Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

{[$Ir_3(cod)_3(\mu_3\text{-}S)_2$]($\mu_3$-S)SnCl}$_2$ – a Ternary Ir-Sn-S cluster with the Iridium Atoms in Three Different Chemical Environments

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1 Synthesis details

1.1 General

All manipulations and reactions were performed under dry Ar atmosphere using standard Schlenk or glovebox techniques. All solvents (ethanol, chloroform, dichloromethane, acetone and toluene) were dried, freshly distilled and stored under Ar prior to use.

1.2 Synthesis of (E/Z)-6-(1-hydrazonoethyl)-2.2'-bipyridine (1)

20 mg ($1\cdot10^{-4}$ mol) of 6-acetyl-bipyridine were dissolved in 20 mL ethanol; 1 mL of hydrazinehydrate (80% in water) was added and the mixture was heated to reflux for 3 hours and stirred additional 12 hours at room temperature. Then, the solution was extracted with chloroform until the organic phase remained colorless. The organic phases were combined, dried over $MgSO_4$, filtered and the solvent was removed *in vacuo*. **1** appeared as yellow solid in 71% yield (15.2 mg).

^{1}H-NMR: 300.1 MHz, $CDCl_3$, δ = 8.74–8.63 (m, 1H); 8.55 (d, 1H, $^2J_{HH}$ = 7.98 Hz); 8.51 (d, 1H, $^2J_{HH}$ = 7.92 Hz); 8.47 (dd, 1H, $^2J_{HH}$ = 7.82 Hz, $^3J_{HH}$ = 0.95 Hz); 8.31 (dd, 1H, $^2J_{HH}$ = 7.74 Hz, $^3J_{HH}$ = 0.86 Hz); 8.30 (dd, 1H, $^2J_{HH}$ = 7.86 Hz, $^3J_{HH}$ = 7.86 Hz); 7.98 (dd, 1H, $^2J_{HH}$ = 7.98 Hz, $^3J_{HH}$ = 0.89 Hz); 7.89–7.78 (m, 1H); 7.77 (dd, 1H, $^2J_{HH}$ = 7.83 Hz, $^3J_{HH}$ = 7.83 Hz); 7.36–7.27 (m, 1H); 5.57 (s, 2H, NH_2); 2.50 (s, 3H, CH_3); 2.38 (s, 3H, CH_3) ppm. The molecule undergoes E/Z-isomerization in solution, shown by the NMR spectrum. ESI($^+$)-HRMS (m/z): calculated 213.1135 $[M+H]^+$, found 213.1130.

1.3 Synthesis of $[(R^{bipy}Sn)_4Sn_2S_{10}]$ (2. R^{bipy}: $CMe_2CH_2C(Me){=}N{-}N{=}C(Me)(C_5H_3N{-}C_5H_4N)$)

30 mg (1 eq, $2.9\cdot10^{-5}$ mol) of $[(R^1Sn)_4S_6]$ (**A**; $R^1 = Me_2CH_2COMe$) and 27 mg (4.4 eq, $1.3\cdot10^{-4}$ mol) of **1** were evacuated. 8 mL of dichloromethane were added under argon atmosphere. The reaction solution was stirred for three days, filtered and layered with 8 mL of acetone. After two weeks a colorless single crystals of **2** were obtained in 35% yield. The poor solubility of **2** only allowed for ESI mass spectrometry.

ESI($^+$)-HRMS (m/z): $[(C_{18}H_{22}N_4Sn)_2SnS_5+H]^+$ (ca. 40%) calculated 1102.9275, found 1102.9277;
$[(C_{18}H_{22}N_4Sn)_2SnS_5+Na]^+$ (ca. 37%) calculated 1125.9104, found 1125.9089;
$\{[(C_{18}H_{22}N_4Sn)_4Sn_2S_{10}+2Na]^{2+}\}_{0.5}$ (ca. 38%) calculated 1125.9100, found 1125.9089;
$[(C_{18}H_{22}N_4Sn)_3S_4]^+$ (ca. 15%) calculated 1363.1248, found 1363.1233.

1.4 Synthesis of $\{[Ir_3(cod)_3(\mu_3\text{-}S)_2](\mu_3\text{-}S)SnCl\}_2$ (3) · 2 CH_2Cl_2

27 mg (4.4 eq, $1.3\cdot10^{-4}$ mol) of **1** and 30 mg (1 eq, $2.9\cdot10^{-5}$ mol) of **A** were evacuated for 30 min and then dissolved in 6 mL dichloromethane under argon atmosphere. The solution was stirred for 20 h. 42 mg (2.2 eq, $6.3\cdot10^{-5}$ mol) of bis(1,5-cyclooctadien)diiridium(I)-dichlorid were evacuated and afterwards dissolved in 5 mL of dichloromethane, resulting in a yellowish orange solution. Both solutions were

mixed, resulting in a dark brown solution that turned into a suspension later on. The reaction solution was stirred for 16 h at room temperature, then filtered and layered with 11 mL of toluene. Within two month very thin, brown, rhombic crystal plates of **3** formed at the wall of the Schlenk tube. Using the same reaction procedure, but omitting the addition of **1**, compound **3** is formed in lower yield and even poorer crystal quality. Resulting crystals are essentially insoluble in all common solvents, hence inhibiting successful analyses from solution. The crystals start to decompose at 132°C.

2 Details of the X-ray diffraction measurement, structure solution and refinement

2.1 General

Single crystal X-ray diffraction experiments for **2** and **3** were performed using a STOE IPDS 2T diffractometer at 100 K with $Mo_{K\alpha}$ radiation and graphite monochromatization ($\lambda = 0.71073$ nm). For details see Table S1. Structure solutions were realized by direct methods, refinements with full-matrix-least-squares against F^2 using SHELXS-97 and SHELXL-2013 software.[1] CCDC 1446774 (**2**) and 1446775 (**3**) contain the supplementary crystallographic data for compounds **2** and **3** in this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. X-ray measurement and structure solution of **2** and **3**.

Compound	**2**	**3**
Empirical formula	$C_{72}H_{84}N_{16}S_{10}Sn_6$	$C_{50}H_{76}Cl_6Ir_6S_6Sn_2$
Formula weight /g·mol^{-1}	2206.29	2472.74
Crystal color, shape	colorless needles	brown rhombic plate
Crystal system	monoclinic	triclinic
Space group	$P\,2_1/c$	$P{-}1$
a /Å	10.8761(2)	10.130(4)
b /Å	38.3489(7)	10.979(4)
c /Å	10.6185(2)	13.757(4)
α /°	90.00	108.21(2)
β /°	94.920(2)	89.91(3)
γ /°	90.00	90.31(3)
V /Å^3	4412.51(14)	1453.3(9)
Z	2	1
ρ_{calc} /g·cm^{-3}	1.661	2.825
$\mu(Mo_{K\alpha})$ /mm^{-1}	1.957	15.049
measurement temperature /K	100	100
2Θ range /°	4.928 – 53.560	3.91 – 47.05
Reflections measured	42486	6149
Independent reflections	18229	6134
R(int)	0.043	0.117
Ind. reflections ($I > 2\sigma(I)$)	7448	1928
Parameters	477	274
Restraints	0	54
R_1 ($I > 2\sigma(I)$)	0.0377	0.0581
wR_2 (all data)	0.0917	0.1427
GooF (all data)	0.967	0.739
Max. peak/hole /e$^-$·Å^{-3}	0.82/−1.15	2.28/−1.51
Absorption correction type[4]	gaussian	gaussian
Min. /Max. transmission	0.443/0.786	0.428/0.782
CCDC number	1446774	1446775

2.2 Details of the structure refinement of compound 2

Sn, S, C and N atoms of the Sn-S complex were refined using anisotropic displacement parameters. H atoms of were calculated using the AFIX 137 (methyl group), AFIX 23 (methylene group) and AFIX 43 (aromatic) command. The highest peak and deepest hole of the final difference Fourier map (0.82 e^{-}·Å^{-3} / –1.15 e^{-}·Å^{-3}) were located at 1.28 Å apart from Sn2 and at 0.87 Å apart from Sn1, respectively. Figure S1 shows the molecular arrangement in the crystal of compound **2**. Table S2 summarizes bond length and angles.

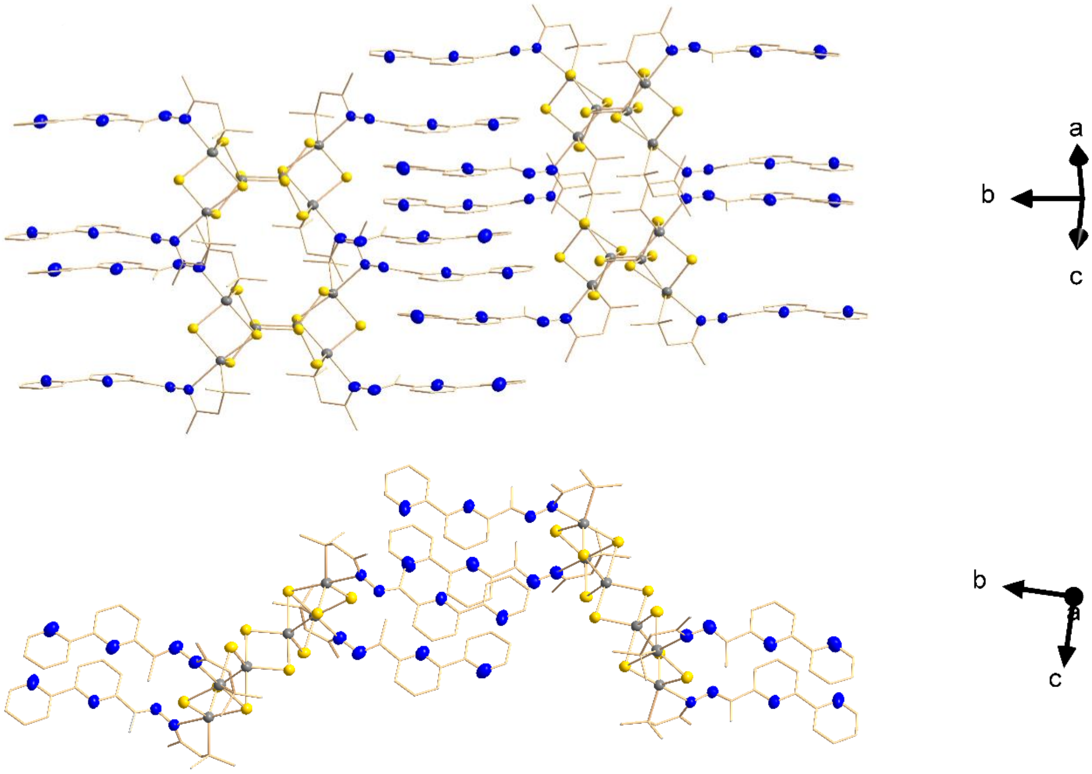


Figure S1. Two different views of the molecular arrangement in **2** (thermal ellipsoids drawn at 50% probability). Color code: Sn, grey, S, yellow, N blue; organic groups shown as wires.

Table S2. Bond length and angles in **2**.

bond or angle	Å or °
Sn−S (Sn$_3$S$_4$ unit)	2.3974(10)-2.4295(11)
Sn3−S5/5’	2.3771(11), 2.4968(10)
Sn3−S4	2.7800(10)
Sn1/2−S4	2.5036(11), 2.5309(10)
Sn1/2−C1/19	2.181(4), 2.174(4)
Sn1/2−N1/5	2.499(3), 2.406(4)
S−Sn−S (cis at Sn3)	85.01(3)-125.29(4)
S2−Sn3−S5’	176.55(3)
S−Sn−S (SnS$_3$C…N)	91.75(3)-113.15(4)
S−Sn−C	101.98(13)-125.49(13)
S−Sn…N$_{cis}$	82.39(8)-94.39(8)
S4−Sn1…N1, S4−Sn2…N5	172.29(9), 177.32(9)
C1−Sn1…N1, C19−Sn2…N5	72.68(14), 75.35(16)

2.3 Details of the structure refinement of compound 3

Ir, Sn, S, Cl and C atoms of the quaternary complex as well as of the solvent molecules were refined using anisotropic displacement parameters. H atoms of CH groups in 1,5-cyclooctadiene were calculated using the AFIX 13 command, H atoms of CH_2 groups in 1,5-cyclooctadiene and dichloromethane were calculated using the AFIX 23 command. The highest peak and deepest hole of the final difference Fourier map ($2.28\ e^{-}\cdot Å^{-3}$ / $-1.51\ e^{-}\cdot Å^{-3}$) were located at 1.13 Å apart from Ir3 and at 1.21 Å apart from S2, respectively. Figure S2 shows a fragment of the crystal structure of compound **3**.

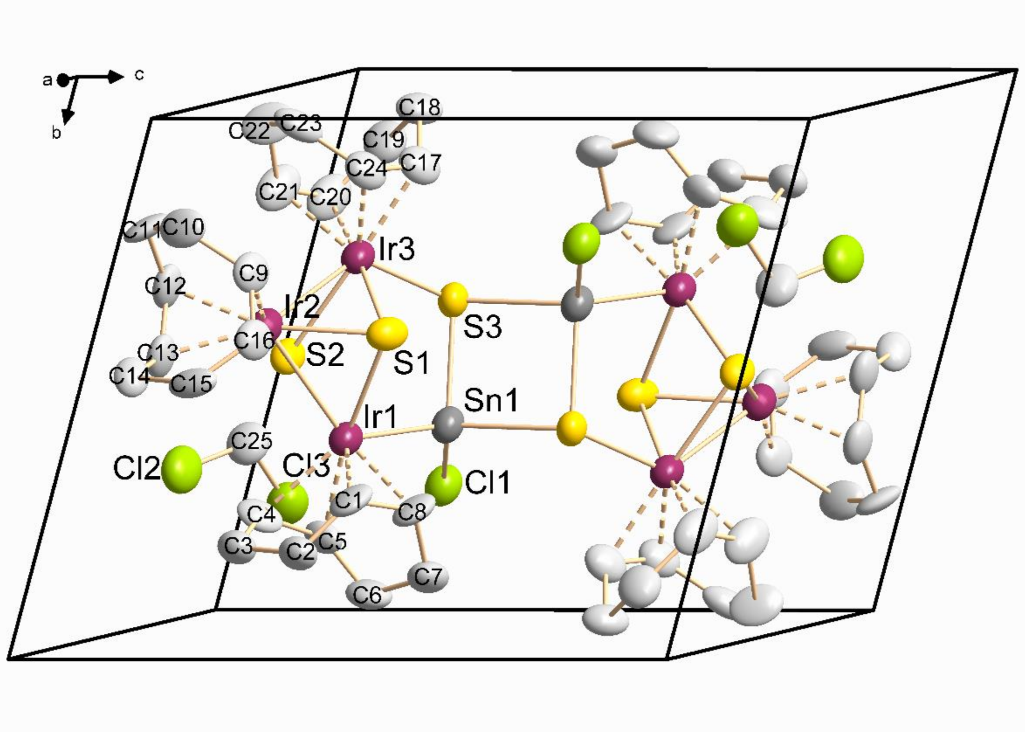


Figure S2. Representation of the unit cell content in **3** with atomic labeling scheme (thermal ellipsoids drawn at 50% probability).

3 Energy dispersive X-ray (EDX) spectroscopy and micro X-ray fluorescence analyses (µ-RFA)

Elemental analysis on **2** was performed using the EDX device Voyager 4.0 of Noran Instruments coupled with the electron microscope CamScan CS 4DV. Data acquisition was performed with an acceleration voltage of 20 kV and 100 s accumulation time. For the analyses, multiple single crystals were used and the data recorded both: various times on one single crystal and various times on other single crystals. S/Sn ratio: 10/6 (calculated), 10.00/5.45 (found).

Elemental analysis on **3** was performed using an M4-Tornado of Bruker with a rhodium target X-ray tube. Data acquisition was performed with 100 s accumulation time. The radiation emitted by the atoms was analyzed: Ir-L, Sn-L, S-K, Cl-K (Figure S4, Table S3).

Table S3. µ-RFA analysis of **3** (Ir-L, Sn-L, S-K, Cl-K); data are given with respect to the Cl content.

Element	Netto	Unn. C [wt %]	Norm. C [wt %]	Atom C [at %] (calc)	Sum formular (calc)	wt % Err. (1-sigma)
Ir –L	1388028	13.04	68.73	37.00 (37.5)	5.63 (6)	0.03
Sn-L	33843	2.94	15.51	13.52 (12.5)	2.06 (2)	0.00
S-K	32717	2.14	11.26	36.34 (37.5)	5.53 (5)	0.00
Cl-K	10439	4.50	4.50	13.14 (12.5)	2.00 (2)	0.00
Total					15.22 (16)	

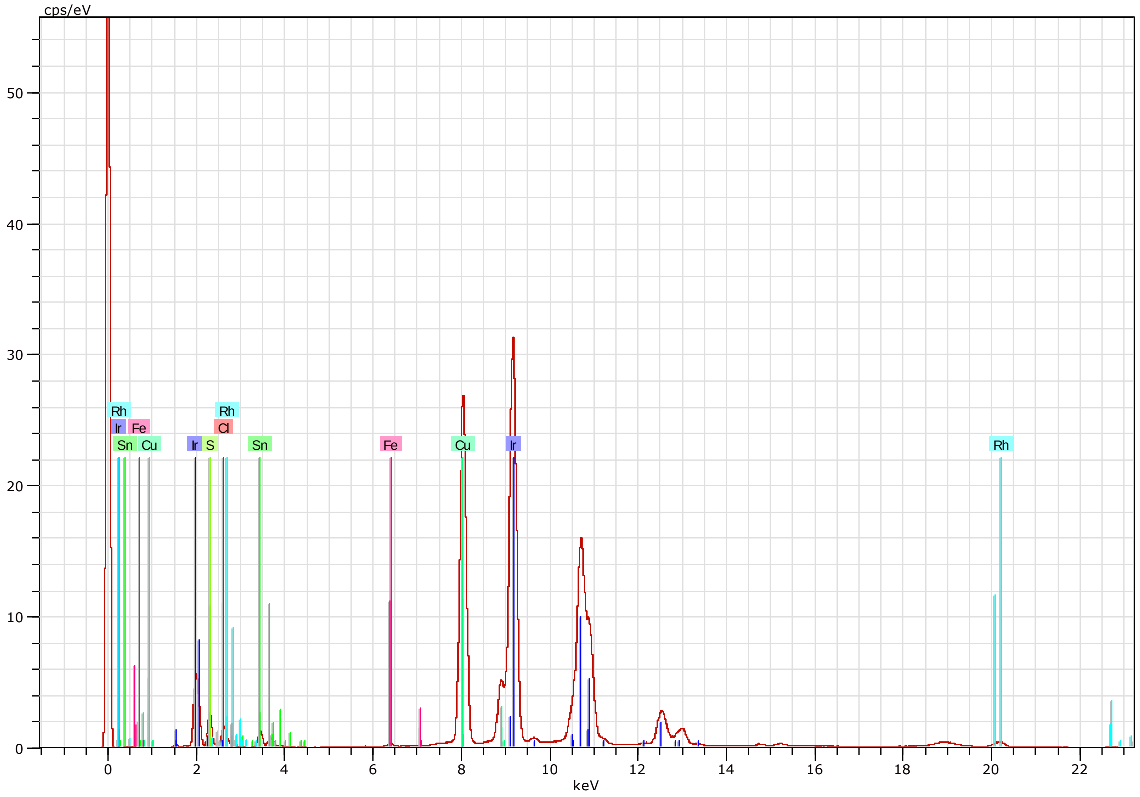


Figure S3. µ-RFA spectrum of a single crystal of **3**, Cu and Fe signals result from the sample holder, Rh signals from the X-ray source.

4 Electrospray ionization mass spectrometry (ESI-MS)

ESI-MS(+) investigations of **2** were performed on a LTQ-FT from Thermo Fischer Scientific. Figure S4 shows the overview spectrum, the zoom onto the main three signal groups and the simulation of isotopic pattern. The very poor solubility of **3** inhibited its investigation by ESI-MS.

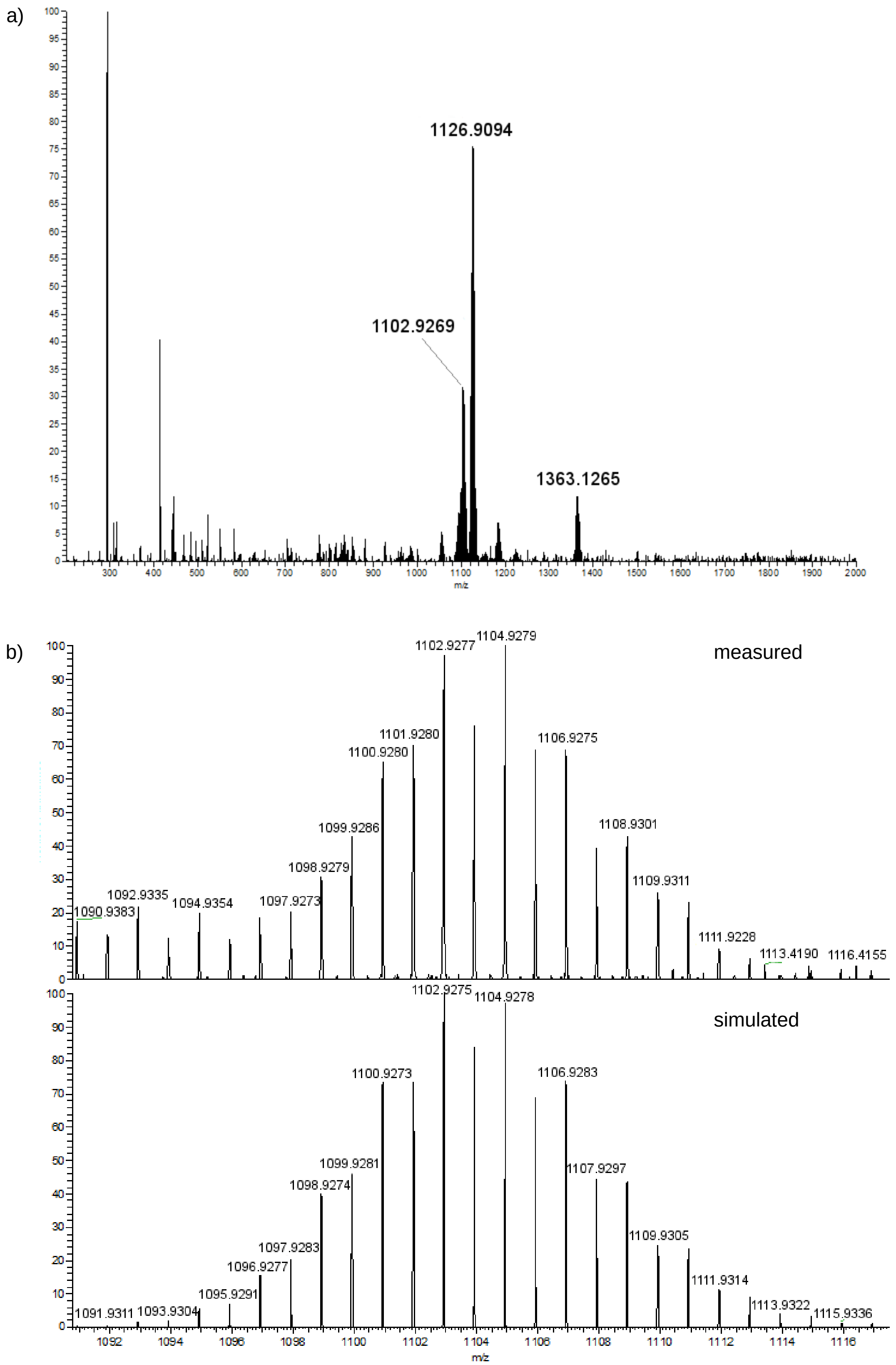


Figure S4. a) ESI($^+$) MS overview spectrum of **2** (in CH$_2$Cl$_2$), indicating main peaks at 1102.9269, 1126.9094 and 1363.12265 m/z. b) ESI($^+$) HR (high resolution) mass cluster with isotopic pattern of [Sn$_3$S$_5$R$^{bipy}{}_2$H]$^+$.

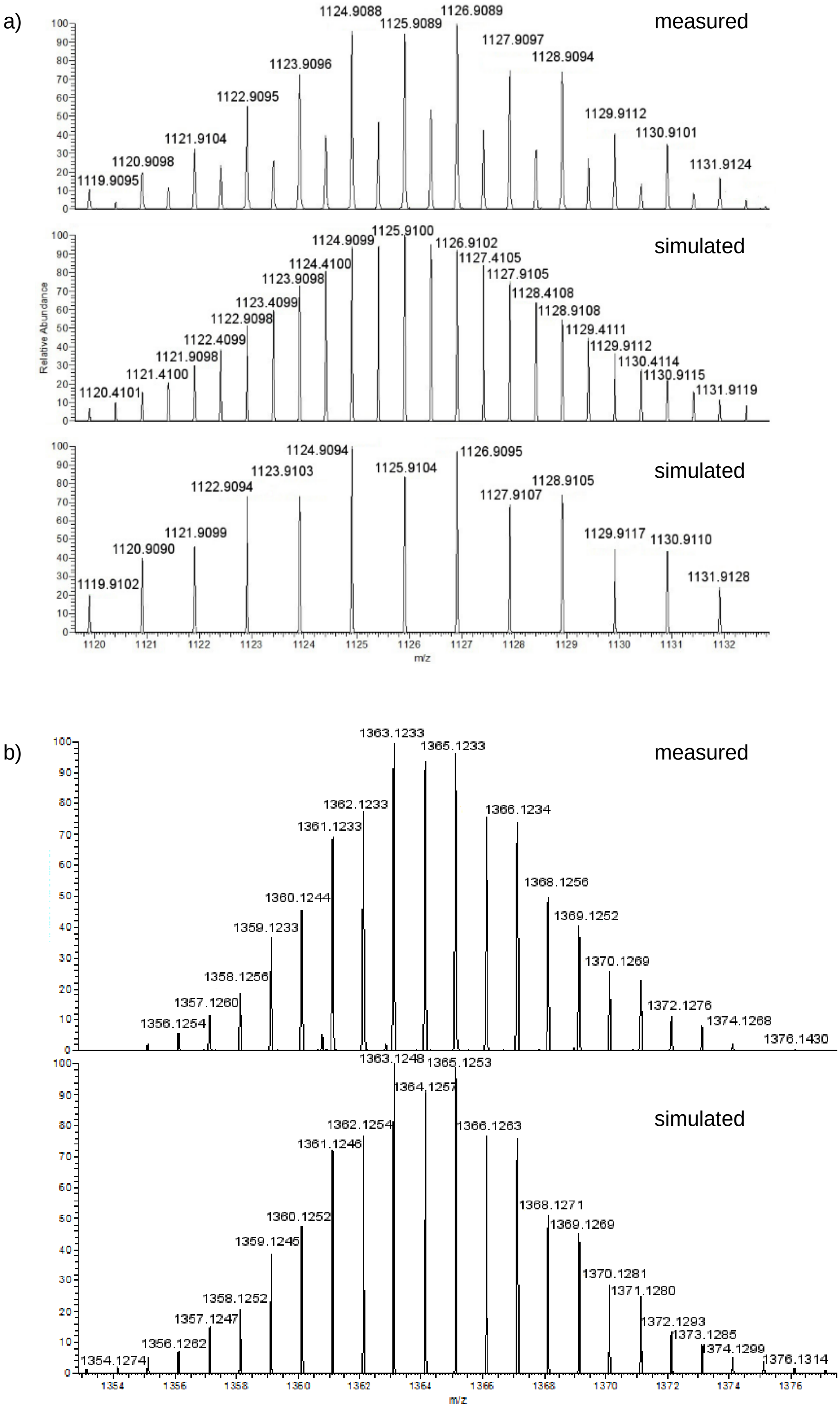


Figure S5. a) ESI(+) HR mass cluster with isotopic pattern of $[Sn_3S_4R^{bipy}{}_3]^+$. b) ESI(+) HR mass cluster with isotopic pattern that turned out to be a combination of two signals, as can be rationalized with the two simulated spectra below that accord with the formulae of $\{[(RBipySn)_4Sn_2S_{10}]Na_2\}^{2+}$ (center) and $\{[(RBipySn)_2S_5]Na\}^+$ bottom.

5 Quantum Chemical Investigations

5.1 Computational methods

DFT calculations were done with the program system TURBOMOLE[2] employing the Becke-Perdew (BP86) functional[3] with def2-TZVP bases[4] and respective fitting bases[5] for the evaluation of the Coulomb matrix. Effective core potentials (ECPs) were used for Sn and Ir atoms, ECP-28[6a] and ECP-60,[6b] respectively. Contour plots were generated with gOpenMol.[7]

5.2 Calculated Structures of $\{[Ir_3(cod)_3(\mu_3\text{-}S)_2](\mu_3\text{-}S)SnCl\}_2$

Table S4 summarizes the structural parameters of the $\{[Ir_3(cod)_3(\mu_3\text{-}S)_2](\mu_3\text{-}S)SnCl\}_2$ molecule in **3** as calculated by DFT methods without symmetry restrictions, in comparison with the results from X-ray diffraction measurements.

Table S4. Summary and comparison of experimental and calculated structural parameters within the inorganic core of $\{[Ir_3(cod)_3(\mu_3\text{-}S)_2](\mu_3\text{-}S)SnCl\}_2$.

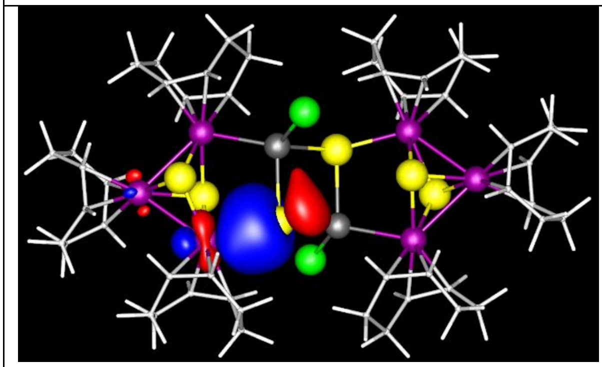
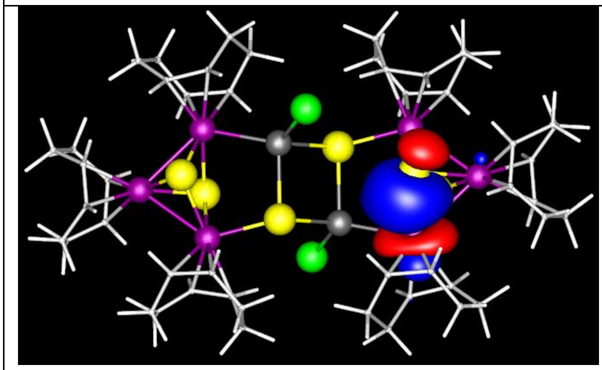
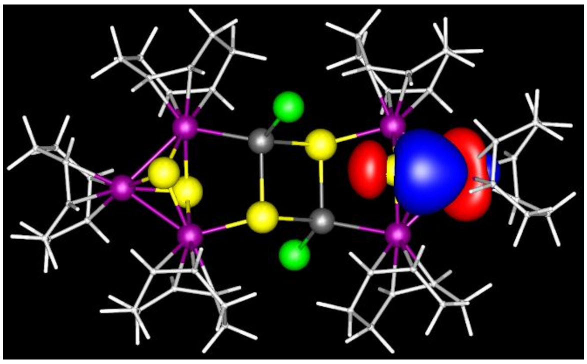
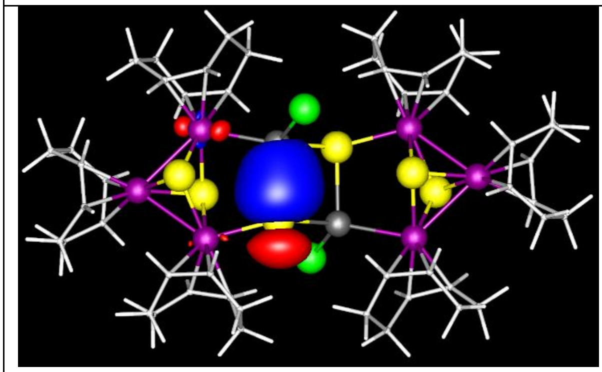
bond or angle	experimental / Å or °	geometry optimization / Å or °	difference (geo−exp) / Å or °
Ir1−Ir2	2.7840 (19)	2.858	0.074
Ir2−Ir3	2.801 (2)	2.880	0.079
Ir1−S1	2.378 (7)	2.394	0.016
Ir2−S1	2.338 (8)	2.347	0.009
Ir3−S1	2.417 (8)	2.431	0.014
Ir1−S2	2.359 (8)	2.396	0.037
Ir2−S2	2.318 (8)	2.345	0.027
Ir3−S2	2.386 (7)	2.417	0.031
Ir1−Sn1	2.556 (3)	2.648	0.092
Ir3−S3	2.445 (7)	2.491	0.046
Sn1−S3	2.513 (7)	2.584	0.071
Sn1−S3'	2.484 (7)	2.540	0.056
Sn1−Cl1	2.380 (8)	2.432	0.052
Ir1-Ir2-Ir3	80.24 (6)	79.105	-1.135
Ir1-(S1,2)-Ir3	98.0 (3)	98.602	0.602
S1-Ir-S2	79.9 (2)	78.702	-1.198
Ir1-Sn1-S3	107.39 (18)	103.993	-3.397
Ir1-Sn1-S3'	121.2 (2)	121.149	-0.051
Ir3-S3-Sn1	98.2 (3)	100.909	2.709
Ir3-S3-Sn1'	122.1 (3)	125.004	2.904
Ir1-Sn1-Cl1	118.4 (2)	120.803	2.403
Cl1-Sn1-S3	107.3 (2)	106.325	-0.975
Cl1-Sn1-S3'	104.2 (3)	105.924	1.724
Sn1-S3-Sn1'	85.9 (2)	85.857	-0.043
S3-Sn1-S3'	94.1 (2)	94.143	0.043

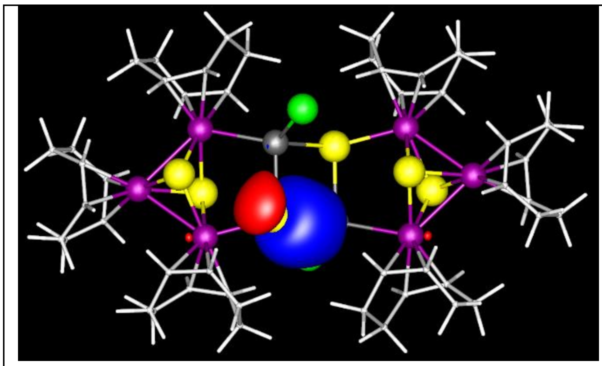
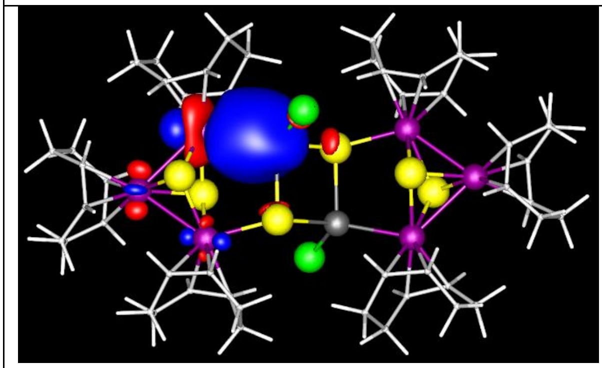
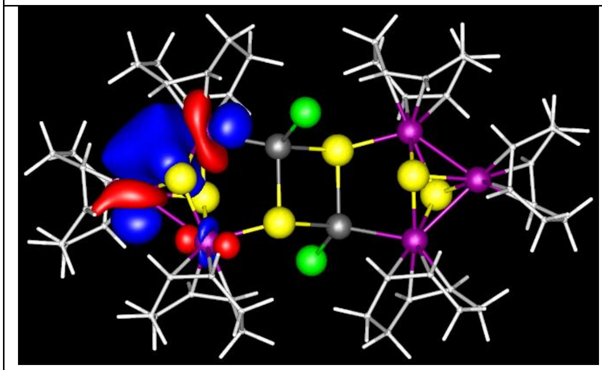
Comparison of the calculated and experimentally observed structural parameters indicate good agreement of both interatomic distances and angles within the error of the method and the typical small bond elongation (up to 0.092 Å here) when using DFT methods.

5.3 Localized Molecular (Valence) Orbitals of {[Ir$_3$(cod)$_3$(μ_3-S)$_2$](μ_3-S)SnCl}$_2$

Table S5 illustrates the localized molecular orbitals (LMOs) as calculated for the valence region of {[Ir$_3$(cod)$_3$(μ_3-S)$_2$](μ_3-S)SnCl}$_2$ using DFT methods and Boys localization of the Kohn-Sham orbitals.[8]

Table S5. Representative localized molecular orbitals (LMOs) of {[Ir$_3$(cod)$_3$(μ_3-S)$_2$](μ_3-S)SnCl}$_2$ as calculated by means of DFT methods. Amplitudes are drawn at 0.05 a.u.

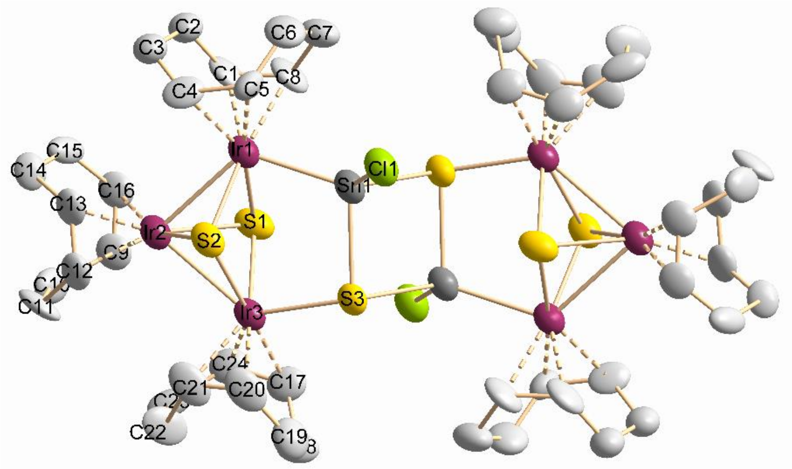
LMO pictures	equivalent LMOs (LMO numbers)	bond
	295, 296	Ir-S
 	297-308	Ir-S
	309, 310	Sn-S

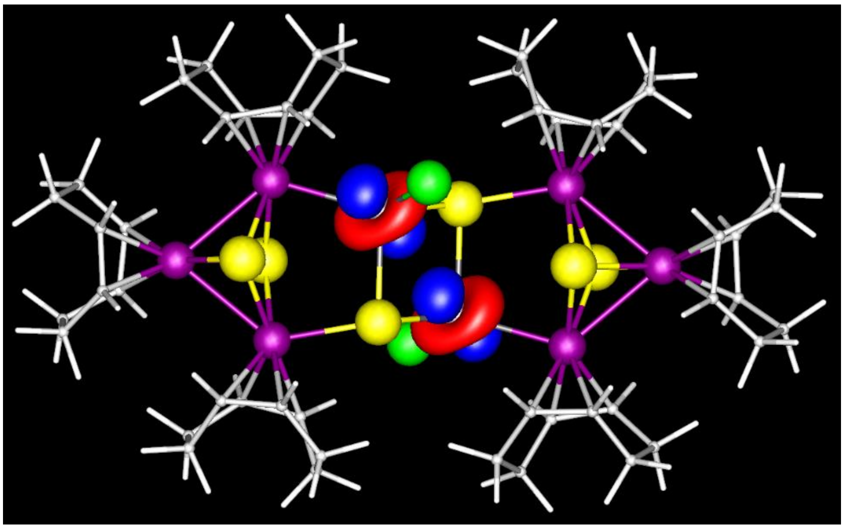
	311, 312	Sn-S
	313, 314	Sn-Ir
	315-318	Ir-Ir

5.4 Canonical (Valence) Molecular Orbitals of $\{[Ir_3(cod)_3(\mu_3\text{-}S)_2](\mu_3\text{-}S)SnCl\}_2$

Table S6 illustrates the canonical molecular orbitals and lists their respective energies as calculated for the valence region of $\{[Ir_3(cod)_3(\mu_3\text{-}S)_2](\mu_3\text{-}S)SnCl\}_2$ using DFT methods.[2-8] Contributions of s, p (and d for Ir) atomic orbitals are given as calculated by Mulliken population analyses.[9] The small discrepancy between total contribution and contributions by s, p and AOs derives from the disregard of d AO contribution (of main group elements) and f AO contribution artefacts.

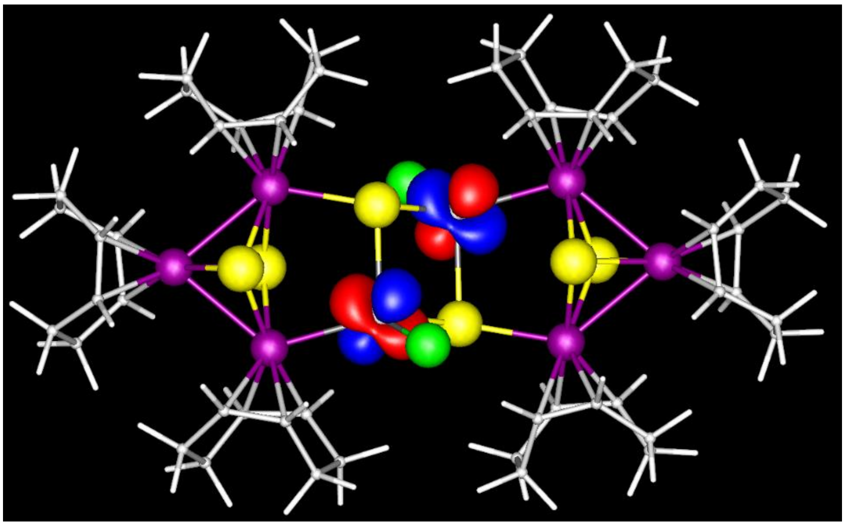
Table S6 Amplitudes, energies and atomic orbital contributions (according to Mulliken population analyses) of representative canonical valence MOs in {[Ir$_3$(cod)$_3$(μ_3-S)$_2$](μ_3-S)SnCl}$_2$. Amplitudes are drawn at 0.033 a.u..





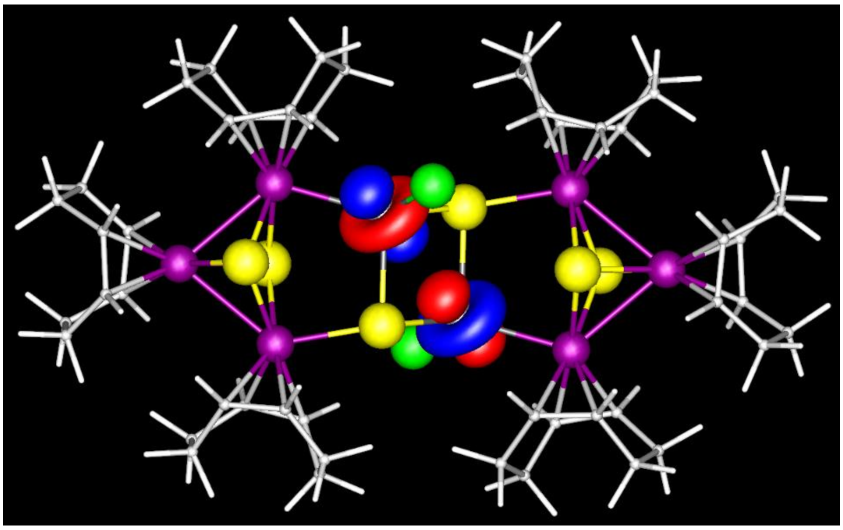
	total	s	p	d
Sn1'	1.00	0.00	0.00	1.00
Sn1	1.00	0.00	0.00	1.00

125a HOMO−193 ε = −25,753eV



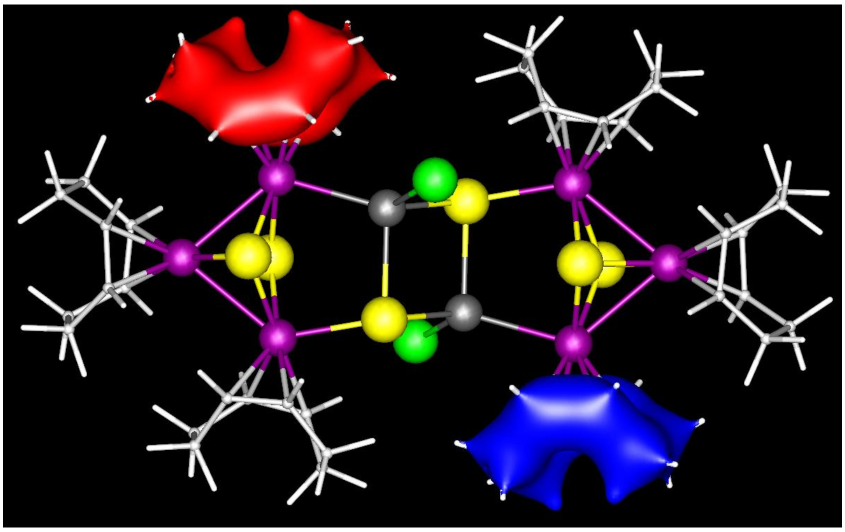
	total	s	p	d
Sn1'	1.00	0.00	0.00	1.00
Sn1	1.00	0.00	0.00	1.00

126a HOMO−192 ε = −25,711 eV



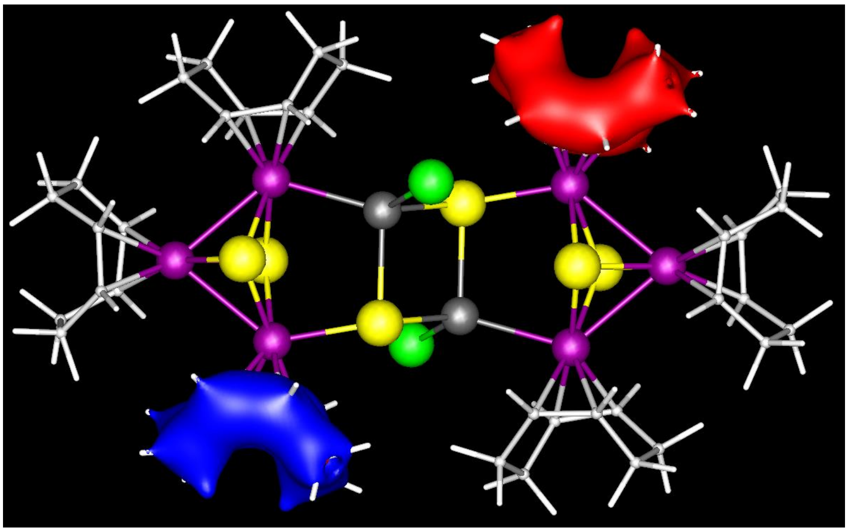
	total	s	p	d
Sn1'	1.00	0.00	0.00	1.00
Sn1	1.00	0.00	0.00	1.00

130a HOMO−188 ε = −25,692 eV



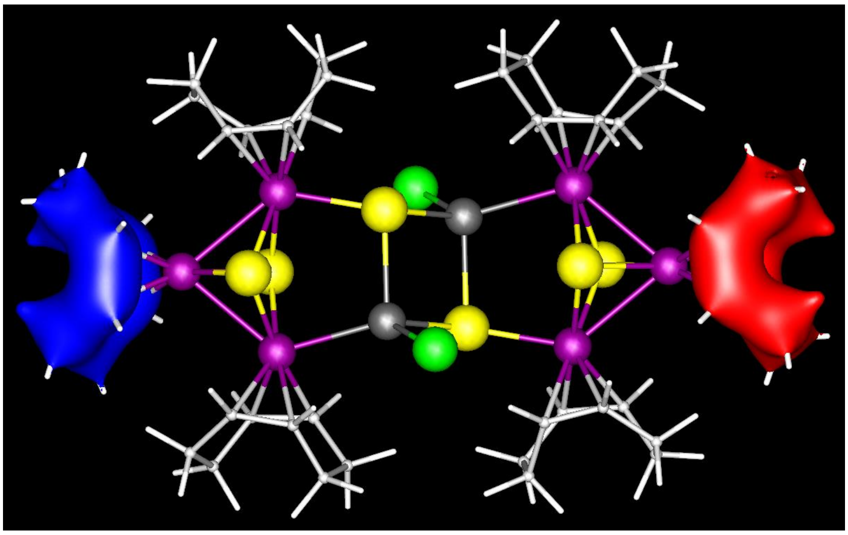
	total	s	p	d
Ir1'	0.05	0.03	0.02	0.00
C1'	0.12	0.11	0.01	
C4'	0.10	0.10	0.01	
C8'	0.10	0.10	0.00	
C5'	0.10	0.10	0.00	
C2'	0.11	0.10	0.01	
C3'	0.09	0.09	0.01	
C7'	0.10	0.09	0.01	
C6'	0.11	0.10	0.01	
Ir1	0.05	0.03	0.02	0.00
C1	0.12	0.11	0.01	
C4	0.10	0.10	0.01	
C8	0.10	0.10	0.00	
C5	0.10	0.10	0.00	
C2	0.11	0.10	0.01	
C3	0.09	0.09	0.01	
C7	0.10	0.09	0.01	
C6	0.11	0.10	0.01	

132a HOMO−186 ε = −21,003 eV



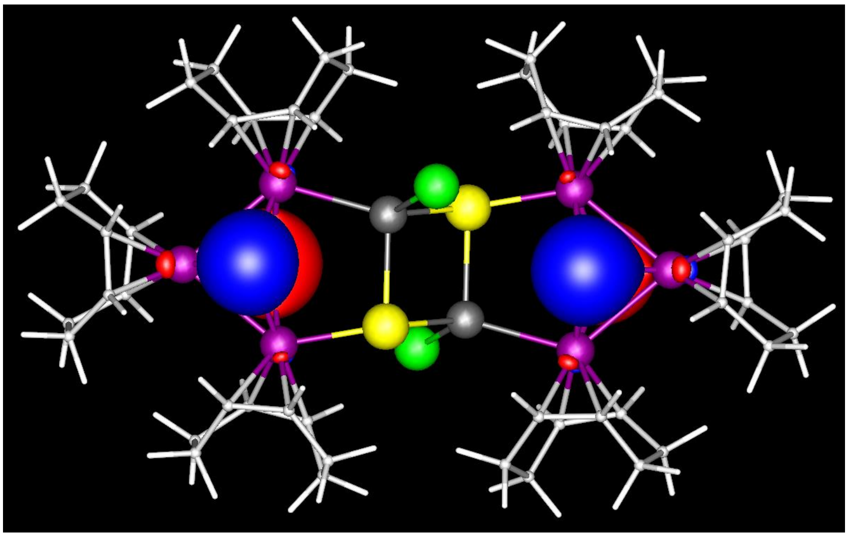
	total	s	p	d
Ir2'	0.02	0.01	0.01	0.00
Ir3'	0.04	0.00	0.03	0.00
C20'	0.08	0.08	0.00	
C24'	0.13	0.12	0.01	
C17'	0.07	0.07	0.00	
C21'	0.13	0.12	0.01	
C19'	0.08	0.08	0.01	
C23'	0.08	0.08	0.01	
C18'	0.12	0.11	0.01	
C22'	0.11	0.10	0.01	
H23a'	0.01	0.01		
Ir3	0.04	0.00	0.03	0.00
Ir2	0.02	0.01	0.01	0.00
C20	0.08	0.08	0.00	
C24	0.13	0.12	0.01	
C17	0.07	0.07	0.00	
C21	0.13	0.12	0.01	
C19	0.08	0.08	0.01	
C23	0.08	0.08	0.01	
C18	0.12	0.11	0.01	
C22	0.11	0.10	0.01	
H23a	0.01	0.01		

133a HOMO−185 ε = −20,890 eV



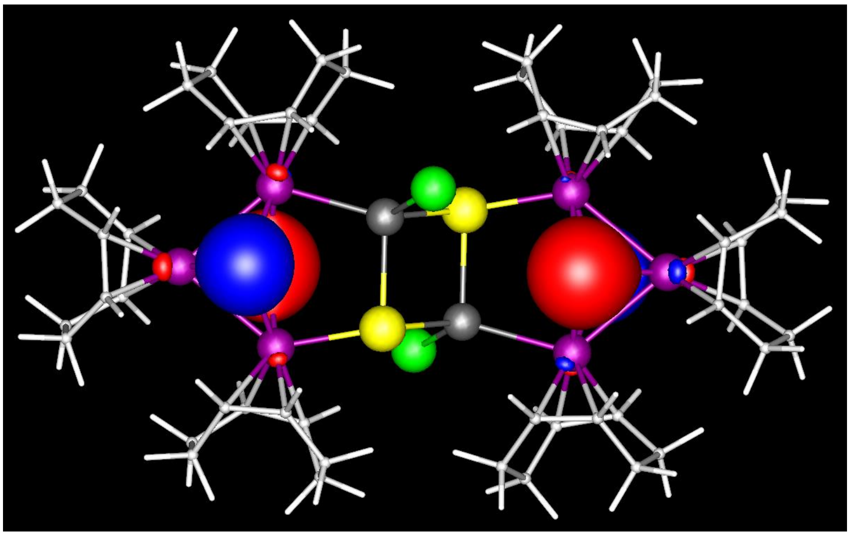
136a HOMO−182 ε = −20,766 eV

	total	s	p	d
C12'	0.09	0.09	0.00	
C10'	0.10	0.10	0.01	
Ir2'	0.06	0.04	0.02	0.00
C13'	0.11	0.10	0.01	
C9'	0.10	0.10	0.01	
C16'	0.09	0.09	0.00	
C14'	0.11	0.10	0.01	
C15'	0.09	0.09	0.01	
Ir2	0.06	0.04	0.02	0.00
C16	0.09	0.09	0.00	
C9	0.10	0.10	0.01	
C13	0.11	0.10	0.01	
C12	0.09	0.09	0.00	
C15	0.09	0.09	0.01	
C10	0.10	0.10	0.01	
C14	0.11	0.10	0.01	
C11	0.09	0.08	0.01	
C11'	0.09	0.08	0.01	



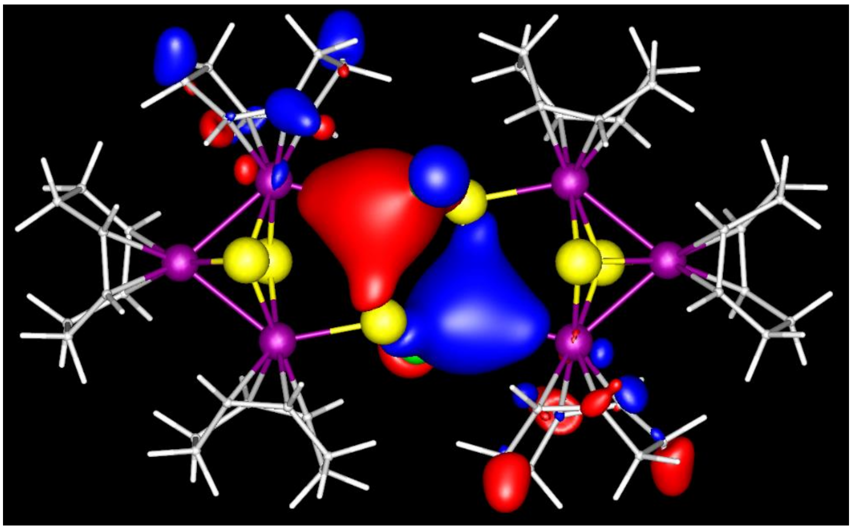
160a HOMO−158 ε = −16,798 eV

	total	s	p	d
Ir2'	0.03	0.00	0.01	0.01
Ir3'	0.02	0.00	0.01	0.02
Ir1'	0.04	0.00	0.01	0.03
S1'	0.44	0.44	0.00	
S2'	0.35	0.35	0.00	
C4'	0.01	0.01	0.00	
C2'	0.01	0.01	0.00	
C3'	0.01	0.01	0.00	
Ir1	0.04	0.00	0.01	0.03
Ir3	0.02	0.00	0.01	0.02
Ir2	0.03	0.00	0.01	0.01
S1	0.44	0.44	0.00	
S2	0.35	0.35	0.00	
C4	0.01	0.01	0.00	
C2	0.01	0.01	0.00	
C3	0.01	0.01	0.00	



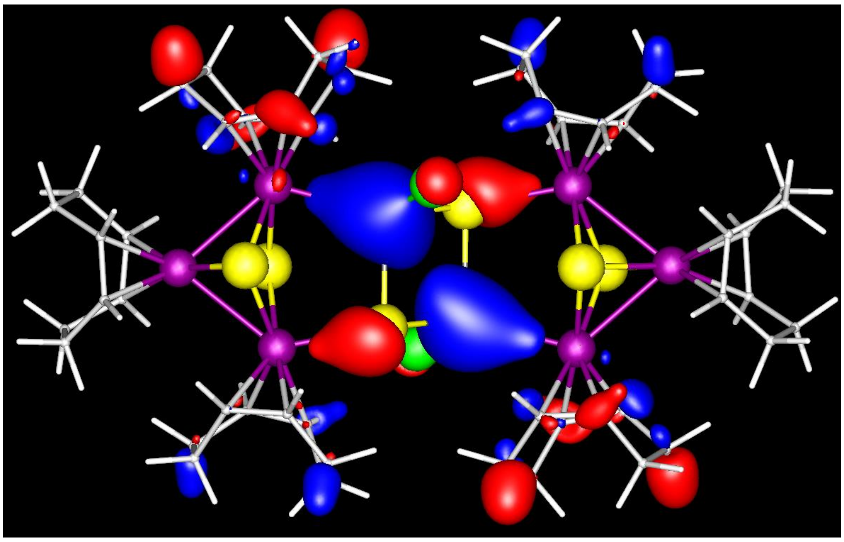
161a HOMO−157 ε = −16,795 eV

	total	s	p	d
Ir2'	0.03	0.00	0.01	0.01
Ir3'	0.02	0.00	0.00	0.02
Ir1'	0.04	0.00	0.01	0.03
S1'	0.49	0.49	0.00	
S2'	0.29	0.29	0.00	
C4'	0.01	0.01	0.00	
C2'	0.01	0.01	0.00	
Ir1	0.04	0.00	0.01	0.03
Ir3	0.02	0.00	0.00	0.02
Ir2	0.03	0.00	0.01	0.01
S1	0.49	0.49	0.00	
S2	0.29	0.29	0.00	
C4	0.01	0.01	0.00	
C2	0.01	0.01	0.00	



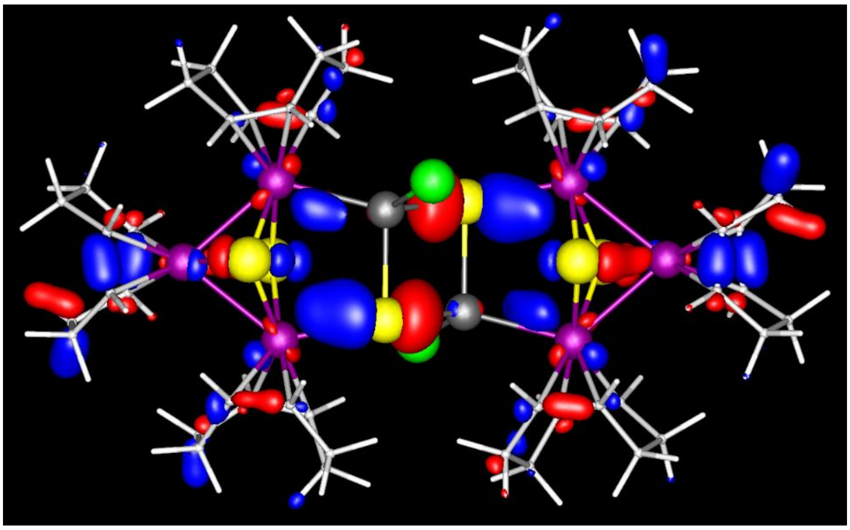
193a HOMO−125 ε = −11,969 eV

	total	s	p	d
Ir2'	0.01	0.00	0.01	0.00
Ir1'	0.08	0.02	0.03	0.03
S1'	0.01	0.00	0.01	
S3'	0.09	0.00	0.09	
Sn1'	0.44	0.43	0.00	
C1'	0.02	0.00	0.01	
C4'	0.02	0.01	0.01	
C8'	0.02	0.00	0.02	
C5'	0.02	0.02	0.01	
Sn1	0.44	0.43	0.00	
S3	0.09	0.00	0.09	
Cl1'	0.08	0.02	0.06	
C3'	0.03	0.01	0.03	
C7'	0.05	0.01	0.04	
H5a'	0.01	0.01		
Ir1	0.08	0.02	0.03	0.03
Cl1	0.08	0.02	0.06	
H3A'	0.02	0.02		
H7a'	0.02	0.02		
Ir2	0.01	0.00	0.01	0.00
S2	0.01	0.00	0.01	
C1	0.02	0.00	0.01	
C4	0.02	0.01	0.01	
C8	0.02	0.00	0.02	
C5	0.02	0.02	0.01	
C3	0.03	0.01	0.03	
C7	0.05	0.01	0.04	
H5a	0.01	0.01		
H3a	0.02	0.02		
H7a	0.02	0.02		



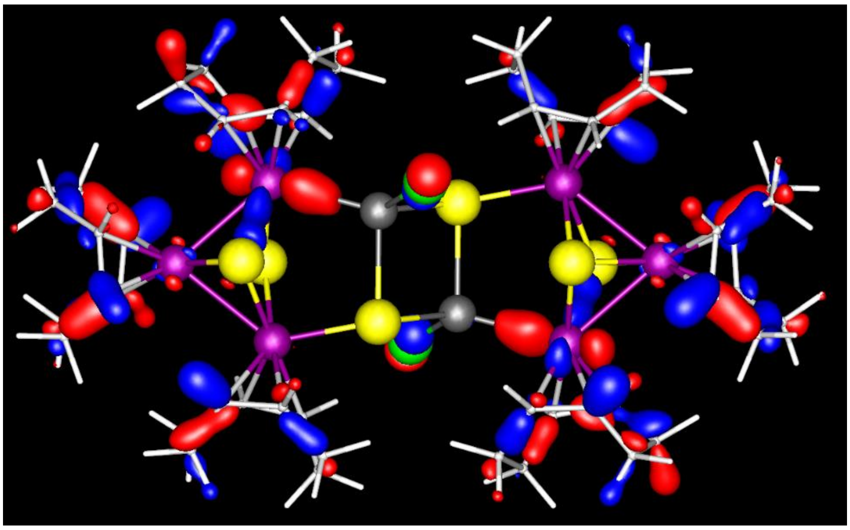
194a HOMO−124; ε = −11,791 eV

	total	s	p	d
Ir2'	0.01	0.00	0.01	0.00
Ir3'	0.04	0.02	0.00	0.01
Ir1'	0.05	0.01	0.01	0.02
S3'	0.12	0.04	0.08	
C20'	0.01	0.00	0.01	
C24'	0.01	0.00	0.01	
C17'	0.01	0.00	0.01	
C21'	0.01	0.00	0.01	
Sn1'	0.24	0.23	0.00	
C1'	0.02	0.00	0.01	
C4'	0.03	0.01	0.03	
C8'	0.03	0.00	0.02	
C5'	0.02	0.01	0.01	
Sn1	0.24	0.23	0.00	
C19'	0.02	0.00	0.02	
C23'	0.02	0.00	0.02	
S3	0.12	0.04	0.08	
Cl1'	0.04	0.01	0.03	
C2'	0.01	0.00	0.01	
C3'	0.04	0.00	0.04	
C7'	0.06	0.00	0.05	
C6'	0.01	0.00	0.01	
Ir1	0.05	0.01	0.01	0.02
Cl1	0.04	0.01	0.03	
H18a'	0.01	0.01		
H23a'	0.01	0.01		
Ir3r	0.04	0.02	0.00	0.01
H3a'	0.03	0.03		
H7a'	0.03	0.03	0.00	
Ir2	0.01	0.00	0.01	0.00
C1	0.02	0.00	0.01	
C4	0.03	0.01	0.03	
C8	0.03	0.00	0.02	
C5	0.02	0.01	0.01	
C20	0.01	0.00	0.01	
C24	0.01	0.00	0.01	
C17	0.01	0.00	0.01	
C21	0.01	0.00	0.01	
C2	0.01	0.00	0.01	
C3	0.04	0.00	0.04	
C7	0.06	0.00	0.05	
C6	0.01	0.00	0.01	
C19	0.02	0.00	0.02	
C23	0.02	0.00	0.02	
H3a	0.03	0.03		
H7a	0.03	0.03	0.00	
H18a	0.01	0.01	0.00	
H23a	0.01	0.01	0.00	



239a HOMO−79; ε = −9,097 eV

	total	s	p	d
C12'	0.02	0.00	0.02	
C10'	0.04	0.00	0.04	
Ir2'	0.04	0.02	0.01	0.02
C13'	0.03	0.00	0.03	
H10a'	0.02	0.02		
H10b'	0.01	0.01		
C9'	0.02	0.00	0.02	
Ir3'	0.06	0.02	0.00	0.04
Ir1'	0.06	0.01	0.01	0.05
S1'	0.06	0.00	0.06	
S2'	0.06	0.00	0.06	
C16'	0.02	0.00	0.02	
S3'	0.16	0.00	0.16	
C20'	0.02	0.00	0.02	
C21'	0.02	0.00	0.01	
Sn1'	0.08	0.00	0.07	
C1'	0.01	0.00	0.01	
C2'	0.02	0.00	0.02	
C5'	0.02	0.00	0.01	
C15'	0.01	0.00	0.01	
Sn1	0.08	0.00	0.07	
C22'	0.02	0.00	0.02	
C23'	0.01	0.00	0.01	
S3	0.16	0.00	0.16	
C3'	0.01	0.00	0.01	
C7'	0.02	0.00	0.02	
Ir1	0.06	0.01	0.01	0.05
H23a'	0.01	0.01		
Ir3	0.06	0.02	0.00	0.04
Ir2	0.04	0.02	0.01	0.02
S1	0.06	0.00	0.06	
S2	0.06	0.00	0.06	
C1	0.01	0.00	0.01	
C8	0.02	0.00	0.02	
C5	0.02	0.00	0.01	
C20	0.02	0.00	0.02	
C21	0.02	0.00	0.01	
C16	0.02	0.00	0.02	
C9	0.02	0.00	0.02	
C13	0.03	0.00	0.03	
C12	0.02	0.00	0.02	
C3	0.01	0.00	0.01	
C7	0.02	0.00	0.02	
C23	0.02	0.00	0.02	
C22	0.01	0.00	0.01	
C15	0.01	0.00	0.01	
C10	0.04	0.00	0.04	
H23a	0.01	0.01		
H10a	0.02	0.02		
H10b	0.01	0.01		



270a HOMO−48; ε = −7,76702eV

	total	s	p	d
C12'	0.04	0.00	0.04	
C10'	0.02	0.00	0.02	
Ir2'	0.04	0.02	0.00	0.02
C13'	0.02	0.00	0.01	
C9'	0.02	0.00	0.02	
Ir3'	0.02	0.00	0.00	0.01
Ir1'	0.09	0.00	0.00	0.08
S1'	0.02	0.00	0.02	
S2'	0.04	0.00	0.04	
C16'	0.04	0.00	0.04	
C14'	0.02	0.00	0.02	
C20'	0.02	0.00	0.02	
C21'	0.03	0.00	0.03	
Sn1'	0.04	0.01	0.03	
C1'	0.04	0.00	0.04	
C4'	0.01	0.00	0.01	
C8'	0.02	0.00	0.01	
C5'	0.02	0.00	0.02	
H16a'	0.03	0.03		
C15'	0.03	0.00	0.02	
Sn1	0.04	0.01	0.03	
C19'	0.02	0.00	0.02	
C22'	0.02	0.00	0.02	
H21a'	0.02	0.02		
Cl1'	0.06	0.00	0.05	
H1a'	0.03	0.03		
C2'	0.01	0.00	0.01	
C3'	0.02	0.00	0.02	
C7'	0.02	0.00	0.02	
C6'	0.01	0.00	0.01	
Ir1	0.09	0.00	0.00	0.08
Cl1	0.06	0.00	0.05	
Ir3	0.02	0.00	0.00	0.01
H2a'	0.01	0.01		
H3a'	0.02	0.02		
Ir2	0.04	0.02	0.00	0.02
S1	0.02	0.00	0.02	
S2	0.04	0.00	0.04	
C1	0.04	0.00	0.04	
C4	0.01	0.00	0.01	
C8	0.02	0.00	0.01	
C5	0.02	0.00	0.02	
C20	0.02	0.00	0.02	
C21	0.03	0.00	0.03	
C16	0.04	0.00	0.04	
C9	0.02	0.00	0.02	
C13	0.02	0.00	0.01	
C12	0.04	0.00	0.04	
H1a	0.03	0.03		
C2	0.01	0.00	0.01	
C3	0.02	0.00	0.02	
C7	0.02	0.00	0.02	
C6	0.01	0.00	0.01	
C19	0.02	0.00	0.02	
C22	0.02	0.00	0.02	
H21a	0.02	0.02		
H16a	0.03	0.03		
C15	0.03	0.00	0.02	
C10	0.02	0.00	0.02	
C14	0.02	0.00	0.02	
C11	0.02	0.00	0.02	
H12a	0.01	0.01		
H2a	0.01	0.01		
H3a	0.02	0.02		
C11'	0.02	0.00	0.02	
H12a'	0.01	0.01		

6 References for the Supporting Information

[1] a) G. W. Sheldrick, *Acta Cryst.* **2008**, *A64.* 112; b) Absorption correction was applied with the program SADABS V2012/1 Bruker AXS Inc. 6300 Enterprise Lane, Madison, WI 53719−1173. USA, **2012**; c) Absorption correction was applied with the programs X-RED and X-SHAPE included in X-Area 1.43. STOE & Cie GmbH, Hilpertstraße 10. D64295 Darmstadt.

[2] TURBOMOLE Version 6.2. (c) TURBOMOLE GmbH 2011. TURBOMOLE is a development of University of Karlsruhe and Faschingszentrum Karlsruhe 1989-2007, TURBOMOLE GmbH since 2007.

[3] a) A. D. Becke, *Phys. Rev. A*, **1988**, *38*, 3098; b) J. P. Perdew, *Phys. Rev. B,* **1996**, *33*, 8822.

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