Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Molecular Engineering of Ruthenium(II) Complexes with(3-Polyamino)phenanthroline Ligands for Developing Reusable Optical Sensors for Cu(II) ions

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Supporting information

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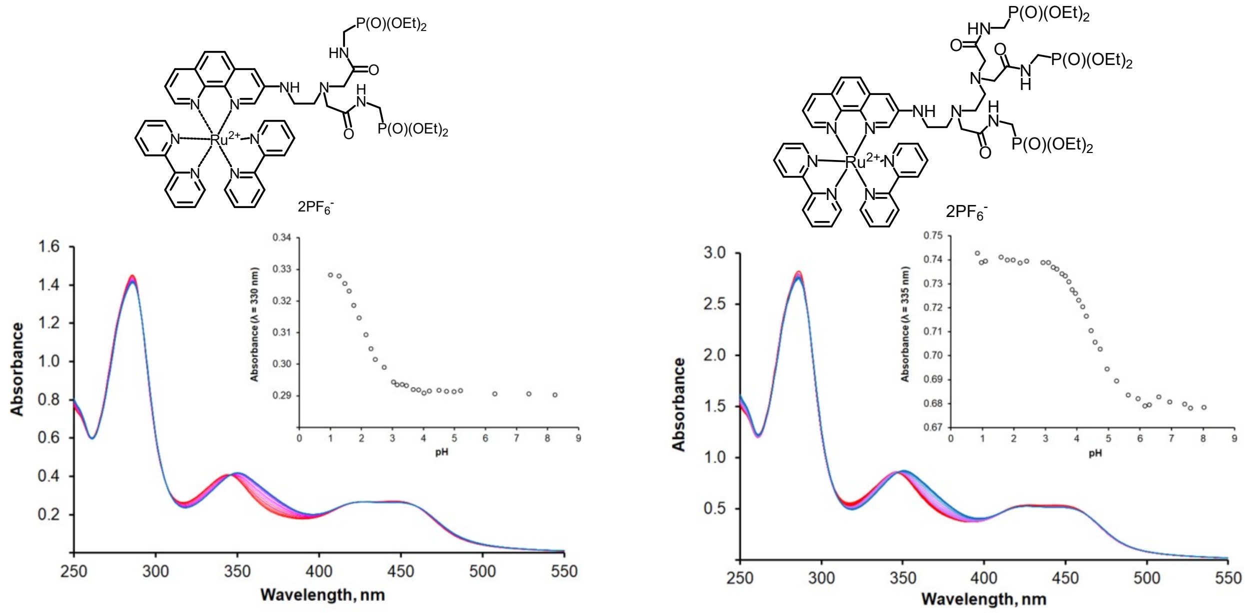
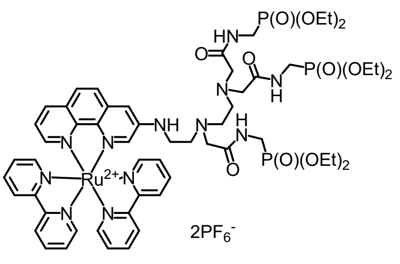
1. Protonation studies of complex Ru(N_3P_3phen)



(a) **(b)**

Figure S1. Comparison of the evolution of the electronic absorption spectra of the compounds **Ru(N_2P_2phen)** (a) and **Ru(N_3P_3phen)** (b) in water as a function of pH. Insets show the pH dependence of the absorbance at λ_{abs} = 335 nm.



Ru(N_3P_3phen)

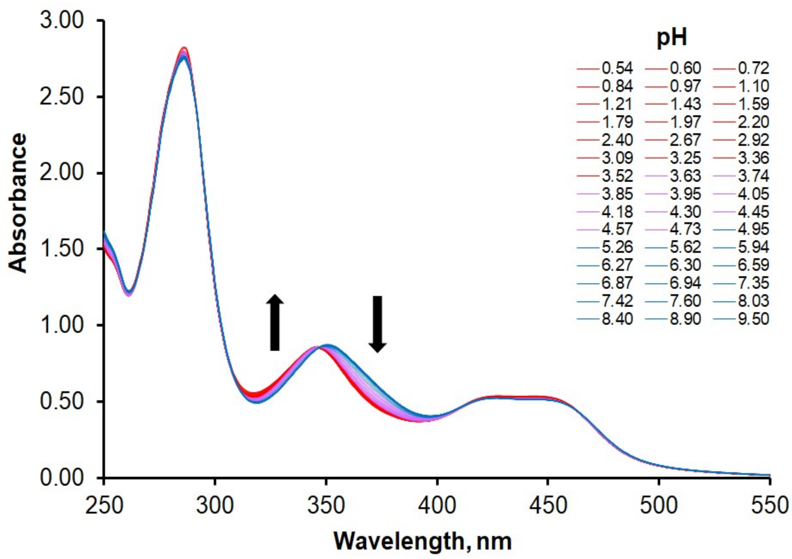


Figure S2. Spectrophotometric titration of **Ru(N_3P_3phen)** in water. [**Ru(N_3P_3phen)**] = 51 μM, I = 0.1 M KCl, pH = 1.0–9.50.

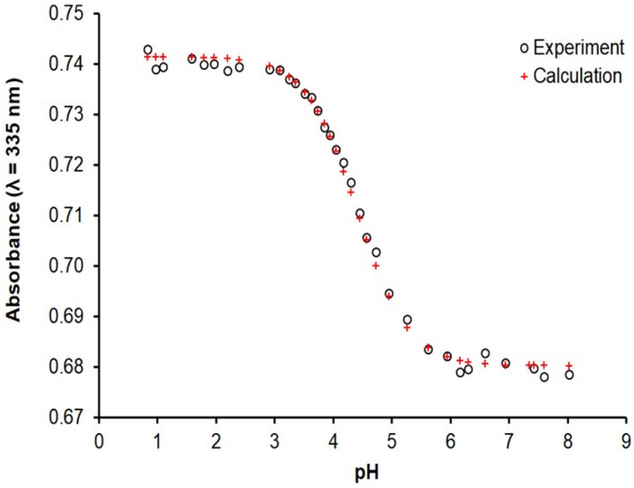
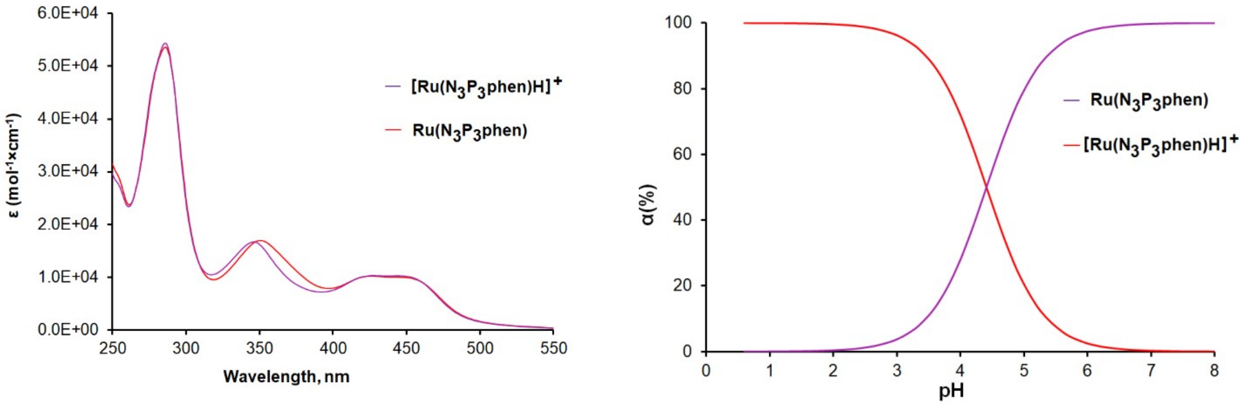
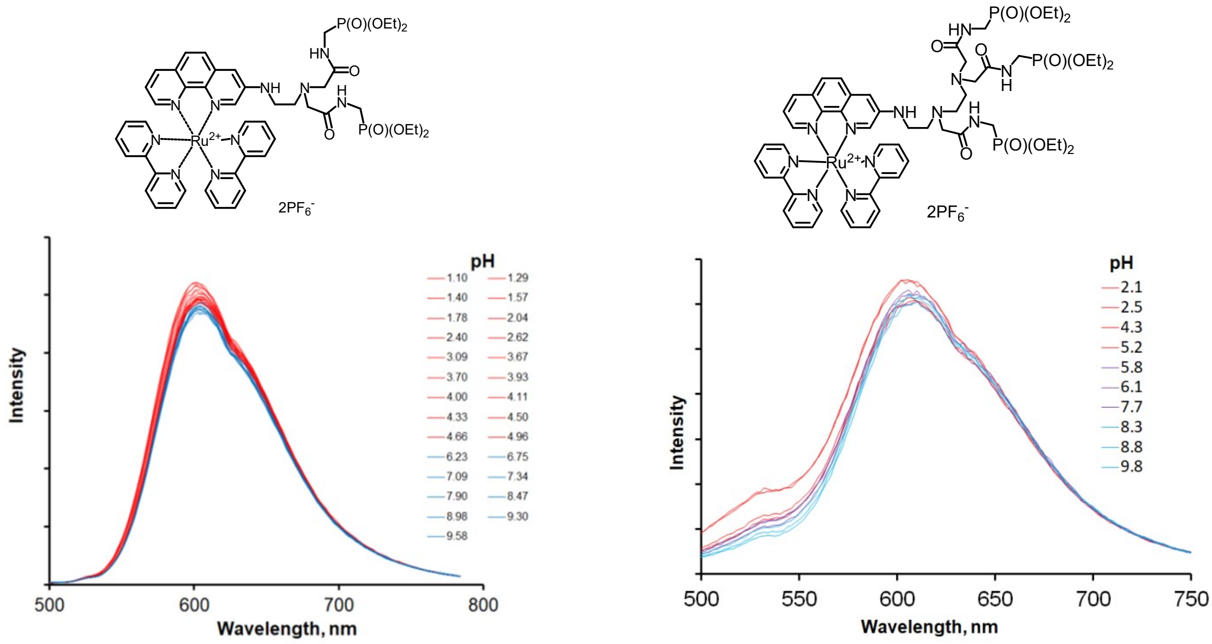


Figure S3. Absorbance changes with pH at λ = 335 nm for **Ru(N$_3$P$_3$phen)** in water as a function of pH.



(a) **(b)**

Figure S4. (a) UV–vis absorption spectra of **Ru(N$_3$P$_3$phen)** and [**Ru(N$_3$P$_3$phen)**H]$^+$ in water calculated using HypSpec program.[1] (b) Species distribution diagram for the **Ru(N$_3$P$_3$phen)**/H$^+$ system in water calculated using HypSpec program.[1]



(a) **(b)**

Figure S5. (a) Fluorimetric titration of **Ru(N$_2$P$_2$phen)** in water. [**Ru(N$_2$P$_2$phen)**] = 6.6 μM, I = 0.1 M KCl, λ_{ex} = 450 nm, pH = 1.1–9.6. (b) Fluorimetric titration of **Ru(N$_3$P$_3$phen)** in water. [**Ru(N$_3$P$_3$phen)**] = 4.7 μM, I = 0.1 M KCl, λ_{ex} = 450 nm, pH = 2.1–9.8.

2. Sensing properties of complex Ru(N_3P_3phen)

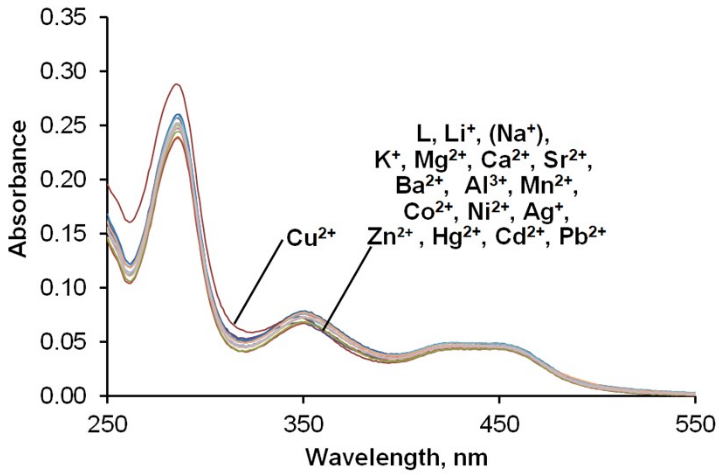


Figure S6. UV–vis absorption spectra of **Ru(N_3P_3phen)** ([**Ru(N_3P_3phen)**] = 4.7 μM, 0.03M HEPES buffer, pH = 7.4) before and after addition of 2 equiv. of metal perchlorates. The spectrum in the presence of sodium perchlorate was recorded without HEPES buffer in deionized water at pH = 5.42.

(a)

(b)

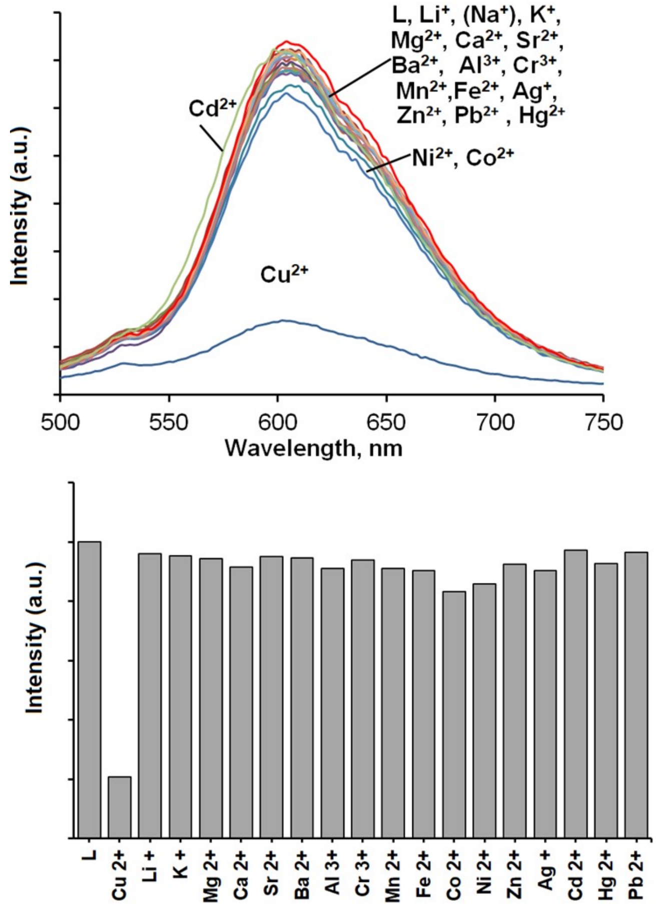


Figure S7. (a) Fluorescence spectra of **Ru(N$_3$P$_3$phen)** ([**Ru(N$_3$P$_3$phen)**] = 4.7 μM, 0.03M HEPES buffer, pH = 7.4, λ_{ex} = 450 nm) before and after addition of 2 equiv. of metal perchlorates. (b) Normalized fluorescence intensity of the studied solutions at λ_{em} = 600 nm. The spectrum in the presence of sodium perchlorate was recorded without HEPES buffer in deionized water at pH = 5.42.

(a)

(b)

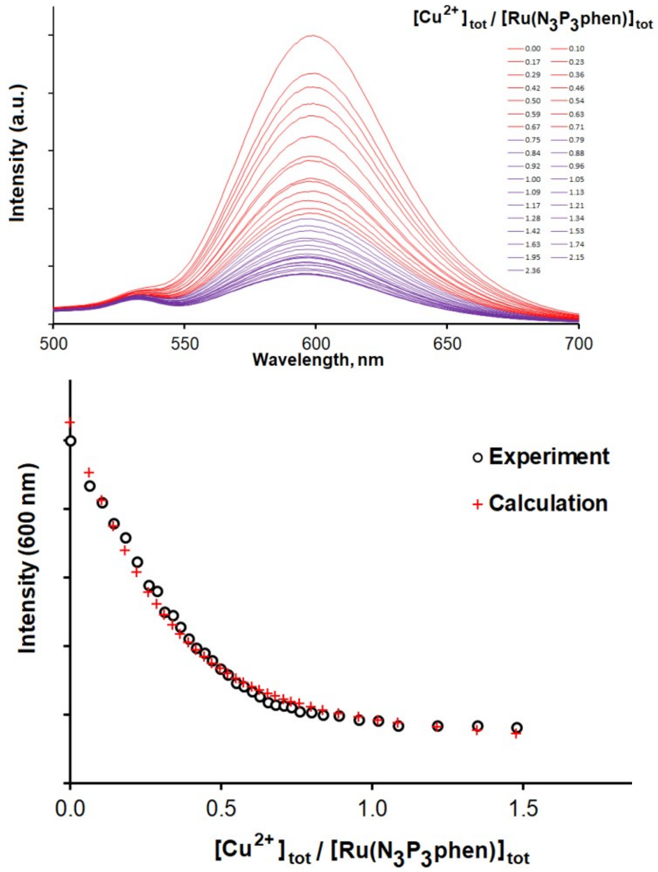
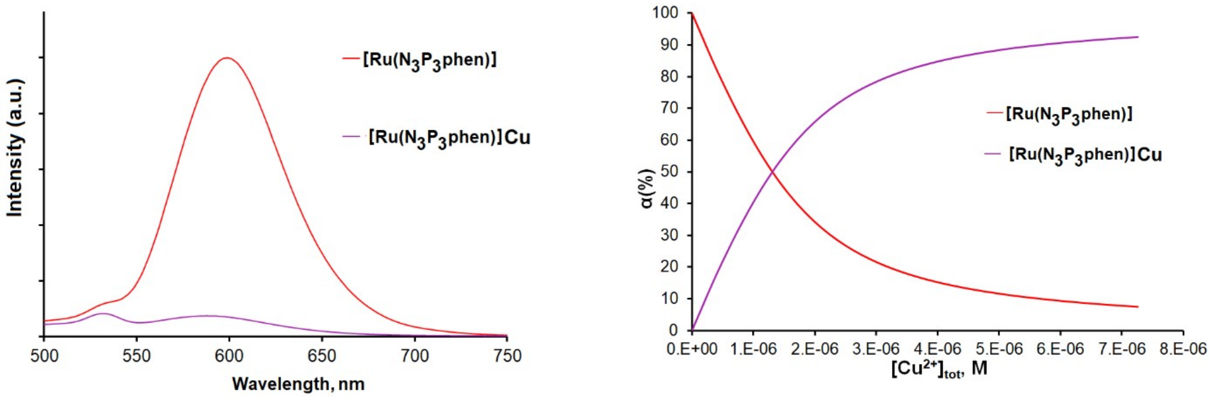


Figure S8. (a) Evolution of the emission spectrum of **Ru(N$_3$P$_3$phen)** ([**Ru(N$_3$P$_3$phen)**] = 5.1 μM, 0.03M HEPES buffer, pH = 7.4, λ_{ex} = 450 nm) upon addition of $Cu(ClO_4)_2$ (0–1.5 equiv.). (b) Changes of the emission intensity as a function of the $[Cu^{2+}]_{tot}$/[**Ru(N$_3$P$_3$phen)**]$_{tot}$ ratio at λ_{em} = 600 nm.



(a) (b)

Figure S9. (a) Normalized fluorescence spectra of **Ru(N$_3$P$_3$phen)** and [Cu(**Ru(N$_3$P$_3$phen)**)]$^{2+}$ in water calculated using HypSpec program.[1] (b) Species distribution diagram for the **Ru(N$_3$P$_3$phen)**/Cu^{2+} system in water calculated using HypSpec program.[1] Data were fit with HypSpec using the following model: Cu^{2+} + L $\rightleftharpoons$ $[CuL]^{2+}$ (log β_{110} = 6.05(5)), L + H^+ $\rightleftharpoons$ LH^+ (log β_{011} = 4.4), Cu^{2+} + H_2O $\rightleftharpoons$ $[Cu(OH)]^+$ + H^+ (log β_{10-1} = –7.95),[2] Cu^{2+} + $2H_2O$ $\rightleftharpoons$ $Cu(OH)_2$ + $2H^+$ (log β_{10-2} = –16.2),[2] $2Cu^{2+}$ + $2H_2O$ $\rightleftharpoons$ $[Cu_2(OH)_2]^{2+}$ + $2H^+$ (log β_{20-2} = –10.43).[2] Detection limit of Cu^{2+} (3σ): 0.02 μM (1.3 ppb).

(a)

(b)

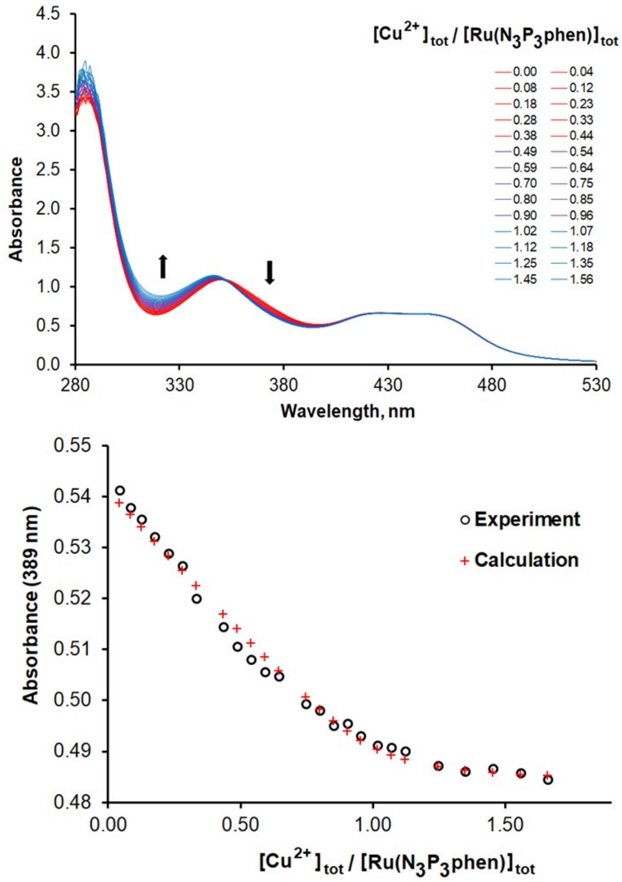
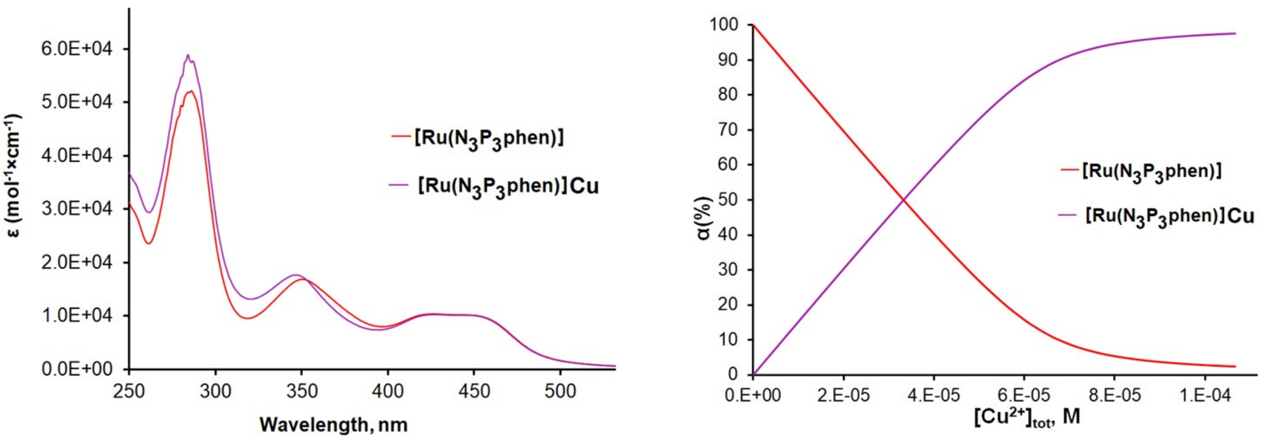


Figure S10. (a) Evolution of the UV–vis absorption spectrum of **Ru(N$_3$P$_3$phen)** ([**Ru(N$_3$P$_3$phen)**] = 64 μM, 0.03M HEPES buffer, pH = 7.4) upon addition of Cu(ClO$_4$)$_2$ (0–1.5 equiv.). (b) Changes of the absorbance as a function of the [Cu^{2+}]$_{tot}$/[**Ru(N$_3$P$_3$phen)**]$_{tot}$ ratio at λ =389 nm.



(a) (b)

Figure S11. (a) UV–vis spectra of **Ru(N$_3$P$_3$phen)** and [Cu(**Ru(N$_3$P$_3$phen)**)]$^{2+}$ in water calculated using HypSpec program.[1] (b) Species distribution diagram for the **Ru(N$_3$P$_3$phen)**/Cu^{2+} system in water calculated using HypSpec program.[1] Data were fit with HypSpec using the following model: $Cu^{2+} + L \rightleftharpoons [CuL]^{2+}$ ($\log \beta_{110} = 5.97(2)$), $L + H^+ \rightleftharpoons LH^+$ ($\log \beta_{011} = 4.4$), $Cu^{2+} + H_2O \rightleftharpoons [Cu(OH)]^+ + H^+$ ($\log \beta_{10-1} = -7.95$),[2] $Cu^{2+} + 2H_2O \rightleftharpoons Cu(OH)_2 + 2H^+$ ($\log \beta_{10-2} = -16.2$),[2] $2Cu^{2+} + 2H_2O \rightleftharpoons [Cu_2(OH)_2]^{2+} + 2H^+$ ($\log \beta_{20-2} = -10.43$).[2]

3. Structural studies of the copper(II) complex of Ru(N_3P_3phen)

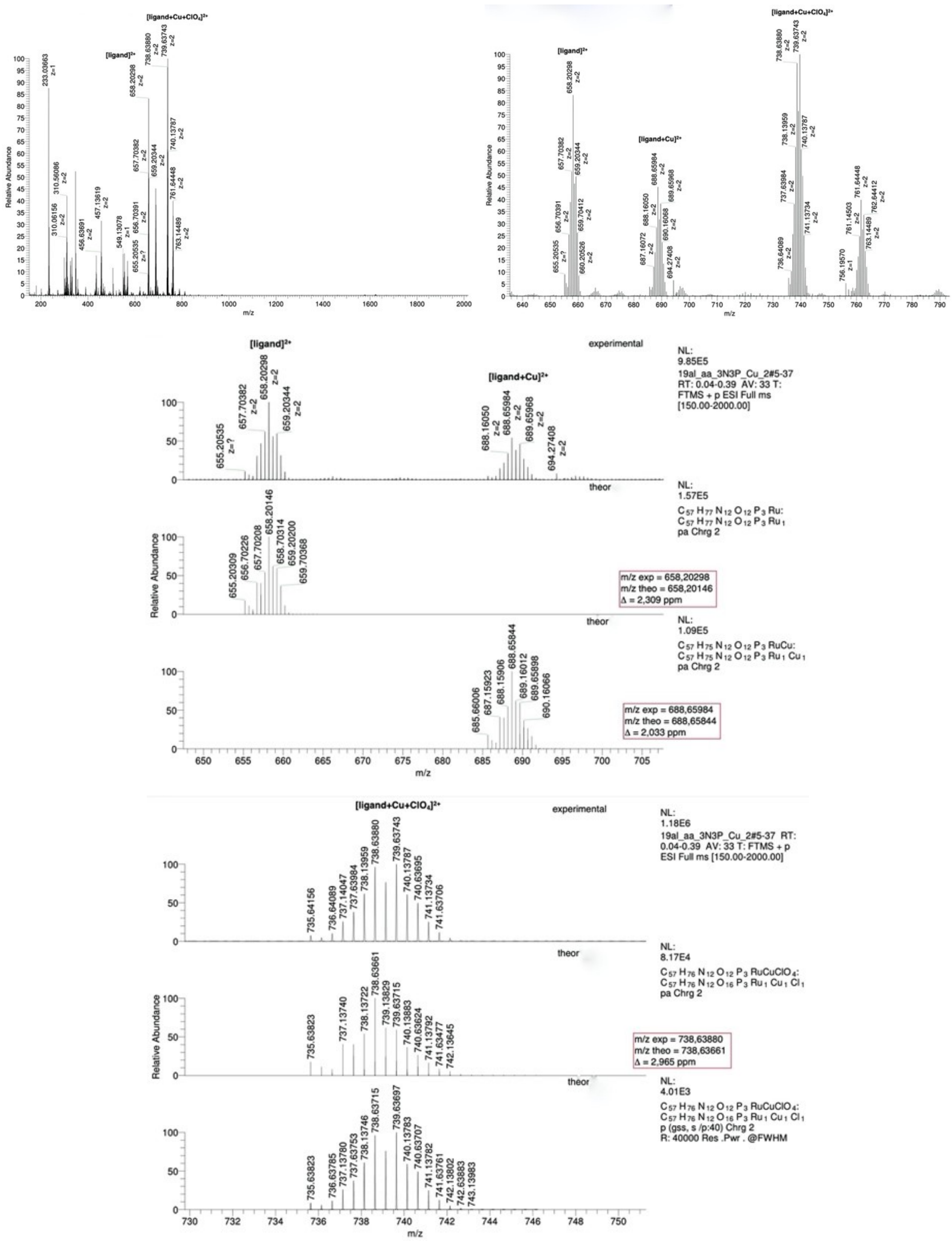


Figure S12. ESI-HRMS spectra of the {Cu[**Ru(N_3P_3phen)**]}$(ClO_4)_2$ complex.

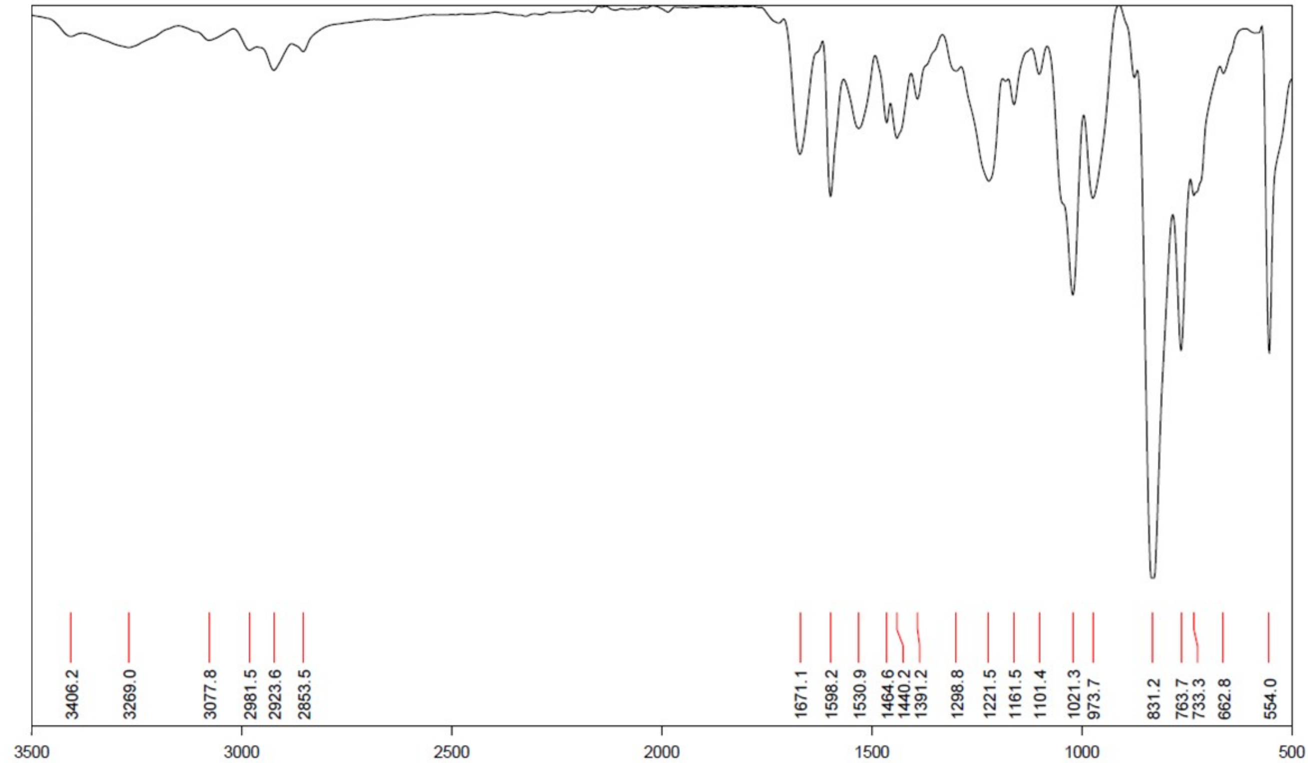


Figure S13. FTIR spectrum of **Ru(N$_3$P$_3$phen)** (neat).

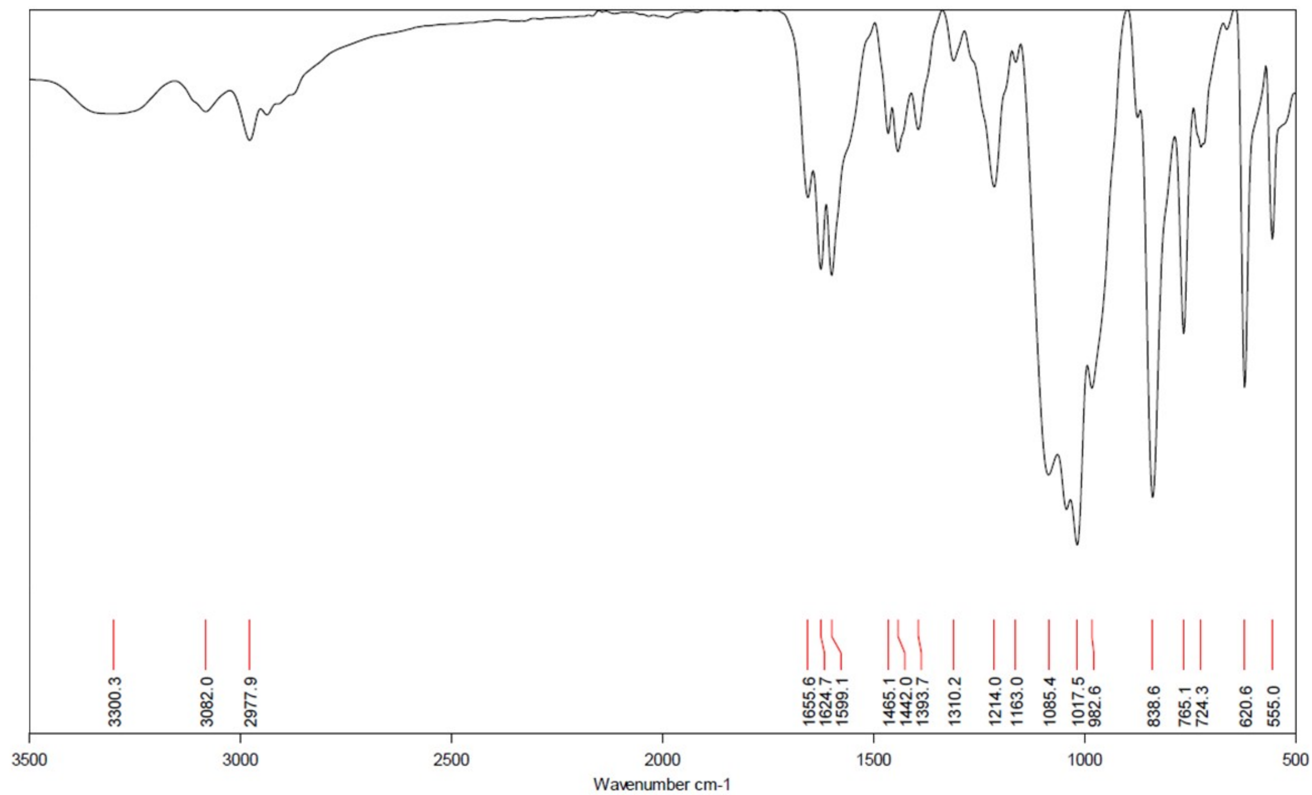


Figure S14. FTIR spectrum of {Cu[**Ru(N$_3$P$_3$phen)**]}(ClO$_4$)$_2$ (neat).

4. DFT studies of the zinc complex with Ru(N_3P_3phen)

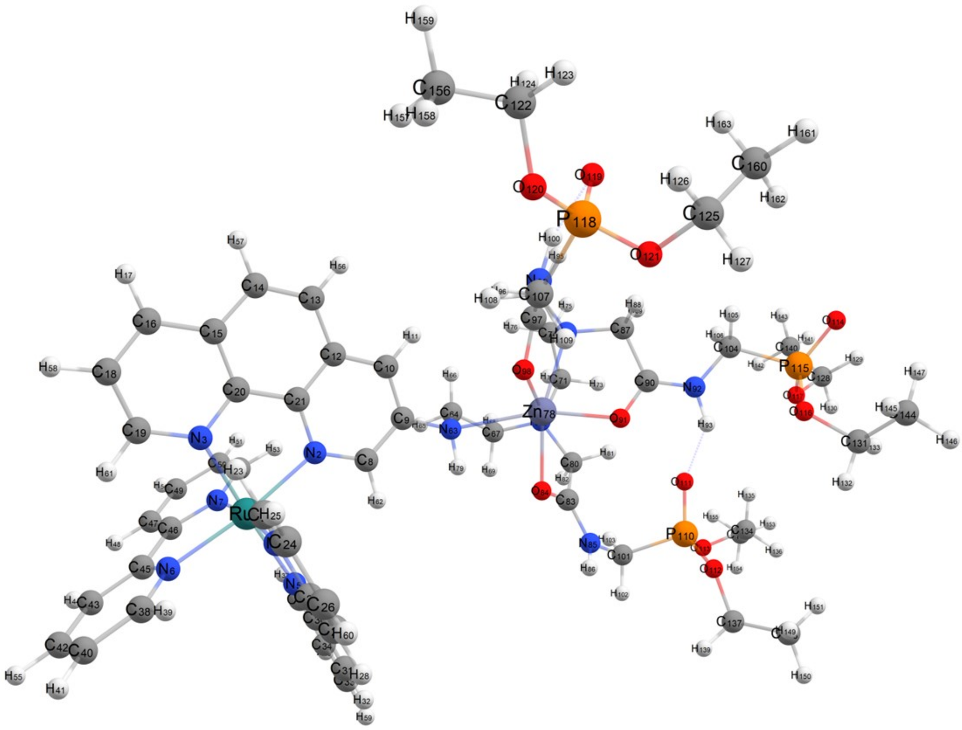


Figure S15. DFT calculated geometry of the bimetallic {Zn[**Ru(N_3P_3phen)**]}$^{4+}$ complex at the B3LYP/6-31G(d,p) level (see text). The more stable *fac*-isomer is shown. Color code for the atoms: C (dark grey), H (light grey), N (blue), O (red), P (orange), Ru (green); Zn (violet).

NUCLEAR COORDINATES -------------------

ATOM	X	Y	Z
Ru	7.769773512	14.221040187	-4.079440352
N	8.986807578	15.934643300	-4.469475560
N	7.286496358	15.451499927	-2.434920383
N	9.413092938	13.230776914	-3.216840550
N	8.426403081	12.997075928	-5.660246727
N	6.372592191	12.716312036	-3.617597325
N	6.017086090	14.934115187	-5.021223698
C	9.831834272	16.160673682	-5.482241658
C	10.536429262	17.377478763	-5.652344959
C	10.342154131	18.382759899	-4.716638662
H	10.858663576	19.332098788	-4.810307879
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C	10.924969510	12.686032120	-1.426942542
H	11.247324168	12.872639641	-0.408732245
C	11.531765761	11.709134562	-2.215583476
C	11.069419519	11.513187153	-3.513860888
H	11.530325534	10.758507648	-4.138774401
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C	3.572966190	15.718923171	-6.129751809
C	4.700148914	16.531124564	-6.249115393
H	4.657712383	17.482723928	-6.766735425
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H	6.793535306	16.703133014	-5.753096594
H	2.621444181	16.018978901	-6.555800595
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H	9.712298299	20.132251162	-2.705114567
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C	15.814747180	20.401975097	-6.920198520
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N	17.523539834	19.281553863	-8.297267547
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O	13.953570569	18.168671149	-4.939070100
N	14.720987586	19.484944273	-3.244743237
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H	15.129519757	14.604880057	-11.745518196
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H	18.561307974	20.823935444	-7.293119998
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O	21.091301112	21.075728539	-8.377038857
P	20.127404416	20.102172615	-8.935611980
O	20.221431145	18.552928015	-8.531230471
O	20.012173204	20.072159133	-10.541182547
P	16.269812365	19.298531256	-1.120982019
O	16.273300385	20.749453194	-1.490307390
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C	15.696744380	19.952533073	1.430551938
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C	20.724281479	21.069406978	-11.360517148
H	21.655305736	21.332481619	-10.855575660
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H	17.531505797	13.020298619	-11.016429371
C	19.865858469	22.292915382	-11.612351981
H	20.389484273	22.969475397	-12.294723491
H	18.910995594	22.020790396	-12.072243971
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C	22.458054995	17.968895053	-7.660261262
H	22.031320837	17.660243414	-6.702068415
H	23.336805391	17.347183839	-7.858581878
H	22.780482884	19.009637298	-7.585000242
C	19.646222503	13.461781839	-10.825355077
H	19.685073817	13.295618880	-9.746062133
H	19.966996941	12.543469921	-11.326232016
H	20.351147282	14.255583056	-11.085332576
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H	19.017282862	17.908890768	-15.131701397
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C	14.554273192	19.605099574	2.358480793
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H	19.910910348	19.819708178	-1.787016613
H	19.020664288	20.696632754	-0.526135641

5. Characterization of Ru(N_2P_2phen)@TiO_2 and Ru(N_3P_3phen)@TiO_2

Table S1. Chemical composition of **Ru(N_2P_2phen)@TiO_2** and **Ru(N_3P_3phen)@TiO_2** materials.

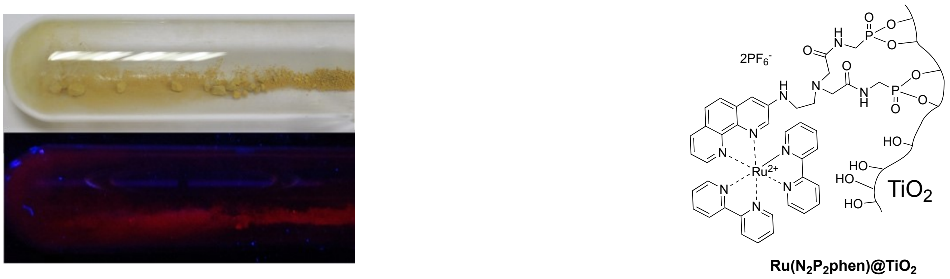
Material	Calculated formula		Elemental analysis[a]					
			%C	%H	%N	%Ti	%P	%Ru
Ru(N_2P_2phen)@TiO_2	$(C_{40}H_{42}N_{10}O_8P_2Ru)(PF_6)_{0.5}Br_{1.5}(TiO_2)_{74}$ $(H_2O)_{44}(C_3H_7OH)_{11}(C_3H_7NO)_{0.5}$	found	10.75	2.49	2.19	42.14	0.92	1.20
		calcd	10.34	2.54	2.08	41.78	0.91	1.19
Ru(N_3P_3phen)@TiO_2	$(C_{45}H_{53}N_{12}O_{12}P_3Ru)(PF_6)_{0.5}Br_{1.5}(TiO_2)_{71}$ $(H_2O)_{49}(C_3H_7OH)_8(C_3H_7NO)_{0.3}$	found	10.26	2.48	2.32	41.23	1.30	1.22
		calcd	10.36	2.76	2.29	40.98	1.31	1.22

[a] P, Ti, and Ru contents were determined by ICP-OES and C, H and N contents were found by combustion analysis.

Table S2. Chemical composition of solids **Ru(N_2P_2phen)@TiO_2** and **Ru(N_3P_3phen)@TiO_2**.

Material	Calculated formula		Elemental analysis[a]					
			N/P	Ti/P	Ti/N	Ti/Ru	N/Ru	P/Ru
Ru(N_2P_2phen)@TiO_2	$(C_{40}H_{42}N_{10}O_8P_2Ru)(PF_6)_{0.5}Br_{1.5}(TiO_2)_{74}$ $(H_2O)_{44}(C_3H_7OH)_{11}(C_3H_7NO)_{0.5}$	found	5.3	29.6	5.6	74.1	13.2	2.5
		calcd	5.0	29.6	5.9	74.0	12.6	2.5
Ru(N_3P_3phen)@TiO_2	$(C_{45}H_{53}N_{12}O_{12}P_3Ru)(PF_6)_{0.5}Br_{1.5}(TiO_2)_{71}$ $(H_2O)_{49}(C_3H_7OH)_8(C_3H_7NO)_{0.3}$	found	3.9	20.5	5.2	71.3	13.7	3.5
		calcd	3.9	20.3	5.2	71.0	13.6	3.5

[a] P, Ti, and Ru contents were determined by ICP-OES and C, H and N contents were found by combustion analysis.



(a) (b)

Figure S16. (a) Picture of the **Ru(N_2P_2phen)@TiO_2** material taken under visible (top) and UV (bottom) light. (b) Schematic presentation of **Ru(N_2P_2phen)@TiO_2**.

(a) (b)

Figure S17. (a) Picture of the **Ru(N_3P_3phen)@TiO_2** material taken under visible (top) and UV (bottom) light. (b) Schematic presentation of **Ru(N_3P_3phen)@TiO_2**.

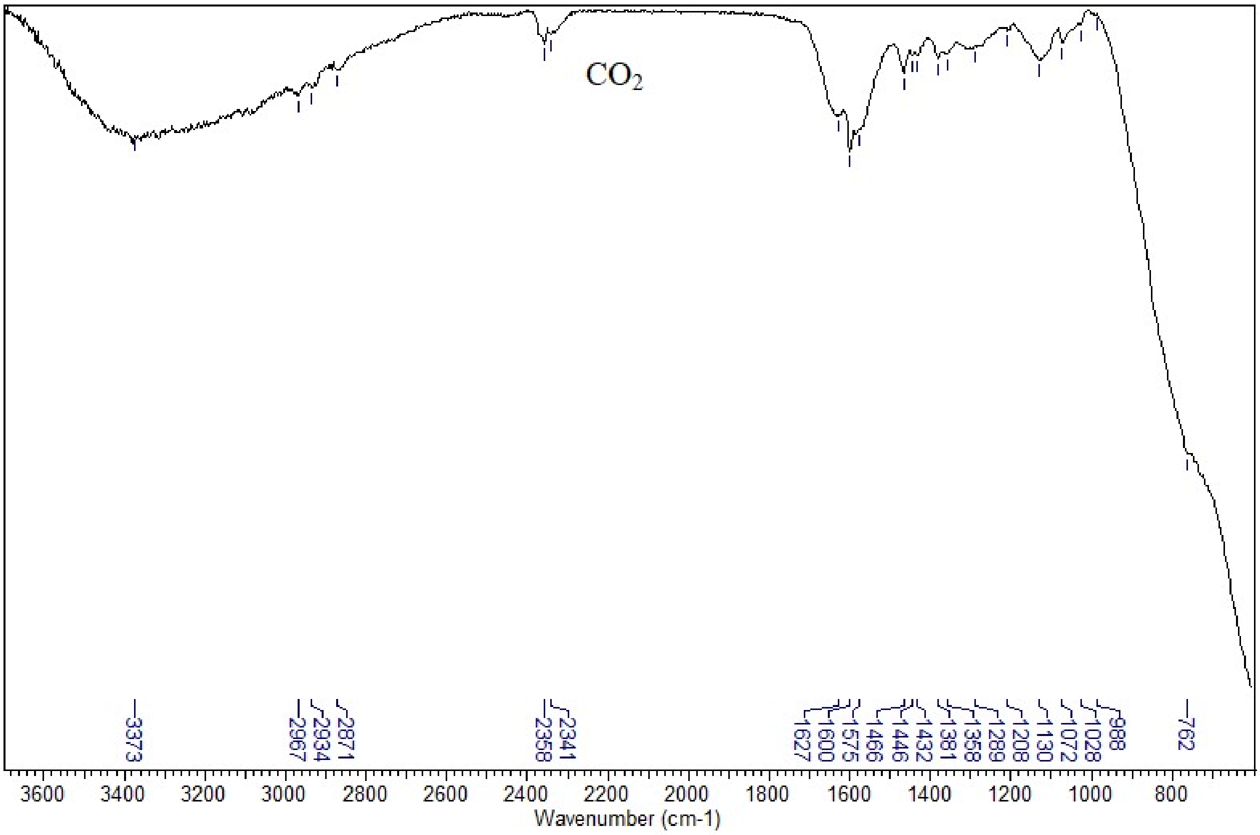


Figure S18. FTIR spectrum of **Ru(N$_2$P$_2$phen)@TiO$_2$** (neat).

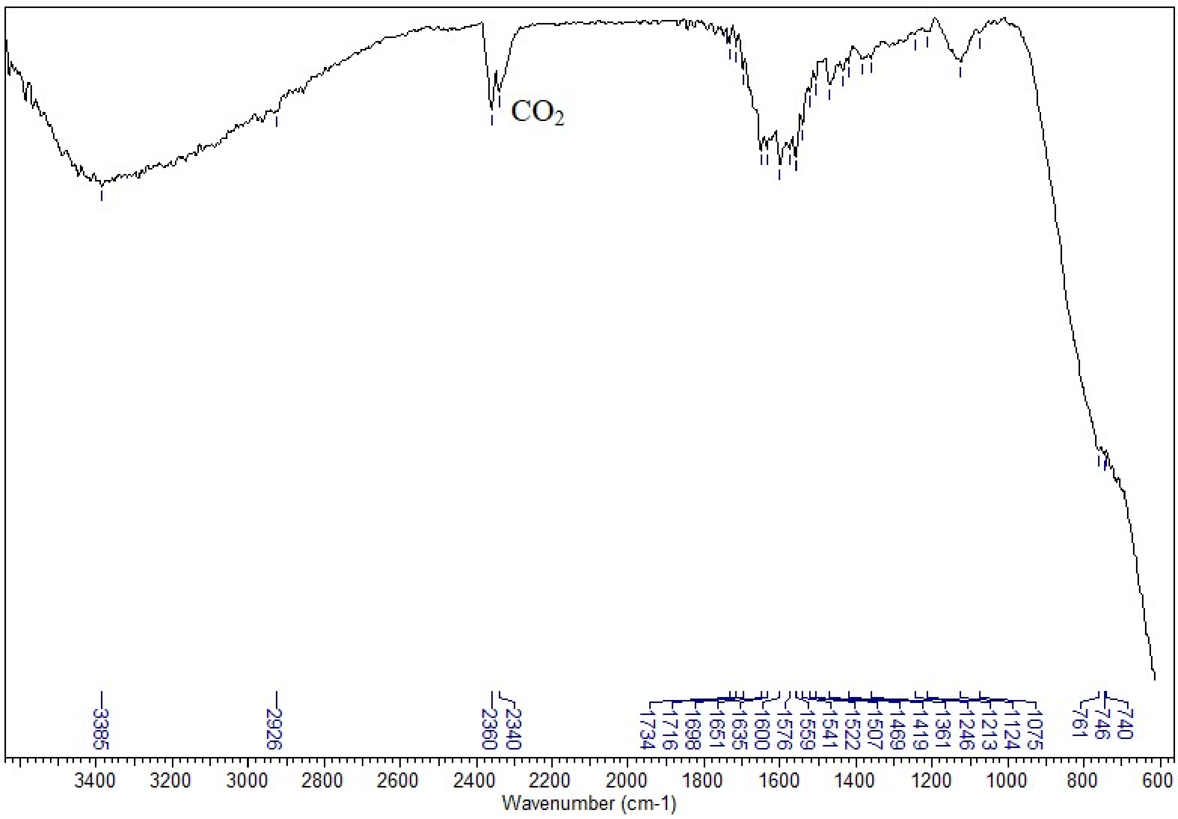
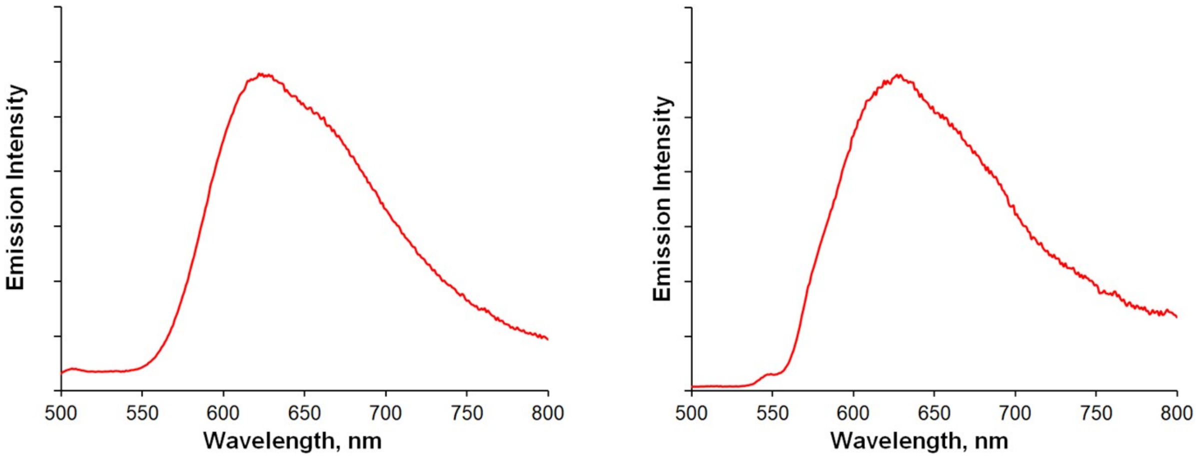


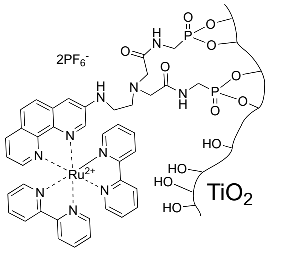
Figure S19. FTIR spectrum of **Ru(N$_3$P$_3$phen)@TiO$_2$** (neat).



(a) **(b)**

Figure S20. Emission spectra of (a) **Ru(N$_2$P$_2$phen)@TiO$_2$** (powder, λ_{ex} = 450 nm) and (b) **Ru(N$_3$P$_3$phen)@TiO$_2$** (powder, λ_{ex} = 450 nm).

6. Studies of sensing properties of $Ru(N_2P_2phen)@TiO_2$



$Ru(N_2P_2phen)@TiO_2$

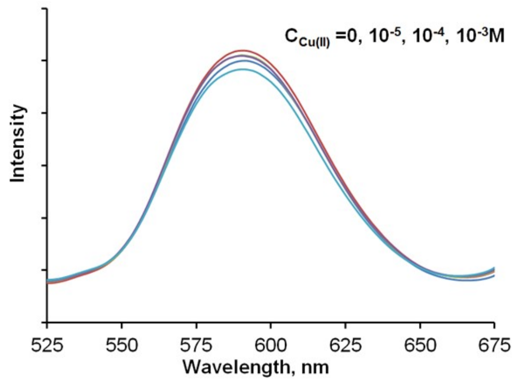
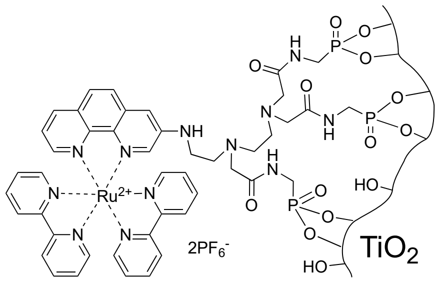


Figure S21. Evolution of the average emission spectrum of a suspension of **$Ru(N_2P_2phen)@TiO_2$** in water (λ_{ex} = 380 nm) in the presence of $Cu(ClO_4)_2$ (c = 0–10^{-3} M).

Comment [MM]: The range is not matching with the conc. given in the Figure.

The color code should be given

7. Sorption studies of Cu^{2+} ions by TiO_2 and Ru(N_3P_3phen)@TiO_2.



Ru(N_3P_3phen)@TiO_2

Procedure. To a standard solution of $Cu(ClO_4)_2$ (c = 133.5 µM = 8545 µg/L), the sorbent was added in a glass vial in air. The suspension was stirred with a magnetic stirrer for 15 min. About 1 mL was passed through a Nylon Syringe Filter (0.22 µm) before the copper concentration in the filtrate was determined by ICP-OES. The loads and the results are summarized in Table S3.

Table S3. Adsorption of Cu(II) ions by TiO_2 and **Ru(N_3P_3phen)@TiO_2**.

Sorbent	Sorbent (mg)	$Cu(ClO_4)_2$ solution (mL)	Cu_{tot}/Ru molar ratio	[Cu] in the filtrate[a] (µg/L)
TiO_2	9	12	-	7879.4
Ru(N_3P_3phen)@TiO_2	10	3	0.33	702.1
Ru(N_3P_3phen)@TiO_2	10	12	1.23	4371.8

[a] Copper(II) concentrations before and after sorption (15 min, r. t.) by the studied solid were determined by ICP-OES.

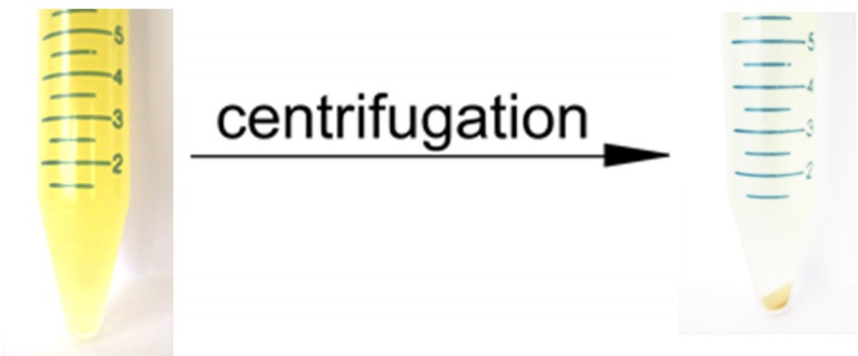


Figure 22. Picture of a suspension of **Ru(N_3P_3phen)@TiO_2** in water before and after centrifugation.

8. NMR spectra

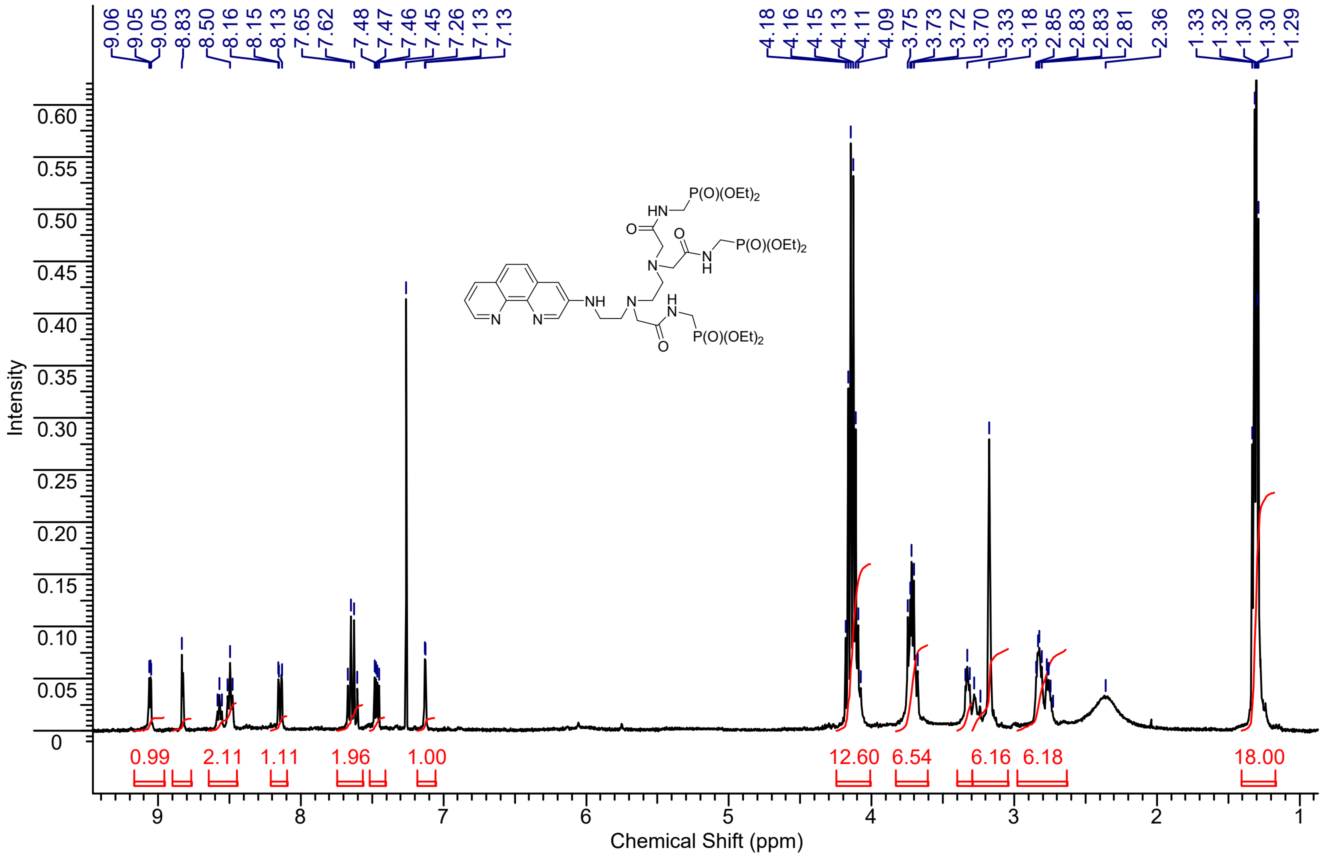


Figure S23. ^{1}H NMR spectrum of **N$_3$P$_3$phen** ($CDCl_3$, 400 MHz, 300 K).

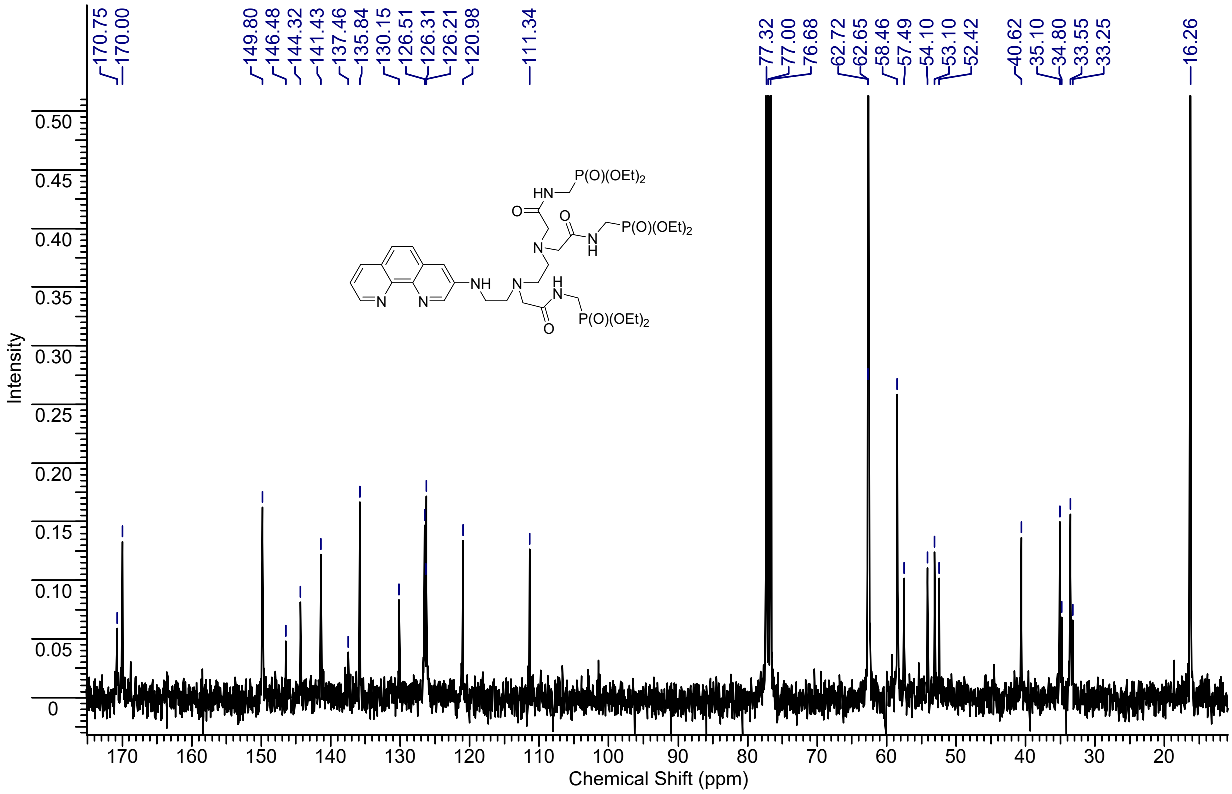


Figure S24. ^{13}C NMR spectrum of **N$_3$P$_3$phen** ($CDCl_3$, 100.6 MHz, 300 K).

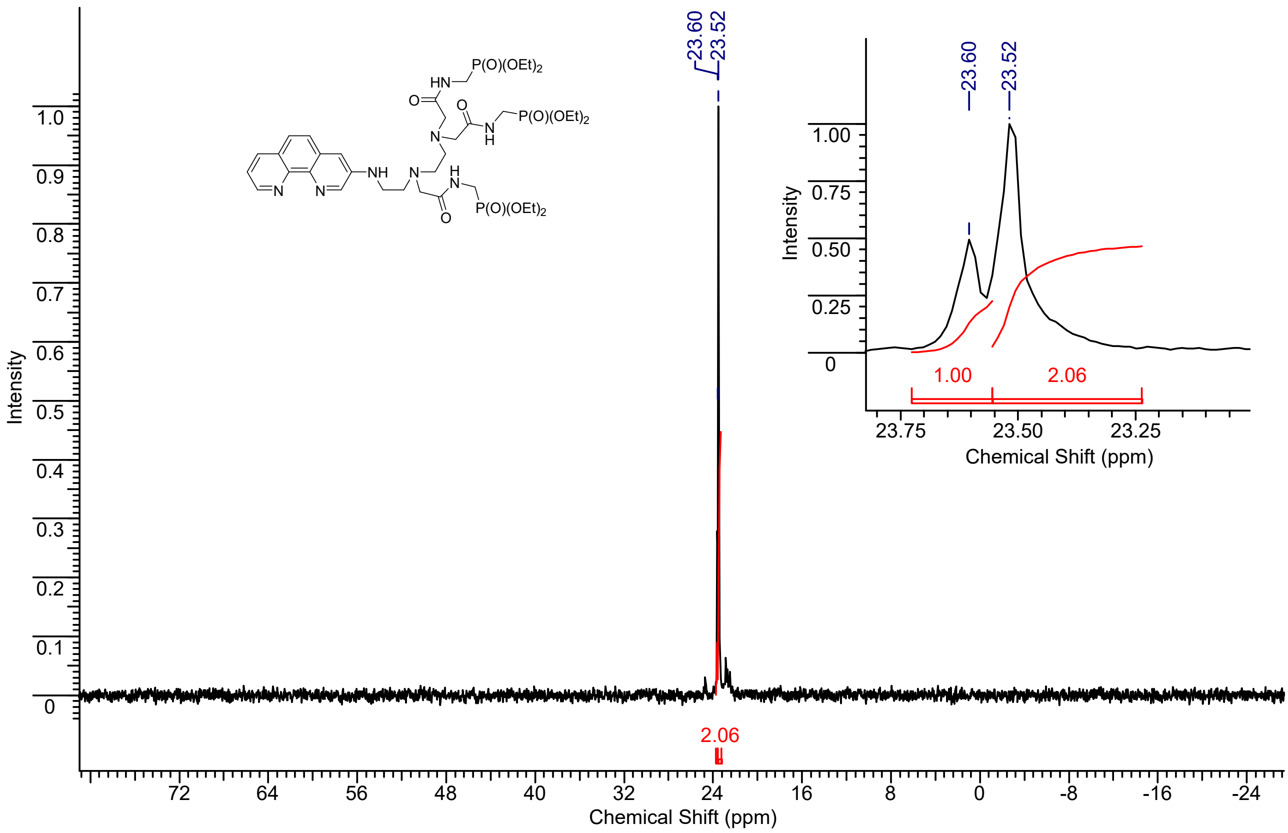


Figure S25. ^{31}P NMR spectrum of **N_3P_3phen** ($CDCl_3$, 162.5 MHz, 300 K).

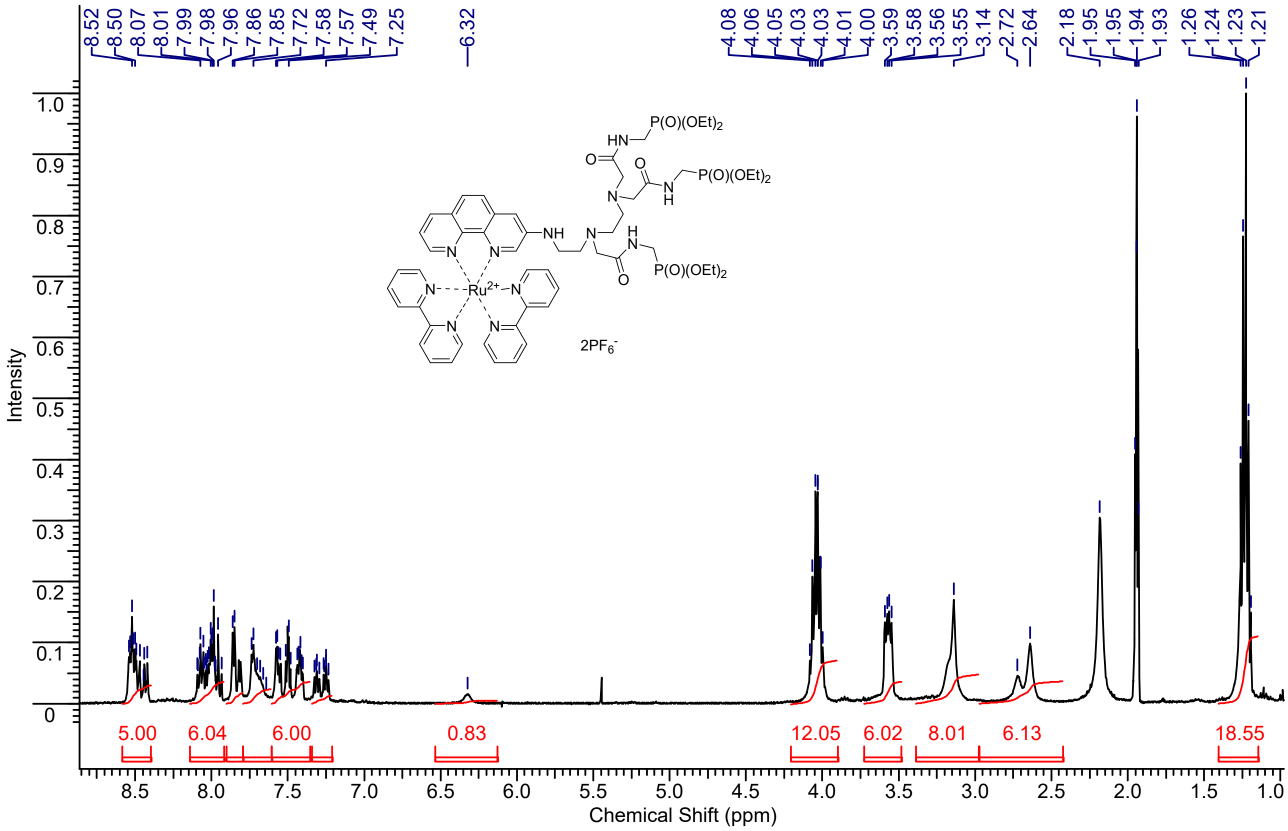


Figure S26. ^{1}H NMR spectrum of **Ru(N_3P_3phen)** (CD_3CN, 400 MHz, 300 K).

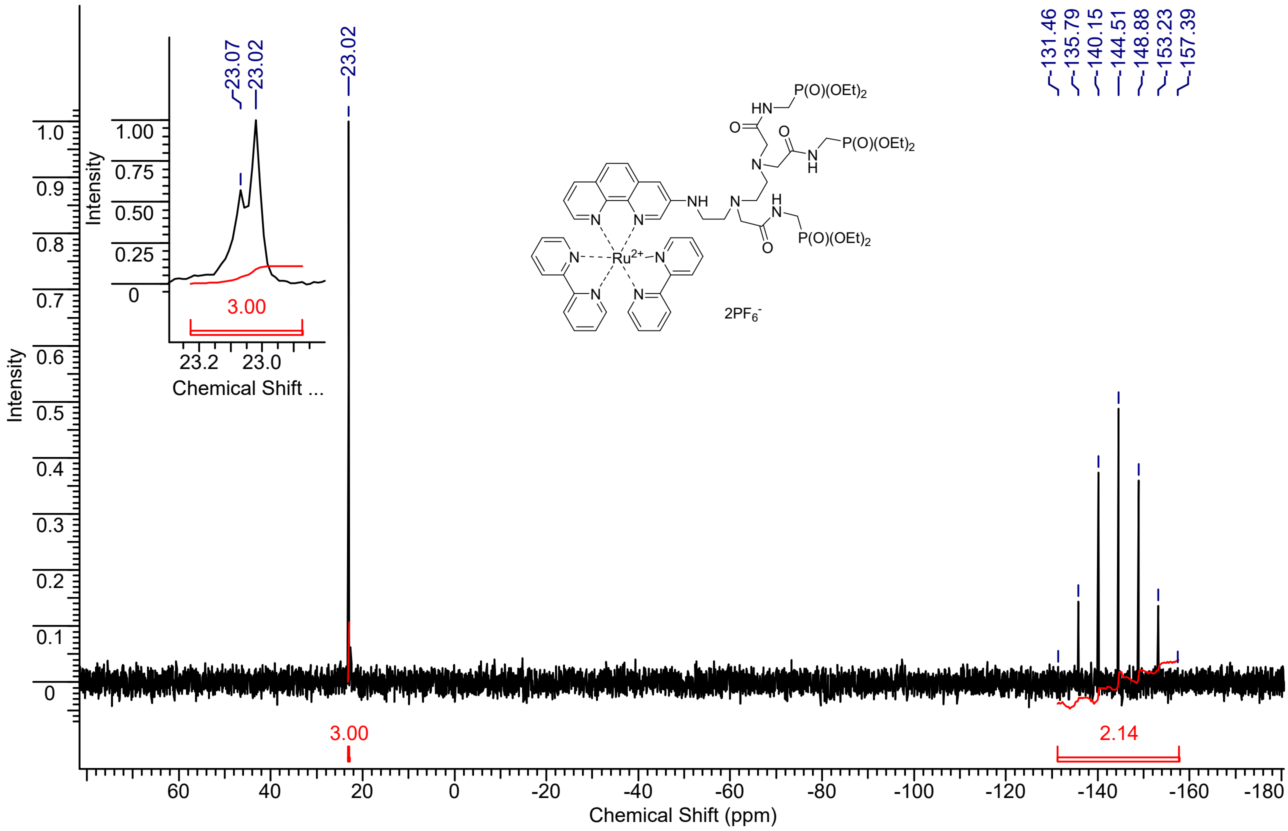


Figure S27. ^{31}P NMR spectrum of **Ru(N$_3$P$_3$phen)** (CD_3CN, 162.5 MHz, 300 K).

9. References

[1] P. Gans, A. Sabatini, A. Vacca, *Talanta* **1996**, *43*, 1739-1753.

[2] K. J. Powell, P. L. Brown, R. H. Byrne, T. Gajda, G. Hefter, S. Sjöberg, H. Wanner, *Pure Appl. Chem.* **2007**, *79*, 895-950.