

# Tetraruthenium Metallamacrocycles With Potentially Coordinating Appended Functionalities

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## NMR Spectra

**IL1**

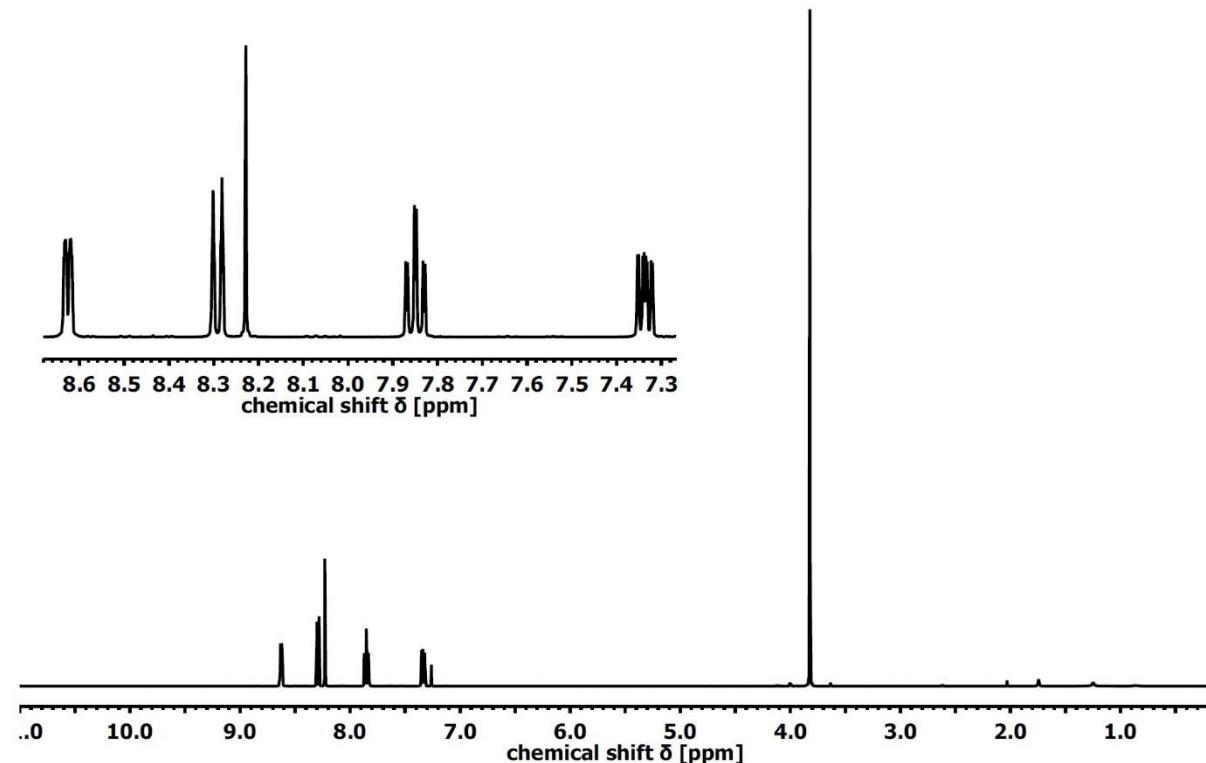


Figure S1: <sup>1</sup>H-NMR spectrum of **IL1** in CDCl<sub>3</sub>

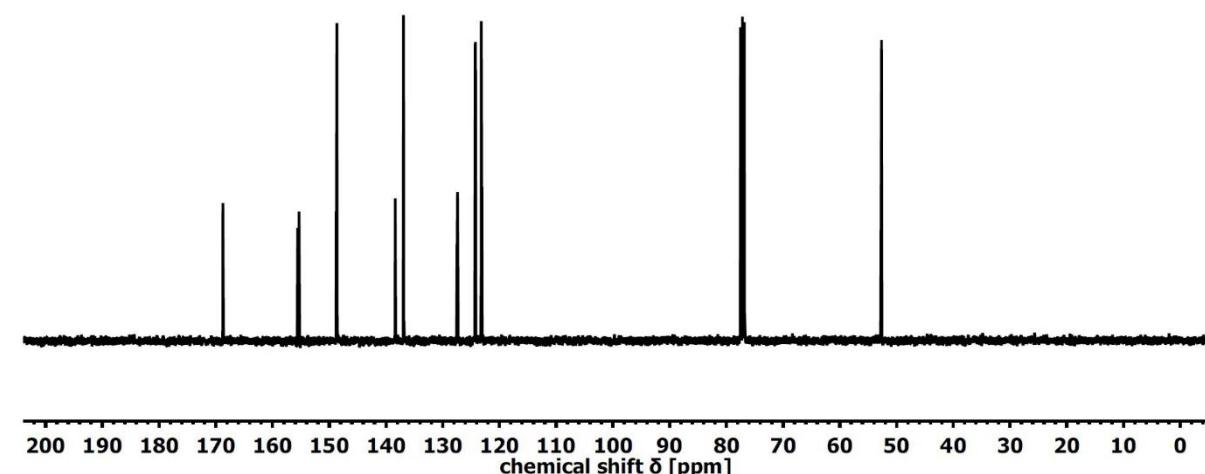


Figure S2: <sup>13</sup>C{<sup>1</sup>H}-NMR spectrum of **IL1** in CDCl<sub>3</sub>

**IL2**

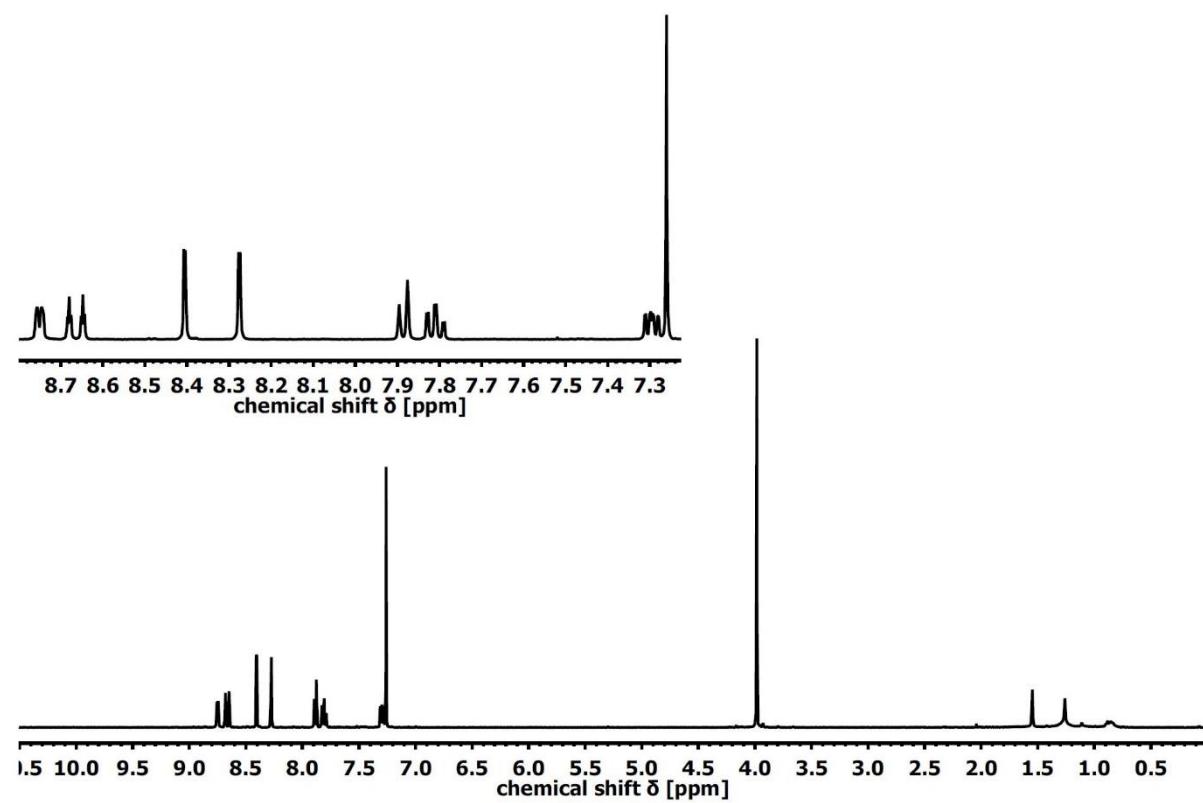


Figure S3:  $^{13}\text{C}\{\text{H}\}$ -NMR spectrum of **IL2** in  $\text{CDCl}_3$

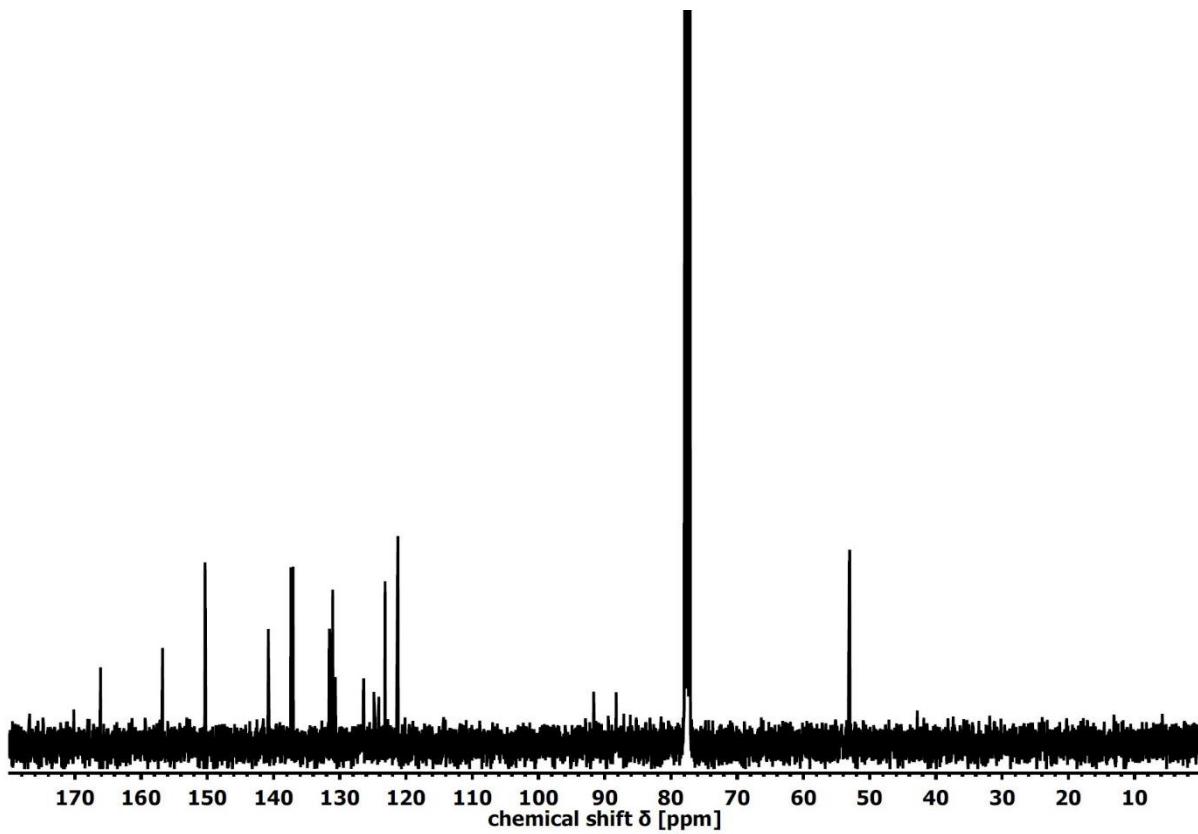


Figure S4:  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **IL2** in  $\text{CDCl}_3$

**IL3**

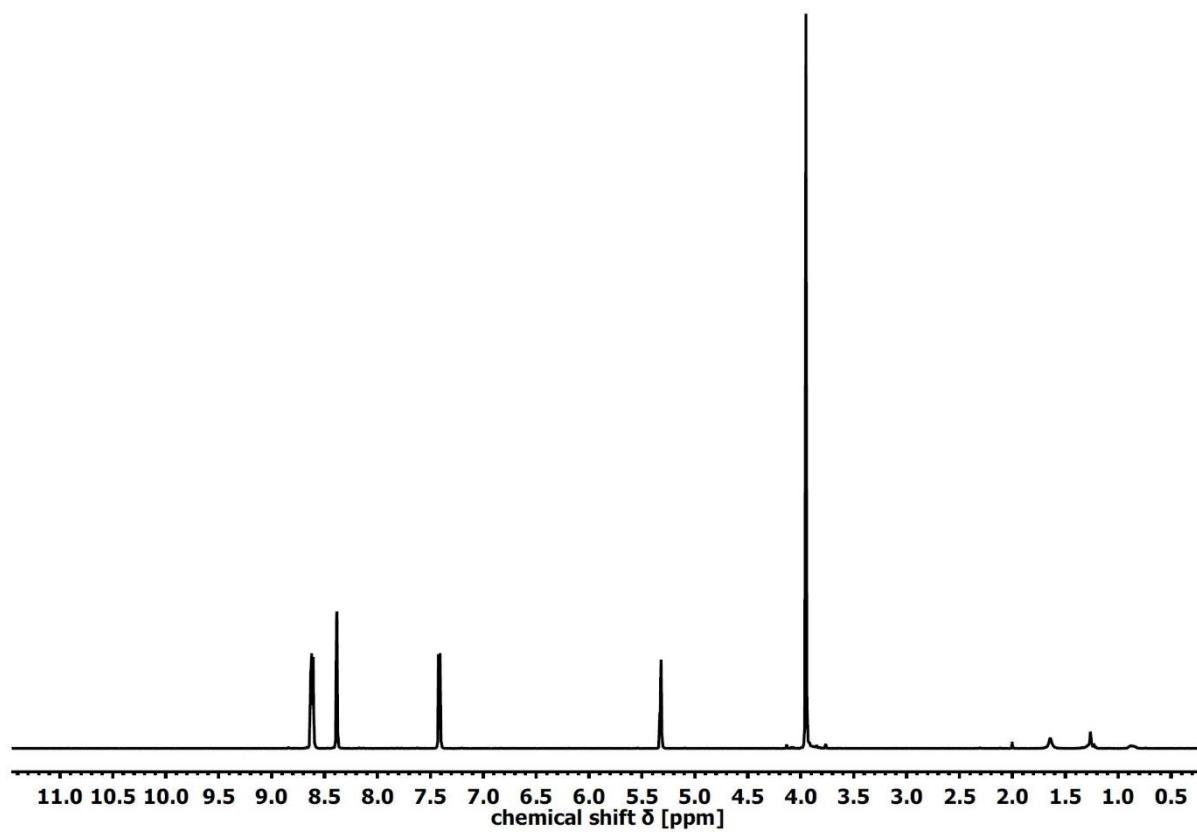


Figure S5:  $^1\text{H}$ -NMR spectrum of **IL3** in  $\text{CDCl}_3$

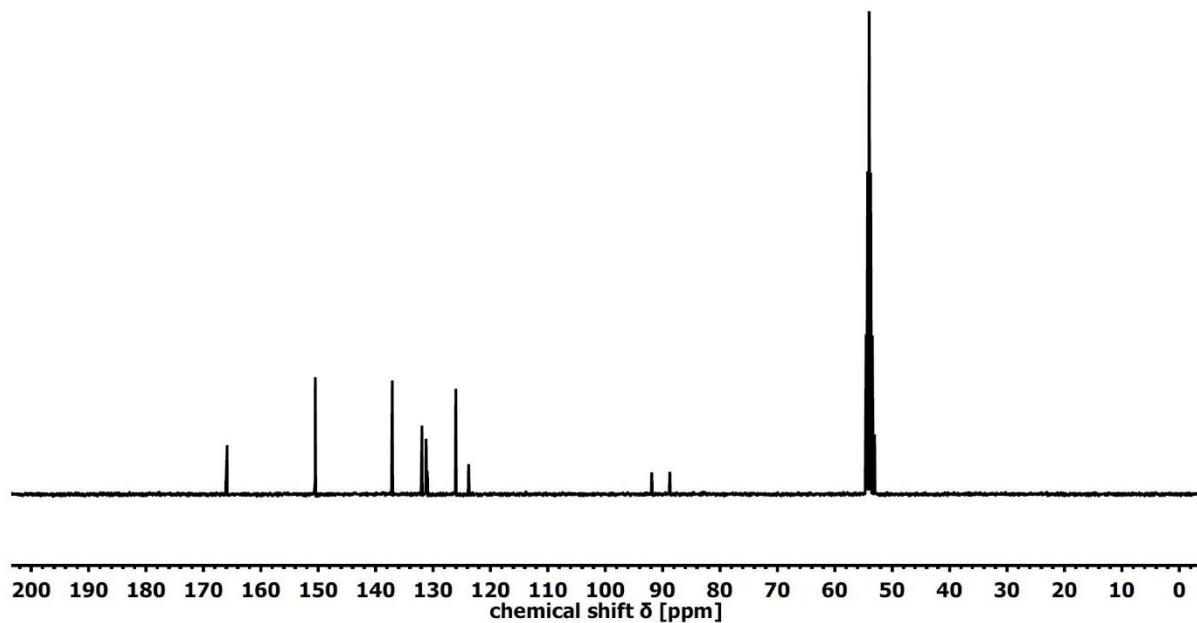


Figure S6:  $^{13}\text{C}\{\text{H}\}$ -NMR spectrum of **IL3** in  $\text{CD}_2\text{Cl}_2$

**IL4**

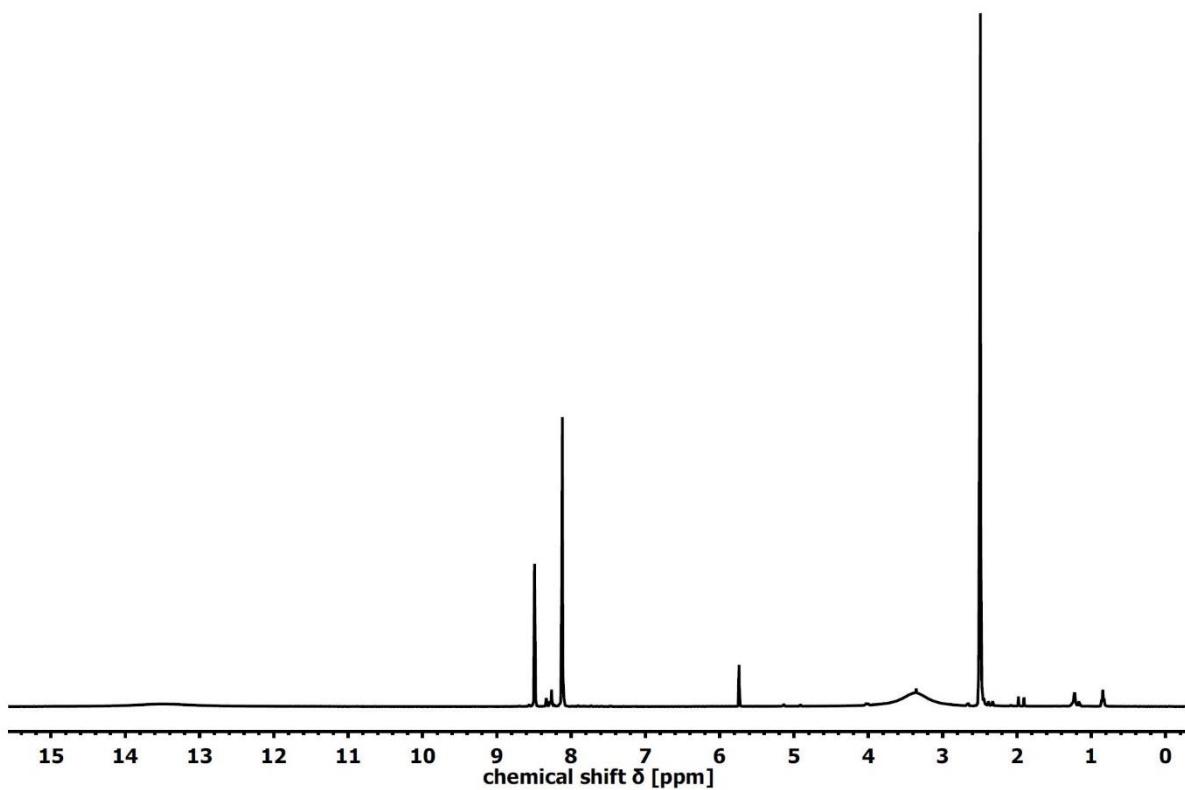


Figure S7: <sup>1</sup>H-NMR spectrum of **IL4** in dmso-d6

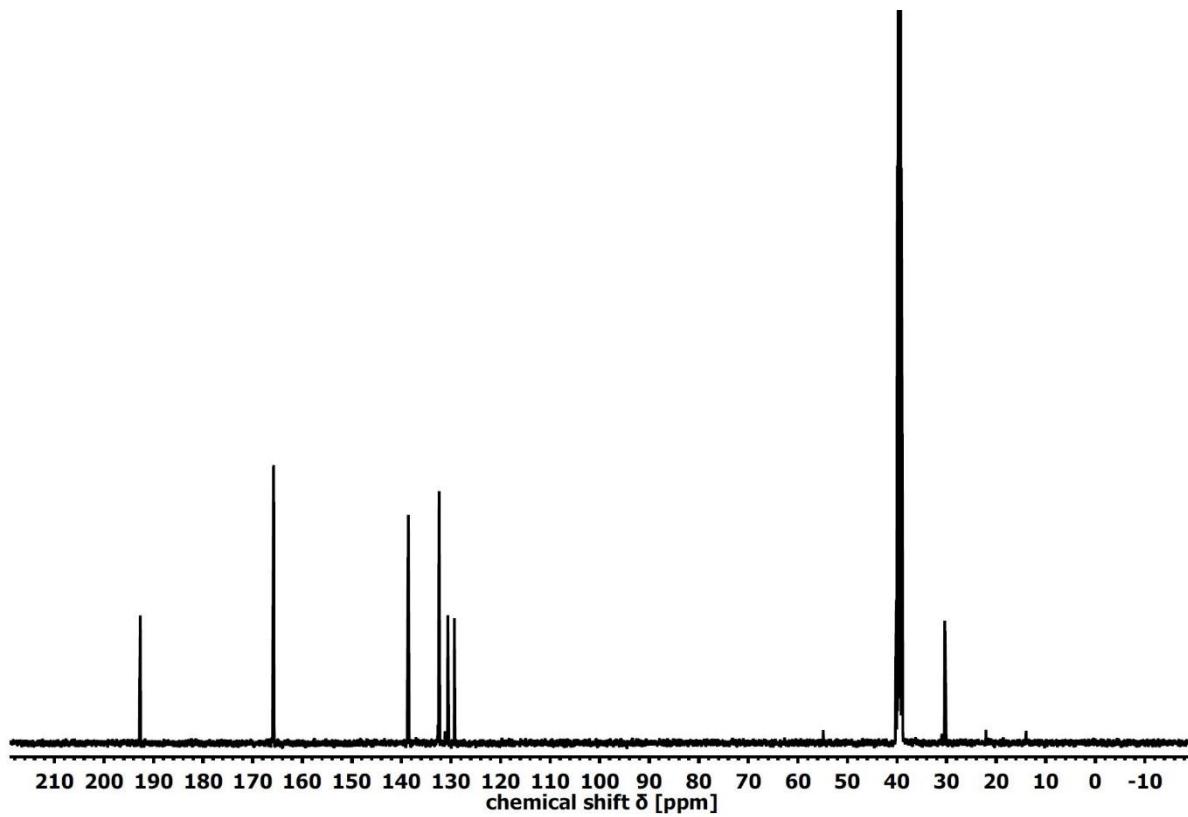


Figure S8:  $^{13}\text{C}\{\text{H}\}$ -NMR spectrum of **IL4** in  $\text{dmso-}d_6$ .

**Complex 1**

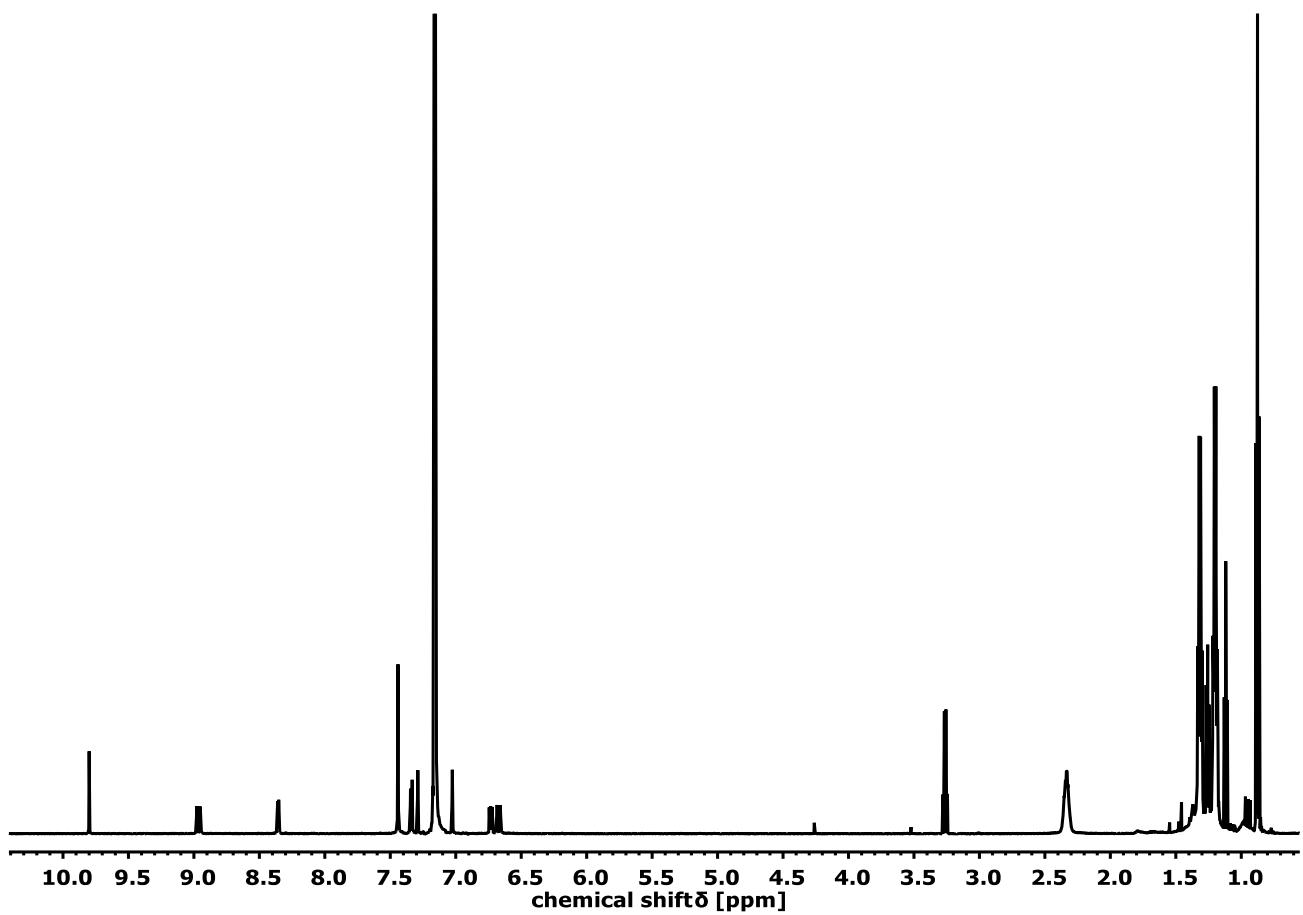


Figure S9:  $^1\text{H}$ -NMR spectrum of **1** in  $\text{C}_6\text{D}_6$ .

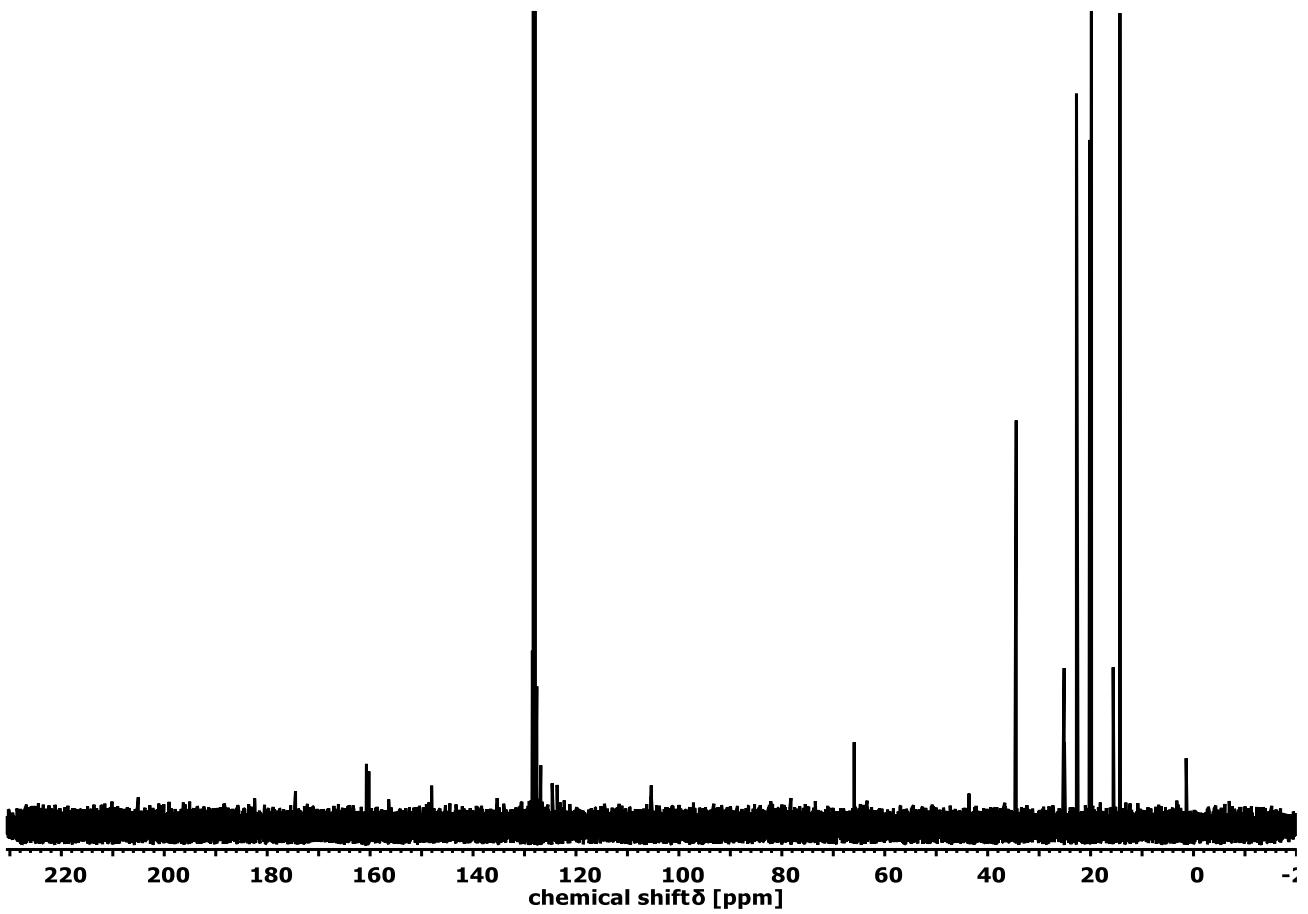


Figure S10:  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **1** in  $\text{C}_6\text{D}_6$ .

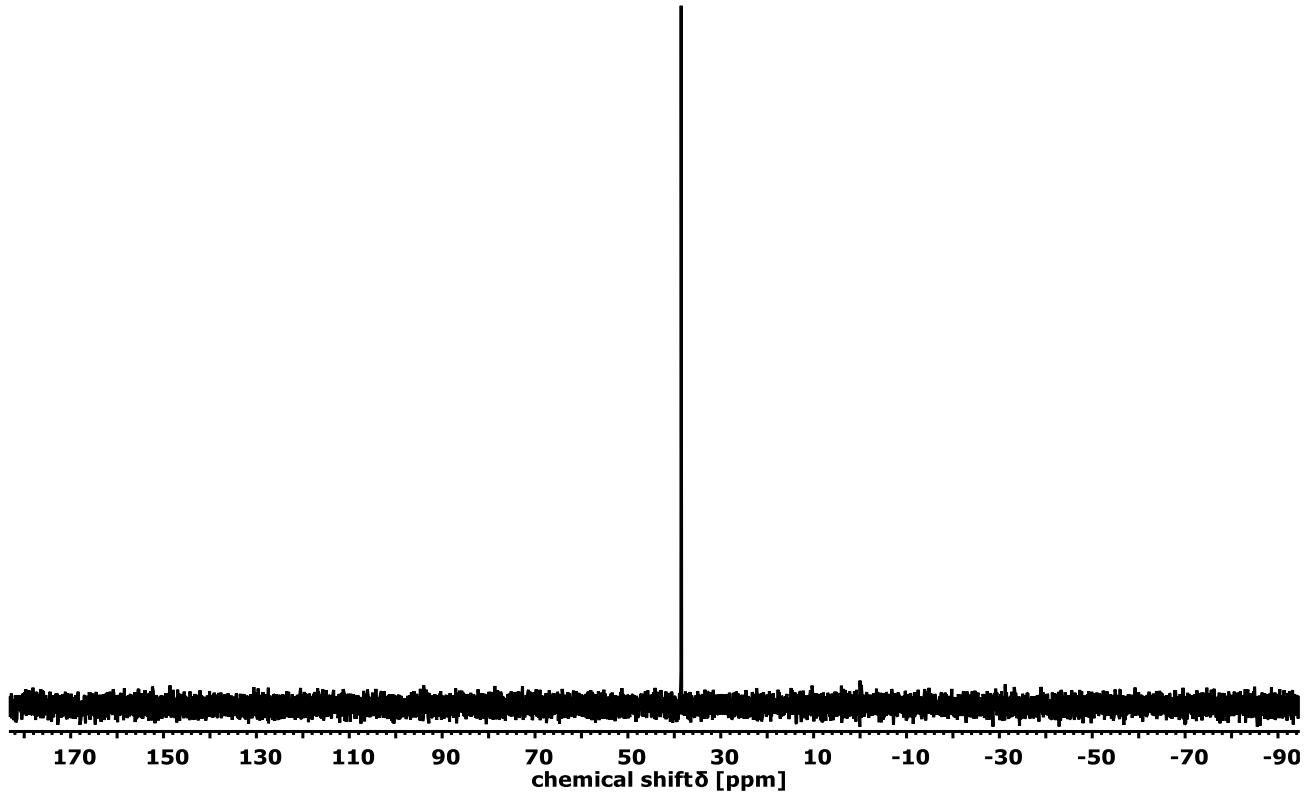


Figure S11:  $^{31}\text{P}\{\text{H}\}$ -NMR spectrum of **1** in  $\text{C}_6\text{D}_6$ .

**Complex 2**

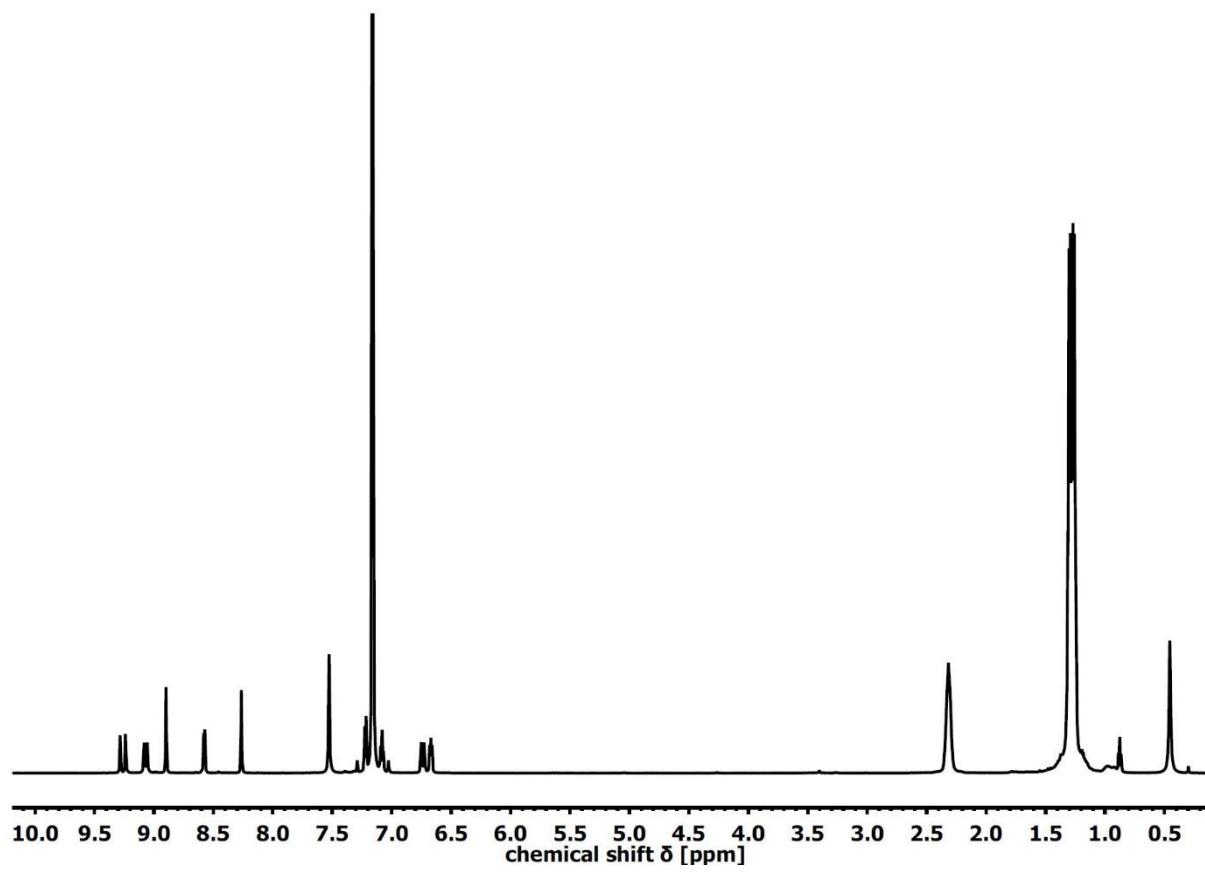


Figure S12:  $^1\text{H}$ -NMR spectrum of **2** in  $\text{C}_6\text{D}_6$ .

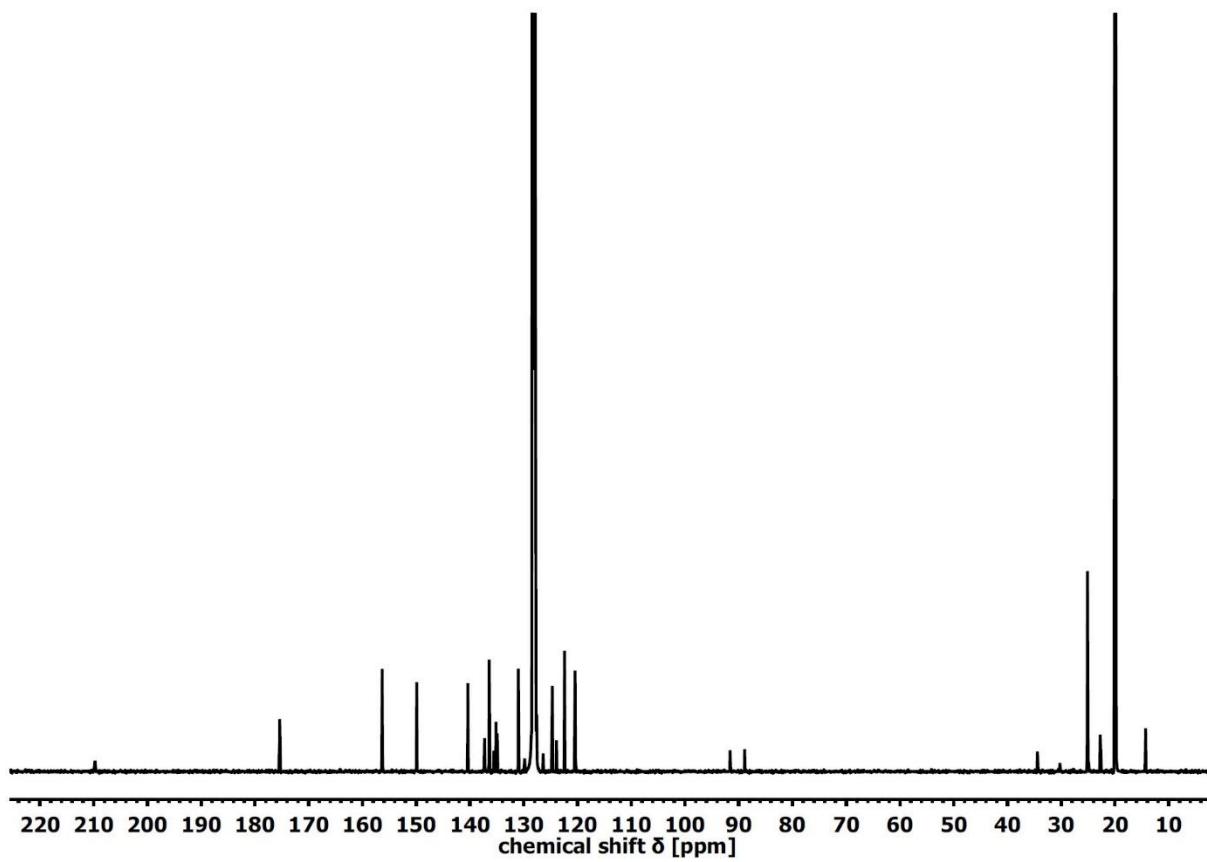


Figure S13:  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **2** in  $\text{C}_6\text{D}_6$

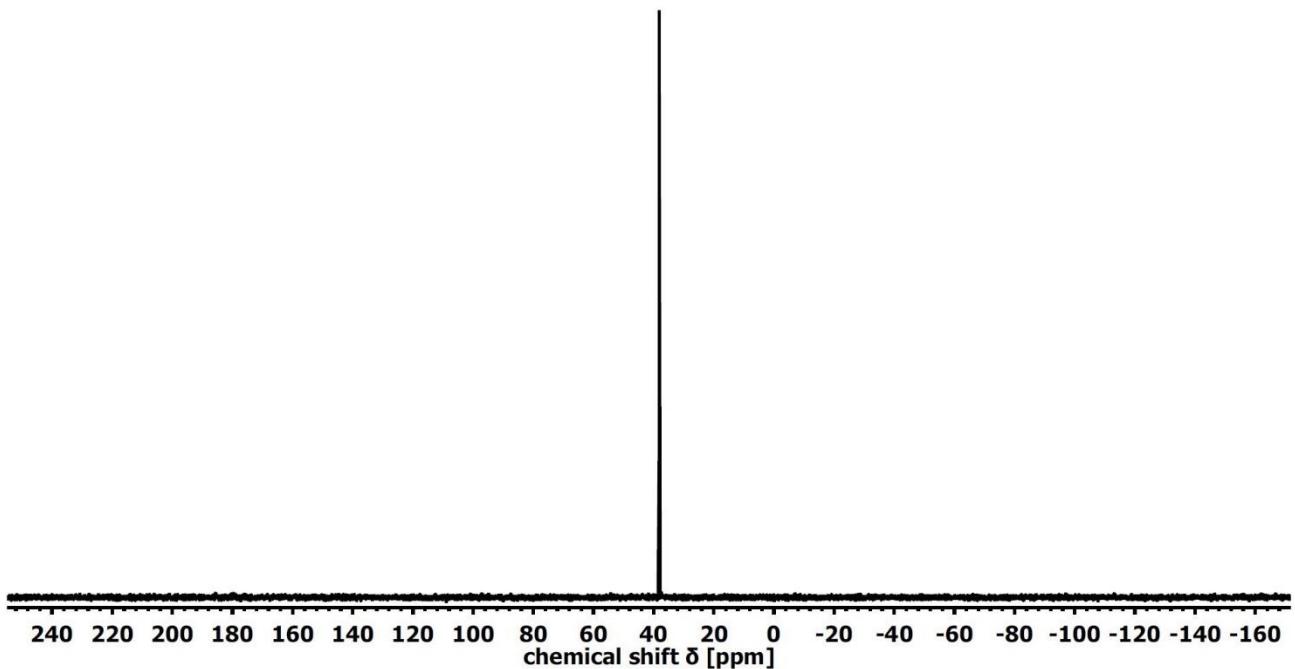


Figure S14:  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of **2** in  $\text{C}_6\text{D}_6$ .

**Complex 3**

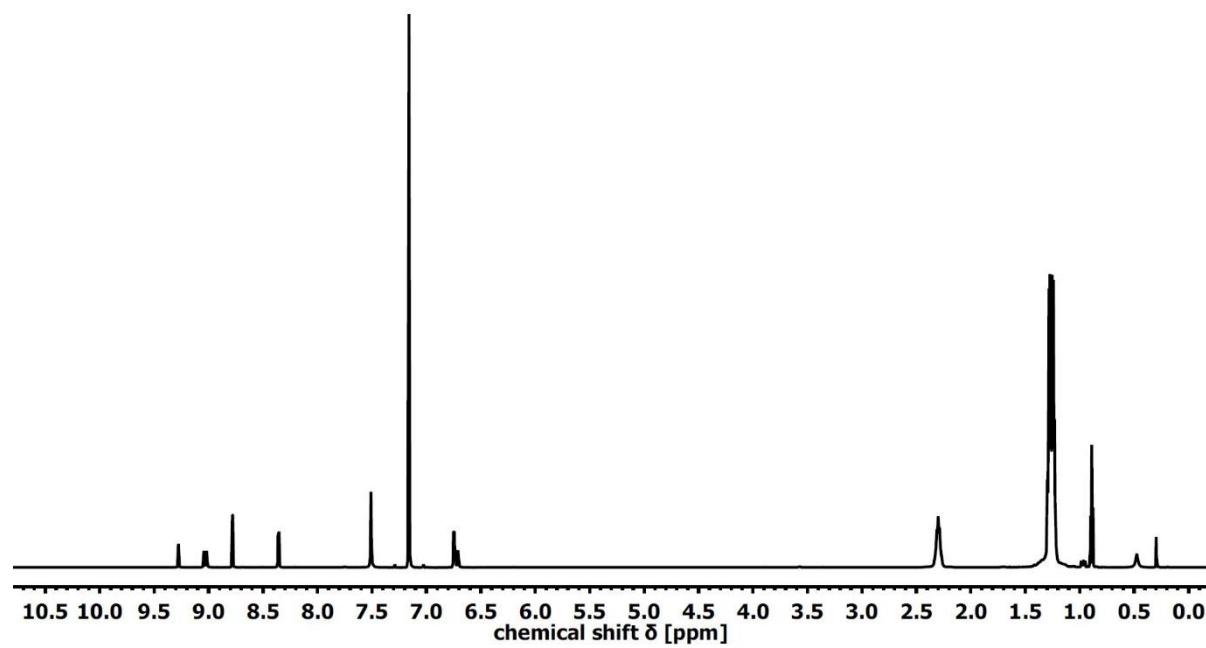


Figure S15:  $^1\text{H}$ -NMR spectrum of **3** in  $\text{C}_6\text{D}_6$

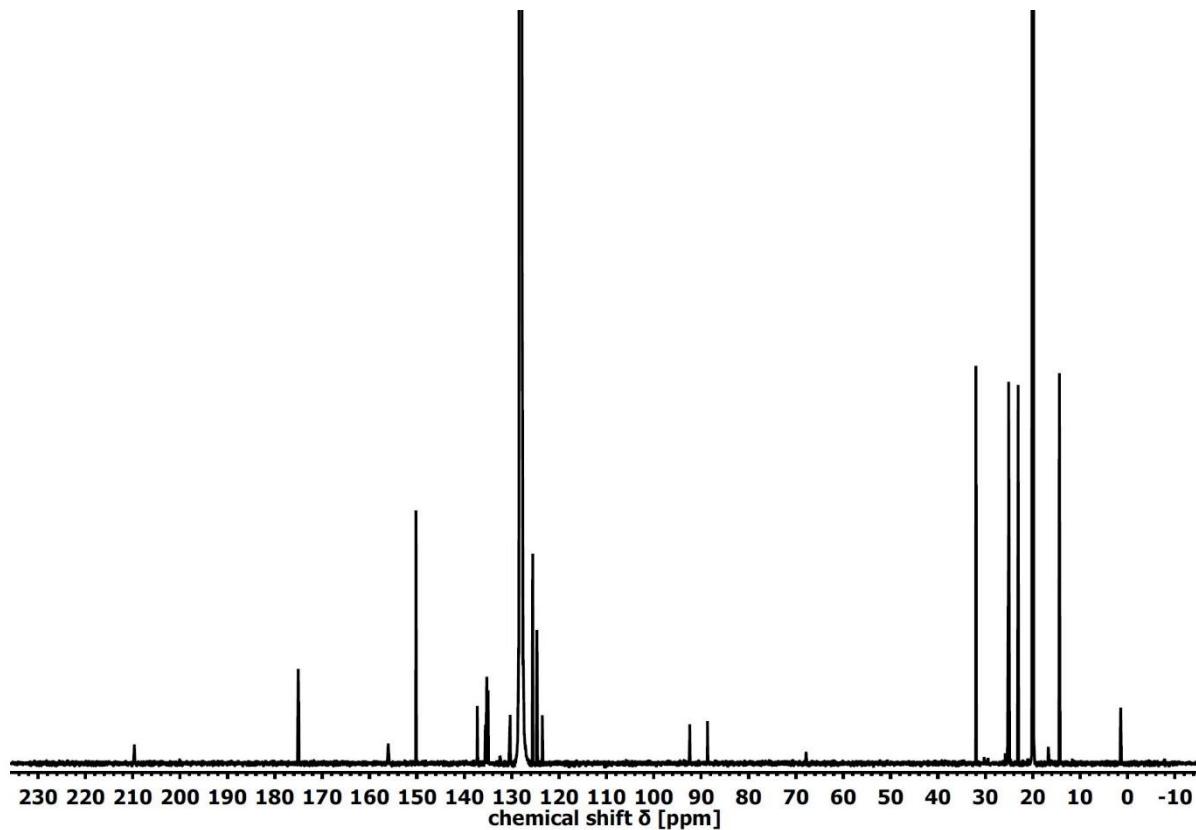


Figure S16:  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **3** in  $\text{C}_6\text{D}_6$

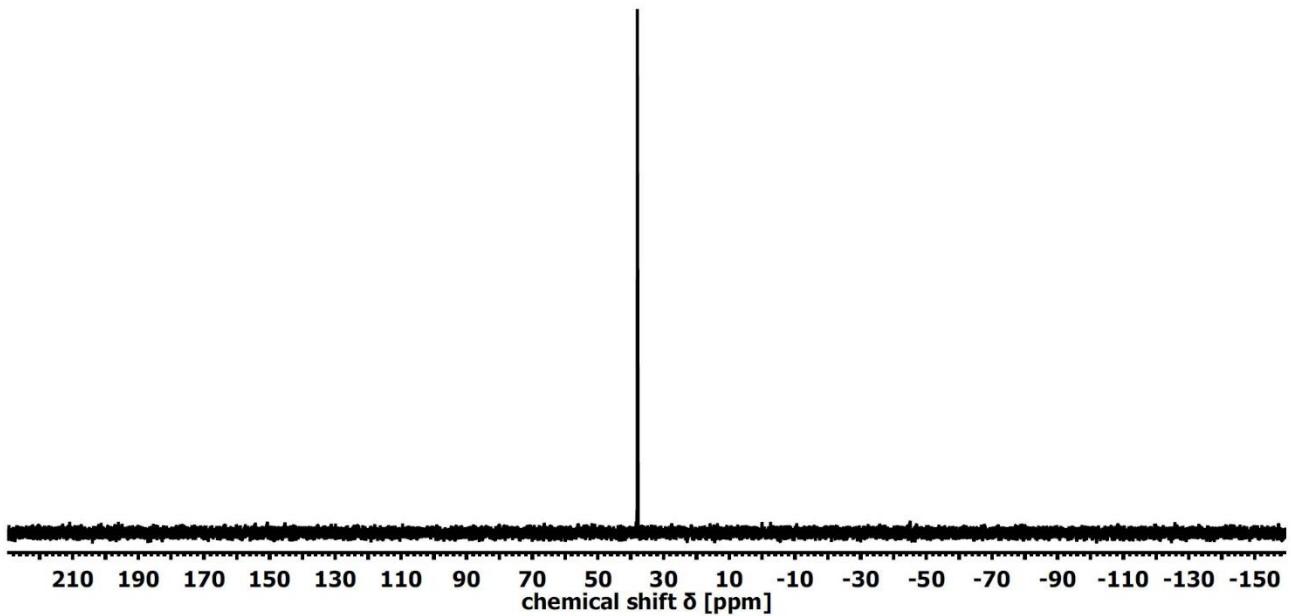


Figure S17:  $^{31}\text{P}\{\text{H}\}$ -NMR spectrum of **3** in  $\text{C}_6\text{D}_6$

#### Complex **4**

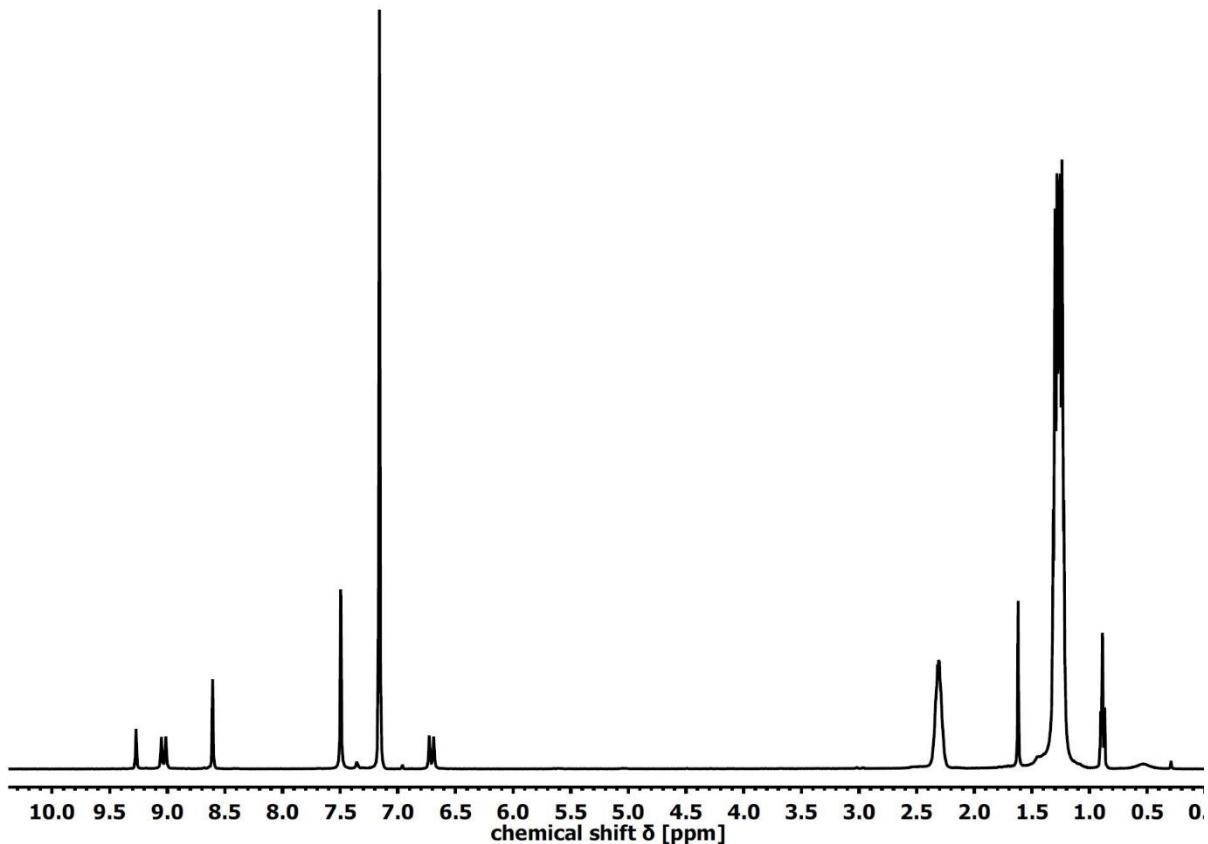


Figure S18 Figure S19:  $^1\text{H}$ -NMR spectrum of **4** in  $\text{C}_6\text{D}_6$

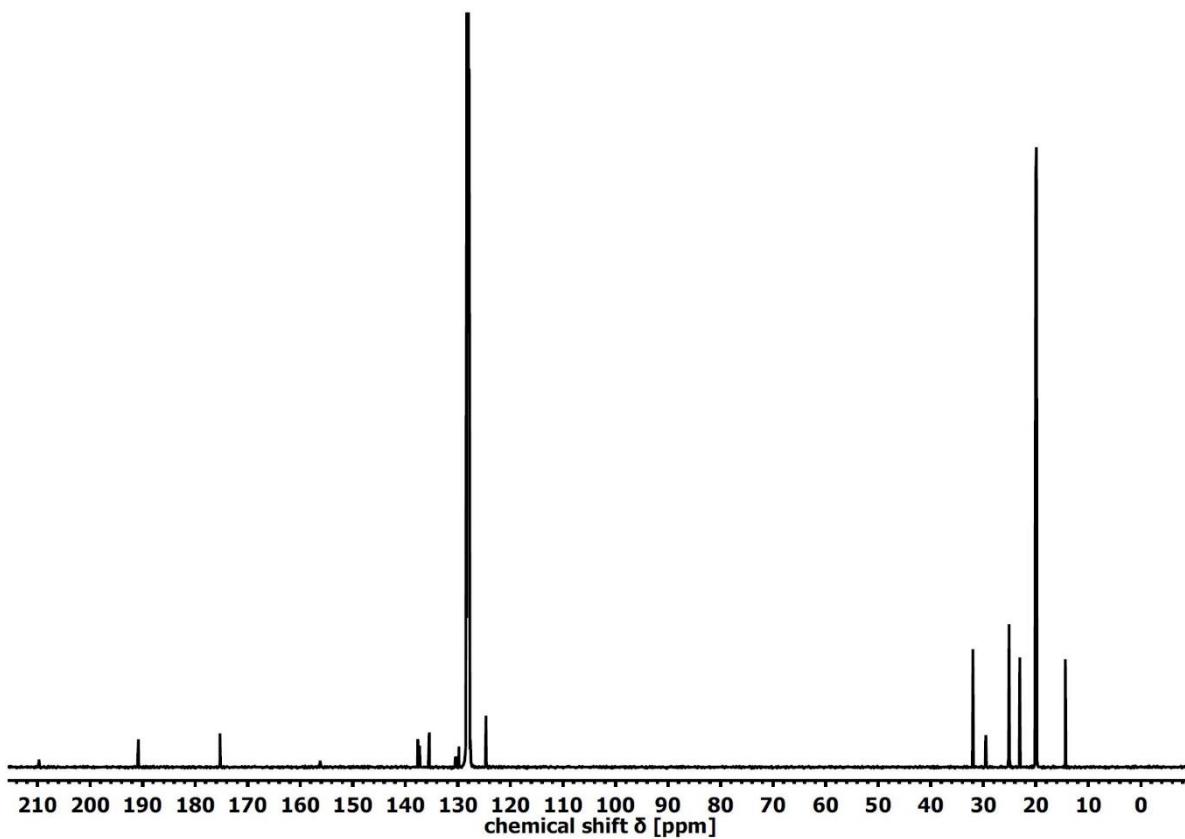


Figure S20:  $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **4** in  $\text{C}_6\text{D}_6$ .

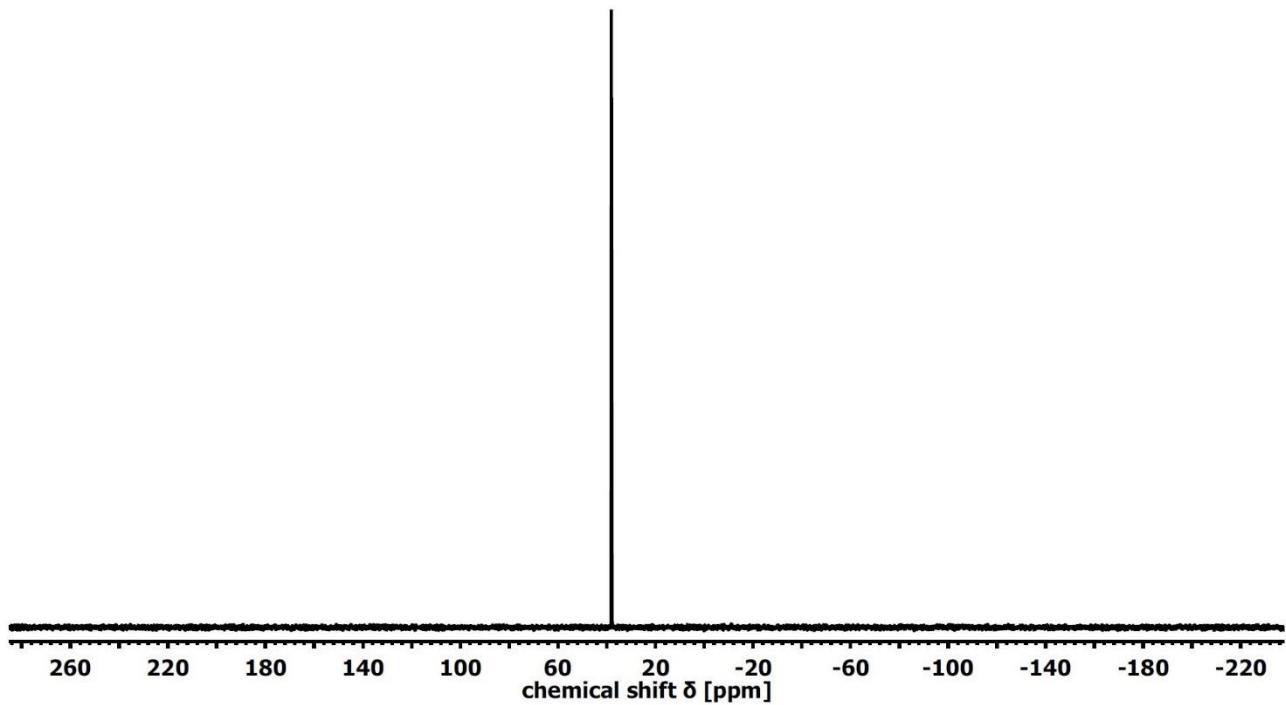


Figure S21:  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of **4** in  $\text{C}_6\text{D}_6$

# ESI-MS

## Complex 1

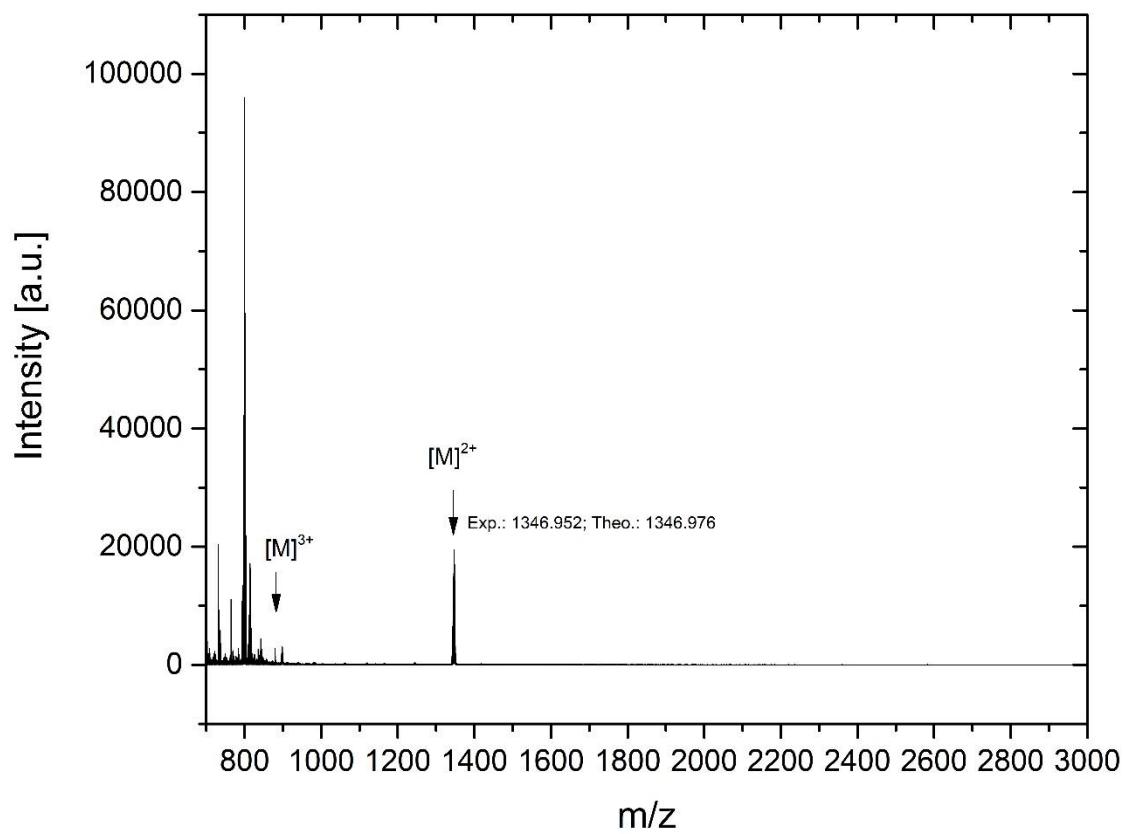


Figure S22: ESI-MS of complex 1.

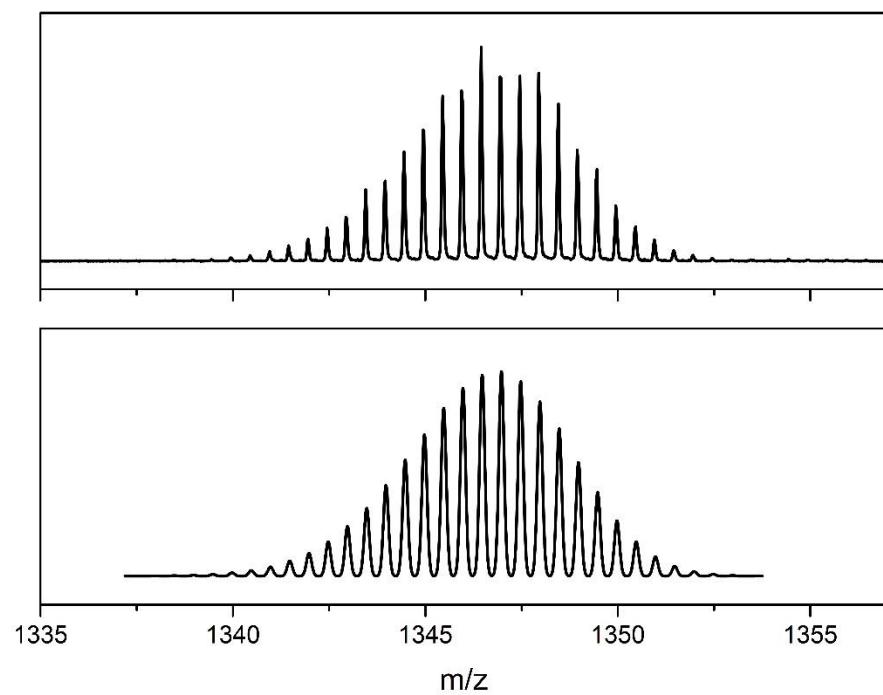


Figure S23:  $[M]^{2+}$  peak: Experimental data (top), calculated (bottom).

## Complex 2

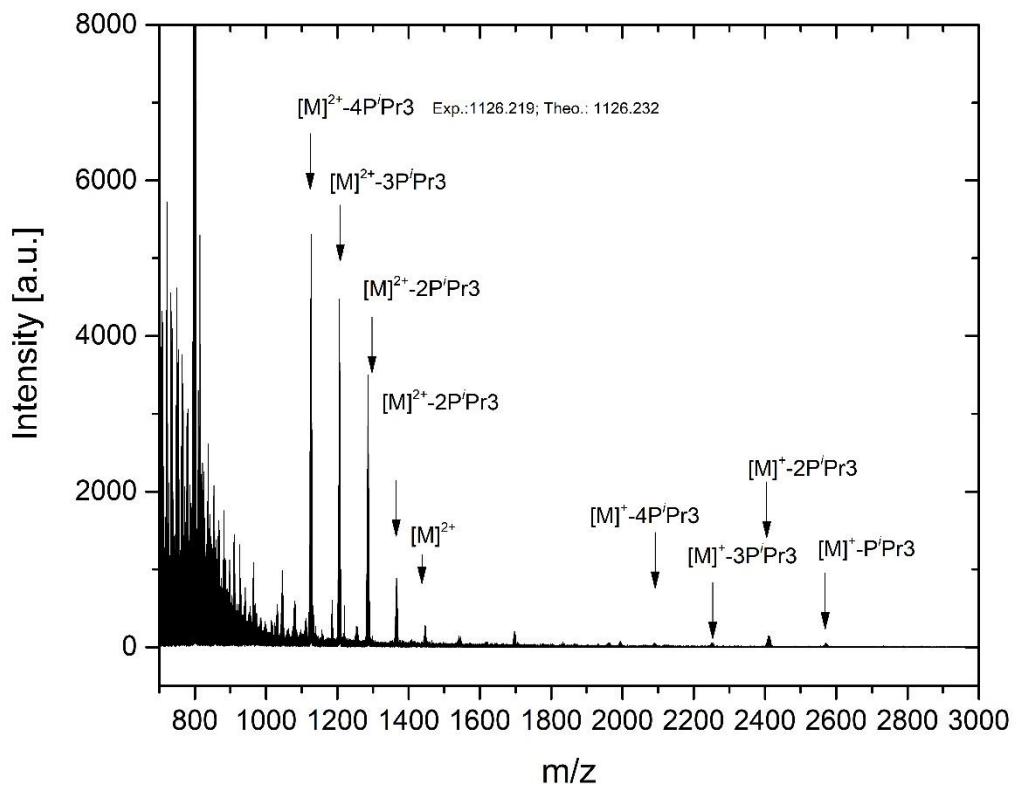


Figure S24: ESI-MS of complex 2.

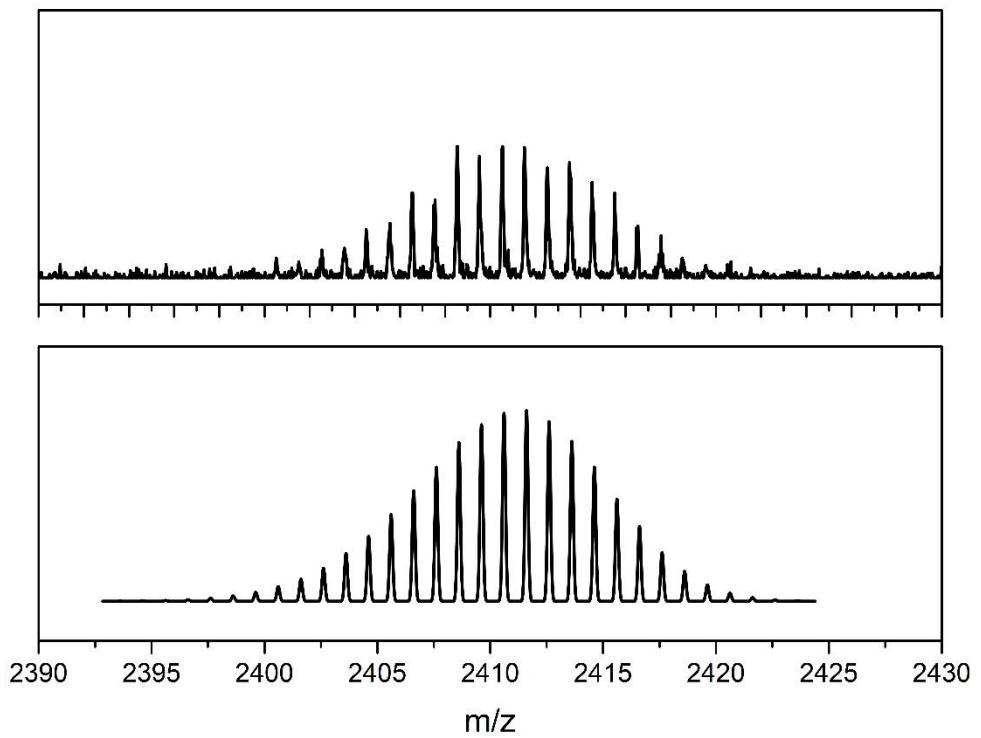


Figure S25:  $[M]^{2+}$ -2 P/Pr<sub>3</sub> peak: Experimental (top), simulation (bottom).

## Complex 4

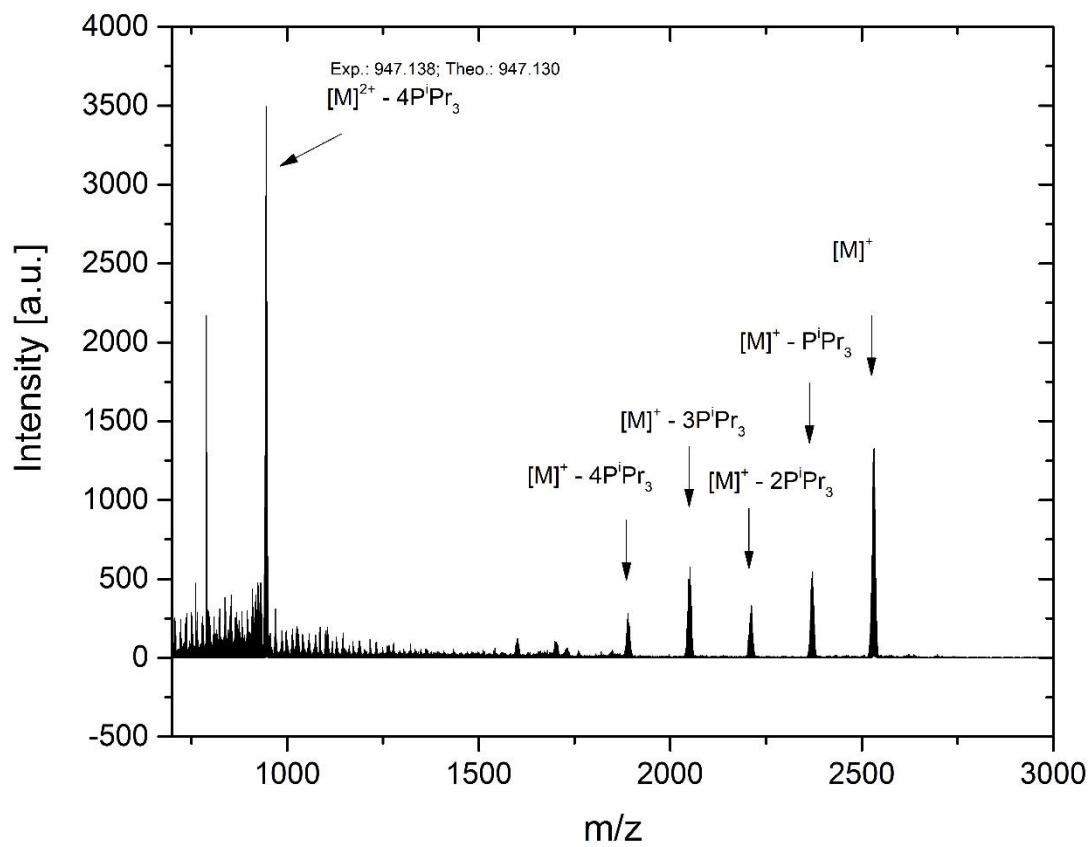


Figure S26: ESI-MS of complex 4.

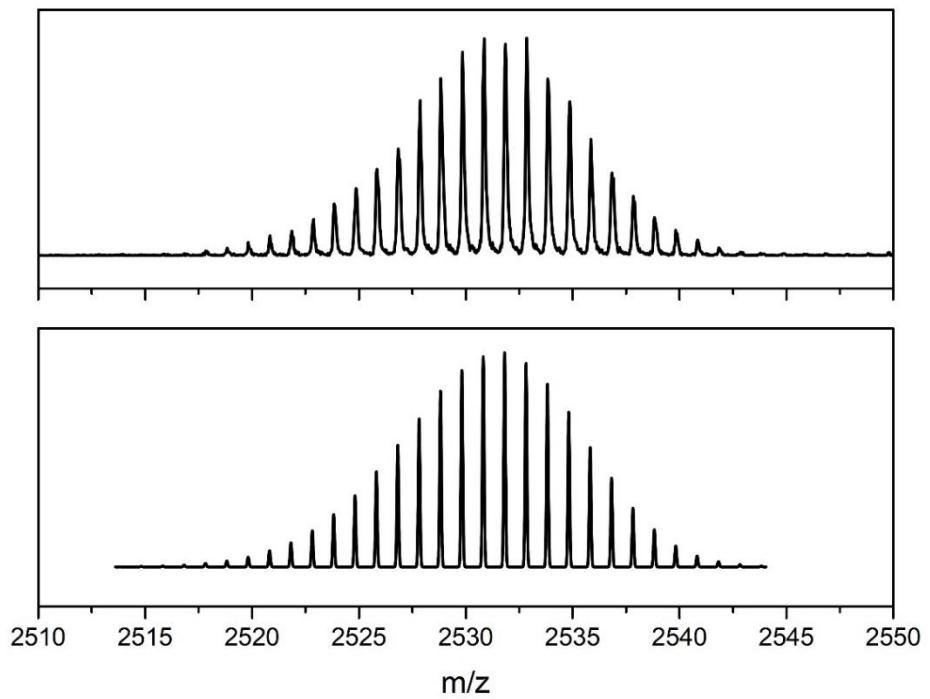


Figure S27:  $[M]^+$  peak: Experimental (top), simulation (bottom).

## X-ray Crystallography

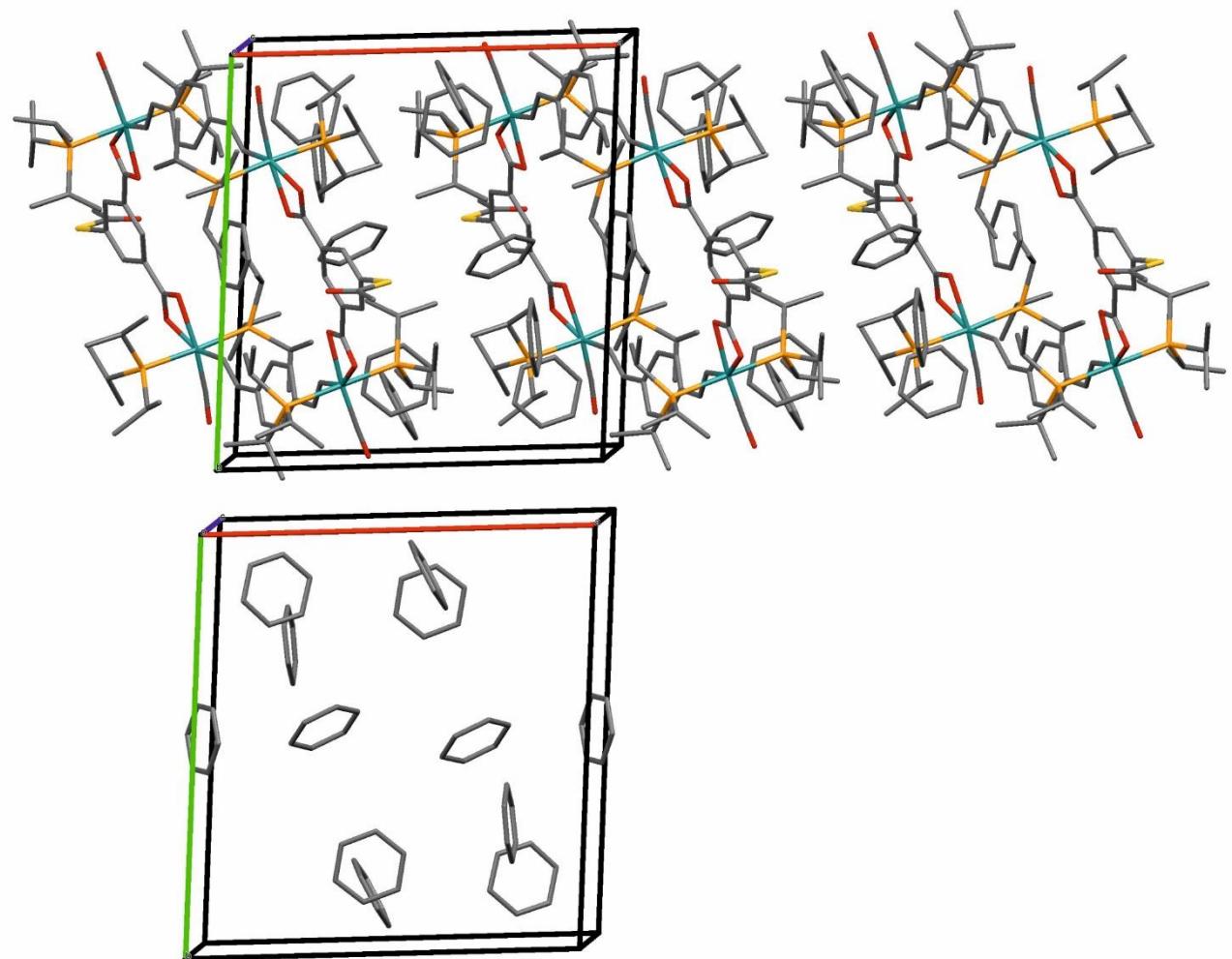


Figure S28: Packing of solvent molecules within the unit cell of macrocycle **4**.

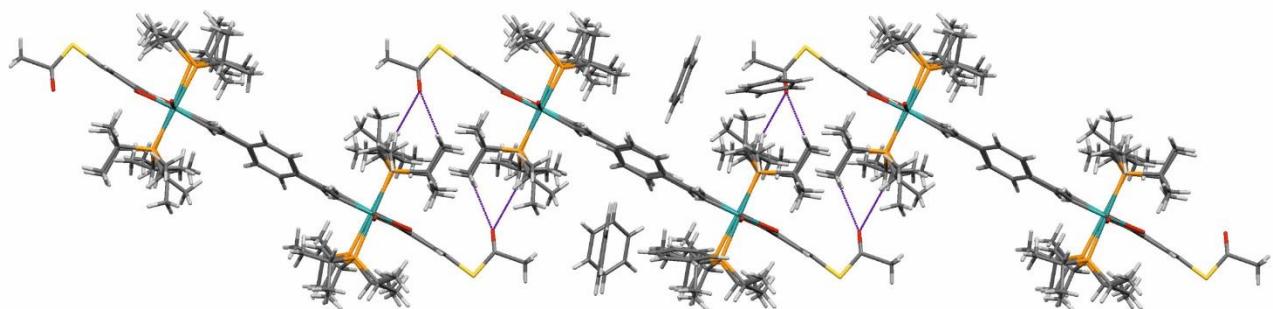


Figure S29: Association of macrocycle **4** in the crystal by hydrogen bonding

Table S1: Crystal and structure refinement data for macrocycle **4**.

<b>4</b>	
<b>Compound</b>	
Formula	C <sub>182</sub> H <sub>262</sub> O <sub>14</sub> P <sub>8</sub> Ru <sub>4</sub> S <sub>2</sub>
D <sub>calc.</sub> / g cm <sup>-3</sup>	1.2418
μ/mm <sup>-1</sup>	0.477
Formula Weight	3390.28
Colour	Yellow
Shape	plate
Size/mm <sup>3</sup>	0.30×0.20×0.10
T/K	100.03
Crystal System	triclinic
Space Group	P-1
a/Å	15.108(3)
b/Å	17.069(2)
c/Å	19.293(3)
α/°	70.272(11)
β/°	75.988(13)
γ/°	88.927(12)
V/Å <sup>3</sup>	4533.1(13)
Z	1
Z'	0.5
Wavelength/Å	0.71073
Radiation type	Mo K <sub>α</sub>
θ <sub>min</sub> /°	1.82
θ <sub>max</sub> /°	25.68
Measured Refl.	39232
Independent Refl.	17156
Reflections with I ≥ σ(I)	4672
R <sub>int</sub>	0.1875
Parameters	971
Restraints	0
Largest Peak	1.3945
Deepest Hole	-2.0282
GooF	0.8167
wR <sub>2</sub> (all data)	0.1389
wR <sub>2</sub>	0.0916
R <sub>1</sub> (all data)	0.2633
R <sub>1</sub>	0.0739

Table S2: Bond lengths [ $\text{\AA}$ ] for **4**.

Atom	Atom	Length/ $\text{\AA}$	Atom	Atom	Length/ $\text{\AA}$
Ru2	P3	2.402(4)	C38	C40	1.572(13)
Ru2	P4	2.402(4)	C35	C36	1.533(13)
Ru2	O4 <sup>1</sup>	2.205(6)	C35	C37	1.515(13)
Ru2	O3 <sup>1</sup>	2.287(6)	C32	C34	1.522(11)
Ru2	C10	1.982(10)	C32	C33	1.515(13)
Ru2	C12	1.763(10)	C29	C31	1.550(12)
Ru1	P1	2.398(4)	C29	C30	1.512(14)
Ru1	P2	2.413(4)	C26	C27	1.521(13)
Ru1	O2	2.183(6)	C26	C28	1.547(14)
Ru1	O1	2.316(6)	C23	C25	1.588(15)
Ru1	C1	1.976(9)	C23	C24	1.544(14)
Ru1	C11	1.764(10)	C50	C52	1.547(12)
S1	C18	1.816(10)	C50	C51	1.500(13)
S1	C21	1.647(14)	C56	C58	1.592(14)
P3	C47	1.818(11)	C56	C57	1.547(12)
P3	C41	1.880(10)	C53	C55	1.564(12)
P3	C44	1.827(10)	C53	C54	1.550(15)
P4	C50	1.847(9)	C47	C48	1.547(14)
P4	C56	1.833(11)	C47	C49	1.551(12)
P4	C53	1.836(10)	C41	C42	1.512(12)
P1	C29	1.838(10)	C41	C43	1.529(12)
P1	C26	1.866(10)	C44	C46	1.547(12)
P1	C23	1.849(12)	C44	C45	1.521(12)
P2	C38	1.864(9)	C89	C88	1.426(18)
P2	C35	1.859(10)	C89	C90	1.398(15)
P2	C32	1.855(9)	C88	C87	1.308(17)
O2	C13	1.266(10)	C91	C90	1.354(15)
O1	C13	1.275(10)	C91	C86	1.387(17)
O6	C12	1.194(10)	C86	C87	1.342(17)
O5	C11	1.194(10)	C60	C59	1.370(15)
O4	C20	1.295(10)	C60	C61	1.376(14)
O3	C20	1.271(11)	C59	C61 <sup>1</sup>	1.399(16)
O7	C21	1.130(13)	C64	C65	1.388(16)
C1	C2	1.361(11)	C64	C63	1.383(17)
C2	C3	1.481(12)	C65	C66	1.389(17)
C3	C8	1.390(13)	C66	C67	1.326(18)
C3	C4	1.396(11)	C67	C62	1.392(16)
C8	C7	1.382(11)	C62	C63	1.347(16)
C7	C6	1.392(11)	C85	C80	1.361(16)
C6	C5	1.367(12)	C85	C84	1.354(17)
C6	C9	1.498(12)	C80	C81	1.355(16)
C5	C4	1.381(11)	C81	C82	1.344(16)
C9	C10	1.310(12)	C82	C83	1.386(17)
C13	C14	1.506(11)	C83	C84	1.399(18)
C14	C15	1.381(12)	C74	C75	1.371(17)
C14	C19	1.392(12)	C74	C79	1.382(17)
C15	C16	1.408(11)	C75	C76	1.387(19)
C16	C20	1.466(13)	C76	C77	1.396(19)
C16	C17	1.392(12)	C77	C78	1.364(19)
C17	C18	1.351(13)	C78	C79	1.391(18)
C18	C19	1.422(12)	C71	C72	1.37(3)
C21	C22	1.665(17)	C71	C70	1.48(4)
C38	C39	1.540(13)	C72	C73	1.31(2)
			C73	C68	1.30(2)
			C68	C69	1.376(19)

Atom	Atom	Length/Å	
C69	C70	1.35(2)	$^{1-x, 1-y, 1-z}$

Table S30: Bond Angles in [°] for 4.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
P4	Ru2	P3	176.83(12)	C53	P4	C50	101.4(5)
O4 <sup>1</sup>	Ru2	P3	90.2(2)	C53	P4	C56	109.5(5)
O4 <sup>1</sup>	Ru2	P4	86.6(2)	C29	P1	Ru1	114.8(4)
O3 <sup>1</sup>	Ru2	P3	87.32(19)	C26	P1	Ru1	112.9(4)
O3 <sup>1</sup>	Ru2	P4	91.02(19)	C26	P1	C29	102.9(5)
O3 <sup>1</sup>	Ru2	O4 <sup>1</sup>	59.1(2)	C23	P1	Ru1	114.0(4)
C10	Ru2	P3	88.6(3)	C23	P1	C29	102.3(5)
C10	Ru2	P4	92.1(3)	C23	P1	C26	108.8(6)
C10	Ru2	O4 <sup>1</sup>	101.9(3)	C38	P2	Ru1	114.3(4)
C10	Ru2	O3 <sup>1</sup>	160.5(3)	C35	P2	Ru1	111.1(4)
C20 <sup>1</sup>	Ru2	P3	89.2(3)	C35	P2	C38	108.6(5)
C20 <sup>1</sup>	Ru2	P4	88.0(3)	C32	P2	Ru1	116.3(4)
C20 <sup>1</sup>	Ru2	O4 <sup>1</sup>	29.8(3)	C32	P2	C38	101.7(4)
C20 <sup>1</sup>	Ru2	O3 <sup>1</sup>	29.3(2)	C13	O2	Ru1	93.5(6)
C20 <sup>1</sup>	Ru2	C10	131.6(4)	C13	O1	Ru1	87.2(5)
C12	Ru2	P3	91.7(4)	C20	O4	Ru2 <sup>1</sup>	92.3(6)
C12	Ru2	P4	91.4(4)	C20	O3	Ru2 <sup>1</sup>	89.3(6)
C12	Ru2	O4 <sup>1</sup>	168.9(4)	C2	C1	Ru1	135.9(8)
C12	Ru2	O3 <sup>1</sup>	110.1(4)	C3	C2	C1	128.2(9)
C12	Ru2	C10	89.1(4)	C8	C3	C2	124.5(8)
C12	Ru2	C20 <sup>1</sup>	139.2(4)	C4	C3	C2	119.2(9)
P2	Ru1	P1	179.72(12)	C4	C3	C8	116.3(9)
O2	Ru1	P1	89.5(2)	C7	C8	C3	121.7(9)
O2	Ru1	P2	90.4(2)	C6	C7	C8	121.4(10)
O1	Ru1	P1	90.72(18)	C5	C6	C7	116.9(9)
O1	Ru1	P2	89.02(18)	C9	C6	C5	121.3(9)
O1	Ru1	O2	58.7(2)	C9	C6	C5	121.7(9)
C1	Ru1	P1	92.3(3)	C4	C5	C6	122.3(9)
C1	Ru1	P2	88.0(3)	C5	C4	C3	121.3(9)
C1	Ru1	O2	97.9(3)	C10	C9	C6	131.8(9)
C1	Ru1	O1	156.3(3)	C9	C10	Ru2	136.6(8)
C13	Ru1	P1	89.4(2)	O2	C13	Ru1	57.3(5)
C13	Ru1	P2	90.4(2)	O1	C13	Ru1	63.3(4)
C13	Ru1	O2	29.2(2)	O1	C13	O2	120.6(8)
C13	Ru1	O1	29.5(2)	C14	C13	Ru1	175.9(8)
C13	Ru1	C1	127.1(4)	C14	C13	O2	119.7(9)
C11	Ru1	P1	87.1(4)	C14	C13	O1	119.7(9)
C11	Ru1	P2	92.9(4)	C15	C14	C13	118.7(9)
C11	Ru1	O2	172.2(4)	C19	C14	C13	121.0(9)
C11	Ru1	O1	114.4(4)	C19	C14	C15	120.3(9)
C11	Ru1	C1	89.3(4)	C16	C15	C14	120.9(9)
C11	Ru1	C13	143.6(4)	C20	C16	C15	120.9(9)
C21	S1	C18	94.3(7)	C17	C16	C20	117.9(9)
C47	P3	Ru2	111.4(4)	O4	C20	Ru2 <sup>1</sup>	120.9(9)
C41	P3	Ru2	116.2(4)	O3	C20	Ru2 <sup>1</sup>	57.9(5)
C41	P3	C47	102.7(5)	O3	C20	O4	61.5(5)
C44	P3	Ru2	120.5(4)	C16	C20	O4	119.3(9)
C44	P3	C47	103.3(5)	C16	C20	O4	174.4(8)
C44	P3	C41	100.4(5)	C16	C20	O3	117.7(9)
C50	P4	Ru2	114.3(4)	C18	C17	C16	123.0(9)
C56	P4	Ru2	113.1(4)	C17	C18	S1	121.5(9)
C56	P4	C50	104.3(5)	C19	C18	S1	122.0(8)
C53	P4	Ru2	113.2(4)	C19	C18	C17	116.6(8)

<b>Atom</b>	<b>Atom</b>	<b>Atom</b>	<b>Angle°</b>	<b>Atom</b>	<b>Atom</b>	<b>Atom</b>	<b>Angle°</b>
C18	C19	C14	118.3(10)	C81	C80	C85	118.3(14)
O6	C12	Ru2	175.1(10)	C82	C81	C80	120.5(15)
O5	C11	Ru1	178.2(11)	C83	C82	C81	122.3(14)
O7	C21	S1	134.6(14)	C84	C83	C82	116.9(14)
C22	C21	S1	111.4(10)	C83	C84	C85	119.0(15)
C22	C21	O7	113.8(14)	C79	C74	C75	119.9(16)
C39	C38	P2	114.0(7)	C76	C75	C74	118.3(18)
C40	C38	P2	115.6(7)	C77	C76	C75	122.4(17)
C40	C38	C39	107.7(9)	C78	C77	C76	118.3(18)
C36	C35	P2	116.8(7)	C79	C78	C77	119.9(18)
C37	C35	P2	113.4(8)	C78	C79	C74	121.2(16)
C37	C35	C36	111.8(10)	C70	C71	C72	107.7(19)
C34	C32	P2	114.1(7)	C73	C72	C71	135(3)
C33	C32	P2	112.0(7)	C68	C73	C72	113(2)
C33	C32	C34	111.1(9)	C69	C68	C73	124(2)
C31	C29	P1	115.6(7)	C70	C69	C68	120(2)
C30	C29	P1	111.7(7)	C69	C70	C71	120(2)
C30	C29	C31	108.2(9)	<hr/>			
C27	C26	P1	113.6(8)	1-x, 1-y,			
C28	C26	P1	117.1(8)				
C28	C26	C27	108.3(10)				
C25	C23	P1	112.0(8)				
C24	C23	P1	115.6(8)				
C24	C23	C25	112.0(11)				
C52	C50	P4	110.3(7)				
C51	C50	P4	117.2(7)				
C51	C50	C52	107.6(8)				
C58	C56	P4	116.2(7)				
C57	C56	P4	115.5(7)				
C57	C56	C58	106.5(9)				
C55	C53	P4	114.1(8)				
C54	C53	P4	114.4(7)				
C54	C53	C55	108.9(9)				
C48	C47	P3	116.3(8)				
C49	C47	P3	114.5(8)				
C49	C47	C48	109.0(9)				
C42	C41	P3	113.9(7)				
C43	C41	P3	111.2(8)				
C43	C41	C42	111.2(8)				
C46	C44	P3	114.5(7)				
C45	C44	P3	118.2(7)				
C45	C44	C46	109.4(9)				
C90	C89	C88	116.9(14)				
C87	C88	C89	121.0(15)				
C86	C91	C90	122.9(13)				
C91	C90	C89	118.7(14)				
C87	C86	C91	117.1(14)				
C86	C87	C88	123.4(16)				
C61	C60	C59	120.9(12)				
C61 <sup>1</sup>	C59	C60	121.0(12)				
C59 <sup>1</sup>	C61	C60	118.1(12)				
C63	C64	C65	120.1(14)				
C66	C65	C64	117.7(14)				
C67	C66	C65	121.4(14)				
C62	C67	C66	121.0(15)				
C63	C62	C67	119.0(14)				
C62	C63	C64	120.7(13)				
C84	C85	C80	123.0(16)				

## Voltammograms of **1,2** and **4**

### Complex **1**

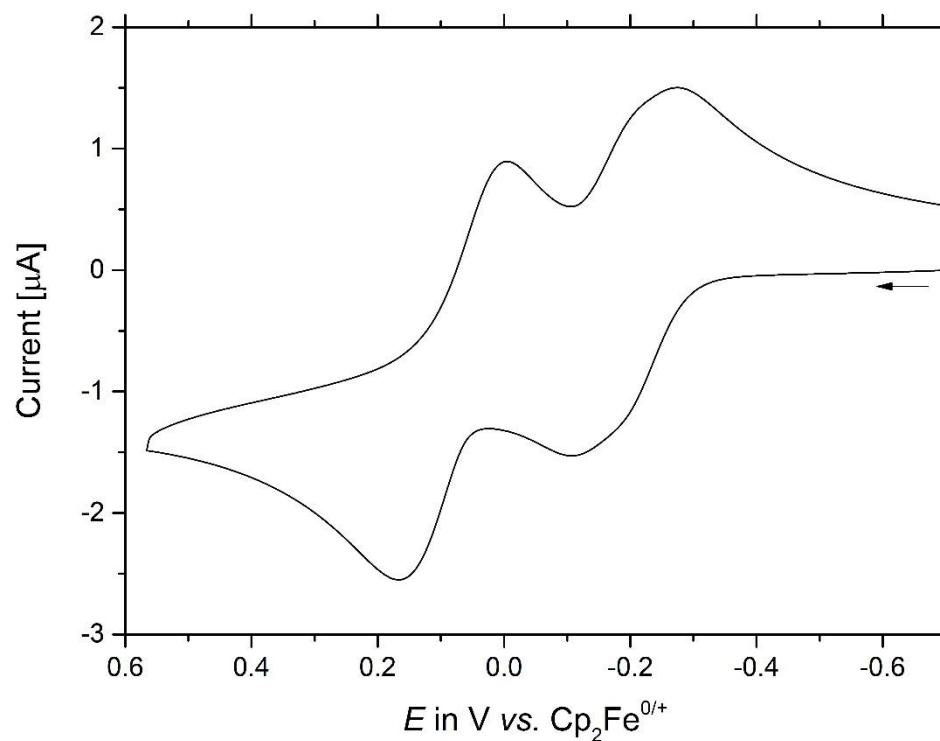


Figure S310: Cyclic voltammogram of **1**.

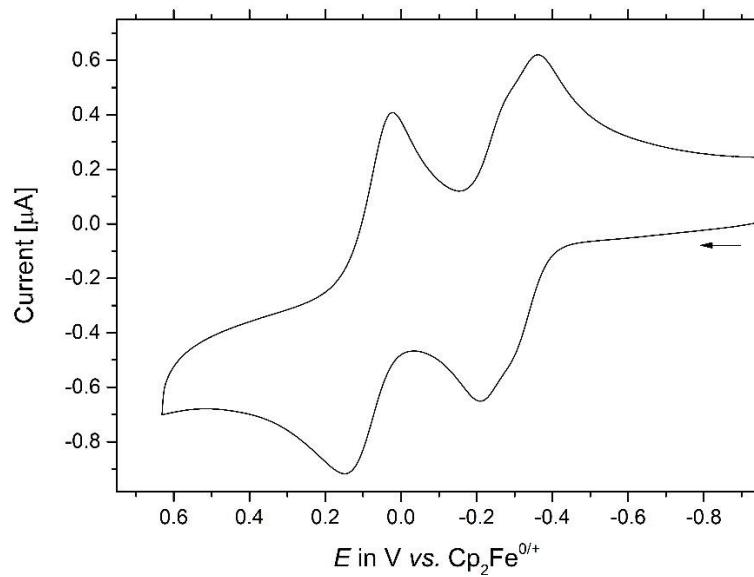


Figure S321: Cyclic voltammogram of **1** (TBA BArF electrolyte).

## Complex 2

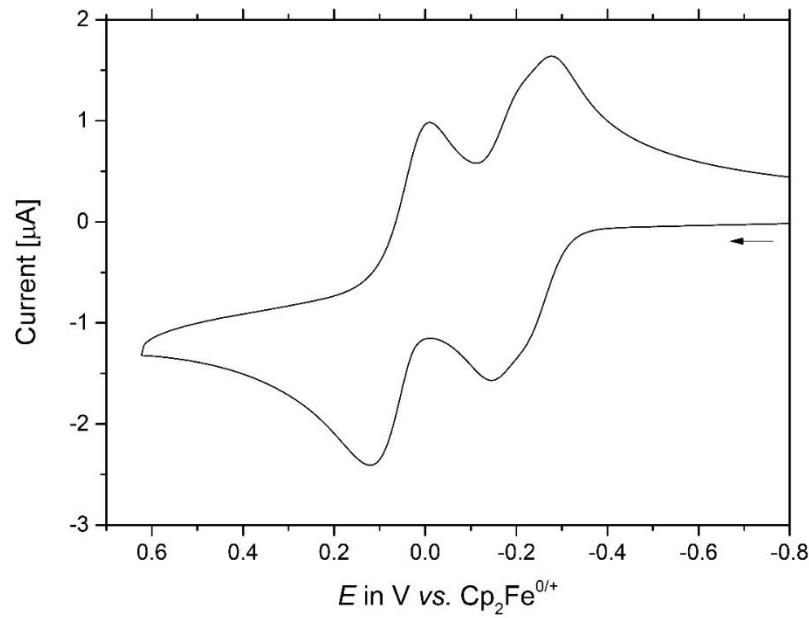


Figure S332: Cyclic voltammogram of **2**.

**Complex 4**

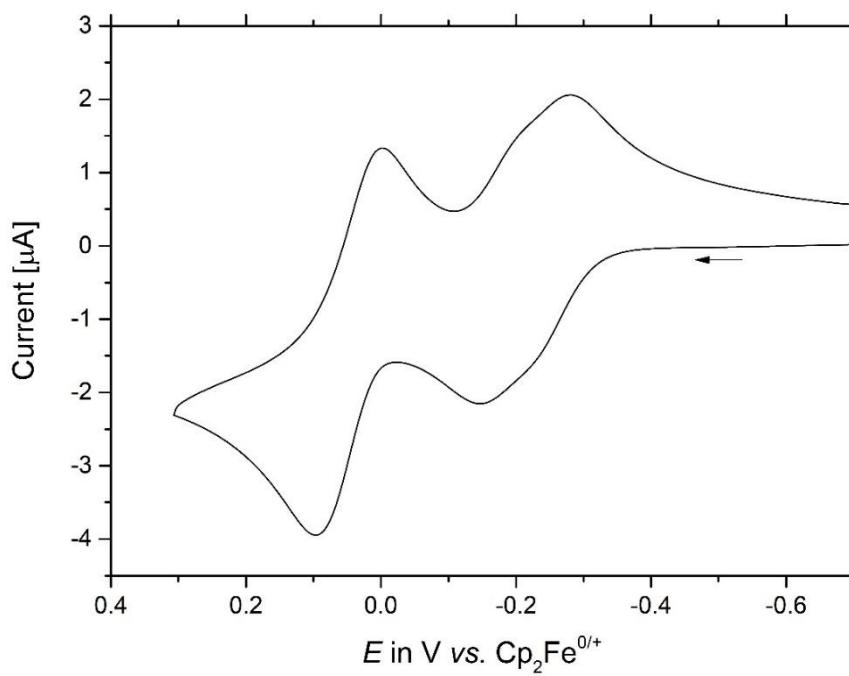


Figure S343: Cyclic voltammogram of **4**.

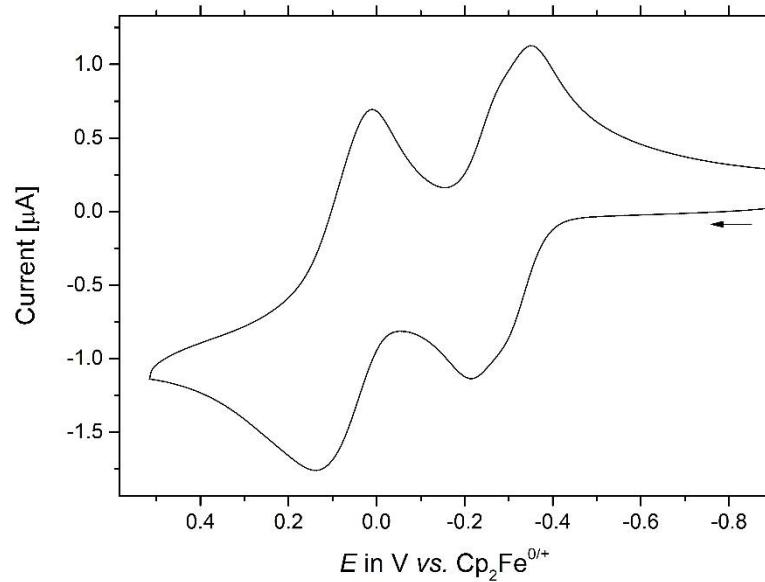


Figure S354 Cyclic voltammogram of **4** (TBA BArF).

## Square Wave voltammetry:

### Complex 1

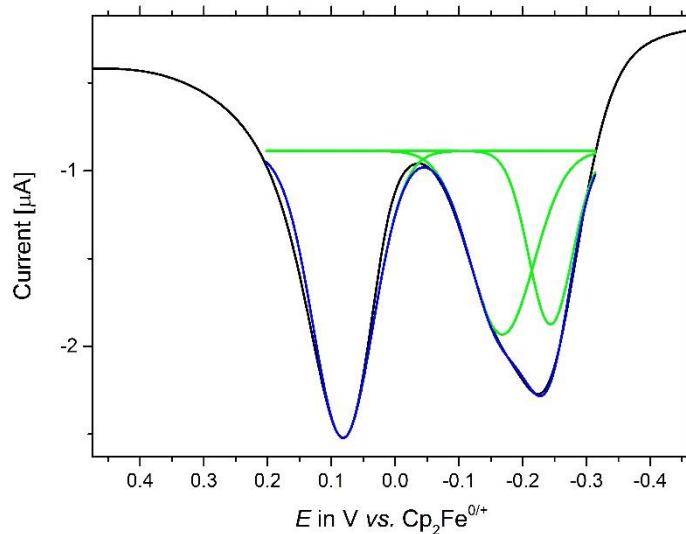


Figure S365: Square wave voltammetric analysis of **1**

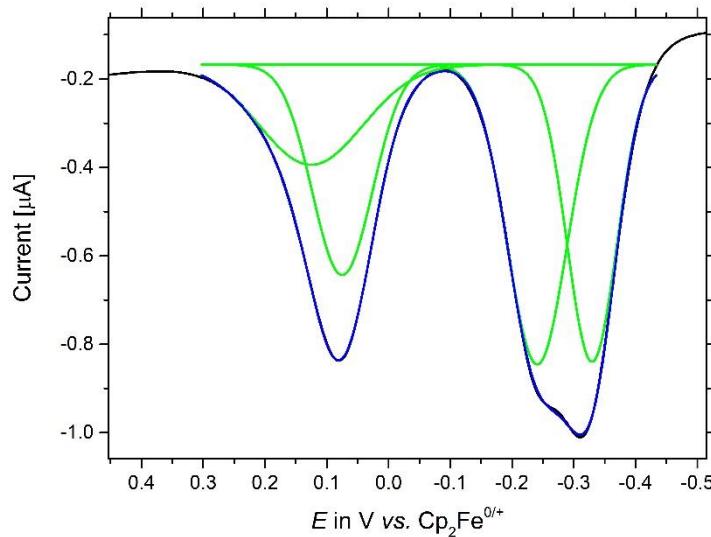


Figure S376 Square wave voltammetric analysis of **1** (TBA BArF).

## Complex 2

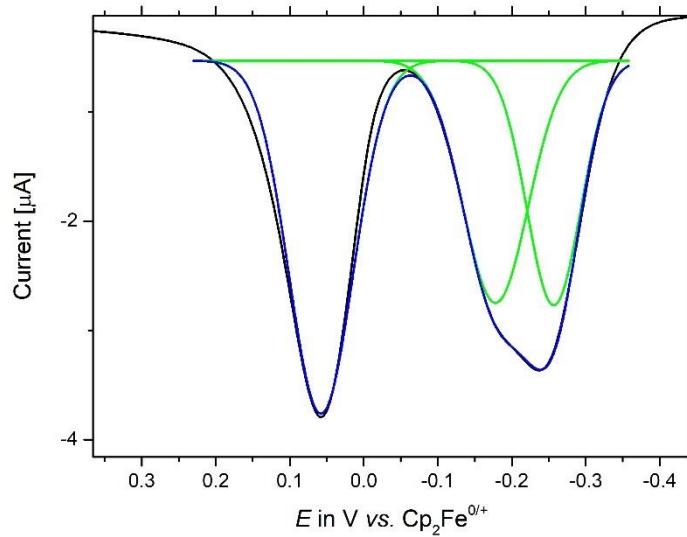


Figure S38: Square wave voltammetric analysis of **2**

## Complex 3

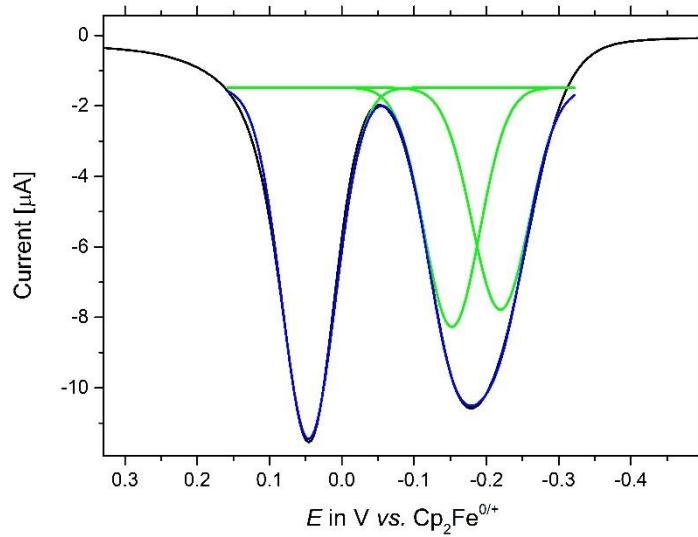


Figure S38: Square wave voltammetric analysis of **3**

**Complex 4**

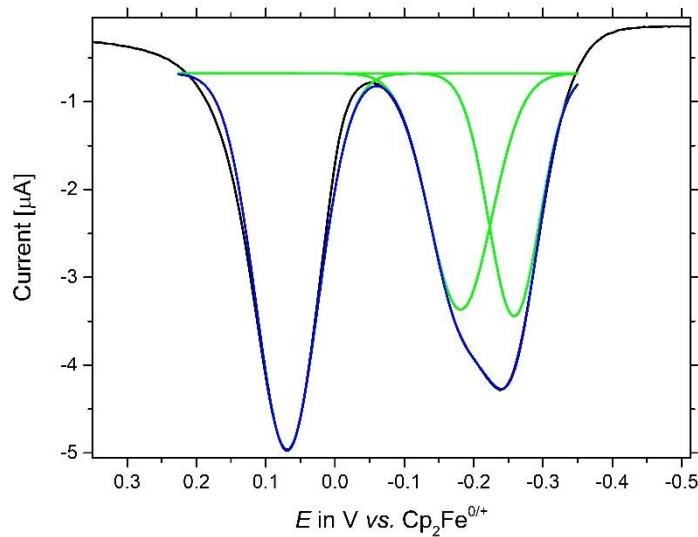


Figure S39: Square wave voltammetric analysis of **4**

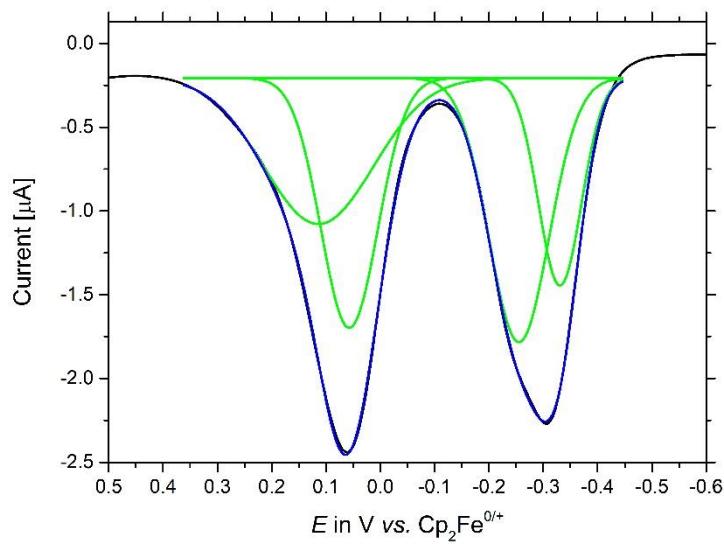


Figure S390 Square wave voltammetric analysis of **4** (TBA BArF).

## Results of IR spectroelectrochemical experiments of **2**, **3** and **4**

### Complex **2**

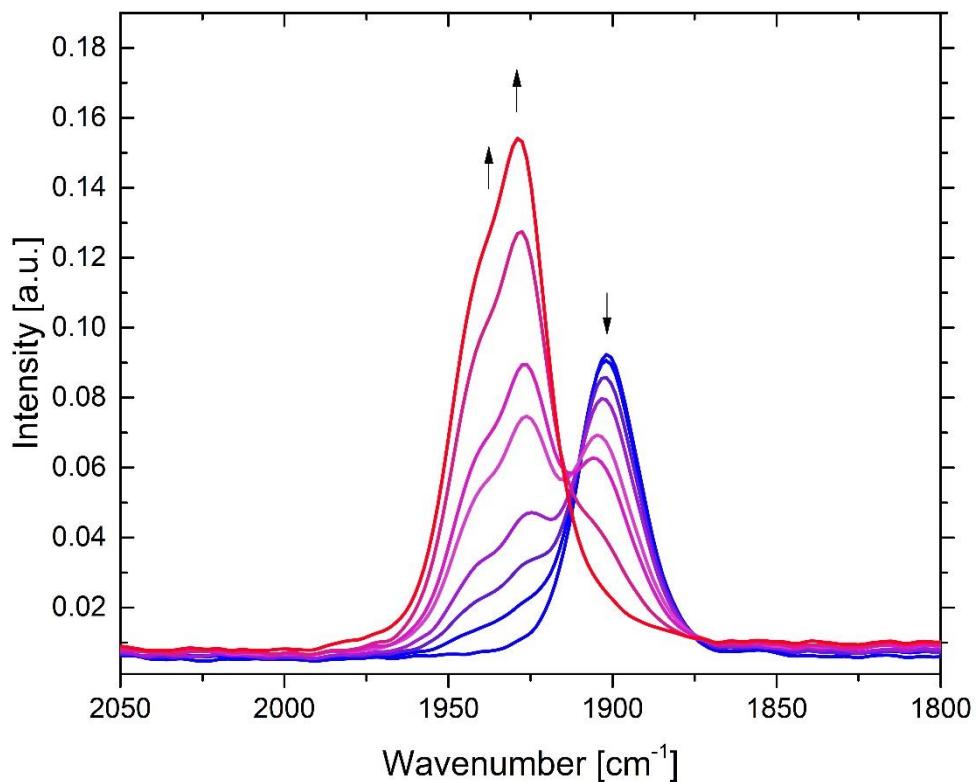


Figure S401: IR spectroscopic changes in the CO-region during the first oxidation of **2** in 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> / TBAPF<sub>6</sub>.

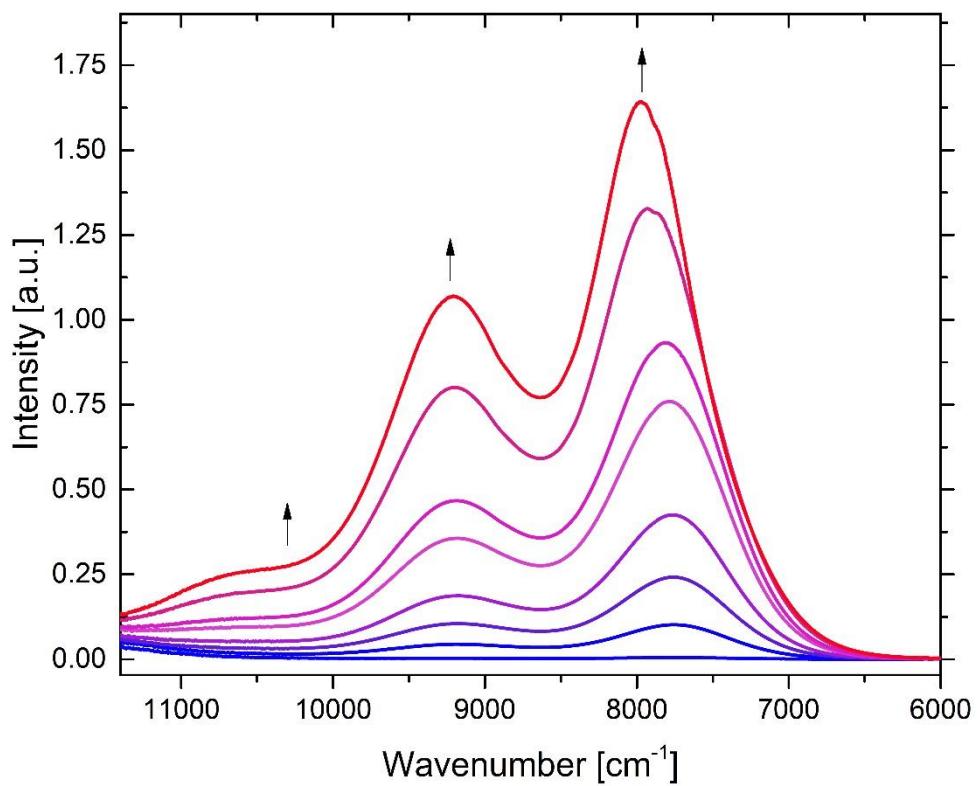


Figure S412: Spectroscopic changes in NIR during the first oxidation of **2** in 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> / TBAPF<sub>6</sub>.

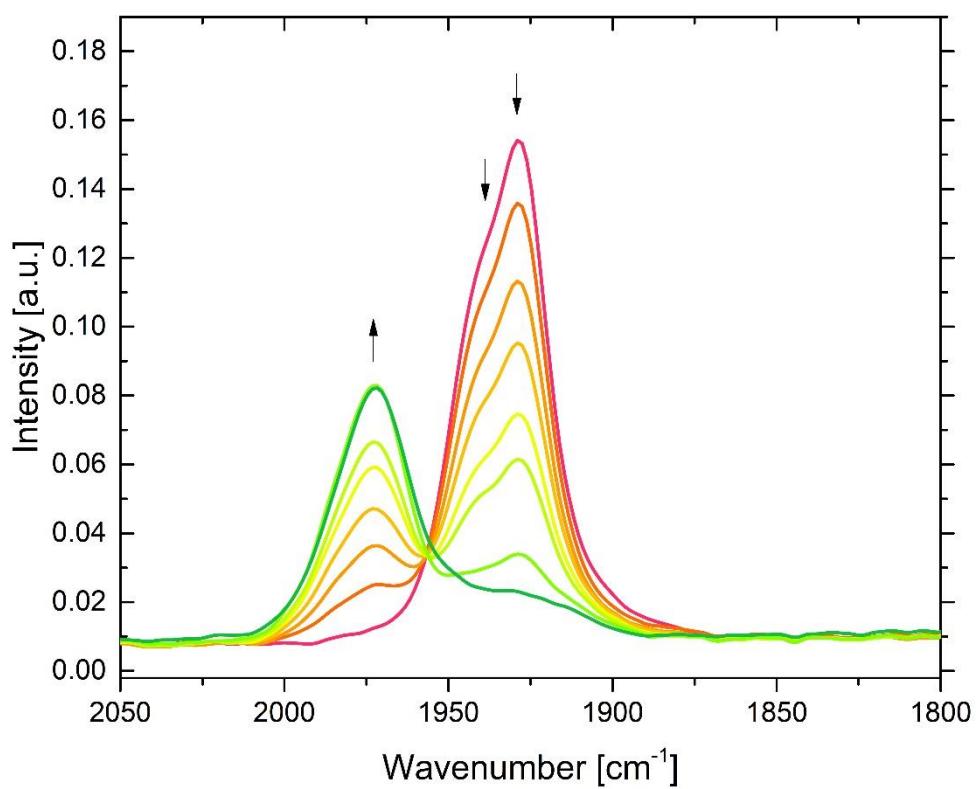


Figure S423: IR spectroscopic changes in the CO-region during the second oxidation of **2** in 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> / TBAPF<sub>6</sub>.

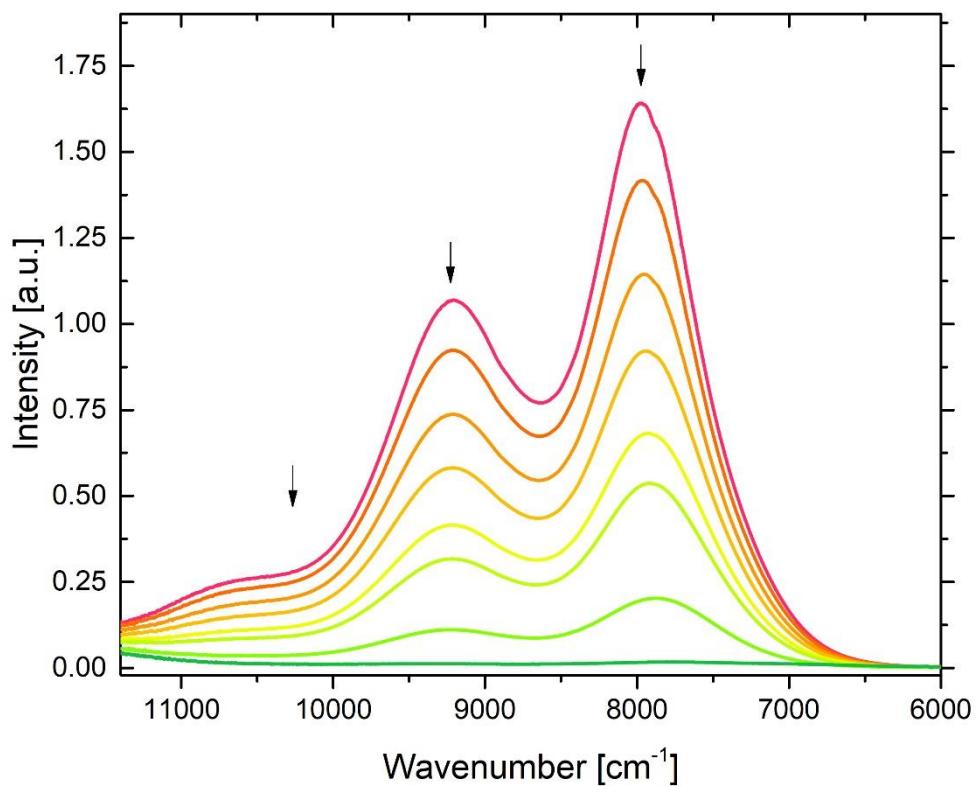


Figure S434: Spectroscopic changes in NIR during the second oxidation of **2** in 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> / TBAPF<sub>6</sub>.

**Complex 3**

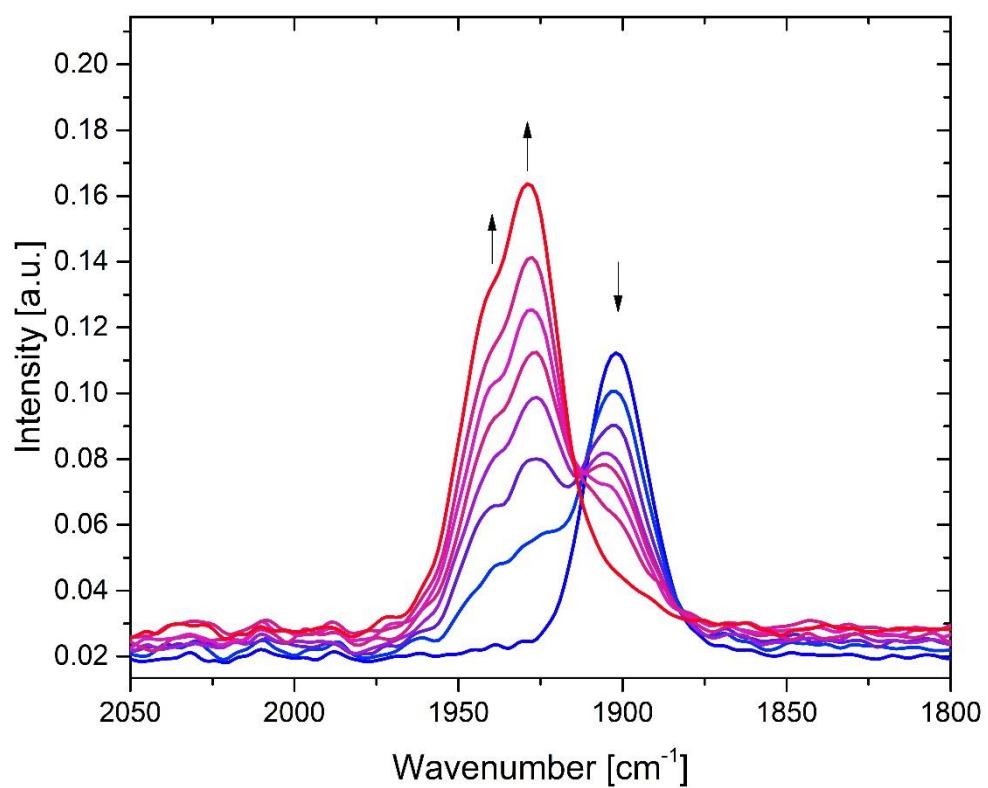


Figure S445: IR spectroscopic changes in the CO-region during the first oxidation of **3** in 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> / TBAPF<sub>6</sub>.

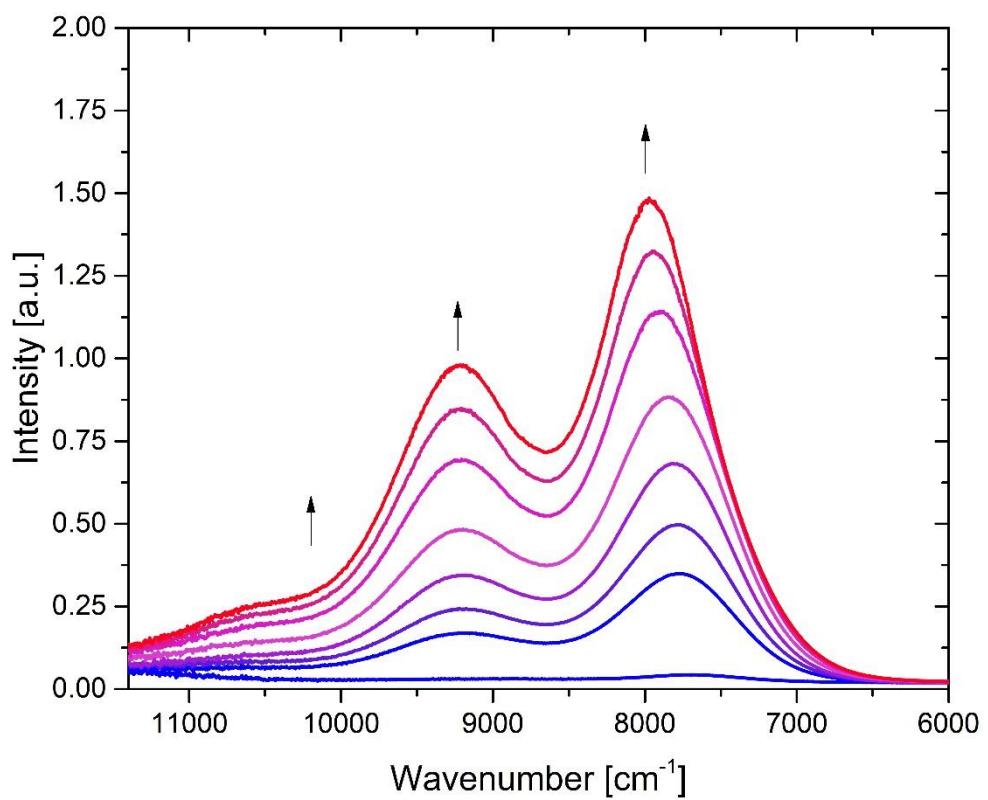


Figure S456: Spectroscopic changes in NIR during the first oxidation of **3** in 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> / TBAPF<sub>6</sub>.

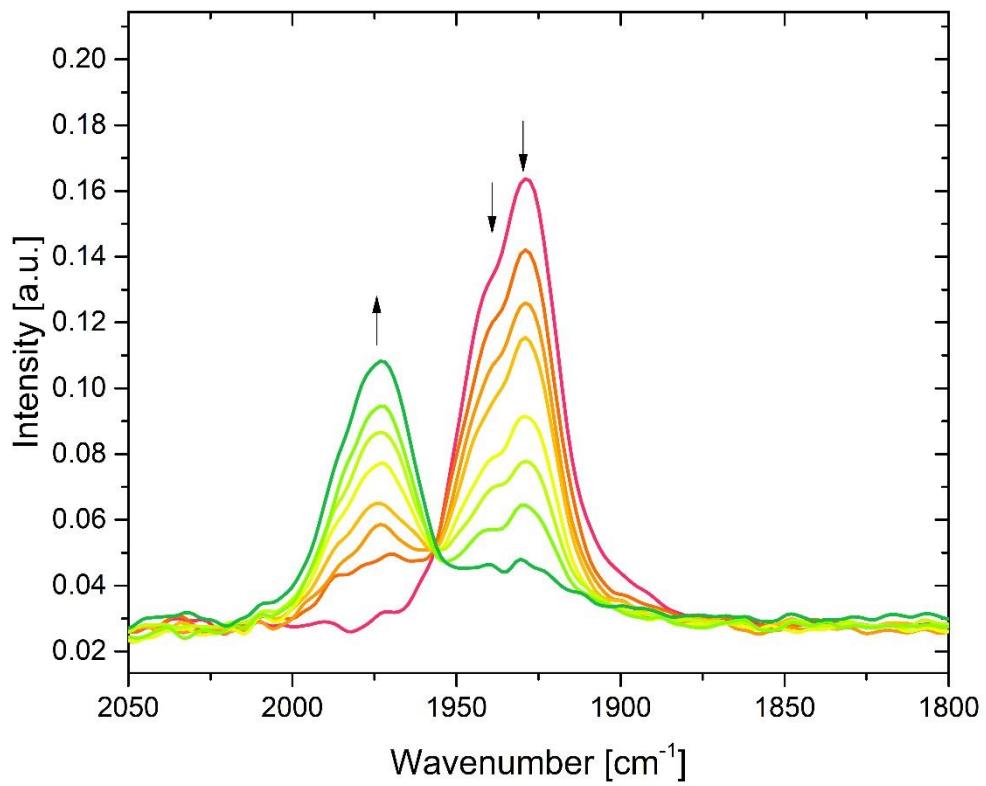


Figure S47: IR spectroscopic changes in the CO-region during the second oxidation of **3** in 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> / TBAPF<sub>6</sub>.

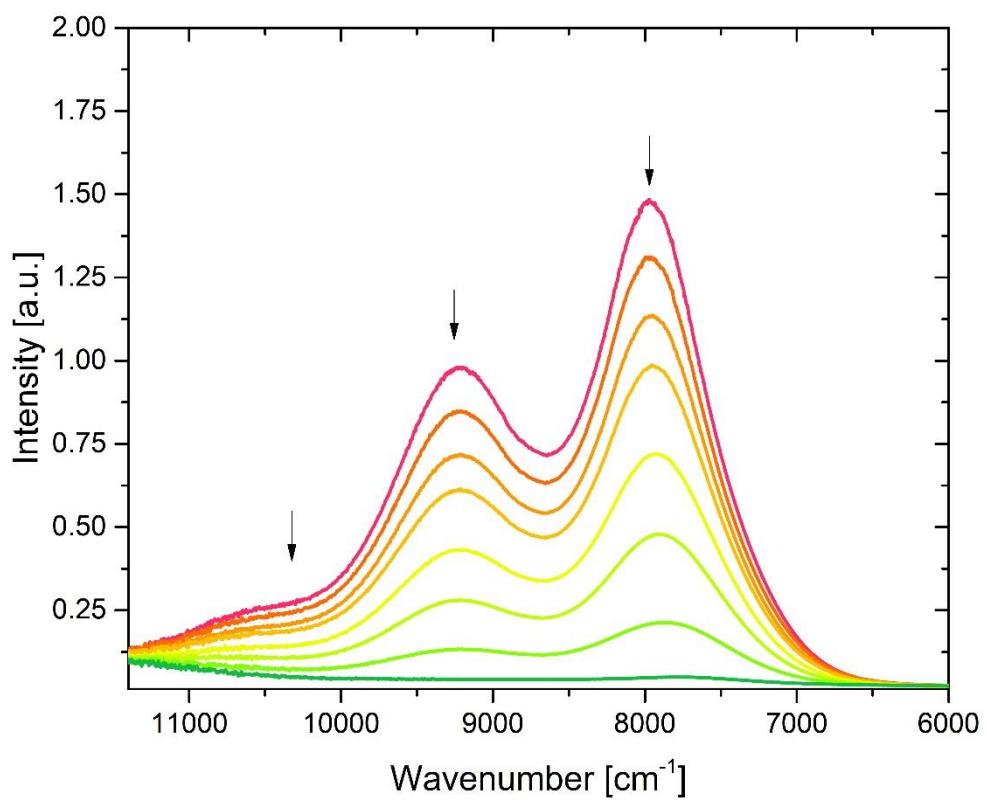


Figure S48: Spectroscopic changes in NIR during the second oxidation of **3** in 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> / TBAPF<sub>6</sub>.

Complex 4

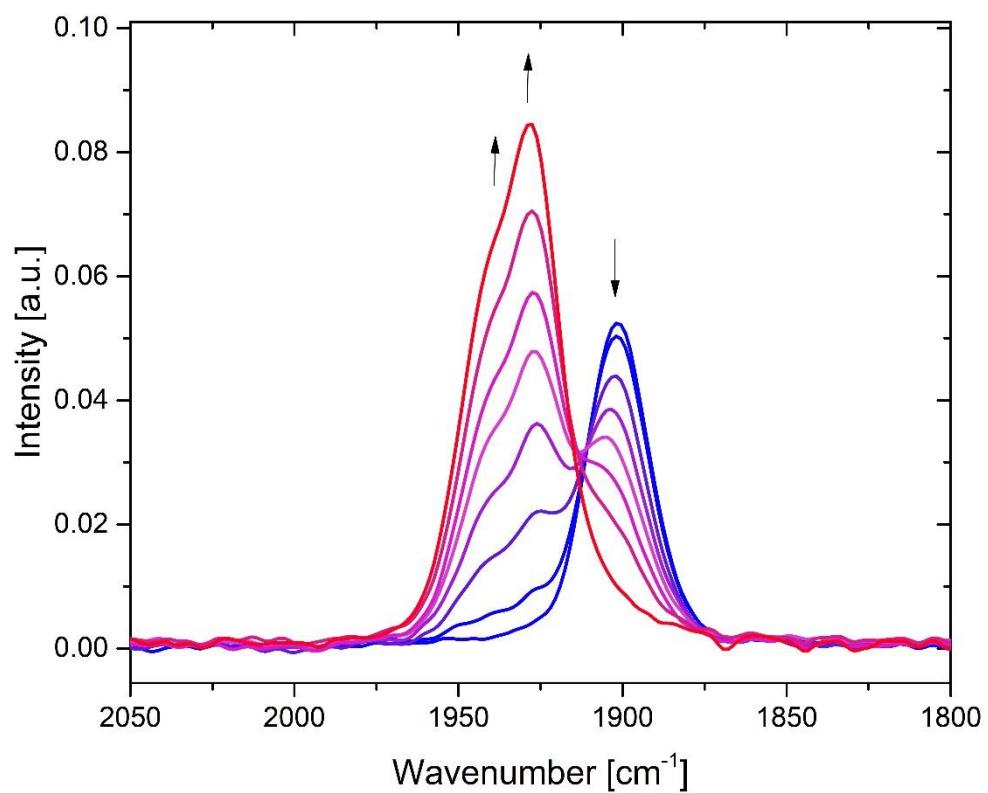


Figure S49: IR spectroscopic changes in the CO-region during the first oxidation of **4** in 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> / TBAPF<sub>6</sub>.

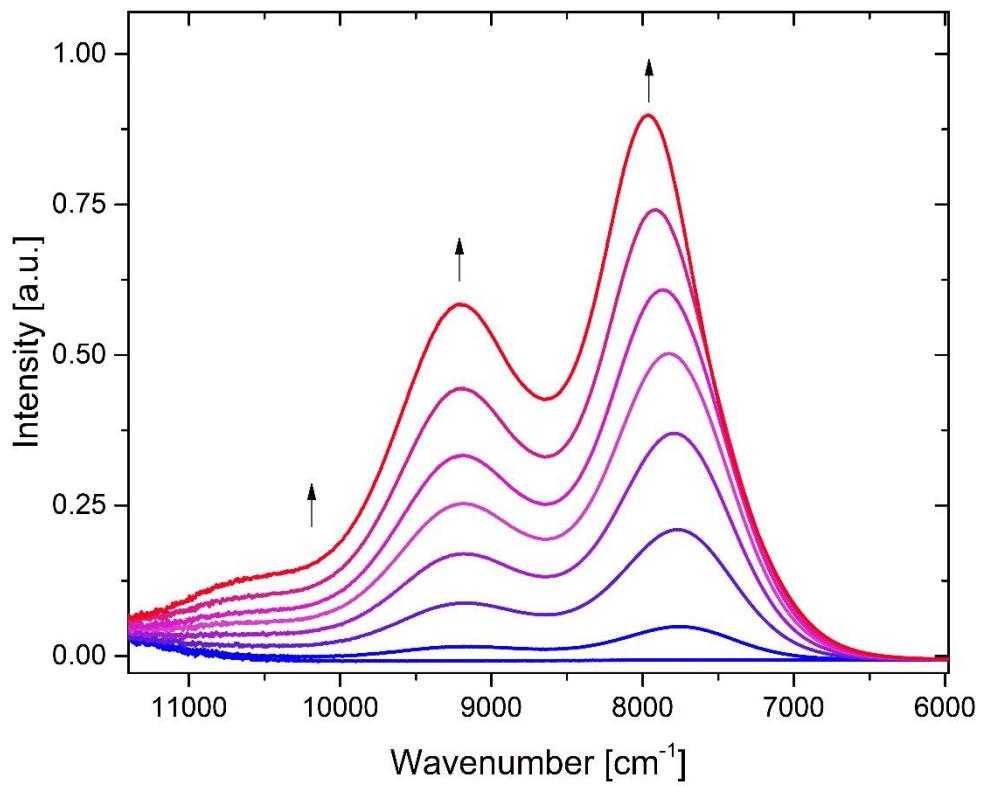


Figure S460: Spectroscopic changes in NIR during the first oxidation of **4** in 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> / TBAPF<sub>6</sub>.

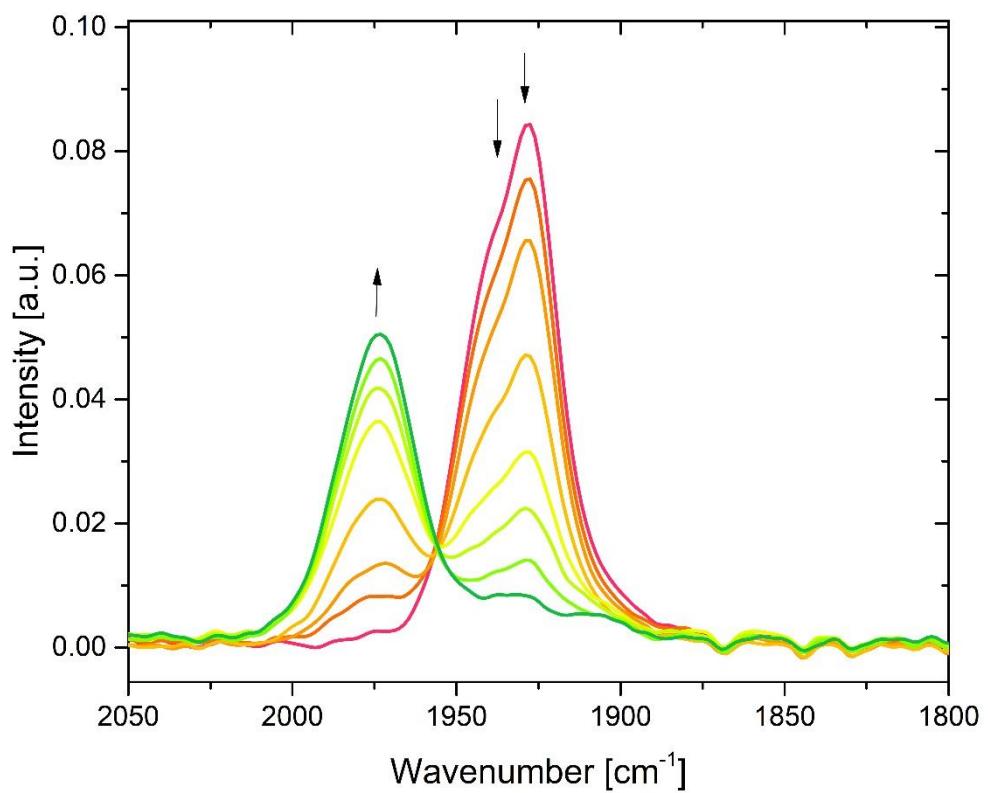


Figure S471: IR spectroscopic changes in the CO-region during the second oxidation of **4** in 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> / TBAPF<sub>6</sub>.

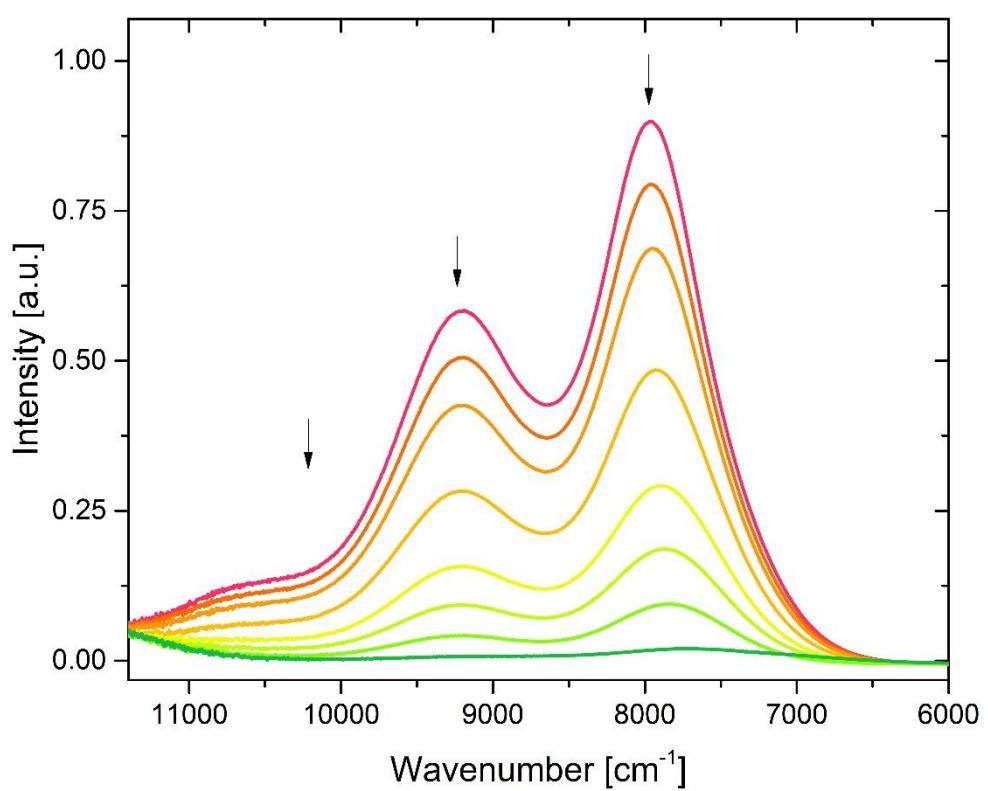


Figure S482: Spectroscopic changes in NIR during the second oxidation of **4** in 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> / TBAPF<sub>6</sub>.

Results of UV/Vis/NIR spectroelectrochemical experiments of  
**1,2 and 4**  
Complex **1**

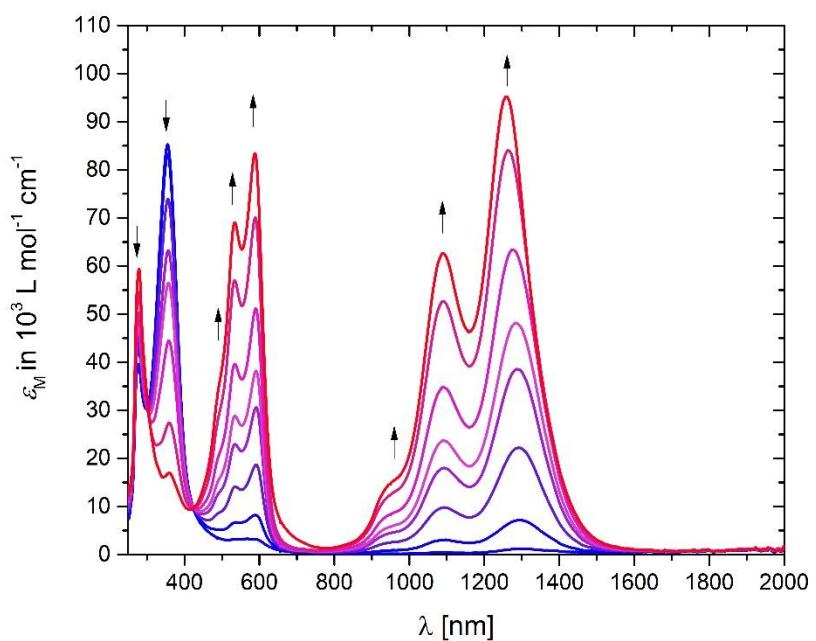


Figure S493: UV/Vis/NIR-SEC for the first oxidation of **1** in  $1,2\text{-C}_2\text{H}_4\text{Cl}_2$  / TBAPF<sub>6</sub>.

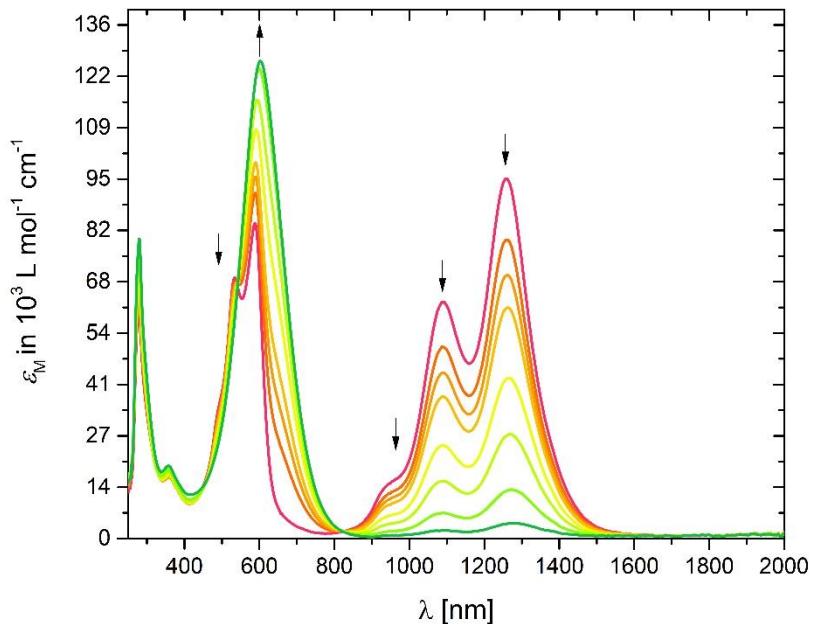


Figure S504: UV/Vis/NIR-SEC for the second oxidation of **1** in  $1,2\text{-C}_2\text{H}_4\text{Cl}_2$  / TBAPF<sub>6</sub>.

## Complex 2

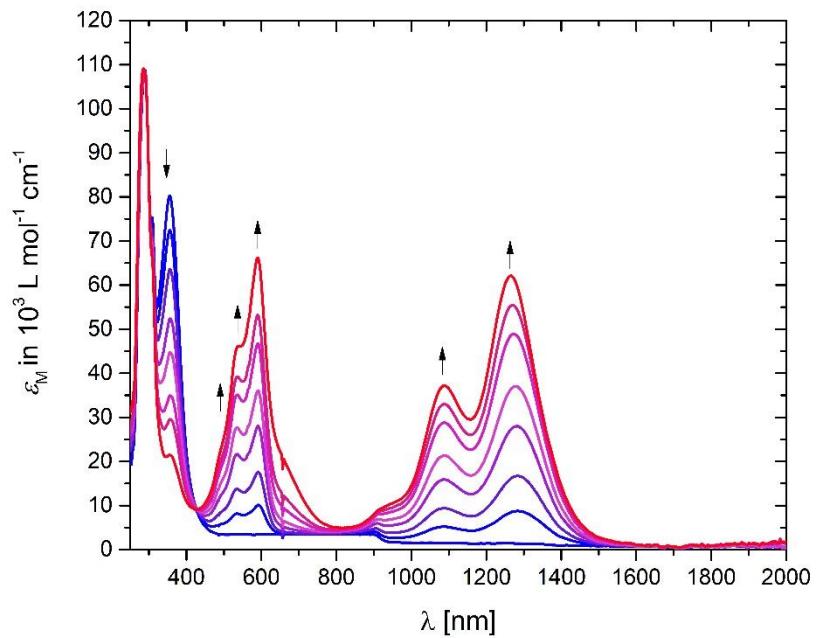


Figure S515: UV/Vis/NIR-SEC for the first oxidation of **2** in 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> / TBAPF<sub>6</sub>.

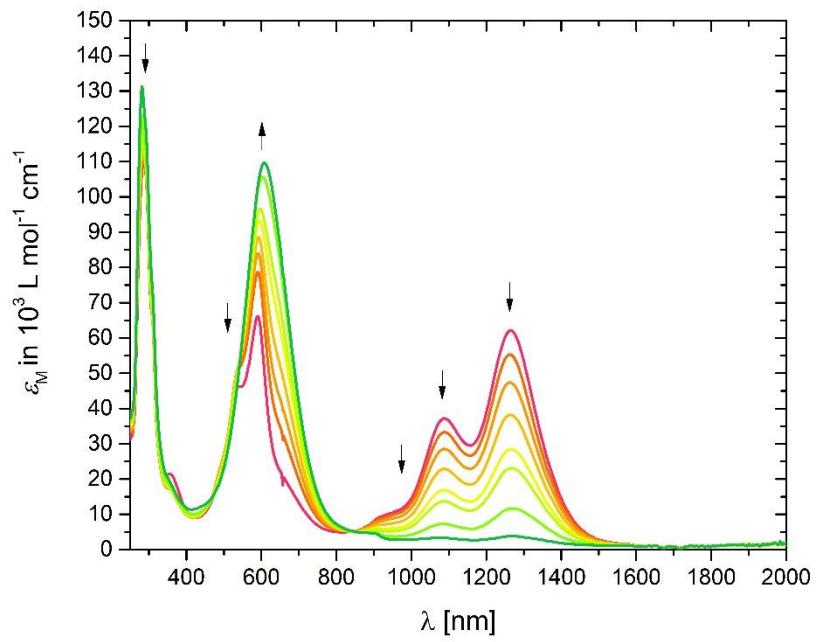


Figure S526: UV/Vis/NIR-SEC for the second oxidation of **2** in 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> / TBAPF<sub>6</sub>.

## Complex 4

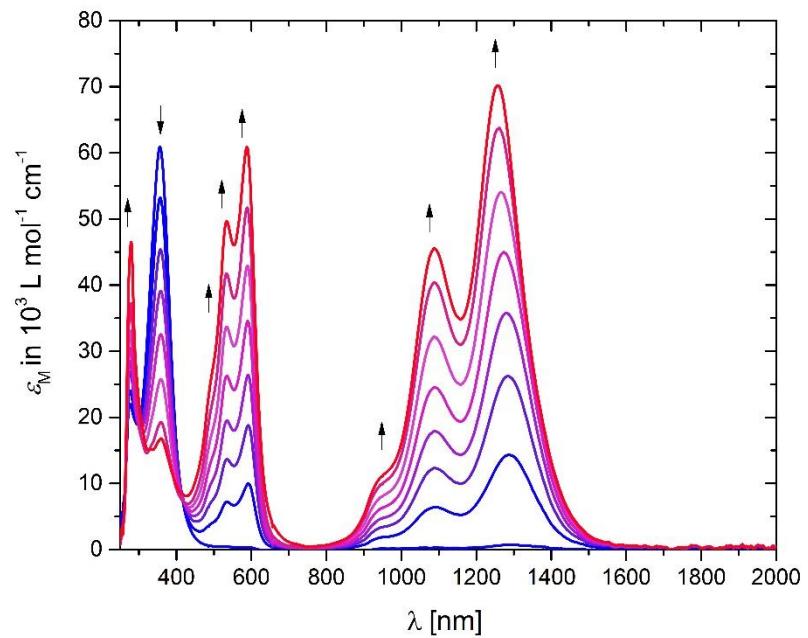


Figure S5753: UV/Vis/NIR-SEC for the first oxidation of **4** in 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> / TBAPF<sub>6</sub>.

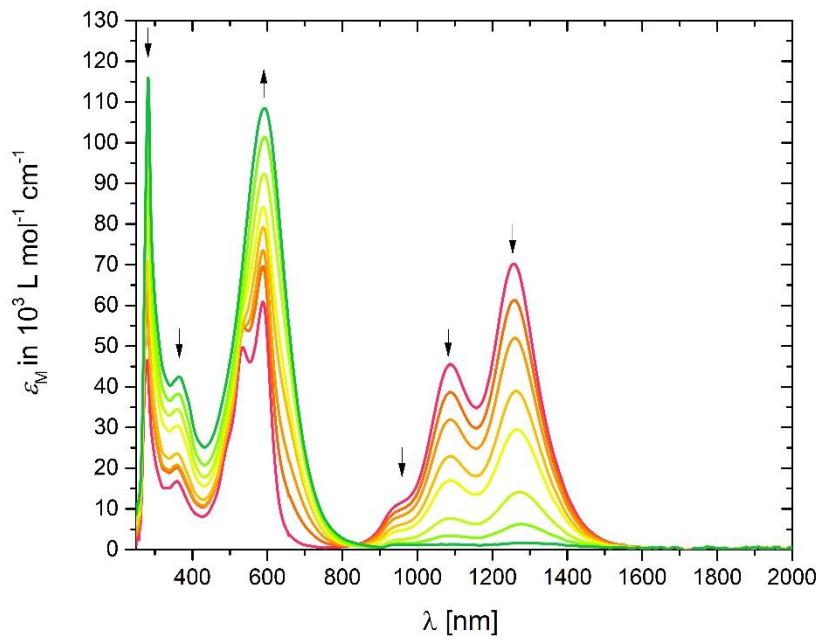


Figure S58: UV/Vis/NIR-SEC for the second oxidation of **4** in 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> / TBAPF<sub>6</sub>.

## EPR spectra of di- and tetracations of macrocycles **1**, **2** and **4**

### Complex **1**

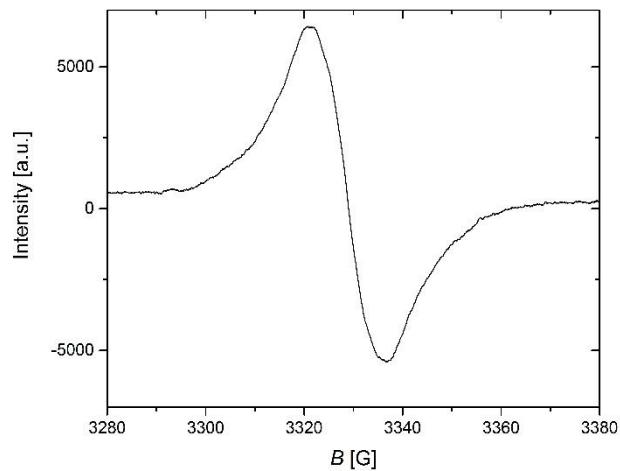


Figure S5954: EPR spectrum of  $[1]^{2+}$  at r.t.

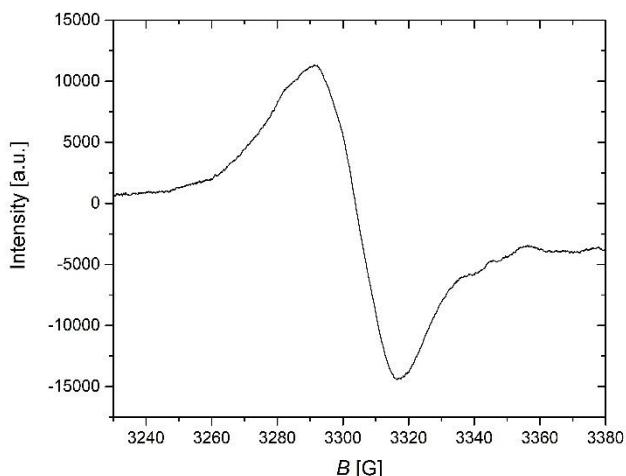


Figure S550: EPR spectrum of  $[1]^{4+}$  at r.t.

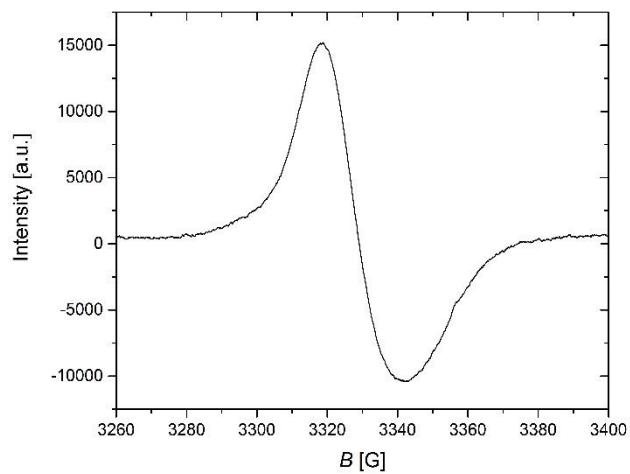


Figure S61: EPR spectrum of  $[1]^{2+}$  at 123 K.

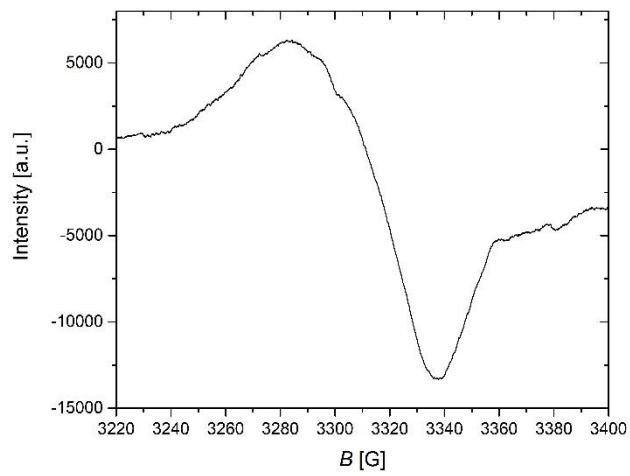


Figure S562: EPR spectrum of  $[1]^{4+}$  at 123 K.

## Complex 2

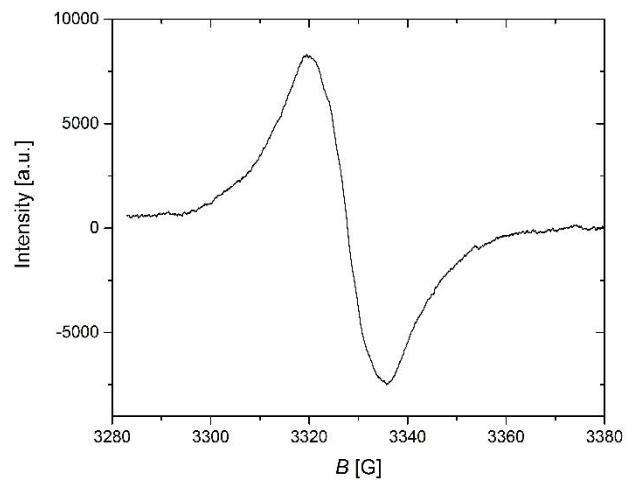


Figure S573: EPR spectrum of  $[2]^{2+}$  at r.t.

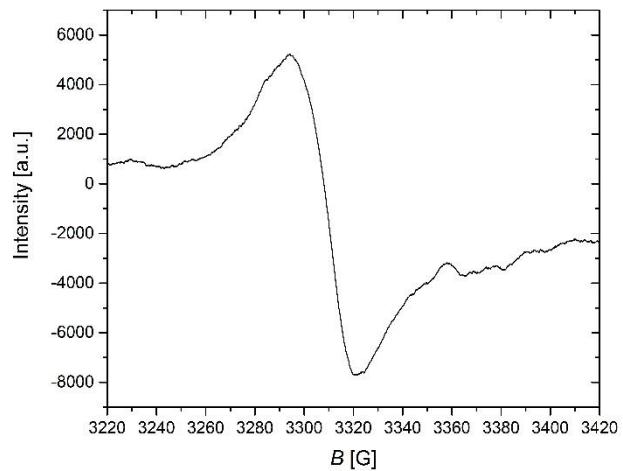


Figure S584: EPR spectrum of  $[2]^{4+}$  at r.t.

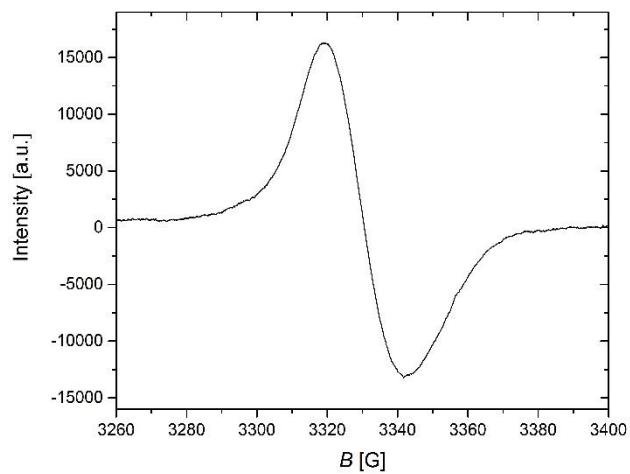


Figure S595: EPR spectrum of  $[2]^{2+}$  at 123 K.

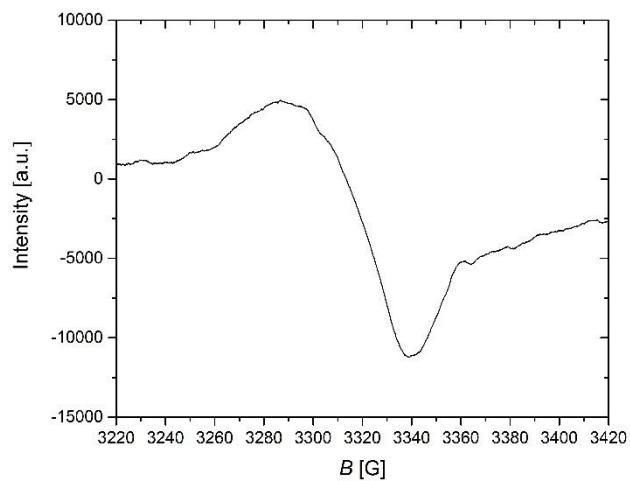


Figure S606: EPR spectrum of  $[2]^{4+}$  at 123 K.

## Complex 4

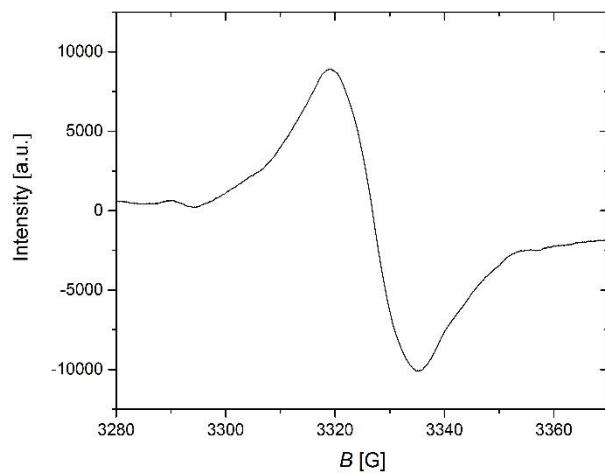


Figure S67: EPR spectrum of  $[4]^{2+}$  at r.t.

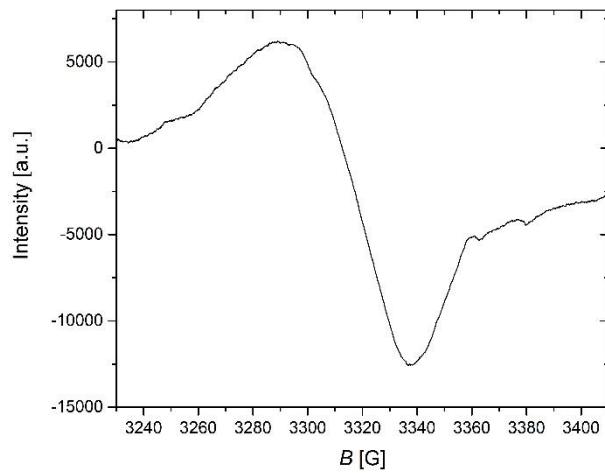


Figure S68: EPR spectrum of  $[4]^{4+}$  at r.t.

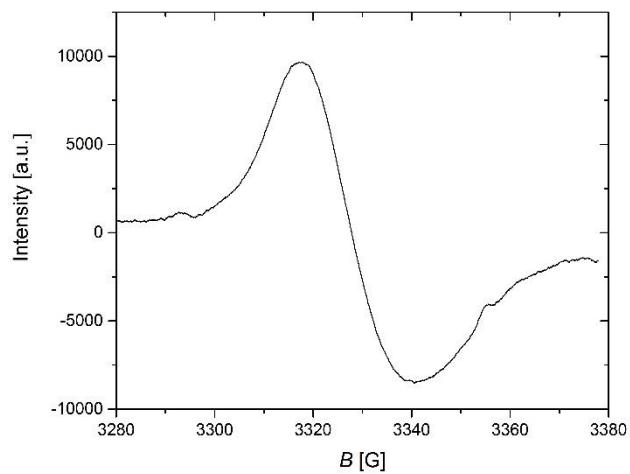


Figure S69: EPR spectrum of  $[4]^{2+}$  at 123 K.

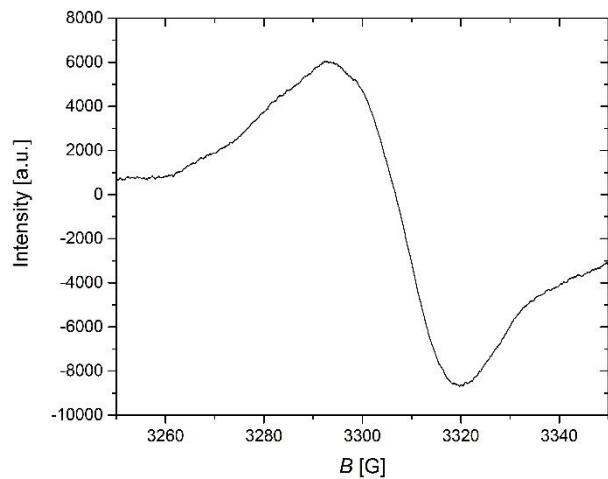


Figure S610: EPR spectrum of  $[4]^{4+}$  at 123 K.