Unraveling the Light-Activated Reaction Mechanism in a Catalytically Competent Key Intermediate of a Multifunctional Molecular Catalyst for Artificial Photosynthesis

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Experimental section

Sample Preparation for spectroscopic and electrochemical experiments

Ru(tpphz)RhCp* was provided by Prof. Rau and synthesized as described in the literature.[3] All spectroscopic and voltammetry experiments, i.e., cyclic voltammetry (CV), chronoamperometry (CA), steady-state absorption spectrophotometry (UV-vis SEC), resonance Raman (rR) SEC and femtosecond time-resolved transient absorption (TA) SEC were performed at room temperature. The complex was dissolved in anhydrous acetonitrile (Sigma-Aldrich) containing 0.1 M tetrabutylammonium hexafluoroborate (TBABF₄) as electrolyte. All solutions were thoroughly degassed with argon prior to each measurement. The measurements were executed with an optical density of 0.3 at 400 nm.

Electrochemical and spectroelectrochemical Instrumentation

UV-vis-SEC, rR-SEC and electrochemical measurements were performed using a three-electrode thin-layer spectroelectrochemical cell with a pathlength of 1 mm (Hellma, Bioanalytical Systems, USA). The three-electrode system contains a Pt counter electrode, an Ag/AgCl pseudo-reference electrode and a glassy carbon working electrode. Cyclic voltammetry and potential-controlled monitoring were performed using a computer-controlled VersaSTAT 3 (Princeton Applied Research) potentiostat. UV-vis and resonance Raman spectra were recorded immediately after applying the respective reduction potential to monitor the accompanied spectral changes. Reoxidation at the corresponding anodic potential fully regenerated the original spectrum, proving that the complex remained stable during the spectroelectrochemical studies. UV-vis spectra were collected in transmission mode by using a product of Avantes Inc., which is comprised of a single-channel fiber-optic spectrometer (AvaSpec-ULS2048XL) equipped with a deuteriumhalogen light source (AvaLight DH-S-BAL).

RR measurements were performed through excitation by visible lasers and detected by an IsoPlane 160 spectrometer (Princeton Instruments, USA) with an entrance slit width of 50 µm and gratings with 600 or 1200 grooves/mm. The rR setup is equipped with 4 excitation lasers: a 405 nm diode laser (TopMode-405-HP, Toptica, Germany), a 473 nm diode-pumped solid-state laser (HB-Laser, Germany), a 532 nm diode-pumped solid-state laser (HB-Laser, Germany) and a 643 nm diode-pumped solid-state DL laser (CrystaLaser, USA). For RR measurements, the laser power was attenuated to approximately 5 mW to reduce photodegradation of the analyte. The Raman signals were recorded by a thermoelectrically cooled CCD camera of 1340 x 100 pixels (PIXIS eXcelon, Princeton Instruments, USA). The band of acetonitrile at 1380 cm⁻¹ was used as a reference for normalizing intensities and wavenumbers. The recorded resonance Raman spectra were background corrected, and the solvent spectrum was subtracted. At 643 nm within the reduction-induced absorption band of Ru(tpphz)RhCp*, no rR signal of the neutral complex has been recorded using the same acquisition parameters.

Transient absorption spectroscopy

A custom-built setup was utilized to acquire fs-TA data. The setup is described in detail elsewhere.[2] Briefly, a white-light supercontinuum probe pulse at 1 kHz repetition rate has been used to analyze the excited-state dynamics. The supercontinuum was generated by focusing a minor part of the output of the Ti:Sapphire amplifier into a CaF₂ plate mounted on a rotating stage. The white light is split into probe and reference. The probe pulse is focused onto the sample by a concave mirror of 500 mm focal length. The spectra of probe and reference are detected by a Czerny-Turner spectrograph of 150 mm focal length (SP2150, Princeton Instruments) equipped with a diode array detector (Pascher Instruments AB, Sweden). For excitation either 403, 492 or 600 nm pulses of approximately 100 fs pulse duration have been used. The repetition rate of the pump pulses has been reduced to 0.5 kHz by
a mechanical chopper, and the polarization is adjusted to the magic angle of 54.7° by a Berek compensator and a polariser. The temporal resolution of the experiment is limited to 300 fs due to strong contributions from coherent artifact signals to the data,[3] which impede a reliable analysis of the pump-probe data by means of multi-exponential fitting at shorter delay times.

For data analysis, first the data was preprocessed to correct for the chirp, and in the following, a sum of exponential functions has been fitted to the data using customized data analysis software (Pascher Instruments AB, Lund, Sweden). The pulse overlap region of ±150 fs has been excluded from the data evaluation due to coherent artefacts in this temporal region. The amplitudes of the exponential fit correspond to the decay associated spectra (DAS). For the investigation of the primary photoinduced processes, the sample was dissolved in anhydrous acetonitrile (OD (400 nm) = 0.4 in a cell with 1 mm path length).

The pump and probe beam pass collinearly through a 1-mm hole in a 0.4 mm thick glassy carbon working electrode. This customized electrode design ensures at the same time high yields of the redox-active species within the observation volume due to the highly resistant glassy carbon material and high transmission despite its opacity. Customized electronics and control software (Pascher Instruments AB, Sweden) allow for simultaneously measuring steady state absorption, current, CV, and TA and ensure jitter-free timing of the datasets.

A prerequisite for TA measurements is a constant concentration of the analyte under investigation during the acquisition period. To warrant constant experimental conditions and analyte concentrations, the current response at fixed potential was monitored and only measurements characterized by constant current throughout the acquisition were selected for further analysis. Transient absorption spectra of the electrochemically reduced complex were recorded at set potentials and constant current response. Steady state UV-vis spectra were simultaneously recorded with time-resolved TA-SEC in order to assess the concentration of the redox active species within the observation volume and the conversion efficiency of the electrochemical process. In addition to current monitoring, absorption spectra were recorded preceding and consecutively each measurement to ensure sample integrity during the measurement. The generation of additional species contributing to the transient absorption spectra cannot be fully excluded since the simultaneous exposure to light and potential of Ru(tpphz)RhCp* may result in degradation products and side reactions. However, measures have been taken to minimize these (current response monitoring, steady state UV-vis spectroscopy).

Computational details

All quantum chemical calculations determining structural and electronic properties of Ru(tpphz)RhCp* were performed using the Gaussian 16 program.[4] The computational costs were reduced without affecting the spectroscopic properties of the complex by approximating the four tert-butyl groups of the two bipyridine ligands by methyl groups. Fully relaxed equilibrium geometries of Ru(tpphz)RhCp* were obtained within the singlet and triplet (with and without Cl) ground state, respectively. Furthermore, the triplet ground state as well as the ground states of the doubly (singlet and triplet) and triply (doublet and quartet) reduced complex following a dissociation of chloride were investigated. All ground state calculations were performed at the density functional level of theory (DFT) by means of the B3LYP[5,6] XC functional. The 6-31G(d) double-ξ basis set[7] was employed for all main group elements, while the relativistic core potential MWB-28[8] was applied with its basis sets for the ruthenium and the rhodium atom. A subsequent vibrational analysis was carried out for each optimized ground state structure to verify that a minimum on the potential energy (hyper-)surface (PES) was obtained.

Excited-state properties such as excitation energies, oscillator strengths and electronic characters were calculated within all (ground state) equilibrium structures at the time-dependent DFT (TDDFT) level of theory. Within the Franck-Condon region, the 150 lowest singlet excited states were calculated.
For all other systems, the number of investigated spin-allowed excitations was increased i) to 300 for the non-reduced triplet (prior and after Cl dissociation) as well as for the doubly reduced singlet and triplet (after Cl’ dissociation), and ii) to 500 for the triply reduced doublet and quartet (after Cl’ dissociation) species. Thereby, the same XC functional, basis set and core potentials were applied as for the preceding ground state calculations. Several joint spectroscopic-theoretical studies on structurally related complexes proved that this computational protocol enables an accurate prediction of ground and excited-states properties with respect to experimental data, e.g. UV-vis absorption, resonance Raman spectra and (spectro-) electrochemical properties. A balanced description of excited states featuring, i.e., metal-to-ligand charge transfer (MLCT), ligand-to-metal charge transfer (LMCT), ligand-to-ligand charge transfer (LLCT), intra-ligand charge transfer (ILCT), intra-ligand (IL) and metal-centered (MC) character, as provided by the present computational setup, is essential to assess the photophysics as well as the photochemistry of transition metal complexes. Effects of interaction with a solvent (acetonitrile: ε = 35.688, n = 1.344) were taken into account on the ground and excited-states properties by the integral equation formalism of the polarizable continuum model. The non-equilibrium procedure of solvation was used for the calculation of the excitation energies within the Franck-Condon region of the respective redox species, which is well adapted for processes where only the fast reorganization of the electronic distribution of the solvent is important. All calculations were performed including D3 dispersion correction with Becke-Johnson damping.

Sample preparation for photocatalysis experiments

For photocatalysis experiments, a 20 µM solution of Ru(tpphz)RhCp* in MeCN:H2O = 1:1 (v:v; 2.5 mL in total) was prepared in a glovebox under argon atmosphere. Then 25 µL of a 20 mM BNA’Br’ (N-benzyl Nicotinamide bromide) aqueous stock solution was added, yielding a final concentration of 200 µM. Additionally, TEA (triethylamine, 0.1 M) serving as sacrificial electron donor and NaH2PO4 (0.08 M) for reducing the basicity of the overall solution were present in the solvent mixture as the 1.25 mL of water were added in two portions (500 µL of an aqueous solution of 0.5 M TEA and 0.4 M NaH2PO4 and 750 µL of pure water). The solution was then transferred into a cuvette with a 10 mm path length (Starna Scientific) and sealed with a screw cap to exclude oxygen diffusion into the sample. Irradiation was performed using one LED stick emitting blue light (λ = 463 nm ± 12 nm, 45-50 mW/cm²) and continuous ventilation using a custom-made air-cooling apparatus, which ensured a constant temperature during the photocatalysis experiment. UV-vis spectra were recorded after defined time intervals of irradiation, and catalytic turnover was determined based on the extinction coefficient (7240 L/mol cm) at 355 nm of the formed BNAH (1,4-dihydro-N-benzyl Nicotinamide).

In the case of the experiment alternating irradiation and thermal reoxidation of the reduced Ru(tpphz)RhCp* complex by substrate conversion, the cuvette was either irradiated as described above or placed into a 40 °C warm water bath.

Sample preparation for CoCp2-reduction experiments for UV-vis spectroscopic investigations

First, a suitable amount of CoCp2 (abcr GmbH, between 3 and 4 mg) was dissolved in a glovebox under an argon atmosphere in a mixture of 1 mL dry acetone:acetonitrile = 1:1 (v:v). Then glass vials were equipped with a suitable amount of Ru(tpphz)RhCp* (typically 0.08106 mg via a DCM stock solution for obtaining 2.5 ml sample with a 20 µM concentration of complex) and the solvent was evaporated. After introducing the glass vials into the glovebox, 1.25 mL degassed MeCN and 1.25 mL degassed H2O were added. Then the appropriate volume (40 µM in 2.5 mL sample) from the CoCp2 stock-solution was added to the glass vial yielding a green colored solution. This solution was transferred into a cuvette with a 10 mm path length (Starna Scientific) and sealed with a screw cap to exclude oxygen diffusion into the sample. In the experiments for nicotinamide reduction, 25 µL of a 20 mM aqueous BNA’Br’ (N-benzyl Nicotinamide bromide) stock solution was additionally transferred into the cuvette. Irradiation of the samples was performed as described above.
Sample preparation for photoreduction experiments for UV-vis spectroscopic investigations

For simple photoreduction experiments using TEA as sacrificial reductant, a 20 µM solution (V = 2.5 mL) of Ru(tpphz)RhCp* in MeCN:H₂O = 1:1 (v:v) prepared under argon atmosphere in a glovebox was additionally charged with 35 µL of TEA (final concentration 0.1 M). Afterwards, the sample was transferred into a cuvette with a 10 mm path length (Starna Scientific) and sealed with a screw cap to exclude oxygen diffusion into the sample. Irradiation of the samples was performed as described above.
Table S1: Calculated vertical excitation energies ($E_e$), wavelengths ($\lambda$), oscillator strengths ($f$), experimental wavelengths ($\lambda_{exp}$) and singly-excited configurations of the main excited singlet-singlet transitions involved in the initial absorption of \textit{Ru(tpphz)RhCp*} within the Franck-Condon region.

| State | Transition | Weight / % | $E_e$ / eV | $\lambda$ / nm | $f$ | $\lambda_{exp}$ / nm$^a$ |
|-------|------------|------------|------------|----------------|----|-------------------|
| $S_2$ | d(Ru)$_{yz}$(256) $\rightarrow$ $\pi_{tpphz}$*(259) (MLCT) | 95 | 2.44 | 508 | 0.060 | - |
| $S_{12}$ | d(Ru)$_{yz}$(256) $\rightarrow$ $\pi_{tpphz}$*(262) (MLCT) | 25 | 2.85 | 435 | 0.091 | 443 |
| $S_{13}$ | d(Ru)$_{yz}$(256) $\rightarrow$ $\pi_{tpphz}$*(263) (MLCT) | 38 | | | | |
| $S_{14}$ | d(Ru)$_{yz}$(257) $\rightarrow$ $\pi_{tpphz}$*(264) (MLCT) | 41 | 2.93 | 423 | 0.228 | 443 |
| $S_{16}$ | d(Ru)$_{yz}$(256) $\rightarrow$ $\pi_{tpphz}$*(264) (MLCT) | 54 | 2.97 | 418 | 0.139 | 443 |
| $S_{17}$ | d(Ru)$_{yz}$(257) $\rightarrow$ $\pi_{tpphz}$*(264) (MLCT) | 41 | | | | |
| $S_{18}$ | d(Rh)$_{yz}$(255) $\rightarrow$ d(Rh)$_{yz}$*(266) (MC) | 84 | 3.04 | 408 | 0.052 | - |
| $S_{19}$ | d(Rh)$_{yz}$(254) $\rightarrow$ $\pi_{tpphz}$*(259) (MLCT) | 90 | 3.25 | 381 | 0.096 | 381 |
| $S_{20}$ | pC(253) $\rightarrow$ $\pi_{tpphz}$*(259) (LLCT) | 72 | 3.57 | 347 | 0.147 | 362 |
| $S_{21}$ | $\pi_{tpphz}$(250) $\rightarrow$ $\pi_{tpphz}$*(259) (IL) | 10 | | | | |
| $S_{22}$ | $\pi_{tpphz}$(252) $\rightarrow$ $\pi_{tpphz}$*(259) (LLCT) | 49 | 3.64 | 341 | 0.228 | 362 |
| $S_{23}$ | $\pi_{tpphz}$(250) $\rightarrow$ $\pi_{tpphz}$*(261) (ILCT) | 27 | | | | |
| $S_{24}$ | $\pi_{tpphz}$(252) $\rightarrow$ $\pi_{tpphz}$*(259) (ILCT) | 49 | 4.06 | 306 | 0.412 | 283 |
| $S_{25}$ | $\pi_{tpphz}$(249) $\rightarrow$ $\pi_{tpphz}$*(260) (IL) | 17 | | | | |
| $S_{26}$ | $\pi_{tpphz}$(251) $\rightarrow$ $\pi_{tpphz}$*(260) (ILCT) | 24 | 4.11 | 301 | 0.552 | 283 |
| $S_{27}$ | $\pi_{tpphz}$(249) $\rightarrow$ $\pi_{tpphz}$*(260) (IL) | 17 | | | | |
| $S_{28}$ | $\pi_{tpphz}$(250) $\rightarrow$ $\pi_{tpphz}$*(261) (ILCT) | 13 | | | | |
| $S_{29}$ | $\pi_{tpphz}$(251) $\rightarrow$ $\pi_{tpphz}$*(264) (LLCT) | 44 | 4.49 | 276 | 0.239 | 283 |
| $S_{30}$ | d(Ru)$_{yz}$(256) $\rightarrow$ $\pi_{tpphz}$*(272) (MLCT) | 20 | | | | |
| $S_{31}$ | $\pi_{tpphz}$(252) $\rightarrow$ $\pi_{tpphz}$*(263) (IL) | 12 | | | | |
| $S_{32}$ | $\pi_{tpphz}$(251) $\rightarrow$ $\pi_{tpphz}$*(263) (IL) | 24 | 4.53 | 274 | 0.574 | 283 |
| $S_{33}$ | $\pi_{tpphz}$(249) $\rightarrow$ $\pi_{tpphz}$*(263) (LLCT) | 24 | | | | |
| $S_{34}$ | $\pi_{tpphz}$(252) $\rightarrow$ $\pi_{tpphz}$*(264) (IL) | 23 | | | | |
| $S_{35}$ | $\pi_{tpphz}$(249) $\rightarrow$ $\pi_{tpphz}$*(264) (ILCT) | 59 | 4.54 | 273 | 0.274 | 283 |
| $S_{36}$ | $\pi_{tpphz}$(252) $\rightarrow$ $\pi_{tpphz}$*(264) (IL) | 11 | | | | |

$^a$ Experimental wavelengths are approximate due to the nature of the Franck-Condon region.


Figure S1: Molecular orbitals involved in bright singlet-singlet excitations of Ru(tpphz)RhCp* within the Franck-Condon region. Hydrogen atoms are omitted for clarity.
Figure S2: Charge density differences of the bright singlet-singlet excitations of Ru(tpphz)RhCp* within the Franck-Condon region. Hydrogen atoms are omitted for clarity.
Table S2: Calculated vertical excitation energies ($E^*$), wavelengths ($\lambda$), oscillator strengths ($f$), spin contamination ($\langle s^2 \rangle$), experimental wavelengths ($\lambda_{\text{exp}}$) and singly-excited configurations of the main triplet-triplet excitations (within the T$_1$ equilibrium structure) involved in the excited-state absorption contributing the transient absorption signal of Ru(tpphz)RhCp*.

| State | Transition | Weight / % | $E^*$ / eV | $\lambda$ / nm | $f$ | $\langle s^2 \rangle$ | $\lambda_{\text{exp}}$ / nm |
|-------|------------|------------|------------|----------------|-----|---------------------|----------------------|
| $T_{24}$ | $\eta_{\text{bpy}}(247\beta) \rightarrow d(\text{Ru})_{\alpha}(258\beta)$ (LMCT) | 74 | 1.92 | 646 | 0.013 | 2.04 | - |
| | $\eta_{\text{tpphz}}(251\beta) \rightarrow d(\text{Ru})_{\alpha}(258\beta)$ (LMCT) | 11 | | | | | |
| | $d(\text{Rh})_{\alpha}(252\beta) \rightarrow d(\text{Ru})_{\alpha}(258\beta)$ (MC) | 9 | | | | | |
| $T_{26}$ | $\eta_{\text{tpphz}}(251\beta) \rightarrow d(\text{Ru})_{\alpha}(258\beta)$ (LMCT) | 35 | 1.96 | 632 | 0.027 | 2.04 | - |
| | $d(\text{Ru})_{\alpha}(249\beta) \rightarrow d(\text{Ru})_{\alpha}(258\beta)$ (MC) | 32 | | | | | |
| | $\eta_{\text{tpphz}}(247\beta) \rightarrow d(\text{Ru})_{\alpha}(258\beta)$ (LMCT) | 16 | | | | | |
| | $\eta_{\text{tpphz}}(254\beta) \rightarrow d(\text{Ru})_{\alpha}(258\beta)$ (LMCT) | 8 | | | | | |
| $T_{27}$ | $\eta_{\text{bpy}}(259\alpha) \rightarrow \eta_{\text{tpphz}}(274\alpha)$ (IL) | 91 | 2.04 | 609 | 0.260 | 2.03 | 593 |
| $T_{52}$ | $d(\text{Rh})_{\alpha}(257\beta) \rightarrow d(\text{Rh})_{\alpha}(258\beta)$ (MC) | 42 | 3.06 | 405 | 0.059 | 2.02 | 435 |
| | $d(\text{Rh})_{\alpha}(258\alpha) \rightarrow d(\text{Rh})_{\alpha}(258\alpha)$ (MC) | 42 | | | | | |
| $T_{76}$ | $\eta_{\text{tpphz}}(256\beta) \rightarrow \eta_{\text{tpphz}}(261\beta)$ (ILCT) | 15 | 3.48 | 357 | 0.142 | 2.91 | 403 |
| | $\eta_{\text{tpphz}}(256\beta) \rightarrow \eta_{\text{tpphz}}(262\beta)$ (ILCT) | 14 | | | | | |
| | $d(\text{Rh})_{\alpha}(257\alpha) \rightarrow \eta_{\text{bpy}}(260\alpha)$ (MLCT) | 14 | | | | | |
| | $\eta_{\text{tpphz}}(255\beta) \rightarrow \eta_{\text{tpphz}}(263\beta)$ (IL) | 10 | | | | | |
| $T_{81}$ | $d(\text{Rh})_{\alpha}(257\alpha) \rightarrow \eta_{\text{bpy}}(260\alpha)$ (MLCT) | 47 | 3.50 | 354 | 0.080 | 2.72 | 403 |
| | $\eta_{\text{tpphz}}(256\beta) \rightarrow \eta_{\text{tpphz}}(262\beta)$ (ILCT) | 11 | | | | | |
| | $\eta_{\text{tpphz}}(256\beta) \rightarrow \eta_{\text{tpphz}}(262\beta)$ (ILCT) | 9 | | | | | |
| $T_{85}$ | $d(\text{Rh})_{\alpha}(257\beta) \rightarrow \eta_{\text{tpphz}}(263\beta)$ (MLCT) | 28 | 3.56 | 348 | 0.055 | 2.92 | 403 |
| | $\eta_{\text{tpphz}}(254\beta) \rightarrow \eta_{\text{bpy}}(259\beta)$ (LLCT) | 17 | | | | | |
| | $\eta_{\text{tpphz}}(254\beta) \rightarrow \eta_{\text{tpphz}}(263\beta)$ (IL) | 12 | | | | | |
| | $\eta_{\text{tpphz}}(254\beta) \rightarrow \eta_{\text{tpphz}}(260\beta)$ (MLCT) | 10 | | | | | |
| | $d(\text{Rh})_{\alpha}(258\alpha) \rightarrow \eta_{\text{tpphz}}(263\alpha)$ (MLCT) | 9 | | | | | |
| $T_{93}$ | $\eta_{\text{tpphz}}(254\beta) \rightarrow \eta_{\text{tpphz}}(263\beta)$ (IL) | 23 | 3.61 | 343 | 0.042 | 3.25 | 403 |
| | $\eta_{\text{tpphz}}(254\beta) \rightarrow \eta_{\text{bpy}}(260\beta)$ (LLCT) | 21 | | | | | |
| | $d(\text{Rh})_{\alpha}(257\alpha) \rightarrow \eta_{\text{tpphz}}(262\alpha)$ (MLCT) | 12 | | | | | |
| $T_{97}$ | $\eta_{\text{tpphz}}(233\beta) \rightarrow d(\text{Ru})_{\alpha}(258\beta)$ (LMCT) | 18 | 3.63 | 341 | 0.054 | 2.27 | 403 |
| | $d(\text{Rh})_{\alpha}(257\alpha) \rightarrow \eta_{\text{tpphz}}(262\alpha)$ (MLCT) | 12 | | | | | |
| | $\eta_{\text{tpphz}}(256\beta) \rightarrow \eta_{\text{tpphz}}(262\beta)$ (ILCT) | 10 | | | | | |
| | $\eta_{\text{tpphz}}(256\beta) \rightarrow \eta_{\text{tpphz}}(261\beta)$ (ILCT) | 10 | | | | | |
| | $\eta_{\text{tpphz}}(254\beta) \rightarrow \eta_{\text{tpphz}}(263\beta)$ (IL) | 7 | | | | | |
| $T_{149}$ | $d(\text{Ru})_{\alpha}(250\beta) \rightarrow \eta_{\text{bpy}}(259\beta)$ (MLCT) | 13 | 4.05 | 306 | 0.311 | 2.57 | 350 |
| | $\eta_{\text{tpphz}}(251\beta) \rightarrow \eta_{\text{bpy}}(260\beta)$ (LLCT) | 11 | | | | | |
| | $d(\text{Ru})_{\alpha}(248\alpha) \rightarrow \eta_{\text{bpy}}(261\alpha)$ (MLCT) | 10 | | | | | |
| $T_{159}$ | $\eta_{\text{tpphz}}(254\beta) \rightarrow \eta_{\text{tpphz}}(263\beta)$ (ILCT) | 36 | 4.12 | 301 | 0.873 | 2.42 | - |
| | $\eta_{\text{tpphz}}(254\beta) \rightarrow \eta_{\text{tpphz}}(263\beta)$ (ILCT) | 18 | | | | | |
| $T_{190}$ | $\eta_{\text{bpy}}(247\beta) \rightarrow \eta_{\text{bpy}}(259\beta)$ (IL) | 13 | 4.30 | 288 | 0.287 | 2.34 | - |
| | $\eta_{\text{bpy}}(248\beta) \rightarrow \eta_{\text{bpy}}(260\beta)$ (IL) | 11 | | | | | |
| | $d(\text{Ru})_{\alpha}(247\alpha) \rightarrow \eta_{\text{bpy}}(261\alpha)$ (MLCT) | 9 | | | | | |
| | $\eta_{\text{bpy}}(251\alpha) \rightarrow \eta_{\text{bpy}}(261\alpha)$ (IL) | 9 | | | | | |
Figure S3: Molecular orbitals involved in bright triplet-triplet excitations of Ru(tpphz)RhCp* within the T1 equilibrium structure. Hydrogen atoms are omitted for clarity.
**Figure S4:** Charge density differences of the bright triplet-triplet excitations of Ru(tpphz)RhCp* within the T₁ equilibrium structure. Hydrogen atoms are omitted for clarity.
Table S3: Calculated vertical excitation energies ($E^*$), wavelengths ($\lambda$), oscillator strengths ($f$), spin contamination ($\langle s^2 \rangle$), experimental wavelengths ($\lambda_{exp}$) and singly-excited configurations of the main triplet-triplet excitations (within the $T_1$ equilibrium structure) involved in the excited-state absorption contributing the transient absorption signal of $\text{Ru(tpphz)RhCp^*}$ (upon $\text{Cl}^-$ dissociation).

| State | Transition | Weight / % | $E^*$ / eV | $\lambda$ / nm | $f$ | $\langle s^2 \rangle$ | $\lambda_{exp}$ / nm |
|-------|------------|------------|------------|----------------|-----|----------------------|---------------------|
| T_{12} | $d(Rh)_{yz}(250\alpha) \rightarrow \pi_{tpphz}^*(256\alpha)$ (MLCT) | 95 | 1.68 | 738 | 0.196 | 1.68 | 750 |
| T_{30} | $\pi_{bpy}(235\beta) \rightarrow d(Ru)_{yz}(249\beta)$ (LMCT) | 97 | 2.71 | 458 | 0.029 | 2.71 | - |
| T_{37} | $\pi_{bpy}(234\beta) \rightarrow d(Ru)_{yz}(249\beta)$ (LMCT) | 81 | 2.86 | 433 | 0.028 | 2.86 | - |
|       | $\pi_{tpphz}(232\beta) \rightarrow d(Ru)_{yz}(249\beta)$ (LMCT) | 14 | 2.89 | 428 | 0.021 | 2.89 | - |
| T_{41} | $\pi_{bpy}(233\beta) \rightarrow d(Ru)_{yz}(249\beta)$ (LMCT) | 80 | 2.89 | 428 | 0.021 | 2.89 | - |
|       | $\pi_{tpphz}(229\beta) \rightarrow d(Ru)_{yz}(249\beta)$ (LMCT) | 6 | 2.89 | 428 | 0.021 | 2.89 | - |
| T_{53} | $d(Rh)_{xz}(247\beta) \rightarrow \pi_{tpphz}^*(255\beta)$ (MLCT) | 52 | 3.08 | 403 | 0.031 | 3.08 | - |
|       | $d(Rh)_{xz}(247\beta) \rightarrow \pi_{tpphz}^*(253\beta)$ (MLCT) | 27 | 3.08 | 403 | 0.031 | 3.08 | - |
| T_{59} | $\pi_{tpphz}(244\beta) \rightarrow \pi_{tpphz}^*(251\beta)$ (ILCT) | 39 | 3.13 | 396 | 0.099 | 2.16 | - |
|       | $d(Rh)_{xz}(242\beta) \rightarrow \pi_{tpphz}^*(251\beta)$ (MLCT) | 25 | 3.13 | 396 | 0.099 | 2.16 | - |
| T_{82} | $\pi_{tpphz}(245\alpha) \rightarrow \pi_{tpphz}^*(251\alpha)$ (ILCT) | 31 | 3.48 | 357 | 0.411 | 2.32 | - |
|       | $\pi_{tpphz}(244\beta) \rightarrow \pi_{tpphz}^*(250\beta)$ (ILCT) | 30 | 3.48 | 357 | 0.411 | 2.32 | - |
|       | $d(Rh)_{xz}(247\beta) \rightarrow \pi_{tpphz}^*(251\alpha)$ (MLCT) | 11 | 3.48 | 357 | 0.411 | 2.32 | - |
|       | $d(Rh)_{xz}(246\beta) \rightarrow \pi_{tpphz}^*(251\alpha)$ (MLCT) | 5 | 3.48 | 357 | 0.411 | 2.32 | - |
| T_{143} | $d(Ru)_{yz}(238\beta) \rightarrow \pi_{tpphz}^*(250\beta)$ (MLCT) | 20 | 4.00 | 310 | 0.432 | 2.59 | - |
|       | $\pi_{bpy}(240\beta) \rightarrow \pi_{tpphz}^*(250\beta)$ (LLCT) | 16 | 4.00 | 310 | 0.432 | 2.59 | - |
|       | $\pi_{tpphz}(243\beta) \rightarrow \pi_{tpphz}^*(255\beta)$ (ILCT) | 11 | 4.00 | 310 | 0.432 | 2.59 | - |
|       | $\pi_{tpphz}(243\beta) \rightarrow \pi_{bpy}^*(253\beta)$ (LLCT) | 8 | 4.00 | 310 | 0.432 | 2.59 | - |
|       | $\pi_{tpphz}(244\alpha) \rightarrow \pi_{bpy}^*(253\alpha)$ (LLCT) | 8 | 4.00 | 310 | 0.432 | 2.59 | - |
|       | $\pi_{bpy}(240\beta) \rightarrow \pi_{tpphz}^*(252\beta)$ (LLCT) | 7 | 4.00 | 310 | 0.432 | 2.59 | - |
| T_{153} | $d(Rh)_{xz}(248\alpha) \rightarrow \pi_{tpphz}^*(257\alpha)$ (MLCT) | 21 | 4.04 | 307 | 0.434 | 2.81 | - |
|       | $\pi_{tpphz}(245\alpha) \rightarrow \pi_{bpy}^*(254\alpha)$ (LLCT) | 15 | 4.04 | 307 | 0.434 | 2.81 | - |
|       | $d(Ru)_{yz}(238\beta) \rightarrow \pi_{tpphz}^*(250\beta)$ (MLCT) | 7 | 4.04 | 307 | 0.434 | 2.81 | - |
Figure S5: Molecular orbitals involved in bright triplet-triplet excitations of Ru(tpphz)RhCp* (upon Cl- dissociation) within the T₁ equilibrium structure. Hydrogen atoms are omitted for clarity.
Figure S6: Charge density differences of the bright triplet-triplet excitations of Ru(tpphz)RhCp* (upon Cl− dissociation) within the T₁ equilibrium structure. Hydrogen atoms are omitted for clarity.
Table S4: Calculated vertical excitation energies ($E^\circ$), wavelengths ($\lambda$), oscillator strengths ($f$), experimental wavelengths ($\lambda_{\text{exp}}$) and singly-excited configurations of the main singlet-singlet excitations (within the $S_0$ equilibrium structure) involved in the UV-vis absorption of the doubly reduced Ru(tpphz)RhCp* (upon Cl$^-$ dissociation).

| State | Transition | Weight / % | $E^\circ$ / eV | $\lambda$ / nm | $f$ | $\lambda_{\text{exp}}$ / nm |
|-------|------------|------------|----------------|----------------|-----|-----------------------------|
| $S_7$ | d(Rh)$_{xz}$(250) → π$_{\text{tpphz}}$* (256) (MLCT/MC) | 93 | 2.05 | 606 | 0.384 | 662 |
| $S_{22}$ | d(Ru)$_{yz}$(246) → π$_{\text{tpphz}}$* (251) (MLCT) | 76 | 2.70 | 459 | 0.174 | 443 |
| | d(Ru)$_{yz}$(246) → π$_{\text{tpphz}}$* (252) (MLCT) | 16 | | | | |
| $S_{27}$ | d(Rh)$_{xy}$(248) → π$_{\text{tpphz}}$* (253) (MLCT) | 80 | 2.84 | 437 | 0.104 | 443 |
| $S_{32}$ | d(Ru)$_{yz}$(245) → π$_{\text{tpphz}}$* (254) (MLCT) | 46 | 2.94 | 421 | 0.154 | 443 |
| | d(Ru)$_{yz}$(246) → π$_{\text{tpphz}}$* (255) (MLCT) | 37 | | | | |
| $S_{34}$ | d(Ru)$_{xy}$(246) → π$_{\text{tpphz}}$* (252) (MLCT) | 34 | 2.96 | 419 | 0.113 | 443 |
| | d(Ru)$_{xy}$(245) → π$_{\text{tpphz}}$* (253) (MLCT) | 23 | | | | |
| | d(Ru)$_{xy}$(245) → π$_{\text{tpphz}}$* (255) (MLCT) | 20 | | | | |
| | d(Ru)$_{yz}$(246) → π$_{\text{tpphz}}$* (251) (MLCT) | 10 | | | | |
| $S_{56}$ | d(Ru)$_{xy}$(245) → π$_{\text{tpphz}}$* (253) (MLCT) | 58 | 3.06 | 405 | 0.072 | 443 |
| | d(Ru)$_{xy}$(245) → π$_{\text{tpphz}}$* (255) (MLCT) | 36 | | | | |
| $S_{45}$ | d(Rh)$_{yz}$(250) → π$_{\text{tpphz}}$* (267) (MLCT) | 89 | 3.24 | 405 | 0.094 | 443 |
| $S_{48}$ | π$_{\text{tpphz}}$(241) → π$_{\text{tpphz}}$* (251) (IL) | 77 | 3.51 | 405 | 0.283 | 443 |
| | π$_{\text{tpphz}}$(242) → π$_{\text{tpphz}}$* (253) (IL) | 10 | | | | |
Figure S7: Molecular orbitals involved in bright singlet-singlet excitations of the doubly reduced Ru(tpphz)RhCp* (upon Cl⁻ dissociation) within the $S_0$ equilibrium structure. Hydrogen atoms are omitted for clarity.
Figure S8: Charge density differences of the bright singlet-singlet excitations of the doubly reduced Ru(tpphz)RhCp* (upon Cl⁻ dissociation) within the $S_0$ equilibrium structure. Hydrogen atoms are omitted for clarity.
Table S5: Calculated vertical excitation energies ($E^*$), wavelengths ($\lambda$), oscillator strengths ($f$), spin contamination ($\langle s^2 \rangle$), experimental wavelengths ($\lambda_{exp}$) and singly-excited configurations of the main triplet-triplet excitations (within the T1 equilibrium structure) involved in the UV-vis absorption of the doubly reduced Ru(tpphz)RhCp* (upon Cl- dissociation).

| State | Transition | Weight / % | $E^*$ / eV | $\lambda$ / nm | $f$ | $\langle s^2 \rangle$ | $\lambda_{exp}$ / nm |
|-------|------------|------------|------------|---------------|----|----------------|------------------|
| T10   | $\pi_{tpphz}\rightarrow\pi_{bpy}^{*}$ (258a) (LMCT) | 97         | 1.76       | 704           | 0.064 | 2.02           | 662              |
| T11   | d(Rh)α(250α) → $\pi_{tpphz}^{*}$(256α) (MLCT) | 92         | 1.90       | 652           | 0.200 | 2.03           | 662              |
| T21   | $\pi_{tpphz}^{*}$(251α) → $\pi_{tpphz}^{*}$(263α) (IL) | 93         | 2.26       | 548           | 0.294 | 2.04           | 616              |
| T42   | d(Ru)α(247β) → $\pi_{bpy}^{*}$(251β) (MLCT) | 28         | 2.82       | 439           | 0.123 | 2.30           | 443              |
|       | d(Ru)α(247α) → $\pi_{bpy}^{*}$(252α) (MLCT) | 19         |           |               |       |                |                  |
|       | d(Ru)α(248β) → $\pi_{bpy}^{*}$(252β) (MLCT) | 15         |           |               |       |                |                  |
|       | d(Ru)α(248α) → $\pi_{bpy}^{*}$(253α) (MLCT) | 11         |           |               |       |                |                  |
|       | d(Ru)α(247β) → d(Rh)α(250β) (MMCT) | 9          |           |               |       |                |                  |
| T48   | d(Ru)α(247α) → $\pi_{tpphz}^{*}$(253α) (MLCT) | 30         | 2.92       | 425           | 0.221 | 2.04           | 443              |
|       | d(Ru)α(247β) → $\pi_{tpphz}^{*}$(252β) (MLCT) | 30         |           |               |       |                |                  |
|       | d(Ru)α(248β) → $\pi_{tpphz}^{*}$(253β) (MLCT) | 11         |           |               |       |                |                  |
|       | d(Ru)α(248α) → $\pi_{tpphz}^{*}$(255α) (MLCT) | 8          |           |               |       |                |                  |
| T61   | d(Ru)α(248β) → $\pi_{tpphz}^{*}$(253β) (MLCT) | 38         | 3.17       | 391           | 0.065 | 2.27           | -                |
|       | d(Ru)α(249β) → $\pi_{tpphz}^{*}$(254β) (MLCT) | 30         |           |               |       |                |                  |
| T71   | $\pi_{cp}\rightarrow(236β)$ → d(Rh)α(250β) (LMCT) | 50         | 3.27       | 379           | 0.070 | 2.18           | -                |
| T75   | d(Ru)α(247β) → $\pi_{tpphz}^{*}$(254β) (MLCT) | 53         | 3.32       | 374           | 0.052 | 2.31           | -                |
|       | d(Ru)α(248β) → $\pi_{tpphz}^{*}$(255β) (MLCT) | 13         |           |               |       |                |                  |
|       | d(Ru)α(248α) → $\pi_{tpphz}^{*}$(255α) (MLCT) | 10         |           |               |       |                |                  |
| T85   | d(Rh)α(250α) → $\pi_{tpphz}^{*}$(263α) (MLCT) | 54         | 3.40       | 365           | 0.041 | 2.33           | -                |
| T98   | $\pi_{tpphz}$(243β) → $\pi_{tpphz}^{*}$(253β) (IL) | 47         | 3.55       | 349           | 0.149 | 2.76           |                  |
|       | $\pi_{tpphz}$(242α) → $\pi_{tpphz}^{*}$(254α) (IL) | 10         |           |               |       |                |                  |
|       | $\pi_{tpphz}$(243β) → $\pi_{bpy}^{*}$(251β) (LLCT) | 8          |           |               |       |                |                  |
**Figure S9**: Molecular orbitals involved in bright triplet-triplet excitations of the doubly reduced Ru(tpphz)RhCp* (upon Cl− dissociation) within the T1 equilibrium structure. Hydrogen atoms are omitted for clarity.
Figure S10: Charge density differences of the bright triplet-triplet excitations of the doubly reduced $\text{Ru(tpphz)RhCp}^*$ (upon Cl$^-$ dissociation) within the $T_1$ equilibrium structure. Hydrogen atoms are omitted for clarity.
Table S6: Calculated vertical excitation energies ($E^\circ$), wavelengths ($\lambda$), oscillator strengths ($f$), spin contamination ($\langle s^2 \rangle$), experimental wavelengths ($\lambda_{\exp}$) and singly-excited configurations of the main doublet-doublet excitations (within the $D_0$ equilibrium structure) involved in the UV-vis absorption of the triply reduced Ru(tpphz)RhCp* (upon Cl$^-$ dissociation).

| State | Transition | Weight / % | $E^\circ$ / eV | $\lambda$ / nm | $f$ | $\langle s^2 \rangle$ | $\lambda_{\exp}$ / nm |
|-------|------------|-------------|----------------|----------------|----|---------------------|----------------------|
| D23   | d(Rh)$_{10}$250α $\rightarrow$ π$_{tpphz}$*256α (MLCT) | 83 | 2.03 | 612 | 0.078 | 1.18 | 663 |
|       | d(Rh)$_{10}$250β $\rightarrow$ π$_{tpphz}$*256β (MLCT) | 9  |       |       |       |       |       |
| D24   | d(Rh)$_{10}$250β $\rightarrow$ π$_{tpphz}$*256β (MLCT) | 73 | 2.04 | 607 | 0.87 | 2.27 | 663 |
|       | d(Rh)$_{10}$250α $\rightarrow$ π$_{tpphz}$*257α (MLCT) | 12 |       |       |       |       |       |
|       | d(Rh)$_{10}$250α $\rightarrow$ π$_{tpphz}$*256α (MLCT) | 12 |       |       |       |       |       |
| D25   | d(Rh)$_{10}$250β $\rightarrow$ π$_{tpphz}$*257β (MLCT) | 44 | 2.08 | 596 | 0.384 | 0.85 | 663 |
|       | d(Rh)$_{10}$250α $\rightarrow$ π$_{tpphz}$*257α (MLCT) | 33 |       |       |       |       |       |
|       | d(Rh)$_{10}$250β $\rightarrow$ π$_{tpphz}$*256β (MLCT) | 11 |       |       |       |       |       |
|       | π$_{tpphz}$*251α $\rightarrow$ π$_{tpphz}$*262α (IL) | 8  |       |       |       |       |       |
| D26   | π$_{tpphz}$*251α $\rightarrow$ π$_{tpphz}$*262α (IL) | 83 | 2.26 | 549 | 0.082 | 0.80 | 663 |
| D29   | d(Ru)$_{7}$245α $\rightarrow$ π$_{tpphz}$*252α (MLCT) | 23 | 2.80 | 443 | 0.121 | 0.78 | 454 |
|       | d(Ru)$_{7}$245β $\rightarrow$ π$_{tpphz}$*251β (MLCT) | 23 |       |       |       |       |       |
|       | d(Ru)$_{7}$246α $\rightarrow$ π$_{tpphz}$*253α (MLCT) | 12 |       |       |       |       |       |
|       | d(Ru)$_{7}$246β $\rightarrow$ π$_{tpphz}$*252β (MLCT) | 12 |       |       |       |       |       |
|       | d(Ru)$_{7}$247α $\rightarrow$ π$_{tpphz}$*254α (MLCT) | 11 |       |       |       |       |       |
|       | d(Ru)$_{7}$247β $\rightarrow$ π$_{tpphz}$*253β (MLCT) | 10 |       |       |       |       |       |
| D30   | π$_{tpphz}$*251α $\rightarrow$ π$_{tpphz}$*268α (ILCT) | 75 | 2.83 | 438 | 0.094 | 0.90 | 454 |
|       | d(Rh)$_{10}$250α $\rightarrow$ π$_{tpphz}$*262α (MLCT) | 9  |       |       |       |       |       |
| D31   | d(Rh)$_{10}$245β $\rightarrow$ π$_{tpphz}$*252β (MLCT) | 28 | 2.91 | 425 | 0.120 | 0.92 | 454 |
|       | d(Rh)$_{10}$245α $\rightarrow$ π$_{tpphz}$*253α (MLCT) | 28 |       |       |       |       |       |
|       | d(Rh)$_{10}$248α $\rightarrow$ π$_{tpphz}$*253α (MLCT) | 17 |       |       |       |       |       |
| D32   | d(Rh)$_{10}$248β $\rightarrow$ π$_{tpphz}$*255β (MLCT) | 66 | 3.13 | 396 | 0.066 | 0.91 | -   |
|       | d(Rh)$_{10}$247α $\rightarrow$ π$_{tpphz}$*255α (MLCT) | 24 |       |       |       |       |       |
| D33   | d(Rh)$_{10}$250α $\rightarrow$ π$_{tpphz}$*268α (MLCT) | 65 | 3.25 | 382 | 0.061 | 1.92 | -   |
|       | d(Rh)$_{10}$250α $\rightarrow$ π$_{tpphz}$*262α (MLCT) | 15 |       |       |       |       |       |
| D34   | d(Rh)$_{10}$247β $\rightarrow$ π$_{tpphz}$*255β (MLCT) | 42 | 3.29 | 377 | 0.078 | 1.07 | -   |
|       | d(Rh)$_{10}$246β $\rightarrow$ π$_{tpphz}$*253β (MLCT) | 13 |       |       |       |       |       |
|       | d(Rh)$_{10}$247α $\rightarrow$ π$_{tpphz}$*255α (MLCT) | 10 |       |       |       |       |       |
| D39   | π$_{tpphz}$241α $\rightarrow$ π$_{tpphz}$*255α (ILCT) | 47 | 4.00 | 310 | 1.037 | 0.92 | -   |
|       | π$_{tpphz}$243β $\rightarrow$ π$_{tpphz}$*255β (ILCT) | 21 |       |       |       |       |       |
| D304  | π$_{tpphz}$237α $\rightarrow$ π$_{tpphz}$*253α (IL) | 9  | 4.53 | 274 | 0.480 | 1.24 | -   |
|       | π$_{tpphz}$237β $\rightarrow$ π$_{tpphz}$*252β (IL) | 9  |       |       |       |       |       |
Figure S11: Molecular orbitals involved in bright doublet-doublet excitations of the triply reduced Ru(tpphz)RhCp* (upon Cl⁻ dissociation) within the D₀ equilibrium structure. Hydrogen atoms are omitted for clarity.
Figure S12: Charge density differences of the bright doublet-doublet excitations of the triply reduced Ru(tpphz)RhCp* (upon Cl⁻ dissociation) within the D₀ equilibrium structure. Hydrogen atoms are omitted for clarity.
**Table S7:** Calculated vertical excitation energies ($E^\circ$), wavelengths ($\lambda$), oscillator strengths ($f$), spin contamination ($\langle s^2 \rangle$), experimental wavelengths ($\lambda_{\text{exp}}$) and singly-excited configurations of the main quartet-quartet excitations (within the Q₁ equilibrium structure) involved in the UV-vis absorption of the triply reduced Ru(tpphz)RhCp⁺ (upon Cl⁻ dissociation).

| State | Transition                                      | Weight / % | $E^\circ$ / eV | $\lambda$ / nm | $f$ | $\langle s^2 \rangle$ | $\lambda_{\text{exp}}$ / nm |
|-------|-------------------------------------------------|------------|----------------|----------------|-----|-----------------------|-----------------------------|
| Q₁₉   | d(Rh)ₓz(250α) → π_{tpphz}*(255α) (MLCT)          | 95         | 1.91           | 647            | 0.246 | 3.79                 | -                           |
| Q₂₅   | π_{tpphz}*(251α) → π_{bpy}*(259α) (LLCT)         | 66         | 2.16           | 575            | 0.236 | 3.87                 | -                           |
|       | π_{bpy}*(251α) → π_{bpy}*(261α) (IL)             | 15         |                |                |       |                       |                             |
|       | π_{bpy}*(251α) → π_{tpphz}*(263α) (LLCT)         | 12         |                |                |       |                       |                             |
| Q₄₄   | π_{bpy}*(252α) → π_{bpy}*(268α) (IL)              | 68         | 2.54           | 487            | 0.092 | 3.81                 | -                           |
|       | π_{bpy}*(252α) → π_{tpphz}*(267α) (LLCT)         | 17         |                |                |       |                       |                             |
| Q₇₃   | d(Rh)ₓz(248β) → π_{tpphz}*(255β) (MLCT)          | 17         | 2.92           | 424            | 0.070 | 4.01                 | -                           |
|       | d(Ru)ᵧx(247β) → π_{tpphz}*(253β) (MLCT)          | 15         |                |                |       |                       |                             |
|       | d(Rh)ₓz(248β) → π_{tpphz}*(253β) (MLCT)          | 12         |                |                |       |                       |                             |
|       | d(Ru)ᵧx(247β) → π_{bpy}*(251β) (MLCT)            | 10         |                |                |       |                       |                             |
|       | d(Ru)ₓz(247β) → π_{tpphz}*(255β) (MLCT)          | 10         |                |                |       |                       |                             |
| Q₁₁₃  | π_{tpphz}(243β) → π_{bpy}*(251β) (LLCT)          | 37         | 3.53           | 352            | 0.146 | 3.98                 | -                           |
|       | π_{bpy}(242β) → π_{bpy}*(251β) (IL)              | 27         |                |                |       |                       |                             |
|       | d(Ru)ₓz(246β) → π_{tpphz}*(251β) (MLCT)          | 8          |                |                |       |                       |                             |
Figure S13: Molecular orbitals involved in bright quartet-quartet excitations of the triply reduced Ru(tpphz)RhCp* (upon Cl− dissociation) within the Q1 equilibrium structure. Hydrogen atoms are omitted for clarity.
Figure S14: Charge density differences of the bright quartet-quartet excitations of the triply reduced \( \text{Ru(tpphz)RhCp}^* \) (upon \( \text{Cl}^- \) dissociation) within the \( Q_1 \) equilibrium structure. Hydrogen atoms are omitted for clarity.
|          | Singlet      | Triplet     |
|----------|--------------|-------------|
| non-reduced | 0.00 eV     | 1.89 eV     |
| doubly reduced | 0.00 eV | 0.17 eV     |
| triply reduced   | 0.00 eV     | 0.58 eV     |

**Figure S15**: Fully optimized equilibrium structures and relative energies of the non-reduced (singlet and triplet), doubly reduced (singlet and triplet) and triply (doublet and quartet) reduced Ru(tpphz)RhCp*; spin densities indicate unpaired electrons for the open-shell species. Hydrogen atoms are omitted for clarity.
Figure S16: Schematic representation of the proposed photophysical pathway for the non-reduced photocatalyst Ru(tpphz)RhCp* upon photoexcitation at 492 nm. First, photoexcitation at 492 nm excites a metal to ligand charge transfer (MLCT) transition from Ru^{II} to the adjacent ligands, i.e., tbbpy and the phenantroline moiety of the tpphz ligand. The 1 ps process contains contributions from $^1$MLCT $\rightarrow$ $^3$MLCT inter-system crossing (ISC), vibrational relaxation and an inter-ligand charge transfer (ILCT) from the tbbpy moiety to the phenanthroline sphere of the tpphz ligand. (Due to the limited temporal resolution and the spectral congestion of the processes, the individual contributions cannot be resolved.) The phenanthroline-centered state relaxes into a phenazine-centered $^3$MLCT state ($\tau_2 = 11$ ps), which decays with a lifetime of 450 ps ($\tau_3$). Finally the complex relaxes on a longer timescale to the ground state via disproportionation and structural reorganization.
Figure S17: Spectroscopic equivalence of chemically (top) and photochemically (bottom) reduced Ru(tpphz)RhCp*. The samples were prepared as described above.
Figure S18: Comparison of the UV-vis spectra of Ru(tpphz)RhCp* after 180 min under photocatalytic conditions (20 µM Ru(tpphz)RhCp*, 200 µM BNA+, MeCN:H2O = 1:1 (v:v), Ar atmosphere, irradiation with one LED-stick, $\lambda = 463$ nm, 45 mW/cm², black trace) with the UV-vis spectra of chemically reduced Ru(tpphz)RhCp* 110 min after addition of 200 µM BNA+ stored either at room temperature (red trace) or stored on the top of a LED-stick ($\lambda = 463$ nm, 45 mW/cm², blue trace). The sample stored on top of the LED-stick showed almost no spectroscopic changes, whereas for the sample stored in the dark at room temperature consumption of Ru(I)tpphzRh(I)Cp* (band decrease at 665nm) concomitant with the formation of BNAH (slight band increase at 355nm, inset) was observed, indicating that irradiation of Ru(I)tpphzRh(I)Cp* indeed leads to a photoinduced discharging process producing a relatively long-lived Rh(II) state and electron density localized on the phenazine moiety of the tpphz-ligand.
Figure S19: A sequentially alternating irradiation/40 °C heating experiment allows for photochemical Rh\textsuperscript{i} generation and thermal Rh\textsuperscript{i} consumption, both processes accompanied by BNA\textsuperscript{+} to BNAH conversion (conditions: 20 µM Ru(tpphz)RhCp\textsuperscript{*}, 200 µM BNA\textsuperscript{+}, MeCN:H\textsubscript{2}O = 1:1 (v:v), Ar atmosphere, irradiation with one LED-stick, \( \lambda = 463 \) nm, 45 mW/cm\textsuperscript{2}). A-C: UV-Vis spectroscopic changes during the irradiation/heating process. Temporal evolution is indicated by a color change from green over blue and purple to red and finally black. Spectra recorded after irradiation are depicted as solid lines, dotted curves represent the spectra obtained after placing the cuvette into a 40 °C water bath or after reoxidizing the sample using air (black dotted curve). D: Absorbance changes at 355 nm (black, BNAH-formation) and 660 nm (blue, Rh\textsuperscript{i} formation and reoxidation) highlight the temporal evolution at characteristic wavelengths. As a result of placing the cuvette into a 40 °C water bath, a strong decrease in the absorbance at 660 nm due to Rh\textsuperscript{i} re-oxidation to Rh\textsuperscript{III} is observed (this is also true for the final reoxidation of the sample using air, avoiding thermal BNA\textsuperscript{+} conversion to occur by quickly bubbling air into the cuvette). E: Comparing absolute absorbance losses at 335 and 660 nm during the four reoxidation processes (1\textsuperscript{st} reoxidation at 40 °C between 40 and 70 min, 2\textsuperscript{nd} reoxidation at 40 °C between 100 and 130 min, 3\textsuperscript{rd} reoxidation at 40 °C between 160 and 180 min and 4\textsuperscript{th} reoxidation using air after 200 min) indicates that reoxidation of the catalyst Ru(tpphz)RhCp\textsuperscript{*} is coupled to an absorbance loss at 355 nm (see 4\textsuperscript{th} reoxidation, where no BNAH was formed due to the fast reoxidation the sample by air). Smaller absorbance losses at 355 nm during the first three 40 °C reoxidations hence indicate BNAH formation coupled to Rh\textsuperscript{i} reoxidation. The sample was prepared as described above.
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