Angewandte Chemie
International Edition

Water Splitting

DOI: 10.1002/anie.200906595

Photochemical Fate: The First Step Determines Efficiency of H_2 Formation with a Supramolecular Photocatalyst**

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Dedicated to Professor Dirk Walther on the occasion of his 70th birthday

The photocatalytic splitting of water into molecular hydrogen and oxygen using sunlight represents a promising solution to the looming energy crisis.[1–3] Despite this potential no large-scale technical processes have been developed. However, each green leaf accomplishes the photocatalytic splitting of water at ambient temperature and low light intensities—an example that provides incentive.[1] Only in the last 20 years has detailed information become available on the structure and the function of the complex molecular apparatus and its subunits, which enable this feat.[4–9] Based on these insights the development of artificial photochemical molecular devices (PMDs) for photoinduced water splitting is feasible, in which a photoredox-active center is linked to a reaction center through a redox-active bridge.[1,10–13] In contrast to the intensively studied intermolecular systems[10,14] these PMDs offer the opportunity to study the connection between intramolecular electron-transfer processes and catalytic conversion on a molecular basis by means of spectroscopy. Strategies for the design of PMDs are thus guided by considering how the photoexcited state determines catalytic activity. The design approaches applied so far have been based on the assumption that the catalytic efficiency is determined predominantly by the electron-storage capability of the bridging ligand in the PMD.[15,16] Herein we scrutinize this assumption using the example of the intramolecular

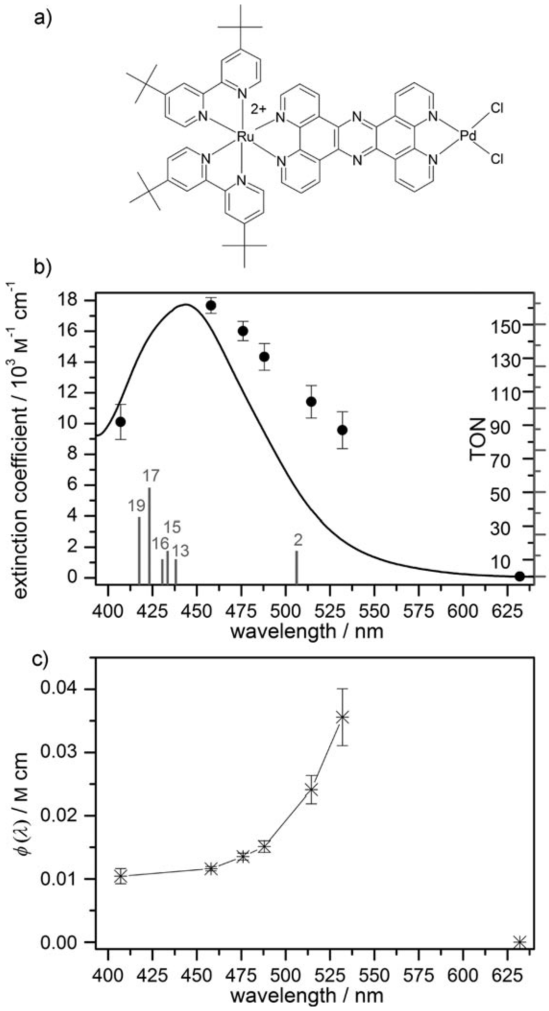

Figure 1. a) Structure of **RuPd**. b) Absorption spectrum of **RuPd** in acetonitrile (——), TON spectrum (●), and the calculated oscillator strengths of the S_n states (gray). c) Efficiency spectrum $\Phi(\lambda)$ of the photon-to-hydrogen conversion of the catalytic process calculated as the ratio of the TON values and the extinction coefficient, normalized to a constant photon flux.

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[**] Correspondence regarding the synthesis and catalysis should be addressed to Prof. Dr. Sven Rau and correspondence concerning the Raman spectra should be addressed to Prof. Dr. Jürgen Popp. This research was supported financially by the Thüringer Ministerium für Bildung, Wissenschaft und Kultur (grant no. B 514-09049). J.P. and B.D. acknowledge financial support from the FCI. S.R. and M.K. thank the DFG and the University of Jena. J.G. thanks the Carl-Zeiss Foundation.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200906595.

H_2-evolving photocatalyst $[(\mathrm{tbbpy})_2\mathrm{Ru}(\mathrm{tpphz})\mathrm{PdCl}_2](\mathrm{PF}_6)_2$ (**RuPd**, Figure 1 a; tbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine, tpphz = tetrapyrido[3,2-a:2′,3′-c:3′′,2′′-h:2′′′,3′′′-j]phenazine).[15] Previous results indicated that photoexcitation of **RuPd** within the metal–ligand charge-transfer (MLCT) band yields an excited state with excess electron density spread over both tbbpy and the tpphz bridging ligand.[17] Herein we describe how catalytic efficiency is linked to the localization of electron density in the initially populated excited state.

The amount of hydrogen produced was measured for various irradiation laser wavelengths (see the Supporting Information). Figure 1 b displays the resulting TON spectrum TON(λ) (TON = turnover number) together with the MLCT absorption spectrum and the oscillator strengths of **RuPd** calculated by TDDFT (time-dependent density functional theory). The maximum TON of 161 is obtained close to the extinction maximum at $\lambda = 458$ nm (Figure 1 b). This TON, which is significantly higher than that in previous investigations, is associated with the addition of 10 vol % H_2O. The activating effect of water might be the result from altered solvent polarity, increased proton mobility, or the propensity of water molecules to act as ligands at the Pd center. For other excitation energies the TON values decrease according to the absorption spectrum. Similar behavior was observed recently for heterogeneous photocatalytic hydrogen production with graphitic C_3N_4 (g-C_3N_4) where the catalytic activity strictly follows the absorption spectrum.[18,19] However, for the supramolecular catalyst **RuPd** remarkable differences between the absorption spectrum and TON(λ) become evident. The extinction coefficient tails off much more steeply in the range of 450 to 550 nm than the TON(λ) values. This finding raises the question whether the absorption of photons of any wavelength within the MLCT band of **RuPd** would yield identical catalysis results. To address this question the TON values were converted into an efficiency spectrum $\Phi(\lambda)$ of the catalysis, which was calculated from the ratio of the TON values and the extinction coefficient of **RuPd** normalized to a constant photon flux (see Figure 1 c and the Supporting Information).

It is clear from Figure 1 c that $\Phi(\lambda)$ increases with increasing wavelength in the range between 400 and 530 nm. $\Phi(630\,\mathrm{nm}) = 0$ indicates a spectral range in which absorbed photons do not result in catalytic activity.

The efficiency spectrum $\Phi(\lambda)$ (Figure 1 c) shows that the extinction coefficient does not correlate with the TON(λ) (Figure 1 b). The absorption of low-energy photons leads to higher catalytic efficiency than the absorption of higher energy photons. Thus the observed discrepancy between $\Phi(\lambda)$ and TON(λ) can be explained by the fact that the absorption spectrum exhibits smaller extinction coefficients for photons of longer wavelengths and lower energy.

With respect to the spectral dependence of hydrogen production, the present study shows that excitation of **RuPd** at shorter wavelengths leads to a higher integrated hydrogen production than excitation at, for example, $\lambda = 514$ nm. However, the photon-to-hydrogen conversion efficiency $\Phi(\lambda)$ shows the opposite trend (Figure 1 c). To examine the molecular mechanism underlying the efficiency spectrum $\Phi(\lambda)$, we characterized the initial starting point of the photochemical reaction, that is, the Franck–Condon region, by means of resonance Raman (RR) spectroscopy. RR spectra contain information about modes that display a large nuclear displacement from the equilibrium geometry at the Franck–Condon point.[20]

For a quantitative analysis the RR spectra were normalized to the solvent band at 1375 cm^{-1} and deconvoluted by fitting them to a sum of Lorentzian profiles. The mode assignment was based on RR spectra of the complex $[(\mathrm{tbbpy})_3\mathrm{Ru}]^{2+}$, and on DFT and TDDFT calculations (Figure 2 a).[17] Figure 2 a displays the quantitative assigment of the modes to different ligands. In Figure 2 b the area of the different ligand-associated modes normalized to the total area of all modes is plotted as a function of the excitation wavelength. This analysis reveals that when the excitation wavelength is shifted to lower energy, the electron density of the excited state shifts from the terminal tbbpy to the tpphz bridging ligand . This result is confirmed by the TDDFT-calculated RR spectra (see Figure 2 and the Supporting Information).

When the electron density distribution of the initially photoexcited state is compared to the efficiency spectrum $\Phi(\lambda)$ (Figure 2 d), it becomes apparent that the latter spectrum correlates strongly with a localization of the electron density on the tpphz bridging ligand. In other words, for increasing pump wavelengths the contribution of the tpphz ligand on the localization of the electron density of the first excited state increases simultaneously with the efficiency spectrum (Figure 2 d). This correlation indicates the importance of the initial photoexcitation for the efficiency of the catalyst: The efficiency of hydrogen production is to a great extent influenced by the localization of the electron density (< 10 fs) of the initial excitation despite the relatively slow Ru→Pd electron transfer (a few 100 ps)[17] and the yet slower diffusion-limited reduction of the charge-separated state by the electron donor. If MLCT results in the transfer of an electron to one of the terminal tbbpy ligands, this excitation is less likely to contribute to hydrogen production than the direct excitation of the tpphz bridging ligand would.

Our results indicate future challenges for the synthesis of PMDs.[2] The Franck–Condon point must be designed in such a way that already the initial electron-transfer step proceeds directionally towards the catalytically active center. This points out the importance of specific ”Franck–Condon design” to be considered along with conventional parameters such as the electron-storage capabilities of the bridging ligand,[21] rapid electron and energy transport within the supramolecular system,[13,22,23] and the stability of the catalytically active charge-separated state.

Based on the correlation between the initial electron density distribution of the excited state (in less than 10 fs) in the supramolecular catalyst, which depends on the excitation wavelength, and the amount of hydrogen formed under identical excitation conditions, the general design concept must be re-examined, and all potential photoaccessible states at the photocenter must be taken into account. A more active photocatalyst should generate a high portion of a bridging-ligand-localized excited state at all incident wavelengths. The optimization approaches implemented so far focusing pri-

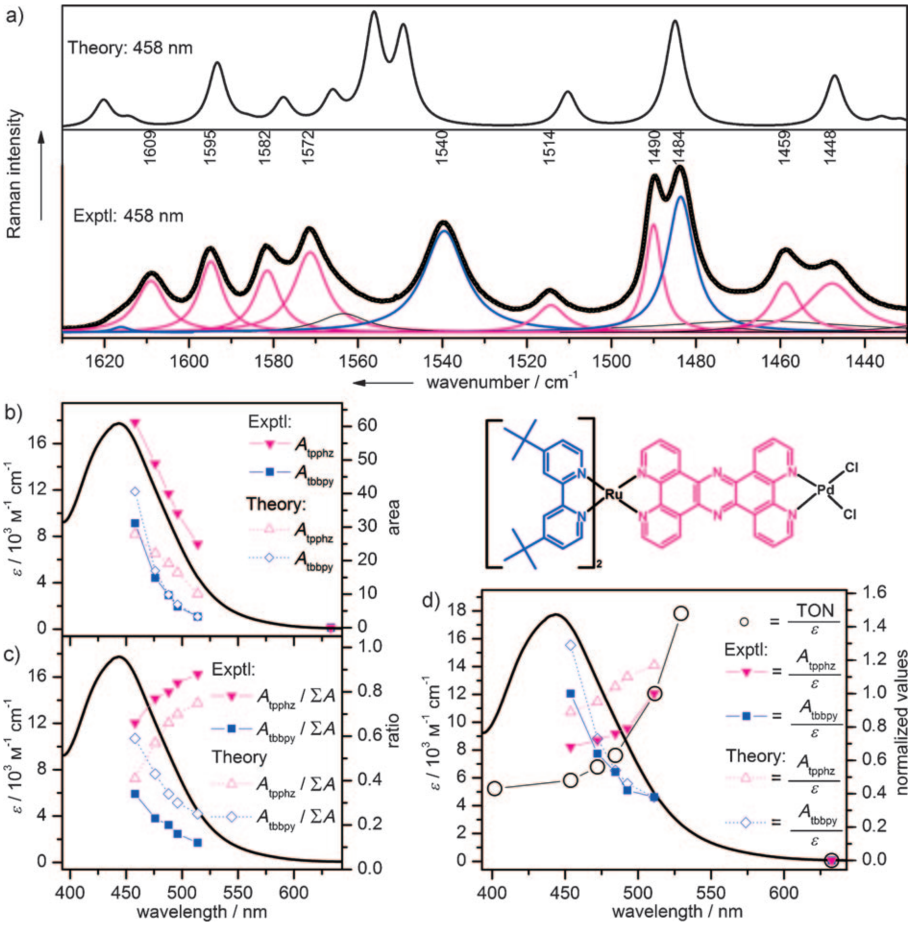

Figure 2. a) TDDFT-calculated resonance Raman (RR) spectrum and experimental RR spectrum (black) of **RuPd** normalized to the acetonitrile solvent band at 1375 cm^{-1} ($\lambda_{excitation} = 458$ nm). The RR spectrum was deconvoluted by fitting to a sum of Lorentzians to determine the vibrational modes of the two ligands, tbbpy (blue) and tpphz (magenta). The overall fit is represented by the yellow dotted line. The same deconvolution procedure was also applied for the excitation wavelengths 476, 488, 496, and 514 nm (see the Supporting Information). b–d) Absorption spectrum of **RuPd**: b) Peak areas of the RR bands of the tbbpy and the tpphz ligands; c) Peak areas of the RR bands of the tbbpy and tpphz ligands divided by the sum of the peak areas of tbbpy and tpphz modes; d) Correlation of initial localization, that is, area of RR bands of tpphz and tbbpy divided by the extinction coefficient, with the efficiency spectrum $\Phi(\lambda)$.

marily on the electron-storage capability of the bridging ligand must be corrected such that terminal ligands are chosen appropriately. In the process it should be ensured that the Franck–Condon point is not localized on the terminal ligands; in other words, optimal terminal ligands should not be able to accept electrons in the electronic excited state. A potential group of ligands that combine these newly defined requirements together with a stabilization of Ru^{II} centers are bibenzimidazoles because they do not contribute to the localization of the first excited state.[24] This observation is very reminiscent of natural photosynthesis where fast and highly efficient directional energy transfer occurs prior to electron transfer from the reaction center, thus limiting detrimental side reactions. The key to unlock the full potential of light-driven molecular catalysis lies in answering the question of how the multitude of initially populated MLCT states can be converted to one reactive state with high efficiency.

Experimental Section

Technical details of the RR spectroscopy can be found in Ref. [20]. Information about the detection and calculation of hydrogen and calculation of the RR spectra can be found in the Supporting Information.

Received: November 23, 2009
Revised: December 14, 2009

Keywords: hydrogen · photocatalysis · resonance Raman spectroscopy · ruthenium · water splitting

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