4.5. Synthesis of Ru and Os complexes

Since the discovery of 2,2'-bipyridine at the end of the nineteenth century,[80] it was extensively used in the complexation of metal ions. Ru and Os complexes of bipyridines are quite attractive because they are chemically, thermally, and photochemically stable and oftenly show fluorescence. Ligands containing two or more 2,2'-bipyridine units can be in principle used as bridges to interconnect metal centers in a well-defined spatial arrangement. Interesting bridging ligands are the bipyridine macrocycles of kind **E** (Chapter 4.1., Figure 27, p. 42). Henze has shown that such macrocycles can from Ru complexes.[17b] Especially interesting would be a mixed Ru/Os complex of such macrocycles because then electron and energy transfer studies could be performed.

Another interesting application of bipyridine containing macrocycles lies in the generation of coordination polymers. The orthogonal sequence of macrocycles in such a polymer would render their solubility higher than normal even without the introduction of flexible chains which otherwise is the main method to increase the solubility of conformationally inflexible macromolecules. These coordination polymers are expected to have novel applications as electronic, magnetic, and materials.

Within a broader investigation of the redox, photophysical, and polymerization properties of bipyridine containing macrocycles, Ru and Os complexes **115-120** were prepared. [81]

The complexations were done with either $[Os(bpy)_2Cl_2]$, or commercially available $[Ru(bpy)_2Cl_2]$. The $[Os(bpy)_2Cl_2]$ source was prepared according to a literature procedure.[82] It starts with the commercially available potassium hexachloroosmate (IV) which was reacted with two equivalents of 2,2'-bipyridine at reflux in DMF, followed by the reduction of $[Os(bpy)_2Cl_2]Cl$ with $Na_2S_2O_4$ to $[Os(bpy)_2Cl_2]$ (Scheme 58).

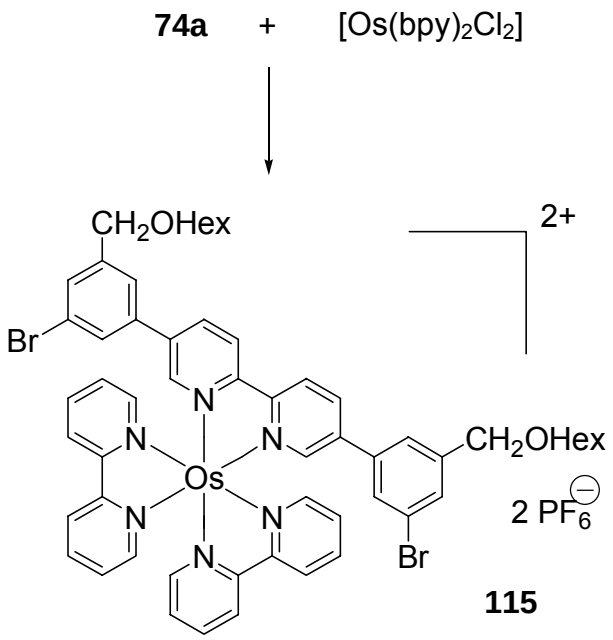
$$K_2[OsCl_6] + 2bpy + 2H_2O \xrightarrow{DMF} [Os(bpy)_2Cl_2]Cl \times 2H_2O + KCl$$

$$2[Os(bpy)_2Cl_2]Cl \times 2H_2O + Na_2S_2O_4 \longrightarrow 2[Os(bpy)_2Cl_2] + H_2SO_4 + 2H_2O$$

Scheme 58. Synthesis of $[Os(bpy)_2Cl_2]$.

4.5.1. Synthesis of Os complex 115

A model Os complex, **115** ([(bpy)$_2$Os(**74a**)]), was prepared by complexation of **74a** with [Os(bpy)$_2$Cl$_2$] in a mixture of ethanol/water at reflux (Scheme 59).



Scheme 59. Synthesis of Os complex **115** from **74a** and [Os(bpy)$_2$Cl$_2$].

During the reaction the color changed from purple to brown-green. The compound was purified by column chromatography through neutral aluminum oxide using DCM/MeOH 95:5. The green fraction was collected and the complex precipitated as PF_6 salt. Complex **115** was fully characterized and gave correct data for combustion analysis. Figure 69 displays its ^{1}H NMR spectrum. It shows two different sets of signals, one for the 2,2'-bipyridine and another one for the bipyridine ligand **74a**.

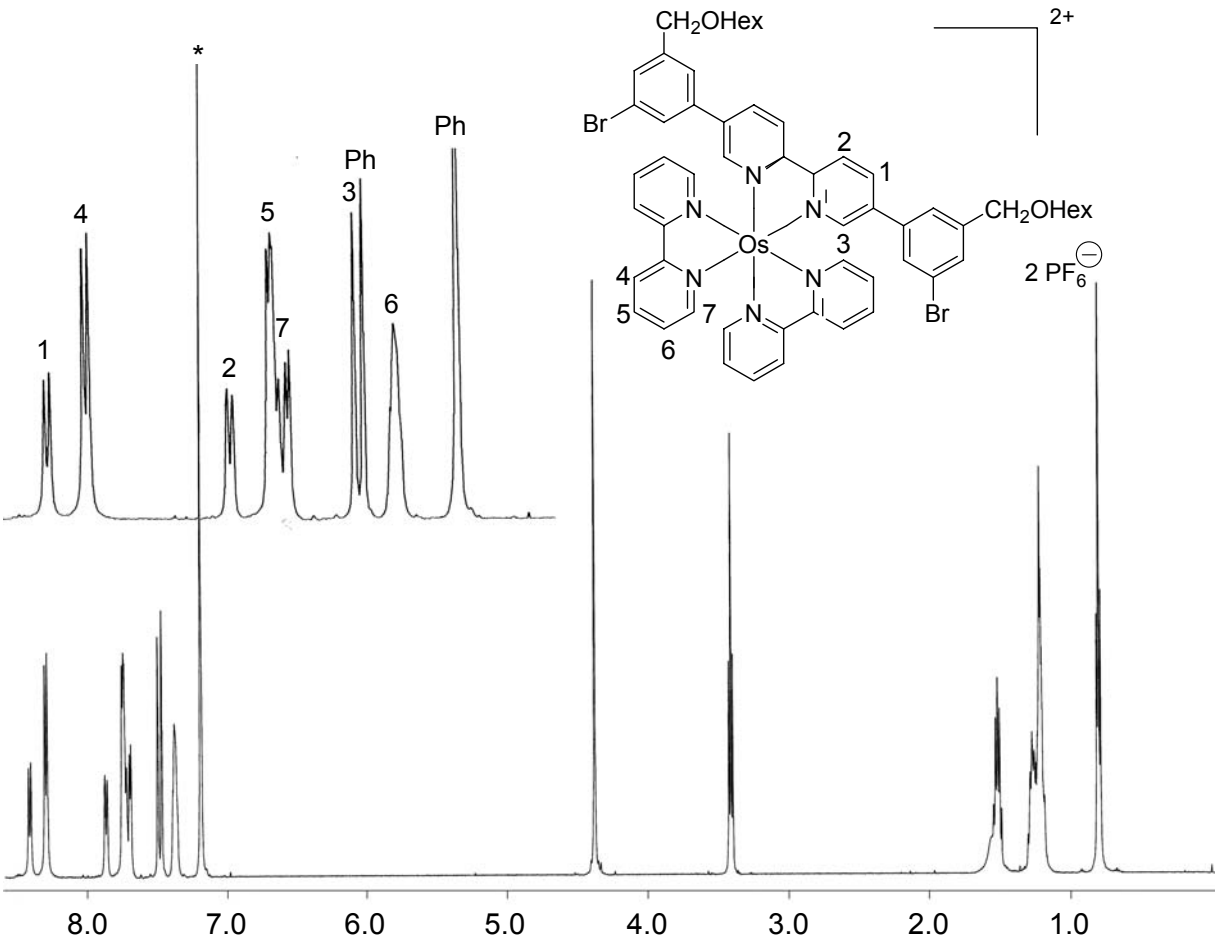
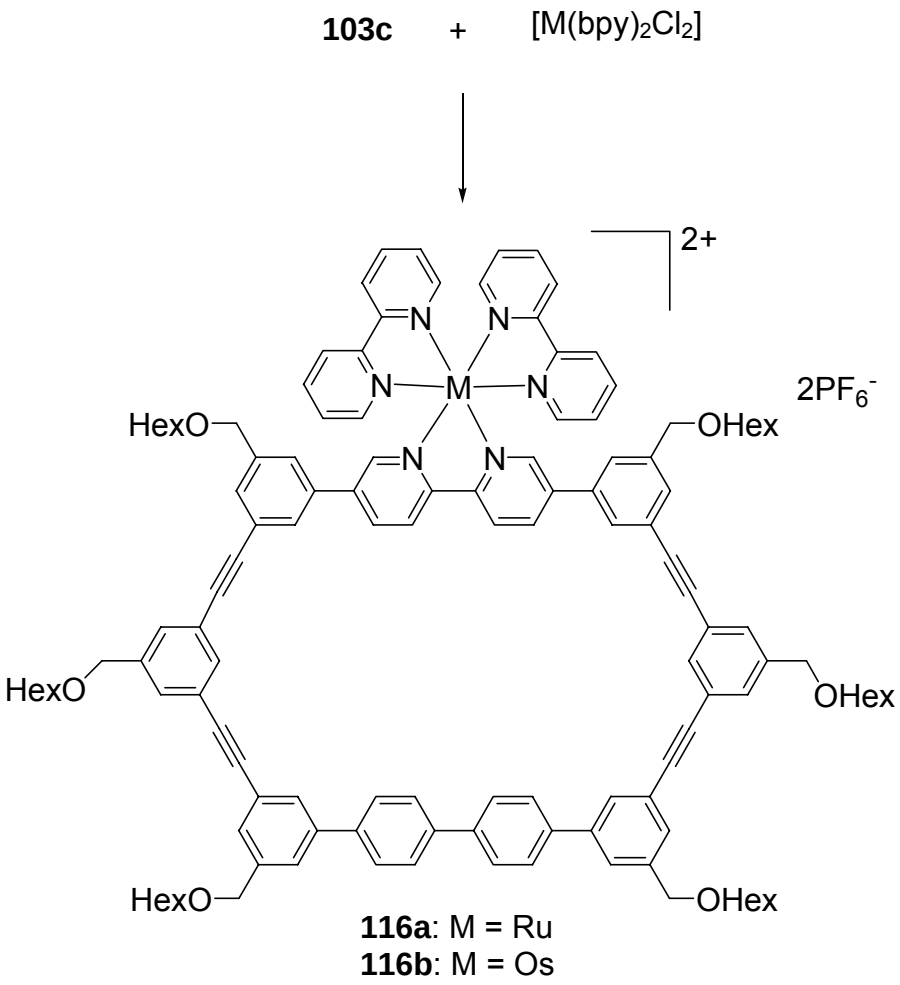


Figure 69. ^{1}H NMR spectrum of compound **115** with the aromatic part enlarged (*: $CDCl_3$, 20 °C, 250 MHz).

4.5.2. Ru and Os complexes of macrocycle 103c

Ru and Os complexes of macrocycle **103c** were prepared by reacting macrocycle **103c** with a small excess of $[Ru(bpy)_2Cl_2]$ or $[Os(bpy)_2Cl_2]$ in a mixture of propylene glycol/dioxane or butanol, respectively (Scheme 60).



Scheme 60. Synthesis of Ru and Os complexes of macrocycle **103c**.

During complexation, the color changed from purple to orange for Ru complex **116a** ($[(bpy)_2Ru(\mathbf{103c})]^{2+}$) and from purple to dark brown-green for the Os complex **116b** ($[(bpy)_2Os(\mathbf{103c})]^{2+}$), respectively. The solvent was removed and the compounds were purified by column chromatography. They contained chlorides as counterions, which again were exchanged by hexafluorophosphates. The complexes were soluble in chloroform, acetonitrile, and nitromethane. Figures 70 and 71 show the ^1H NMR spectra of complexes **116a** and **116b**, respectively, with the aromatic parts enlarged.

Two sets of signals were observed for each of the two pyridines of the bipyridine ligands and one set for those of the cycle's bipyridine. The MALDI-TOF mass spectra of **116a** and **116b** were recorded in dithranol matrix and show signals at *m/z* = 2102, 1957 for **116a** and *m/z* = 2192, 2047 for **116b** which were assigned to $[M\text{-}PF_6]^+$ and $[M\text{-}2PF_6]^+$, respectively (Figure 72 and 73).

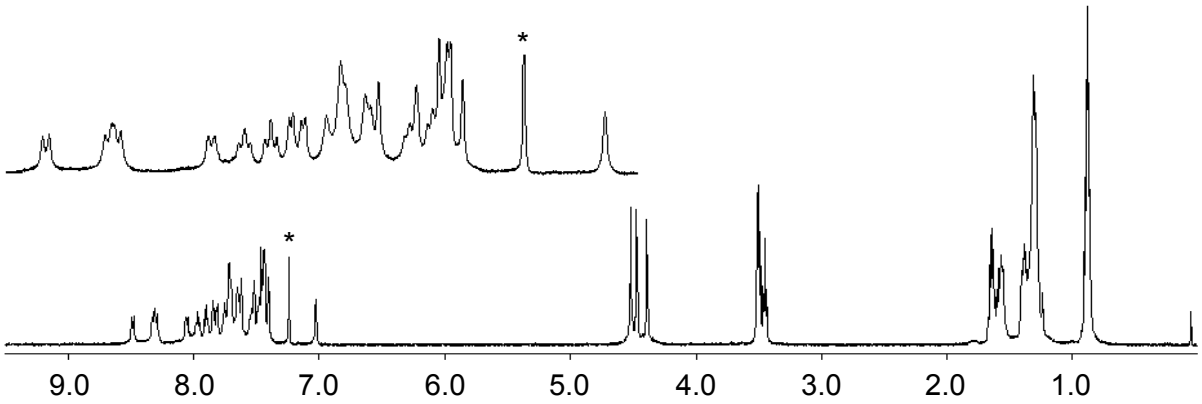


Figure 70. ^{1}H NMR spectrum of **116a** (*: $CDCl_3$, 500 MHz, 20 °C) with the aromatic part enlarged.

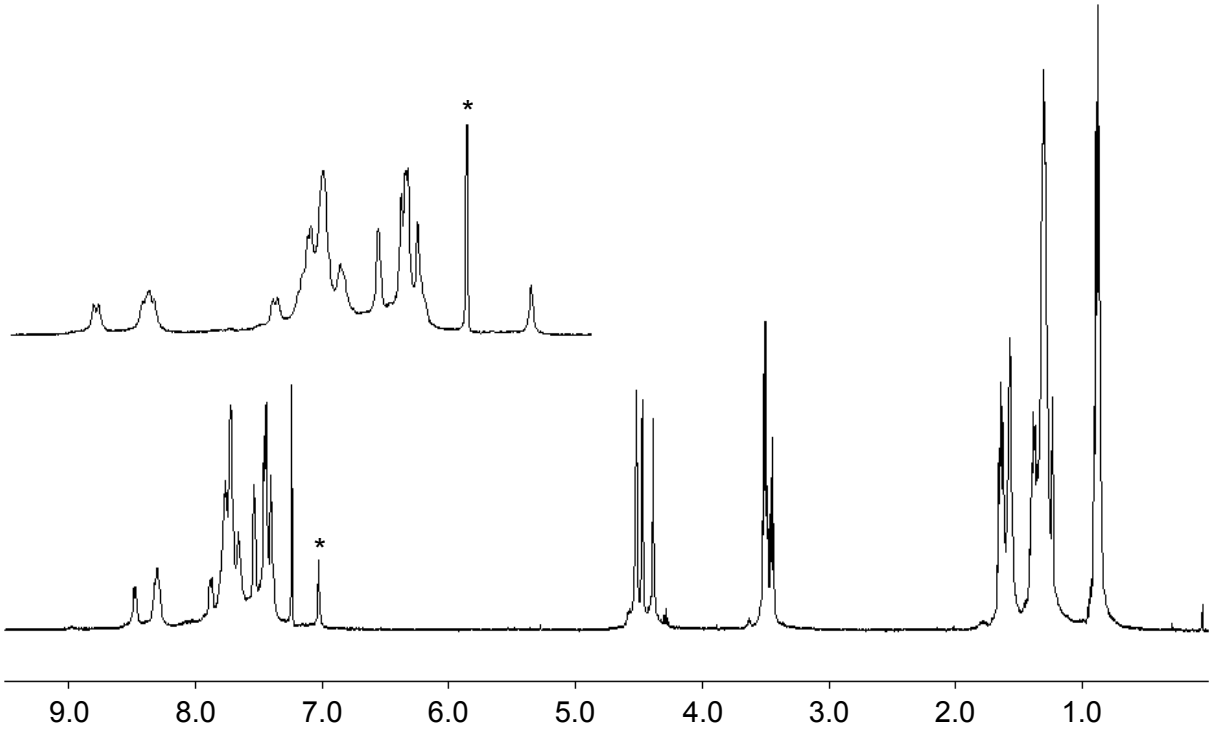


Figure 71. ^{1}H NMR spectrum of **116b** (*: $CDCl_3$, 500 MHz, 20 °C) with the aromatic part enlarged.

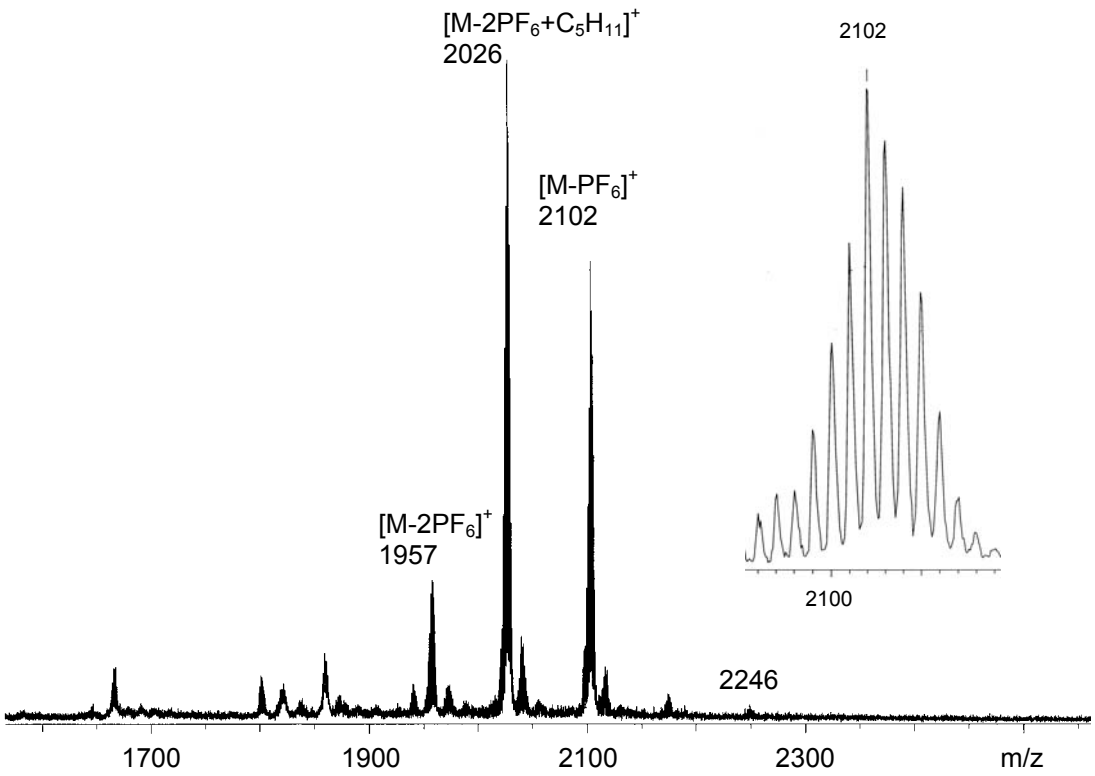


Figure 72. MALDI-TOF mass spectrum (ditranol matrix) of **116a**. Insert: expanded and amplified isotope pattern of the MALDI-TOF mass signal of **116a** at *m/z* = 2102 $[M\text{-}PF_6]^+$. For a comparison of the observed and calculated intensities, see table 3.

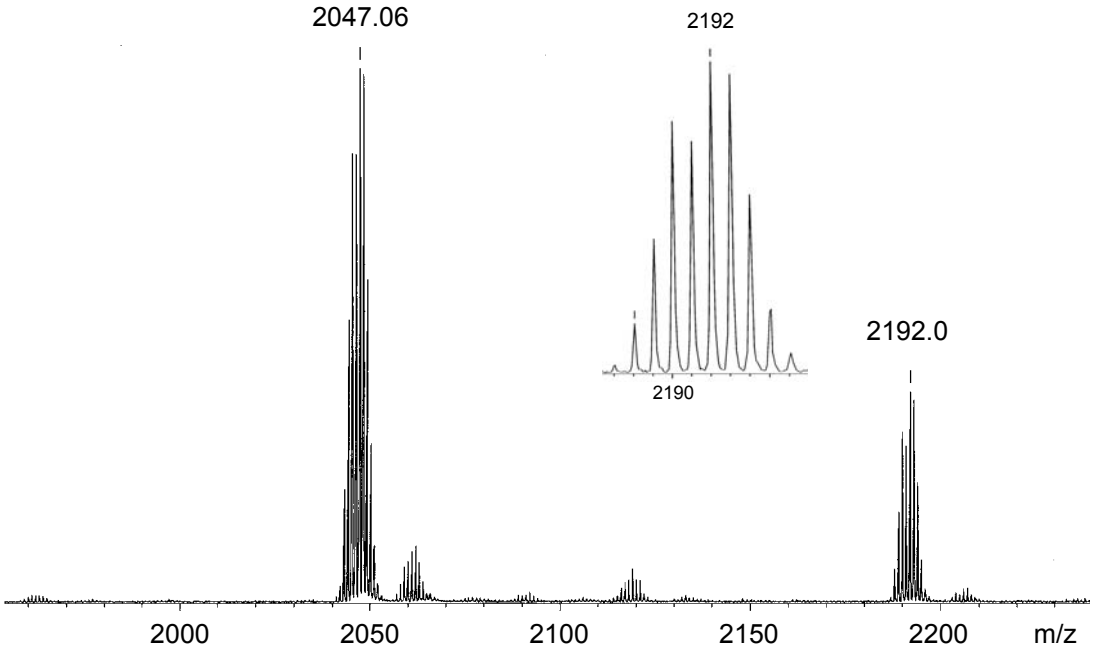


Figure 73. MALDI-TOF mass spectrum (ditranol matrix) of **116b**. Insert: expanded and amplified isotope pattern of the MALDI-TOF mass signal of **116b** at

m/z = 2192 $[M\text{-}PF_6]^+$. For a comparison of the observed and calculated intensities, see table 4.

The experimental isotopic distribution for the peak at $[M\text{-}PF_6]^+$ was compared to the calculated one and they were found to be in good agreement. Table 3 and 4 contain this comparison for the signals at *m/z* = 2102 and 2192 of **116a** and **116b**, respectively.

Table 3. Calculated and experimental isotope intensities for the MALDI-TOF signal of **116a** at *m/z* = 2102 ($[M\text{-}PF_6]^+$).

Mass	Calcd	Found
2098	10	15
2099	24	27.5
2100	45	26.4
2001	66	67
2102	100	100
2103	94	88.6
2104	82	78.6
2105	60	56.4
2106	34	31.4

Tabele 4. Calculated and experimental isotope intensities for the MALDI-TOF signal of **116b** at *m/z* = 2192 ($[M\text{-}PF_6]^+$).

Mass	Calcd	Found
2188	23	16
2189	48.6	43
2190	82	81
2191	78	75
2192	100	100
2193	96	96
2194	60.7	57
2195	27.7	21
2196	9.7	6

4.5.3. Synthesis of the Os complex of macrocycle 10

The complexation of **10** with Os was more difficult to achieve. Different solvent mixtures were tried, but the expected color change from purple to dark green was not observed. Finally the cycle was treated in butanol at 140 °C with an excess of $Os(bpy)_2Cl_2$ for five days.[83] The structure of the product was established to be that of complex **117** ($[(bpy)_2Os(\mathbf{10})Os(bpy)_2]^{4+}$) on the basis of mass spectrometric and NMR spectroscopic studies. The MALDI-TOF mass spectrum recorded in a dithranol matrix showed a number of characteristic signals and proved unambiguously the complex formation (Figure 74). Characteristic is the identical mass difference

between the signals at *m/z* = 2758, 2613, 2468 that proves the step-wise fragmentation of the three PF_6^- groups. Table 5 shows the assignment of the signals.

Table 5. Assignments and fragmentation of MALDI-TOF mass spectrum signals of **117**.

Mass	Assigned formula	Fragmentation
2758	$C_{132}H_{124}N_{12}O_4Os_2P_3F_{18}$	$[M\text{-}PF_6]^+$
2613	$C_{132}H_{124}N_{12}O_4Os_2P_2F_{12}$	$[M\text{-}2PF_6]^+$
2468	$C_{132}H_{124}N_{12}O_4Os_2PF_6$	$[M\text{-}3PF_6]^+$
1966	$C_{112}H_{108}N_8O_4OsPF_6$	$[M\text{-}3PF_6\text{-}2bpy\text{-}Os]^+$
1821	$C_{112}H_{108}N_8O_4Os$	$[M\text{-}4PF_6\text{-}2bpy\text{-}Os]^+$

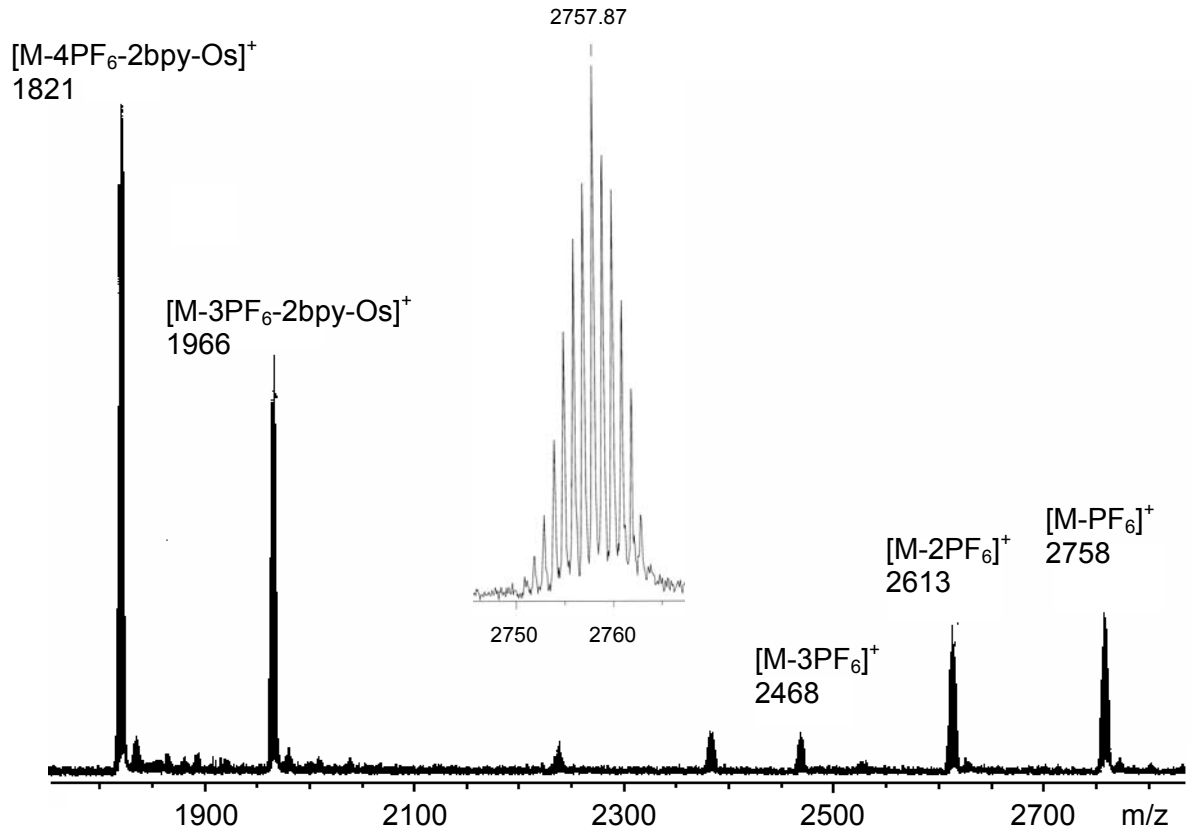


Figure 74. MALDI-TOF mass spectrum (dithranol matrix) of **117**. Insert: expanded and amplified isotope pattern of the MALDI-TOF mass signal of **117** at *m/z* = 2758.86 $[M\text{-}PF_6]^+$. For the fragmentation pattern, see Tabele 5. For a comparison of the observed and calculated intensities, see table 6.

Table 6. Calculated and experimental isotope intensities for the MALDI-TOF signal of **117** *m/z* = 2758.86

Mass	Calcd	Found
2752.86	8	8.5
2753.86	17	16
2754.86	33	30
2755.86	50	50
2756.86	70	67
2757.86	84	78
2758.87	100	100
2759.86	86	83
2760.86	76	77
2761.86	59	56
2762.86	35	39
2763.86	16	16

The dinuclear complex **117** has two enantiomeri forms (Λ,Λ and Δ,Δ) and one *meso* form (Δ,Λ) figure 75. The ^{1}H NMR spectrum is therefore quite complex. Two sets of signals are observed for the bpy ligands and one set for the macrocycle (Figure 76). The assignment of these sets could nevertheless be achieved by means of COSY and HMQC experiments.

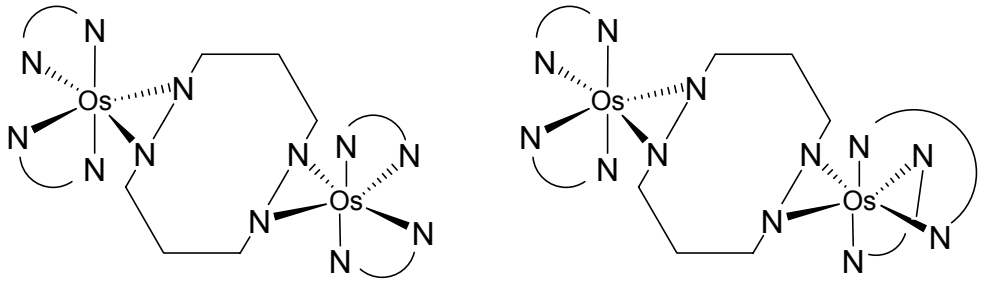


Figure 75. Cartoon representation of two stereoisomeris forms of **117**: Λ,Δ (left), Λ,Λ (right).

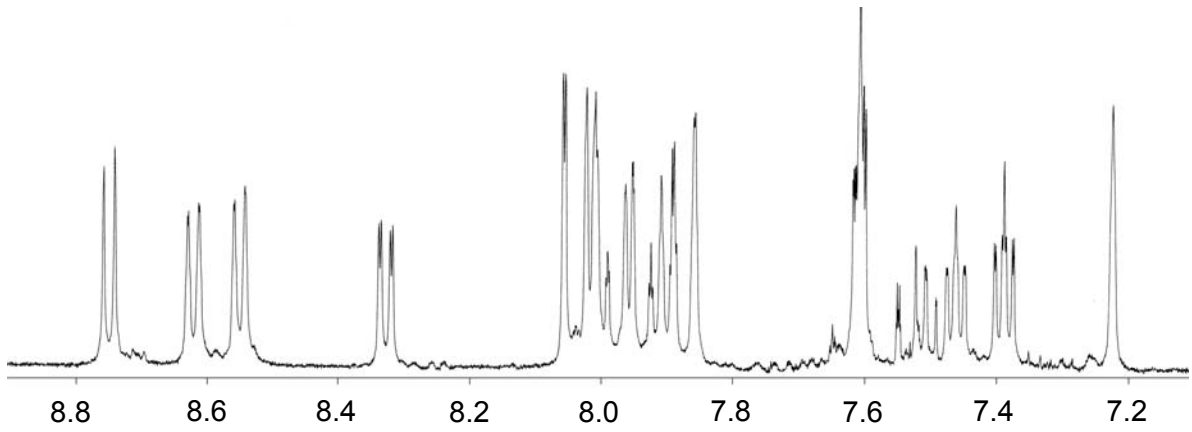
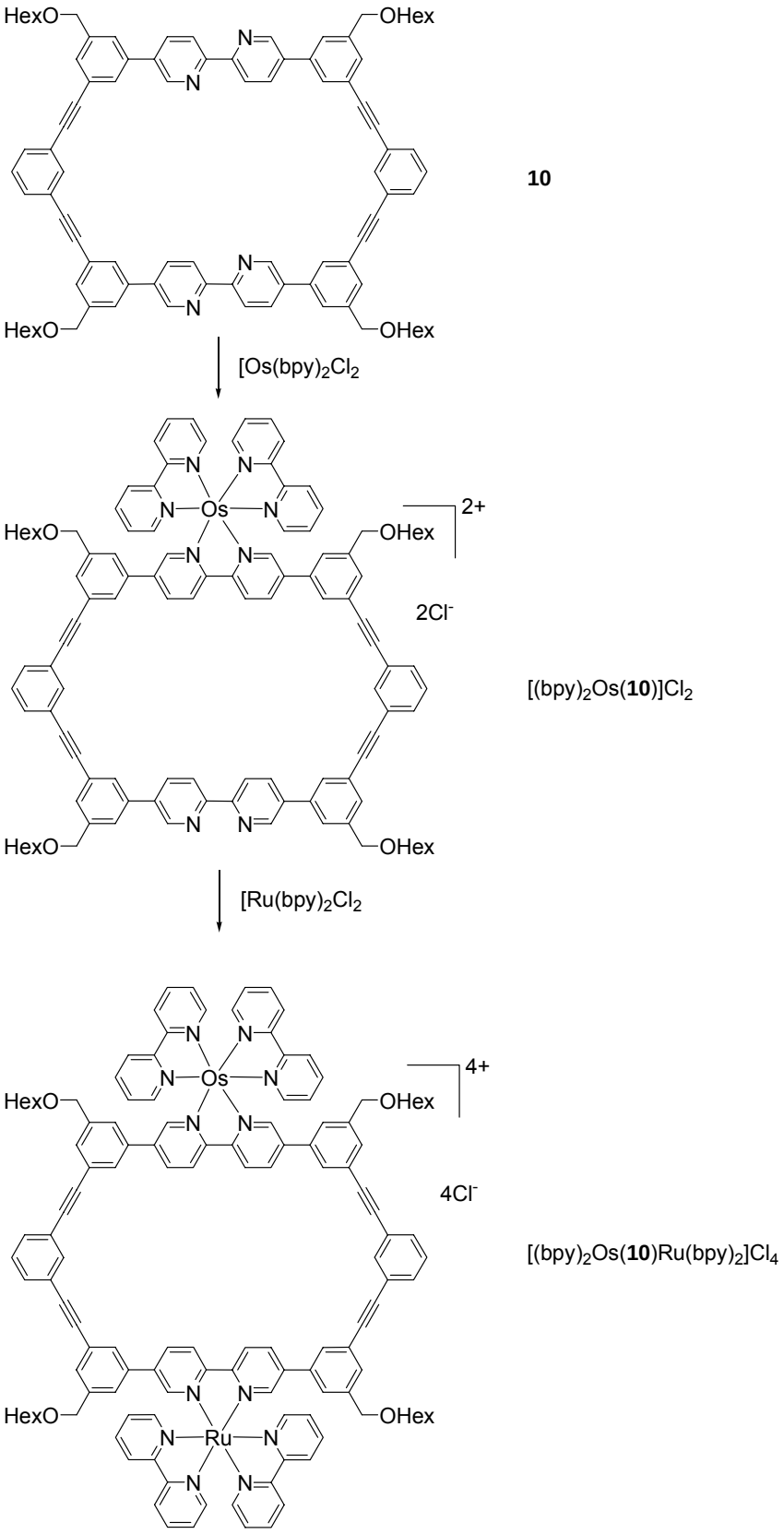


Figure 76. ^{1}H NMR spectrum of the stereoisomeric mixture of **117** (CD_3NO_2, 20 °C, 500 MHz).

4.5.4. Synthesis of the mixed Ru/Os complex 118

The synthesis of the heterobinuclear complex **118** was more complex specifically for purification reasons (Scheme 61).[48]



Scheme 61. The synthesis of heterodinuclear complex **118**.

In the first step the mononuclear Os complex $[(bpy)_2Os(\mathbf{10})]Cl_2$ was prepared by reacting the $[Os(bpy)_2Cl_2]$ with an excess of macrocycle **10**. During this step the formation of some homobinuclear $[(bpy)_2Os(\mathbf{10})Os(bpy)_2]Cl_2$ was unavoidable. Repetitive column chromatography under specific conditions was used in order to obtain highly pure mononuclear complex (See experimental part). The ^1H NMR spectrum and MALDI-TOF mass spectrum, as well as the TLC, proved the purity of the mononuclear complex $[(bpy)_2Os(\mathbf{10})]Cl_2$. The ^1H NMR spectrum of $[(bpy)_2Os(\mathbf{10})]Cl_2$ showed broad signals. Characteristic for this complex are the two different signals for benzyl-H at δ = 4.43 and 4.52 ppm. The MALDI-TOF mass spectrum of $[(bpy)_2Os(\mathbf{10})]Cl_2$ in dithranol matrix showed a number of characteristic signals with regard to mass they correspond to and the isotope patterns (Figure 77).

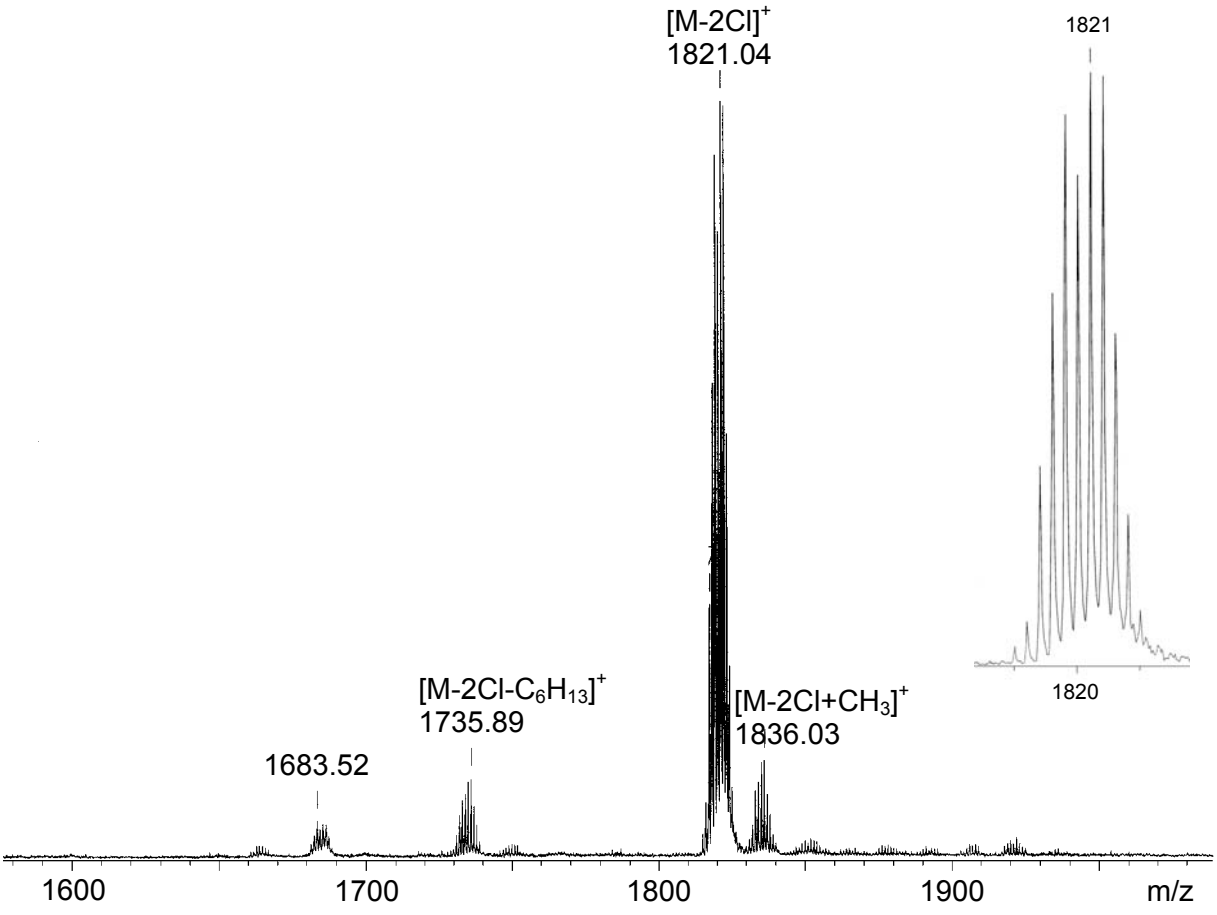


Figure 77. MALDI-TOF mass spectrum (dithranol matrix) of complex $[(bpy)_2Os(\mathbf{10})]Cl_2$. Insert: expanded and amplified isotope pattern of the signal at *m/z* = 1821 $[M\text{-}2Cl]^+$. For a comparison of the observed and calculated intensities, see table 7.

Table 7. Calculated and experimental isotope intensities for the MALDI-TOF signal of complex $[(bpy)_2Os(\mathbf{10})]Cl_2$ at *m/z* = 1821.04

Mass	Calcd	Found
1816	6	7.4
1817	25	34
1818	51	63
1819	85	93.7
1820	74	83
1821	100	100
1822	91	99.6
1823	52	56.3
1824	21	57.4
1825	7	9.2

Having achieved pure $[(bpy)_2Os(\mathbf{10})]Cl_2$, the synthesis of the mixed complex in the second step was no problem. For that purpose the mononuclear complex $[(bpy)_2Os(\mathbf{10})]Cl_2$ was reacted with $[Ru(bpy)_2Cl_2]$. The purification of the compound was done by column chromatography. The complex was precipitated as PF_6 salt.

The structure of the isolated complex was established to be that of the heterobinuclear complex **118** ($[(bpy)_2Ru(\mathbf{10})Os(bpy)_2]^{4+}$) on the basis of mass spectrometric and NMR spectroscopic studies. The MALDI-TOF spectrum of the complex in dithranol shows two characteristic signals at *m/z* = 2670 and 2525, corresponding exactly to that calculated for $[M\text{-}PF_6]^+$ and $[M\text{-}2PF_6]^+$, respectively (Figure 78). The experimental isotopic distribution at *m/z* = 2669.8 was compared to that calculated one and was found to be in good agreement (Table 8).

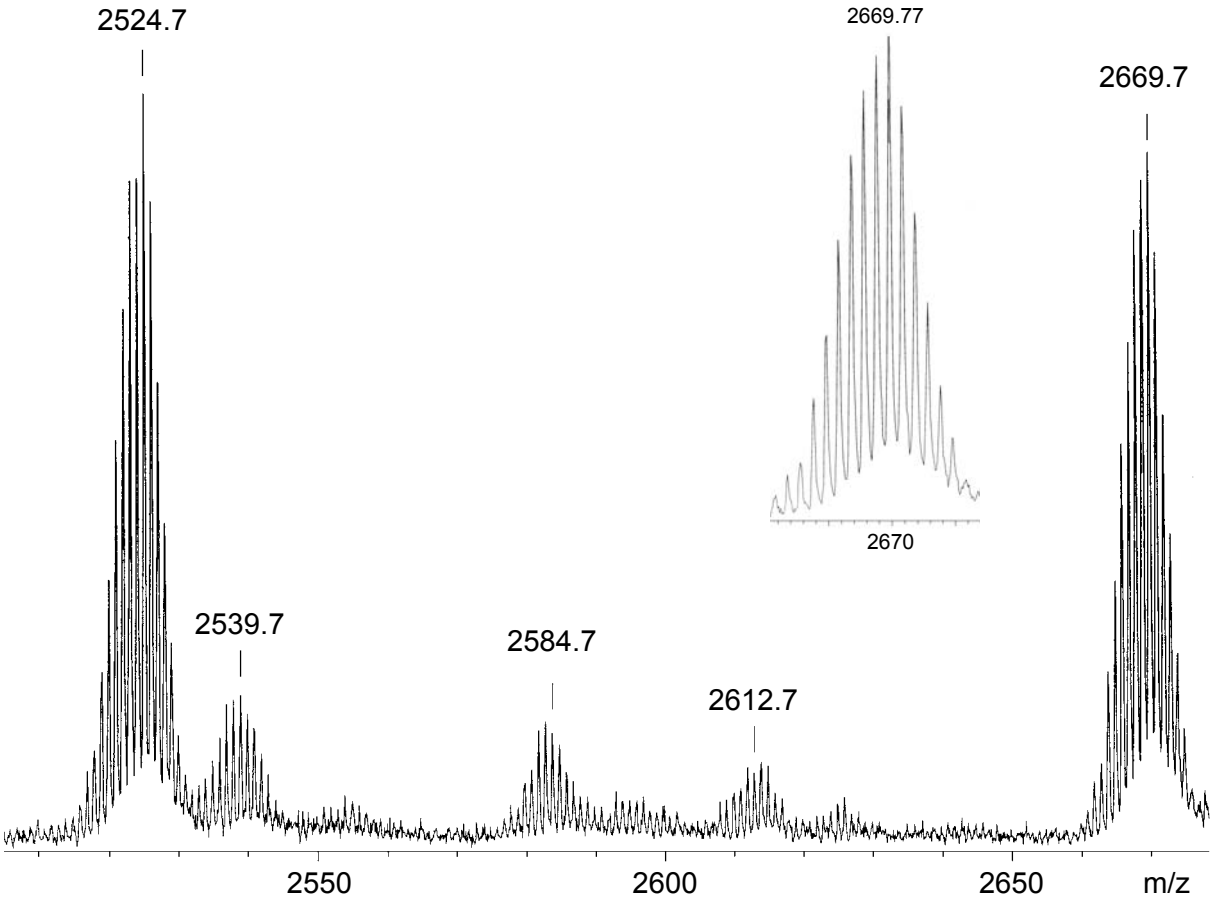


Figure 78. MALDI-TOF mass spectrum (dithranol matrix) of **118** in reflector mode. Insert: expanded and amplified isotope pattern of the MALDI-TOF mass signal at *m/z* = 2669.77 $[M\text{-}PF_6]^+$.

Table 8. Calculated and experimental isotope intensities for the MALDI-TOF signal of **118** at *m/z* = 2669.8.

Mass	Calcd	Found
2664.8	38	38.3
2665.8	55	57.8
2666.8	75	75
2667.8	93	88.7
2668.8	96	95.7
2669.8	100	100
2670.8	82	85.8
2671.8	60	63
2672.8	40	44.7

The complex **118** exists as a mixture of diastereoisomers and therefore its ^{1}H NMR spectrum is quite complex. Four sets of signals are observed for the bipyridine ligands and two sets for those of the cycle. The assignment of the protons was nevertheless possible using COSY and HMQC experiments (Figure 79).

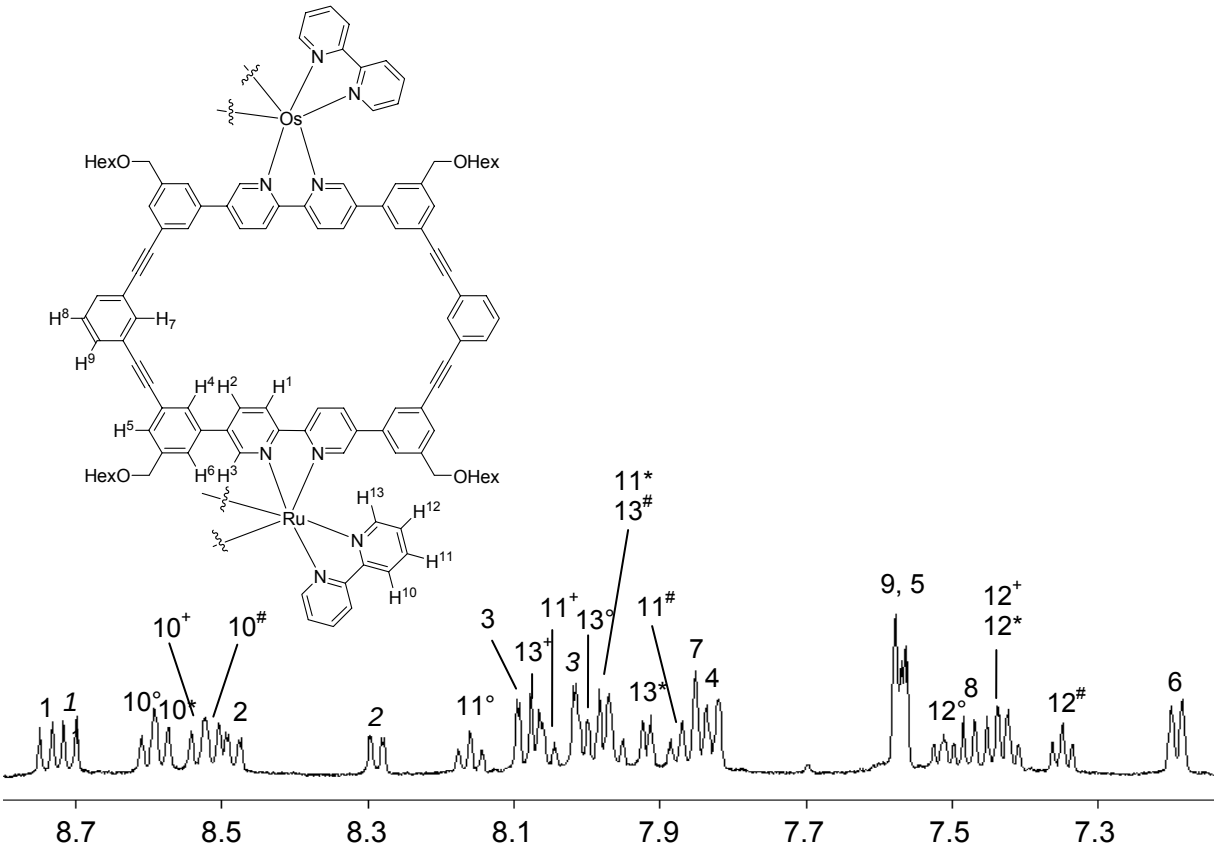


Figure 79. ^{1}H NMR spectrum of the mixed Ru/Os complex **118** (CD_3NO_2, 20 °C, 500 MHz) with signal assignment.

4.5.5. Synthesis of model compounds 119a,b and 120

Bidentate bridging ligands can give rise to multinuclear transition metal complexes like for example coordination polymers. Only a few examples of coordination polymers are known in literature.[84] Rehahn prepared soluble and high molecular-weight ruthenium (II) coordination polymers by using highly pure [Ru(bpy)Cl_3] and a bridging ligand monomer (Figure 80).

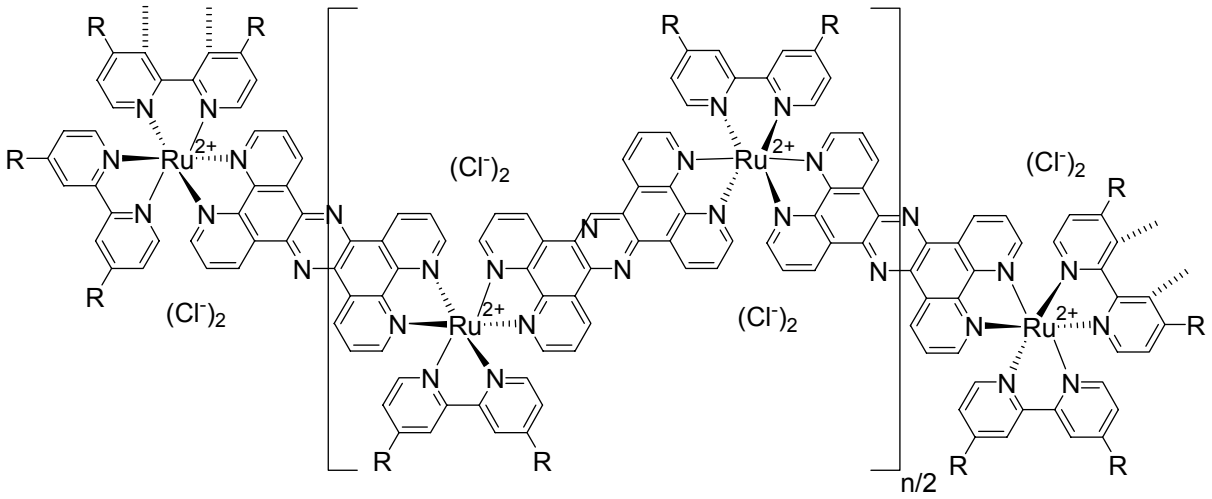
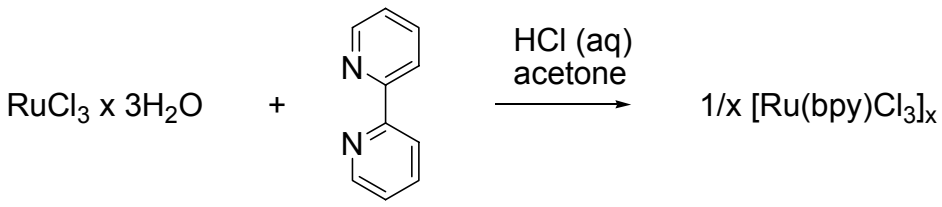


Figure 80. Coordination polymers of a bridging ligand by Rehahn.

In order to achieve high molecular weight polymer, high purity and an exact 1:1 proportion of the monomers is required. In our case macrocycle **10** and $[Ru(bpy)Cl_3]$ were selected as monomers for the polymerization. Rehahn has shown that when $[Ru(bpy)Cl_3]$ was prepared according to literature procedure[85] a low molecular weight polymer was formed. The reason were impurities in $[Ru(bpy)Cl_3]$ which contained some $RuCl_3$ and $[Ru(bpy)_2Cl_2]$ which produced defects in polymer structure and acted as end group, respectively. It was impossible to purify $[Ru(bpy)Cl_3]$ due to its polymeric constitution. Therefore its synthesis had to be changed. This was accomplished by Rehahn who developed a procedure which gave highly pure $[Ru(bpy)Cl_3]$.[84b] He used only 0.35 M hydrochloric acid together with acetone, and the bipyridine solution was syringed within about 10 h to the $RuCl_3 \times 2H_2O$ in aqueous 0.35 M hydrochloric acid (Scheme 62). In this way, the formation of the $[Ru(bpy)_2Cl_2]$ can be suppressed. This procedure was also employed in the present work.



Scheme 62. Synthesis of highly pure $[Ru(bpy)Cl_3]$ by Rehahn.

$[Ru(bpy)Cl_3]$ is a paramagnetic compound, which rendered an assessment of its purity by ^1H NMR spectroscopy impossible. This task was nevertheless achieved by converting it into another Ru(II) complex, by reacting the Ru-monomer with a second ligand.

It was not clear from the beginning whether two macrocycles can coordinate to one Ru. For this purpose three model compounds **119a**,**b** and **120** were synthesized. Two equivalents of ligands **74a** or **74b** were reacted with $[Ru(bpy)Cl_3]$ in a mixture of dioxane/ethanol/water 2:2:1, at reflux. During reaction the color changed from purple to orange. The complexes were isolated as PF_6^- salts in 85% yield. During complexation of **74b**, the THP group was cleaved off to give the diol **119b** instead of the expected THP-protected analogue.

It should be mentioned here that complexes **119** are of additional interest as models for nanoconstructions with shape-persistent macrocycles having two bipyridine units. This compound is very poorly soluble in common organic solvents like DCM, chloroform, nitromethane, and acetonitrile, but soluble in DMSO. The purity of **119b** was assessed from its ^1H NMR spectrum (Figure 81). Both complexes were fully characterized and gave correct elemental analysis. The FAB mass spectrum displayed two fragmentation peaks at *m/z* = 1791 and 1646 for **119a** and at *m/z* = 1451 and 1306 for **119b** corresponding to $[M\text{-}PF_6]^+$ and $[M\text{-}2PF_6]^+$.

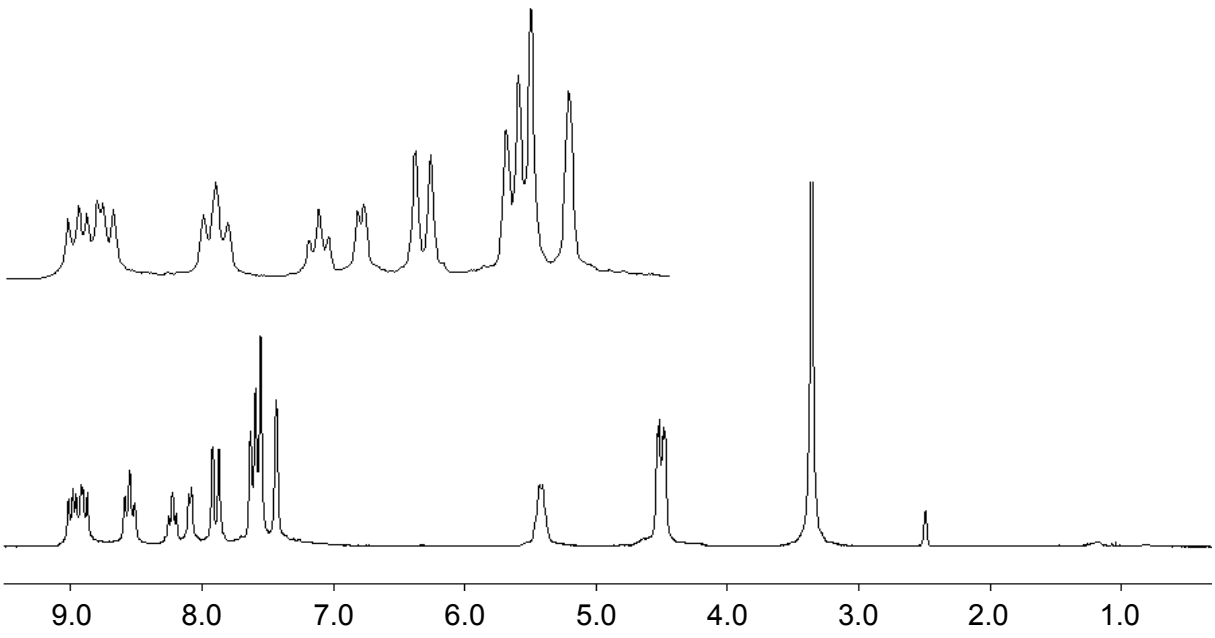
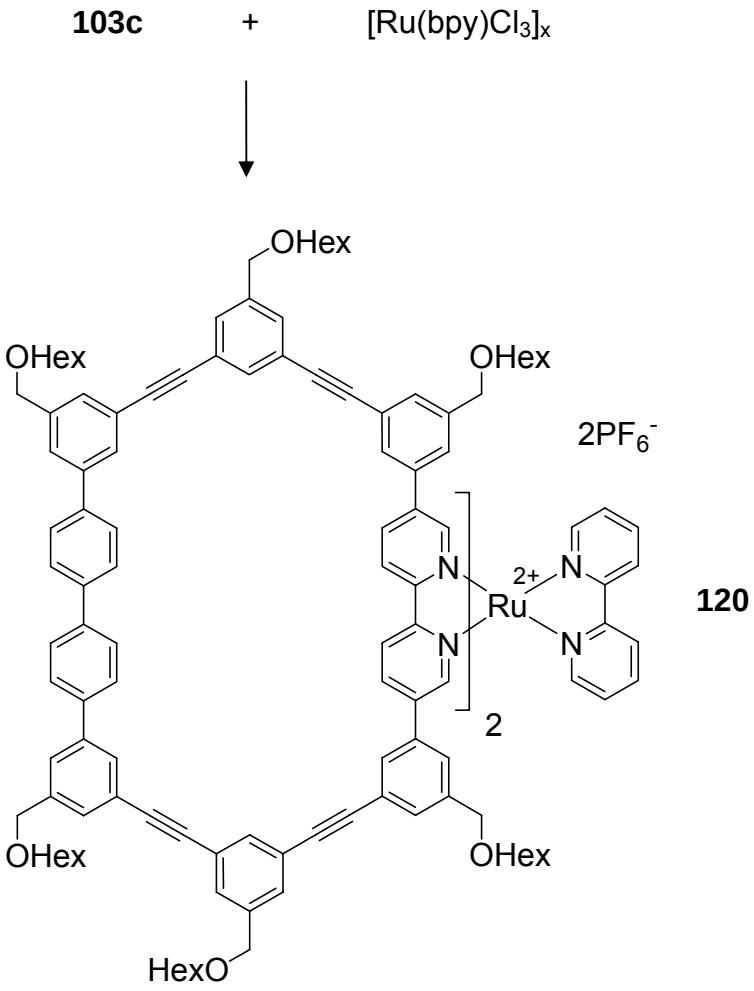


Figure 81. ^1H NMR spectrum of compound **119b** with the aromatic part enlarged (DMSO, 250 MHz, 20 °C).

In next step the monofunctional bipyridine macrocycle **103c** was complexed with $[Ru(bpy)Cl_3]$ to give **120** (Scheme 63). During reaction the expected change of color was observed from purple to blue-green and brown orange. The complex was isolated by column chromatography. Its ^1H NMR spectrum shows the expected signals, but they were broad. The MALDI-TOF spectrum shows a set of signals attributable to characteristic fragmentation ions of the complex (Figure 82).



Scheme 63. Synthesis of complex **120**.

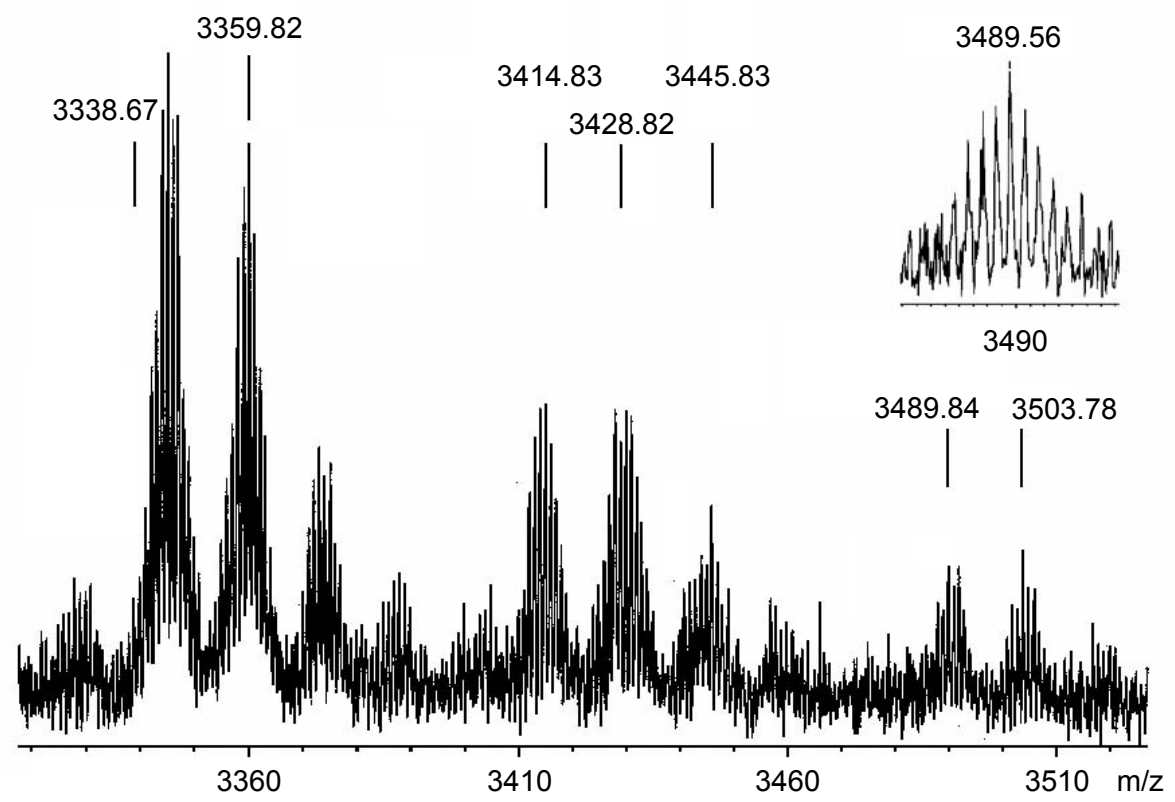


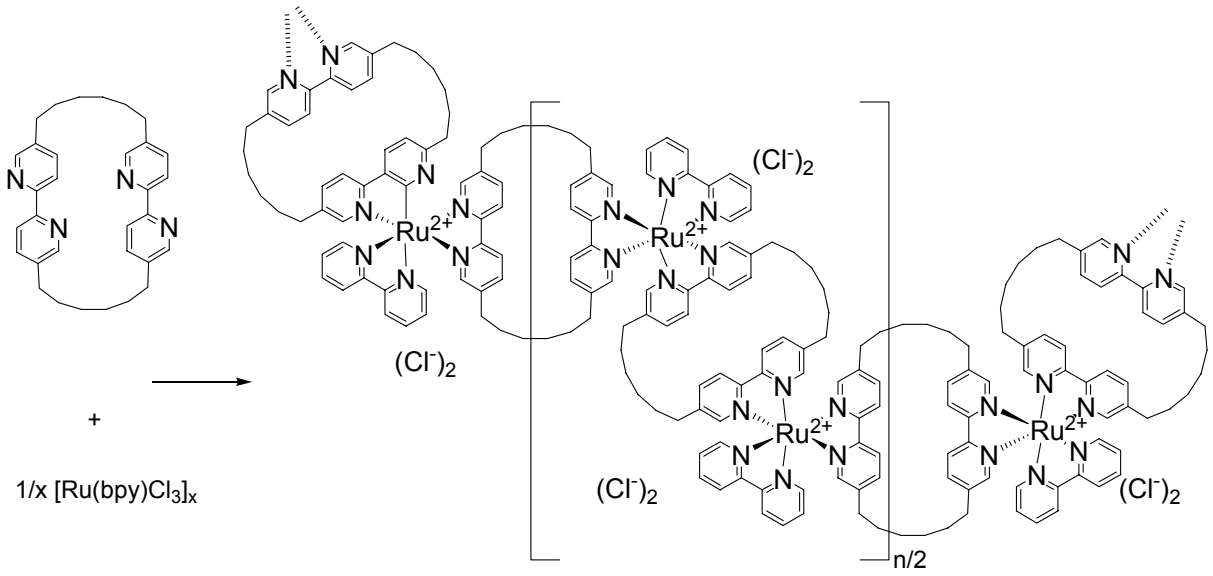
Figure 82. MALDI-TOF mass spectrum (dithranol matrix) of **120**. For the fragmentation pattern, see Table 9. Insert: Extended and amplified isotope pattern of the MALDI-TOF mass spectral signal of **120** at *m/z* = 1489.84 $[M\text{-}PF_6]^+$.

Table 9. Assignments and fragmentation of some MALDI-TOF mass spectrum signals of complex **120**.

Mass	Assigned formula	Fragmentation
3503.76	$C_{227}H_{255}N_6O_{12}RuPF_6$	$[M+CH_3\text{-}PF_6]^+$
3489.84	$C_{226}H_{253}N_6O_{12}RuPF_6$	$[M\text{-}PF_6]^+$
3445.83	$C_{223}H_{245}N_6O_{12}RuPF_6$	$[M\text{-}PF_6\text{-}C_3H_7]^+$
3359.82	$C_{227}H_{256}N_6O_{12}Ru$	$[M+H+CH_3\text{-}2PF_6]^+$
3344.84	$C_{226}H_{253}N_6O_{12}Ru$	$[M+H\text{-}2PF_6]^+$

The low yield in which the complex **120** formed makes one pessimistic regarding the polymerization reaction where high conversions are strictly required. For the initial polymerization, the bifunctional cycle **10** was reacted with equimolar amounts of $[Ru(bpy)Cl_3]$ (Scheme 64). The large difference between the molar masses of macrocycle **10** and $[Ru(bpy)Cl_3]$ made the achievement of an exact 1 : 1

stoichiometry an experimental challenge. Precipitation of the reaction product with NH_4PF_6 gave an oligomeric material (MALDI-TOF MS: P_n = 5). An accurate determination of the molecular weight of such compounds is a complex matter because they represent polyelectrolytes. Further optimization is certainly required to increase the molar mass.



Scheme 64. Synthesis of coordination polymer from macrocycle **10** and $Ru(bpy)Cl_3$.