

Supporting Information

Photo-CIDNP reveals different protonation sites
depending on the primary step
of the photo-induced electron/proton transfer process
with Ru(II) polyazaaromatic complexes.

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Experimental Aspects

Materials.

[Ru(TAP)₂(HAT)]Cl₂ was synthesized and purified as previously described.^[1] *N*-acetyl-tyrosine (*N*-Ac-Tyr) and guanosine-5'-monophosphate (GMP) disodium salt were purchased from Sigma-Aldrich and used without further purification. Hydroquinone (H₂Q) was purchased from Sigma-Aldrich and was sublimed prior to use. 4,4-dimethyl-4-silapentane-1-sulfonic acid sodium salt (DSS) was purchased from Riedel-de Haën and was used as received. For the NMR measurements, a concentrated phosphate buffer (100 mM, pH ~ 7) was prepared in D₂O using D₃PO₄ (Isotec) and NaOD (Sigma). Buffered aqueous solutions were otherwise prepared with Millipore Milli-Q water using sodium phosphate monobasic and dibasic salts (Riedel-de Haën). The pH of the solutions was adjusted by addition of (H/D)Cl or NaO(H/D) and was measured using a Consort P601 pH meter. For both the NMR and transient absorption measurements, the solutions were deoxygenated by bubbling with argon (Air Liquide, Belgium) for at least 30 min.

Stern-Volmer Measurements.

Stern-Volmer measurements were performed under air in a quartz cell of 10 mm optical path length that was filled with 2 mL of solution buffered at the desired pH containing [Ru(TAP)₂(HAT)]Cl₂ with an absorbance of 0.1 at 440 nm (about 10 μM), 150 mM NaCl, 10 mM phosphate buffer and the quencher with a concentration of 20 mM for GMP and 25 mM for H₂Q and *N*-Ac-Tyr. The quencher concentration was gradually diluted without changing the concentration of the other compounds. Emission spectra were recorded with a Shimadzu RF-5301 PC spectrofluorimeter equipped with a Hamamatsu R928 red-sensitive photomultiplier tube. The spectra were corrected for the instrument response. The luminescence lifetime data were measured using the same excitation source and the same monochromator as described here above (see Flash Photolysis Measurements). The solutions were placed in a quartz cell of 10 mm optical path length. The signal at selected wavelength was analysed via a photomultiplier (R928, Hamamatsu). The signal was recorded with a digital oscilloscope (HP 54200A), connected through the IEEE488 interface to a personal computer, and was averaged over at least 16 laser shots.

Transient absorption measurements.

The transient absorption experiments were performed in a cross-beam configuration by using the excitation source composed of a frequency-tripled (355 nm) Nd:YAG Q-switched laser (Continuum Inc.) coupled with an optical parametric oscillator (Continuum Inc.) covering the wavelength region ranging from 410 to 2300 nm with a maximum pulse energy from 10 to 120 mJ depending on the wavelength. The average pulse duration was 5 ns. As a probe source, a 150 W, xenon arc lamp producing a continuous spectral distribution ranging from 190 to 2600 nm was used. The grating Czerny-Turner monochromator (Spectra Pro 2300i, Acton Research Corp.) was used for the spectral selection. The solutions were placed in a quartz cell of 10 mm optical path length for the analytical beam and 1 mL sample volume. The transient absorption spectra were measured in the 250-650 nm spectral range with a gated intensified CCD camera (PI-MAX, 1024x256 pixels, Princeton Instruments) coupled to a monochromator (the detection gate was 2 ns). The time delays for probing, following the laser excitation pulse, were controlled by a programmable time generator (Princeton Instruments). The experiments were performed under argon in a quartz cell of 10 mm optical path length that was filled with 3 mL of solution at the desired pH containing [Ru(TAP)₂(HAT)]Cl₂ with a concentration of about 100 μM, 150 mM NaCl, 10 mM phosphate and the quencher. The quencher concentration was adjusted based on the results of the Stern-Volmer experiments so as to reach a quenching level between 80 and 90%. The ground-state absorption spectra were measured using a Perkin-Elmer (Lambda 40 or Lambda 45) UV-vis spectrometer.

NMR measurements.

Samples were prepared by mixing suitable volumes of aqueous (D_2O) stock solutions of $[Ru(TAP)_2(HAT)]Cl_2$, electron donor, DSS (2,2-dimethyl-2-silapentane-5-sulfonate sodium salt) and phosphate buffer. The pH was adjusted at the desired value using NaOD or DCl; it was not corrected for deuterium isotope effect. D_2O was then added to reach a volume of 600 μL and the following concentrations: ~ 0.1 mM $[Ru(TAP)_2(HAT)]Cl_2$, ~ 2 mM electron donor, 0.2 mM DSS and 10 mM phosphate buffer. Hence, the photo-CIDNP experiments were conducted with buffered D_2O solutions but, for easy reading, the results (structures, acid-base equilibriums ...) are described as it was with H_2O .

A different sample was prepared for each pH value. It was transferred into a standard 5 mm NMR tube and thoroughly deoxygenated prior to careful introduction of the optical fiber and sealing with Parafilm. The samples were illuminated in the NMR magnet, from above, via a 1 mm diameter optical fiber positioned inside a coaxial insert (Wilmad WGS 5BL) whose tip was about 3 mm above the top of the NMR receiver coil, as illustrated in **Figure S1**. The light source was a continuous wave argon ion laser (Innova 70C series laser model, Coherent) operating at 488 nm. A mechanical shutter controlled by the NMR spectrometer was employed to produce light pulses. The actual output power of the laser at 488 nm, ~ 2.6 W, and the output power from the optical fiber within the coaxial insert, ~ 1.0 W, were measured before each series of experiments.

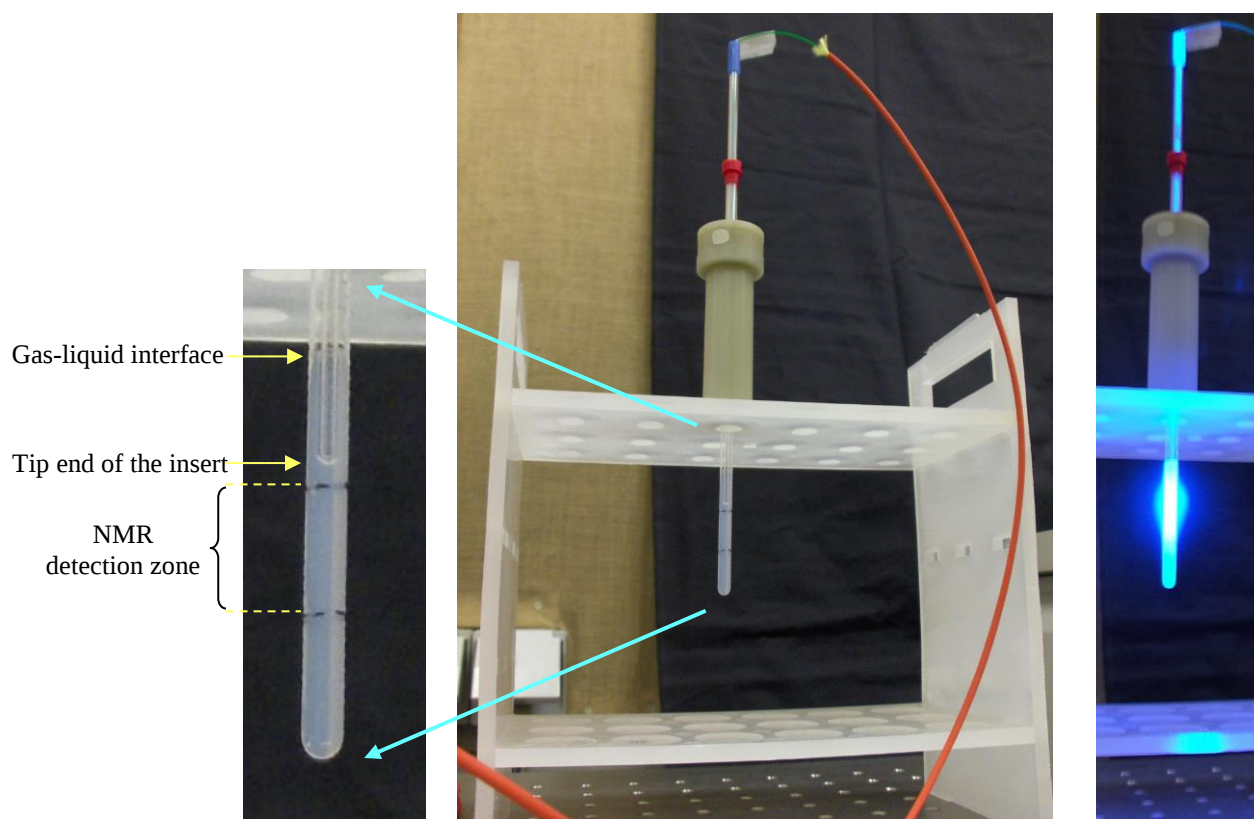


Figure S1: Sample set-up for photo-CIDNP experiment (a dilute polymer colloid was used to get strong light dispersion).

The NMR measurements were carried out at 298 K on a 600 MHz Varian VNMRs spectrometer equipped with a standard 5 mm Triple Inverse z-Gradient probe. The pulse sequence used for the ^1H photo-CIDNP experiments is depicted in **Figure S2**. The illumination period of 100 ms was followed by a short delay prior to the non-selective ^1H RF pulse and subsequent acquisition of the free induction decay (FID). The spectral width was about 16 ppm centered at the signal of the solvent (HDO). The processing of the NMR spectra comprised exponential apodization of the FID ($\text{lb} = 2$ Hz), zero-filling (spectrum digital resolution of 0.07 Hz/point) and calibration of the chemical shift scale with respect to the methyl signal of DSS ($\delta = 0.00$ ppm).

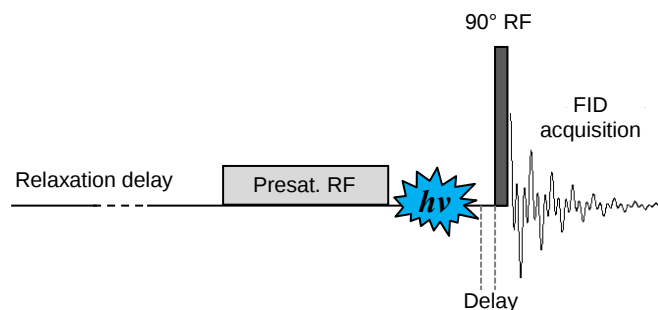


Figure S2: ^1H NMR pulse sequence used for the photo-CIDNP experiments. The duration of the successive components is not represented on scale: the relaxation delay (12 s) is followed by (i) continuous-wave radio frequency (RF) irradiation for presaturation of the signal of the solvent (3 s), (ii) blue-light illumination for photo-CIDNP spectra (100 ms) or a corresponding waiting delay for control spectra, (iii) a short delay (10 or 20 ms) intended to allow radical recombination so as to avoid paramagnetic broadening of the NMR signals, (iv) high-power non-selective RF pulse (5.8 μs) and (v) acquisition of the FID (2 s). The sequence was repeated 12 or 16 times.

Photo-CIDNP experiments were carried out for a total of 28 freshly prepared samples. At least three ^1H NMR spectra were recorded for each sample: a first control spectrum without sample illumination (first “dark spectrum” referred to as D1), a spectrum with blue-light illumination (spectrum L1) and a second control spectrum without sample illumination (spectrum D2). The photo-CIDNP enhancements were calculated using integral data from spectra D1, L1 and D2 according to the following equation:

$$\text{photo-CIDNP enhancement (\%)} = 100 \times (I_{\text{L1}} - I_{\text{D}}) / I_{\text{D}} \quad \text{with} \quad I_{\text{D}} = (I_{\text{D1}} + I_{\text{D2}}) / 2$$

TAP H-3 and H-6 give rise to distinct ^1H NMR signals but the corresponding photo-CIDNP enhancements were not significantly different. Global enhancement data are therefore given for these signals and similarly for TAP H-2 and H-7.

Decreasing photo-CIDNP enhancements were observed at $\text{pH} > 5$. Besides, significant broadening of the signals of $[\text{Ru}(\text{TAP})_2(\text{HAT})]^{2+}$ occurred in the presence of *N*-Ac-Tyr (see **Figure S8**) and, to a lesser extent, with GMP (no broadening was observed for the signals of the electron donors). This is due to electron self-exchange that shortens the ^1H longitudinal relaxation time and therefore inhibits or prevents the buildup of nonequilibrium nuclear polarization during steady-state illumination. Accumulation of the monoreduced complex in solution may occur if the oxidized quencher is involved in leak reactions. Electron self-exchange then also occurs during acquisition of the FID and yields broadening of the ^1H signals of the complex.

pH effects on the photoluminescence

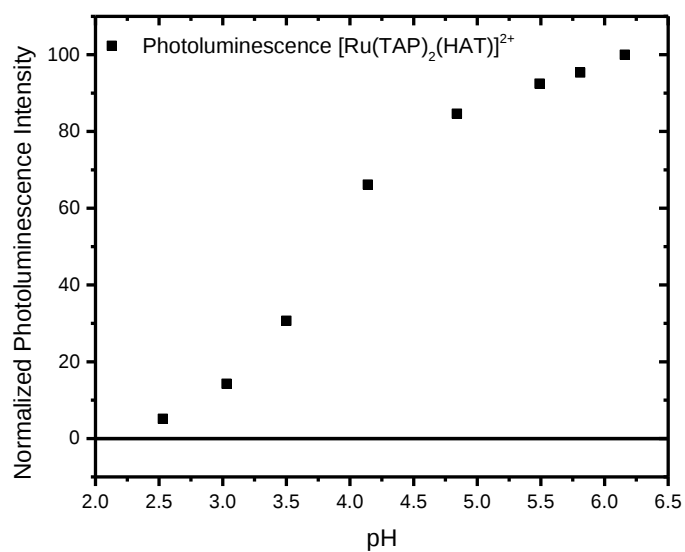


Figure S3. pH effect on the photoluminescence intensity of $[\text{Ru}(\text{TAP})_2(\text{HAT})]\text{Cl}_2$ at 608 nm, normalized with respect to the value measured around pH 6.

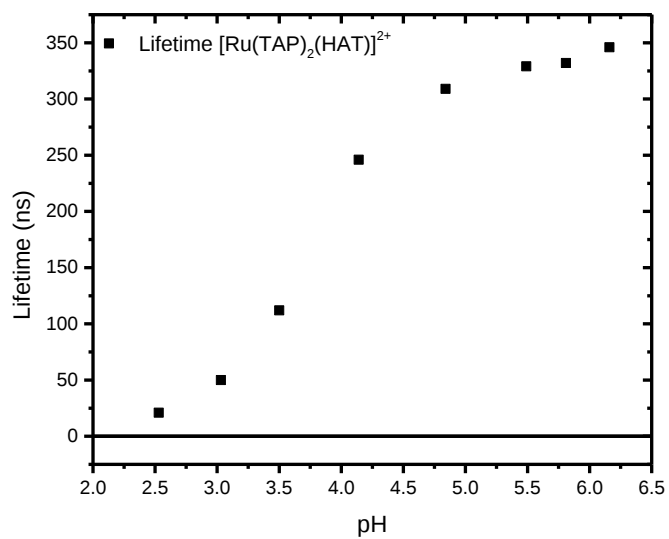


Figure S4. pH effect on the lifetime of the unprotonated excited state of $[\text{Ru}(\text{TAP})_2(\text{HAT})]\text{Cl}_2$, as determined from the photoluminescence at 608 nm.

Estimation of ΔG_{ET}° – Stern-Volmer plots – Transient absorption spectra

The Gibbs free energy change (ΔG_{ET}°) of the PET processes were determined according to the following equation:

$$\Delta G_{ET}^{\circ} = F \left(E_{D^{\bullet+}/D}^{\circ} - E_{A/A^{\bullet-}}^{\circ} \right) - \Delta E_{00} \quad (1)$$

$E_{D^{\bullet+}/D}^{\circ}$ is the oxidation potential of the electron donor, $E_{A/A^{\bullet-}}^{\circ}$ is the reduction potential of the electron acceptor, F is Faraday's constant and ΔE_{00} is the energy of the $^3\text{MLCT}$ excited state of the complex with respect to the ground state (approximated by the energy of the emission maximum).

ΔE_{00} for the unprotonated excited state $[\text{Ru}(\text{TAP})_2(\text{HAT})]^{2+*}$ was approximated to 2.04 eV, which corresponds to 608 nm for λ_{max} emission. The reduction potential of the excited complex is then estimated as:

$$E_{A/A^{\bullet-}}^{\circ} + \Delta E_{00} = -0.68 + 2.04 = +1.36 \text{ V vs SCE.}$$

The values used for the oxidation potential of the electron donors are 0.46 V vs SCE for H_2Q ,^[2, 3, 4] 0.85 V vs SCE for $N\text{-Ac-Tyr}$ ^[5] and 1.07 V vs SCE^[6] (as determined from pulsed radiolysis) or 1.25 V vs SCE^[7] (as determined from electrochemical oxidation) for GMP.

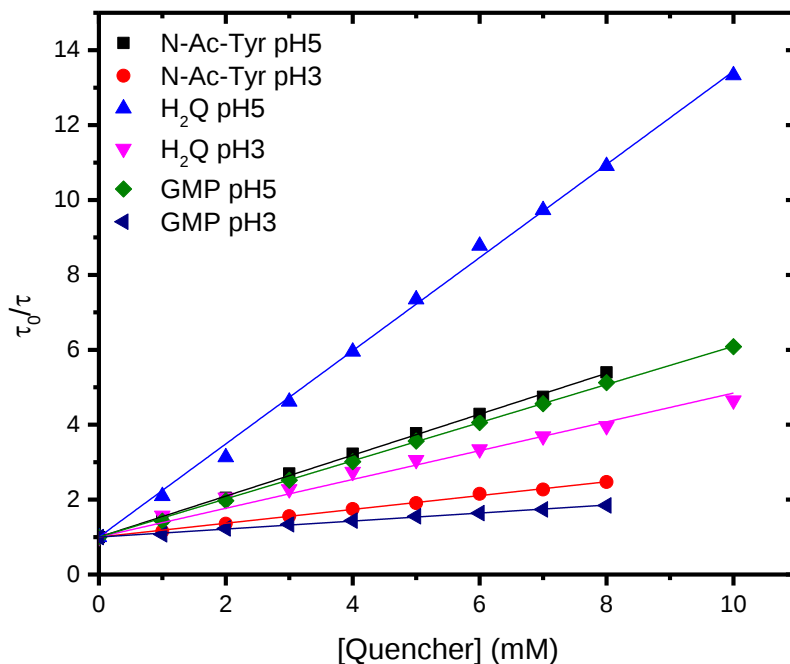


Figure S5. Stern-Volmer plot for the quenching of the excited state of $[\text{Ru}(\text{TAP})_2(\text{HAT})]^{2+}$ by H_2Q , $N\text{-Ac-Tyr}$ and GMP, in the presence of 150 mM NaCl and 10 mM phosphate buffer, at pH 3 and 5.

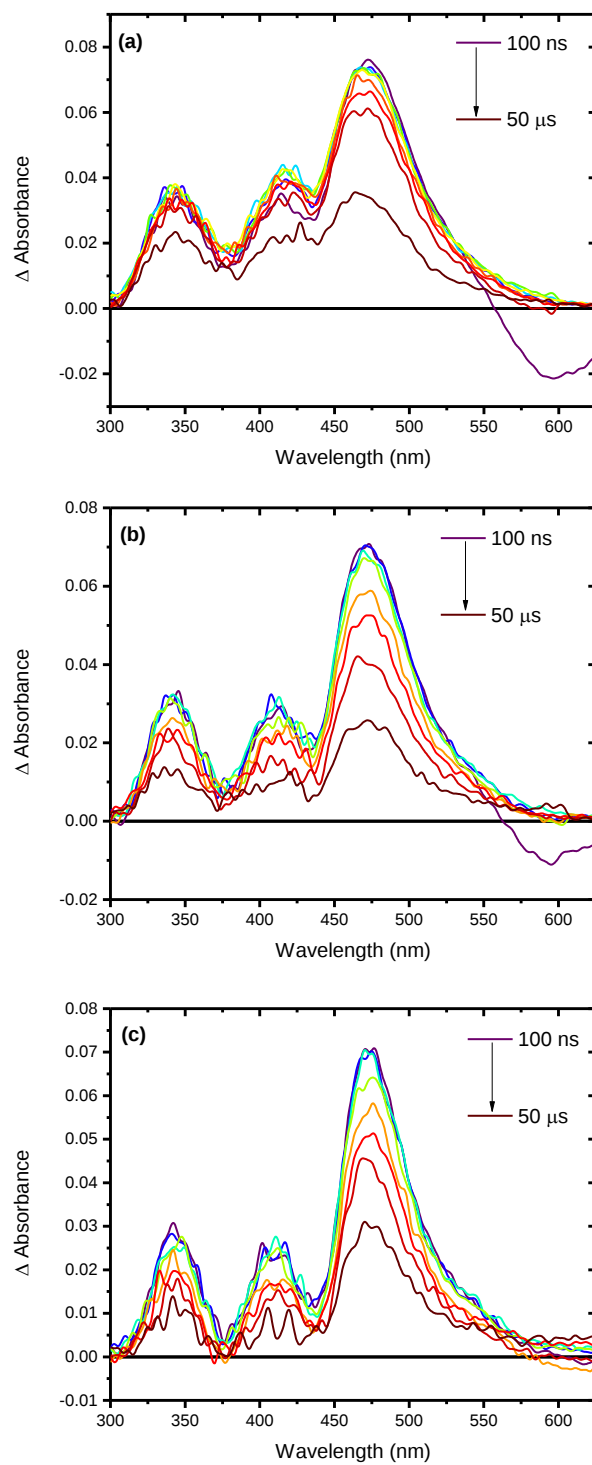


Figure S6. Transient absorption spectra for the complex $[\text{Ru}(\text{TAP})_2(\text{HAT})]^{2+}$ in the presence of 10 mM H_2Q , 150 mM NaCl , 10 mM phosphate buffer (a) at pH 5, (b) pH 3 and (c) pH 1.

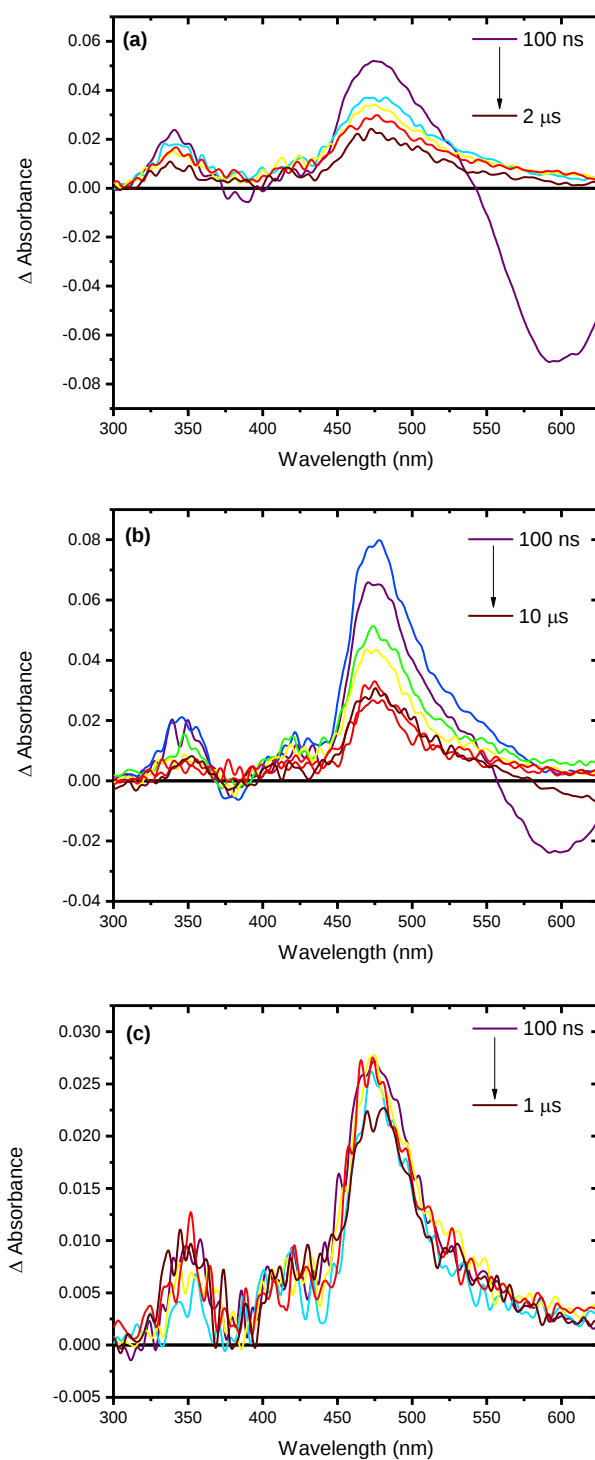
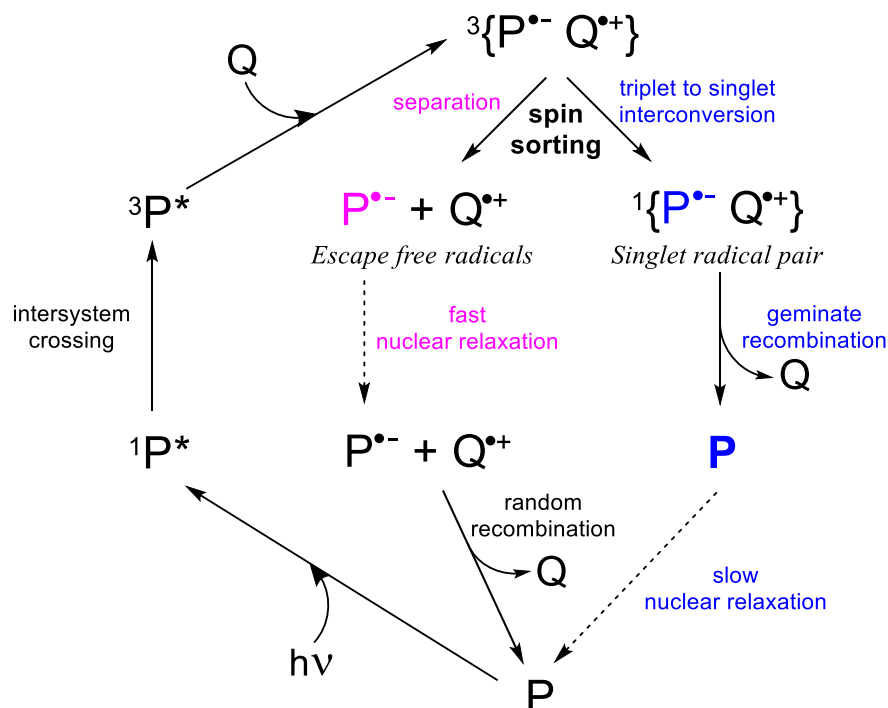


Figure S7. Transient absorption spectra for the complex $[\text{Ru}(\text{TAP})_2(\text{HAT})]^{2+}$ in the presence of 10 mM *N*-Ac-Tyr, 150 mM NaCl, 10 mM phosphate buffer (a) at pH 5, (b) pH 3 and (c) pH 1.

Fundamentals of photo-CIDNP in solution

The IUPAC definition of CIDNP (Chemically Induced Dynamic Nuclear Polarization) is “non-Boltzmann nuclear spin state distribution produced in thermal or photochemical reactions, usually from colligation and diffusion, or disproportionation of radical pairs, and detected by NMR spectroscopy by enhanced absorption or emission signals.”^[8] The radical pair mechanism, which relies on the ability of electron-nuclear spin interactions to alter the recombination probability of radical pairs, is currently accepted as the origin of photo-CIDNP in solution. A simplified description of this mechanism is presented in the framework of the present study here below, considering a cyclic photoreaction. The reader is referred to literature for general and comprehensive descriptions.^[9, 10,11,12,13,14,15]



Scheme S1. Basic processes involved in CIDNP production for the photosensitizer of a cyclic photoreaction.

P stands for the photosensitizer and **Q** for the quencher. Proton transfer and self-exchange processes are not represented. Species generated with a non-Boltzmann nuclear spin state distribution are colored in magenta (escape polarization) or blue (geminate polarization). In contrast to most studies reported in the literature, our work deals with ^1H photo-CIDNP on the photosensitizer rather than on the quencher. Hence, the spin sorting process is illustrated with nuclear polarization on **P**. Besides, it is considered that fast paramagnetic nuclear relaxation annihilates the escape polarization before random recombination and, consequently, that no cancellation of the geminate polarization occurs. Polarization arising from so-called F-pairs, *i.e.* radical pairs formed by random reencounter of free radicals, is also ignored.

The basic processes involved in the production of photo-CIDNP are depicted in **Scheme S1**, where possible proton transfers were ignored for the sake of clarity. The photosensitizer (**P**), *i.e.* $[\text{Ru}(\text{TAP})_2(\text{HAT})]^{2+}$ in the present study, is promoted to a singlet excited state ($^1P^*$) by light absorption and reaches a triplet excited state ($^3P^*$) via intersystem crossing. For polycyclic aromatic Ru(II) complexes, the quantum yield of intersystem crossing between the $^1\text{MLCT}$ and $^3\text{MLCT}$ excited states is 100 %. Reductive quenching of this triplet excited state yields a triplet radical pair, referred to as $^3\{P^{\bullet-} Q^{\bullet+}\}$, which separates into free radicals (escape radicals) unless a competing event occurs during its lifetime. In cyclic photoreactions, this event consists of triplet (T_0) to singlet conversion followed

by back electron transfer, yielding the so-called geminate recombination products, *i.e.* the diamagnetic parent compounds. The spin-orbit coupling is the primary cause of intersystem crossing but this does not yield CIDNP. Hyperfine couplings may also induce triplet to singlet interconversion and this mechanism is responsible for nuclear spin-state sorting (also simply referred to as spin sorting). Accordingly, a fraction of the geminate recombination products and the corresponding amount of free radicals (escape radicals) are generated with equal but opposite nuclear polarizations, which are simply referred to as escape and geminate polarizations. Escape polarizations are carried out by paramagnetic species and are therefore rather short-lived. They are strongly reduced by nuclear relaxation before the diamagnetic parent compounds are finally recovered by random recombination. In contrast, geminate polarizations are carried out by diamagnetic species, which are characterized by much longer ^1H longitudinal relaxation times. Hence, geminate polarizations that are produced on the 10^{-9} s - 10^{-10} s timescale can be detected much later by NMR. As Boltzmann equilibrium at room temperature corresponds to almost equipopulated nuclear spin states, significant signal enhancements can be detected even though the spin sorting process is not very efficient.

Photo-CIDNP enhancements can be positive or negative, depending on the sign of the hyperfine coupling constant notably, and can be observed for both the photosensitizer and the quencher. The ^1H photo-CIDNP enhancements observed so far for Ru(II) polycyclic aromatic complexes have all been positive, in agreement with DFT calculations. However, both positive and negative photo-CIDNP enhancements were observed for *N*-Ac-Tyr (**Figure S8c**), in agreement with literature.^[12] As mentioned before, oxidized tyrosine is involved in leak reactions and broadening of the ^1H signals of $[\text{Ru}(\text{TAP})_2(\text{HAT})]^{2+}$ was observed at $\text{pH} > 5$ due to electron self-exchange. Important broadening that prevents the measurements of meaningful photo-CIDNP enhancement occurs at $\text{pH} 7$ (**Figure S8b**); it is noteworthy that no other signals are broadened (**Figures S8a,c**).

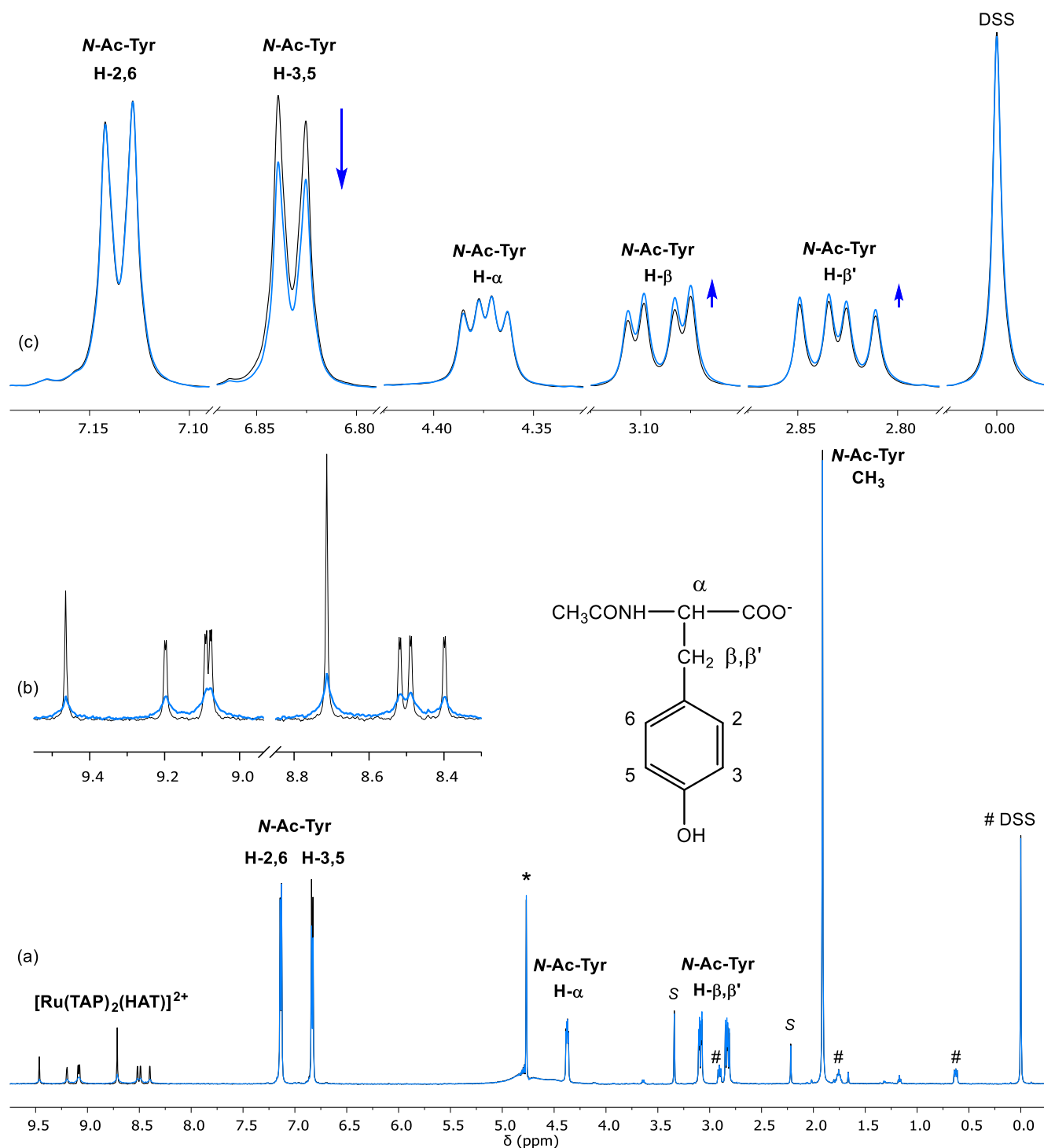


Figure S8. ^1H NMR spectra recorded in the presence of 2 mM *N*-Ac-Tyr at pH 7. The equilibrium spectrum is in black and the spectrum recorded with sample illumination is superimposed in blue: (a) Region showing all of the signals, (b) region showing the signals of $[\text{Ru}(\text{TAP})_2(\text{HAT})]^{2+}$ and (c) regions showing the methyl signal of DSS and various signals of *N*-Ac-Tyr (the acetyl signal is not shown). *S* = trace of solvent (acetone at 2.22 ppm and methanol at 3.34 ppm); * = residual signal of HDO after presaturation. The spectra reveal a significant negative photo-CIDNP enhancement for *N*-Ac-Tyr H-3,5 (c) and weak, but detectable, positive enhancements for H- β and H- β' (c). Broadening of the signal of the complex after illumination is due to electron self-exchange (b).

DFT Calculations

The DFT calculations were carried out following the same method (B3LYP/6-31G*/Stuttgart using COSMO model) as previously used with the complexes $[\text{Ru}(\text{TAP})_3]^{2+}$ and $[\text{Ru}(\text{TAP})_2(\text{Phen})]^{2+}$ in water.^[16]

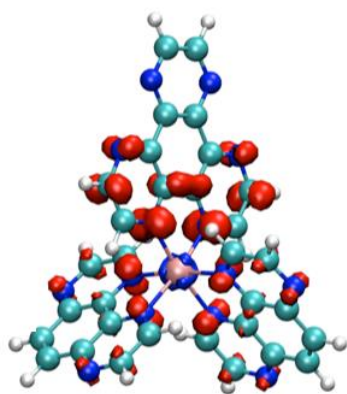
The electron-spin density was plotted with constant contours of +0.003 (red) and -0.003 (blue). Ru, C, N, and H atoms are colored in pink, turquoise, blue and white, respectively.

The data reported in Tables S1-S5 are average values over equivalent positions in the diamagnetic unprotonated complex (and over positions giving unresolved ^1H NMR signals) because the polarization is detected on this species. The paramagnetic relaxation factors ($Ax^2 + 3Rh^2$) are given for information purposes. Ax and Rh are the axially and rhombicity of the anisotropic part of the hyperfine interaction tensor, respectively:

$$Ax = 2A_{zz} - (A_{xx} + A_{yy})$$

$$Rh = A_{yy} - A_{xx}$$

Unprotonated monoreduced complex

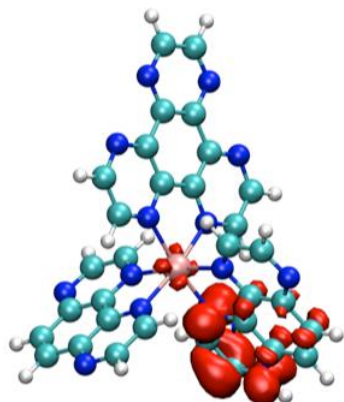


Electron-spin density of the monoreduced complex $[\text{Ru}(\text{TAP})_2(\text{HAT})]^{*+}$.

	A_{iso} (mT)	$Ax^2 + 3Rh^2$ (10^{-2} mT ²)
TAP H-2	-0.108	4.87
TAP H-7	-0.108	4.71
TAP H-3	-0.023	2.66
TAP H-6	-0.010	0.90
TAP H-9,10	0.005	0.26
HAT H-2,7	-0.259	25.61
HAT H-3,6	-0.016	2.99
HAT H-10,11	0.006	0.09

Table S1. Average ^1H Fermi-contact terms (A_{iso}) and paramagnetic relaxation factors ($Ax^2 + 3Rh^2$) calculated for $[\text{Ru}(\text{TAP})_2(\text{HAT})]^{*+}$.

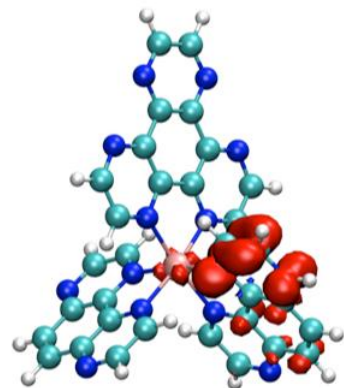
Monoreduced complex protonated on a TAP ligand



Electron-spin density of the monoreduced complex
 $[\text{Ru}(\text{TAP})(\text{TAP-H})^\bullet(\text{HAT})]^{2+}$
 protonated on the nitrogen atom N-1 of a TAP ligand.

	A_{iso} (mT)	$Ax^2 + 3Rh^2$ (10^{-2} mT ²)
TAP H-2	-0.319	86.81
TAP H-7	-0.032	1.79
TAP H-3	-0.071	17.56
TAP H-6	0.000	7.36
TAP H-9,10	-0.053	6.20
<i>TAP H⁺</i>	<i>-0.782</i>	<i>547.34</i>
HAT H-2,7	-0.001	0.70
HAT H-3,6	-0.001	4.27
HAT H-10,11	0.000	0.06

Table S2. Average ¹H Fermi-contact terms (A_{iso}) and paramagnetic relaxation factors ($Ax^2 + 3Rh^2$) calculated for $[\text{Ru}(\text{TAP})(\text{TAP-H})^\bullet(\text{HAT})]^{2+}$ protonated on the nitrogen atom N-1 of the ligand TAP or TAP'.

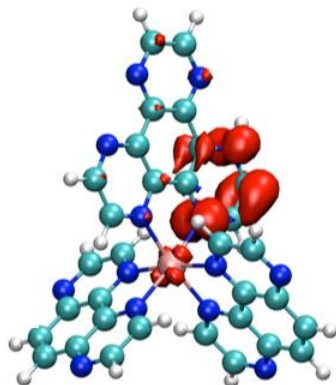


Electron-spin density of the monoreduced complex
 $[\text{Ru}(\text{TAP})(\text{TAP-H})^\bullet(\text{HAT})]^{2+}$
 protonated on the nitrogen atom N-8 of a TAP ligand.

	A_{iso} (mT)	$Ax^2 + 3Rh^2$ (10^{-2} mT ²)
TAP H-2	-0.033	1.55
TAP H-7	-0.324	89.93
TAP H-3	-0.001	1.70
TAP H-6	-0.065	18.15
TAP H-9,10	-0.054	6.41
<i>TAP H⁺</i>	<i>-0.780</i>	<i>541.62</i>
HAT H-2,7	0.003	0.67
HAT H-3,6	-0.005	14.88
HAT H-10,11	0.000	0.03

Table S3. Average ¹H Fermi-contact terms (A_{iso}) and paramagnetic relaxation factors ($Ax^2 + 3Rh^2$) calculated for $[\text{Ru}(\text{TAP})(\text{TAP-H})^\bullet(\text{HAT})]^{2+}$ protonated on the nitrogen atom N-8 of the ligand TAP or TAP'.

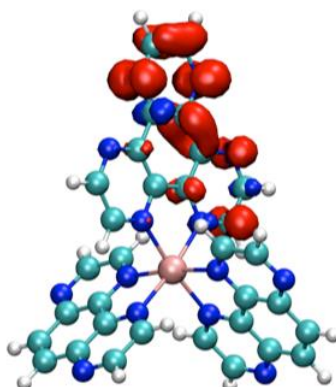
Monoreduced complex protonated on the HAT ligand



Electron-spin density of the monoreduced complex
 $[\text{Ru}(\text{TAP})_2(\text{HAT-H})]^{2+}$
 protonated on the nitrogen atom N-1 of the HAT ligand.

	A_{iso} (mT)	$Ax^2 + 3Rh^2$ (10^{-2} mT ²)
TAP H-2	0.003	0.49
TAP H-7	-0.002	0.19
TAP H-3	-0.001	8.18
TAP H-6	-0.003	1.27
TAP H-9,10	0.003	0.49
HAT H-2,7	-0.357	88.30
HAT H-3,6	-0.054	17.32
HAT H-10,11	-0.031	2.52
<i>HAT H⁺</i>	<i>-0.801</i>	<i>544.19</i>

Table S4. Average ¹H Fermi-contact terms (A_{iso}) and paramagnetic relaxation factors ($Ax^2 + 3Rh^2$) calculated for $[\text{Ru}(\text{TAP})_2(\text{HAT-H})]^{2+}$ protonated on N-1 or N-8.



Electron-spin density of the monoreduced complex
 $[\text{Ru}(\text{TAP})_2(\text{HAT-H})]^{2+}$
 protonated on the nitrogen atom N-12 of the HAT ligand.

	A_{iso} (mT)	$Ax^2 + 3Rh^2$ (10^{-2} mT ²)
TAP H-2	-0.001	0.15
TAP H-7	0.000	0.04
TAP H-3	0.001	0.88
TAP H-6	0.000	0.15
TAP H-9,10	0.000	0.03
HAT H-2,7	0.016	3.13
HAT H-3,6	-0.177	28.22
HAT H-10,11	-0.355	68.92
<i>HAT H⁺</i>	<i>-0.839</i>	<i>546.43</i>

Table S5. Average ¹H Fermi-contact terms (A_{iso}) and paramagnetic relaxation factors ($Ax^2 + 3Rh^2$) calculated for $[\text{Ru}(\text{TAP})_2(\text{HAT-H})]^{2+}$ protonated on N-9 or N-12.

**Cartesian Coordinates (in Å) of the equilibrium geometry of
[Ru(TAP)₂(HAT)]²⁺**

Ru	0.00000000	0.00000000	0.51916067
N	-1.07758126	-0.78362465	-1.09617303
N	1.07758126	0.78362465	-1.09617303
C	-0.57444622	-0.41847821	-2.32017439
C	0.57444622	0.41847821	-2.32017439
C	-2.15256307	-1.58854437	-1.11204344
C	2.15256307	1.58854437	-1.11204344
C	-1.17171614	-0.85868915	-3.52305881
C	1.17171614	0.85868915	-3.52305881
C	-2.71916511	-2.01367579	-2.31770162
C	2.71916511	2.01367579	-2.31770162
H	-2.55948532	-1.89042251	-0.15371521
H	2.55948532	1.89042251	-0.15371521
C	-0.57175399	-0.41959901	-4.78860330
C	0.57175399	0.41959901	-4.78860330
H	-3.58632699	-2.66829168	-2.30432480
H	3.58632699	2.66829168	-2.30432480
H	-2.57169029	0.31093313	2.53708681
H	2.57169029	-0.31093313	2.53708681
C	-2.13763129	-0.66195196	2.73917346
C	2.13763129	0.66195196	2.73917346
C	-2.67392991	-1.51234407	3.72009936
C	2.67392991	1.51234407	3.72009936
N	-1.06953309	-1.02043068	2.01405637
N	1.06953309	1.02043068	2.01405637
H	-3.53700772	-1.18677903	4.29469020
H	3.53700772	1.18677903	4.29469020
N	-2.17933555	-2.71954397	3.99961786
N	2.17933555	2.71954397	3.99961786
C	-0.53720247	-2.25448416	2.29939979
C	0.53720247	2.25448416	2.29939979
C	-1.10035496	-3.10131189	3.28639795
C	1.10035496	3.10131189	3.28639795
C	0.60624366	-2.65501008	1.57652951
C	-0.60624366	2.65501008	1.57652951
C	-0.48360974	-4.38177240	3.51838675
C	0.48360974	4.38177240	3.51838675
C	1.20351433	-3.91827954	1.81290186
C	-1.20351433	3.91827954	1.81290186
N	1.10911089	-1.77834113	0.64564820
N	-1.10911089	1.77834113	0.64564820
C	0.61856114	-4.77217881	2.81411305
C	-0.61856114	4.77217881	2.81411305
H	-0.93012158	-5.01849376	4.27480618
H	0.93012158	5.01849376	4.27480618
N	2.28753594	-4.31857886	1.11777644
N	-2.28753594	4.31857886	1.11777644
C	2.18500864	-2.19958362	-0.03326546
C	-2.18500864	2.19958362	-0.03326546
H	1.08946632	-5.73511688	2.98225198
H	-1.08946632	5.73511688	2.98225198
C	2.75512834	-3.46009748	0.20947654
C	-2.75512834	3.46009748	0.20947654
H	2.59770760	-1.52807669	-0.77765830
H	-2.59770760	1.52807669	-0.77765830
H	3.62336933	-3.77222043	-0.36478340
H	-3.62336933	3.77222043	-0.36478340
N	-1.13364410	-0.83616555	-5.94024371
N	1.13364410	0.83616555	-5.94024371
C	-0.56707340	-0.42026607	-7.06185576
C	0.56707340	0.42026607	-7.06185576
H	1.01250524	0.75402759	-7.99654496
H	-1.01250524	-0.75402759	-7.99654496
N	2.24670277	1.65767200	-3.51772365
N	-2.24670277	-1.65767200	-3.51772365

**Cartesian Coordinates (in Å) of the equilibrium geometry of
[Ru(TAP)(TAP-H)⁺(HAT)]²⁺ protonated on N-1**

Ru	-0.00565106	-0.51695995	-0.00393226
N	-0.78773622	1.10832565	1.08114587
N	0.78091987	1.10489276	-1.08651656
C	-0.42221410	2.32210807	0.57696183
C	0.42116512	2.32036239	-0.58124365
C	-1.57716569	1.11932605	2.15955822
C	1.56828435	1.11367628	-2.16625450
C	-0.84901670	3.52869679	1.16868929
C	0.85330051	3.52561936	-1.17131089
C	-1.99402266	2.33510670	2.73495557
C	1.99161053	2.32827778	-2.73930669
H	-1.87732065	0.16327115	2.57229220
H	1.86274082	0.15646638	-2.58012755
C	-0.41128861	4.79252438	0.57257552
C	0.42221603	4.79103592	-0.57313445
H	-2.63587415	2.32227687	3.61235280
H	2.63354296	2.31334994	-3.61658913
H	0.31519940	-2.53915775	2.56301924
H	-0.33442040	-2.53346051	-2.56719597
C	-0.66043819	-2.73988241	2.13512083
C	0.64092748	-2.73934314	-2.13979040
C	-1.51941570	-3.72264300	2.68133148
C	1.48625764	-3.73308341	-2.69851113
N	-1.02616674	-2.02290274	1.07200357
N	1.01472566	-2.02754326	-1.08069115
H	-1.19408812	-4.29567736	3.54604959
H	1.14696339	-4.29803362	-3.56286158
N	-2.71883154	-3.99083255	2.19289335
N	2.68265365	-4.01300788	-2.21860574
C	-2.25814766	-2.29839203	0.54788698
C	2.25145777	-2.31442593	-0.55362393
C	-3.10977370	-3.27771291	1.10935145
C	3.08780970	-3.30712871	-1.13327718
C	-2.67285269	-1.56235714	-0.59469545
C	2.66102219	-1.58687199	0.58677588
C	-4.39642671	-3.50684763	0.50993749
C	4.36196063	-3.55128972	-0.54786676
C	-3.94161175	-1.79979287	-1.17217187
C	3.92574246	-1.85384948	1.13472321
N	-1.80689860	-0.63675083	-1.10520222
N	1.77912076	-0.65080376	1.10496251
C	-4.79590009	-2.79704077	-0.58709895
C	4.76832691	-2.83989910	0.55779423
H	-5.03031167	-4.26232659	0.96202233
H	4.99231249	-4.31069364	-0.99766307
N	-4.34627595	-1.09982915	-2.25924660
N	4.29391501	-1.11909478	2.24625237
C	-2.22815557	0.04292773	-2.17221970
C	2.21888572	0.04744933	2.19585745
H	-5.76233442	-2.96087108	-1.05200051
H	5.74077219	-3.03217484	1.00192373
C	-3.50221218	-0.20048049	-2.73631361
C	3.44406272	-0.16711513	2.76836868
H	-1.55927090	0.78457019	-2.59377560
H	1.55240044	0.79373686	2.60972466
H	-3.81854971	0.36976431	-3.60599298
H	3.79233059	0.38404110	3.63181271
N	-0.82031706	5.94315675	1.14080115
N	0.83840684	5.94031379	-1.13868473
C	-0.40465142	7.06418527	0.57405583
C	0.42876705	7.06282916	-0.57014202
H	0.75919912	7.99700513	-1.01785098
H	-0.72971691	7.99952966	1.02340977
N	1.64586689	3.51481097	-2.26015902
N	-1.64074083	3.52029026	2.25801714
H	5.20001197	-1.27452132	2.67185890

**Cartesian Coordinates (in Å) of the equilibrium geometry of
[Ru(TAP)(TAP-H)⁺(HAT)]²⁺ protonated on N-8**

Ru	0.00663497	0.51551563	0.00483915
N	0.79228687	-1.12110630	1.07984101
N	-0.79981040	-1.10329389	-1.07336932
C	0.41684744	-2.33109550	0.57384675
C	-0.43952981	-2.32159609	-0.57537960
C	1.59565368	-1.13987488	2.14744267
C	-1.59973453	-1.10376273	-2.14364650
C	0.84684969	-3.54178869	1.15461721
C	-0.88213910	-3.52313262	-1.16582602
C	2.01507047	-2.35962926	2.71269366
C	-2.03357526	-2.31509282	-2.71670919
H	1.90529834	-0.18640360	2.55943908
H	-1.89312280	-0.14179792	-2.54725350
C	0.39802347	-4.80155248	0.55825854
C	-0.44854936	-4.79263099	-0.57782014
H	2.66665875	-2.35291990	3.58287811
H	-2.68506844	-2.29546717	-3.58683827
H	-0.27775604	2.52916154	2.58732965
H	0.33669046	2.55722820	-2.58828960
C	0.69287721	2.72519012	2.14578865
C	-0.63474680	2.76266199	-2.15598118
C	1.56134699	3.70286996	2.68555187
C	-1.43448194	3.73219063	-2.70011659
N	1.04224175	2.01067792	1.07538888
N	-1.00789050	2.01863046	-1.07057690
H	1.24746657	4.27319575	3.55616182
H	-1.14099379	4.32080038	-3.55912405
N	2.75555612	3.96969021	2.18361894
N	-2.67292142	3.99436066	-2.15299177
C	2.26993171	2.28317487	0.53943648
C	-2.24558511	2.32055784	-0.52361936
C	3.13113450	3.25782799	1.09389945
C	-3.11038001	3.29775271	-1.04204530
C	2.66859051	1.54914969	-0.60958430
C	-2.65345433	1.59577438	0.61889575
C	4.41147254	3.48412003	0.48015111
C	-4.37119063	3.54024636	-0.43622431
C	3.93080467	1.78440920	-1.20204446
C	-3.91519211	1.83202726	1.23005110
N	1.79305737	0.62791629	-1.11193524
N	-1.78388680	0.65639924	1.11975072
C	4.79557211	2.77651245	-0.62378098
C	-4.76721475	2.82580803	0.67126886
H	5.05327606	4.23560675	0.92754586
H	-5.02583149	4.29728230	-0.85837677
N	4.31956387	1.08731203	-2.29667458
N	-4.30450575	1.12681411	2.32144343
C	2.19813829	-0.04852269	-2.18778491
C	-2.19310043	-0.02260665	2.18740522
H	5.75717806	2.93799353	-1.09932514
H	-5.72787055	2.99701259	1.14446117
C	3.46613317	0.19309138	-2.76657907
C	-3.45996634	0.22231070	2.77817535
H	1.52126272	-0.78544219	-2.60489972
H	-1.52347356	-0.77098429	2.59669941
H	3.76989119	-0.37521105	-3.64219333
H	-3.76273802	-0.35362886	3.64896183
N	0.80953243	-5.95557365	1.11731789
N	-0.87480455	-5.93837407	-1.14295330
C	0.38276161	-7.07316078	0.55205865
C	-0.46348394	-7.06443992	-0.58276022
H	-0.80286493	-7.99578393	-1.02965034
H	0.70885976	-8.01113596	0.99504430
N	-1.68568139	-3.50455993	-2.24636418
N	1.65140712	-3.54110796	2.23446550
H	-3.26131030	4.71332028	-2.55736514

**Cartesian Coordinates (in Å) of the equilibrium geometry of
[Ru(TAP)₂(HAT-H)]²⁺ protonated on N-1**

Ru	0.00153714	-0.52916986	0.00173319
N	-0.79884049	1.09913438	1.08530938
N	0.78365532	1.09029871	-1.09059969
C	-0.43617554	2.32023363	0.58291338
C	0.40911617	2.31842812	-0.56504269
C	-1.59866174	1.10205008	2.15468010
C	1.61024086	1.13988564	-2.18306448
C	-0.88501203	3.52153338	1.18949020
C	0.81390986	3.53127291	-1.10652475
C	-2.03343713	2.30910352	2.73724928
C	2.03258466	2.31482717	-2.74595147
H	-1.89621310	0.14154667	2.55913037
H	1.92813304	0.19484654	-2.60537327
C	-0.45706835	4.78751055	0.60964074
C	0.38623661	4.77785398	-0.52717907
H	-2.68232065	2.28702333	3.60871336
H	2.68219207	2.34880252	-3.60987482
H	0.30575193	-2.56079469	2.57746324
H	-0.29716006	-2.54585306	-2.57652069
C	-0.66455092	-2.76131545	2.13672612
C	0.67450755	-2.74323979	-2.13785532
C	-1.52309019	-3.75083648	2.67098209
C	1.54076778	-3.72098722	-2.68089142
N	-1.02340563	-2.04075704	1.07332734
N	1.02891391	-2.02899415	-1.06847101
H	-1.20525115	-4.32235100	3.53944716
H	1.22671364	-4.28741962	-3.55428550
N	-2.71445596	-4.02583494	2.16677588
N	2.73421691	-3.99175749	-2.17951778
C	-2.24780416	-2.32249964	0.53486918
C	2.25671968	-2.30399788	-0.53465448
C	-3.09792396	-3.31156965	1.08140001
C	3.11325474	-3.28293338	-1.08897134
C	-2.65452560	-1.58532650	-0.60996907
C	2.65952383	-1.56975231	0.61272065
C	-4.37608170	-3.54911538	0.46724121
C	4.39394706	-3.51442643	-0.47759943
C	-3.91449334	-1.83203771	-1.20276977
C	3.92158304	-1.81029778	1.20296562
N	-1.78852223	-0.65289844	-1.10962172
N	1.78700952	-0.64548507	1.11620488
C	-4.76911376	-2.83709943	-0.63074591
C	4.78295524	-2.80544232	0.62375683
H	-5.00765310	-4.31182506	0.91059156
H	5.03121216	-4.26928321	-0.92633324
N	-4.30983751	-1.13502951	-2.29494200
N	4.31335501	-1.11613350	2.29820028
C	-2.20084552	0.02475713	-2.18147044
C	2.19553037	0.02781974	2.19259007
H	-5.72983544	-3.00448455	-1.10646612
H	5.74595539	-2.96705957	1.09682534
C	-3.46607224	-0.22940621	-2.76155182
C	3.46266685	-0.21988392	2.77048959
H	-1.52990968	0.77162778	-2.59059058
H	1.52171349	0.76729689	2.61055358
H	-3.77737408	0.33596905	-3.63632825
H	3.76893121	0.34353872	3.64833492
N	-0.86571851	5.95026140	1.15494286
N	0.81839286	5.91703487	-1.11323178
C	-0.43985260	7.06028009	0.57488015
C	0.40684813	7.04775588	-0.56417771
H	0.74144032	7.97636926	-1.01848283
H	-0.76621197	8.00302713	1.00671383
N	1.62793173	3.51864216	-2.20861934
N	-1.68369660	3.49960476	2.26963756
H	1.91461466	4.41686419	-2.58889169

**Cartesian Coordinates (in Å) of the equilibrium geometry of
[Ru(TAP)₂(HAT-H)]²⁺ protonated on N-12**

Ru	0.00022715	-0.53404297	0.00294848
N	-0.80440738	1.08572907	1.09156449
N	0.78726571	1.10264284	-1.07466537
C	-0.43815930	2.29921463	0.58489432
C	0.41490786	2.29506199	-0.56512028
C	-1.60366906	1.09656914	2.16390492
C	1.59481946	1.12709603	-2.16050038
C	-0.87754263	3.50528629	1.17282977
C	0.83965188	3.52064539	-1.13900210
C	-2.02991917	2.31097932	2.73319018
C	2.00993488	2.35658178	-2.71690247
H	-1.90495784	0.14045635	2.57690771
H	1.90538140	0.17903004	-2.57997918
C	-0.44478655	4.78647627	0.58738137
C	0.40382481	4.73013779	-0.55554375
H	-2.67593057	2.30126422	3.60694063
H	2.65795442	2.34776626	-3.59053106
H	0.30853190	-2.56435612	2.57651977
H	-0.29594544	-2.54894116	-2.58242382
C	-0.66155523	-2.76633800	2.13568067
C	0.67520744	-2.74685479	-2.14248952
C	-1.52069437	-3.75444928	2.67236750
C	1.54019757	-3.72716574	-2.68437510
N	-1.02042304	-2.04819796	1.07051686
N	1.03011914	-2.03212911	-1.07386419
H	-1.20255981	-4.32452787	3.54178704
H	1.22504418	-4.29513419	-3.55635486
N	-2.71230029	-4.02851868	2.16909636
N	2.73375056	-3.99640322	-2.18349529
C	-2.24580838	-2.32832236	0.53368292
C	2.25716702	-2.30799174	-0.53898689
C	-3.09662549	-3.31516271	1.08347139
C	3.11408051	-3.28626585	-1.09442646
C	-2.65453021	-1.59017520	-0.60997380
C	2.66121993	-1.57426477	0.60853072
C	-4.37681050	-3.55097449	0.47275023
C	4.39617289	-3.51666370	-0.48533309
C	-3.91708525	-1.83412926	-1.19819932
C	3.92564504	-1.81261406	1.19510826
N	-1.78959942	-0.65802722	-1.11158379
N	1.79008127	-0.65067630	1.11488528
C	-4.77148221	-2.83839141	-0.62451314
C	4.78660139	-2.80771479	0.61536057
H	-5.00858523	-4.31243300	0.91805010
H	5.03275063	-4.27142796	-0.93533843
N	-4.31584709	-1.13441496	-2.28757404
N	4.32022980	-1.11631949	2.28815572
C	-2.20409875	0.02043871	-2.18245880
C	2.20152133	0.02496867	2.18893841
H	-5.73299448	-3.00447931	-1.09895074
H	5.74957406	-2.96945789	1.08862087
C	-3.47268299	-0.23088977	-2.75780535
C	3.47130612	-0.22085979	2.76308288
H	-1.53437021	0.76565101	-2.59713895
H	1.52931732	0.76511049	2.60835610
H	-3.78524471	0.33579384	-3.63147725
H	3.77978900	0.34369524	3.63967418
N	-0.85471102	5.91947571	1.14025988
N	0.79942013	5.94133433	-1.09324275
C	-0.43184222	7.08173622	0.56875186
C	0.38501236	7.11670857	-0.53624772
H	0.72685990	8.03278687	-1.00170557
H	-0.77166881	8.00281893	1.02888943
N	1.65643288	3.53892481	-2.24088286
N	-1.67642722	3.49645290	2.25267117
H	1.40550046	5.91543567	-1.90828750

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