The effect of peripheral bipyridine ligands on the photocatalytic hydrogen production activity of Ru/Pd catalysts

Gurmeet Singh Bindra, a Martin Schulz, a Avishek Paul, a Suraj Soman, a Robert Groarke, a Jane Inglis, a Mary T. Pryce, a Wesley R. Browne, b Sven Rau, c Brian J. Maclean d and Johannes G. Vos* a

Received 29th June 2011, Accepted 23rd August 2011
DOI: 10.1039/c1dt11241d

A pyrazine bridged ruthenium/palladium bimetallic photocatalyst with peripheral 4,4’-dicarboxyethyl-2,2’-bipyridine ligands, \( \text{EtOOC-RuPd} \), is reported, together with its 2,2’-bipyridine analogue. Upon irradiation with visible light, \( \text{EtOOC-RuPd} \) catalyses the production of hydrogen gas whereas the complex RuPd does not.

Hydrogen is widely perceived to be one of the primary replacement fuels, in particular for transport, due to its exceptionally high energy density/mass ratio. The photocatalytic production of hydrogen is therefore a major challenge in converting solar energy directly to chemical energy. One of the most promising approaches towards this goal is the use of molecular photocatalysts that utilise visible light to drive proton reduction and it can be envisaged that such systems comprise of a light-harvesting antenna (photosensitiser) that can donate electrons to a catalytically active centre to which it is connected via a bridging ligand.

Due to their exceptional photophysical and redox properties Ru(II) polypyridyl complexes are an excellent choice as the light harvesting centre while Pd(II) or Pt(II) are the metal of choice for the catalytically active centres. Alternative combinations already reported are Re/Co, Ru/Pd, Ru/Pt, Os/Rh, Ru/Rh, Pt/Co, Ir/Rh. The intramolecular approach in which a bridging ligand facilitates photoinduced electron transfer from the light harvesting centre to the hydrogen forming centre requires vectorial electron transfer to be mediated by the bridging ligand. This realisation has led to the application of bridging ligands that are more electron deficient than the peripheral ligands. However, recently Rau et al. have proposed that in addition to the final (lowest lying) excited state, higher lying excited (Franck–Condon) states can also play an important role, as seen from the excitation wavelength dependency of turnover numbers (TONs). However, other factors such as lifetime of the charge separated states and secondary processes during the multiple electron transfer steps may influence catalytic activity.

Here we report direct evidence of the importance of the peripheral 2,2’-bipyridyl (bpy) ligands in the photocatalytic process. The photocatalytic activity of the Ru(II)/Pd(II) complex based on the non-substituted 2,2’-bipyridyl (bpy) ligand (RuPd) is contrasted with that of the analogous heterobimetallic complex in which the more electron deficient 4,4’-di(carboxyethyl)bipyridine ligand replaces bpy (i.e. \( \text{EtOOC-RuPd} \)). The structures of both complexes are shown in Fig. 1. The bridging ligand is 2,5-dicarboxyethyl-2,2’-bipyridine (2,5-dpp).

In agreement with the earlier report by Sakai and Ozawa, the complex RuPd was found to show no photocatalytic activity towards hydrogen production. In stark contrast we found that the dinuclear catalyst \( \text{EtOOC-RuPd} \) could achieve TONs for \( \text{H}_2 \) production of up to 400 (32 \( \mu \text{mol} \) after 18 h).

Photocatalytic reactions were performed by irradiation of the reaction mixtures at 470 nm using triethylamine (TEA) as the terminal reductant to regenerate the Ru(II) complex. The presence of water was found to be a key factor for photocatalytic hydrogen production, with hydrogen formation not observed in its absence. The role played by water in the catalysis is however manifold: (1) as a source of protons, and hence an increase in water content accelerates to a certain point the reaction, (2) to facilitate...
proton-transfer and (3) to increase solvent polarity thereby stabilizing polar intermediates. Control experiments with the mononuclear precursor compounds Ru and EtOOC-Ru confirmed the necessity of the presence of the Pd(II) centre. The time-dependence of dihydrogen formation is shown in Fig. S2 (ESI†). Different behaviour is observed for the preformed complex EtOOC-RuPd and the in situ formed complex (i.e. EtOOC-Ru + Pd(CHCN)2Cl2, 1:1 molar ratio). Both graphs show a sigmoidal time profile eventually reaching a plateau that indicates deactivation of the catalyst. An induction period was observed with dihydrogen production reaching a maximum after ca. 3.5 h for EtOOC-RuPd and ca. 5.5 h for EtOOC-Ru + Pd(CHCN)2Cl2. The longer induction period for the in situ formed binuclear complex supports the conclusion that the active catalyst is a binuclear EtOOC-Ru/Pd complex. For further details on the photocatalytic reactions see the ESI.†

Colloid formation has been discussed as a possible process in catalysis with Ru/Pd complexes13–14 and although this behaviour cannot be excluded in the present system it is important to note that the formation of a precipitate was not observed during the photocatalysis with either RuPd or EtOOC-RuPd.‡

Previous investigations have shown that the 2,5-dpp bridge enables relatively strong coupling between the metal centres and that the emissive state of the [(bpy)Ru-(2,5-dpp)]+ and [(bpy)Ru-(2,5-dpp)-Ru(bpy)]2+ compounds is dpp-based.15–21 Absorption spectroscopy shows that RuPd and EtOOC-RuPd have similar features with the intraligand and metal-to-hp charge transfer bands being shifted towards lower energy by ca. 15–40 nm. However, the lowest energy MLCT of EtOOC-RuPd is shifted by 10 nm to higher energy compared with the RuPd complex (Table 1). Similarly the emission spectrum of EtOOC-RuPd is shifted by 30 nm to the blue compared to RuPd. Due to the lower π* energy of the EtOOC-bpy ligands they are better π-acceptors which leads to a stabilisation of the ground state and is manifested in a red shift of 40 nm in the 1MLCT ← GS transition involving the peripheral bpy/(EtOOC)2bpy ligands. This is in agreement with the higher oxidation potential of EtOOC-RuPd with respect to RuPd. These data suggest as expected that the π*-energy levels for the carboxyethyl ligands are lower in energy than those of the bpy ligands. The UV/Vis absorption spectrum of the complex undergoes several changes already when TEA is added, as indicated by absorption and emission spectroscopy. Similar changes are observed when following the photocatalysis by absorption spectroscopy, assigned tentatively to exchange of the chloride ligands.

The dramatic differences in the photocatalytic activities towards H2 production between the polypyridyl-Ru/Pd complexes RuPd and EtOOC-RuPd, i.e. with the former inactive and the latter highly active (TONs of 400), is surprising. Both heterobimetallic complexes exhibit very short excited state lifetimes, indicating efficient interaction between the two metal centres (electron transfer quenching). The observations indicate the importance of the peripheral ligand for photoinduced electron transfer as proposed earlier by Rau et al.11 It is also important to note that hydrogen formation is not directly linked to the formation of precipitates as is observed for other systems.14

Further investigations concerning the nature of the electron transfer and additional factors governing the overall catalytic activity of intramolecular photocatalysts such as the nature and location of the involved electronic states are in progress.

This research is supported by the EPA grant 2008-ET-MS-3-S2, the SFI under Grants No. 07/SRC/B1160, 08/RFP/CHE1349, the Netherlands Organisation for Scientific Research through a VIDI grant (WRB) and the German Research Association (DFG SFB 583, GRK 1626; SR).

Notes and references

†TONs were determined by gas chromatography after irradiation of the reaction mixture for 18 h. Reaction mixture: cat. = 4.08 × 10−4 M, c(TEA) = 2.15 M, 5 vol% of water in acetonitrile. The mixture was irradiated with an LED torch at 470 nm. The TON is the average of three independent measurements.

‡The addition of mercury has been proposed as a method to identify the involvement of colloids (by quenching their activity). In the present system however addition of mercury leads to decomposition of the complexes even in the absence of light and hence this standard test is not applicable here. It should be noted that the coordination of PdCl2 to both Ru and EtCOO-Ru would be essentially the same and hence dissociation to form Pd-colloids would be expected from both complexes if it occurred. The absence of H2 evolution in the case of RuPd suggests that Pd dissociation to yield an active colloid does not occur in the present system.

Table 1 Photophysical and electrochemical properties of the dinuclear complexes RuPd, EtOOC-RuPd and their mononuclear precursors Ru, EtOOC-Ru

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Abs. (log e)/nm</th>
<th>Em./nm</th>
<th>τ/ns</th>
<th>Oxidation/+mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuPd</td>
<td>539 (4.00)</td>
<td>807</td>
<td>&lt; 0.5</td>
<td>+1.56</td>
</tr>
<tr>
<td>EtOOC-RuPd</td>
<td>526 (4.20)</td>
<td>778</td>
<td>&lt; 0.5</td>
<td>+1.75</td>
</tr>
<tr>
<td>Ru</td>
<td>483 (3.98)</td>
<td>685</td>
<td>266</td>
<td>+1.33</td>
</tr>
<tr>
<td>EtOOC-Ru</td>
<td>467 (4.25)</td>
<td>630</td>
<td>564</td>
<td>+1.68</td>
</tr>
</tbody>
</table>

* Determined by time correlated single photon counting at 293 K in aerated acetonitrile solution. † From cyclic voltammetry in acetonitrile (0.1 M TBAPF6) vs. Ag/AgCl. All data were acquired at 293 K.