

## Molecular “Fingerhaken”\* based on multiple $\pi$ -interactions

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## 1. Pictures for elucidation of “Fingerhakel”



## 2. Concentration dependent $^1\text{H}$ -NMR spectra

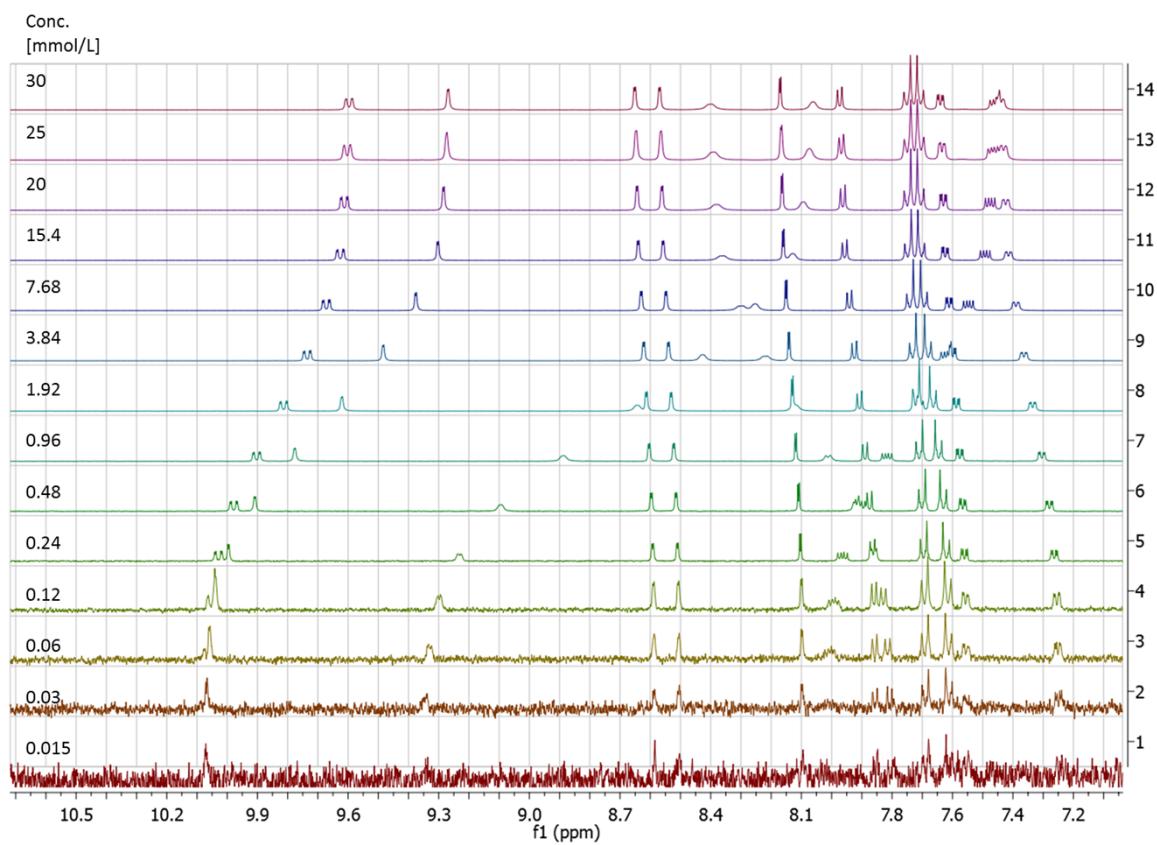


Figure 1: concentration dependent  $^1\text{H}$ -NMR spectra of  $\text{Ru}(\text{tbp})_2\text{tpphz}$  as a  $\text{PF}_6$  salt in Acetonitrile.

### 3. Peak assignment in the $^1\text{H-NMR}$ spectra

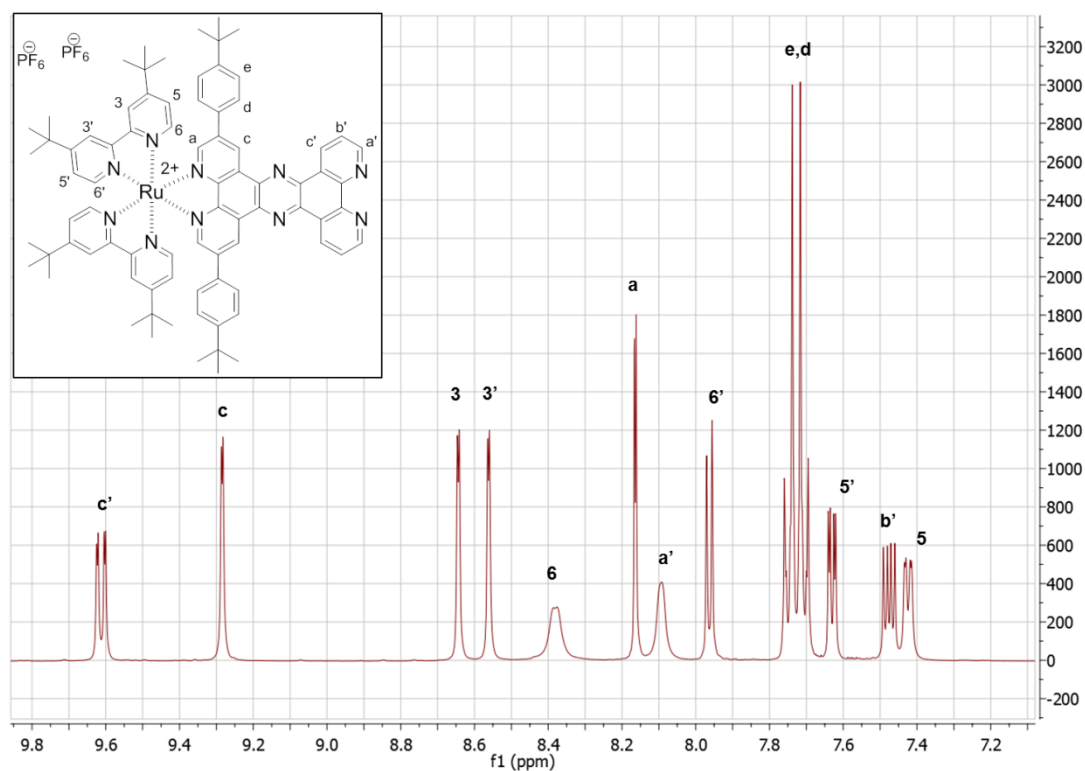


Figure 3: H-NMR of  $\text{Ru}(\text{tpb})_2\text{tpphz}$  (20 mM) in Acetonitrile. The assignment of the signals was carried out with the aid of different NMR-techniques (COSY, HSQC, HMBC).

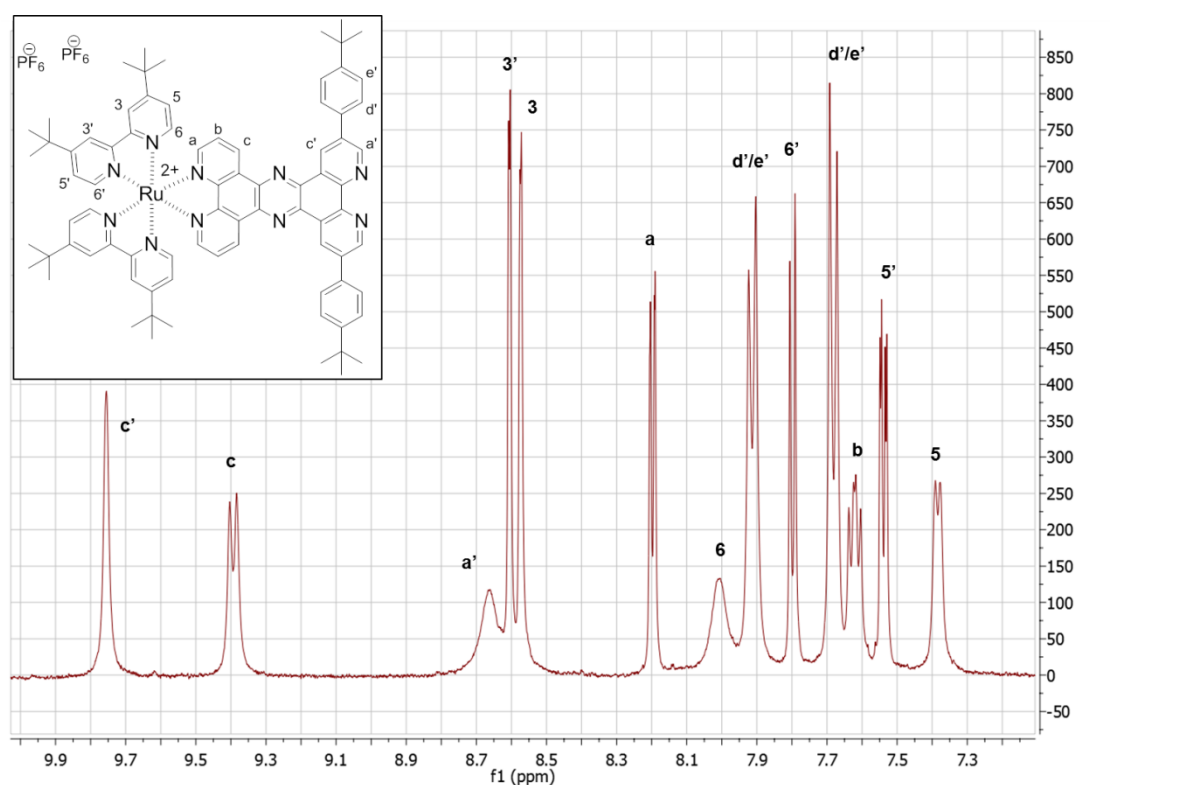


Figure 4: H-NMR of  $\text{Ru}(\text{tpphz})(\text{tpb})_2$  (1.92 mM) in Acetonitrile. The assignment of the signals was carried out with the aid of different NMR-techniques (COSY, HSQC, HMBC) and analogy.

#### 4. Comments on the modified methodology of the calculation $K_D$ of **Rutpphz**

This publication introduces a different value for  $K_D$  of **Rutpphz** ( $Ru = Ru^{2+}(tbbpy)_2$ ,  $tbbpy = 4,4'$ -di-*tert.*-butyl-2,2'-bipyridine and  $tpphz = \text{tetrapyrido}[3,2-a:2',3':c:3'',2'']\text{-}h:2''',3'''\text{-}j$ ]phenazine) than the cited article in this publication (Ref. 5 of manuscript):  $289 \pm 17 \text{ M}^{-1}$  (new) against  $122 \pm 19 \text{ M}^{-1}$  (old). This deviation is caused by the use of more data points and a modification of the methodology of the calculation of the dimerization constant, which improves the accuracy of the calculation. The old value of the dimerization constant was produced by taking the average of the determined constants of the  $^1\text{H-NMR}$  signals of two protons of the  $tpphz$  ligand, yielded from local non linear least squares fit curves.<sup>1,2</sup> The disadvantages of this method are a relatively high standard error of 15.6 % and the fact that the effect of the interaction is analyzed using only two protons. The concentration dependent  $^1\text{H-NMR}$  spectra of **Rutpphz** however show that the interaction influences the ppm value of nearly every proton. Thus the change of the signal position of more than two protons should be usable for the determination of the dimerization constant.

Consequently the new value was determined by the use of global non linear least squares curve fitting of the  $^1\text{H-NMR}$  signals of five protons. The use of this modified methodology together with more data points yielded a reduction of the percentage of the standard error from 15.6 % to 5.9 %. All other effects and details of this modification of the calculation methodology will be described and a separate publication, which is written at the time. The overall advantages of global fitting over local approaches are also described by P. Thordarson.<sup>3</sup>

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<sup>1</sup> V. Steullet and D. W. Dixon, *Chem. Soc., Perkin Trans. 2*, 1999, 1547.

<sup>2</sup> N. R. de Tacconi, R. Chitakunye, F. M. MacDonnell and R. O. Lezna, *J. Phys. Chem. A*, 2008, **112**, 497.

<sup>3</sup> P. Thordarson, *Chem. Soc. Rev.*, 2011, **40**, 1305.

## 5. Details to the calculation on the dimerization constant $K_D$

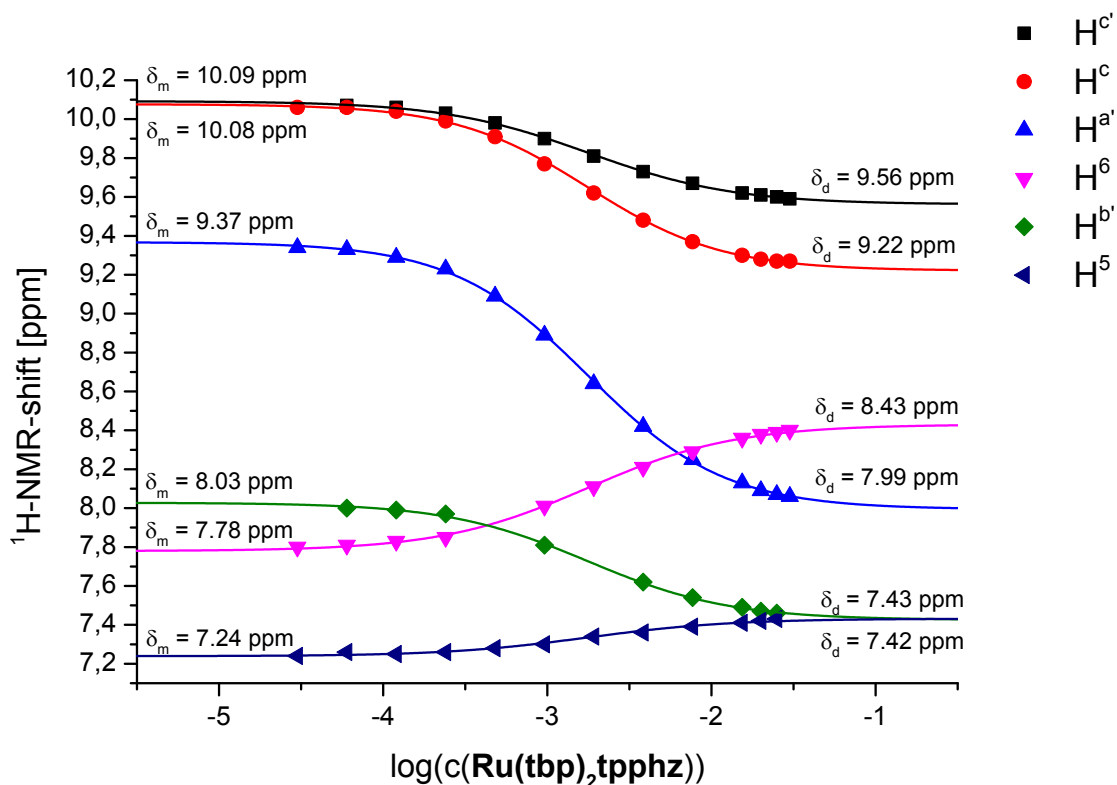


Figure 5: Plot of the shift of the ppm values of the protons  $c'$ ,  $c$ ,  $a'$ ,  $6$ ,  $b'$  and  $5$  of  $\text{Ru}(\text{tbp})_2\text{tpphz}$  versus the logarithm of the concentration of the complex. Extrapolation of the data points with a Boltzmann function yields the ppm values of the pure monomer ( $\delta_m$ ) and the pure dimer ( $\delta_d$ ).<sup>4</sup>

$$y = A2 + \frac{(A1 - A2)}{\left(1 + e^{\left(\frac{x - x_0}{dx}\right)}\right)}$$

Fit statistics: reduced  $\chi^2 = 4.77 \cdot 10^{-5}$ , adjusted  $R^2 = 1$ .

Fit parameters:  $x_0$  is shared for all curves due to the global fit;  $A1 = \delta_m$ ,  $A2 = \delta_d$ ,  $x = c(\text{Ru}(\text{tbp})_2\text{tpphz})$  and  $y = {}^1\text{H-NMR-shift}$ .  $dx$  is adjusted during the fit.

<sup>4</sup> V. Steullet and D. W. Dixon, *Chem. Soc., Perkin Trans. 2*, **1999**, 1547.

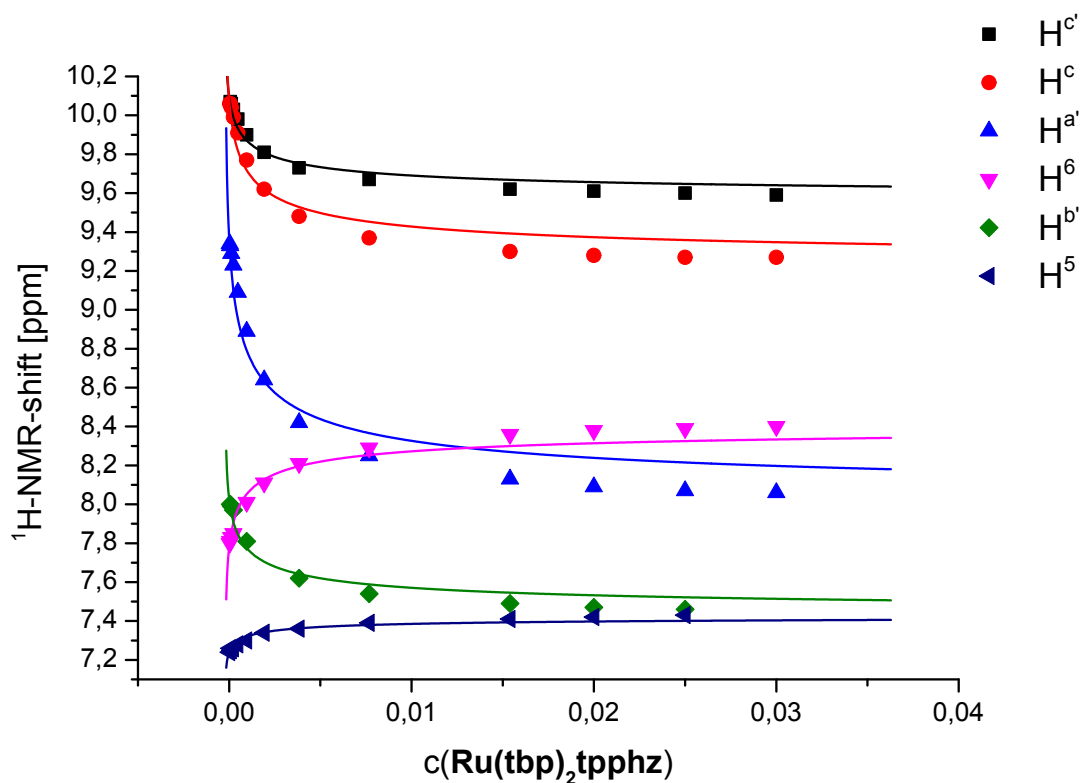


Figure 6: Plot of the shift of the ppm values of the protons  $c'$ ,  $c$ ,  $a'$ ,  $6$ ,  $b'$  and  $5$  of  $\text{Ru}(\text{tbp})_2\text{tpphz}$  versus the concentration of the complex. The data points were treated with a least squares global fitting procedure using the following equation to yield the Dimerization constant  $K_D = 647 \pm 46 \text{ M}^{-1.5}$

$$\delta_{obs} = \delta_m + (\delta_d - \delta_m) \frac{\sqrt{1 + 8K_D[M]} - 1}{\sqrt{1 + 8K_D[M]} + 1}$$

Fit statistics: reduced  $\chi^2 = 0,00301$ , adjusted  $R^2 = 0.99972$ .

Fit parameters:  $K_D$  is shared for all curves due to the global fit;  $\delta_m$  and  $\delta_d$  were set as a constant for each proton using the values shown in Figure 5.

<sup>5</sup> J.-S. Chen and R. B. Shirts, *The Journal of Physical Chemistry*, **1985**, *89*, 1643.

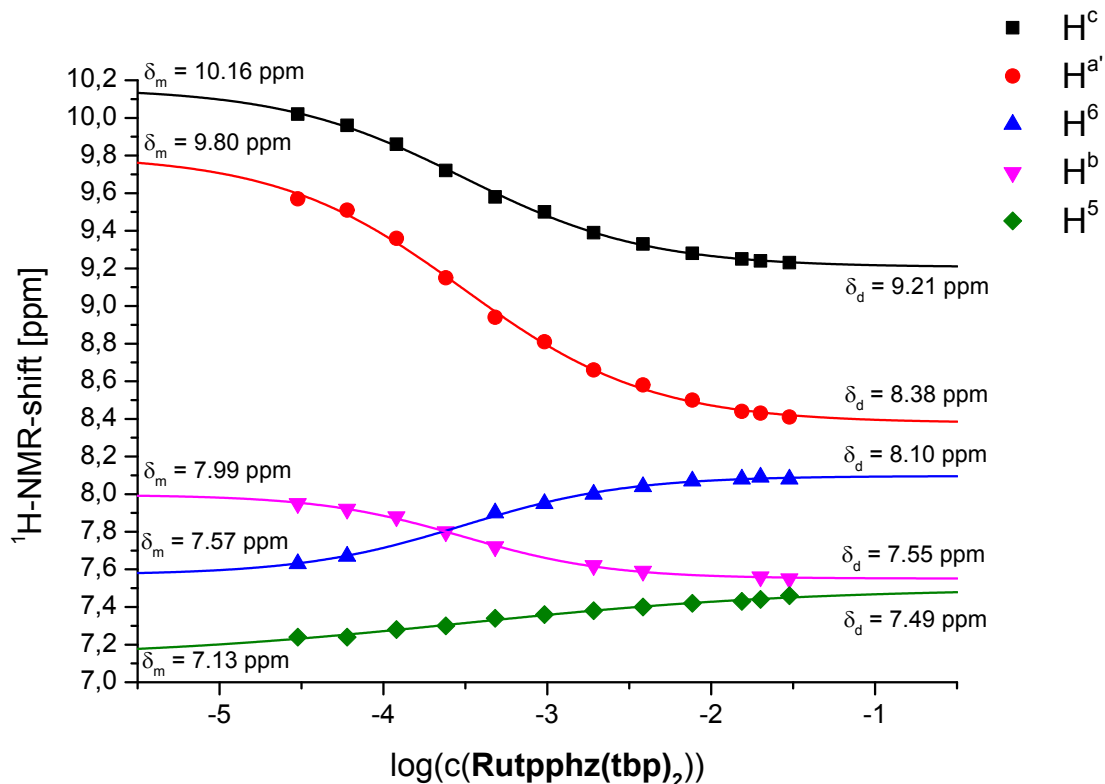


Figure 7: Plot of the shift of the ppm values of the protons c, a', 6, b and 5 of **Rutpphz(tbp)<sub>2</sub>** versus the logarithm of the concentration of the complex. Extrapolation of the data points with a Boltzmann function yields the ppm values of the pure monomer ( $\delta_m$ ) and the pure dimer ( $\delta_d$ ).<sup>4</sup>

$$y = A2 + \frac{(A1 - A2)}{\left(1 + e^{\left(\frac{x - x_0}{dx}\right)}\right)}$$

Fit statistics: reduced  $\chi^2 = 1.55 \cdot 10^{-4}$ , adjusted  $R^2 = 0.99979$ .

Fit parameters:  $x_0$  is shared for all curves due to the global fit;  $A1 = \delta_m$ ,  $A2 = \delta_d$ ,  $x = c(\text{Rutpphz}(\text{tbp})_2)$  and  $y = {}^1\text{H-NMR-shift}$ .  $dx$  is adjusted during the fit.

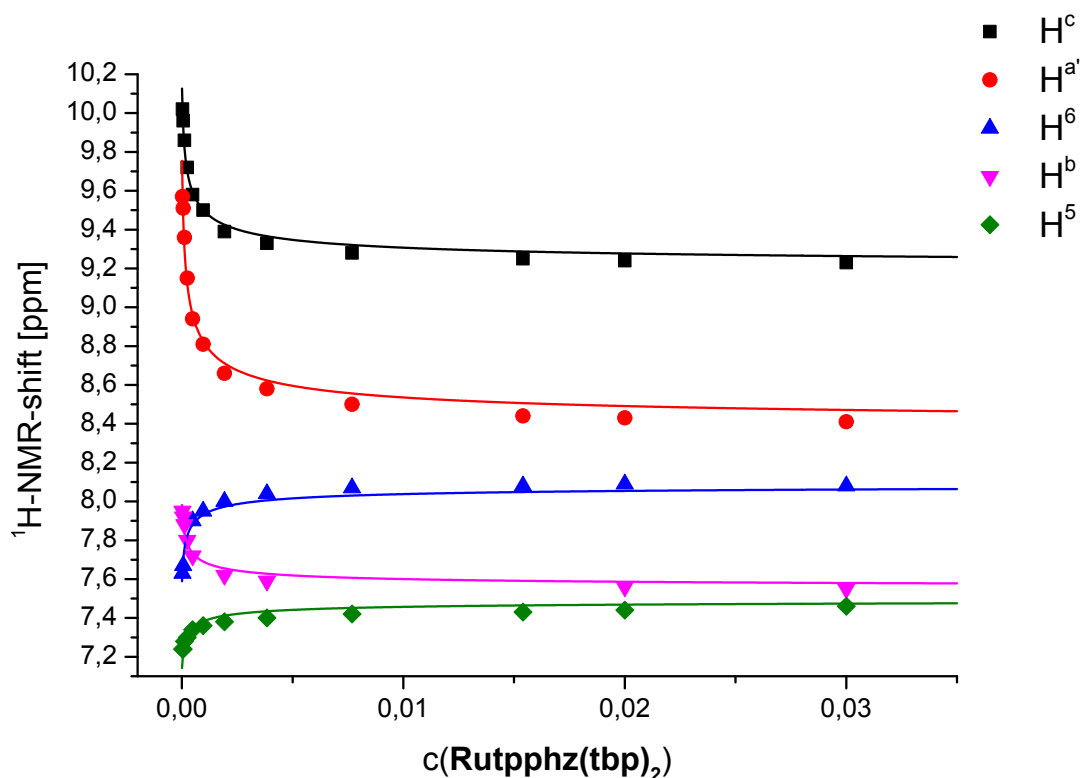


Figure 8: Plot of the shift of the ppm values of the protons c, a', 6, b and 5 of **Rutpphz(tbp)<sub>2</sub>** versus the concentration of the complex. The data points were treated with a least squares global fitting procedure using the following equation to yield the Dimerization constant  $K_D = 3634 \pm 176 \text{ M}^{-1.5}$

$$\delta_{obs} = \delta_m + (\delta_d - \delta_m) \frac{\sqrt{1 + 8K_D[M]} - 1}{\sqrt{1 + 8K_D[M]} + 1}$$

Fit statistics: reduced  $\chi^2 = 0.00125$ , adjusted  $R^2 = 0.99832$ .

Fit parameters:  $K_D$  is shared for all curves due to the global fit;  $\delta_m$  and  $\delta_d$  were set as a constant for each proton using the values shown in Figure 7.

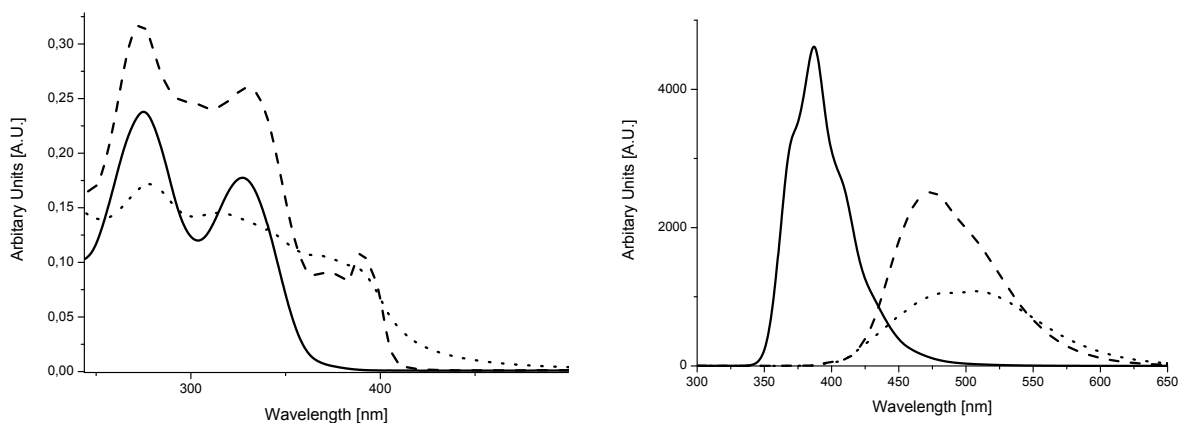


## 6. Change of the photophysical properties of $\text{tpphz}(\text{tbp})_2$

In an experiment we prepared a stock solution ( $66.0 \mu\text{m}$ ) and measured immediately the absorption- and emission-properties ( $5 \mu\text{m}$ ) (dashed line in figures below). The stock solution was held under ambient light for 15 d. Afterwards again the absorption and emission properties were measured (dotted line in the figures below).

The absorption bands at 273 nm and 330 nm decrease significantly and the fine structure of the bands between 350 nm and 400 nm disappears. The emission band at 473 nm decreases and a new emission band rises at 503 nm.

The reason for this behavior is not clear yet. One possible explanation could be a complicated aggregation processes in solution, maybe enhanced by the  $\pi$ -attraction, which leads to this change of photo physical properties. Further investigation into this interesting behavior is underway.



Left: Absorption spectra and right: emission spectra of  $\text{phen}(\text{tbp})_2$  (solid),  $\text{tpphz}(\text{tbp})_2$  solution freshly prepared (dashed),  $\text{tpphz}(\text{tbp})_2$  after 15 d in solution with  $\text{CH}_2\text{Cl}_2$  (DCM).

## 7. Details to the crystal structures

Table 1. Crystal data and structure refinement for **phenBr<sub>2</sub>O<sub>2</sub>X**

Empirical formula	C <sub>15</sub> H <sub>10</sub> Br <sub>2</sub> N <sub>2</sub> O <sub>2</sub>	
Formula weight	410.07	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	<i>P</i> -1	
Unit cell dimensions	a = 6.9502(7) Å	α = 82.560(7)°.
	b = 10.2517(9) Å	β = 78.404(8)°.
	c = 10.6485(9) Å	γ = 75.662(8)°.
Volume	717.54(12) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.898 Mg/m <sup>3</sup>	
Absorption coefficient	5.653 mm <sup>-1</sup>	
F(000)	400	
Crystal size	0.3807 x 0.1388 x 0.0429 mm <sup>3</sup>	
Theta range for data collection	3.441 to 26.372°.	
Index ranges	-8 ≤ h ≤ 8, -12 ≤ k ≤ 10, -13 ≤ l ≤ 13	
Reflections collected	5644	
Independent reflections	2927 [R(int) = 0.0317]	
Completeness to theta = 25.242°	99.7 %	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	2927 / 0 / 192	
Goodness-of-fit on F <sup>2</sup>	1.108	
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0394, wR <sub>2</sub> = 0.1080	
R indices (all data)	R <sub>1</sub> = 0.0474, wR <sub>2</sub> = 0.1148	
Largest diff. peak and hole	1.027 and -0.758 e·Å <sup>-3</sup>	

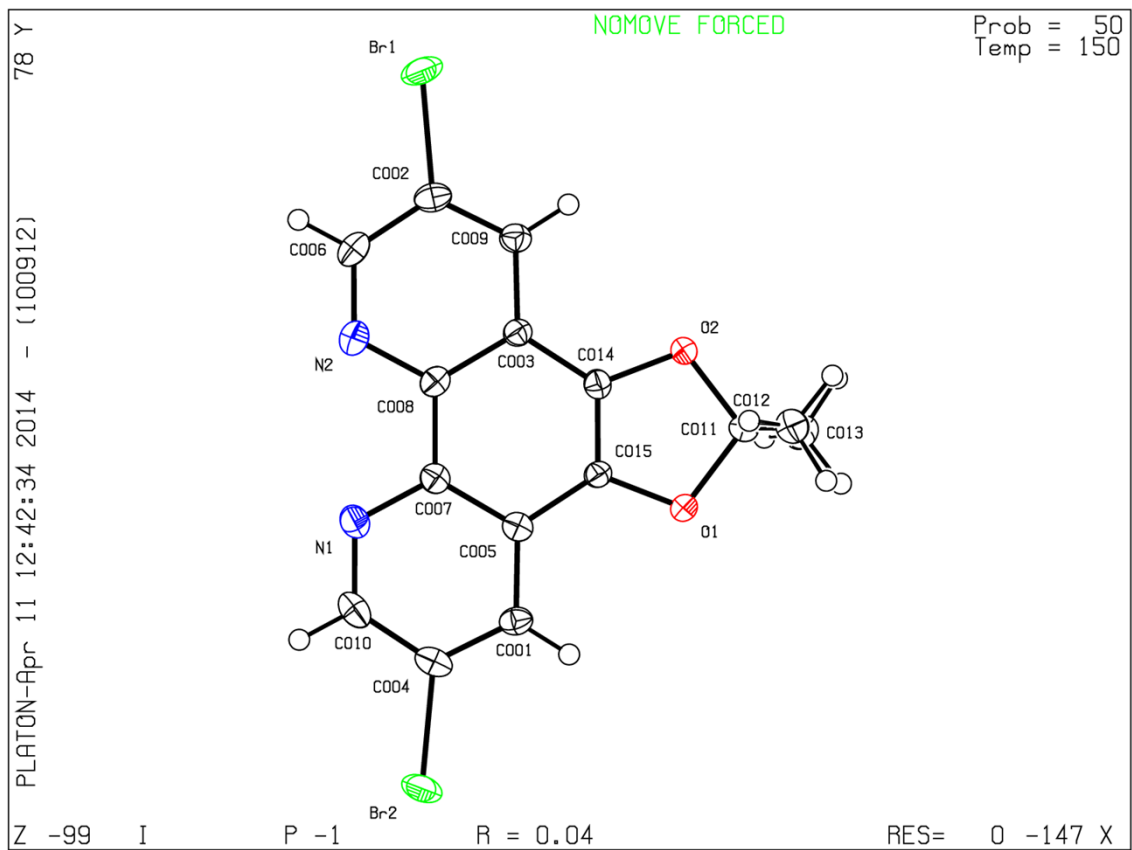


Figure 9: ORTEP representation of **phenBr<sub>2</sub>O<sub>2</sub>X**, probability ellipsoids given at 50 %.

Table 2. Crystal data and structure refinement for **phen(tbp)<sub>2</sub>O<sub>2</sub>X**

Empirical formula	C <sub>36</sub> H <sub>37</sub> Cl <sub>3</sub> N <sub>2</sub> O <sub>2</sub>	
Formula weight	636.02	
Temperature	150(2) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	<i>P</i> -1	
Unit cell dimensions	a = 10.9557(7) Å	α = 104.299(5)°.
	b = 11.8569(7) Å	β = 109.647(6)°.
	c = 14.1102(9) Å	γ = 95.094(5)°.
Volume	1642.82(19) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.286 Mg/m <sup>3</sup>	
Absorption coefficient	2.792 mm <sup>-1</sup>	
F(000)	668	
Crystal size	0.3391 x 0.1704 x 0.151 mm <sup>3</sup>	
Theta range for data collection	7.593 to 73.963°.	
Index ranges	-13 ≤ h ≤ 12, -14 ≤ k ≤ 14, -17 ≤ l ≤ 17	
Reflections collected	11349	
Independent reflections	6421 [R(int) = 0.0188]	
Completeness to theta = 67.684°	99.5 %	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	6421 / 0 / 420	
Goodness-of-fit on F <sup>2</sup>	1.028	
Final R indices [I > 2σ(I)]	R1 = 0.0561, wR2 = 0.1450	
R indices (all data)	R1 = 0.0588, wR2 = 0.1474	
Largest diff. peak and hole	1.322 and -0.537 e·Å <sup>-3</sup>	

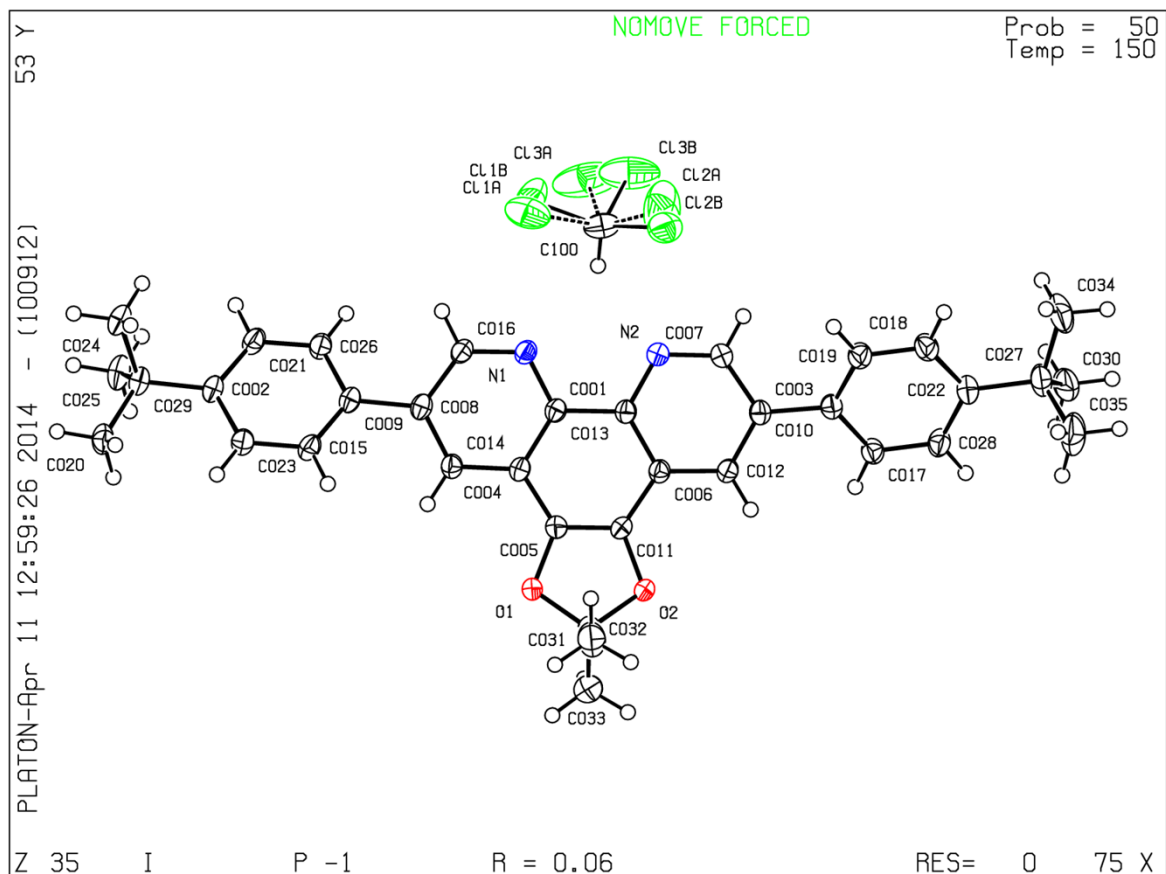


Figure 10: ORTEP representation of  $\text{phen}(\text{tbp})_2\text{O}_2\text{X}$ , probability ellipsoids given at 50 %.

Table 3. Crystal data and structure refinement for **phen(tbp)<sub>2</sub>**.

Empirical formula	C <sub>32</sub> H <sub>32</sub> N <sub>2</sub>	
Formula weight	444.59	
Temperature	180(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	
Unit cell dimensions	<i>a</i> = 16.2831(12) Å	$\alpha = 90^\circ$ .
	<i>b</i> = 9.4620(5) Å	$\beta = 115.158(8)^\circ$ .
	<i>c</i> = 17.5232(11) Å	$\gamma = 90^\circ$ .
Volume	2443.7(3) Å <sup>3</sup>	
<i>Z</i>	4	
Density (calculated)	1.208 Mg/m <sup>3</sup>	
Absorption coefficient	0.531 mm <sup>-1</sup>	
F(000)	952	
Crystal size	0.2384 x 0.0985 x 0.0427 mm <sup>3</sup>	
Theta range for data collection	7.604 to 74.114°.	
Index ranges	-20 ≤ <i>h</i> ≤ 16, -11 ≤ <i>k</i> ≤ 11, -21 ≤ <i>l</i> ≤ 21	
Reflections collected	10148	
Independent reflections	4800 [R(int) = 0.0306]	
Completeness to theta = 67.679°	99.6 %	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	4800 / 0 / 335	
Goodness-of-fit on F <sup>2</sup>	1.037	
Final R indices [I > 2σ(I)]	R1 = 0.0670, wR2 = 0.1870	
R indices (all data)	R1 = 0.0980, wR2 = 0.2194	
Largest diff. peak and hole	0.486 and -0.231 e·Å <sup>-3</sup>	

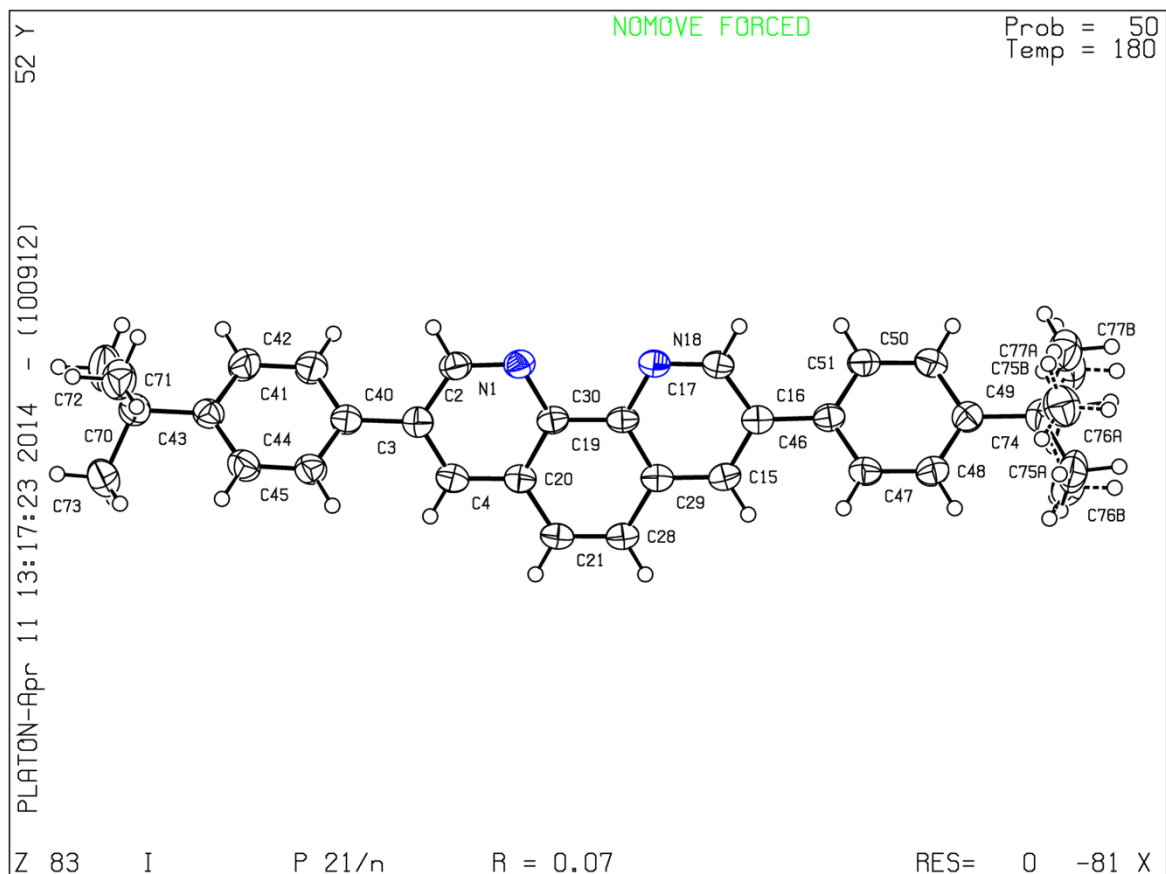


Figure 11: ORTEP representation of **phen(tbp)<sub>2</sub>**, probability ellipsoids given at 50 %. The *tert*-butyl group on the right-hand side is calculated on two alternative conformations.

Table 4. Crystal data and structure refinement for **phen(tbp)<sub>2</sub>O<sub>2</sub>**.

Empirical formula	C <sub>32</sub> H <sub>30</sub> N <sub>2</sub> O <sub>2</sub>	
Formula weight	474.58	
Temperature	150(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	<i>P</i> -1	
Unit cell dimensions	a = 6.3897(4) Å	α = 97.594(6)°.
	b = 10.1543(7) Å	β = 91.675(5)°.
	c = 19.0511(13) Å	γ = 92.920(6)°.
Volume	1222.85(14) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.289 Mg/m <sup>3</sup>	
Absorption coefficient	0.630 mm <sup>-1</sup>	
F(000)	504	
Crystal size	0.2878 x 0.077 x 0.048 mm <sup>3</sup>	
Theta range for data collection	7.412 to 73.739°.	
Index ranges	-7 ≤ h ≤ 7, -12 ≤ k ≤ 10, -23 ≤ l ≤ 23	
Reflections collected	14141	
Independent reflections	4802 [R(int) = 0.0317]	
Completeness to theta = 67.679°	99.7 %	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	4802 / 0 / 325	
Goodness-of-fit on F <sup>2</sup>	1.079	
Final R indices [I > 2σ(I)]	R1 = 0.0467, wR2 = 0.1165	
R indices (all data)	R1 = 0.0653, wR2 = 0.1285	
Largest diff. peak and hole	0.241 and -0.192 e·Å <sup>-3</sup>	



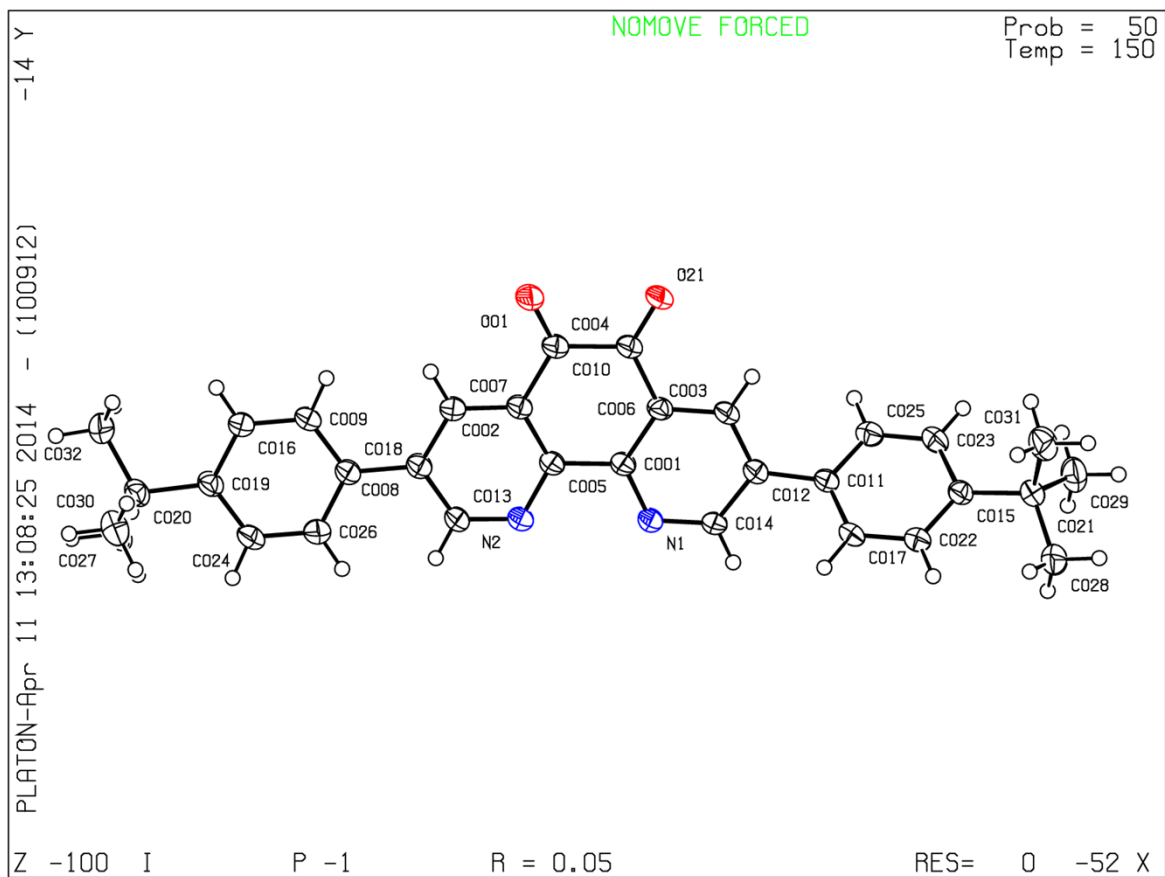


Figure 12: ORTEP representation of **phen(tbp)<sub>2</sub>O<sub>2</sub>**, probability ellipsoids given at 50

Table 5. Crystal data and structure refinement for **tpphz(tbp)<sub>2</sub>**.

Empirical formula	C <sub>47</sub> H <sub>42</sub> Cl <sub>6</sub> N <sub>6</sub>	
Formula weight	903.56	
Temperature	180(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.6741(4) Å	α = 73.800(4)°.
	b = 15.7010(6) Å	β = 88.093(4)°.
	c = 19.5176(8) Å	γ = 86.939(4)°.
Volume	2254.68(18) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.331 Mg/m <sup>3</sup>	
Absorption coefficient	3.790 mm <sup>-1</sup>	
F(000)	936	
Crystal size	0.1408 x 0.0925 x 0.044 mm <sup>3</sup>	
Theta range for data collection	7.397 to 74.491°.	
Index ranges	-9 ≤ h ≤ 9, -14 ≤ k ≤ 19, -23 ≤ l ≤ 24	
Reflections collected	22502	
Independent reflections	9194 [R(int) = 0.0424]	
Completeness to theta = 67.679°	99.7 %	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	9194 / 0 / 542	
Goodness-of-fit on F <sup>2</sup>	1.114	
Final R indices [I > 2σ(I)]	R1 = 0.0730, wR2 = 0.2191	
R indices (all data)	R1 = 0.0945, wR2 = 0.2337	
Largest diff. peak and hole	1.090 and -0.514 e·Å <sup>-3</sup>	

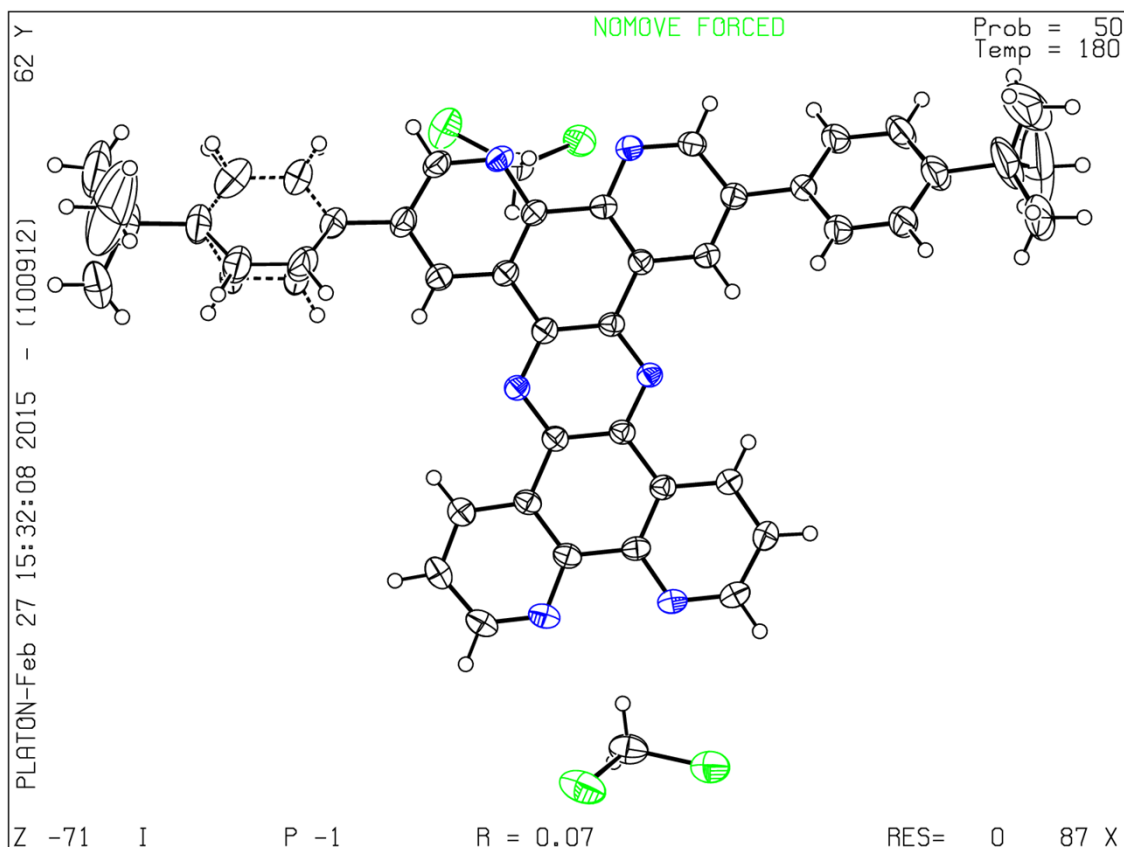


Figure 13: ORTEP representation of **tpphz(tbp)<sub>2</sub>**, probability ellipsoids given at 50 %. The anisotropic parameters of the C-atoms in the *tert.*-butyl- are enlarged due to structural disorder. The phenyl substituent on the left-hand side is calculated in two alternative conformations with respect to their twist relative to the adjacent pyridyl moiety.

Table 6. Crystal data and structure refinement for **Ru(tbp)<sub>2</sub>tpphz**.

Empirical formula	C <sub>96</sub> H <sub>108</sub> F <sub>12</sub> N <sub>18</sub> P <sub>2</sub> Ru	
Formula weight	1905.01	
Temperature	180(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 51.8116(7) Å	α = 90°.
	b = 15.1574(2) Å	β = 91.5900(10)°.
	c = 25.2431(3) Å	γ = 90°.
Volume	19816.5(4) Å <sup>3</sup>	
Z	8	
Density (calculated)	1.277 Mg/m <sup>3</sup>	
Absorption coefficient	2.222 mm <sup>-1</sup>	
F(000)	7936	
Crystal size	0.2072 x 0.1366 x 0.0946 mm <sup>3</sup>	
Theta range for data collection	7.452 to 72.564°.	
Index ranges	-47 ≤ h ≤ 62, -18 ≤ k ≤ 18, -31 ≤ l ≤ 30	
Reflections collected	56735	
Independent reflections	19053 [R(int) = 0.0289]	
Completeness to theta = 67.679°	99.3 %	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	19053 / 6 / 991	
Goodness-of-fit on F <sup>2</sup>	0.780	
Final R indices [I > 2σ(I)]	R1 = 0.0495, wR2 = 0.1341	
R indices (all data)	R1 = 0.0675, wR2 = 0.1472	
Largest diff. peak and hole	0.725 and -0.588 e·Å <sup>-3</sup>	

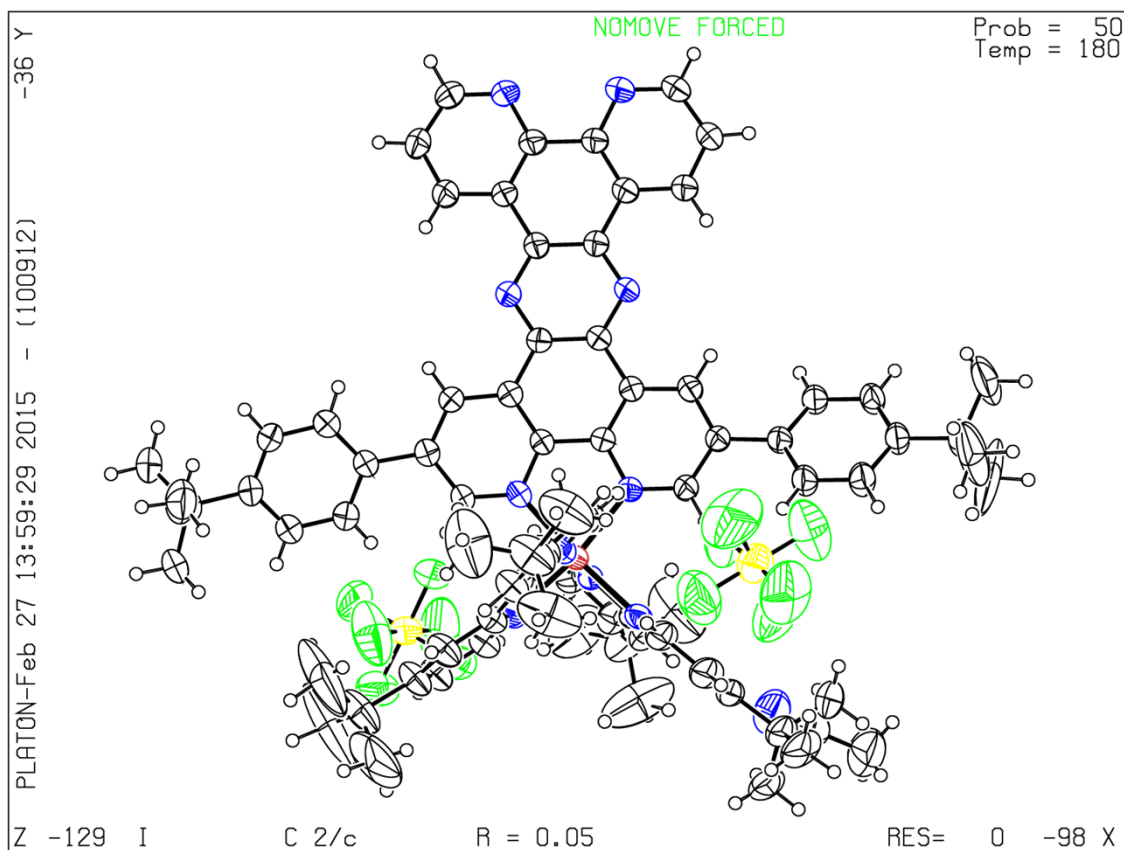


Figure 14: ORTEP representation of **Ru(tbp)<sub>2</sub>tpphz**, probability ellipsoids given at 50 %. The anisotropic parameters of the C-atoms in the *tert.*-butyl-groups and of the F-atoms in the PF<sub>6</sub><sup>-</sup>-anion are enlarged due to structural disorder.

Table 7. Crystal data and structure refinement for **Rutpphz(tbp)<sub>2</sub>**.

Empirical formula	C <sub>85.50</sub> H <sub>95</sub> Cl <sub>11</sub> F <sub>12</sub> N <sub>10</sub> P <sub>2</sub> Ru
Formula weight	2043.67
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C 2/c
Unit cell dimensions	a = 45.6046(9) Å      α = 90°. b = 22.1737(4) Å      β = 116.956(3)°. c = 21.5480(6) Å      γ = 90°.
Volume	19422.5(9) Å <sup>3</sup>
Z	8
Density (calculated)	1.398 Mg/m <sup>3</sup>
Absorption coefficient	0.567 mm <sup>-1</sup>
F(000)	8376
Crystal size	0.122 x 0.1019 x 0.0639 mm <sup>3</sup>
Theta range for data collection	3.408 to 26.372°.
Index ranges	-56 ≤ h ≤ 56, -27 ≤ k ≤ 26, -26 ≤ l ≤ 24
Reflections collected	62965
Independent reflections	19815 [R(int) = 0.0580]
Completeness to theta = 25.242°	99.7 %
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	19815 / 0 / 1037
Goodness-of-fit on F <sup>2</sup>	0.985
Final R indices [I > 2σ(I)]	R1 = 0.0531, wR2 = 0.1383
R indices (all data)	R1 = 0.0793, wR2 = 0.1510
Largest diff. peak and hole	0.608 and -0.496 e·Å <sup>-3</sup>

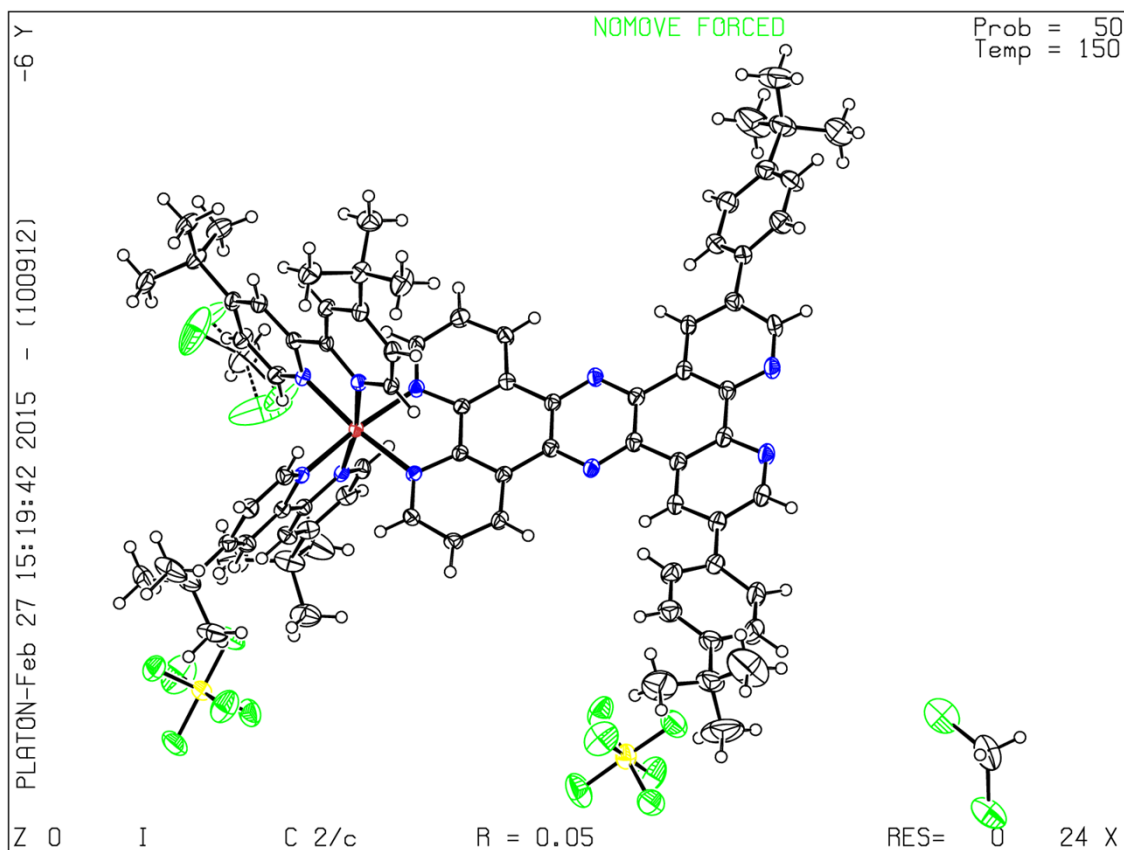


Figure 15: ORTEP representation of **Rutpphz(tbp)<sub>2</sub>**, probability ellipsoids given at 50 %. The anisotropic parameters of the C-atoms in the *tert.*-butyl-groups, of the F-atoms in the hexafluorophosphate-anion and of the Cl-atoms in dichloromethane are enlarged due to structural disorder.

Table 8. Crystal data and structure refinement for **Ru(tbp)<sub>2</sub>tpphzRu**

Empirical formula	C <sub>143.50</sub> H <sub>198</sub> F <sub>24</sub> N <sub>14</sub> O <sub>5.50</sub> P <sub>4</sub> Ru <sub>2</sub>	
Formula weight	2989.17	
Temperature	150(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	I 2/a	
Unit cell dimensions	a = 19.8215(8) Å	α = 90°.
	b = 44.8370(12) Å	β = 106.727(3)°.
	c = 19.8740(5) Å	γ = 90°.
Volume	16915.4(10) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.174 Mg/m <sup>3</sup>	
Absorption coefficient	2.450 mm <sup>-1</sup>	
F(000)	6260	
Crystal size	0.2754 x 0.1604 x 0.1417 mm <sup>3</sup>	
Theta range for data collection	7.480 to 74.464°.	
Index ranges	-24 ≤ h ≤ 14, -56 ≤ k ≤ 52, -23 ≤ l ≤ 22	
Reflections collected	26007	
Independent reflections	14622 [R(int) = 0.0349]	
Completeness to theta = 67.679°	86.3 %	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	14622 / 46 / 977	
Goodness-of-fit on F <sup>2</sup>	1.062	
Final R indices [I > 2σ(I)]	R1 = 0.0658, wR2 = 0.1932	
R indices (all data)	R1 = 0.0926, wR2 = 0.2178	
Largest diff. peak and hole	0.978 and -0.669 e·Å <sup>-3</sup>	



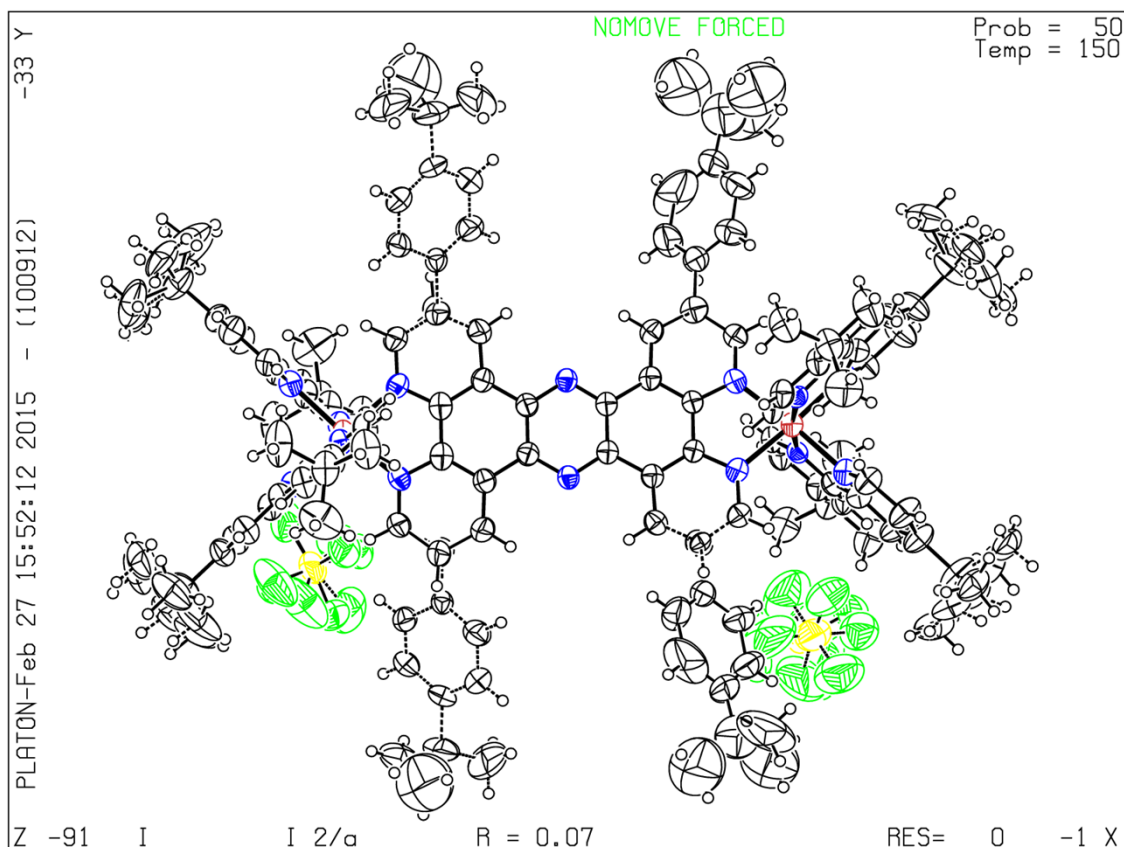


Figure 16: ORTEP representation of **Ru(tbp)<sub>2</sub>tpphzRu**, probability ellipsoids given at 50 %. The anisotropic parameters of the C-atoms in the *tert*-butyl-groups and of the F-atoms in the PF<sub>6</sub>-anion are enlarged due to structural disorder. The *tert*-butylphenyl substituents can be found on either side of the bridging ligand with respect to the crystal packing. Adjacent PF<sub>6</sub>-anions are found on different positions in the lattice accordingly.

Table 9. Crystal data and structure refinement for **Ru(tbp)<sub>2</sub>phen**.

Empirical formula	C <sub>75</sub> H <sub>90.50</sub> F <sub>12</sub> N <sub>9.50</sub> P <sub>2</sub> Ru	
Formula weight	1516.07	
Temperature	180(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 15.7991(4) Å	α = 104.461(2)°.
	b = 16.8342(4) Å	β = 116.670(3)°.
	c = 16.8521(5) Å	γ = 92.680(2)°.
Volume	3812.4(2) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.321 Mg/m <sup>3</sup>	
Absorption coefficient	2.711 mm <sup>-1</sup>	
F(000)	1578	
Crystal size	0.2341 x 0.1185 x 0.0612 mm <sup>3</sup>	
Theta range for data collection	7.407 to 74.493°.	
Index ranges	-19 ≤ h ≤ 15, -20 ≤ k ≤ 20, -19 ≤ l ≤ 21	
Reflections collected	42405	
Independent reflections	15533 [R(int) = 0.0357]	
Completeness to theta = 67.679°	99.7 %	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	15533 / 0 / 979	
Goodness-of-fit on F <sup>2</sup>	1.039	
Final R indices [I > 2σ(I)]	R1 = 0.0430, wR2 = 0.1126	
R indices (all data)	R1 = 0.0499, wR2 = 0.1200	
Largest diff. peak and hole	1.138 and -0.824 e·Å <sup>-3</sup>	

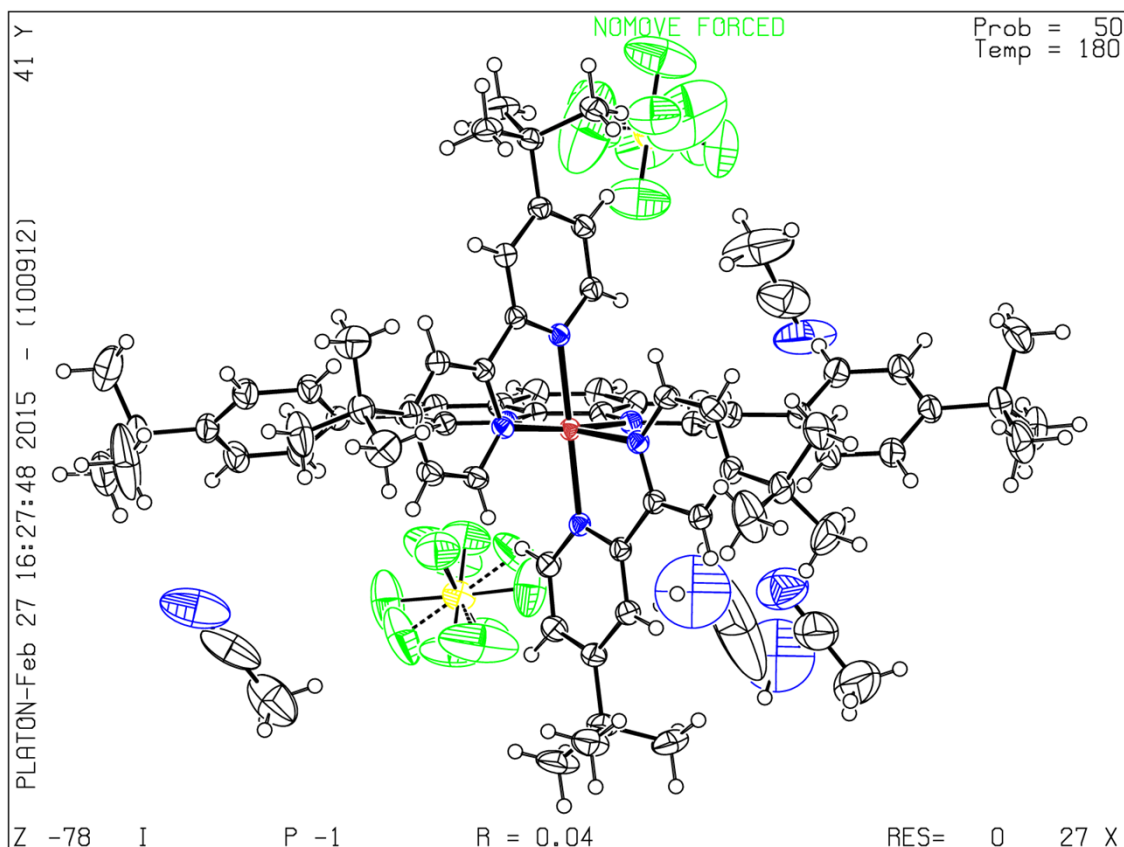


Figure 17: ORTEP representation of **Ru(tbp)<sub>2</sub>phen(PF<sub>6</sub>)<sub>2</sub>**, probability ellipsoids given at 50 %. The anisotropic parameters of the C-atoms in the *tert.*-butyl-groups and of the F-atoms in the PF<sub>6</sub>-anion are enlarged due to structural disorder. One molecule of water is distributed between two alternative positions.