University of Groningen

The critical role played by the catalytic moiety in the early-time photodynamics of hydrogen generating bimetallic photocatalysts

Pan, Qing; Mecozzi, Francesco; Korterik, Jeroen P.; Vos, Johannes G.; Browne, Wesley R.; Huijser, Annemarie

Published in:
 Chemphyschem

DOI:
[10.1002/cphc.201600458](https://doi.org/10.1002/cphc.201600458)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
 Publisher's PDF, also known as Version of record

Publication date:
 2016

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Pan, Q., Mecozzi, F., Korterik, J. P., Vos, J. G., Browne, W. R., & Huijser, A. (2016). The critical role played by the catalytic moiety in the early-time photodynamics of hydrogen generating bimetallic photocatalysts. *Chemphyschem*, 17(17), 2654-2659. <https://doi.org/10.1002/cphc.201600458>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

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

Qing Pan,^[a] Francesco Mecozzi,^[b] Jeroen P. Korterik,^[a] Johannes G. Vos,^[c] Wesley R. Browne,^[b] and Annemarie Huijser^{*[a]}

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 10² 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 10² 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.

Figure 1. Molecular structure of **RuPd** (left) and **RuPt** (right). The mononuclear Ru precursor is denoted as **Ru**, S = solvent (acetonitrile).

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 Pt-Cl₂ unit with Pt-I₂ 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':5',2''-terpyridine (tpy) bridging ligand.^[9b,12] The absorption spectra are provided in Figure S1 of the Supporting Information (SI). Both complexes show comparable photocatalytic performance under similar re-

[a] Q. Pan, J. P. Korterik, Dr. A. Huijser
MESA + Institute for Nanotechnology
University of Twente, P.O. Box 217
7500 AE Enschede (The Netherlands)
E-mail: j.m.huijser@utwente.nl

[b] F. Mecozzi, Prof. Dr. W. R. Browne
Molecular Inorganic Chemistry
Stratingh Institute for Chemistry
University of Groningen, 9747 AG, Groningen (The Netherlands)

[c] Prof. Dr. J. G. Vos
SRC for Solar Energy Conversion
School of Chemical Sciences, Dublin City University
Glasnevin, Dublin 9 (Ireland)

Supporting Information for this article can be found under
<http://dx.doi.org/10.1002/cphc.201600458>.

action conditions with respect to turnover number and turnover frequency for 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 (λ_{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 ($^1\text{MLCT}$) 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 ($^3\text{MLCT}$) 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.^[7b,15] In the present contribution we compare **RuPd** and **RuPt** by using a generalized model, which combines ILET and vibrational cooling as $^3\text{MLCT}_{\text{bpy}} \rightarrow ^3\text{MLCT}_{\text{tpy}}$ internal conversion (IC).^[16] This model is equivalent to a sequential model in global analysis, and gives time constants of 5.3 ± 0.5 ps for **Ru** and 7.0 ± 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 spectrotemporal 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 $^3\text{MLCT}_{\text{bpy}}$ and $^3\text{MLCT}_{\text{tpy}}$ states are populated, in agreement with our recent resonance Raman studies.^[12] EAS1 evolves into EAS2 over 865 ± 445 fs (τ_1),^[18] with the latter spectrum showing reduced absorption for both the bpy^- and tpy^- ligand-centered bands. These data indicate the presence of a third excited state in addition to the $^3\text{MLCT}_{\text{bpy}}$ and $^3\text{MLCT}_{\text{tpy}}$ states, which absorbs less between 350 and 450 nm and quenches these $^3\text{MLCT}$ states as shown in Figure 4. This state will be referred to as T_3 , where T indicates the triplet character and the subscript distinguishes it from $^3\text{MLCT}_{\text{bpy}}$ and $^3\text{MLCT}_{\text{tpy}}$ triplet states. Importantly, this $^3\text{MLCT} \rightarrow T_3$ quenching process is incomplete, with EAS2 further evolving into EAS3 over 4.1 ± 0.4 ps (τ_2). This value resembles the $^3\text{MLCT}_{\text{bpy}} \rightarrow ^3\text{MLCT}_{\text{tpy}}$ IC time constant discussed above for **RuPd** (7.0 ± 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 **RuPd** (Figure S3). However, as compared to **RuPd** the tpy^- 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^- 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 ± 11 ps (τ_3). The tpy^- ligand-centered band at about 420 nm increases concom-

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.

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) $^3\text{MLCT}_{\text{bpy}} \rightarrow ^3\text{MLCT}_{\text{tpy}}$ internal conversion, C) quenching of the $^3\text{MLCT}$ states by the T_3 state.

itant with a decrease in ESA > 520 nm. The origin of this spectral development will be discussed below.

The new T_3 state in RuPt is likely associated with the Pt^{II} moiety, as it is not observed in Ru and RuPd. The T_3 state quenches the $^3\text{MLCT}_{\text{bpy}}$ and $^3\text{MLCT}_{\text{tpy}}$ 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 T_3 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 ($\lambda_{\text{exc}} = 480$ nm) and 3B ($\lambda_{\text{exc}} = 516$ 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 $^3\text{MLCT}_{\text{tpy}}/^3\text{MLCT}_{\text{bpy}}$ population ratio directly after intersystem crossing.

The EAS1 $\rightarrow$ EAS2 developments shown in Figures 3A and 3B suggest that as compared to the $^3\text{MLCT}$ states, the T_3 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 $\lambda_{\text{exc}} = 527$ 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 τ_1 and τ_3 values obtained upon excitation at shorter wavelengths (Table 1). The 980 ± 184 fs time constant (EAS1 $\rightarrow$ EAS2) indicates quenching of $^3\text{MLCT}$ states by the T_3 state. Notably, $^3\text{MLCT}_{\text{bpy}} \rightarrow ^3\text{MLCT}_{\text{tpy}}$ IC is not observed with excitation at 527 nm, possibly due to the relatively minor population of the $^3\text{MLCT}_{\text{bpy}}$ state. EAS2 further develops into EAS3 over 99 ± 12 ps, showing a decrease in amplitude > 530 nm similar to the EAS3 $\rightarrow$ EAS4 transition in Figure 3A ($\lambda_{\text{exc}} = 480$ nm) and 3B ($\lambda_{\text{exc}} = 516$ nm), indicating that the ~ 100 ps process is inde-

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

λ_{exc}		480 nm	516 nm	527 nm	Assignment
Ru	τ_1 (ps)	5.3 ± 0.5	4.5 ± 0.4	N.A.	$^3\text{MLCT}_{\text{bpy}} \rightarrow ^3\text{MLCT}_{\text{tpy}}$
RuPd	τ_1 (ps)	7.0 ± 0.5	10.7 ± 0.7	N.A.	$^3\text{MLCT}_{\text{bpy}} \rightarrow ^3\text{MLCT}_{\text{tpy}}$
RuPt	$\tau_1^{[18]}$ (fs)	865 ± 445	600 ± 398	980 ± 184	$^3\text{MLCT} \rightarrow T_3$
	τ_2 (ps)	4.1 ± 0.4	5.1 ± 0.5	N.A.	$^3\text{MLCT}_{\text{bpy}} \rightarrow ^3\text{MLCT}_{\text{tpy}}$
	τ_3 (ps)	117 ± 11	136 ± 20	99 ± 12	Charge redistribution tpy-Pt-I moiety

Figure 5. A) TA spectra of **RuPt** obtained at 527 nm excitation. Fits are represented by solid curves. B) EAS obtained from global analysis using a sequential model.

pendent of λ_{exc} . A contribution from solvated electrons is unlikely, as otherwise a signal increase over ~ 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^[20] 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^[21]) is not consistent with the presence of solvated electrons. The ~ 100 ps process observed for **RuPt** only may be related to the T_3 state. Importantly, delocalization of the lowest unoccupied molecular orbital (i.e. which is involved in the T_3 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.^[22] 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-ns or faster equilibration between the T_3 state and the $^3\text{MLCT}$ states is unlikely. Excitation at 527 nm likely results in population of the T_3 state predominantly, while at 480 nm the $^3\text{MLCT}$ states are populated substantially. The T_3 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 $^3\text{MLCT}$ states into the T_3 state, resulting in a substantial proportion of the molecules in the sample relaxing to local minima on the $^3\text{MLCT}$ potential energy surfaces. Note that this non-equilibrated population differs remarkably from a recent work on a series of heteroleptic Ru^{II} complexes showing the establishment of a Boltzmann-distributed population of the $^3\text{MLCT}$ states over about 100 ps in-

dependent of λ_{exc} .^[23] A consequence of this non-equilibrated population is the bi-exponential photoluminescence decay.^[12] It was proposed earlier that the formation of two non-equilibrated emissive states can occur for certain combinations of ligands.^[24] 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.,^[25] it was proposed that for some Ru^{II}-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 S9 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 of the tpy⁻ ligand-centered band at about 420 nm and the bpy⁻ ligand-centered band at about 370 nm provides insight into the initial $^3\text{MLCT}_{\text{tpy}}/{}^3\text{MLCT}_{\text{bpy}}$ population ratio upon increasing λ_{exc} , while this trend is opposite for **RuPt** (Figure 3). EAS2 represents the spectrum after $^3\text{MLCT}_{\text{bpy}} \rightarrow {}^3\text{MLCT}_{\text{tpy}}$ IC. 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 $^3\text{MLCT}_{\text{tpy}}$ state becomes less with increasing λ_{exc} . This trend is in agreement with the slower IC time constant of 10.7 ± 0.7 ps obtained by exciting **RuPd** at 516 nm as compared to the value obtained at $\lambda_{\text{exc}} = 480$ nm (7.0 ± 0.5 ps). This trend can be rationalized by the formation

Figure 6. EAS of RuPd at 480 nm (A) and 516 nm (B) excitation.

of a cooler $^3\text{MLCT}_{\text{bpy}}$ 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.^[14] Note that a mono-exponential photoluminescence decay was observed for Ru,^[12,14] suggesting a thermally equilibrated population of the $^3\text{MLCT}$ states. However, the EAS at $\lambda_{\text{exc}}=480$ and 516 nm are different (Figure S4). This apparent discrepancy may be explained by a non-equilibrated population of $^3\text{MLCT}$ states with similar lifetimes.

The λ_{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 absorptivity.^[9b,26] If the same population distribution of THEXI states would have been reached independent of λ_{exc} , $\Phi(\lambda)$ can be expected to be independent of λ_{exc} . However, earlier studies on RuPd showed an increase of $\Phi(\lambda)$ as λ_{exc} increases.^[9b] A similar $\Phi(\lambda)$ response was found by Popp et al. for a related photocatalyst.^[26] Resonance Raman studies on the latter photocatalyst indicate that increasing λ_{exc} leads to a larger population of Franck-Condon states localized on the bridging ligand, suggesting that the initial electron density localization in the Franck-Condon region determines the photocatalytic reactivity.^[26] In a recent TA study on the same Ru/Pd photocatalyst, a long-lived (>1 ps) coherent vibrational motion was observed.^[27] As this phenomenon only occurs at high λ_{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 λ_{exc} reduces the $^3\text{MLCT}_{\text{bpy}} \rightarrow ^3\text{MLCT}_{\text{tpy}}$ IC rate, likely due to population of a cooler $^3\text{MLCT}_{\text{bpy}}$ 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.^[8c,9a,12] 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 $^3\text{MLCT}_{\text{bpy}} \rightarrow ^3\text{MLCT}_{\text{tpy}}$ IC process takes place within several ps, likely competing with vibrational cooling. The $^3\text{MLCT}_{\text{tpy}}/^3\text{MLCT}_{\text{bpy}}$ population ratio appears to be λ_{exc} dependent, which may allow the $\Phi(\lambda)$ observed to be rationalized. For RuPt, more complex photodynamics are observed involving a lower-lying T_3 excited state quenching $^3\text{MLCT}$ states on a sub-ps timescale. With sufficient high excitation photon energy (e.g. 480 nm, 2.58 eV), $^3\text{MLCT}_{\text{bpy}} \rightarrow ^3\text{MLCT}_{\text{tpy}}$ 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_3 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.^[9b,12] The TA setup was described in detail earlier.^[14] 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 pump pulse had a full width at half maximum (FWHM) bandwidth of 7 nm and a 50 fs pulse duration. The 516 nm pump pulse had a FWHM bandwidth of 6 nm and a 74 fs pulse duration. The 527 nm pump pulse 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: 3.7×10^{14} photons/(cm² pulse), 516 nm: 5.1×10^{14} photons/(cm² pulse), 527 nm: 4.4×10^{14} 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.^[28]

Acknowledgements

This work is supported by the Dutch Organization for Scientific Research (NWO), the EU COST Action CM-1202 (PERSPECT-H₂O, short-term scientific mission 16737), the Sectorplan for Physics and Chemistry, the European Research Council (Consolidator Investigator Grant no. 279549, WRB, FM) and Funding from the Ministry of Education, Culture and Science (Gravity program 024.001.035, WRB).

Keywords: molecular photocatalysis • non-equilibrated excited states • photodynamics • ruthenium • transient absorption

- [1] a) A. Juris, V. Balzani, F. Barigelli, S. Campagna, P. Belser, A. Vonzelewsky, *Coord. Chem. Rev.* **1988**, *84*, 85–277; b) S. Campagna, F. Puntoriero, F. Nastasi, G. Bergamini, V. Balzani, *Photochemistry and Photophysics of Coordination Compounds I* **2007**, *280*, 117–214.
- [2] a) A. Company, G. Sabenya, M. González-Bejar, L. Gomez, M. Clemancey, G. Blondin, A. J. Jasniowski, M. Puri, W. R. Browne, J. M. Latour, L. Que, M. Costas, J. Perez-Prieto, J. Lloret-Fillol, *J. Am. Chem. Soc.* **2014**, *136*, 4624–4633; b) C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.* **2013**, *113*, 5322–5363.
- [3] a) H. Ozawa, M. A. Haga, K. Sakai, *J. Am. Chem. Soc.* **2006**, *128*, 4926–4927; b) N. Kaveevivitchai, R. Chitta, R. F. Zong, M. El Ojaimi, R. P. Thummel, *J. Am. Chem. Soc.* **2012**, *134*, 10721–10724.
- [4] a) J. H. Alstrum-Acevedo, M. K. Brennaman, T. J. Meyer, *Inorg. Chem.* **2005**, *44*, 6802–6827; b) L. Alibabaei, M. K. Brennaman, M. R. Norris, B. Kalanyan, W. J. Song, M. D. Losego, J. J. Concepcion, R. A. Binstead, G. N. Parsons, T. J. Meyer, *Proc. Natl. Acad. Sci. USA* **2013**, *110*, 20008–20013; c) K. Fan, F. S. Li, L. Wang, Q. Daniel, E. Gabrielsson, L. C. Sun, *Phys. Chem. Chem. Phys.* **2014**, *16*, 25234–25240.
- [5] N. Armaroli, V. Balzani, *Angew. Chem. Int. Ed.* **2007**, *46*, 52–66; *Angew. Chem.* **2007**, *119*, 52–67.
- [6] L. Hammarström, *Acc. Chem. Res.* **2015**, *48*, 840–850.
- [7] a) M. Karnahl, C. Kuhnt, F. Ma, A. Yartsev, M. Schmitt, B. Dietzek, S. Rau, J. Popp, *ChemPhysChem* **2011**, *12*, 2101–2109; b) S. Tschierlei, M. Presselt, C. Kuhnt, A. Yartsev, T. Pascher, V. Sundström, M. Karnahl, M. Schwalbe, B. Schafer, S. Rau, M. Schmitt, B. Dietzek, J. Popp, *Chem. Eur. J.* **2009**, *15*, 7678–7688.
- [8] a) H. Ozawa, Y. Yokoyama, M. Haga, K. Sakai, *Dalton Trans.* **2007**, 1197–1206; b) Y. Halpin, M. T. Pryce, S. Rau, D. Dini, J. G. Vos, *Dalton Trans.* **2013**, 42, 16243–16254; c) T. Kowacs, Q. Pan, P. Lang, L. O'Reilly, S. Rau, W. R. Browne, M. T. Pryce, A. Huijser, J. G. Vos, *Faraday Discuss.* **2015**, *185*, 143–170.
- [9] a) G. S. Bindra, M. Schulz, A. Paul, S. Soman, R. Groarke, J. Inglis, M. T. Pryce, W. R. Browne, S. Rau, B. J. Maclean, J. G. Vos, *Dalton Trans.* **2011**, *40*, 10812–10814; b) G. S. Bindra, M. Schulz, A. Paul, R. Groarke, S. Soman, J. L. Inglis, W. R. Browne, M. G. Pfeffer, S. Rau, B. J. Maclean, M. T. Pryce, J. G. Vos, *Dalton Trans.* **2012**, *41*, 13050–13059; c) C. V. Suneesh, B. Balan, H. Ozawa, Y. Nakamura, T. Katayama, M. Muramatsu, Y. Nagasawa, H. Miyasaka, K. Sakai, *Phys. Chem. Chem. Phys.* **2014**, *16*, 1607–1616; d) L. Zedler, J. Guthmüller, I. R. de Moraes, S. Kupfer, S. Kriek, M. Schmitt, J. Popp, S. Rau, B. Dietzek, *Chem. Commun.* **2014**, *50*, 5227–5229.
- [10] M. G. Pfeffer, B. Schafer, G. Smolentsev, J. Uhlig, E. Nazarenko, J. Guthmüller, C. Kuhnt, M. Wachtler, B. Dietzek, V. Sundström, S. Rau, *Angew. Chem. Int. Ed.* **2015**, *54*, 5044–5048; *Angew. Chem.* **2015**, *127*, 5132–5136.
- [11] M. G. Pfeffer, T. Kowacs, M. Wachtler, J. Guthmüller, B. Dietzek, J. G. Vos, S. Rau, *Angew. Chem. Int. Ed.* **2015**, *54*, 6627–6631; *Angew. Chem.* **2015**, *127*, 6727–6731.
- [12] T. Kowacs, L. O'Reilly, Q. Pan, A. Huijser, P. Lang, S. Rau, W. R. Browne, M. T. Pryce, J. G. Vos, *Inorg. Chem.* **2016**, *55*, 2685–2690.
- [13] a) A. Cannizzo, F. van Mourik, W. Gawelda, G. Zgrablic, C. Bressler, M. Chergui, *Angew. Chem. Int. Ed.* **2006**, *45*, 3174–3176; *Angew. Chem.* **2006**, *118*, 3246–3248; b) A. T. Yeh, C. V. Shank, J. K. McCusker, *Science* **2000**, *289*, 935–938.
- [14] Q. Pan, F. Mecozzi, J. P. Korterik, D. Sharma, J. L. Herek, J. G. Vos, W. R. Browne, A. Huijser, *J. Phys. Chem. C* **2014**, *118*, 20799–20806.
- [15] C. Goze, C. Leiggener, S. X. Liu, L. Sanguinet, E. Levillain, A. Hauser, S. Decurtins, *ChemPhysChem* **2007**, *8*, 1504–1512.
- [16] Both ILET and vibrational cooling (VC) contribute to the IC rate constant via $1/\tau_{IC} = 1/\tau_{ILET} + 1/\tau_{VC}$, where τ_{IC} , τ_{ILET} and τ_{VC} refer to the time constants for effective IC, ILET and VC, respectively.
- [17] S. Wallin, J. Davidsson, J. Modin, L. Hammarström, *J. Phys. Chem. A* **2005**, *109*, 4697–4704.
- [18] Accurate determination of τ_1 is challenging, as quenching of the ³MLCT_{bpy} and ³MLCT_{tpy} states by T₃ does not necessarily occur with a same rate. Furthermore, the occurrence of band overlap, minor signal changes of the tpy[−] ligand-centered band, and the absorptivity uncertainty of the T₃ state cause a relatively large uncertainty of τ_1 . Nevertheless, as τ_1 is at a distinct order of magnitude as compared to τ_2 and τ_3 , the overall fit based on a sequential model is not significantly influenced.
- [19] The TA data and global fits based on a two-component sequential model are provided in Figure S6. Note that a global fit using a single exponent (one-component sequential model) yields a time constant of 116 ± 19 ps as shown in Figure S7. However, this model results in a poor fit of the GSB signal, as illustrated in Figure S8 and the kinetic traces at 475 nm in Figure S6–S7.
- [20] S. C. Doan, B. J. Schwartz, *J. Phys. Chem. B* **2013**, *117*, 4216–4221.
- [21] These data will be discussed in a time-resolved L-edge X-ray absorption study, probing processes occurring at the Pt moiety.
- [22] H. Ozawa, K. Sakai, *Chem. Commun.* **2011**, 47, 2227–2242.
- [23] C. W. Stark, W. J. Schreier, J. Lucon, E. Edwards, T. Douglas, B. Kohler, *J. Phys. Chem. A* **2015**, *119*, 4813–4824.
- [24] E. C. Glazer, D. Magde, Y. Tor, *J. Am. Chem. Soc.* **2007**, *129*, 8544–8551.
- [25] L. K. Orman, D. R. Anderson, T. Yabe, J. B. Hopkins, *Adv. Chem.* **1990**, *226*, 253–266.
- [26] S. Tschierlei, M. Karnahl, M. Presselt, B. Dietzek, J. Guthmüller, L. González, M. Schmitt, S. Rau, J. Popp, *Angew. Chem. Int. Ed.* **2010**, *49*, 3981–3984; *Angew. Chem.* **2010**, *122*, 4073–4076.
- [27] M. Wachtler, J. Guthmüller, S. Kupfer, M. Maiuri, D. Brida, J. Popp, S. Rau, G. Cerullo, B. Dietzek, *Chem. Eur. J.* **2015**, *21*, 7668–7674.
- [28] J. J. Snellenburg, S. P. Laptinok, R. Seger, K. M. Mullen, I. H. M. van Stokkum, *J. Stat. Softw.* **2012**, *49*, 1–22.

Manuscript received: May 5, 2016

Accepted Article published: June 3, 2016

Final Article published: July 5, 2016