

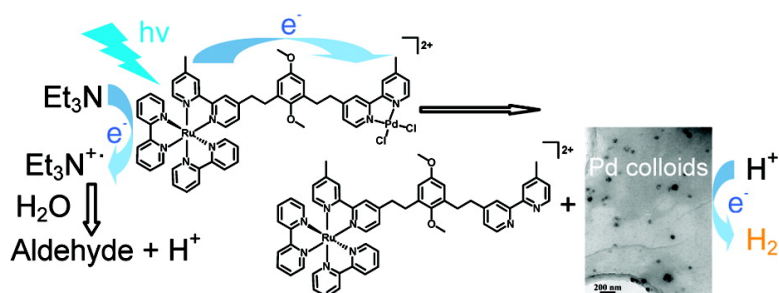
Communication

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The Role of Colloid Formation in the Photoinduced H₂ Production with a Ru^{II}–Pd^{II} Supramolecular Complex: A Study by GC, XPS, and TEM

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The search for efficient solar energy conversion schemes has refueled the interest in supramolecular assemblies for photoinduced H₂ production.^{1–3} The multimolecular systems developed in the late 1970s were based on chromophores such as ruthenium(II) polypyridyl complexes, a sacrificial electron donor, an electron mediator (e.g., methyl viologen), and a metal oxide/metal colloidal catalyst.^{4,5} In contrast to these early systems, supramolecular complexes would benefit from the specific location of the redox-active components to promote the desired charge separation. Furthermore, utilizing homogeneous catalysts in such assemblies would allow precise tuning of the metal catalyst for efficient H₂ production. Along these lines, Sakai and co-workers recently described a supramolecular complex composed of a ruthenium(II) polypyridyl complex covalently linked to a 2,2'-bipyridyl Pd^{II} complex.¹ Upon irradiation of an aqueous solution of the dinuclear complex in the presence of EDTA as sacrificial electron donor, photoinduced H₂ production was achieved (4.8 turnovers).^{1a} Rau et al. studied a rigid dinuclear system composed of a ruthenium(II) polypyridyl-type complex linked to a Pd^{II} unit via a tetrapyrrophenazine (tpphz) bridge and reported 56 turnovers in CH₃CN/triethylamine (TEA) mixtures, where TEA functions as both electron and proton source.² The details of the mechanism for H₂ production with the reported dinuclear complexes remain unclear, however. This prompted us to study a similar Ru^{II}–Pd^{II} dinuclear complex, Ru–DMB–Pd (Figure 1, inset).⁶ Herein we report on the photoinduced H₂ production in CH₃CN/TEA solutions of Ru–DMB–Pd. As metal colloids of group 10 are active H₂ production catalysts,⁵ we focused on the potential formation of Pd colloids by photodegradation of the complex and their possible role in H₂ evolution. For this purpose, we have analyzed the reaction mixture at different stages of the H₂ formation reaction by transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS).

Ru–DMB–Pd was synthesized from the previously published Ru–DMB–bpy (bpy = 2,2'-bipyridine)⁷ lacking the Pd^{II} unit and was characterized by NMR spectroscopy, ESI mass spectrometry, and electrochemistry (Supporting Information). The electrochemical data indicate that photoreduction of the Pd^{II} complex could proceed via reductive quenching of the Ru chromophore by the amine,⁸ while direct electron transfer from the ³MLCT (metal-to-ligand charge transfer) state of the Ru chromophore is thermodynamically less feasible.

Photoinduced H₂ production with Ru–DMB–Pd was studied under continuous illumination with visible light from a tungsten filament lamp. A cutoff filter ($\lambda \geq 475$ nm) allowed for excitation into the MLCT band of the Ru unit while avoiding excitation of

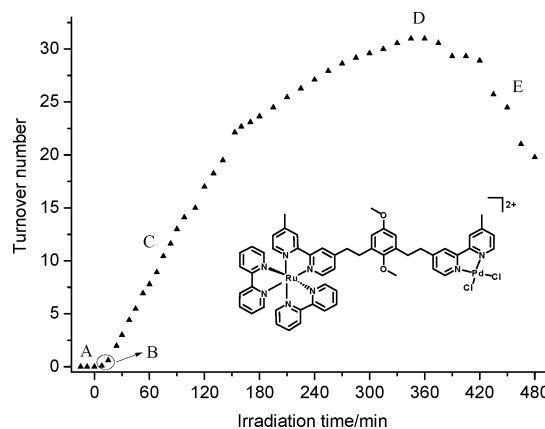


Figure 1. The evolution of H₂ as a function of time for the visible light irradiation ($\lambda \geq 475$ nm) of 50 μ M Ru–DMB–Pd in CH₃CN/TEA solution; inset: molecular structure of Ru–DMB–Pd.

the Pd^{II} unit (Supporting Information). The illumination experiments were performed in deaerated solutions of Ru–DMB–Pd (50 μ M) in CH₃CN/TEA (2:1 v/v), and H₂ formation was monitored on-line by GC analysis of the headspace above the reaction mixture.⁹ Figure 1 shows a typical plot of the amount of H₂ formed as a function of illumination time. Irrespective of the actual mechanism of H₂ formation, the amount is expressed as a formal turnover number based on the initial quantity of Ru–DMB–Pd. No H₂ was formed in the dark (A), and initial H₂ evolution (B) was only observed after an induction time of several minutes. Maximum rates of H₂ production (C) exceeded 10 turnovers per hour, and the peak amount accumulated in the illumination apparatus corresponds to more than 30 turnovers after a few hours (D). The illumination was usually terminated after around 8 h (E).¹⁰ Control experiments under similar conditions using Ru–DMB–bpy lacking the Pd^{II} unit showed negligible H₂ production, demonstrating that a Pd catalyst is responsible for the H₂ formation with Ru–DMB–Pd.¹¹ However, bimolecular experiments using Ru–DMB–bpy or [Ru(bpy)₃]²⁺ as chromophore and Pd(4,4'-Me₂-bpy)Cl₂ as catalyst resulted in H₂ production rates comparable to that of the Ru–DMB–Pd system (Supporting Information). This result indicates that the H₂ production with Ru–DMB–Pd is not necessarily an intramolecular process in the intact supramolecule.

To investigate the potential formation of colloids and their involvement in H₂ production, TEM and XPS measurements were carried out on samples of the reaction mixture at different reaction stages (Figures 2 and 3). In the TEM measurements of solutions cast on copper grids, small Pd nanoparticles (<5 nm) appeared already at the catalysis start point (B) (Figure 2a) while 45 min of irradiation (C) in the same experimental run resulted in much larger

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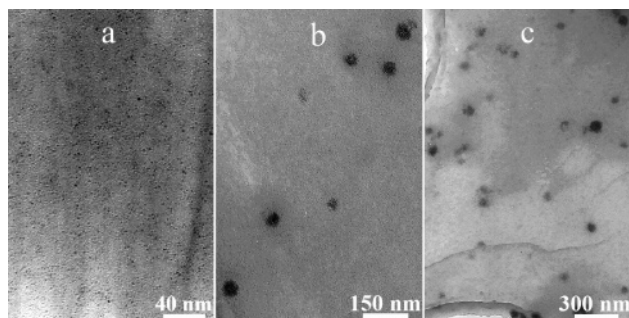


Figure 2. TEM images of samples taken from (a) catalysis start point; (b) maximum rate; (c) end stage.

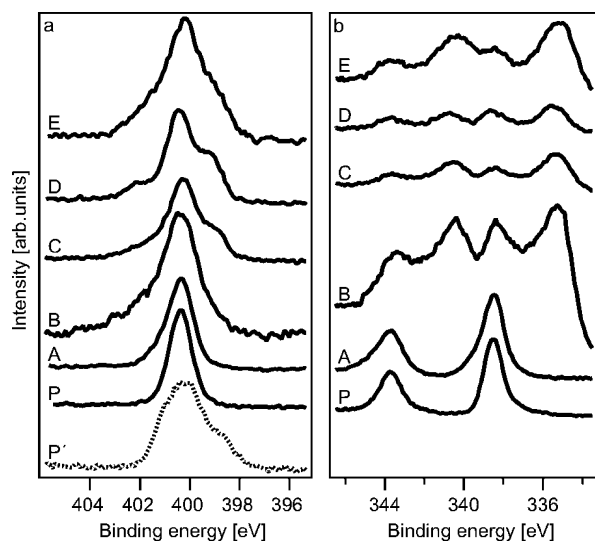


Figure 3. XPS spectra of (a) N 1s, (b) Pd 3d measured at different reaction stages: (A) before irradiation; (B) catalysis start point; (C) maximum rate; (D) maximum TON; (E) end stage and as isolated powders of Ru-DMB-Pd (P, solid traces) and Ru-DMB-bpy (P', dashed trace).

(30–50 nm) colloids (Figure 2b). At the end stage (E), even more colloids were detected, suggesting further dissociation of Pd from Ru-DMB-Pd (Figure 2c). The notion of photoinduced release of Pd from Ru-DMB-Pd was corroborated by ESI-MS data from illuminated samples of the reaction mixture that showed major peaks of the mono- (at $m/z = 1090$) and double-charged (at $m/z = 473$) ions from the Ru-DMB-bpy complex lacking the Pd unit (Supporting Information).

To monitor both Pd colloids and molecular Pd species, XPS measurements on evaporated samples were carried out at the reaction stages A–E as well as on the isolated powders of Ru-DMB-Pd and Ru-DMB-bpy (Figure 3). As shown in Figure 3a, the N 1s spectrum of Ru-DMB-bpy (trace P') is built up by two peaks at binding energies of 400.1 and 399.0 eV, originating from nitrogen coordinated to Ru and nitrogen in the free bpy, respectively. In contrast, the N 1s spectrum of Ru-DMB-Pd (trace P) is built up by a single peak at a binding energy of 400.1 eV, showing that the nitrogen atoms coordinated to Pd have a N 1s binding energy very similar to those coordinated to Ru. Moreover, the Pd 3d spectrum of Ru-DMB-Pd (Figure 3b, trace P) shows a single spin-orbit split (Pd 3d_{5/2} and Pd 3d_{3/2}) signal at binding energies expected for Pd^{II}.¹² Dissolving Ru-DMB-Pd in CH₃CN/TEA prior to irradiation had no effect on either N 1s or Pd 3d peak positions (traces A), confirming that no dissociation of Pd from Ru-DMB-

Pd occurred at this stage.¹³ During irradiation (traces B–E), a build up of the N 1s signal at the position of free bpy indicates a gradual dissociation of Pd from Ru-DMB-Pd. At the same time, a new spin-orbit split peak with a 3.2 eV shift is evident in the Pd 3d spectra in accordance with reduction of Pd^{II} to Pd⁰.¹² The valence change of Pd and the appearance of free bpy can be associated with the formation of metallic Pd colloids via release of Pd from the photoreduced Ru-DMB-Pd complex. Assuming that Pd colloids are the actual catalyst for proton reduction, the induction period for H₂ production could be related to the photoinduced formation of the colloidal catalyst.

In summary, we have described a Ru^{II}-Pd^{II} dinuclear complex and have shown that H₂ is generated upon visible light irradiation of this complex in the presence of TEA as sacrificial electron and proton donor. As evidenced by XPS and TEM measurements, Pd is released from the complex upon illumination and the appearance of Pd⁰/colloids strongly correlates in time with the formation of H₂. From our data, we cannot exclude the formation of H₂ by homogeneous catalysis on the dinuclear complex, but our results strongly suggest that heterogeneous catalysis on the Pd colloids has a major contribution to the observed H₂ formation. These results emphasize that the mechanistic interpretation of H₂ production with supramolecular systems in general requires careful consideration of alternative mechanisms.

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Supporting Information Available: Synthetic and experimental details; ESI-MS, NMR, CV, and UV-vis characterization of Ru-DMB-Pd; control experiments and XPS data for Ru. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (9) The headspace to liquid ratio of the illumination apparatus was sufficiently large to neglect dissolved H₂ for quantification.
- (10) At the end stage, the H₂ concentration decreased, which can be associated with leakage or consumption of the produced H₂.
- (11) A control experiment using Pd(4,4'-Me₂-bpy)Cl₂ without the Ru chromophore in the CH₃CN/TEA mixture showed no H₂ production.
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- (13) Note that no nitrogen signal can be associated with the volatile CH₃CN/TEA mixture due to the high vacuum in the sample chamber (Supporting Information).

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