ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Trapping of $ZnCl_2$ by bipyridyl-functionalized organotin sulfide clusters, and its effect on optical properties

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1. Experimental details

a. General remarks

All synthesis steps were carried out under argon atmosphere with exclusion of air and moisture. All solvents were purified and dried prior to use. [(R^1Sn)$_4$S$_6$] (**A**) (R^1 = $CMe_2CH_2CMeN–NH_2$) and [($R^{6\text{-}bipy}$Sn)$_4$Sn$_2$S$_{10}$] (**B**) ($R^{6\text{-}bipy}$= $CMe_2CH_2C(Me)N$-NC(Me)-*o*-$C_{10}H_7N_2$) were synthesized according to procedures reported in the literature. [1] Further chemicals were purchased from Sigma-Aldrich and used as received. ^{1}H NMR spectra were recorded with a Bruker AVII 300 spectrometer at 300K. ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were recorded with a Bruker AVIII 500 spectrometer. ESI mass spectra were recorded with a Finnigan LTQ-FT Ultra mass spectrometer (Thermo Fischer Scientific). All samples were handled under argon and dissolved in dry solvents, Hamilton syringes (250 µL) were used for sample injection via syringe pump infusion. Overview Spectra are shown as well as high resolution spectra of the molecular signals with calculated isotopic patterns of the associated molecular ion.

b. Syntheses and analyses

Synthesis of [(R^{Phen}Sn)$_4$S$_6$] (1) (R^{Phen} = $CMe_2CH_2C(Me)N$-NC(H)$C_{12}H_7N_2$)

[(R^NSn)$_4$S$_6$] (**A**) [R^N = $CMe_2CH_2CMeN–NH_2$] (100 mg, 0.089 mmol) was dissolved in 10 mL DCM and a solution of 1,10-phenanthroline-5-carboxaldehyde[2] (115 mg, 0.535 mmol) in 10 mL DCM was added. The pale yellow mixture was stirred for 48 h at room temperature. Layering of the solution with n-hexane (1:1.25) yielded pale yellow crystals of **1**. **^{1}H NMR** (300 MHz, CD_2Cl_2, 25 °C): δ = 10.38 (s, 1 H, C(N)*H*), 9.67 (dd, *J* = 8.5, 1.7 Hz, 1H), 9.26 (dd, *J* = 4.4, 1.8 Hz, 1H), 9.18 (dd, *J* = 4.3, 1.7 Hz, 1H), 8.42 (dd, *J* = 8.1, 1.7 Hz, 1H), 8.36 (s, 1H), 7.73 (ddd, *J* = 8.0, 4.3, 2.4 Hz, 2H), 2.74(s, 2H, CH_2), 1.89 (s, 3H, CH_3, CMe), 1.28 (s, 6 H, CH_3, Me_2) ppm. **^{13}C NMR** (75 MHz, CD_2Cl_2, 25 °C): δ = 193.2, 153.7, 151.3, 140.3, 137.9, 134.9, 134.1, 132.9, 131.0, 127.5, 126.3, 126.1, 124.6, 124.2, 123.6, 123.2, 27.1, 26.9, 19.4 ppm. **^{119}Sn NMR** (187 MHz, CD_2Cl_2, 25 °C): δ = -44 ppm. HRMS (ESI$^+$): m/z calc.: 1881.0940 $[M+H]^+$ found: 1881.0953.

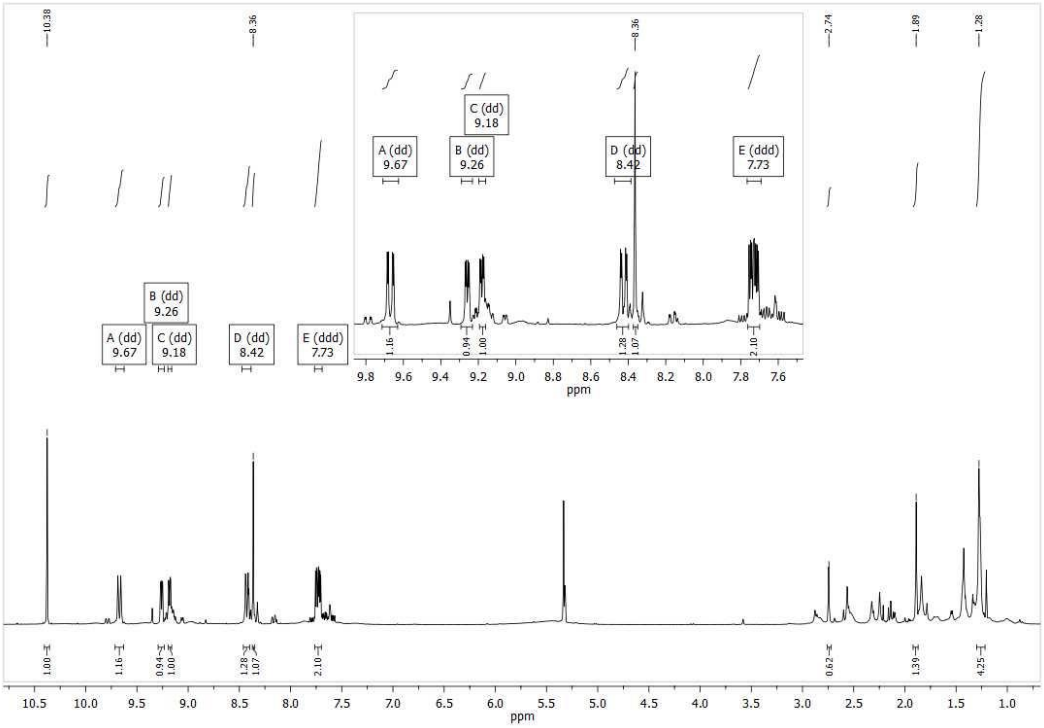


Figure S1: ^{1}H NMR spectrum of **1** in CD_2Cl_2. The magnified section shows the aromatic region with visible coupling pattern, signals with low intensity arise from non-reacted starting material.

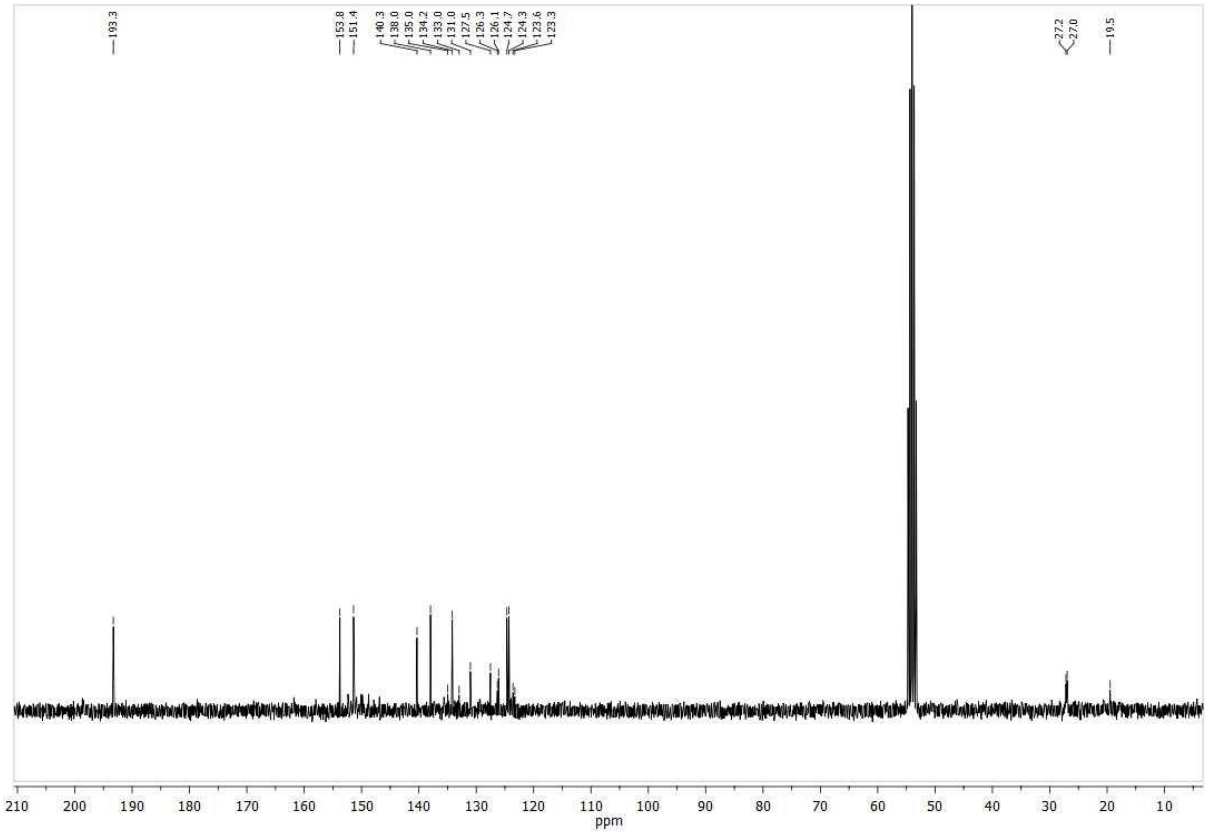


Figure S2: ^{13}C NMR spectrum of **1** in CD_2Cl_2.

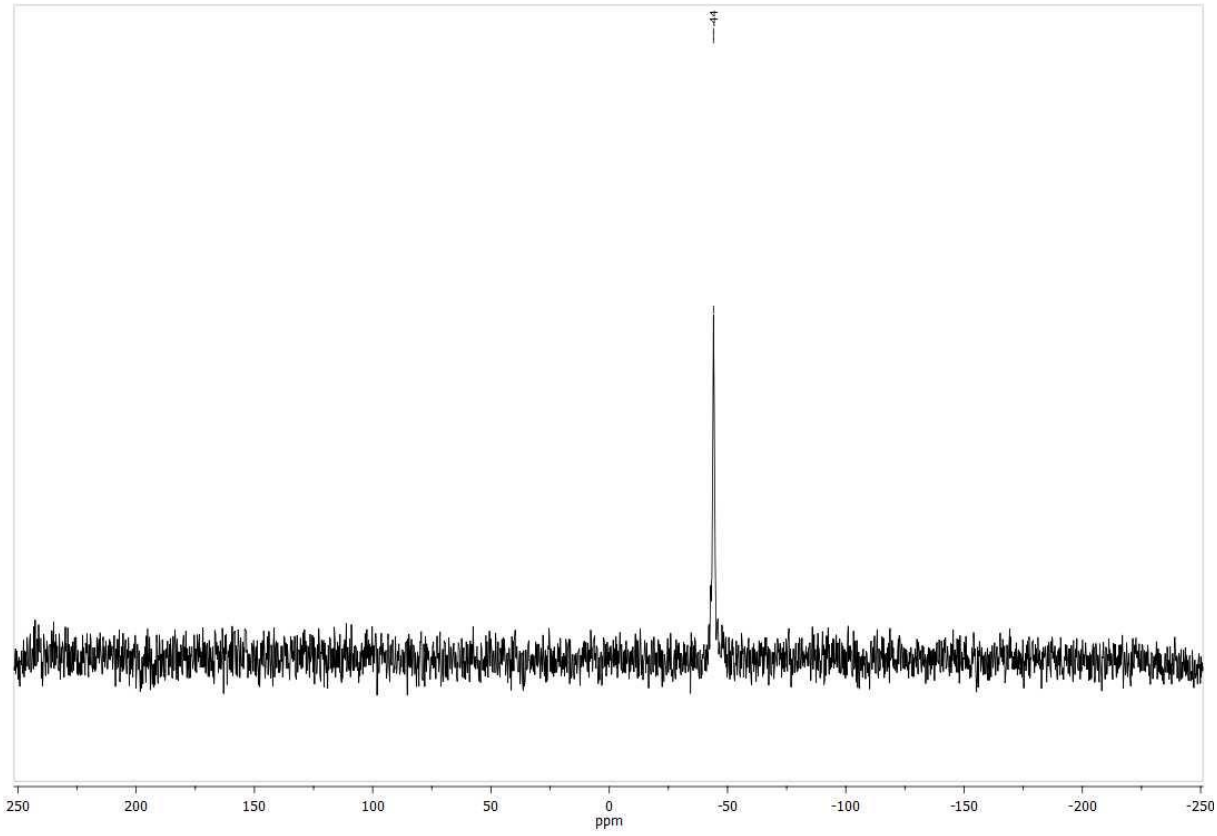


Figure S3: ^{119}Sn NMR spectrum of **1** in CD_2Cl_2.

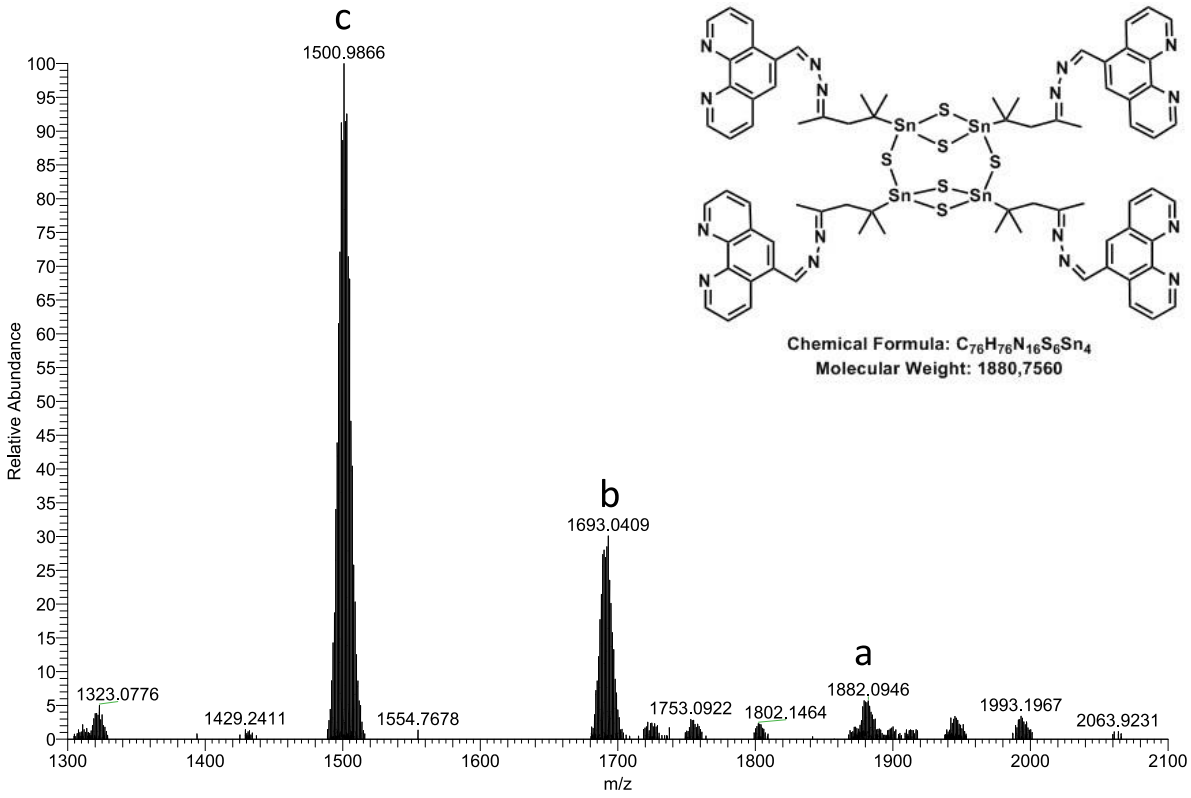


Figure S4: ESI$^+$ mass spectrum of a product solution of **1** with labeled peaks, that could be assigned to the molecule or molecular fragments.

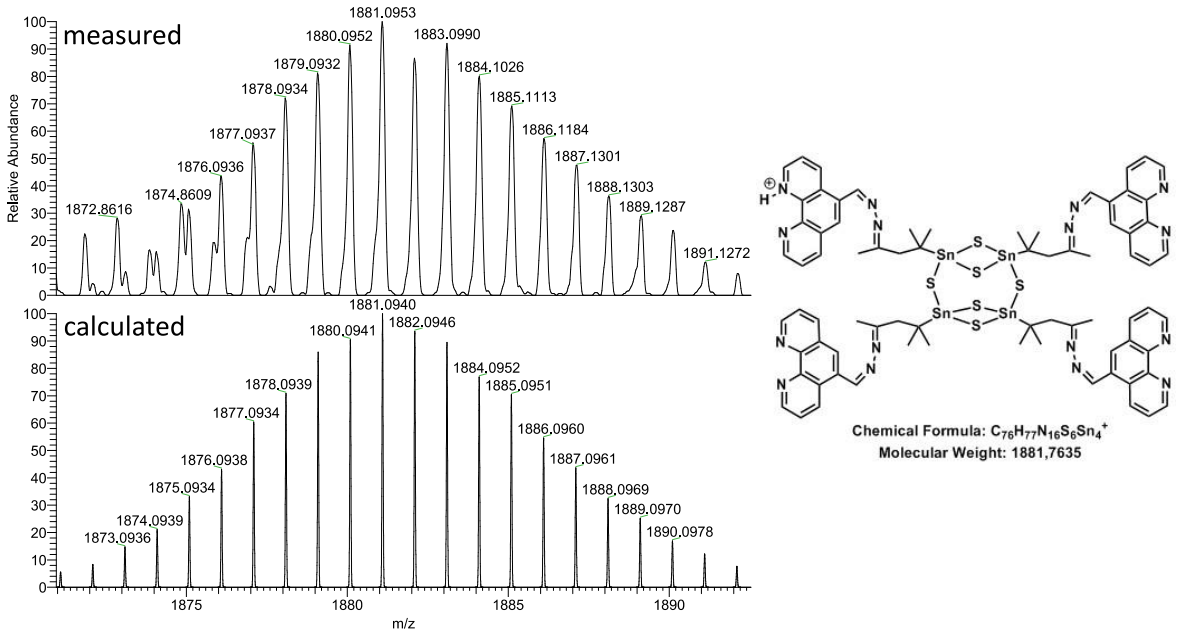


Figure S5: HR-ESI$^+$ mass spectrum and calculated isotopic pattern for fragment a with the sum formula $[C_{76}H_{76}N_{16}S_6Sn_4\text{-}H]^+$.

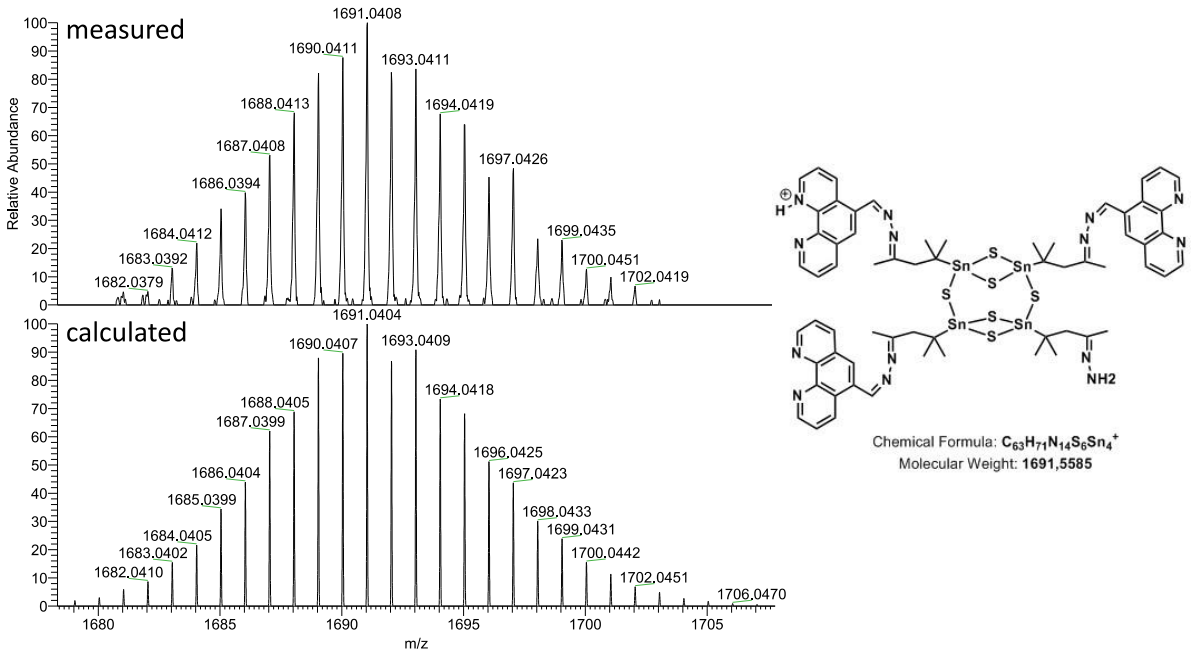


Figure S6: HR-ESI$^+$ mass spectrum and calculated isotopic pattern for fragment b with the sum formula $[C_{63}H_{70}N_{14}S_6Sn_4\text{-}H]^+$.

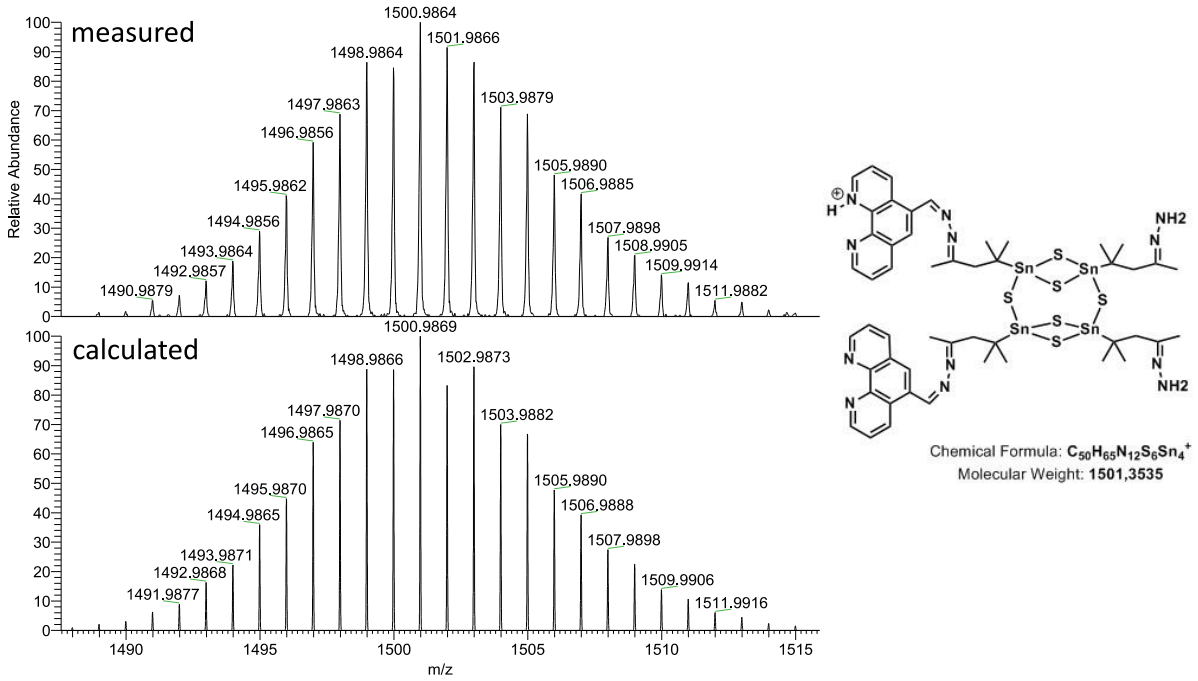


Figure S7: HR-ESI$^+$ mass spectrum and calculated isotopic pattern for fragment c with the sum formula $[C_{50}H_{64}N_{12}S_6Sn_4\text{-}H]^+$.

Synthesis of [($R^{p\text{-}bipy}$Sn)$_4$S$_6$](2) ($R^{p\text{-}bipy}$= $CMe_2CH_2C(Me)N\text{-}NC(H)\text{-}p\text{-}C_{10}H_7N_2$)

[(R^1Sn)$_4$S$_6$] (**A**) [R^1 = $CMe_2CH_2CMeN–NH_2$] (555 mg, 0.496 mmol) was dissolved in 120 mL DCM and a solution of [2,2´-bipyridine]-4-carbaldehyde[3] (394 mg, 2.139 mmol) in 10 mL DCM was added. The mixture was stirred for 48 h at room temperature. Layering of the solution with n-hexane (1:1) yielded pale yellow crystals of **2**. The Yield was determined from 5 mL aliquots of the whole reaction. Yield: 0.029 g (85 %, 0.0162 mmol; calculated on basis of **A**). Elemental analysis: found (calc.): C 42.56 (45.76), H 5.01 (4.29), N 10.09 (12.56), S 8.24 % (10.78 %). **^{1}H NMR** (300 MHz, CD_2Cl_2, 25 °C): δ = 9.28 (s, 1 H, C(N)*H*), 8.67(s,1H), 8.64 (ddd, *J* = 4.7, 1.6, 0.8 Hz, 1H), 8.19 (d, *J* = 4.8 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.73 (td, *J* = 7.7, 1.8 Hz, 1H), 7.45 (dd, *J* = 5.0, 1.5 Hz, 1H), 7.3 (ddd, J = 7.5, 4.8, 1.1 Hz, 1H), 2.73 (s, $^3J_{H\text{-}119Sn}$= 69 Hz, 2H, CH_2), 2.20 (s, 3H, CH_3, CMe), 1.42 (s, $^3J_{H\text{-}119Sn}$= 67 Hz, 6 H, CH_3, Me_2) ppm. **^{13}C NMR** (75 MHz, CD_2Cl_2, 25°C) δ = 20.4, 26.6, 38.5, 51.6, 121.5, 124.1, 124.2, 137.0, 142.5, 149.6, 150.0, 153.2, 156.3, 156.7, 159.4, 161.9 ppm. **^{119}Sn NMR** (187 MHz, CD_2Cl_2, 25 °C): δ = 43 ppm. HRMS (ESI$^+$): m/z calc.: 1785.0937 $[M+H]^+$ found: 1785.0973.

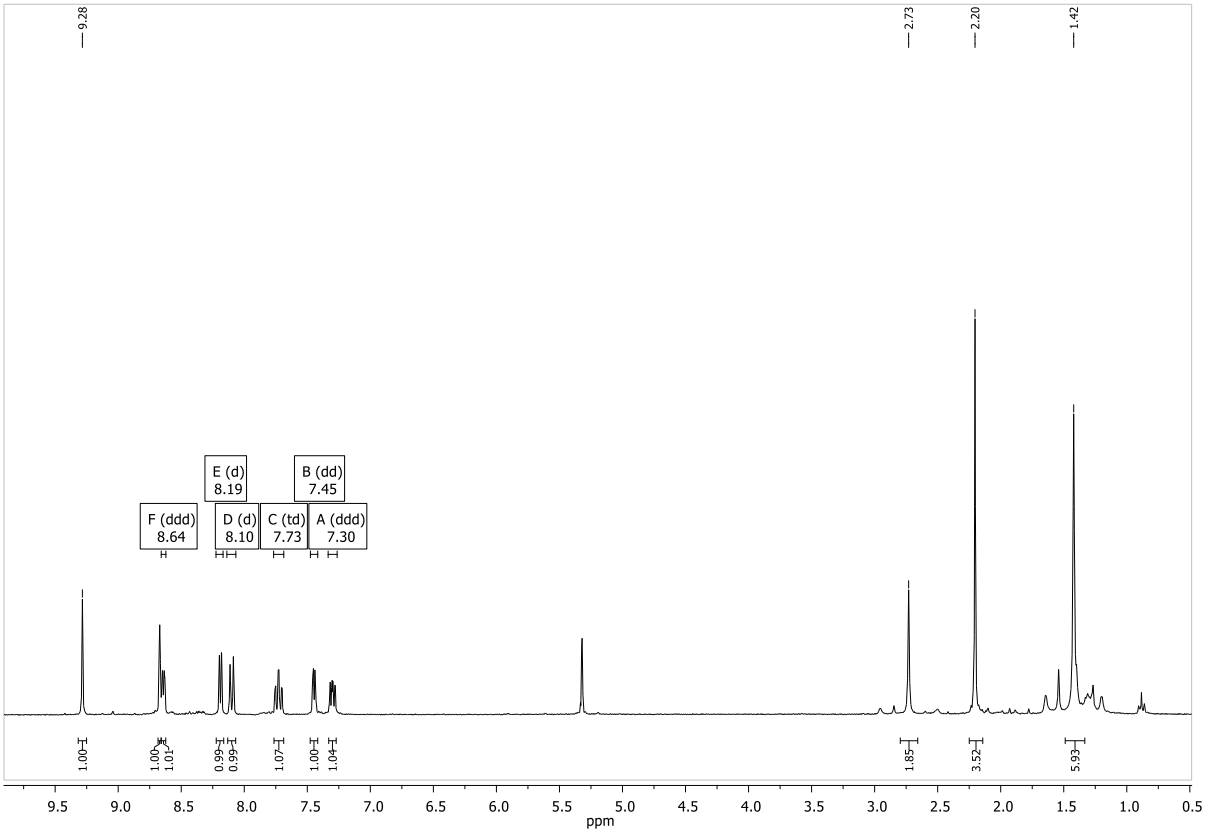


Figure S8: ^{1}H NMR spectrum of **2** in CD_2Cl_2.

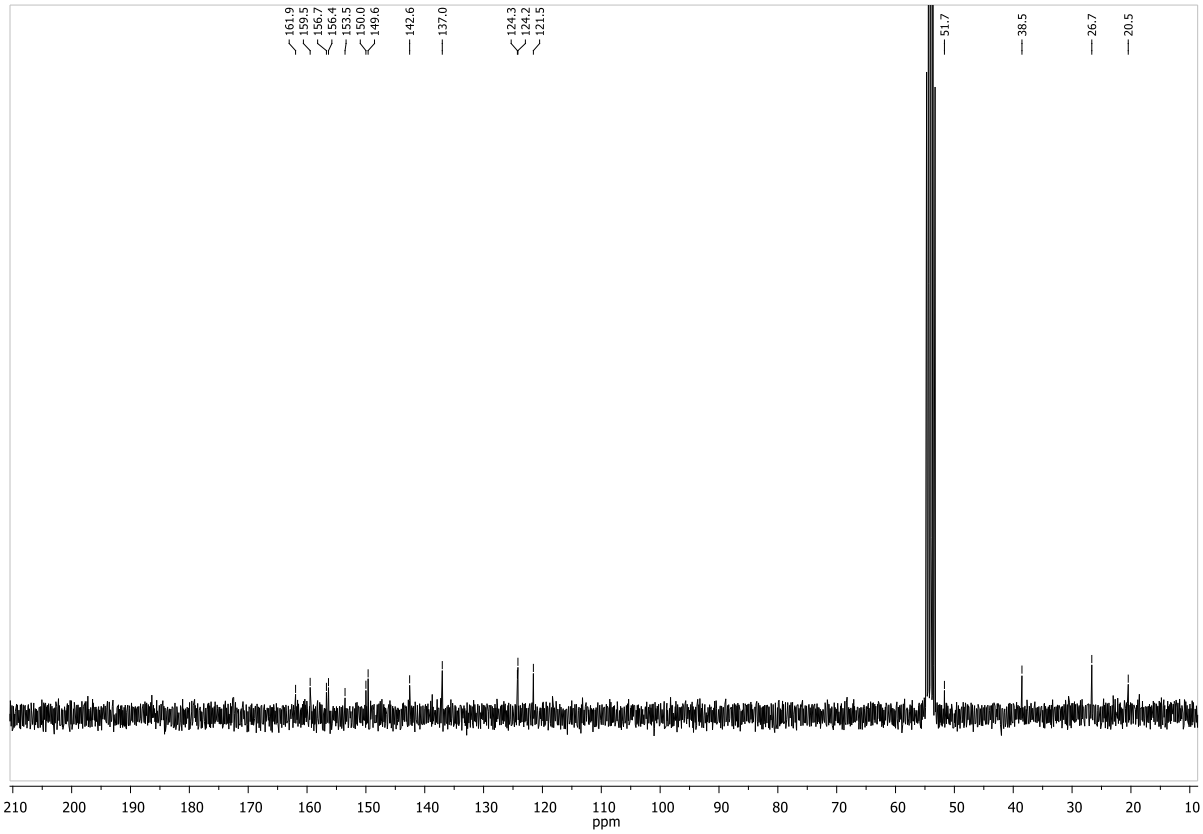


Figure S9: ^{13}C NMR spectrum of **2** in CD_2Cl_2.

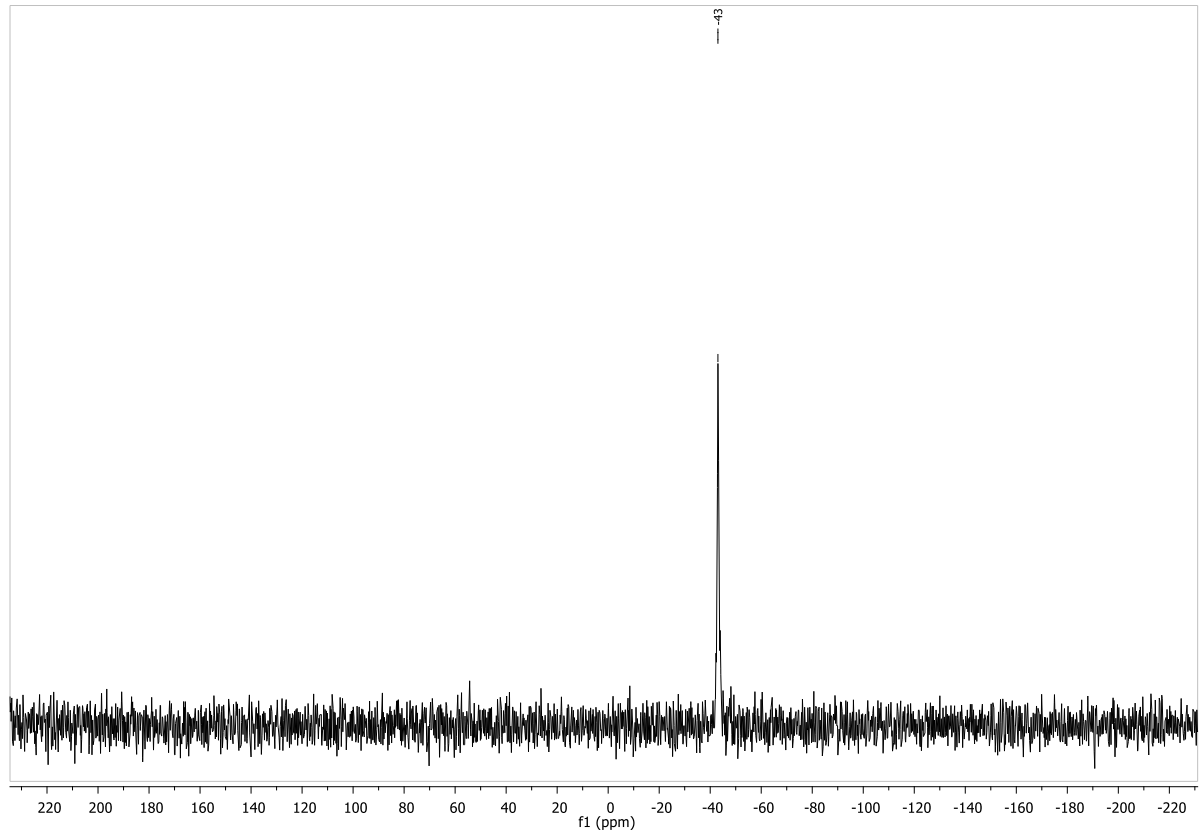


Figure S10: ^{119}Sn NMR spectrum of **2** in CD_2Cl_2.

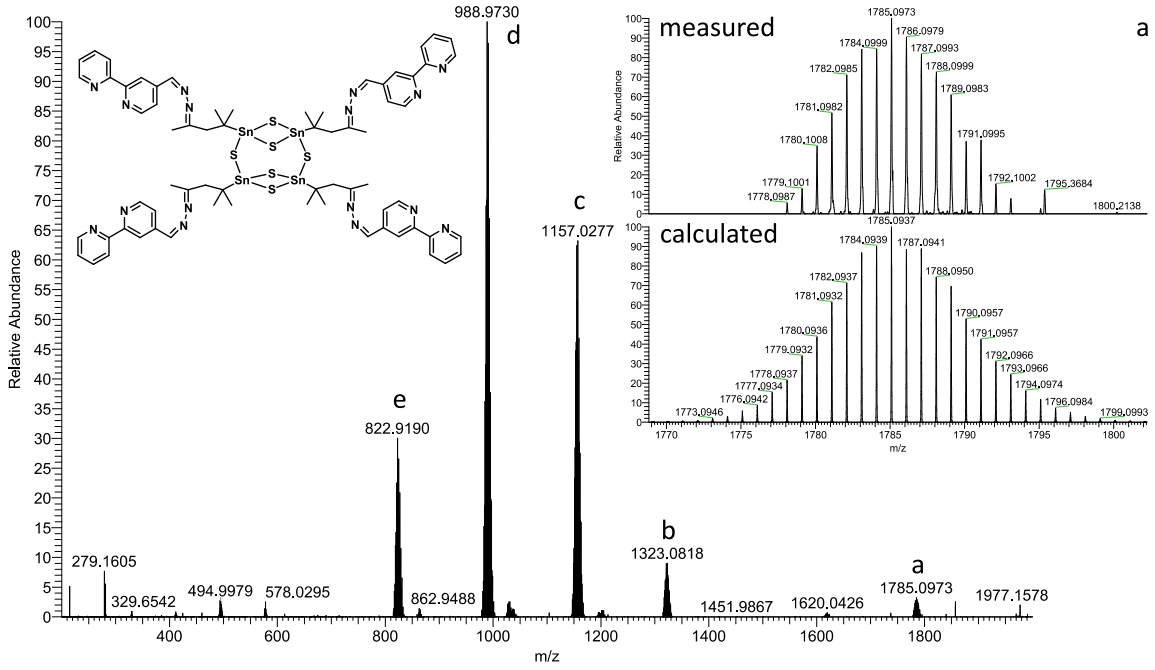


Figure S11: ESI^+ mass spectrum of a product solution of **2** with HR-MS spectrum and calculated isotopic pattern for compound **2** with the sum formula $[C_{68}H_{76}N_{16}S_6Sn_4\text{-}H]^+$.

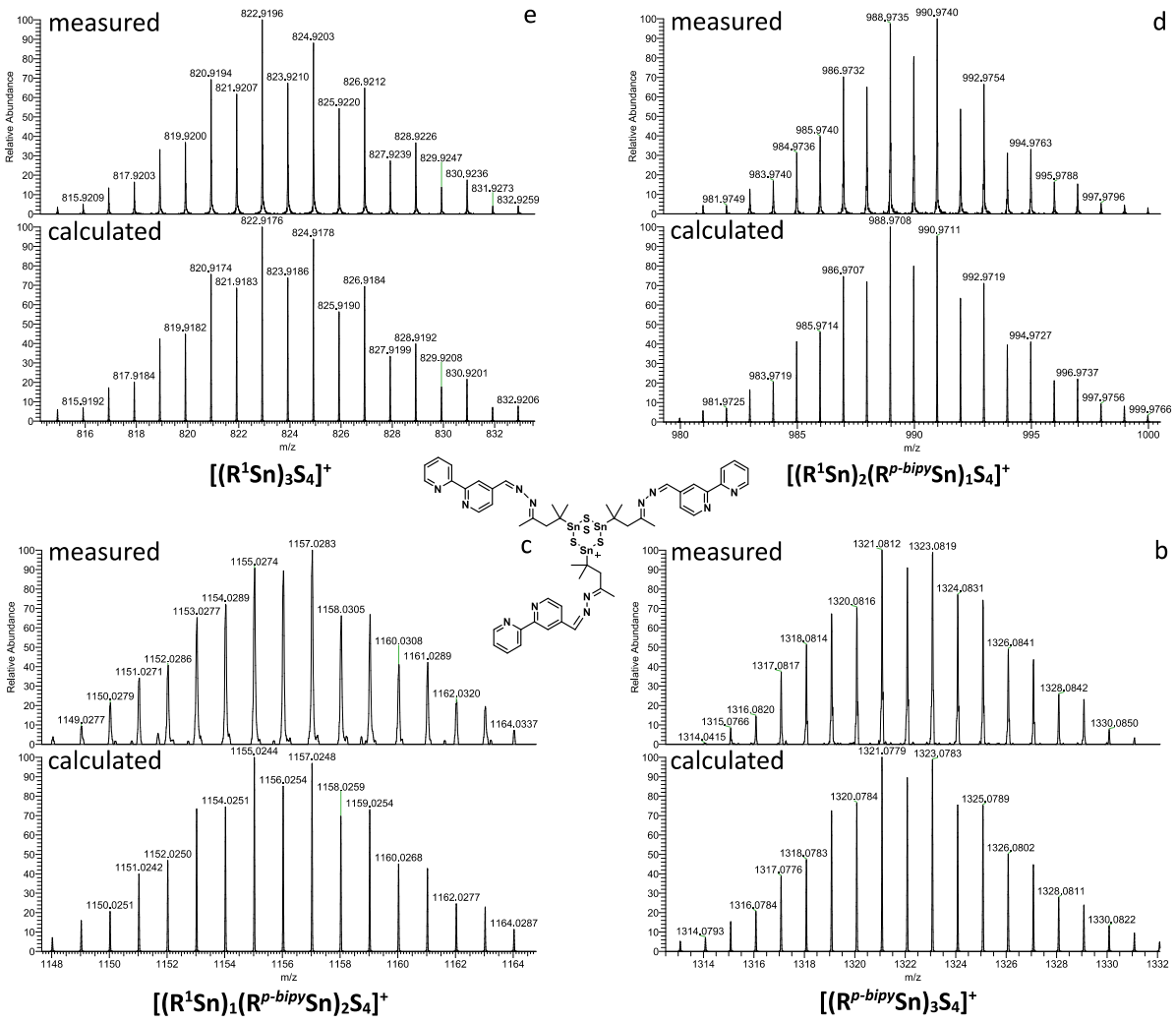


Figure S12: HR-ESI$^+$ mass spectra and calculated spectra of fragments detected in product solution of **2**. The four shown species originate from the known rearrangement of tinsulfide clusters in mass spectrometry measurements from the DD-like topology with the core composition $[Sn_4S_6]$ to the ionized DHC topology with the core composition $[Sn_3S_4]$. The four Signals arise from the DHC molecule with three (b), two (c), one (d) and zero (e) attached bipyridine ligands to it, which is determined by the matching of mass and isotopic pattern of measured and calculated spectra.

Synthesis of $[Zn(C_{12}H_7N_2CHO)Cl_2]_2$ (4)

To a solution of 1,10-phenanthroline-5-carboxaldehyde (71 mg, 0.34 mmol) in 25 mL DCM, a suspension of solid $ZnCl_2$ (46 mg, 0.33 mmol) in 5 mL DCM was added and the mixture stirred overnight. After filtration, the solution is layered with n-pentane and after several days' crystalline colorless bars of **4** can be found.

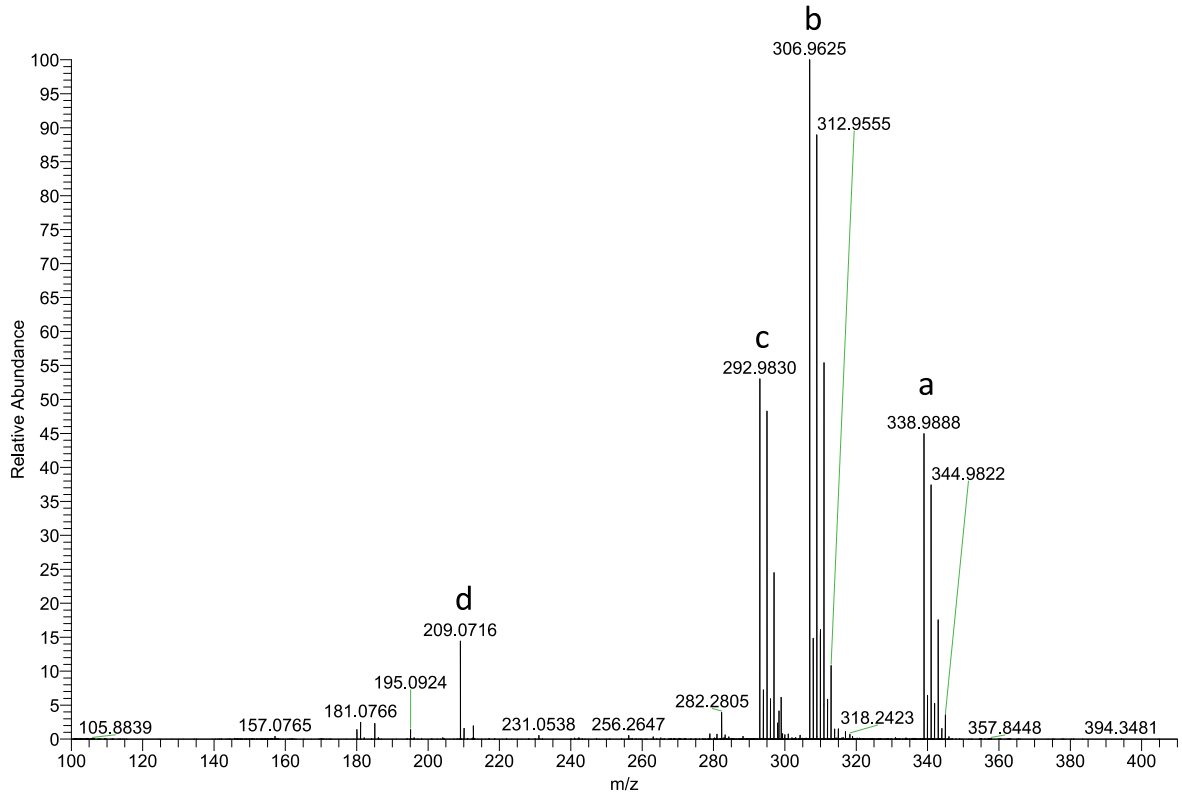


Figure S13: Overview ESI$^+$ mass spectrum of a product solution of **4**.

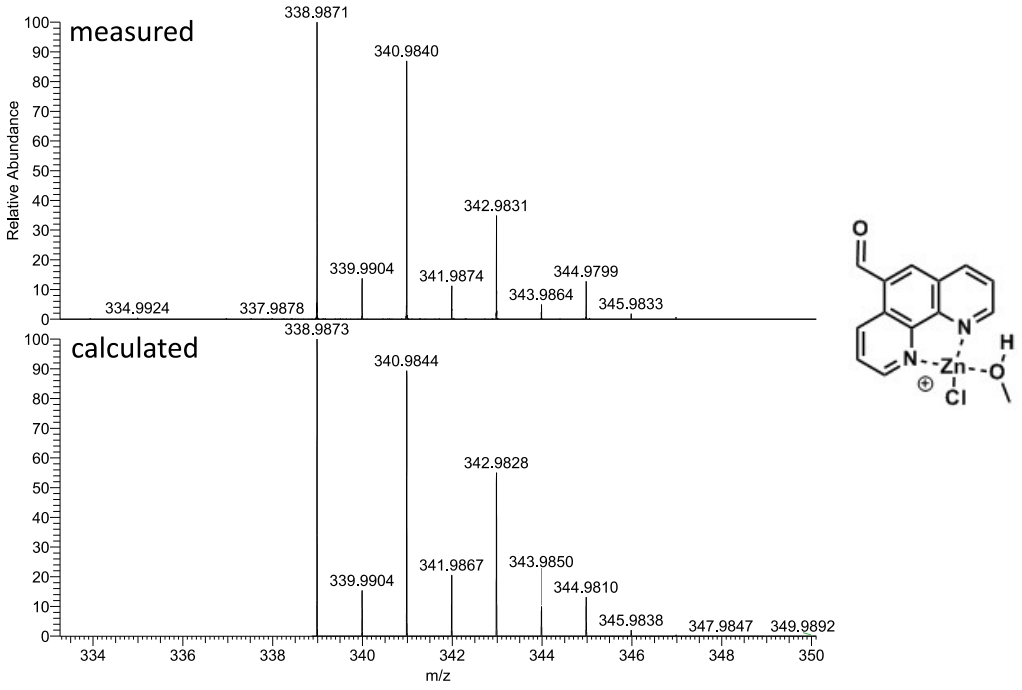


Figure S14: HR-ESI$^+$ mass spectrum and calculated isotopic pattern for fragment a with the sum formula $[C_{13}H_8N_2O\text{-}ZnCl\text{-}CH_3OH]^+$.

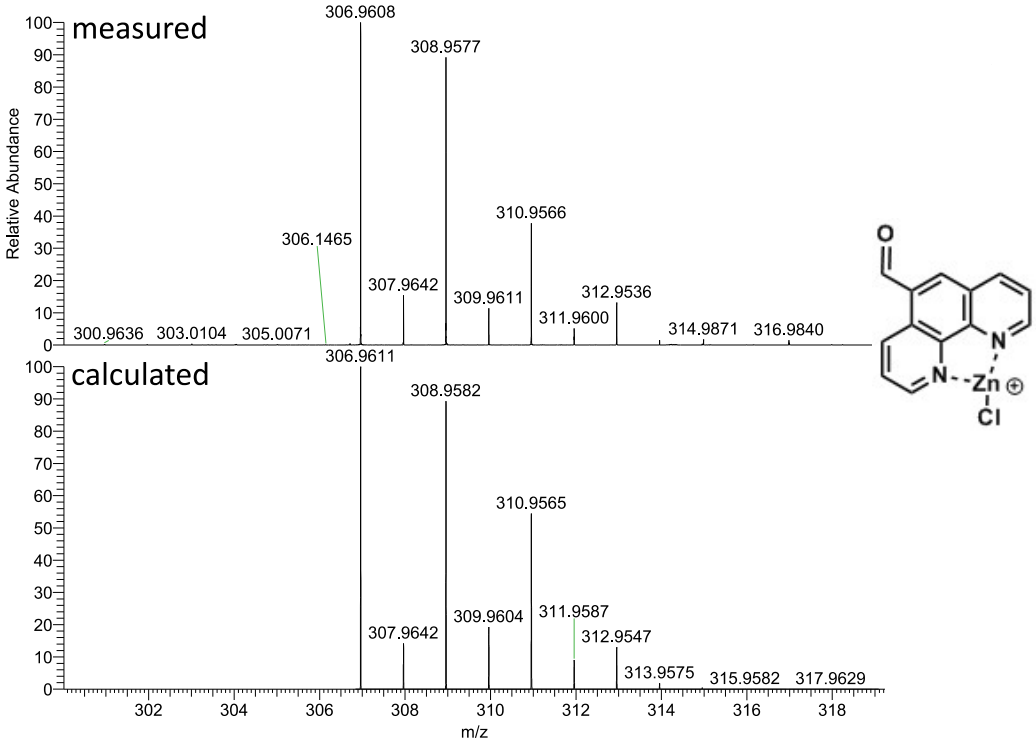


Figure S15: HR-ESI$^+$ mass spectrum and calculated isotopic pattern for fragment b with the sum formula $[C_{13}H_8N_2O\text{-}ZnCl]^+$.

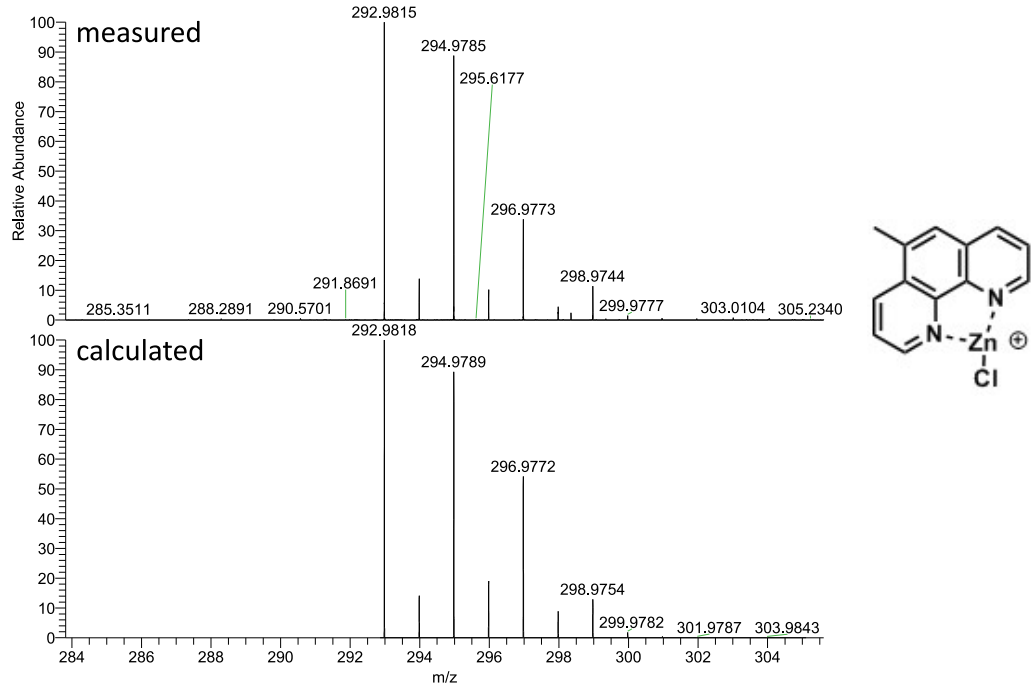


Figure S16: HR-ESI$^+$ mass spectrum and calculated isotopic pattern for fragment c with the sum formula $[C_{13}H_{10}N_2\text{-}ZnCl]^+$.

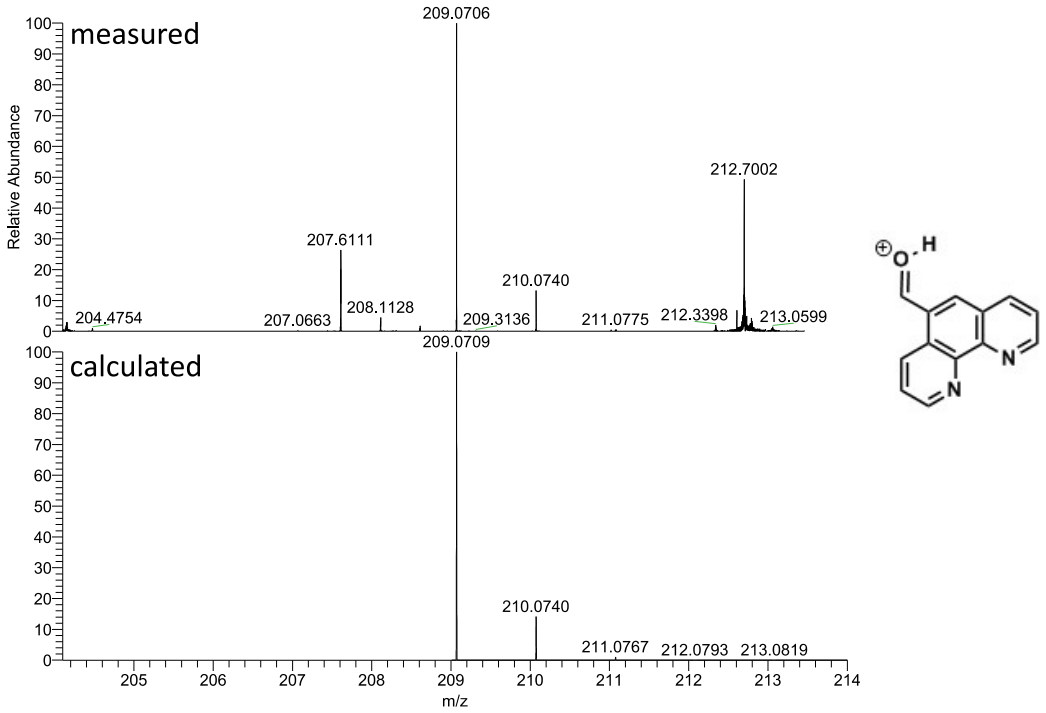


Figure S17: HR-ESI$^+$ mass spectrum and calculated isotopic pattern for fragment d with the sum formula $[C_{13}H_8N_2O\text{-}H]^+$.

Synthesis of $[(R^{p\text{-}bipy}ZnCl_2Sn)_4S_6]$(5) ($R^{p\text{-}bipy}$= $CMe_2CH_2C(Me)N\text{-}NC(H)\text{-}p\text{-}C_{10}H_7N_2$)

2 (50 mg, 0.028 mmol) was dissolved in 15 mL DCM. A suspension of solid $ZnCl_2$ (25 mg, 0.188 mmol) in 5 mL DCM was added to the solution. The solid dissolved throughout reaction and pale yellow crystals of **5** were formed after several weeks. The solubility of the product is insufficient for NMR measurements, but allows ESI$^+$-measurement. HRMS (ESI$^+$): m/z calc.: 2158.7088 $[M\text{-}ZnCl_3]^+$ found: 2158.7187.

The overview (Fig. S18) shows the mass spectrum after reaction of compound **2** with $ZnCl_2$. As the molecular compound has to be charged for a measurement, a chlorine atom is detached during ionization process. Three molecular Signals can be assigned to compound **5**. The molecule with the sum formula $(R^{p\text{-}bipy}Sn)_4S_6$ with one attached $ZnCl^+$ unit (c, m/z= 1484.98) is found as well as the molecule with a $ZnCl_2$ and a $ZnCl^+$ unit (b, m/z=2020.85) attached to it. And the highest molecule to be detected has two $ZnCl_2$ units and a $ZnCl^+$ unit (a, m/z=2156.71) attached to it. During the ionization process the DD-like topology molecules with the core composition $[Sn_4S_6]$ can undergo a rearrangement to the charged DHC topology with the core composition $[Sn_3S_4]$. These rearrangement products can be seen in this spectrum as the DHC-core with three (d), two (e) and one (f) bipyridine units attached to it.

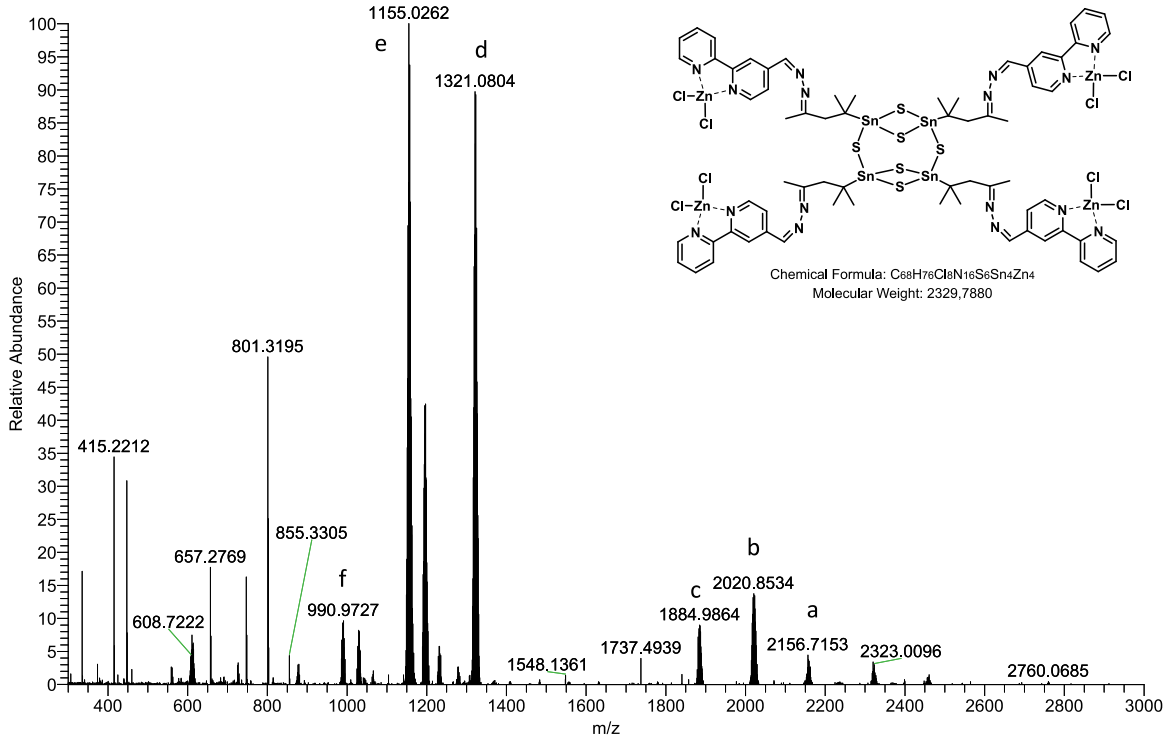


Figure S18: Overview ESI$^+$ mass spectrum of a product solution of **5**.

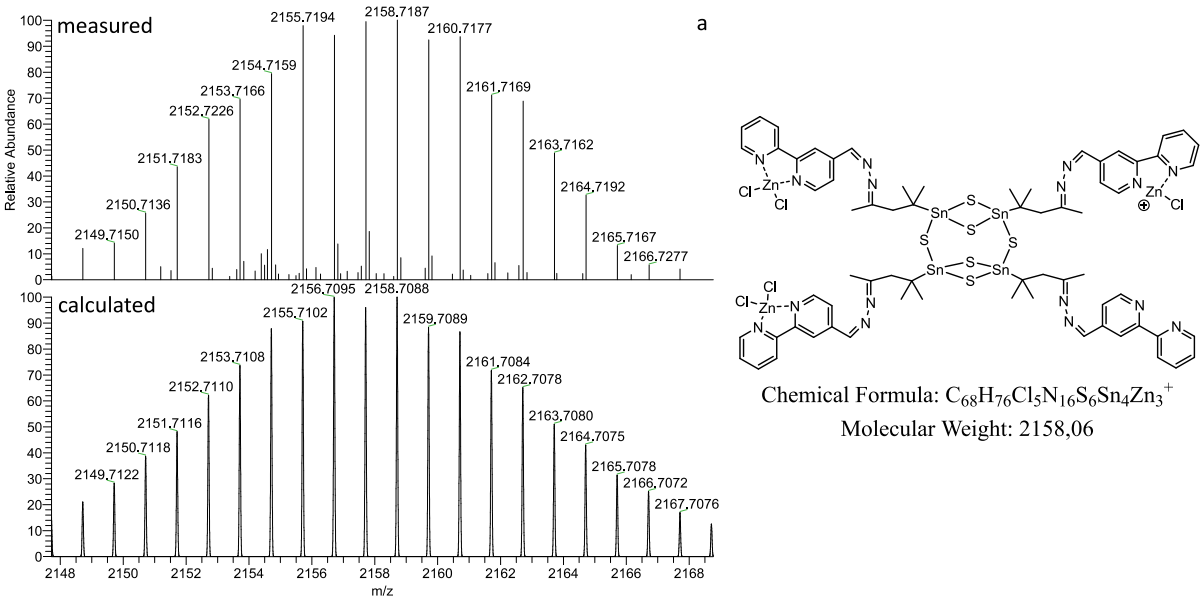
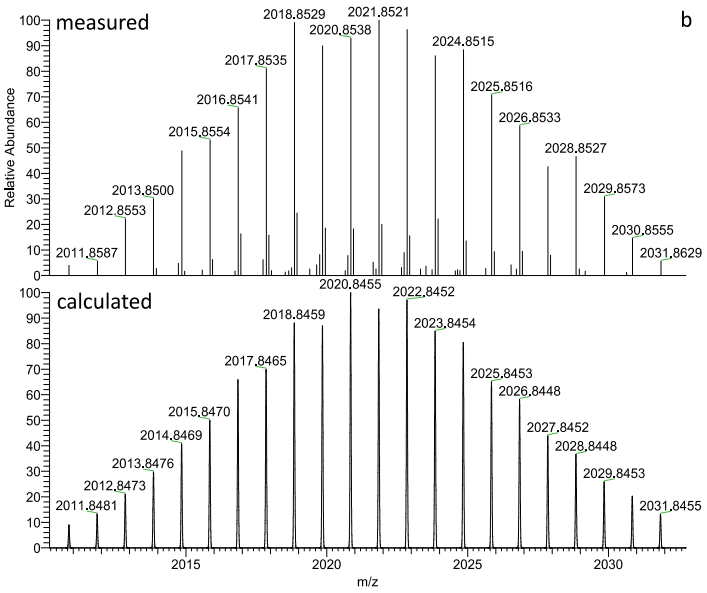
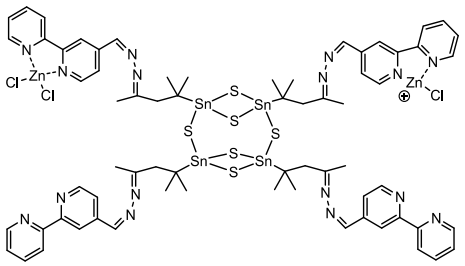


Figure S19: HR-ESI$^+$ mass spectrum and calculated isotopic pattern for fragment a with the sum formula $[C_{68}H_{76}N_{16}S_6Sn_4\text{-}Zn_3Cl_5]^+$.

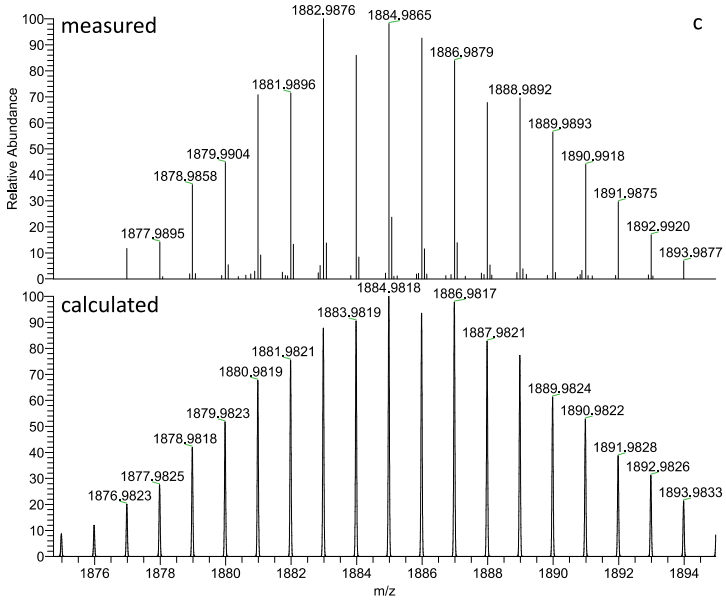


b

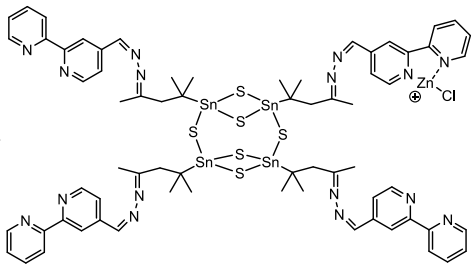


Chemical Formula: $C_{68}H_{76}Cl_3N_{16}S_6Sn_4Zn_2^+$
Molecular Weight: 2021,78

Figure S20: HR-ESI$^+$ mass spectrum and calculated isotopic pattern for fragment b with the sum formula $[C_{68}H_{76}N_{16}S_6Sn_4\text{-}Zn_2Cl_3]^+$.



c



Chemical Formula: $C_{68}H_{76}ClN_{16}S_6Sn_4Zn^+$
Molecular Weight: 1885,50

Figure S21: HR-ESI$^+$ mass spectrum and calculated isotopic pattern for fragment c with the sum formula $[C_{68}H_{76}N_{16}S_6Sn_4\text{-}ZnCl]^+$.

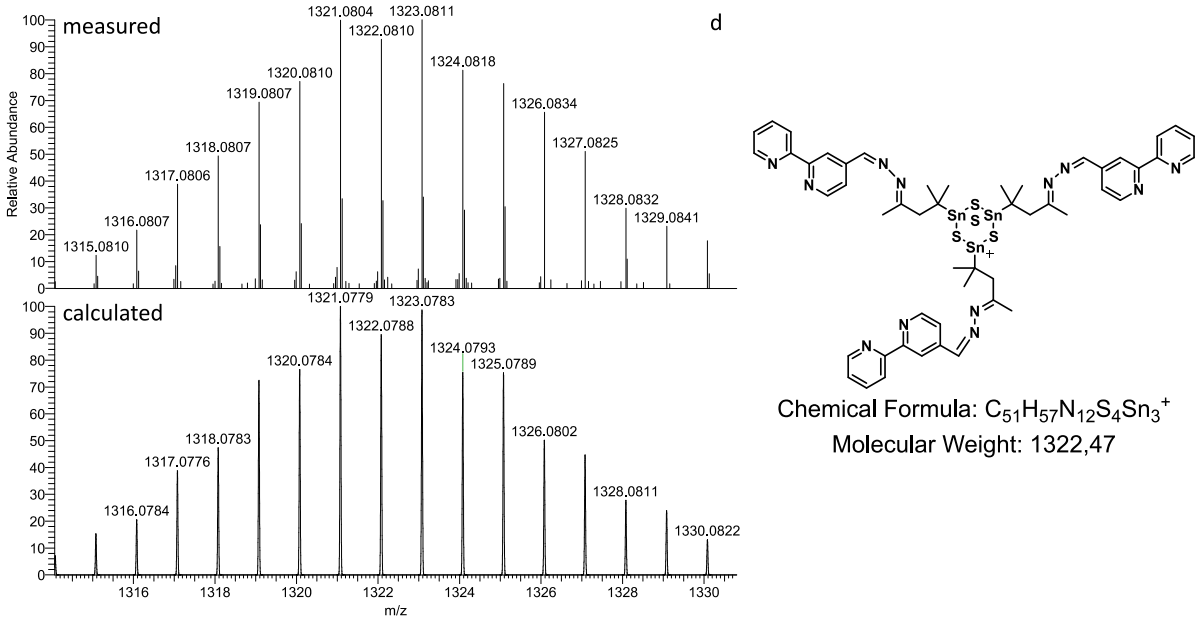


Figure S22: HR-ESI$^+$ mass spectrum and calculated isotopic pattern for fragment d with the sum formula $[C_{51}H_{57}N_{12}S_4Sn_3]^+$.

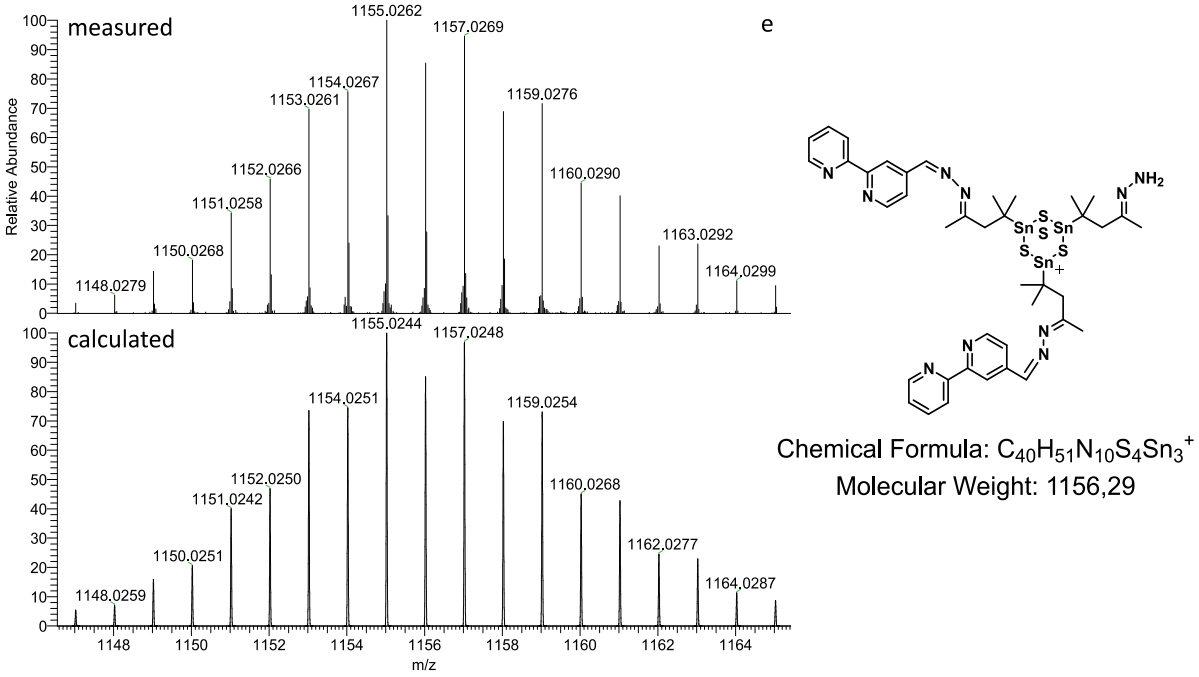


Figure S23: HR-ESI$^+$ mass spectrum and calculated isotopic pattern for fragment e with the sum formula $[C_{40}H_{51}N_{10}S_4Sn_3]^+$.

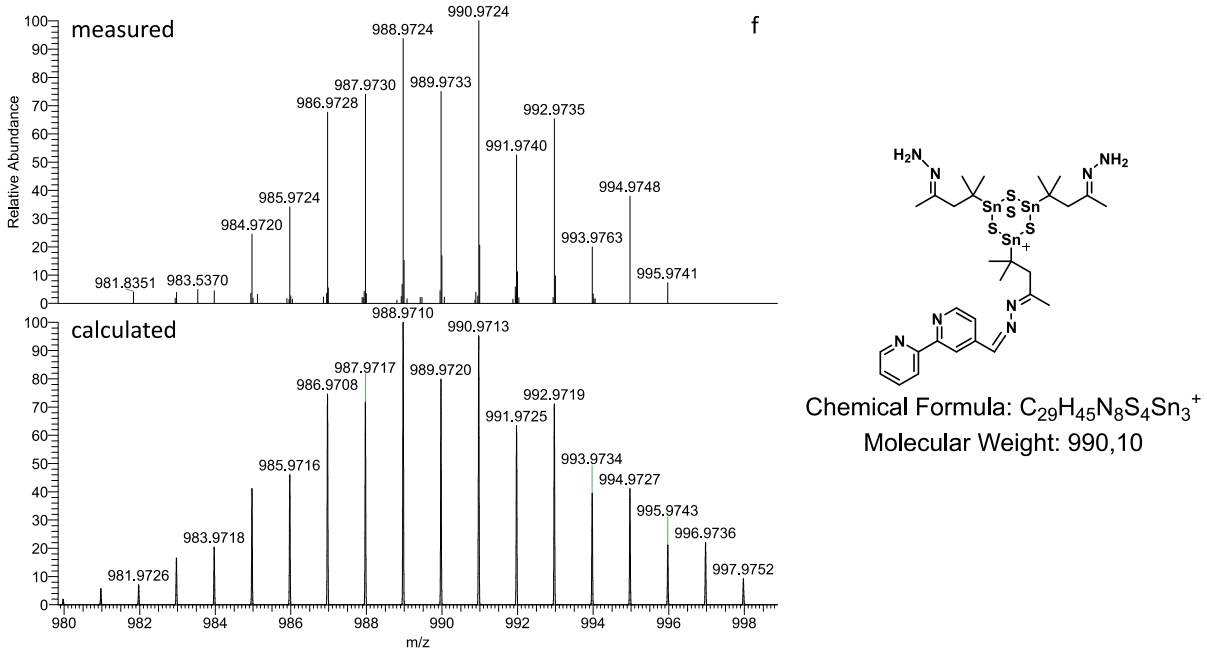


Figure S24: HR-ESI$^+$ mass spectrum and calculated isotopic pattern for fragment f with the sum formula $[C_{29}H_{45}N_8S_4Sn_3]^+$.

Synthesis of $C_{10}H_7N_2CHOZnCl_2$ (6)

To a solution of 2,2´bipyridine-4-carbaldehyde (30 mg, 0.162 mmol) in 3 mL DCM solid $ZnCl_2$ (56 mg, 0.41 mmol) was added and stirred for 2 days. The resulting solution was filtered and layered with *n*-hexane. Colorless crystals of **6** form within few days.

Synthesis of {Co[η^3-(N,N- Bipy)]Cl_2} (7)

A solution of **B** (20.6 mg, 0.009 mmol) in 6 mL DCM was layered with a solution of $[Co(PPh_3)_2Cl_2]$ (148.8 mg, 0.074 mmol) in 12 mL THF. Green Crystals of **7** form within few days.

Synthesis of [Ru(dmso)η^3-(N,N-Bipy)Cl_2] (8)

$[Ru(dmso)_4Cl_2]$ (52.4 mg, 0.01 mmol) was dissolved in 4 mL DCM, added to a solution of **B** (90.4 mg 0.041mmol) in 4 mL DCM and stirred at room temperature for 16 h. After filtration and layering with toluene crystals of **3** can be isolated.

2. Single crystal X-ray diffraction measurement and crystallographic details

a. General remarks

X-ray crystal structures of compound **1** to **6** were measured using a STOE StadiVari diffractometer applying a Cu-Kα X-ray radiation source (λ=1.54186). Single-crystal X-ray analysis of compound **7** and **8** were performed on a STOE IPDS 2T diffractometer applying a Mo-Kα X-ray source (λ= 0.71073 Å). All measurements were carried out at 100 K. Reflection Data were processed with X-Area 1[4]. The structures were solved by intrinsic Phase methods in SHELXT[5] and refined by full-matrix-least-squares refinement against F^2 in SHELXL [6] using the Olex2 [7] user interface. Non-carbon atoms in all structures are shown with thermal ellipsoids at 50% probability. Carbon atoms are drawn as wires, hydrogen atoms are omitted for clarity. Table S1 to S4 summarize data collection and refinement details.

Crystallographic data and refinement details

Table S1 Crystallographic data and refinement results of compound **1** and **2**.

compound	**1**	**2**
Empirical formula	$C_{79.5}H_{83}Cl_7N_{16}S_6Sn_4$	$C_{68}H_{77}N_{16}OS_6Sn_4$
Formula weight /g mol^{-1}	2177.88	1801.57
Crystal color, shape	light yellow, block	light yellow, plate
Crystal system	orthorhombic	monoclinic
Space group	$Pna2_1$	$P2/c$
a /Å	25.9881(11)	15.6802(3)
b /Å	22.3278(7)	20.3433(3)
c /Å	15.5336(5)	12.4505(2)
α /°	90	90
β /°	90	109.1940(10)
γ /°	90	90
V /Å^3	9013.5(6)	3750.77(11)
Z	4	2
ρ_{calc} /g·cm^{-3}	1.605	1.595
μ(Cu K$_\alpha$) / mm^{-1}	12.331	12.448
Absorption correction type	spherical	spherical
Min. / max. transmission	0.0099/0.0419	0.0970/0.8062
2Θ range / °	6.802-129.992	5.96-140.11
Reflections measured	138809	37792
R(int)	0.0726	0.0463
Independent reflections	15178	7353
Parameters	1094	497
Restraints	25	1
$R1/wR2$ ($I > 2\sigma(I)$)	0.0534/0.1306	0.0341/0.0850
$R1/wR2$ (all data)	0.0696/0.1366	0.0431/0.0885
GooF (all data)	0.910	0.986
Max. peak/hole /e$^-$·Å^{-3}	1.56/−0.57	0.802/−0.902
Flack Parameter	0.038(4)	
CCDC number	1989633	1989631

Table S2 Crystallographic data and refinement results of compound **3** and **4**.

compound	**3**	**4**
Empirical formula	$C_{22}H_{16}N_6$	$C_{26}H_{16}Cl_4N_4O_2Zn_2$
Formula weight /g mol^{-1}	364.41	688.97
Crystal color, shape	Colorless, block	Colorless, needle
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$C2/c$
a /Å	7.9437(5)	19.5229(5)
b /Å	10.9876(5)	18.0694(3)
c /Å	10.2274(5)	8.8084(2)
α /°	90	90
β /°	90.435(4)	102.320(2)
γ /°	90	90
V /Å^3	892.64(8)	3035.76(12)
Z	2	4
ρ_{calc} /g·cm^{-3}	1.356	1.507
μ(Cu K$_\alpha$) / mm^{-1}	0.678	5.427
Absorption correction type	spherical	spherical
Min. / max. transmission	0.893/0.935	0.497/0.812
2Θ range / °	11.822 - 142.134	9.274-144.672
Reflections measured	14268	27673
R(int)	0.0375	0.0502
Independent reflections	1725	2983
Parameters	127	172
Restraints	0	0
$R1/wR2$ ($I > 2\sigma(I)$)	0.0320/0.0750	0.0309/0.0768
$R1/wR2$ (all data)	0.0510/0.0788	0.0375/0.0784
GooF (all data)	0.939	0.902
Max. peak/hole /e$^-$·Å^{-3}	0.18/−0.14	0.28/−0.58
CCDC number	1989628	1989630

Table S3 Crystallographic data and refinement results of compound **5** and **6**.

compound	**5**	**6**
Empirical formula	$C_{68}H_{76}Cl_8N_{16}S_6Sn_4Zn_4$	$C_{11}H_8Cl_2N_2OZn$
Formula weight /g mol^{-1}	2329.64	320.46
Crystal color, shape	Light yellow, plate	colorless, plate
Crystal system	Tetragonal	triclinic
Space group	$P4_22_12$	$P\bar{1}$
a /Å	23.7332(11)	8.2052(6)
b /Å	23.7332(11)	8.6043(5)
c /Å	11.4025(7)	9.7408(6)
α /°	90	98.959(5)
β /°	90	97.490(6)
γ /°	90	115.238(5)
V /Å^3	6422.6(7)	599.38(7)
Z	2	2
ρ_{calc} /g·cm^{-3}	1.205	1.776
μ(Cu K$_\alpha$) / mm^{-1}	9.598	6.812
Absorption correction type	spherical	spherical
Min. / max. transmission	0.0001/0.0136	0.0219/0.3306
2*Θ* range / °	8.604-84.848	9.422-134.99
Reflections measured	25938	10770
R(int)	0.0686	0.1034
Independent reflections	2233	2150
Parameters	218	154
Restraints	132	0
*R*1/*wR*2 ($I > 2\sigma(I)$)	0.0868/0.2081	0.0487/0.1049
*R*1/*wR*2 (all data)	0.1108/0.2328	0.0883/0.1115
GooF (all data)	0.947	0.763
Max. peak/hole /e$^-$·Å^{-3}	0.59/−0.39	0.55/−0.35
Flack parameter	0.06(4)	–
CCDC number	1989635	1989629

Table S4 Crystallographic data and refinement results of compound **7** and **8**.

compound	**7**	**8**
Empirical formula	$C_{12}H_{12}Cl_2CoN_4$	$C_{35}H_{44}Cl_4N_8O_2Ru_2S_2$
Formula weight /g mol^{-1}	342.09	1016.84
Crystal color, shape	Dark green, block	Brown block
Crystal system	monoclinic	triclinic
Space group	*P*2/*c*	$P\bar{1}$
a /Å	10.6519(10)	8.2648(10)
b /Å	8.1804(6)	10.0946(9)
c /Å	15.5453(15)	12.9476(16)
α /°	90	104.143(9)
β /°	97.892(8)	101.316(10)
γ /°	90	100.545(9)
V /Å^3	1341.7(2)	996.4(2)
Z	4	1
ρ_{calc} /g·cm^{-3}	1.693	1.695
μ(Mo K_α) / mm^{-1}	1.666	1.175
Absorption correction type	numerical	numerical
Min. / max. transmission	0.1046/0.1275	0.813, 0.934
2*Θ* range / °	3.860-53.834	4.614 - 51.222°
Reflections measured	9641	7900
R(int)	0.0490	0.0350
Independent reflections	2841	3682
Parameters	174	248
Restraints	0	0
*R*1/*wR*2 ($I > 2\sigma(I)$)	0.0461/0.1050	0.0295/0.0763
*R*1/*wR*2 (all data)	0.0805/0.1124	0.0347/0.0785
GooF (all data)	0.786	1.050
Max. peak/hole /e$^-$·Å^{-3}	0.80/−0.42	1.13/−0.40
CCDC number	1989632	1989634

b. Supplementary crystal structure figures

Molecular structure and packing diagram of compound 1

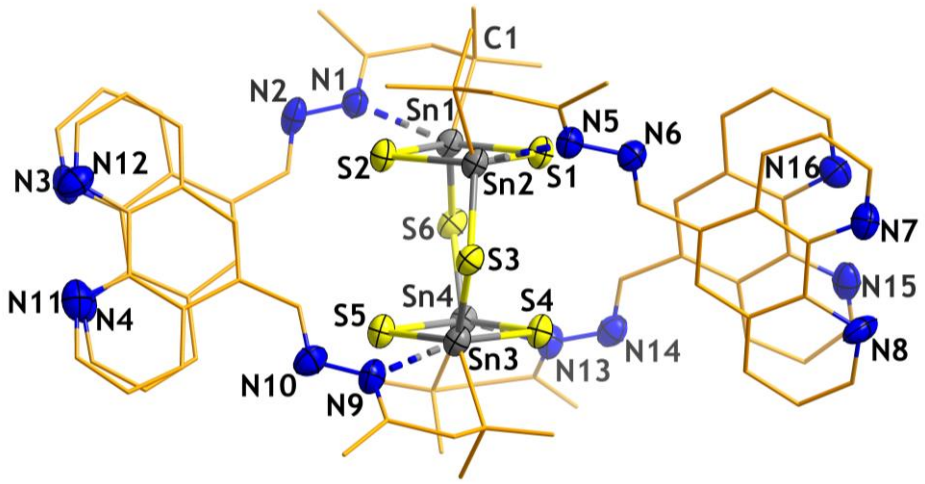


Figure S25: Molecular structure of compound **1** in side view, shown without the inorganic part of the minor disordered domains. Thermal ellipsoids are shown at 50% probability, carbon atoms drawn as wires and hydrogen atoms omitted for clarity. The cocrystallised 3.5 molecules of CH_2Cl_2 also omitted.

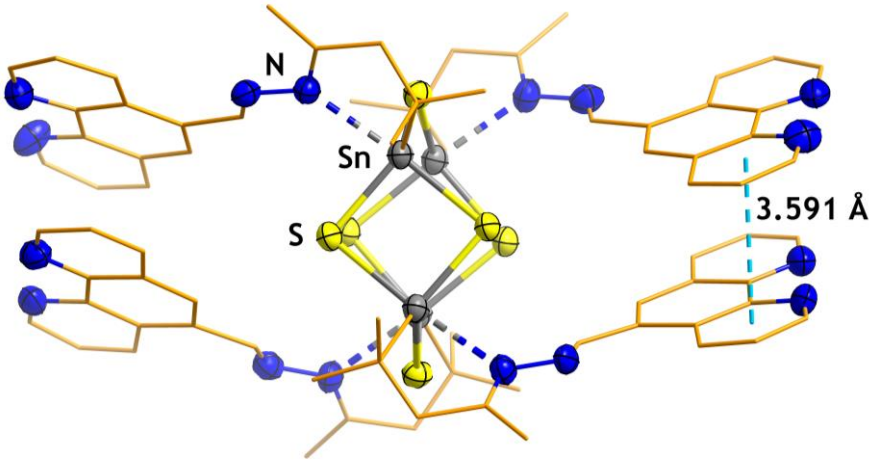


Figure S26: Molecular structure of compound **1** in top view shown without the inorganic part of the minor disordered domains. Thermal ellipsoids are shown at 50% probability, carbon atoms drawn as wires and hydrogen atoms omitted for clarity. The cocrystallised 3.5 molecules of CH_2Cl_2 also omitted. The shortest centroid distance of the organic ligands is highlighted.

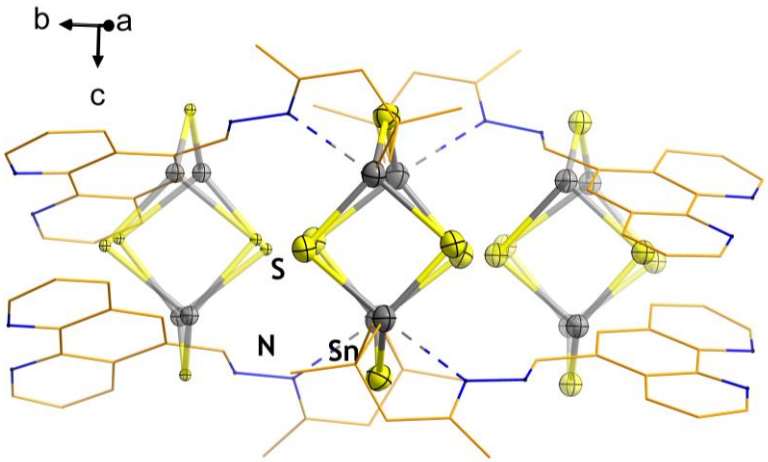


Figure S27: Molecular structure of compound **1** in top view, shown with the inorganic part of the minor disordered domains. The crystal structure exhibits three domains with refined occupancies of 90.82%, 6.5% and 2.68%, respectively. During the refinement of the major domain, we found thermal displacement parameters of C19, C27, C46 and C76 to be unusually elongated. Isotropic refinement revealed electron densities in close proximity which were attributed to Sn ions of domains 2 (Sn1A, Sn2A) and 3 (Sn3B, Sn4B). Subsequently, sulfur atoms of the minor domains were located from difference fourier maps. The disorder affects the whole molecule, but as the minor parts sum up to an occupancy of 9.18% the lighter atoms cannot be found and refined. The disordered molecules are shifted along the *b* axis by 4.45-4.54 Å and in the *ab*-plane by 1.96-1.97 Å (See Figure S28) Thermal ellipsoids are shown at 50% probability, carbon and nitrogen atoms drawn as wires and hydrogen atoms omitted for clarity. The co-crystallised 3.5 molecules of CH_2Cl_2 also omitted.

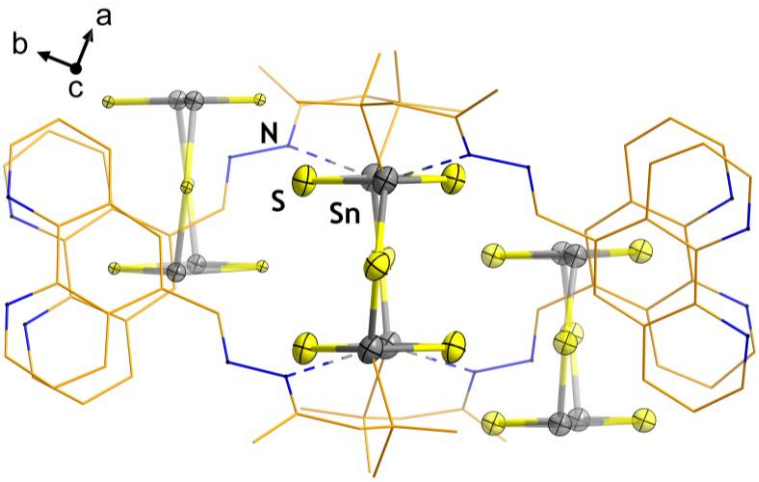


Figure S28: Molecular structure of compound **1** in side view, shown with the inorganic part of the minor disordered domains. The crystal structure comprises three domains, with the main part having an occupancy of 90.82%, the second part an occupancy of 6.5% and the third part with an occupancy of 2.68%. The disorder affects the whole molecule, but as the minor parts sum up to an occupancy of 9.18% the lighter atoms cannot be found and refined. The disordered molecules are shifted along the *ab* plane by 1.96-1.97 Å, which corresponds to half the height of the molecule. Thermal ellipsoids are shown at 50% probability, carbon and nitrogen atoms drawn as wires and hydrogen atoms omitted for clarity. The cocrystallised 3.5 molecules of CH_2Cl_2 also omitted.

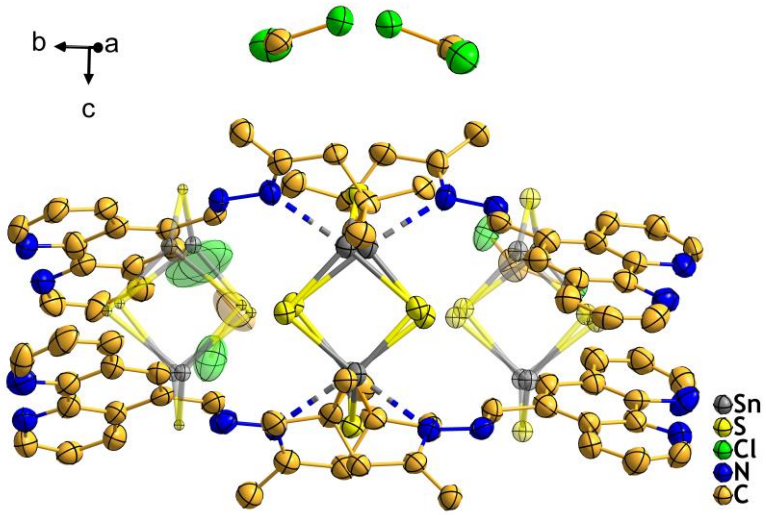


Figure S29: Asymetric unit in the crystal structure of compound **1**, disorderd inorganic part and cocrystallised CH_2Cl_2 molecules displayed. Not fully occupied positions are shown semi transparent. Thermal ellipsoids are shown at 50% probability.

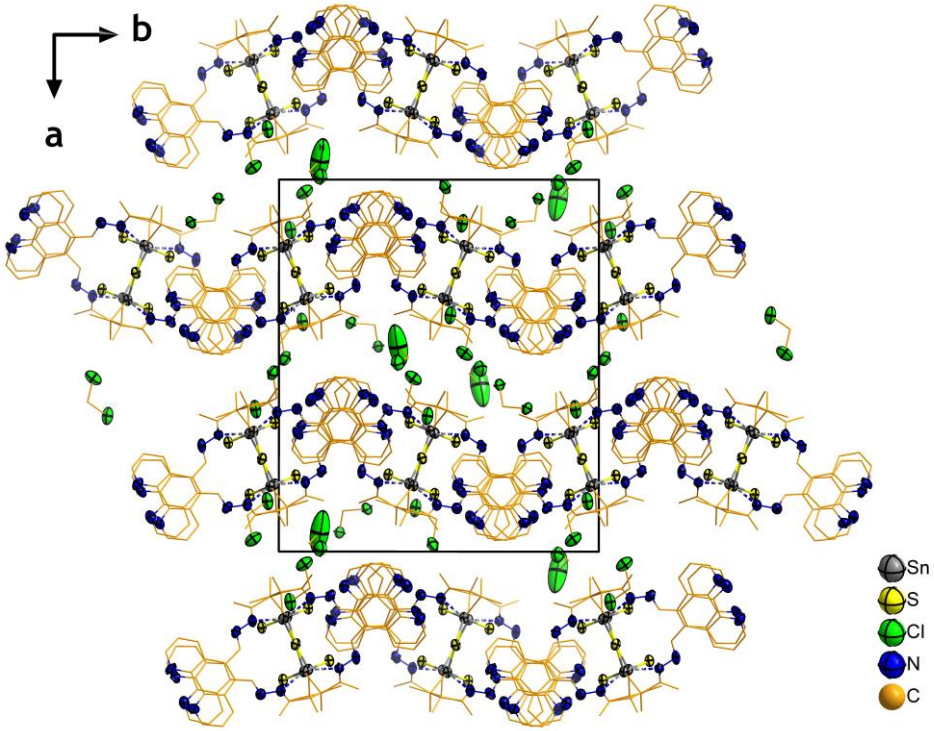


Figure S30: Packing of molecules of compound **1** in the unit cell with view along [001] shown without the inorganic part of the minor disordered domains. Thermal ellipsoids are shown at 50% probability, carbon atoms drawn as wires and hydrogen atoms omitted for clarity.

Molecular structure and packing diagram of compound 2

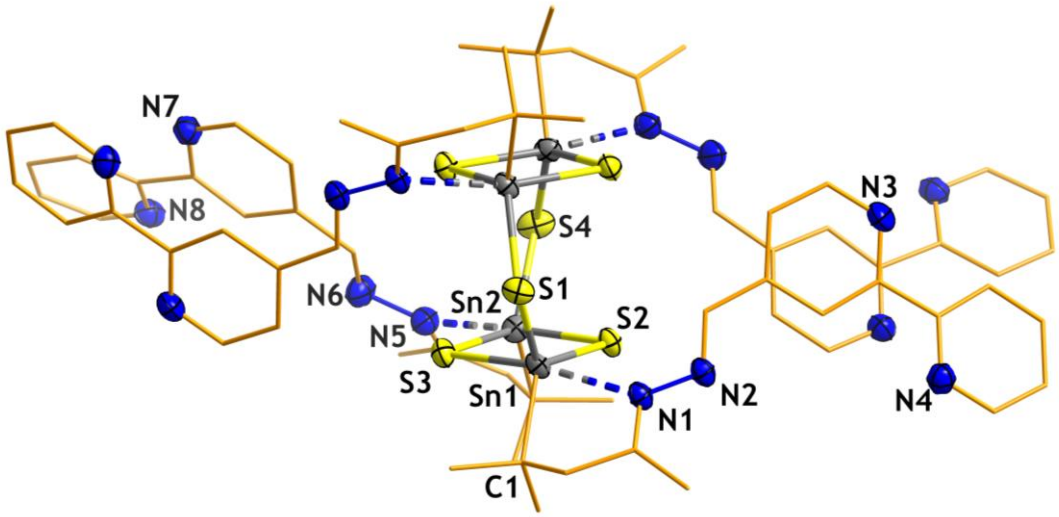


Figure S31: Molecular structure of compound **2** in side view shown without the disorder in the organic chain connecting the bypiridin ligand to the tinsulfide-core. Thermal ellipsoids are shown at 50% probability, carbon atoms drawn as wires and hydrogen atoms omitted. The cocrystallised water molecule is also omitted.

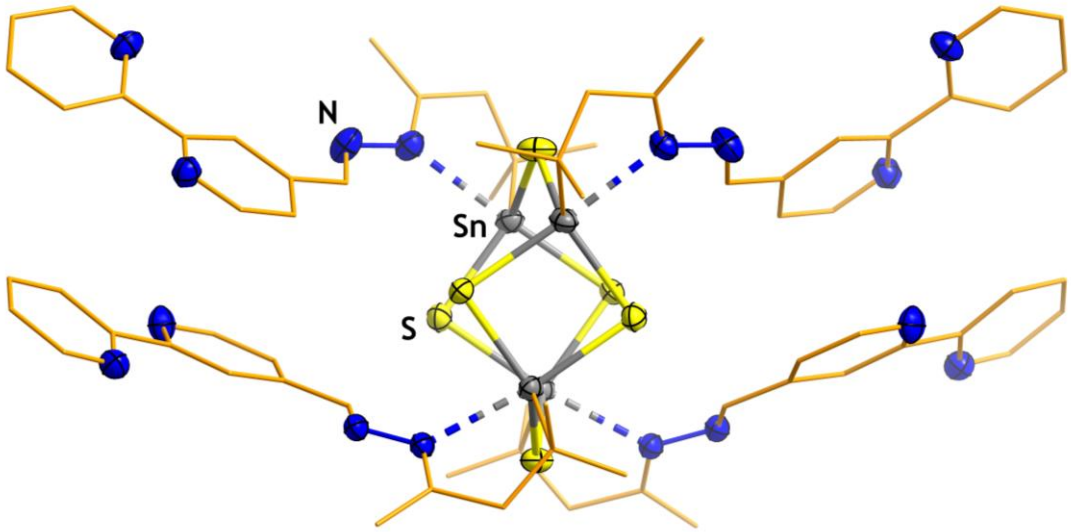


Figure S32: Molecular structure of compound **2** in top view shown without the disorder in the organic chain connecting the bypiridin ligand to the tinsulfide-core. Thermal ellipsoids are shown at 50% probability, carbon atoms drawn as wires and hydrogen atoms omitted. The cocrystallised water molecule is also omitted.

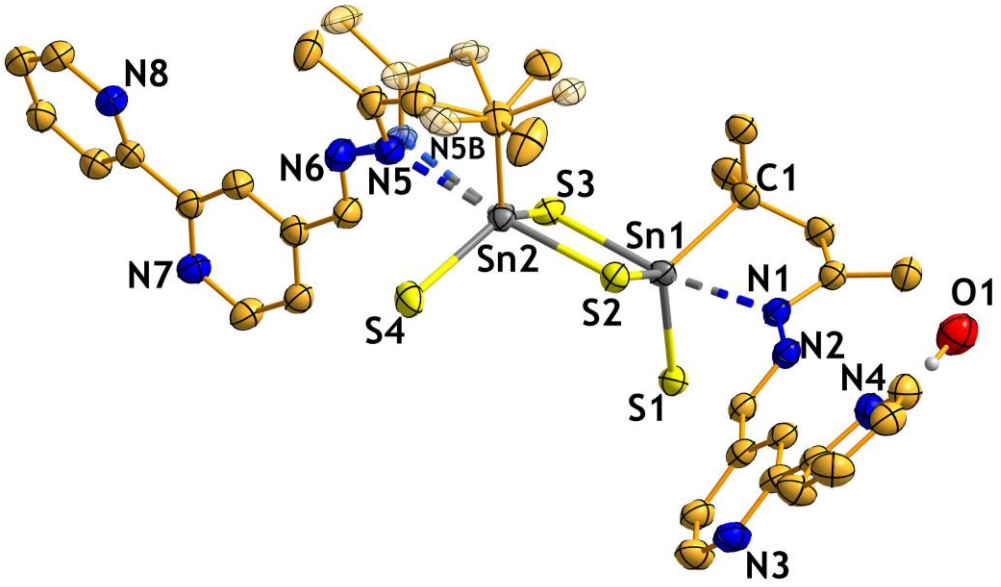


Figure S33: Asymetric unit in the crystal structure of compound **2**, disorderd organic part and cocrystallised water molecule displayed. Thermal ellipsoids are shown at 50% probability.

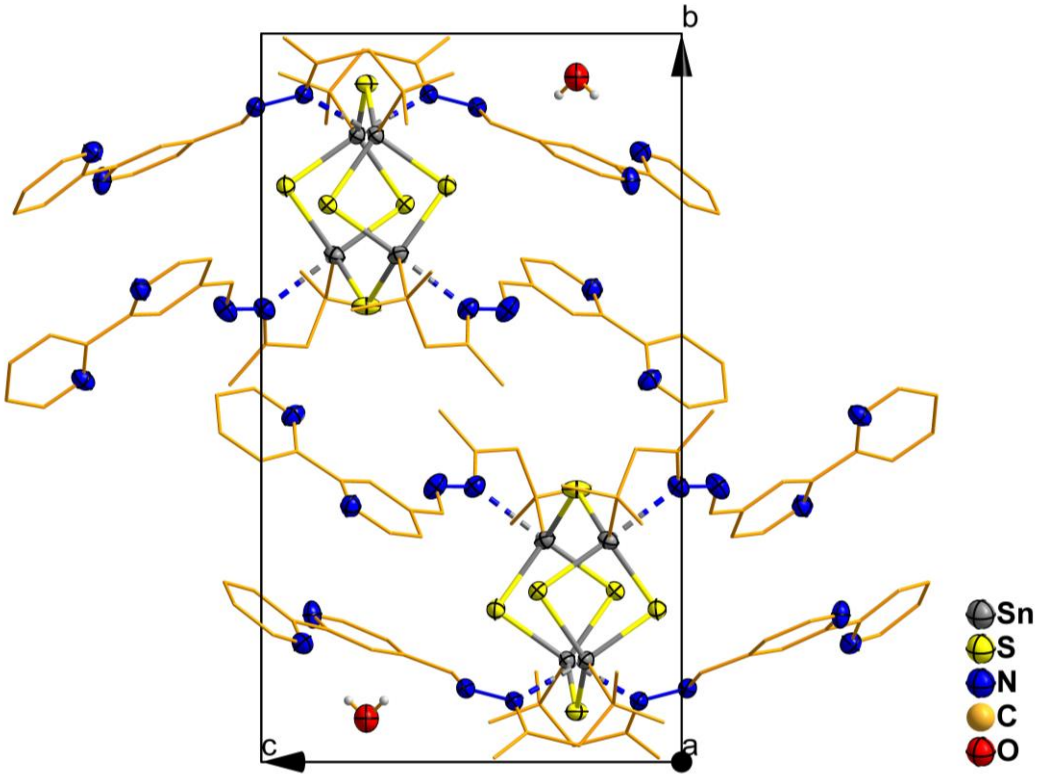


Figure S34: Packing of molecules of compound **2** in the unit cell with view along [100]. Thermal ellipsoids are shown at 50% probability, carbon atoms drawn as wires and hydrogen atoms omitted for clarity.

Molecular structure and packing diagram of compound 3

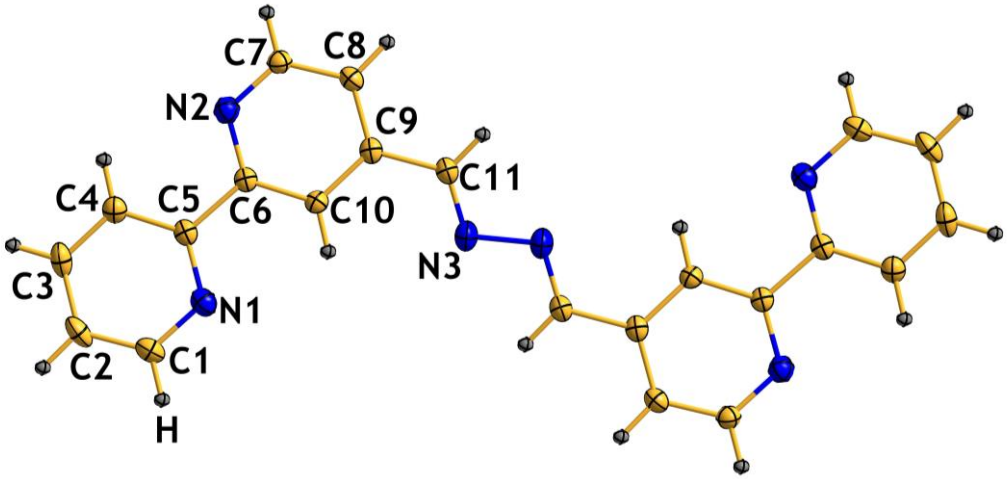


Figure S35: Molecular structure of compound **3**. Thermal ellipsoids are shown at 50% probability.

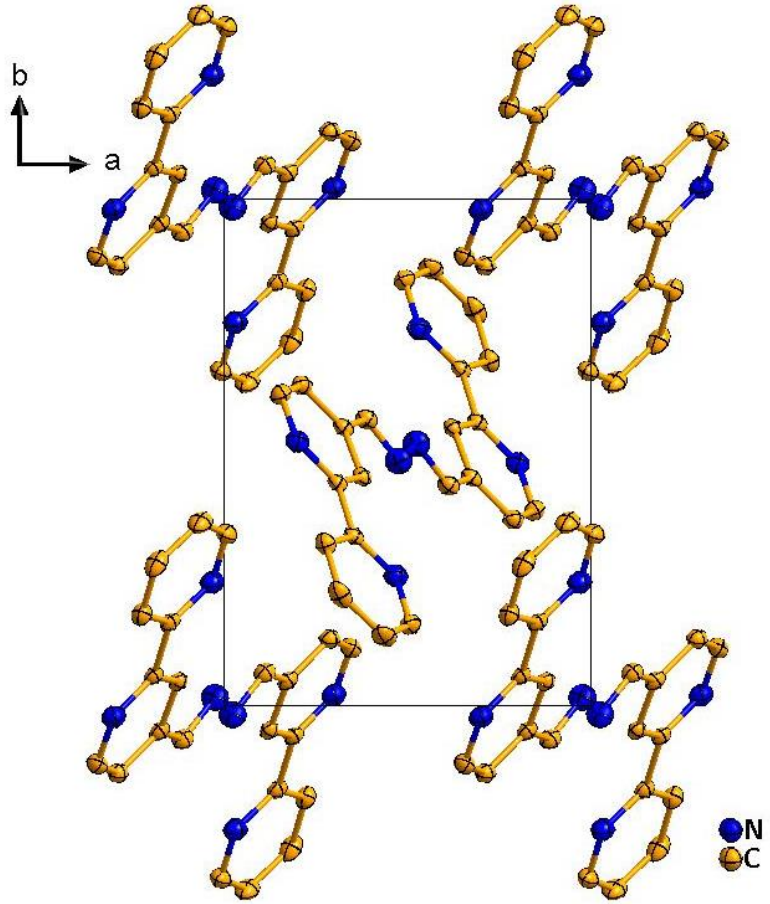


Figure S36: Packing of molecules of compound **3** in the unit cell with view along [001]. Thermal ellipsoids are shown at 50% probability, hydrogen atoms omitted for clarity.

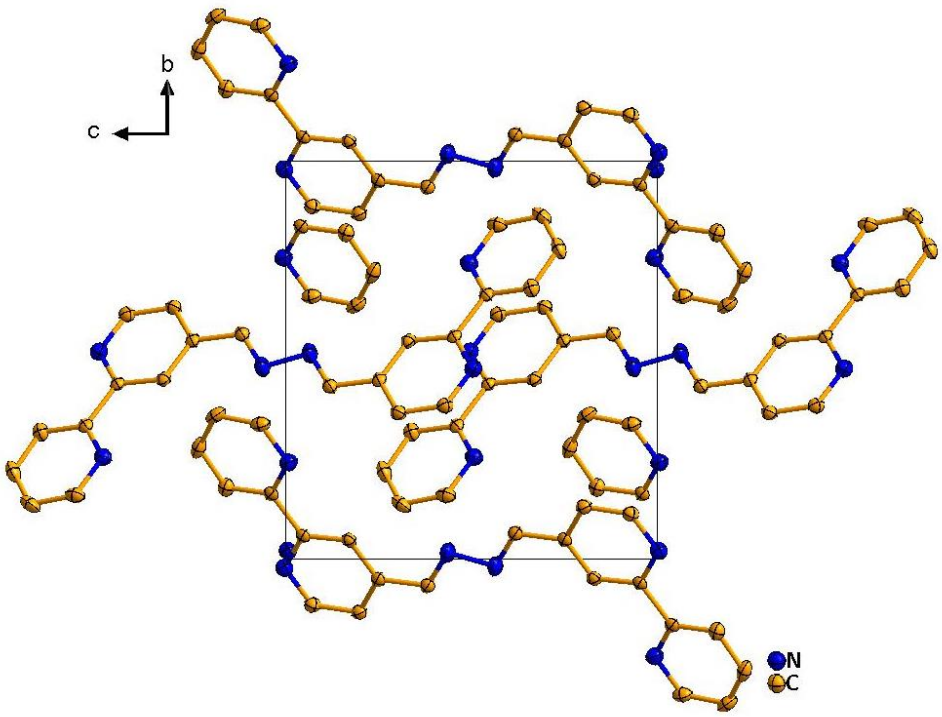


Figure S37: Packing of molecules of compound **3** in the unit cell with view along [100]. Thermal ellipsoids are shown at 50% probability, hydrogen atoms omitted for clarity.

Molecular structure and packing diagram of compound 4

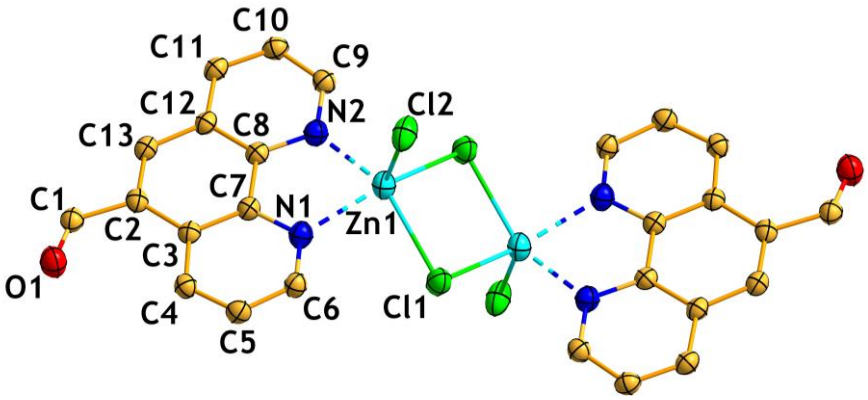


Figure S38: Molecular structure of compound **4**. Thermal ellipsoids are shown at 50% probability, carbon atoms drawn as wires and hydrogen atoms omitted.

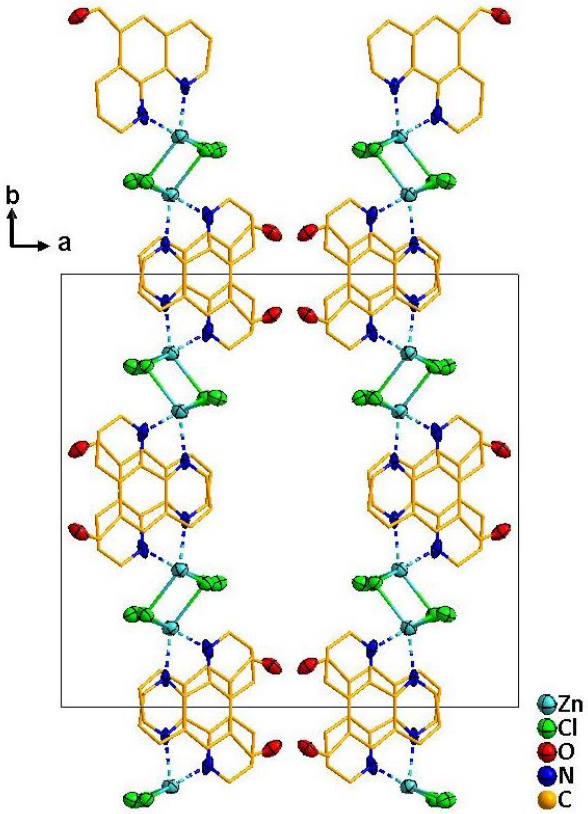


Figure S39: Packing of molecules of compound **4** in the unit cell with view along [001]. Thermal ellipsoids are shown at 50% probability, carbon atoms drawn as wires and hydrogen atoms omitted for clarity.

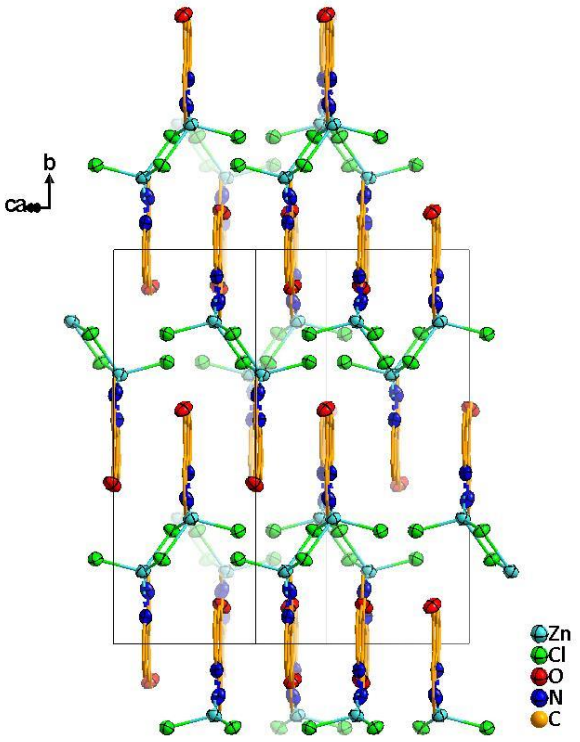


Figure S40: Packing of molecules of compound **4** in the unit cell. Thermal ellipsoids are shown at 50% probability, carbon atoms drawn as wires and hydrogen atoms omitted for clarity.

Molecular structure and packing diagram of compound 5

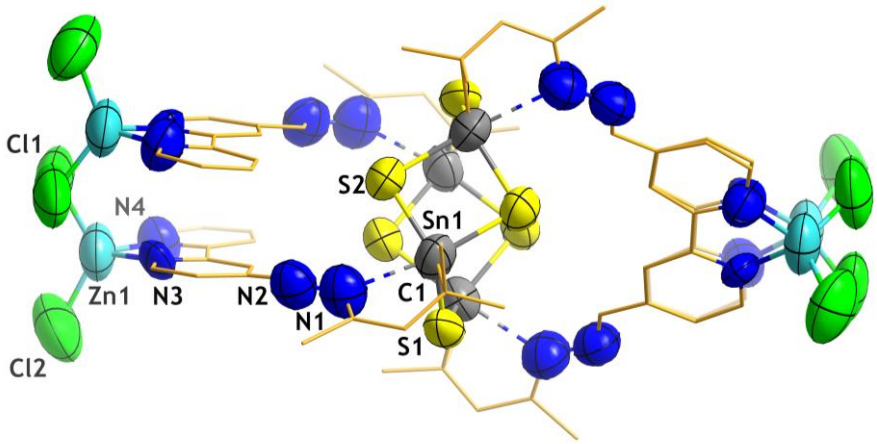


Figure S41: Molecular structure of compound **5** in top view. Thermal ellipsoids are shown at 50% probability, carbon atoms drawn as wires and hydrogen atoms omitted for clarity.

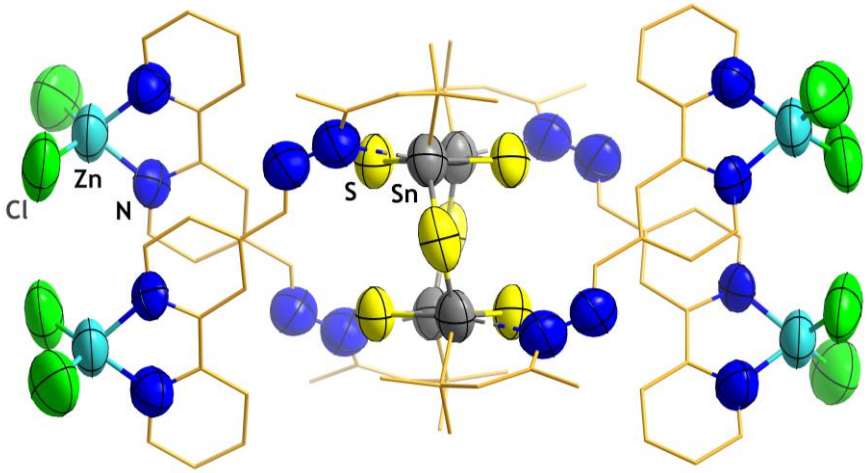


Figure S42: Molecular structure of compound **5** in side view. Thermal ellipsoids are shown at 50% probability, carbon atoms drawn as wires and hydrogen atoms omitted for clarity.

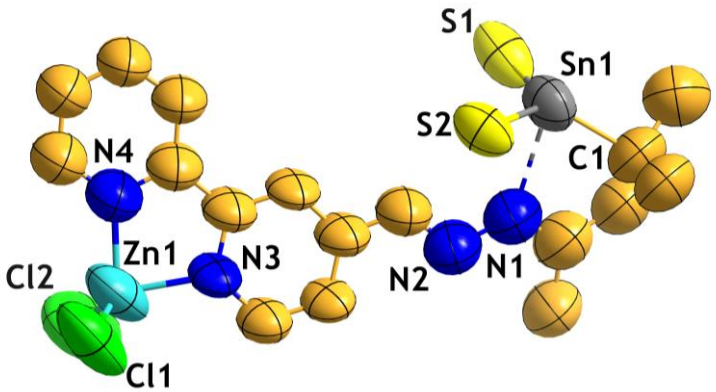


Figure S43: Asymetric unit in the crystal structure of compound **5**. Thermal ellipsoids are shown at 50% probability.

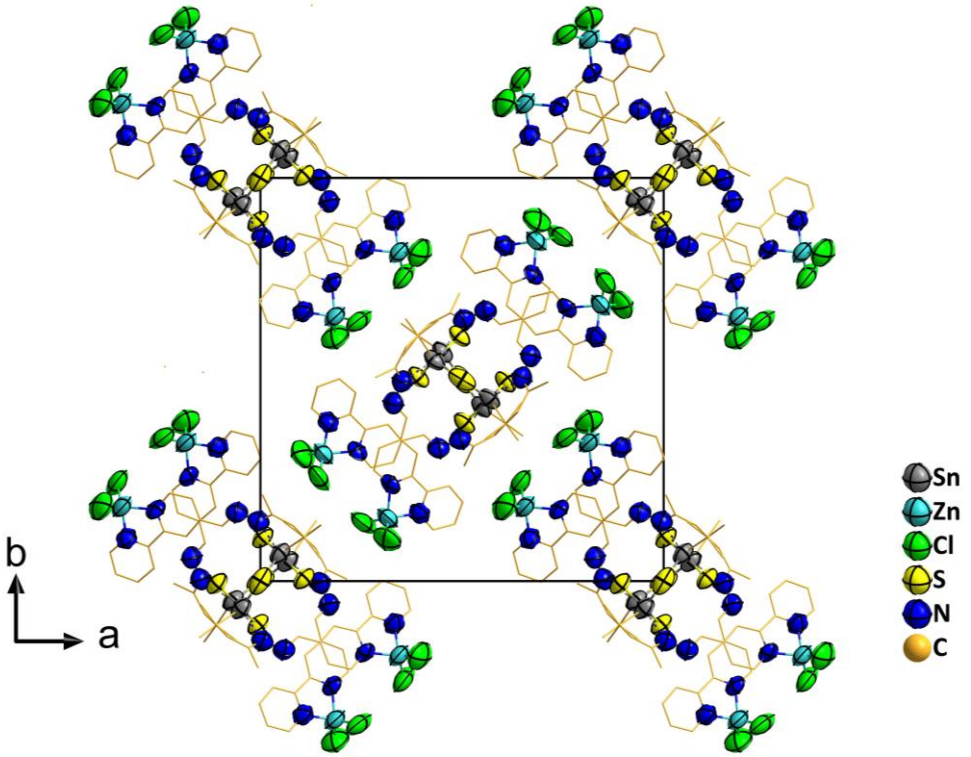


Figure S44: Packing of molecules of compound **5** in the unit cell with view along [001]. Thermal ellipsoids are shown at 50% probability, carbon atoms drawn as wires and hydrogen atoms omitted for clarity.

Molecular structure and packing diagram of compound 6

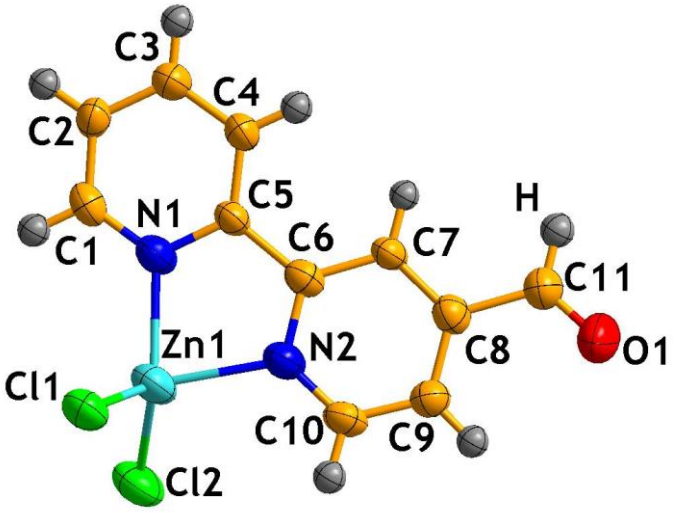


Figure S45: Molecular structure of compound **6**. Thermal ellipsoids are shown at 50% probability.

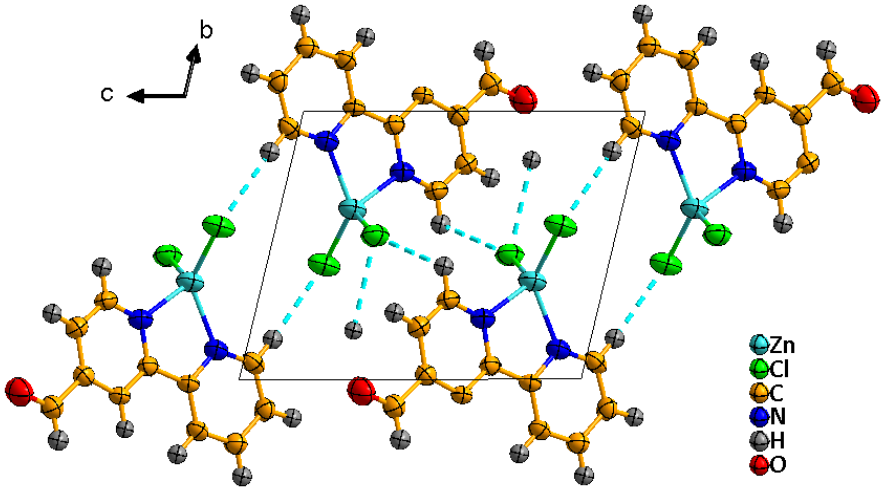


Figure S46: Packing of molecules of compound **6** in the unit cell with view along [100]. Thermal ellipsoids are shown at 50% probability, hydrogen bridging shown in light blue.

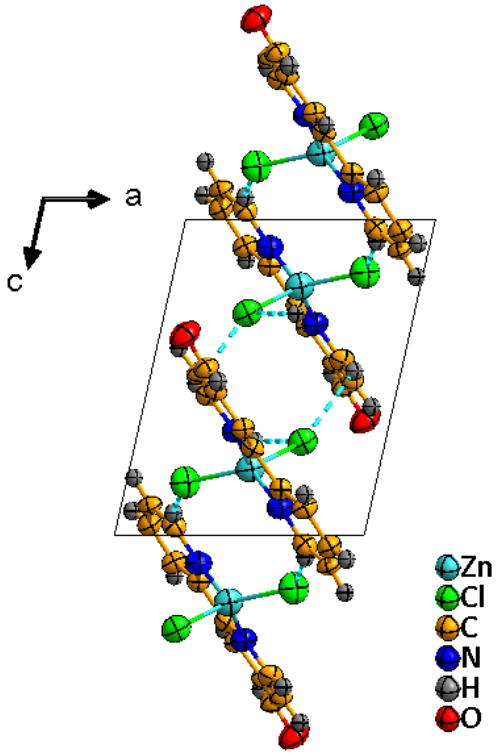


Figure S47: Packing of molecules of compound **6** in the unit cell with view along [010]. Thermal ellipsoids are shown at 50% probability, hydrogen bridging shown in light blue.

Molecular structure and packing diagram of compound 7

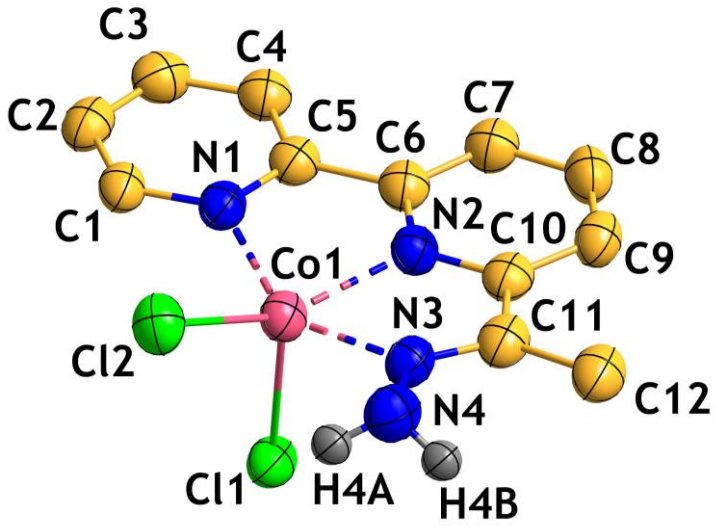


Figure S48: Molecular structure of compound **7** with thermal ellipsoids are shown at 50% probability, hydrogen atoms only shown at functional hydrazone group, other hydrogen atoms omitted for clarity.

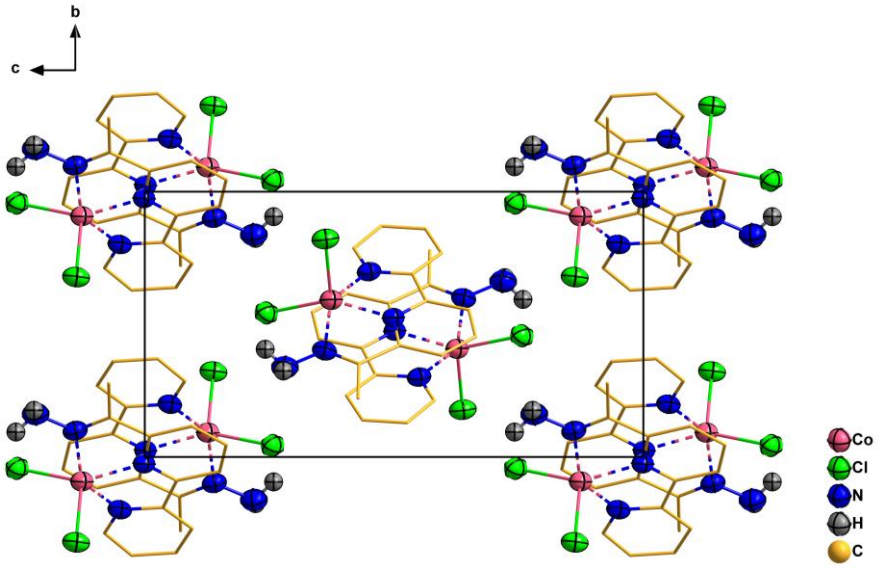


Figure S49: Packing of molecules of compound **7** in the unit cell with view along [100]. Thermal ellipsoids are shown at 50% probability, carbon atoms drawn as wires and hydrogen atoms omitted for clarity.

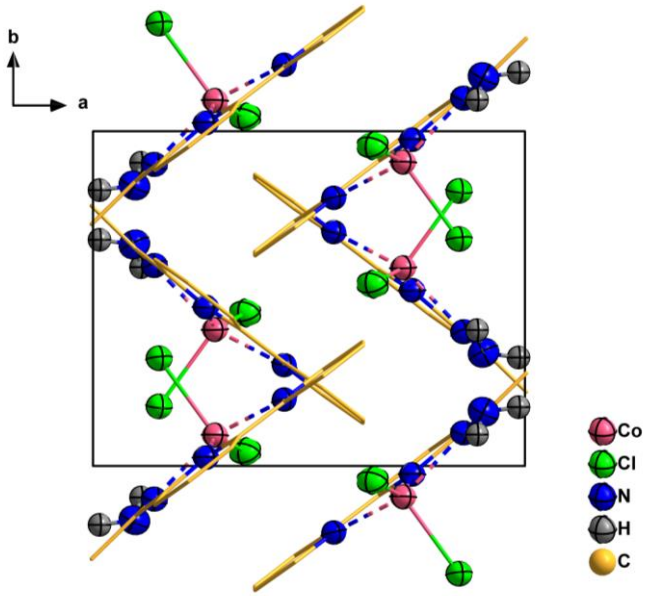


Figure S50: Packing of Molecules of compound **7** in the unit cell with view along [001]. Thermal ellipsoids are shown at 50% probability, carbon atoms drawn as wires and hydrogen atoms omitted for clarity.

Molecular structure and packing diagram of compound 8

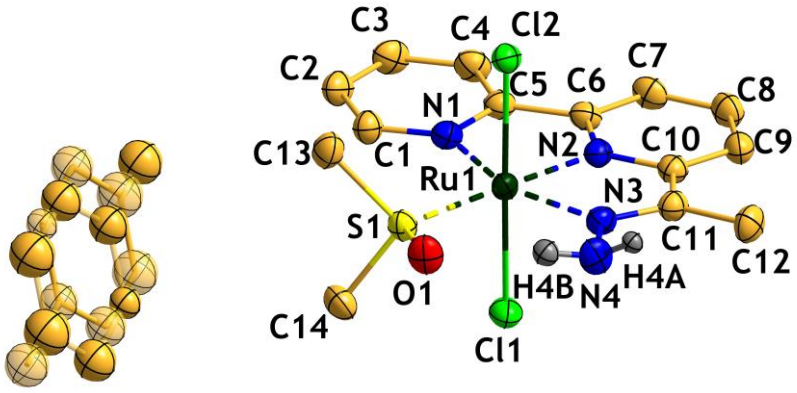


Figure S51: Molecular structure of compound **8** with thermal ellipsoids are shown at 50% probability. Hydrogen atoms only shown at functional hydrazone group, other hydrogen atoms omitted for clarity. The disordered toluene molecule is displayed with a semi-transparent part.

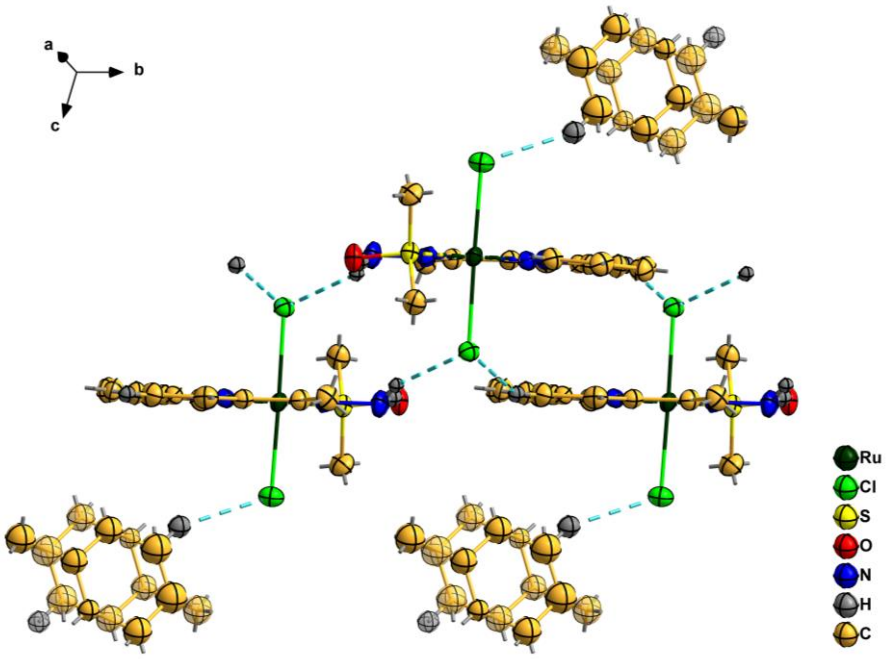


Figure S52: Hydrogen bonds between chlorine atoms and Hydrogen atoms connected to the functional hydrazone group or the solvent molecule in solid state of compound **8**. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms only shown at hydrogen bond positions for clarity.

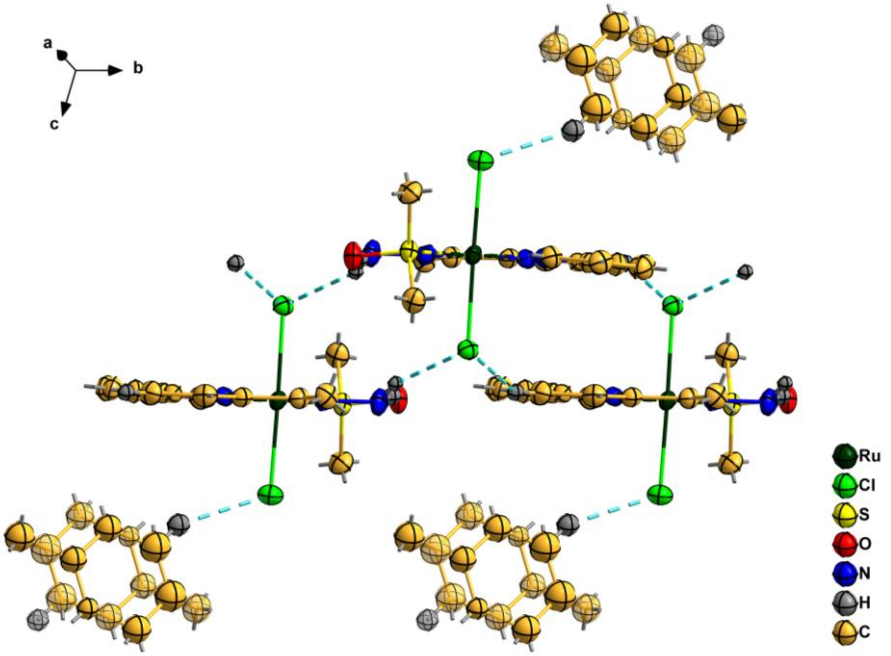


Figure S53: Packing of molecules of compound **8** in the unit cell with view along [010]. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms omitted for clarity.

3. Overview of the compounds involved in this study

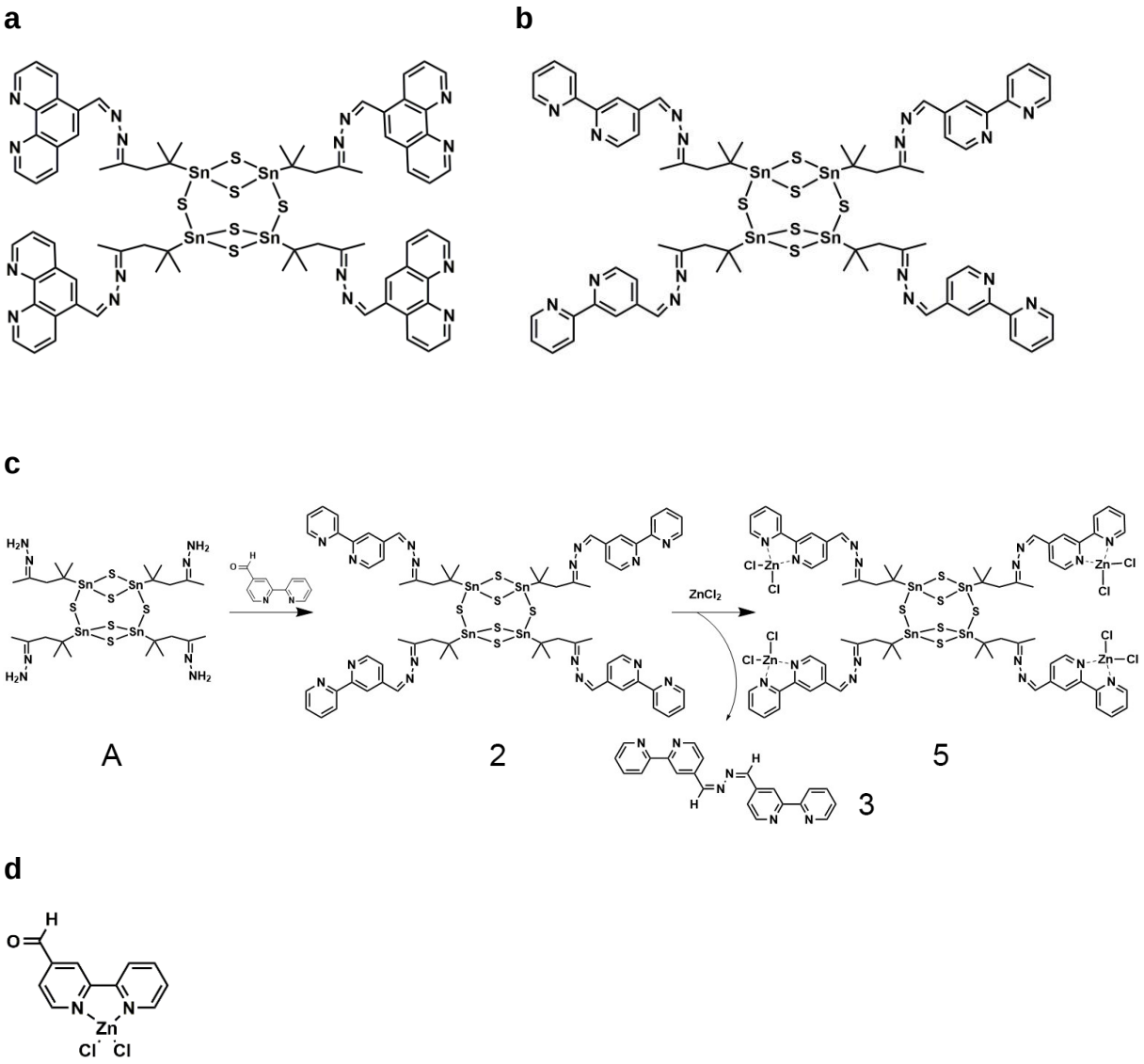


Figure S54: Schematic drawings of (a) compound **1**, (b) compound **2**, (c) the reaction pathway leading from **A** to the formation of compound **2** and finally **5**, thereby indicating all reactants and also the by-product **3**, (d) compound **4** resulting from a reaction of compound **1** with $ZnCl_2$. Further structural diagrams to be found along with the mass spectra shown above.

4. References for the supporting information

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