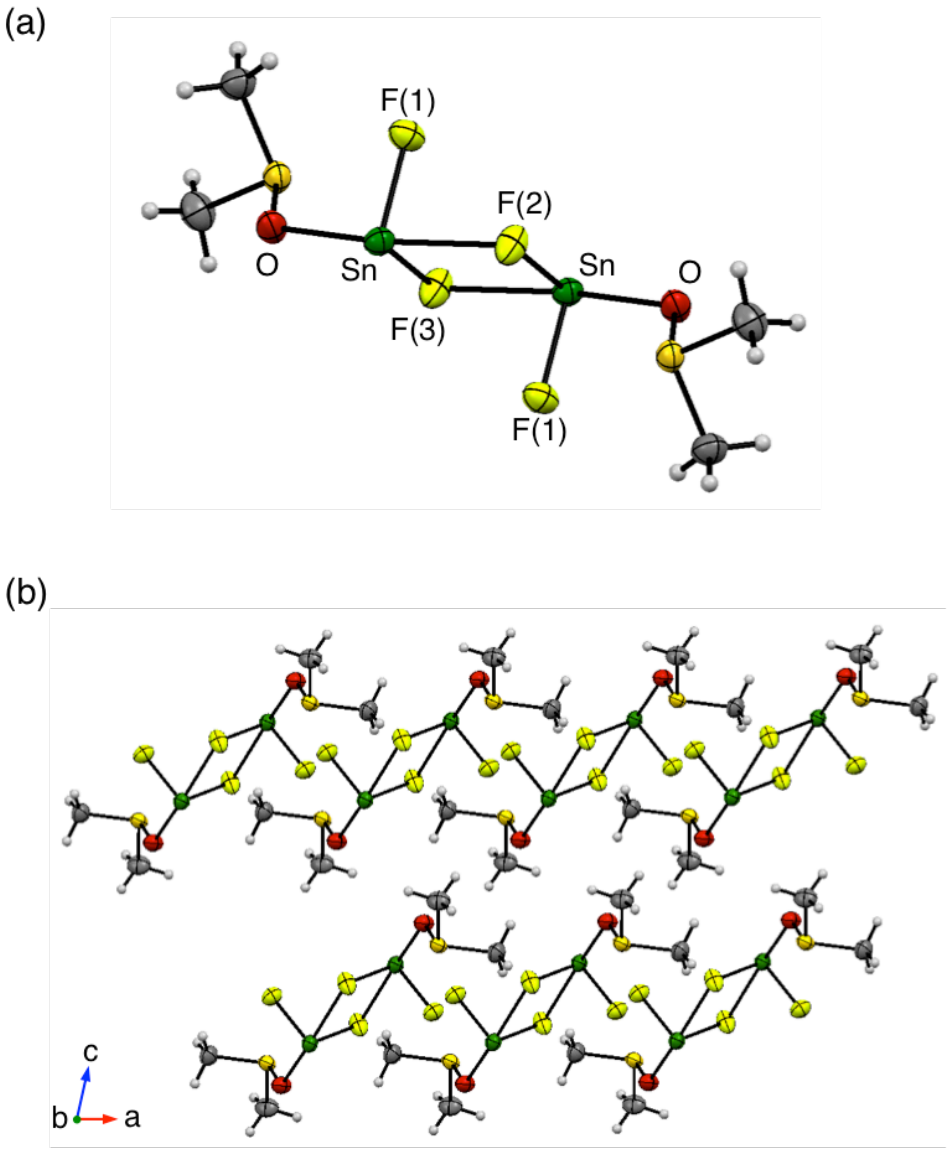

Figure S9. X-ray crystal structure of $[Sn_2F_4(dmso)_2]$: (a) molecular structure and (b) packing structure along with *b* axis. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å): Sn–O 2.3758(18); Sn–F(1) 2.0127(14); Sn–F(2) 2.2843(15); Sn–F(3) 2.1164(14).

[$SnCl_2$(dmf)]

Single crystals of [$SnCl_2$(dmf)] suitable for X-ray diffraction analysis were obtained by diffusion of toluene into a solution of $SnCl_2$ in DMF at room temperature. Intensity data were collected at 100 K on a Bruker Single Crystal CCD X-ray Diffractometer (SMART APEX II ULTRA) with Mo Kα radiation (λ = 0.71073 Å) and graphite monochromater. A total of 23252 reflections were measured with a maximum 2θ angle of 51.0˚, of which 8312 were independent reflections (R_{int} = 0.0545). The structure was solved by direct methods (SHELXS-97[1]) and refined by the full-matrix least-squares on F^2 (SHELXL-97[1]). The dimethylamino groups in one of DMF molecules were disordered, which was solved using appropriate models. Thus, two sets of dimethylamino groups, *i.e.*, (C1–N1–C2) and (C3–N1–C4) were placed and their occupancies were refined to be 0.58 and 0.42, respectively.

All non-hydrogen atoms were refined anisotropically except for C3 and C4. All hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $C_{18}H_{42}Cl_{12}N_6O_6Sn_6$; FW = 1576.12, crystal size 0.10 × 0.10 × 0.03 mm, Orthorhombic, $P2_12_12_1$, a = 22.560(16) Å, b = 35.33(2) Å, c = 5.919(4) Å, V = 4717(6) Å^3, Z = 4, D_c = 2.219 g/cm^3. The refinement converged to R_1 = 0.0343, wR_2 = 0.0622 ($I > 2\sigma(I)$), GOF = 0.990.

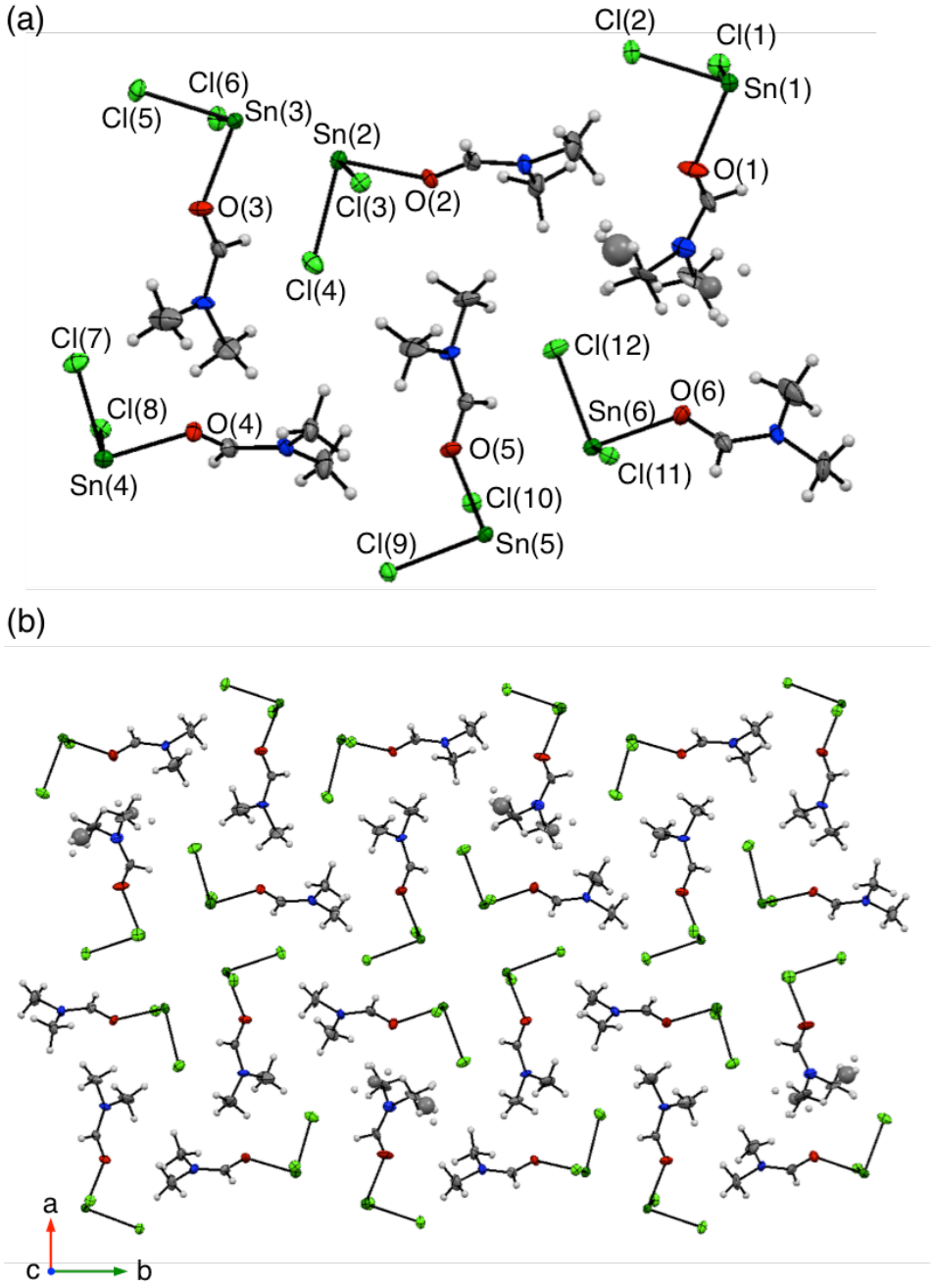

Figure S10. X-ray crystal structure of [$SnCl_2$(dmf)]: (a) molecular structure and (b) packing structure along with *c* axis. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å): Sn(1)–O(1) 2.223(5); Sn(1)–Cl(1) 2.528(3); Sn(1)–Cl(2) 2.444(2); Sn(2)–O(2) 2.218(5); Sn(2)–Cl(3) 2.524(3); Sn(2)–Cl(4) 2.492(3); Sn(3)–O(3) 2.193(5); Sn(3)–Cl(5) 2.444(2); Sn(3)–Cl(6) 2.515(3); Sn(4)–O(4) 2.197(5); Sn(4)–Cl(7) 2.462(2); Sn(4)–Cl(8) 2.511(3); Sn(5)–O(5) 2.223(5); Sn(5)–Cl(9) 2.435(2); Sn(5)–Cl(10) 2.529(3); Sn(6)–O(6) 2.221(5); Sn(6)–Cl(11) 2.524(3); Sn(6)–Cl(12) 2.470(2).

Solubility of SnI_2 Complex in DMSO

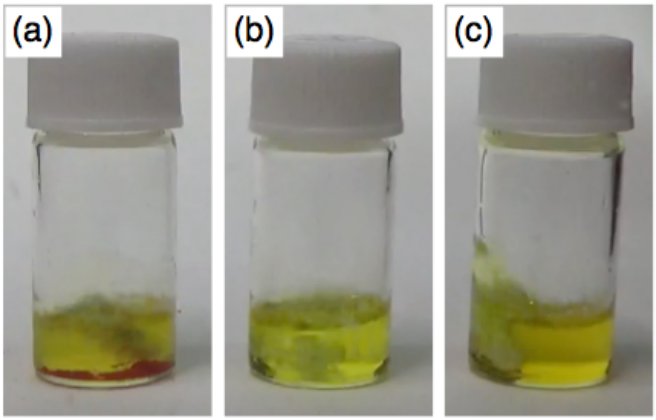

Figure S11. Photographs of 1.5 M DMSO solution of SnI_2 after stirring at 50 °C for 10 min prepared from different precursors by using (a) sublimed SnI_2, (b) [SnI_2(dmf)], or (c) [SnI_2(dmso)] as a precursor material, respectively.

Preparation of Film Sample of Sn-based Perovskite

Film Sample of $MASnI_3$

A 1.5 M solution of $MASnI_3$ was prepared using [$SnI_2(dmso)_2$] (793.2 mg, 1.5 mmol) and methylammonium iodide (MAI, 238.5 mg, 1.5 mmol) in DMSO (1 mL). The mixed powders were dissolved for 30 min at 25 ˚C, followed by filtering with a PTFE membrane filter (0.45 μm). The resulting solution (200 μL) was then spin-coated on a cleaned glass substrate at 5000 rpm for 7s. Anti-solvent dripping was performed using 450 μL toluene at 3 s before the spin-coating process stopped. The substrate was then annealed on a hotplate with the procedure of 35 ˚C for 5 min, 45 ˚C for 5 min, and 70 ˚C for 20 min. After annealing, 50 mg/mL PMMA solution in chlorobenzene (PhCl) was spin-coating on the top of $MASnI_3$ film at 1500 rpm for 45 s.

Film Sample of $FASnI_3$

A 1.5 M solution of $FASnI_3$ was prepared using [$SnI_2(dmso)_2$] (793.2 mg, 1.5 mmol) and formamidinium iodide (FAI, 258.0 mg, 1.5 mmol) (1:1 molar ratio) as starting materials. These powders were dissolved in DMF (0.75 mL): DMSO (0.25 mL) mixed solvent with a volume ratio of 3:1 for 30 min at 25 ˚C. The solution was filtered with a PTFE membrane filter (0.45 μm). A 200 μL of the solution was then spin-coated on a cleaned glass substrate at 4000 rpm for 60 s. Anti-solvent dripping was performed using 450 μL toluene at 5 s before the spin-coating process stopped. The substrate was then annealed on a hotplate with the procedure of 35 ˚C for 5 min, 45 ˚C for 5 min, and 70 ˚C for 20 min. After annealing, 50 mg/mL PMMA solution in PhCl was spin-coated on the top of $FASnI_3$ film at 1500 rpm for 45 s.

Film Sample of $FASnI_3$ with 10 mol% SnF_2

In a similar manner to $FASnI_3$ film, the powders of [$SnI_2(dmso)_2$] (793.2 mg, 1.5 mmol) and formamidinium iodide (FAI, 258.0 mg, 1.5 mmol, TCI) (1:1 molar ratio) as starting materials and SnF_2 (23.5 mg, 0.15 mmol) were dissolved in DMF (0.75 mL): DMSO (0.25 mL) mixed solvent with a volume ratio of 3:1 at 25 ˚C. After filtration with a 0.45 μm filter, a 200 μL

solution was spin-coated on a cleaned glass substrate at 4000 rpm for 60 s. Anti-solvent dripping was performed using 450 μL toluene at 5 s before the spin-coating process stopped. The substrate was then annealed on a hotplate with the procedure of 35 ˚C for 5 min, 45 ˚C for 5 min, and 70 ˚C for 20 min. After annealing, 50 mg/mL PMMA solution in PhCl was spin-coating on the top of $FASnI_3$ film at 1500 rpm for 45 s.

Preparation of Crystalline Sample of $MASnI_3$

[SnI_2(dmf)] (445 mg, 1.00 mmol) and MAI (158 mg, 1.00 mmol) were dissolved in ethanol (3 mL), and the reaction mixture was stirred at 80 °C for 30 min. The pale green solution was cooled down to give blackish green crystalline powder (355 mg, 0.667 mmol, 67%), which were collected by filtration, washed with ethanol, and dried under vacuum.

Preparation of Crystalline Sample of $FASnI_3$

In a similar manner to $MASnI_3$, from a solution of [SnI_2(dmf)] (176 mg, 0.395 mmol) and FAI (65.4 mg, 0.380 mmol) in ethanol (1.5 mL), 133 mg (0.244 mmol, 61%) of $FASnI_3$ of crystalline powder was obtained.

Optical Characterization

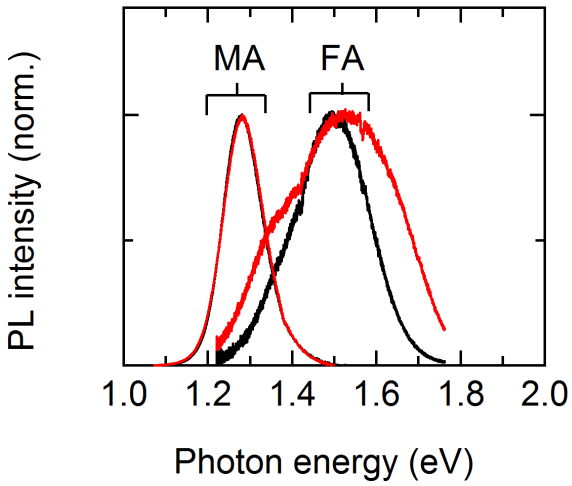

Figure S12. PL spectra of $MASnI_3$ and $FASnI_3$ fabricated without SnF_2 before (black solid line) and after (red solid line) air exposure (~15 min).

Figure S12 shows the PL spectra of $MASnI_3$ and $FASnI_3$ prepared without SnF_2 additive before (black solid line) and after (red solid line) air exposure of ~15 min. During the exposure to air atmosphere, the absorption measurements were performed under air; no change in the spectral shape was observed for the film sample of $MASnI_3$, while the spectrum for $FASnI_3$ film showed significant broadening after air exposure, indicating sample degradation by air oxidation of $FASnI_3$ film despite PMMA protection on the surface. To avoid the degradation effect on photophysical properties, the film of $FASnI_3$ with 10% SnF_2 were prepared, which is well-known for improving the sample stability.[2] XRD measurement on the film of $FASnI_3$ with 10% SnF_2 confirmed identical XRD pattern to that of the film of for $FASnI_3$.

XRD Patterns of $FASnI_3$ with 0-20 mol% SnF_2

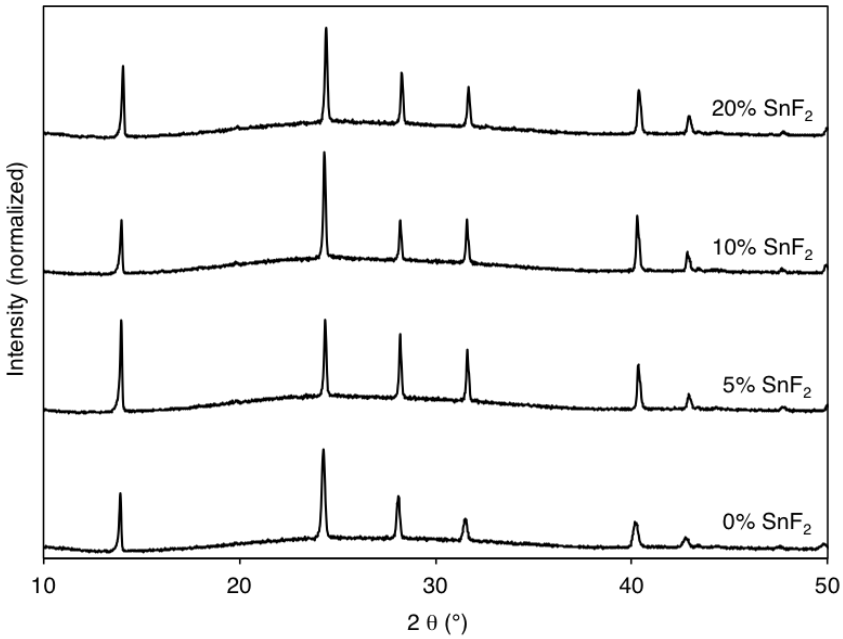

Figure S13. XRD patterns of the film for $FASnI_3$ with 0, 5, 10, and 20 mol% SnF_2.

Thermogravimetric Analysis

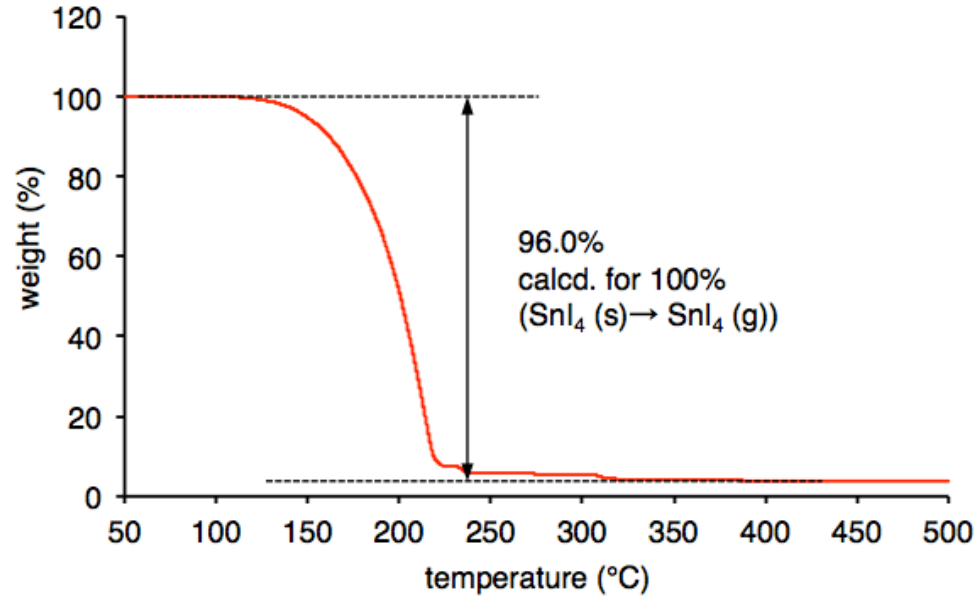

Figure S14. Thermogravimetric analysis of sublimed SnI_4 heating at 5 °C/min under N_2.

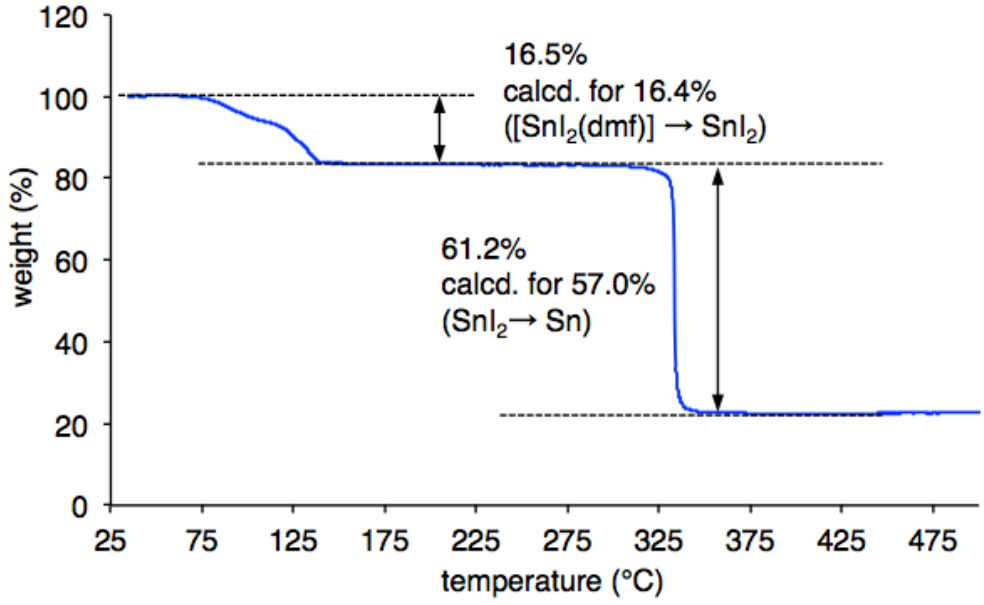

Figure S15. Thermogravimetric analysis of $[SnI_2(dmf)]$ heating at 5 °C/min under N_2.

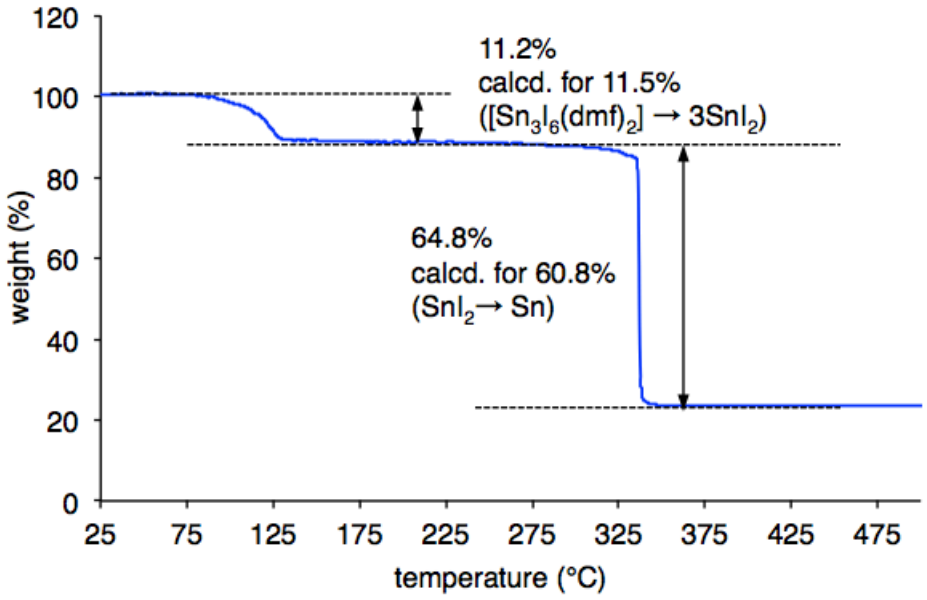

Figure S16. Thermogravimetric analysis of $[Sn_3I_6(dmf)_2]$ heating at 5 °C/min under N_2.

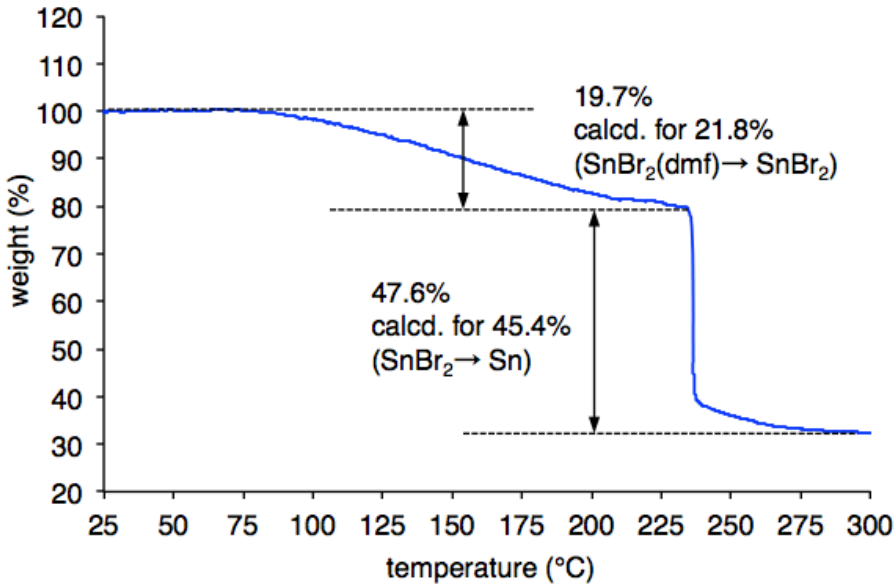

Figure S17. Thermogravimetric analysis of $[SnBr_2(dmf)]$ heating at 5 °C/min under N_2.

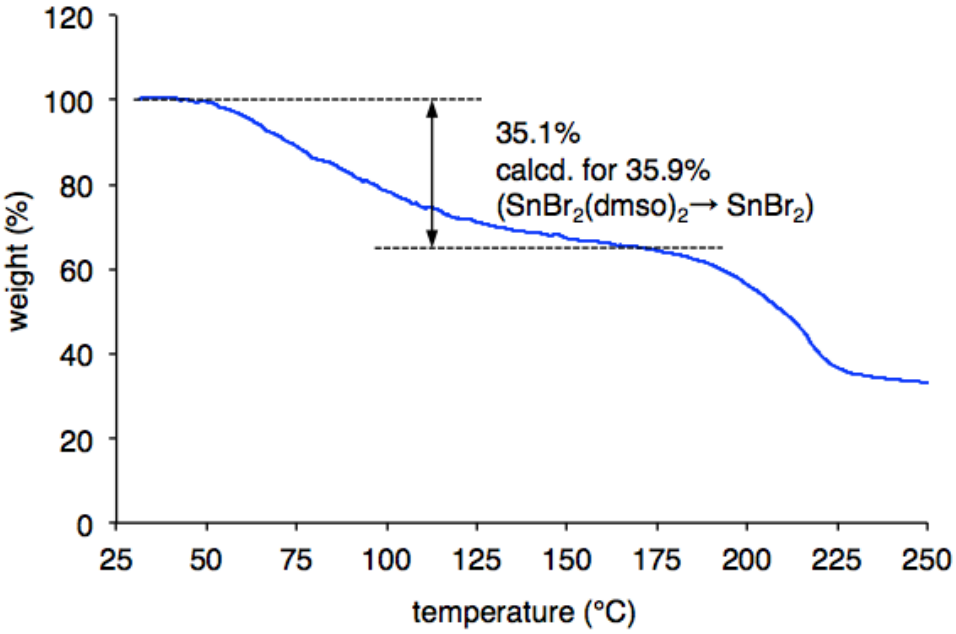

Figure S18. Thermogravimetric analysis of $[SnBr_2(dmso)_2]$ heating at 5 °C/min under N_2.

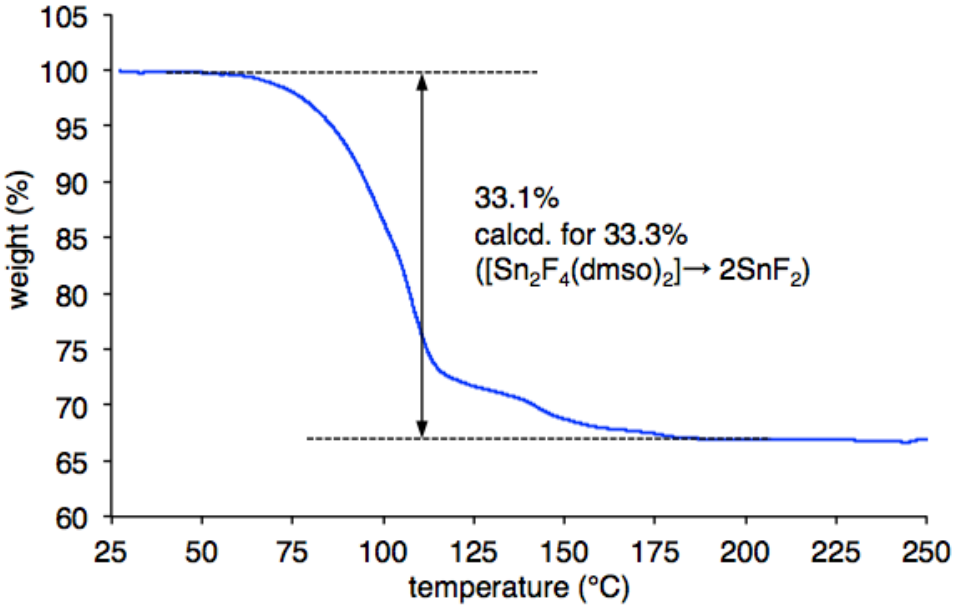

Figure S19. Thermogravimetric analysis of $[Sn_2F_4(dmso)_2]$ heating at 5 °C/min under N_2.

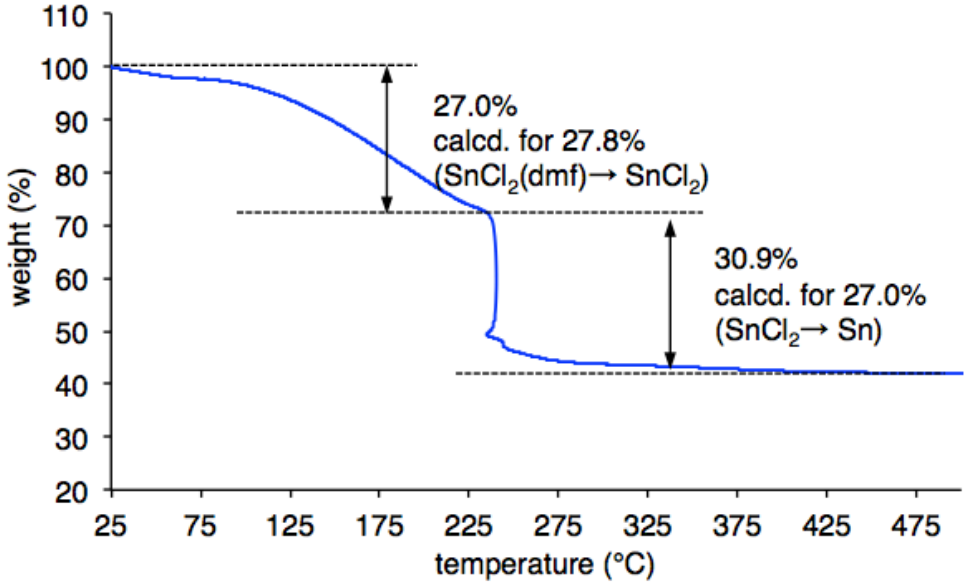

Figure S20. Thermogravimetric analysis of [$SnCl_2$(dmf)] heating at 5 °C/min under N_2.

^{119}Sn MAS NMR Spectra

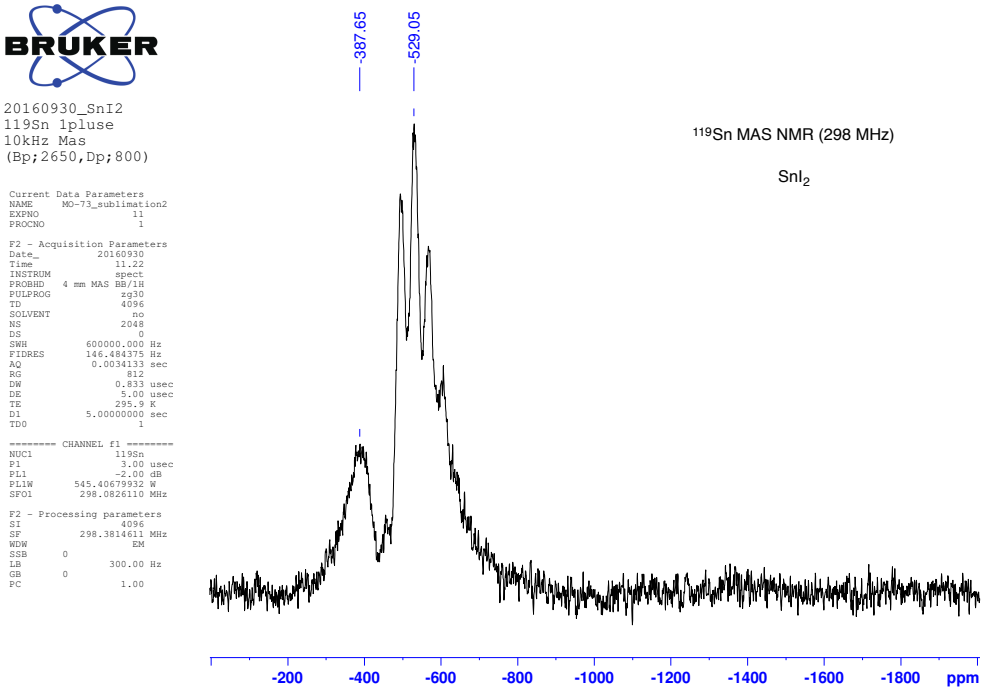

Figure S21. ^{119}Sn MAS NMR spectrum (298 MHz) of sublimed SnI_2.

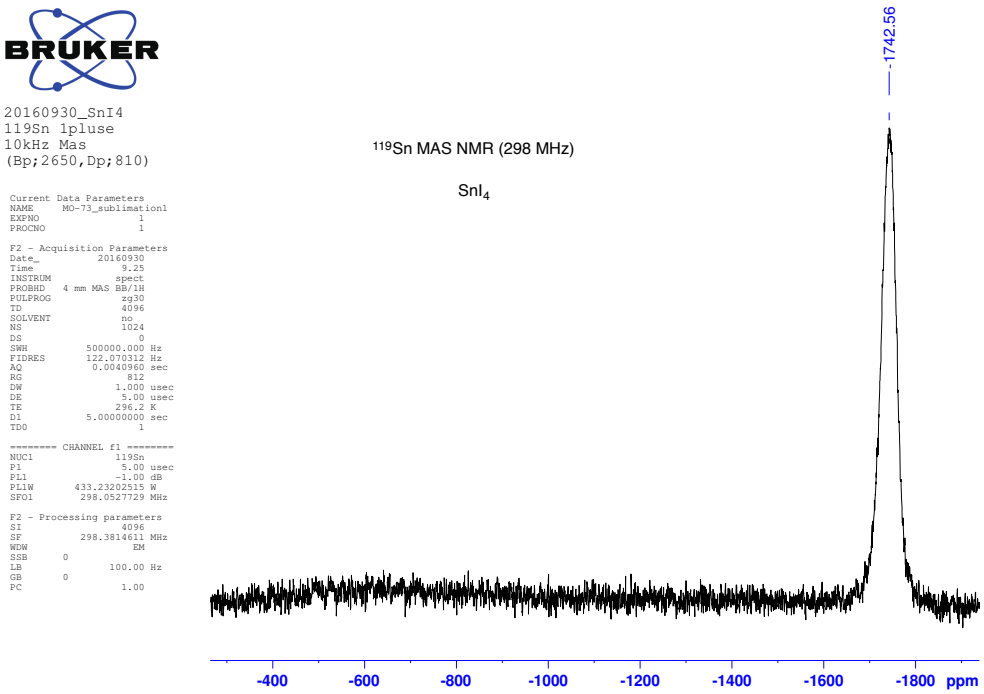

Figure S22. ^{119}Sn MAS NMR spectrum (298 MHz) of sublimed SnI_4.

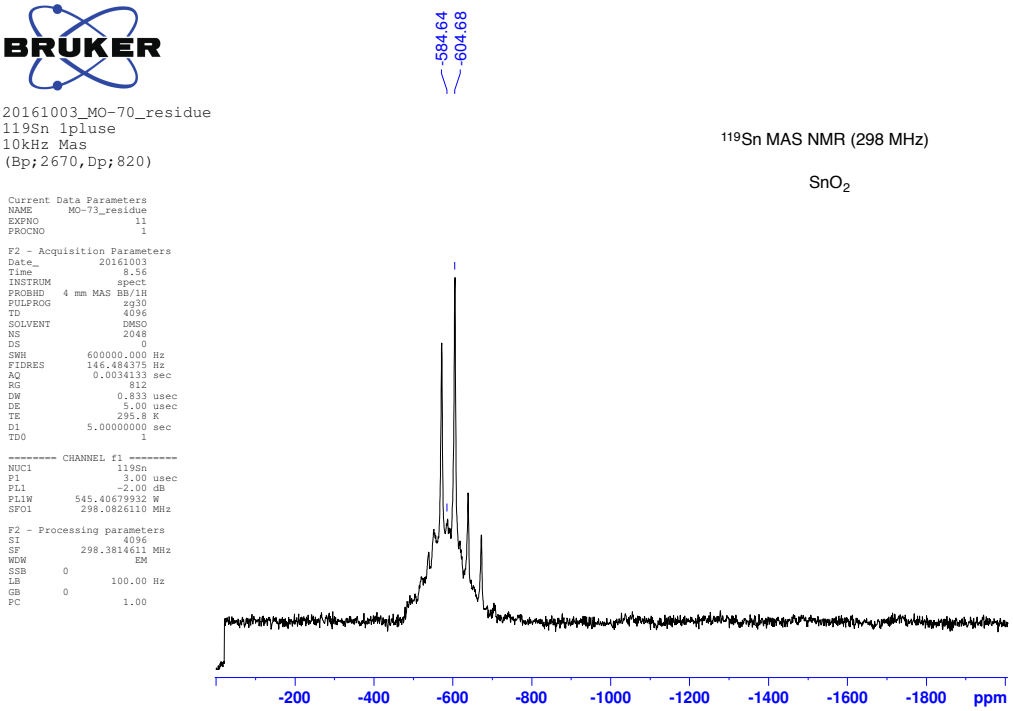

Figure S23. ^{119}Sn MAS NMR spectrum (298 MHz) of residual dark brown solids in sublimation of commercially available sample of SnI_2 (SnO_2).

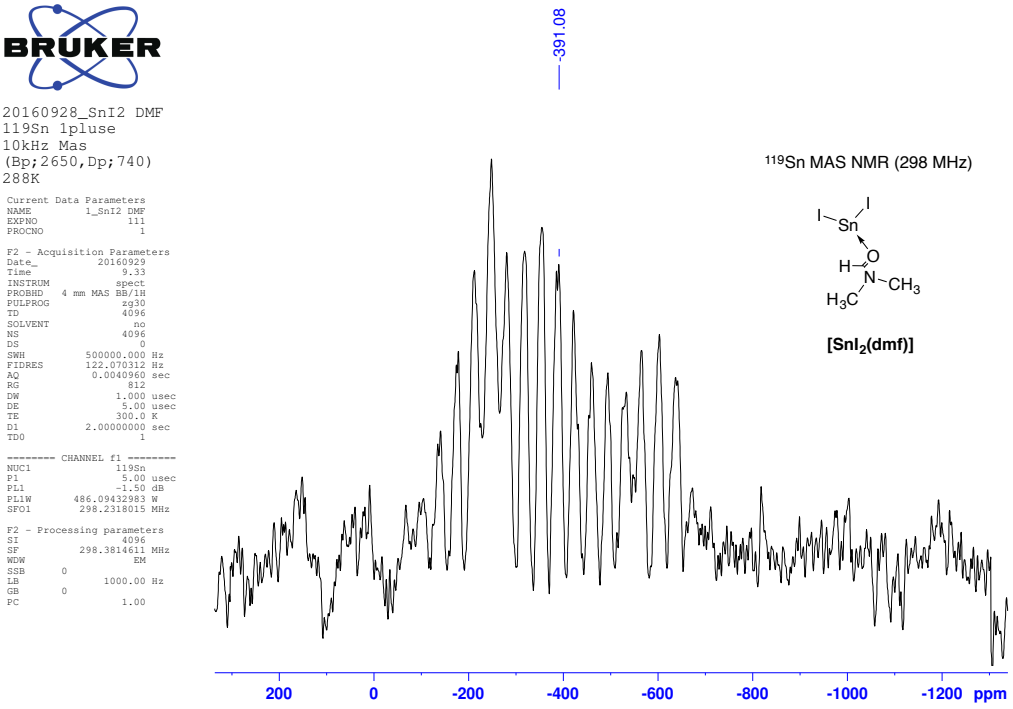

Figure S24. ^{119}Sn MAS NMR spectrum (298 MHz) of [SnI_2(dmf)].

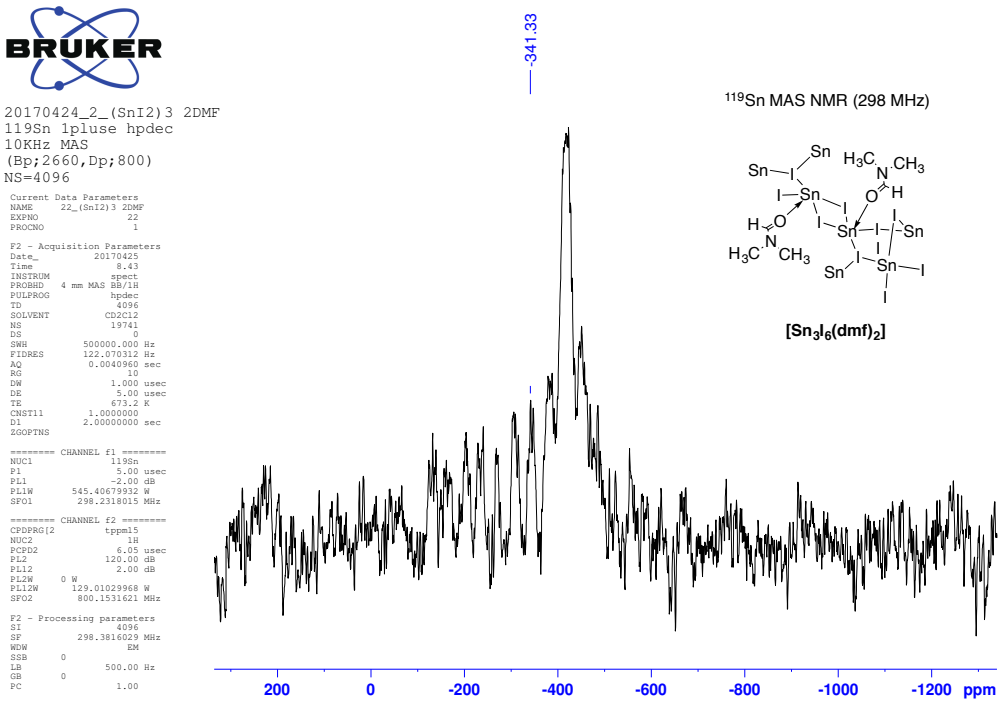

Figure S25. ^{119}Sn MAS NMR spectrum (298 MHz) of $[Sn_3I_6(dmf)_2]$.

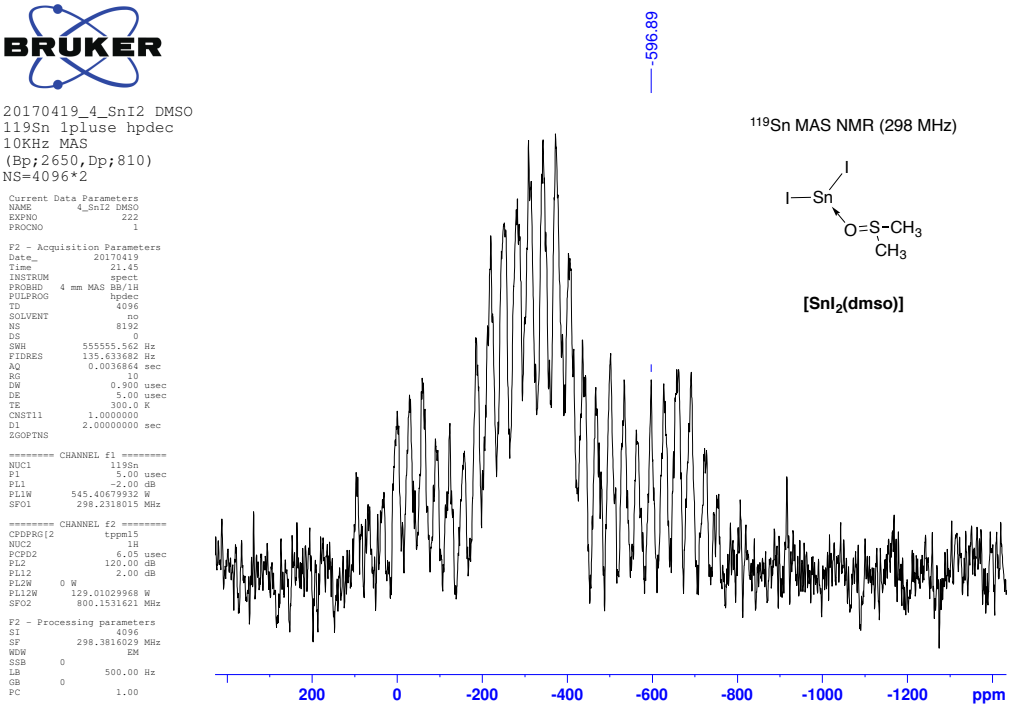

Figure S26. ^{119}Sn MAS NMR spectrum (298 MHz) of $[SnI_2(dmso)]$.

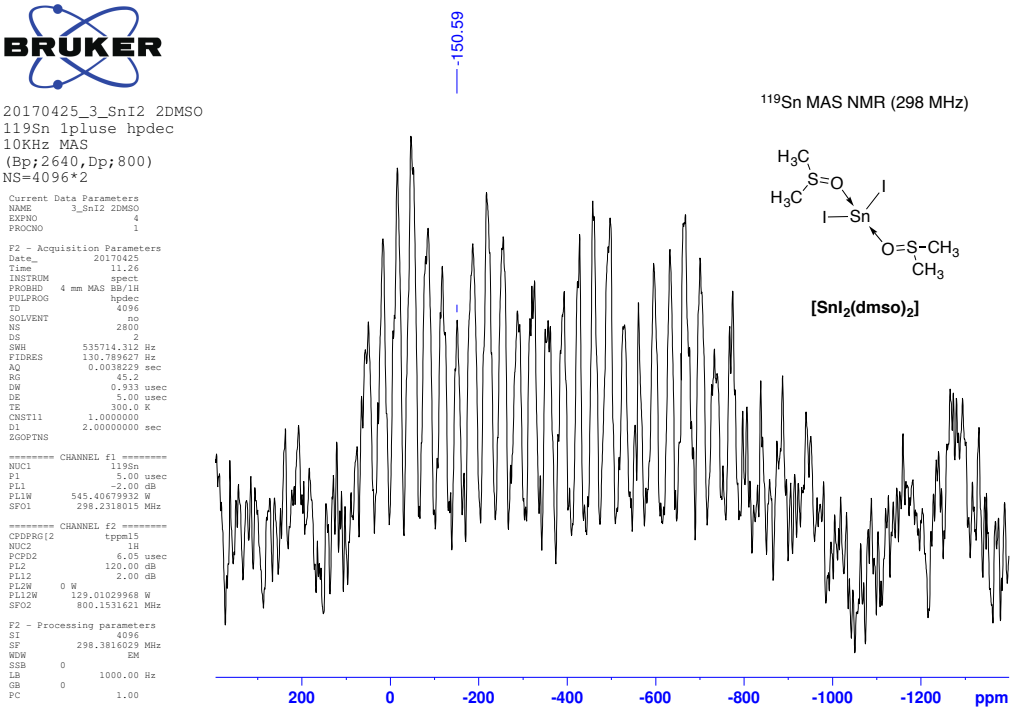

Figure S27. ^{119}Sn MAS NMR spectrum (298 MHz) of $[SnI_2(dmso)_2]$.

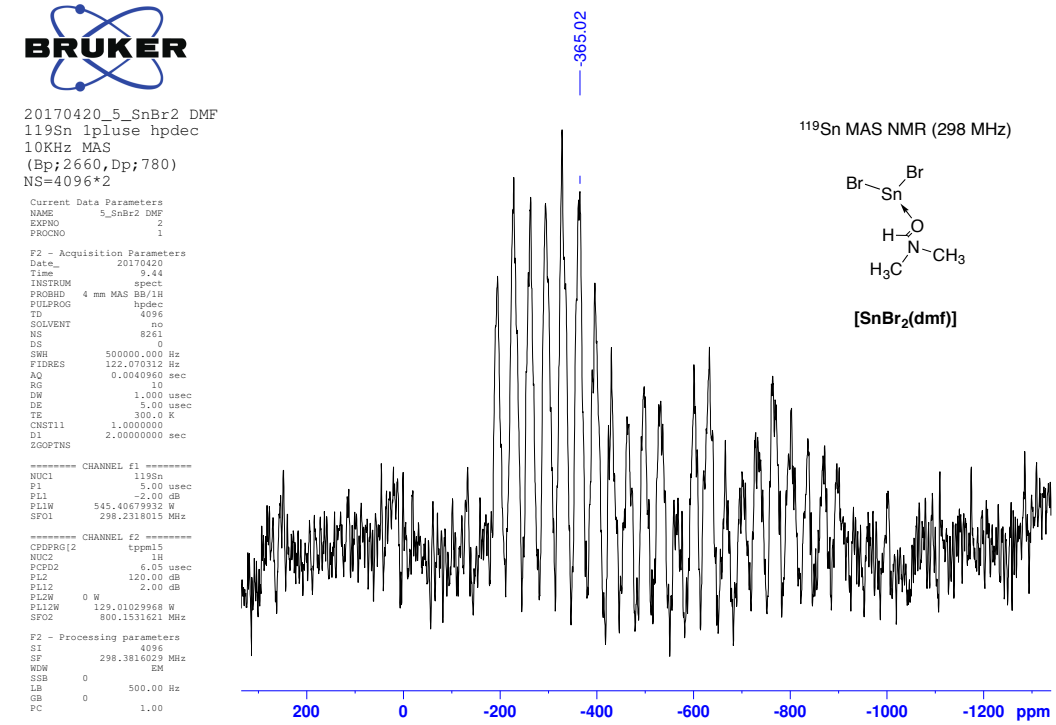

Figure S28. ^{119}Sn MAS NMR spectrum (298 MHz) of $[SnBr_2(dmf)]$.

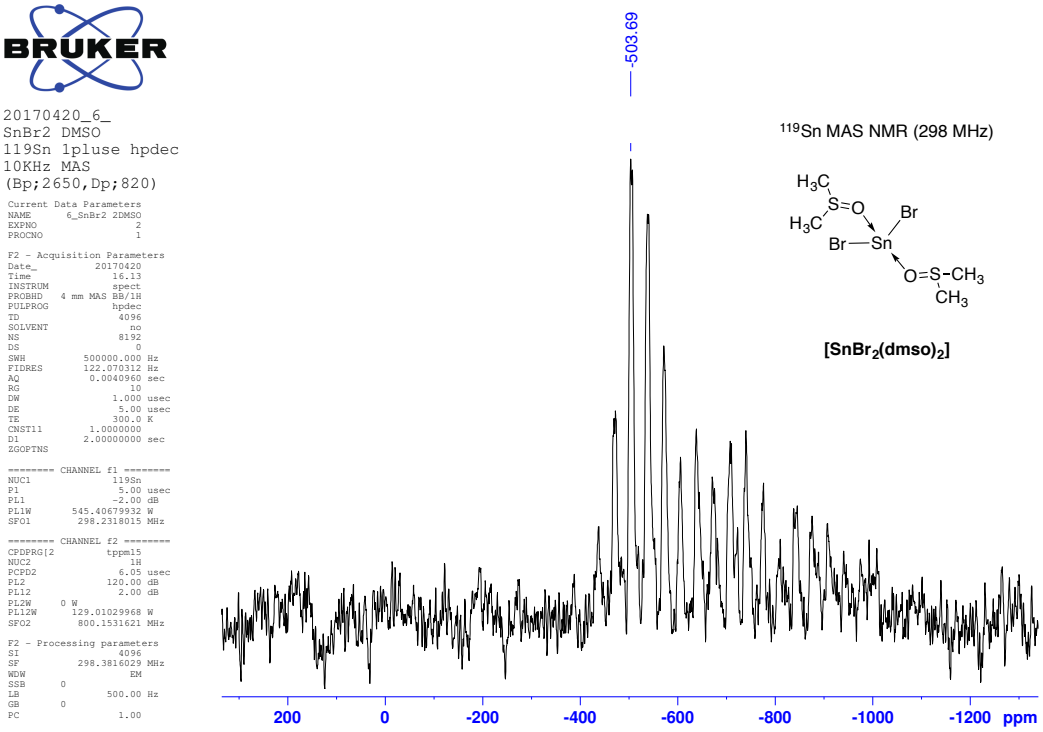

Figure S29. ^{119}Sn MAS NMR spectrum (298 MHz) of $[SnBr_2(dmso)_2]$.

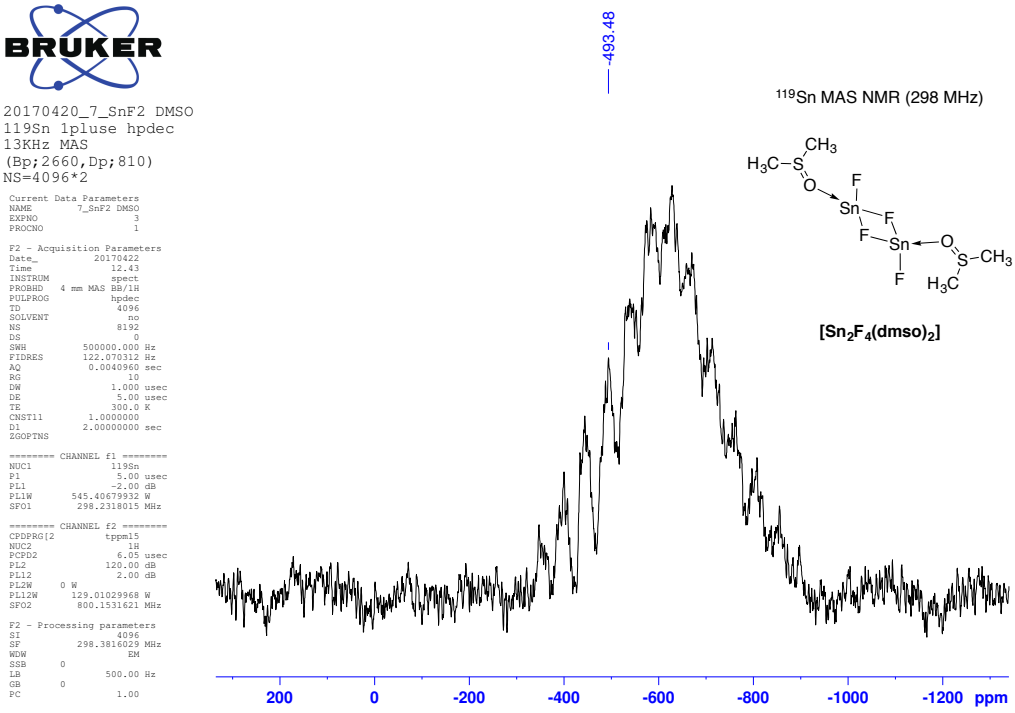

Figure S30. ^{119}Sn MAS NMR spectrum (298 MHz) of $[Sn_2F_4(dmso)_2]$.

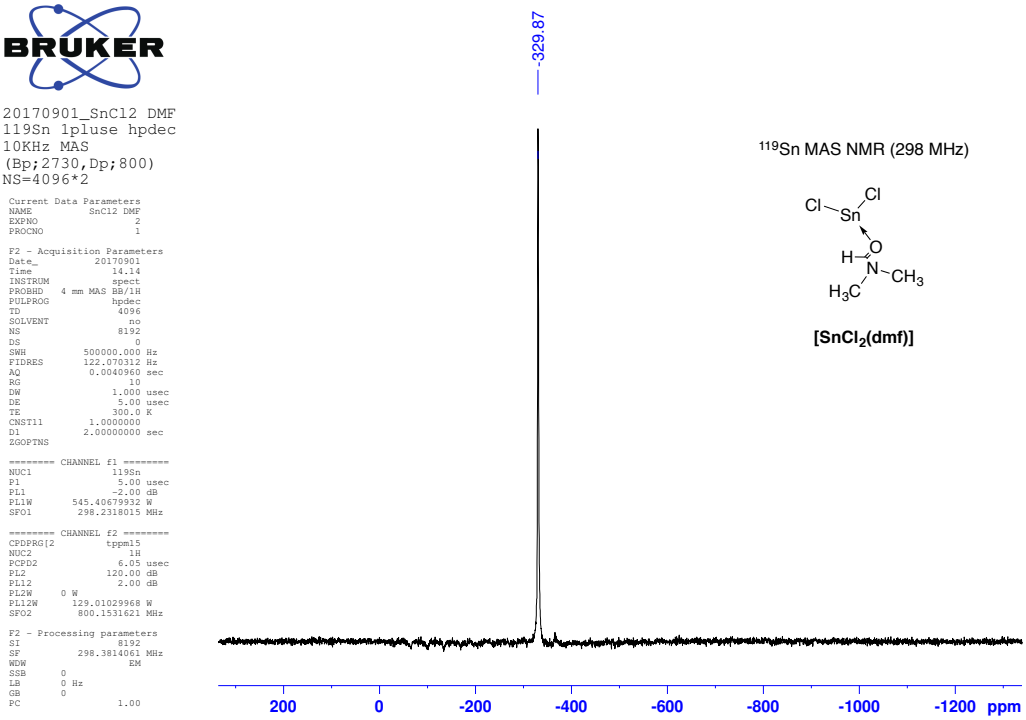

Figure S31. ^{119}Sn MAS NMR spectrum (298 MHz) of [$SnCl_2$(dmf)].

References

1. Sheldrick, G. M. SHELX-97, Program for the Refinement of Crystal Structures; University of Göttingen: Göttingen, Germany, 1997.

2. a) Chung, I.; Lee, B.; He, J.; Chang, R. P. H.; Kanatzidis, M. G. *Nature* **2012**, *485*, 486–489. b) Kumar, M. H.; Dharani, S.; Leong, W. L.; Boix, P. P.; Prabhakar, R. R.; Baikie, T.; Shi, C.; Ding, H.; Ramesh, R.; Asta, M.; Grätzel, M.; Mhaisalkar, S. G.; Mathews, N. *Adv. Mater.* **2014**, *26*, 7122–7127. c) Kontos, A. G.; Kaltzoglou, A.; Siranidi, E.; Palles, D.; Angeli, G. K.; Arfanis, M. K.; Psycharis, V.; Raptis, Y. S.; Kamitsos, E. I.; Trikalitis, P. N.; Stoumpos, C. C.; Kanatzidis, M. G.; Falaras, P. *Inorg. Chem.* **2017**. *56*, 84–91.