

Supplementary data

Formation and Mixed-valent Behaviour of a Substituted Tetraferrocenylstannane

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General procedures: All reactions were performed under argon atmosphere unless otherwise noted. Dichloromethane was dried over CaH_2 and distilled prior to use. All reagents were used as received from commercial suppliers. The copper bronze was purchased from Alfa Aesar (Bronze powder Cu:Sn 90:10 wt%, 100 mesh). NMR spectra were recorded on a Bruker Avance DRX 400 spectrometer at 400.31 MHz (^1H), 100.07 MHz ($^{13}\text{C}\{^1\text{H}\}$) and 149.28 MHz (^{119}Sn). All resonances are reported in ppm versus the solvent signal as internal standard [CDCl_3 (^1H : $\delta = 7.26$; ^{13}C : $\delta = 77.0$ ppm); CD_2Cl_2 (^1H : $\delta = 5.32$; ^{13}C : $\delta = 53.8$ ppm)] or SnMe_4 (^{119}Sn : $\delta = 0$ ppm) as external standard. IR spectra were recorded with a BioRad Excalibur FTS 3100 spectrometer using CsI disks. Electrochemical experiments were carried out on a BioLogic SP-50 voltammetric analyzer using a glassy carbon working electrode, a platinum wire as counter electrode and a 0.01 M Ag/AgNO_3 electrode as reference electrode. The measurements were carried out at a scan rate of 100 mV s^{-1} for cyclic voltammetry experiments and at 10 mV s^{-1} for square wave voltammetry experiments using 0.1 M $(n\text{Bu}_4\text{N})(\text{PF}_6)$ as supporting electrolyte in CH_2Cl_2 . Potentials are given relative to the ferrocene/ferrocenium couple ($E_{1/2} = 225 \pm 5 \text{ mV}$ under the experimental conditions). UV/Vis/NIR spectra were recorded on a Varian Cary 5000 spectrometer using 1.0 cm cells (Hellma, suprasil). FD mass spectra were recorded on a FD Finnigan MAT90 spectrometer. ^{57}Fe Mößbauer measurements of powder samples were performed in transmission geometry using a constant-acceleration spectrometer and the source $^{57}\text{Co}(\text{Rh})$. The Recoil 1.03 Mössbauer Analysis Software was used to fit the experimental spectra.^[S0] Isomer shift values are quoted relative to $\alpha\text{-Fe}$ at 293 K. Melting points were determined using a Gallenkamp capillary melting point apparatus MFB 595 010 and were not corrected. Elemental analyses were performed by the microanalytical laboratory of the chemical institutes of the University of Mainz.

Crystal Structure Determinations: Intensity data were collected with a Bruker AXS Smart1000 CCD diffractometer with an APEX II detector and an Oxford cooling system and corrected for absorption and other effects using Mo- K_{α} radiation ($\lambda = 0.71073 \text{ \AA}$) at 173(2) K. The diffraction frames were integrated using the SAINT package and most were corrected for absorption with MULABS.^[S1,S2] The structures were solved by direct methods and refined by the full-matrix method based on F^2 using the SHELXTL software package.^[S3,S4] All non-hydrogen atoms were refined anisotropically while the positions of all hydrogen atoms were generated with appropriate geometric constraints and allowed to ride on their respective parent carbon atoms with fixed isotropic thermal parameters.

Density functional calculations were carried out with the Gaussian03/DFT series^[S5] of programs. The B3LYP formulation of density functional theory was used employing the LANL2DZ basis set. No symmetry constraints were imposed on the molecules. No solvent modeling was employed.

Synthesis of 2:

Activation of copper bronze: 20 g copper bronze (10% Sn) were stirred for 10 min in a solution of I_2 in acetone (2%, 200 ml). After filtration the bronze was washed several times with conc. HCl/acetone (1:1, 100 ml) to remove CuI, finally with acetone and with diethyl ether to remove residual HCl and dried in vacuo.

4.84 g (15 mmol) 1-bromo-ferrocene-1'-carboxylic acid methyl ester Br-Fn-COOMe^[S6] and 10 g activated copper bronze were mixed and filled in an Argon flushed Schlenk flask. The Schlenk flask was heated to 130°C for 18 h. The resulting red residue was extracted with dichloromethane until the washings were nearly colorless. The organic extracts were washed with 5% aqueous ammonia solution (2× 100 mL), water (1× 100 mL) and brine (1× 100 mL) and dried over $MgSO_4$. The solvent was removed in vacuum and the residue was chromatographed on silica using dichloromethane / ethyl acetate. The first band eluted (CH_2Cl_2) was starting material and debrominated starting material. The second band (CH_2Cl_2 / ethyl acetate 20:1) furnished biferrocene **1** (1.95 g; 4.0 mmol, 53%) and the following band yielded 135 mg (0.12 mmol, 3%) $Sn(FnCOOMe)_4$ **2** as an orange powder. Crystals suitable for X-ray crystallographic analysis were obtained from dichloromethane / diethyl ether by slow evaporation at room temperature.

Oxidation of **2** using $[N(p\text{-C}_6\text{H}_4\text{Br})_3]\text{SbCl}_6$:

66 mg (0.06 mmol) **2** were dissolved in CH_2Cl_2 (20 ml) and 50 mg (0.06 mmol) tris(4-bromophenyl)ammoniumyl hexachloroantimonate dissolved in dichloromethane (20 ml) were added dropwise over five minutes. After stirring for 45 minutes the solvent was evaporated and the residue was washed with petroleum ether 40/60 / diethyl ether (1:1, 1×50 ml) and diethyl ether (2×50 ml). The green residue was dissolved in dichloromethane (5 ml) and precipitated with diethyl ether (50 ml) yielding a green powder (77 mg, 0.05 mmol, 89%, calculated for $[\mathbf{2}]\text{SbCl}_6$).

[S0] K. Lagarec, D. G. Rancourt, *Nucl. Instrum. Methods Phys. Res. B* 1997, **129**, 266.

[S1] SMART Data Collection and SAINT-Plus Data Processing Software for the SMART System (various versions); Bruker Analytical X-Ray Instruments, Inc.: Madison, WI, 2000.

[S2] B. Blessing, *Acta Cryst.* 1995, **A51**, 33.

[S3] G. M. Sheldrick, SHELXTL, Version 5.1; Bruker AXS: Madison, WI, 1998.

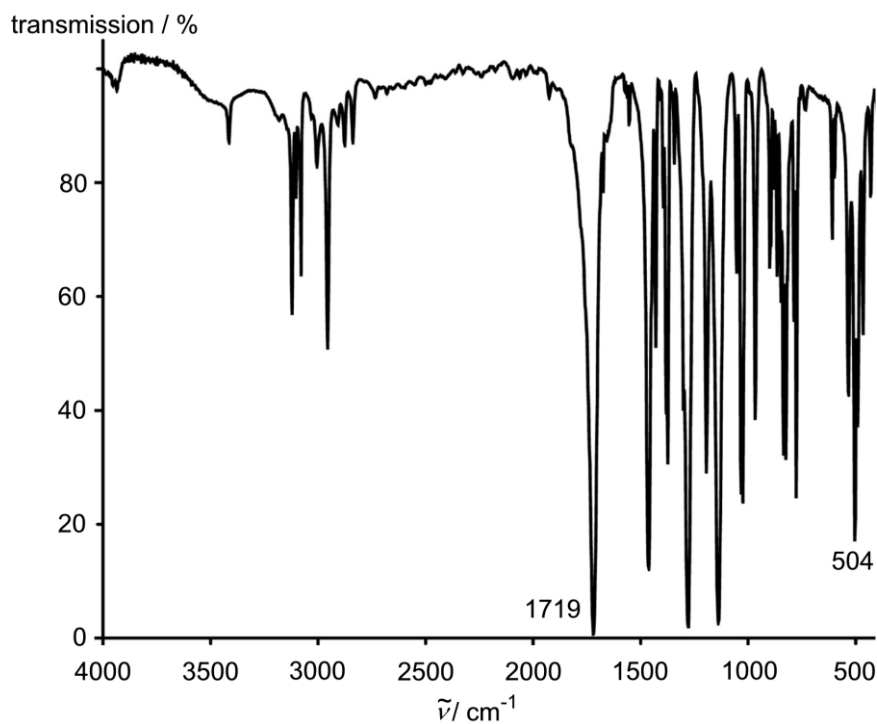
[S4] G. M. Sheldrick, SHELXL-97; University of Göttingen, Göttingen, Germany, 1997.

[S5] Gaussian 03, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

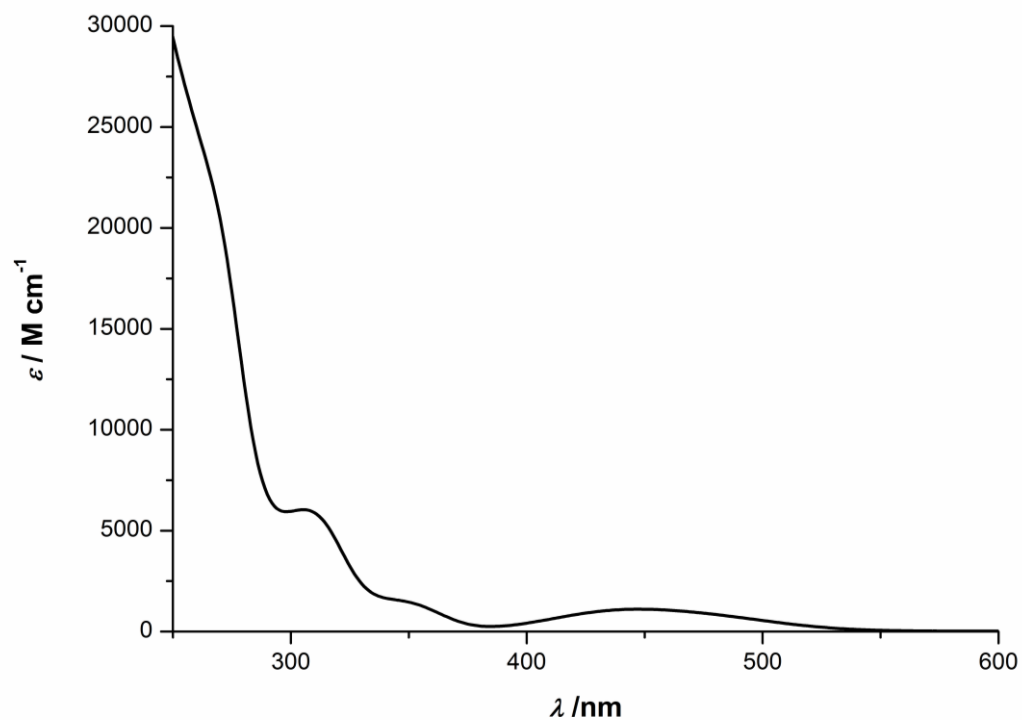
[S6] A. N. Nesmeyanov, V. A. Sazonova, V. N. Drozd, *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya* 1962, 45.

Analytical data of 2: orange crystals. Mp: >250°C (decomp.). Anal.: Calc. for $C_{48}H_{44}O_8Fe_4Sn$ (1090.95): C, 52.85; H, 4.07%. Found: C, 52.59; H 4.18%. FD-MS (m/z): 1092 $[M]^+$. 1H NMR (400 MHz, $CDCl_3$, δ / ppm): 4.71 (s, 2H, $H^{7,10}$), 4.54 (s, 2H, $H^{3,4}$), 4.37 (s, 2H, $H^{2,5}$), 4.15 (s, 2H, $H^{8,9}$), 3.81 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ / ppm): 171.9 (CO), 75.4 ($C^{3,4}$, $^3J(^{117,119}Sn^{13}C) = 44.4$ Hz), 73.3 ($C^{2,5}$, $^3J(^{117,119}Sn^{13}C) = 54.7$ Hz), 71.9 ($C^{8,9}$), 71.4 (C^6), 70.4 ($C^{7,10}$), 69.7 (C^1 , $^1J(^{119}Sn^{13}C) = 601$ Hz, $^1J(^{117}Sn^{13}C) = 574$ Hz), 51.7 (s, CH_3). $^{119}Sn\{^1H\}$ NMR (149 MHz, $CDCl_3$, δ / ppm): -65.3. UV/VIS (CH_2Cl_2 , nm / ϵ): 228 (68870), 305 (6040), 448 (1110). IR (CsI, cm^{-1}): 3121 (m, CH_{Cp}), 3102 (w, CH_{Cp}), 3078 (m, CH_{Cp}), 2995 (m, CH_{CH_3}), 1719 (vs, C=O), 1464 (vs), 1278 (vs, C-O), 1138 (vs), 504 (m, Sn-C).

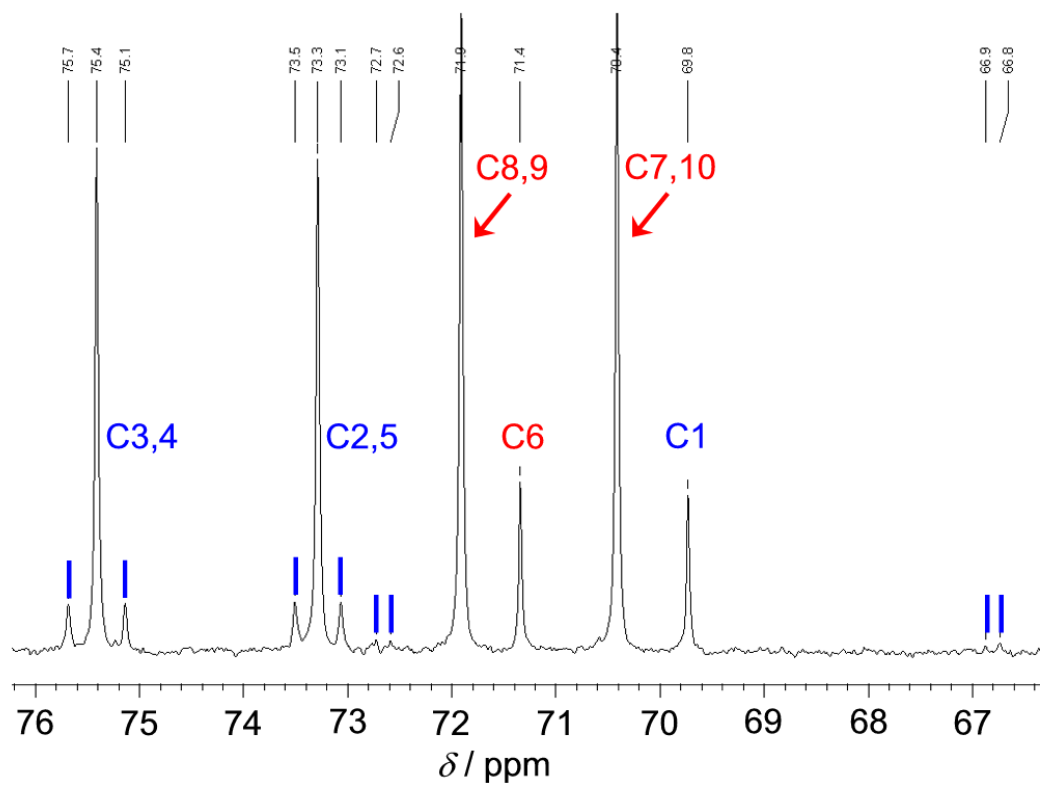
IR spectrum of 2 in CsI



UV/Vis spectrum of **2** in CH₂Cl₂

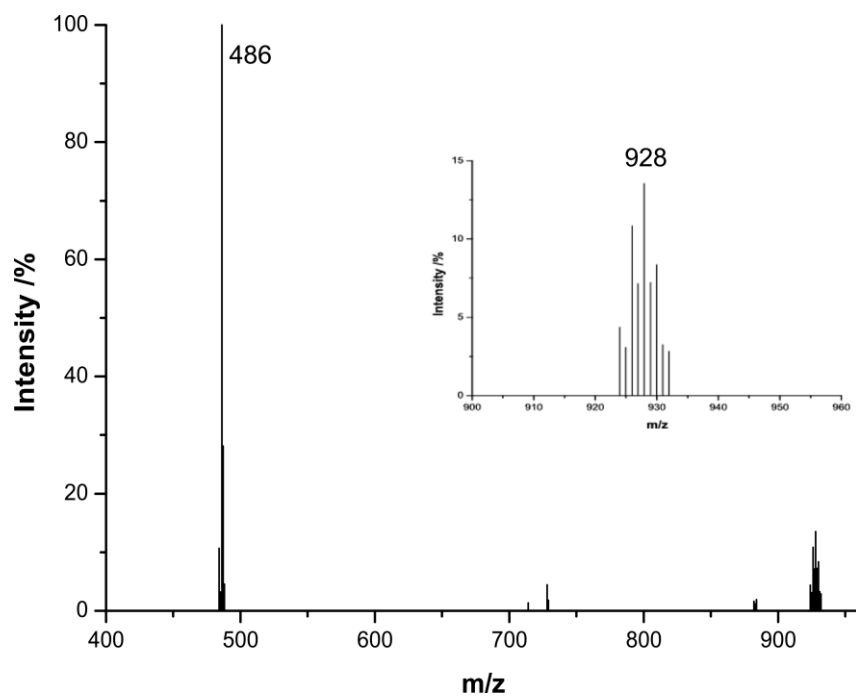


Partial ¹³C NMR spectrum of **2** in CDCl₃

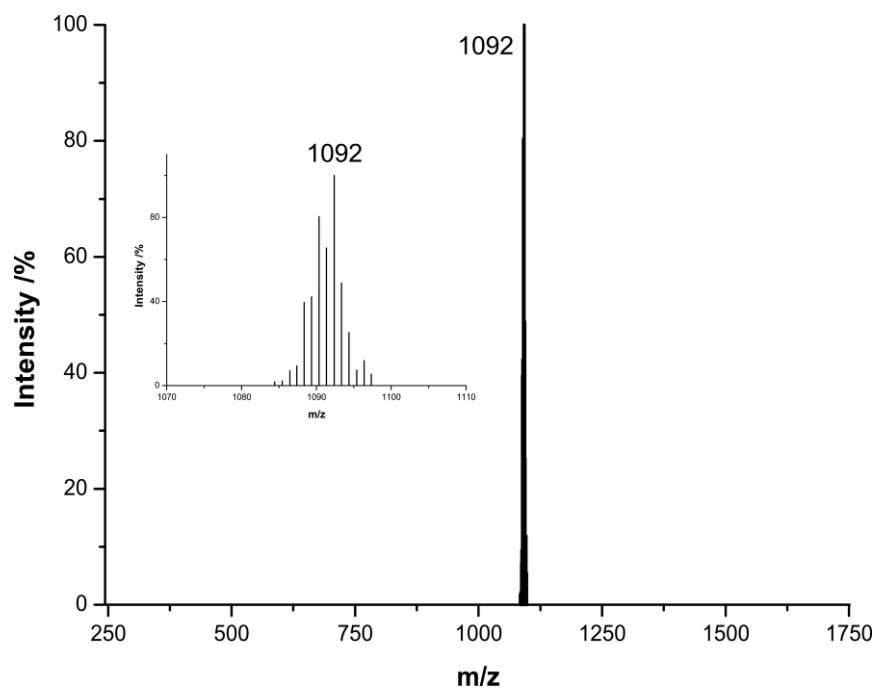


FD mass spectrum of 1 ($m/z = 486$) and bromo-tri(ferrocenyl)stannane

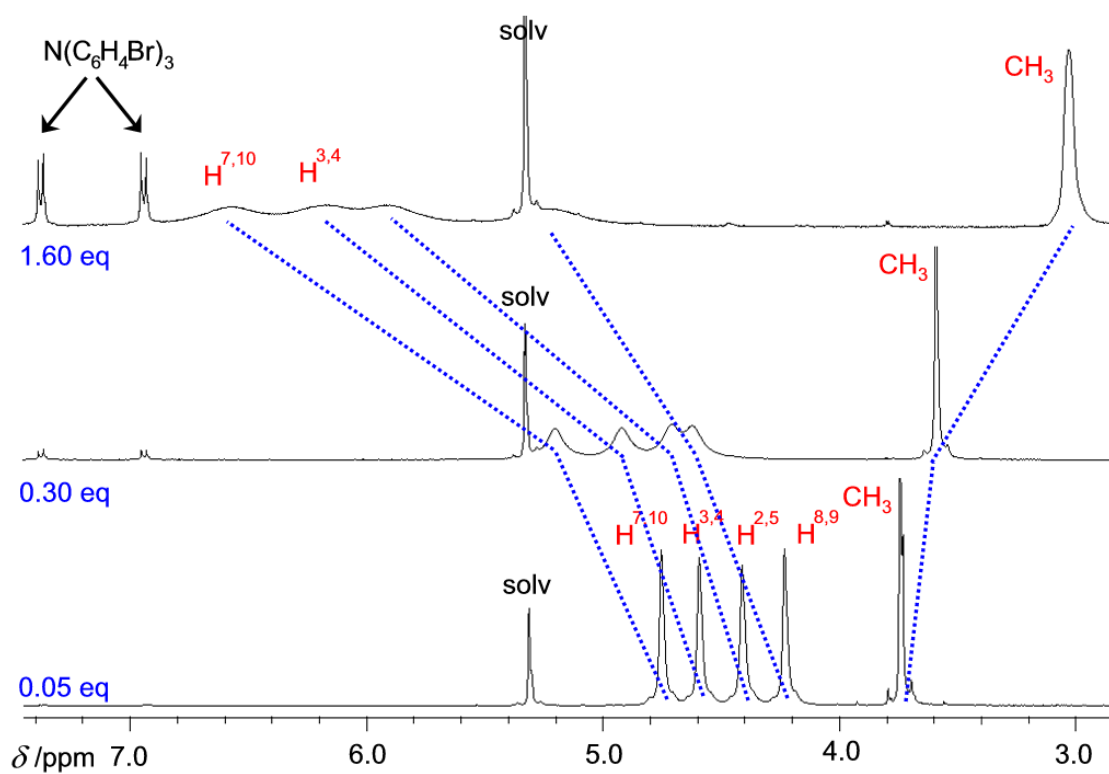
$[(C_5H_4COOCH_3)(C_5H_4)Fe]_3SnBr$ ($m/z = 928$)



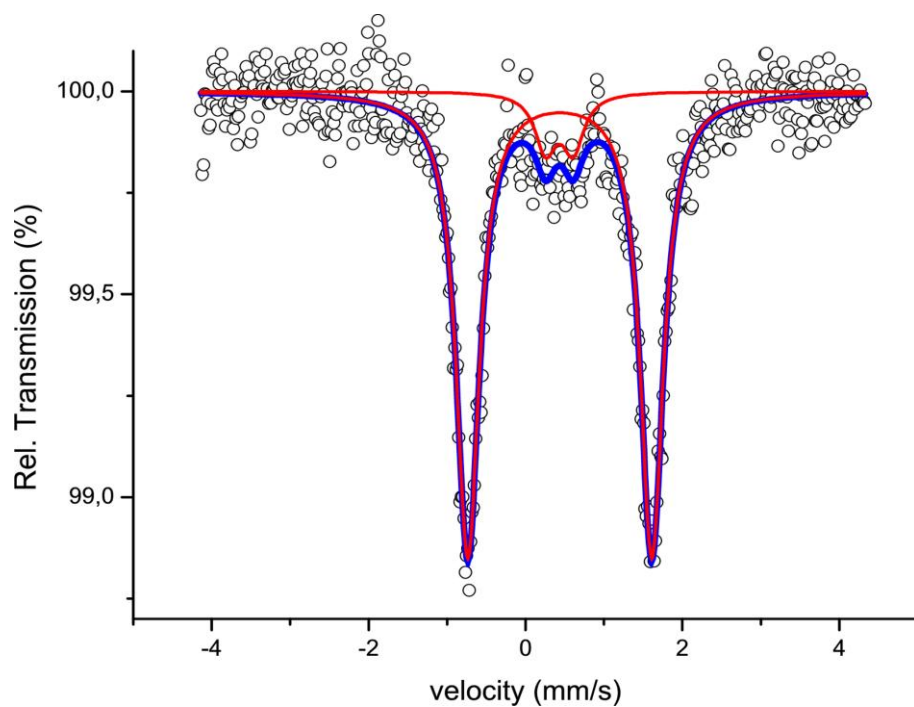
FD mass spectrum of 2 ($m/z = 1092$)



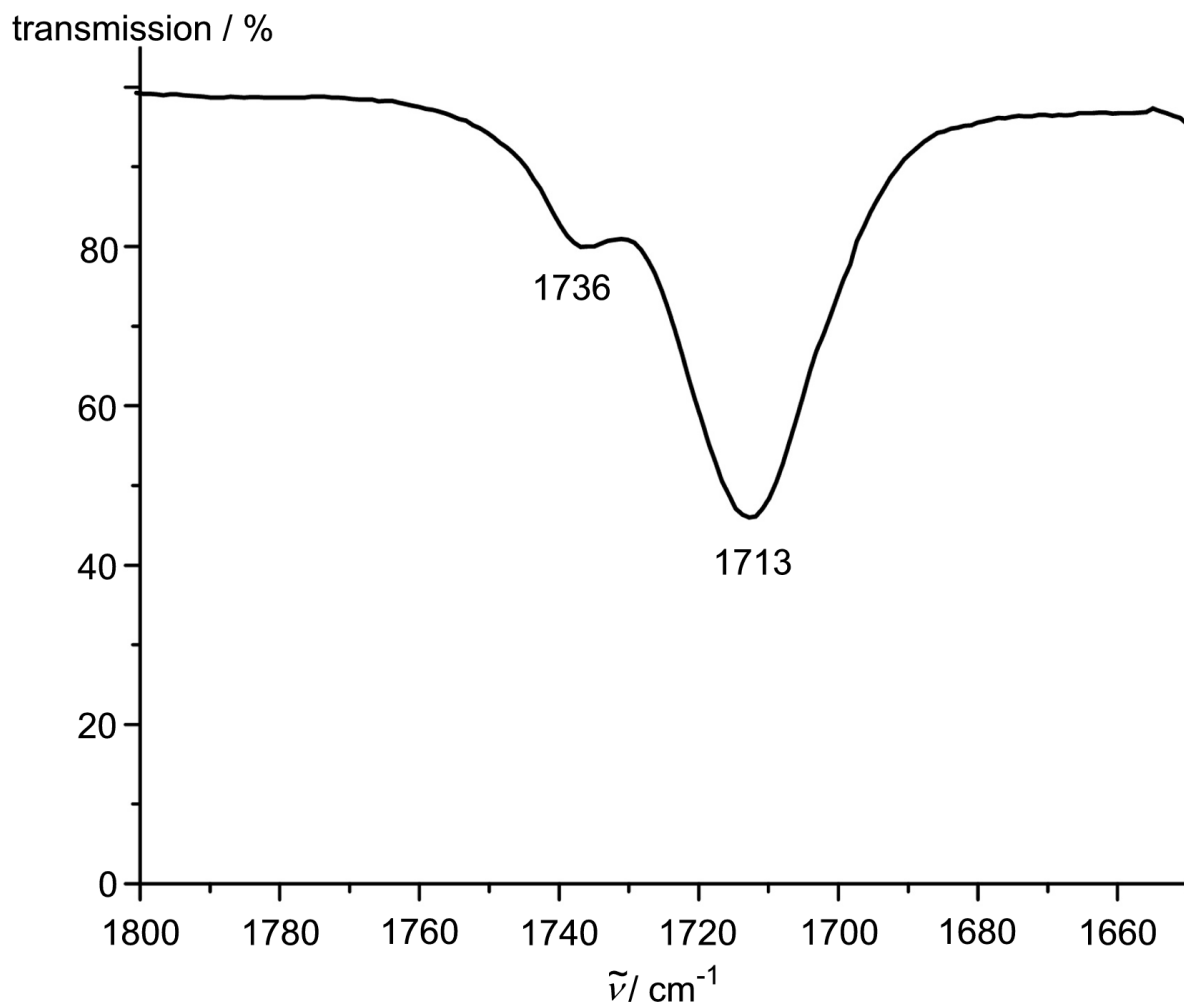
Paramagnetic ^1H NMR spectra of **2 + $[\text{N}(p\text{-C}_6\text{H}_4\text{Br})_3]\text{SbCl}_6$ (0.05 – 1.6 eq) in CD_2Cl_2**



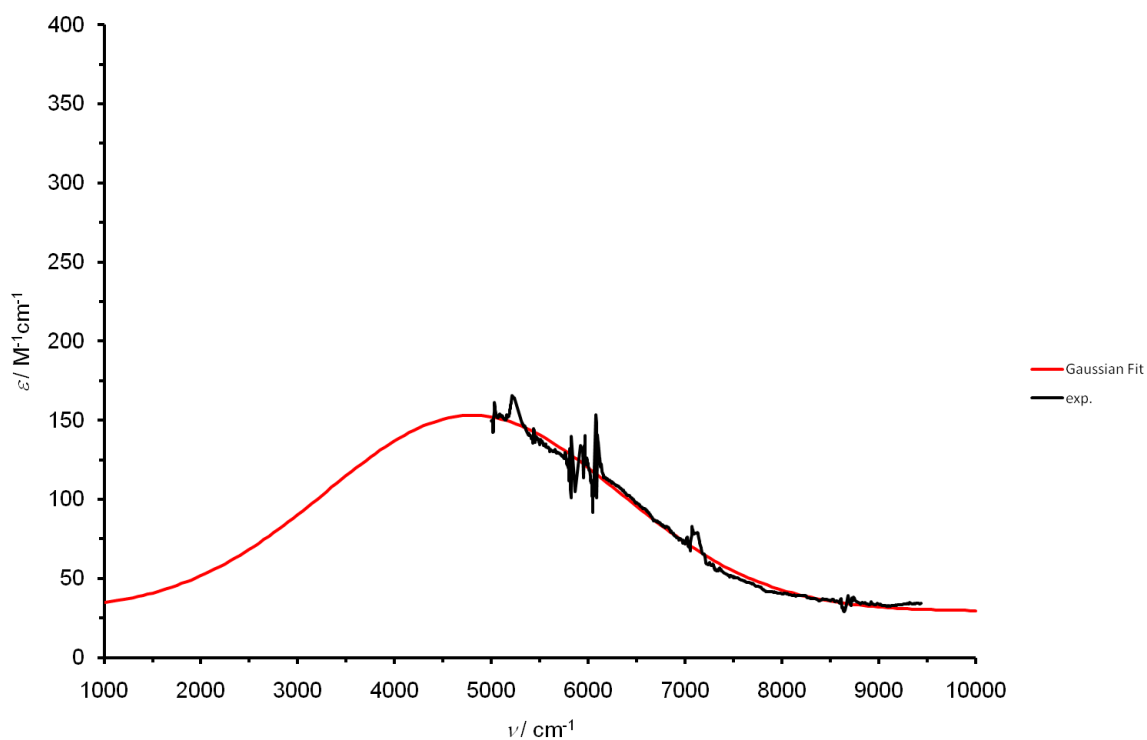
Mössbauer spectrum of partially oxidized **2 at 295 K**



IR spectrum of partially oxidized 2 at 295 K in CH₂Cl₂ (CO region)

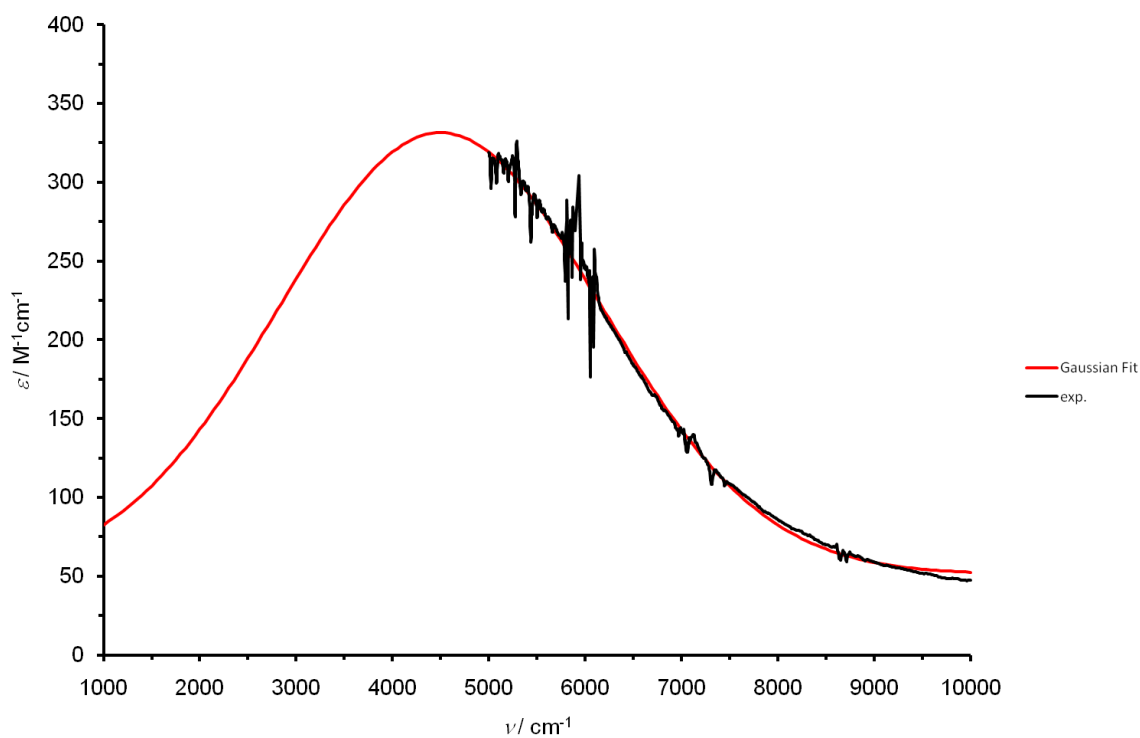


Gaussian band shape fit of the IVCT bands of $[2]^+$



$$y_0 = 29 \text{ M}^{-1} \text{ cm}^{-1}; x_c = 4803 \text{ cm}^{-1}; w = 3035 \text{ cm}^{-1}; A = 470906 \text{ M}^{-1} \text{ cm}^{-2}; R^2 = 0.98562.$$

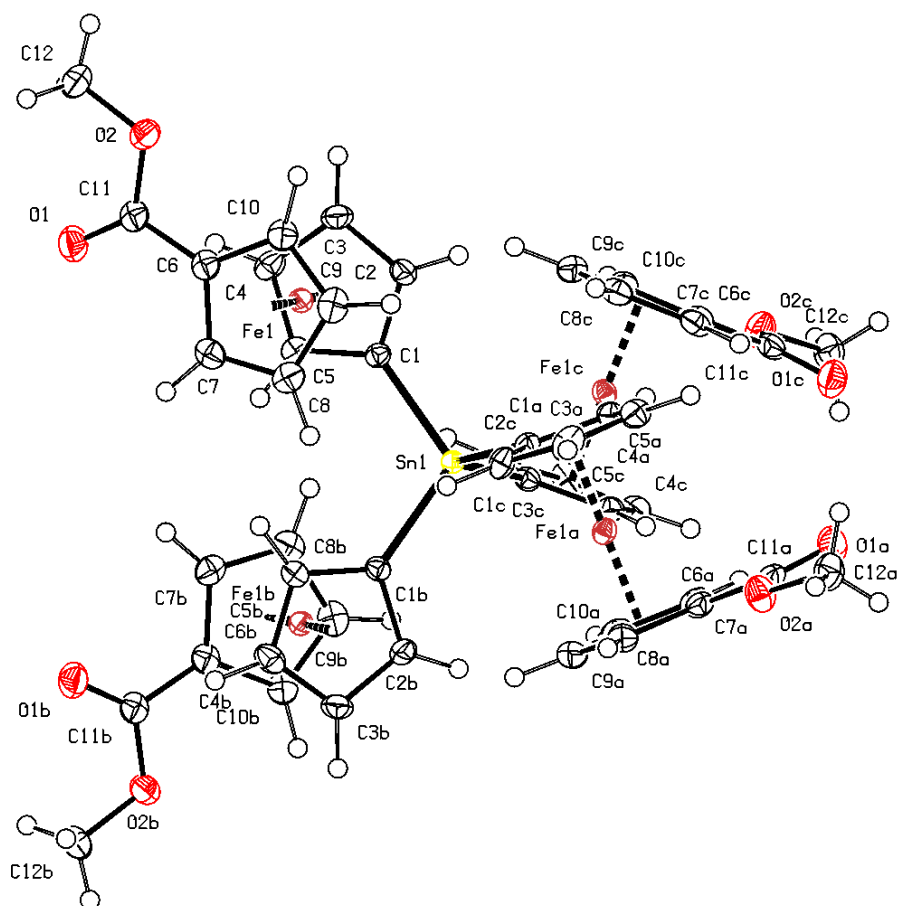
Gaussian band shape fit of the IVCT band of $[2]^{2+}$



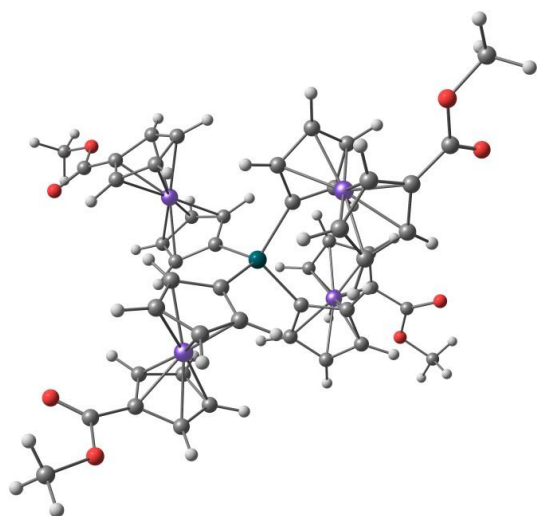
$$y_0 = 51 \text{ M}^{-1} \text{ cm}^{-1}; x_c = 4499 \text{ cm}^{-1}; w = 3345 \text{ cm}^{-1}; A = 1174639 \text{ M}^{-1} \text{ cm}^{-2}; R^2 = 0.99474.$$

Details of the X-ray crystallography of 2

$C_{48}H_{44}Fe_4O_8Sn$, $M = 1090.92$, $T = 173(2)$ K, crystal size $0.33 \times 0.25 \times 0.18$ mm³, tetragonal, space group $I4_1/a$, $a = b = 19.8605(4)$, $c = 10.4054(5)$ Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 4104.3(2)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.765$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 2.038$ mm⁻¹, 12350 collected reflections, 2480 unique reflections, $R_1 [I > 2\sigma(I)] = 0.0275$, $wR_2 = 0.0549$ (all data), $S = 1.013$, largest diff. peak and hole 0.349 and -0.455 e Å⁻³.



DFT optimised cartesian coordinates of 2



50	-0.000150000	-0.000049000	-0.000191000
26	2.516191000	0.544893000	-2.818891000
6	1.225576000	1.196838000	-1.236931000
6	0.832254000	1.783750000	-2.505151000
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6	1.926506000	2.564236000	-3.026112000
1	1.933833000	3.108927000	-3.959830000
6	3.019303000	2.466152000	-2.089300000
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DFT optimised cartesian coordinates of [2]⁺

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6	-7.581683000	-1.438900000	1.331812000
1	-8.367624000	-2.187649000	1.431898000
1	-8.002572000	-0.430061000	1.290471000
1	-6.866734000	-1.506213000	2.158023000
8	-5.505994000	0.041426000	0.320088000
8	-6.915906000	-1.761232000	0.054363000
26	2.546496000	1.084415000	-2.349196000
6	0.895176000	-0.240989000	-2.019737000
6	0.689963000	0.547604000	-3.224584000
1	-0.138985000	1.216906000	-3.414803000
6	1.763217000	0.279554000	-4.147744000
1	1.885854000	0.719748000	-5.127361000
6	2.651197000	-0.670511000	-3.528005000
1	3.567158000	-1.058582000	-3.951249000
6	2.128523000	-0.984602000	-2.223976000
1	2.588705000	-1.658816000	-1.515925000
6	4.515851000	1.806860000	-2.259209000
6	4.028807000	1.579397000	-0.917927000
1	4.481851000	0.900867000	-0.209359000
6	2.886424000	2.428378000	-0.722156000
1	2.311183000	2.508174000	0.189785000
6	2.667495000	3.179768000	-1.939826000
1	1.902545000	3.925128000	-2.110261000
6	3.674534000	2.798066000	-2.888938000
1	3.801657000	3.172685000	-3.893403000
6	5.667119000	1.100754000	-2.849393000
6	7.126122000	0.958246000	-4.792950000
1	7.190568000	1.470406000	-5.753422000
1	8.029984000	1.119813000	-4.198142000
1	6.967187000	-0.116297000	-4.927140000
8	6.312903000	0.196507000	-2.287411000
8	5.961965000	1.565658000	-4.116486000
26	1.605871000	-2.338040000	2.100920000
6	0.465418000	-0.658171000	1.469667000
6	-0.139181000	-1.289473000	2.634530000
1	-1.120836000	-1.742036000	2.674517000
6	0.800413000	-1.246908000	3.729473000
1	0.643174000	-1.648654000	4.720606000
6	2.001209000	-0.601378000	3.256089000
1	2.907811000	-0.445549000	3.824123000
6	1.800559000	-0.244043000	1.874149000
1	2.535742000	0.228654000	1.239306000
6	3.207451000	-3.664495000	2.374770000
6	3.101813000	-3.324809000	0.972947000

1	3.883447000	-2.850212000	0.396957000
6	1.809352000	-3.758428000	0.518540000
1	1.420561000	-3.669580000	-0.485954000
6	1.115450000	-4.361556000	1.633817000
1	0.120478000	-4.782479000	1.605637000
6	1.978849000	-4.310062000	2.779933000
1	1.770722000	-4.679635000	3.772830000
6	4.379032000	-3.358319000	3.213707000
6	5.392853000	-3.683215000	5.402915000
1	5.103909000	-4.189675000	6.324410000
1	6.298588000	-4.125510000	4.977550000
1	5.556947000	-2.614416000	5.573238000
8	5.375446000	-2.709855000	2.841953000
8	4.253838000	-3.885406000	4.485666000

Spin density plot of [2]⁺ (contour value 0.001 a.u.); isotropic Fermi contact couplings at selected hydrogen atoms in MHz

