Supporting Information

Resonance-Raman spectro-electrochemistry of intermediates in molecular artificial photosynthesis of bimetallic complexes

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Experimental details

The ruthenium complexes **Ru**, **RuPd** and **RuPt** were prepared according to published procedures.^{1,2} All solutions were prepared in acetonitrile (ACN, HPLC-grade, Aldrich), which

5 was dried over calcium hydride and distilled twice. Prior to each measurement oxygen was removed by purging the solutions with argon. Electrochemical and spectro-electrochemical data were obtained using a thin layer quartz glass spectro-electrochemical cell (Bioanalytical Systems, Inc) equipped with Pt-gauze, Ptcounter and Ag/AgCl-pseudo-reference electrodes. The thickness of the investigated layer of

- 10 solution is 1 mm. The total sample volume in the cell is 500 μ l. For SEC and cyclic voltammetry (CV) solutions of **Ru**, **RuPd** and **RuPt** (100 μ M) in ACN containing 0.1 M TBABF₄ electrolyte were used. All solutions were thoroughly degassed with Argon prior to each measurement. The reduction products were analyzed by UV-vis absorption and resonance-Raman (RR) spectroscopy.
- 15 During the measurements the observed current is constant which implies continuous generation of the analyte. Even though the measurements are performed in a thin layer in the SEC-cell, the total sample volume of 500 μ l supplies educt during the course of the measurements. Therefore, we assume a quasi-constant concentration of species during the measurements, since the analyte is continuously generated.
- UV-vis absorption spectra were measured at room temperature with a double beam Cary 5000 UV-vis spectrometer (Varian) with 1 nm spectral resolution.
 RR spectra were excited by the visible lines of an Ar ion laser (Coherent, Innova 300C) and recorded with an Acton SpectraPro 2758i spectrometer (entrance slit width 100 μm, focal length 750 mm, grating 600/mm). Transmission geometry was employed for the *in situ* RR
- 25 spectro-electrochemical experiments. The Raman signals were detected using a liquidnitrogen cooled CCD (SPEC-10, Roper Scientific). The spectra have been normalized with respect to an ACN band, i.e., to the solvent signal, prior to subtraction of the solvent spectrum. By normalizing to the solvent Raman signal we correct the spectra for changes in the laser intensity at the focus due to changes in the absorption of the solution as well as differences in the adjustment of the optical path for different measurements.
- 30 differences in the adjustment of the optical path for different measurements. In the cell a diffusion controlled mixture of educt and reduction products is present. Still, by analyzing the changes in the acquired spectra we can precisely determine structural changes upon reduction by comparing the spectra at the reduction potential with the ocp (open circuit potential) spectrum, which are both normalized to the solvent. Upon complete electrolysis the
- 35 spectroscopic signal intensity would simply be higher. In principle it is also possible to disentangle the contributions of educt and reduction product by decomposing the measured spectrum into an ocp-like spectrum corresponding to residual educt and the product spectrum. However, such spectral processing is not trivial since resonance-Raman spectra are affected by a broad background from luminescence of trace amounts of byproducts of the synthesis
- 40 despite purification. This luminescence does also vary upon changing the voltage. For complete electrolysis a different and more complex cell arrangement needs to be used, as described in detail in Q. Hu, A. S. Hinman, *Anal. Chem.* **2000**, *72*, 3233–3235.; R. S. Czernuszewicz, K. A. Macor, *J. Raman Spectrosc.* **1988**, *19*, 553–557.^{3,4}
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Theoretical methods

Quantum chemical calculations were performed with the GAUSSIAN 09 program.³ The geometry and vibrational frequencies of the ground state was obtained by means of density functional theory (DFT) using the XC functional B3LYP. The 28-electron (60-electron) relativistic effective core potential MWB was used with its basis set for the ruthenium (platinum) atom. The 6-31G(d) double- ζ basis set was employed for the ligands. To correct for the lack of anharmonicity and the approximate treatment of electron correlation, the

- 10 harmonic frequencies were scaled by the factor 0.97. The vertical excitation energies (200 states) and oscillator strengths were obtained from time dependent DFT (TDDFT) calculations within the adiabatic approximation with the same XC functional, pseudopotential and basis set. The effects of the interaction with a solvent (acetonitrile, ϵ =35.688, n=1.344) on the geometry and excitation energies were taken into account by the integral equation
- 15 formalism of the polarizable continuum model (IEFPCM). The nonequilibrium procedure of solvation was used for the calculation of the excitation energies, which is well adapted for processes where only the fast reorganization of the electronic distribution of the solvent is important. Finally, it should be mentioned that the four *tert*-butyl groups of the original catalyst were approximated in the calculations by methyl groups. This allows a reduction of
- 20 the computational cost of the simulations without affecting the spectroscopic properties of the complexes.The RR spectra of the non-reduced and reduced **RuPt** were obtained with a method described

in details in the literature.^{4,5} This requires the calculation of excited state gradients for the states involved in the IL and MLCT bands. The CAM-B3LYP XC functional was employed for the computation of the gradients because this method provided the most accurate RR spectra for the related RuPd compound.⁴

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Scheme S1 Light-induced electron transfer (red shaded) and electrochemical reduction (blue shaded) of a dinuclear hydrogen-evolving **RuM** (M=Pd) photocatalyst. Intermediates of the photochemical path under catalytic conditions are difficult to access, but can be mimicked and characterized by *in situ* spectro-electrochemical techniques.



Figure S1 Comparison of the steady state absorption spectra of RuPd (black graph) and RuPt (blue graph) dissolved in ACN / 0.1 M TBABF₄.



Figure S2 Difference UV-vis absorption spectra obtained during reduction of RuPd.









Figure S4 Calculated molecular orbitals involved in photo-excitation of single reduced **RuPt**. The MLCT at around 450 nm is dominated by charge transfer into acceptor orbitals of the tbbpy ligand (A). Only minor contributions arise from the Ru-to-tpphz MLCT transition (B). The lowest energy transition at around 600 nm is assigned to an intraligand π - π * charge transfer localized on the tpphz fragment (C).



Figure S5 Resonance-Raman spectro-electrochemical response of **Ru** (A), **RuPd** (B) and **RuPt** (C) during electrochemically reduction in ACN / 0.1 M Bu₄NBF₄, excited at 458 nm. Vibrational resonances of the reduced species (red spectra) assigned to tbbpy modes (marked with a cross) either increase or remain unchanged in intensity whereas the modes, assigned to the tpphz ligand (marked with a hash key) are decreased by approximately 20% in intensity for all three complexes.

For band assignment of RR spectral features the nonresonant Raman spectrum of the tpphz ligand has been used because in case of a delocalized aromatic electronic configuration the Raman resonances of ring breathing modes of the cyclic aromatic structure have a large Raman cross section, since the polarization is strongly changing during the vibration. Upon electronic transition the photoelectron is also directed to the aromatic system, which is why vibrations of the aromatic system are enhanced. Therefore, the same vibrations are visible in resonant and nonresonant Raman spectra of this aromatic tpphz ligand. Indeed the RR spectrum of the reduced **RuPt** excited at 514 nm is in excellent agreement with the nonresonant Raman spectrum of the free tpphz ligand [M. Karnahl, S. Tschierlei, C. Kuhnt, B. Dietzek, M. Schmitt, J. Popp, M. Schwalbe, S. Krieck, H. Görls, F. W. Heinemann, et al., *Dalton Trans. Camb. Engl. 2003* 2010, *39*, 2359–2370].



Figure S6 Wavelength dependent resonance-Raman spectra of **RuPt** dissolved in ACN. The applied Raman excitation wavelengths match the lowest energy MLCT absorption band of **RuPt**. Spectral data were decomposed by Lorentz fits into the contribution of vibrational modes of the tbbpy-ligands (blue labelled) and of the tpphz-ligand (magenta labelled bands). An increasing contribution of the tpphz ligand to the FC point with decreasing excitation energy is observed.

It should be noted that during the spectro-electrochemical RR experiments a diffusion-controlled mixture of reduced and non-reduced species is present in the laser focus volume.
I.e., the experimental spectra at 514 nm excitation are the superposition of the RR spectra of the non-reduced species and the reduced species possessing MLCT and IL transitions (Fig S7 B). This explains the only qualitative agreement of the experimental and theoretical RR

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spectra (Fig. S7). The calculated spectra are based on the structure of the pure reduction states of **RuPt**, but all energetically allowed transitions were taken into account, e.g., for the single reduced species electronic resonances with the tpphz IL π - π^* transition and the MLCT transition. Qualitatively, there is good agreement between experiment and calculations indicating charge transfer to the tpphz bridging ligand upon photoactivation (Fig. S8).

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Figure S7 TDDFT-calculated (A) and experimental (B) resonance-Raman spectra of non-reduced (black) and electrochemically reduced (red) **RuPt**, excited at 514 nm. Experiment and calculations are in qualitatively good agreement, indicating charge transfer to the tpphz bridging ligand upon photoactivation.



Figure S8 Most prominent resonance-Raman active vibrations of reduced RuPt (λ_{exc} = 514nm). Resonance-Raman features are primarily assigned to tpphz modes.



Figure S9 RR spectra of **RuPt**, excited at 458 nm (left) and at 514 nm (right) before applying potential (black curve) and after recovery upon reoxidation of the reduced species at more positive potentials (blue curve). Only minor alterations in the spectra prove the general reversibility and recovery upon reoxidation of the reduced **RuPt**.