The Critical Role Played by the Catalytic Moiety in the Early-Time Photodynamics of Hydrogen-Generating Bimetallic Photocatalysts


The effect of the catalytic moiety on the early-time photodynamics of Ru/M (M = Pt or Pd) bimetallic photocatalysts is studied by ultrafast transient absorption spectroscopy. In comparison to the Ru/Pd photocatalyst described earlier, the Ru/Pt analogue shows complex excited-state dynamics with three distinct kinetic components ranging from sub-ps to 10^2 ps, requiring a more sophisticated photophysical model than that developed earlier for the Ru/Pd complex. In the Ru/Pt photocatalyst, an additional lower-lying excited state is proposed to quench the hot higher-lying triplet metal-to-ligand charge transfer states. Furthermore, a strong excitation wavelength dependence on the population of excited states is observed for both the Ru/Pt and Ru/Pd complexes, indicating a non-equilibrated distribution even on the 10^1 ps timescale. These insights shed light on the significant impact of the catalytic moiety on the fundamental early-time photophysics of Ru-based photocatalysts.

Ru^II-polypyridyl complexes continue to attract interest due to their remarkable photophysical and photochemical properties.[1] Their excited-state redox properties and excellent stability as visible-light harvesting components are especially suited in photocatalysis.[2] For example, bimetallic Ru^II complexes have demonstrated both light-induced proton reduction and water oxidation,[3] highlighting their potential in photocatalytic water splitting by using sunlight[4] for renewable fuel production.[5] Large-scale devices based on light-driven molecular photocatalysts have yet to be realized, primarily due to kinetic limitations. Hence, a great deal of focus has been placed on achieving a detailed kinetic understanding of the fundamental aspects of the photodynamical processes to guide the design of new photocatalysts.[6] In particular, understanding the early-time photodynamics[7] that follow photoexcitation is essential in addressing subsequent steps in the overall process of solar-to-fuel conversion.

The reactivity of bimetallic Ru/Pt and Ru/Pd photocatalysts for proton reduction has been shown to depend strongly on the specific molecular structure of the compounds, both in regard to the bridging ligand connecting the metal atoms and the peripheral ligands.[8] These classes of photocatalysts are in general based on a Ru-polypyridyl photosensitizer connected to a catalytic moiety via a bridging ligand (see Figure 1). Several recent studies have focused on the relation between overall photocatalytic reactivity and the nature of the bridging and peripheral ligands.[9] Less attention, however, has been directed towards understanding the influence of the catalytic center on the early-time photodynamics of the photosensitizer unit.

Recently, Rau et al. reported that the early-time photodynamics of two Ru/MCl₂ photocatalysts, where M = Pd or Pt, were similar, despite different photocatalytic efficiencies of the complexes.[10] Furthermore, it was noted that replacing the PtCl₂ unit with PtI₂ improved both the photocatalytic reactivity and stability, though again the early-time photodynamics were not altered.[11] These results suggest that, although the overall photocatalytic performance can be influenced strongly by a change in the catalytic moiety, the early-time photodynamics are not necessarily affected.

We have recently developed a series of Ru/Pd and Ru/Pt photocatalysts (RuPd and RuPt, Figure 1) with 2,2'-bipyridine (bpy) peripheral ligands and a 2,2'-S₂;2'-terpyridine (tpy) bridging ligand.[12] The absorption spectra are provided in Figure S1 of the Supporting Information (SI). Both complexes show comparable photocatalytic performance under similar re-
action conditions with respect to turnover number and turnover frequency for \( \text{H}_2 \) generation. This observation raises the question whether or not the catalytic moiety has only a marginal effect on the early-time photodynamics of the photosensitizer in general.

The present work focuses on the early-time photodynamics of the complexes Ru, RuPd and RuPt using fs transient absorption (TA) spectroscopy and addresses the important role of the catalytic moiety. Mechanistic insight into the dynamics is achieved from excitation wavelength (\( \lambda_{\text{exc}} \)) dependent studies. We recently studied the early-time photodynamics of Ru and RuPd that follow excitation at 480 nm into their singlet metal-to-ligand charge transfer (1 MLCT) states. A photophysical model was established through target analysis of the TA data, in which rapid intersystem crossing within 100 fs\(^{[13]} \) into triplet metal-to-ligand charge transfer (3 MLCT) states is followed by inter-ligand electron transfer (ILET) towards the bridging ligand. The latter process proceeds on the early ps timescale across the triplet excited state manifold in competition with vibrational cooling.\(^{[14]} \) Note that this ILET process is different from intra-ligand electron transfer.\(^{[15,16]} \) In the present contribution we compare RuPd and RuPt by using a generalized model, which combines ILET and vibrational cooling as 3 MLCT\(^{bpy} \rightarrow 3 \text{ MLCT}^{tpy} \) internal conversion (IC).\(^{[16]} \) This model is equivalent to a sequential model in global analysis, and gives time constants of 5.3 \( \pm \) 0.5 ps for Ru and 7.0 \( \pm \) 0.5 ps for RuPd. The TA data, fits and the evolution associated spectra (EAS) are provided in Figures S2–S4.

The TA spectra of RuPt (Figure 2A, \( \lambda_{\text{exc}} = 480 \) nm) are qualitatively similar to those observed for Ru and RuPd,\(^{[14]} \) allowing for assignment of the individual bands by analogy. The negative band between 440 and 520 nm is due to ground state bleach (GSB), while the broad excited state absorption (ESA) band \( > 520 \) nm is associated with ligand-to-metal charge-transfer transitions. The ESA bands at about 420 and 375 nm are likely due to ligand-centered \( \pi^* - \pi \) transitions of the tpy and bpy radical anions, respectively.\(^{[14,17]} \) The kinetic traces of RuPt (Figure 2B), however, illustrate that the temporal evolution of these bands is more complex than for Ru and RuPd. The ESA signal at 371 nm decays bi-exponentially over several ps following photoexcitation. Notably, the ESA signal at this wavelength, and at 420 nm, increases again after about 100 ps. Furthermore, the negative signal at 475 nm recovers, likely due to contributions from ESA overlapping with the GSB signal (see below).

Interpretation of the TA data shown in Figure 2 is not straightforward due to the overlap of the individual bands. The complex spectrototemporal behavior of RuPt requires three time constants to achieve a global fit using a sequential model. The EAS obtained (Figure 3A) provide insight into the nature of the overlapping TA bands. EAS1 is representative of the TA spectrum at early times, that is, immediately after intersystem crossing. The coexistence of the ESA bands around 375 nm and 420 nm indicates that both 3 MLCT\(^{bpy} \) and 3 MLCT\(^{tpy} \) states are populated, in agreement with our recent resonance Raman studies.\(^{[12]} \) EAS1 evolves into EAS2 over 865 \( \pm \) 445 fs (\( \tau_i \));\(^{[18]} \) with the latter spectrum showing reduced absorption for both the bpy\(^{\cdot -} \) and tpy\(^{\cdot -} \) ligand-centered bands. These data indicate the presence of a third excited state in addition to the 3 MLCT\(^{bpy} \) and 3 MLCT\(^{tpy} \) states, which absorbs less between 350 and 450 nm and quenches these 3 MLCT states as shown in Figure 4. This state will be referred to as \( \text{T}_3 \), where T indicates the triplet character and the subscript distinguishes it from 3 MLCT\(^{bpy} \) and 3 MLCT\(^{tpy} \) triplet states. Importantly, this 3 MLCT \( \rightarrow \text{T}_3 \) quenching process is incomplete, with EAS2 further evolving into EAS3 over 4.1 \( \pm \) 0.4 ps (\( \tau_i \)). This value resembles the 3 MLCT\(^{bpy} \) \( \rightarrow 3 \text{ MLCT}^{tpy} \) IC time constant discussed above for RuPd (7.0 \( \pm \) 0.5 ps) and is likely associated with a similar process. This assignment is supported by the signal increase around 420 nm concomitant with a signal decrease below ca. 385 nm, similar to the TA results obtained for RuPt (Figure S3). However, as compared to RuPd the tpy\(^{\cdot -} \) ligand-centered band at about 420 nm of RuPt is relatively broad and overlaps with the GSB. As a result of the rise of this tpy\(^{\cdot -} \) ligand-centered band over time, the kinetic trace at 475 nm (Figure 2B) shows a decrease in amplitude over time. EAS3 develops into EAS4 with a time constant of 117 \( \pm \) 11 ps (\( \tau_i \)). The tpy\(^{\cdot -} \) ligand-centered band at about 420 nm increases concom-

![Figure 2](image-url)  
*Figure 2. TA spectra at 480 nm excitation (A) and kinetic traces at key wavelengths (B) for RuPt. Fits based on a sequential model are represented as solid curves.*
itant with a decrease in ESA > 520 nm. The origin of this spectral development will be discussed below.

The new T₃ state in RuPt is likely associated with the Ptᴵᴵ moiety, as it is not observed in Ru and RuPd. The T₃ state quenches the ³ MLCT_bpy and ³ MLCT_tpy states at a sub-ps time-scale and is likely lower in energy. Excitation at longer wavelengths would be expected to enhance the direct population of the T₃ state and provide insight into its nature. The evolution of the spectral features obtained with excitation at 516 nm (Figure S5) is qualitatively analogous to that observed at 480 nm excitation, and global fitting using a sequential model yields a similar set of three time constants (Table 1). The EAS obtained provide insight into the nature of overlapping TA bands. Comparison of the individual EAS shown in Figure 3A (λ_exc = 480 nm) and 3B (λ_exc = 516 nm) evidences changes in intensities, indicating a change in excited state population distribution with excitation wavelength. EAS1 in Figure 3B shows that with excitation at 516 nm the tpy ligand-centered band around 420 nm is more intense than the bpy ligand-centered band at ca. 375 nm, while EAS1 in Figure 3A shows that this order is reverse with excitation at 480 nm. This difference indicates that exciting RuPt at longer wavelengths results in an increase in the initial ³ MLCT_tpy/³ MLCT_bpy population ratio directly after intersystem crossing.

The EAS1 → EAS2 developments shown in Figures 3A and 3B suggest that as compared to the ³ MLCT states, the T₃ state absorbs weakly < 450 nm and strongly > 530 nm. This interpretation is supported by the data at 527 nm excitation (Figure 5A) clearly showing these features. The minor signal development < 450 nm with λ_exc = 527 nm complicates global analysis. Nevertheless, tentative fitting[19] yields the EAS shown in Figure 5B and time constants of 980 ± 184 fs and 99 ± 12 ps, which agree with the τ₁ and τ₂ values obtained upon excitation at shorter wavelengths (Table 1). The 980 ± 184 fs time constant (EAS1 → EAS2) indicates quenching of ³ MLCT states by the T₃ state. Notably, ³ MLCT_bpy → ³ MLCT_tpy IC is not observed with excitation at 527 nm, possibly due to the relatively minor population of the ³ MLCT_tpy state. EAS2 further develops into EAS3 over 99 ± 12 ps, showing a decrease in amplitude > 530 nm similar to the EAS3 → EAS4 transition in Figure 3A (λ_exc = 480 nm) and 3B (λ_exc = 516 nm), indicating that the ~ 100 ps process is inde-

### Table 1. Overview of the obtained time constants and their assignment.

<table>
<thead>
<tr>
<th>λ_exc</th>
<th>480 nm</th>
<th>516 nm</th>
<th>527 nm</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru</td>
<td>τ₁ (ps)</td>
<td>5.3 ± 0.5</td>
<td>4.5 ± 0.4</td>
<td>N.A.</td>
</tr>
<tr>
<td>RuPd</td>
<td>τ₁ (ps)</td>
<td>7.0 ± 0.5</td>
<td>10.7 ± 0.7</td>
<td>N.A.</td>
</tr>
<tr>
<td>RuPt</td>
<td>τ₁ (fs)</td>
<td>865 ± 445</td>
<td>600 ± 398</td>
<td>980 ± 184</td>
</tr>
<tr>
<td></td>
<td>τ₁ (ps)</td>
<td>4.1 ± 0.4</td>
<td>5.1 ± 0.5</td>
<td>N.A.</td>
</tr>
<tr>
<td></td>
<td>τ₂ (ps)</td>
<td>117 ± 11</td>
<td>136 ± 20</td>
<td>99 ± 12</td>
</tr>
</tbody>
</table>

Figure 3. EAS of RuPt at 480 nm (A) and 516 nm (B) excitation, obtained from a global fitting of the TA data using a sequential model.

Figure 4. Overview of processes following intersystem crossing into the triplet manifold. For simplicity the singlet potential energy surfaces and the ground state are not shown. A) Vibrational cooling, B) ³ MLCT_tpy → ³ MLCT_bpy internal conversion, C) quenching of the ³ MLCT states by the T₃ state.

Figure 4. Overview of processes following intersystem crossing into the triplet manifold. For simplicity the singlet potential energy surfaces and the ground state are not shown. A) Vibrational cooling, B) ³ MLCT_tpy → ³ MLCT_bpy internal conversion, C) quenching of the ³ MLCT states by the T₃ state.
dependent of $\lambda_{\text{exc}}$. A contribution from solvated electrons is unlikely, as otherwise a signal increase over $\sim 80$ ps (rather than the current signal decrease) and an isosbestic point at about 660 nm due to equilibration between solvated electrons and solvated dimer anions would have been observed. Furthermore, the decay time of the ESA band $>530$ nm (which matches the photoluminescence lifetime of RuPt of about 300 ns at $\lambda_{\text{exc}} = 532$ nm) is not consistent with the presence of solvated electrons. The $\sim 100$ ps process observed for RuPt only may be related to the T$_1$ state. Importantly, delocalization of the lowest unoccupied molecular orbital (i.e. which is involved in the T$_1$ state) over the bridging ligand is likely to involve some mixing with the Pt d-orbitals as observed for a related Ru/Pt complex with a bipyridyl-based bridging ligand. This increased delocalization in RuPt may rationalize the weak ESA signal $<450$ nm. Electron density redistribution over the tpy-Pt-I moiety accompanied by solvent reorientation can be expected to change the platinum bond lengths, through changes in backbonding effects, which will be investigated in future studies by X-ray absorption techniques.

The pronounced excitation wavelength dependence observed for RuPt indicates that a thermally equilibrated excited (THEXI) state distribution is not reached even at 500 ps after photoexcitation, and sub-nm or faster equilibration between the T$_1$ state and the $^3$MLCT states is unlikely. Excitation at 527 nm likely results in population of the T$_1$ state predominantly, while at 480 nm the $^3$MLCT states are populated substantially. The T$_1$ state is unlikely to involve localization of electron density on the ligands (i.e. bpy and tpy radical anions) as it has only weak absorption below 450 nm. This state is more likely associated with the Pt moiety, as it is not observed for Ru and RuPd. A competing vibrational cooling process may be inhibiting complete quenching of hot $^3$MLCT states into the T$_1$ state, resulting in a substantial proportion of the molecules in the sample relaxing to local minima on the $^3$MLCT potential energy surfaces. Note that this non-equilibrated population differs remarkably from a recent work on a series of heteroleptic Ru$^+$ complexes showing the establishment of a Boltzmann-distributed population of the $^3$MLCT states over about 100 ps independent of $\lambda_{\text{exc}}$.

A consequence of this non-equilibrated population is the bi-exponential photoluminescence decay. It was proposed earlier that the formation of two non-equilibrated emissive states can occur for certain combinations of ligands. The present study provides, to the best of our knowledge, the first ultrafast photodynamical evidence that the population of these non-equilibrated states can be controlled by variation in excitation wavelength, that is, the final distribution depends on the Franck-Condon states populated initially. It is of note that in earlier temperature-dependent ps transient Raman studies by Hopkins et al., it was proposed that for some Ru$^+$-polypyridyl complexes ILET might occur $>500$ ns, resulting in a non-equilibrated population of excited states. The fs time resolution of our work allows this conclusion to be extended, that is, even though inter-ligand IC occurs at an early ps timescale, excited states can remain non-equilibrated at longer timescales.

The complex early-time photodynamics of RuPt discussed above raise the question as to whether an excitation wavelength dependence is also present in Ru and RuPd, prompting us to record TA data for these two complexes with excitation at 516 nm (Figure 59 and S10). The EAS of RuPd (Figure 6A, $\lambda_{\text{exc}} = 480$ nm and Figure 6B, $\lambda_{\text{exc}} = 516$ nm) show an excitation wavelength dependence, though much less than for RuPt. ESA1 represents the spectrum immediately after intersystem crossing from the Franck-Condon states. Therefore, comparison of the intensities at 370 and 420 nm in the individual EAS2 in Figure 6A and 6B hence indicates that the population of the relaxed $^3$MLCT$_{\text{tpy}}$ state becomes less with increasing $\lambda_{\text{exc}}$ while this trend is opposite for RuPt. ESA2 represents the spectrum after $^3$MLCT$_{\text{tpy}}$ to $^3$MLCT$_{\text{tpy}}$ IC. Comparison of the intensities at 370 and 420 nm in the individual ESA2 in Figure 6A and 6B hence indicates that the population of the relaxed $^3$MLCT$_{\text{tpy}}$ state becomes less with increasing $\lambda_{\text{exc}}$. This trend is in agreement with the slower IC time constant of $10.7 \pm 0.7$ ps obtained by exciting RuPd at 516 nm as compared to the value obtained at $\lambda_{\text{exc}} = 480$ nm (7.0 $\pm$ 0.5 ps). This trend can be rationalized by the formation of...
of a cooler $^1$MLCT$_{bpy}$ state and hence a higher effective barrier to IC. As a result, a greater proportion of molecules relax to an excited state localized at the peripheral bpy ligands as local energetic minima. Hence, a non-equilibrated excited state population is also present in RuPd, leading to a bi-exponential photoluminescence decay. Note that a mono-exponential photoluminescence decay was observed for RuPd, suggesting a thermally equilibrated population of the $^3$MLCT states. However, the EAS at $\lambda_{exc}=480$ and 516 nm are different (Figure S4). This apparent discrepancy may be explained by a non-equilibrated population of $^3$MLCT states with similar lifetimes.

The $\lambda_{exc}$ dependent photodynamics may have a major impact on $\Phi(\lambda)$ for photocatalytic H$_2$ generation, that is, the wavelength-dependent H$_2$ turnover number corrected for the molar absorbptivity. If the same population distribution of THEXI states would have been reached independent of $\lambda_{exc}$, $\Phi(\lambda)$ can be expected to be independent of $\lambda_{exc}$. However, earlier studies on RuPd showed an increase of $\Phi(\lambda)$ as $\lambda_{exc}$ increases. A similar $\Phi(\lambda)$ response was found by Popp et al. for a related photocatalyst. Resonance Raman studies on the latter photocatalyst indicate that increasing $\lambda_{exc}$ leads to a larger population of Franck-Condor states localized on the bridging ligand, suggesting that the initial electron density localization in the Franck-Condor region determines the photocatalytic reactivity. In a recent TA study on the same Ru/Pd photocatalyst, a long-lived ($>1$ ps) coherent vibrational motion was observed. As this phenomenon only occurs at high $\lambda_{exc}$ values and is absent in the mononuclear Ru precursor, it may be associated to the bridging ligand and influenced by the Pd catalytic moiety. These results highlight the importance of the bridging ligand with regard to $\Phi(\lambda)$.

On the other hand, the present study indicates that increasing $\lambda_{exc}$ reduces the $^3$MLCT$_{bpy}$ $\rightarrow$ $^3$MLCT$_{tpy}$ IC rate, likely due to population of a cooler $^3$MLCT$_{bpy}$ state, effectively increasing the barrier height to IC. As a result, an increased electron density population relaxes at the peripheral bpy ligands as local energetic minima. Considering their remote position relative to the catalytic moiety, this effect seems to be in contradiction with the higher $\Phi(\lambda)$ value observed at longer wavelengths. This result indicates that the peripheral bpy ligands may play a more important role for photocatalytic H$_2$ generation than so far considered. Importantly, we observed that functionalizing the peripheral bpy ligands of Ru/Pt and Ru/Pd photocatalysts with electron withdrawing ester groups significantly increases the H$_2$ evolution reactivity. The question is hence to what extent the early-time population of the peripheral ligands affects the subsequent photoelectrochemical processes occurring at longer timescales.

In summary, ultrafast TA studies on two analogous bimetallic photocatalysts RuPd and RuPt show that the catalytic moiety has a strong impact on the early-time photodynamics of the photosensitizer unit. A substantial dependence of excitation wavelength is observed for both complexes, indicating that population of the excited states has not equilibrated even 500 ps after photoexcitation. For RuPd, a $^3$MLCT$_{bpy}$ $\rightarrow$ $^3$MLCT$_{tpy}$ IC process takes place within several ps, likely competing with vibrational cooling. The $^3$MLCT$_{tpy}$/$^3$MLCT$_{bpy}$ population ratio appears to be $\lambda_{exc}$ dependent, which may allow the $\Phi(\lambda)$ observed to be rationalized. For RuPt, more complex photodynamics are observed involving a lower-lying $T_1$ excited state quenching $^3$MLCT states on a sub-ps timescale. With sufficient high excitation photon energy (e.g. 480 nm, 2.58 eV), $^3$MLCT$_{bpy}$ $\rightarrow$ $^3$MLCT$_{tpy}$ IC is also observed to occur within a few ps, analogous to RuPd. However, lower excitation photon energies (e.g. 527 nm, 2.35 eV) are likely to result in predominant population of the $T_1$ state, which is possibly related to the Pt moiety. A time-resolved L-edge x-ray absorption spectroscopy study exclusively probing processes occurring at the Pt moiety is currently underway.

**Experimental Section**

The synthesis and characterization of the complexes were published in previous work. The TA setup was described in detail earlier. Samples were prepared by dissolving the complexes in anhydrous acetonitrile (Sigma–Aldrich, purity > 99.9%) in 1 mm path length quartz cuvettes. The RuPt concentration was 0.53 mM for TA using 480 nm excitation, corresponding to an optical density (OD) of 0.45. The RuPt sample used for experiments at 516 nm excitation had an OD of 0.17 (i.e. 0.56 mm), while for measurements
at 527 nm excitation the sample had an OD of 0.12 (i.e. 0.59 mm). RuPd and Ru samples have similar ODs as compared to those of RuPt. The polarization angle between the pump and probe was set at magic angle (54.7°). The 480 nm pulse pump had a full width at half maximum (FWHM) bandwidth of 7 nm and a 50 fs pulse duration. The 516 nm pulse pump had a FWHM bandwidth of 6 nm and a 74 fs pulse duration. The 527 nm pulse pump had a FWHM bandwidth of 7 nm and a 68 fs pulse duration. In all cases the pulse durations were within a 10 fs range of the transform limit, assuming a Gaussian pulse shape and a time-bandwidth product of 0.44. The excitation power was kept sufficiently low (480 nm: 3.7×10¹⁰ photons/(cm² pulse), 516 nm: 5.1×10¹⁰ photons/(cm² pulse), 527 nm: 4.4×10¹⁰ photons/(cm² pulse)) and verified to be in the linear regime. The TA data were numerically corrected for chirp and analyzed using the open-source program Glo- taran.21,22

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