Early-time Photodynamics of Ruthenium-based Photocatalysts for Light-induced Hydrogen Generation

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**EARLY-TIME PHOTODYNAMICS OF
RUTHENIUM-BASED PHOTOCATALYSTS
FOR LIGHT-INDUCED HYDROGEN
GENERATION**

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EARLY-TIME PHOTODYNAMICS OF RUTHENIUM-BASED PHOTOCATALYSTS FOR LIGHT-INDUCED HYDROGEN GENERATION

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Abbreviation list

Abbreviation	Description
CFT	Crystal field theory
DAS	Decay associated spectra
DFT	Density functional theory
EAS	Evolution associated spectra
ESA	Excited state absorption
FC	Frank-Condon
FWHM	Full width at half maximum
GDD	Group delay dispersion
GS	Ground state
GSB	Ground state bleach
GVD	Group velocity dispersion
HOMO	Highest occupied molecular orbital
IC	Internal conversion
ILET	Inter-ligand electron transfer
ISC	Intersystem crossing
LC	Ligand-centered
LFT	Ligand field theory
LMCT	Ligand-to-metal charge transfer
LUMO	Lowest unoccupied molecular orbital
MC	Metal-centered
MCP	Micro channel plate
MLCT	Metal-to-ligand charge transfer
MO	Molecular orbital
NHE	Normal hydrogen electrode
NOPA	Non-collinear optical parametric amplifier
OD	Optical density
OPA	Optical parametric amplifier
PL	Photoluminescence
rR	Resonance Raman
SAS	Species associated spectra
SCE	Saturated calomel electrode
SHG	Second harmonic generation
SVD	Singular value decomposition
TA	Transient absorption
TCSPC	Time correlated single photon counting
TEA	Triethylamine
TOF	Turnover frequency

TON	Turnover number
TRPL	Time-resolved photoluminescence
VC	Vibrational cooling
WLC	White light continuum

Abbreviation

Ligand

2,3-dpp	2,3-di(pyridine-2-yl)pyrazine
2,5-tpy (tpy)	2,2':5',2''-terpyridine
2,6-tpy	2,2':6',2''-terpyridine
bpph	4,7-diphenyl-1,10-phenanthroline
bpy	2,2'-bipyridine
dceb	4,4'-diethoxycarbonyl-2,2'-bipyridine

Abstract

This thesis aims to provide a fundamental understanding of the early-time photodynamics of a series of Ru/M (M = Pd or Pt) bimetallic photocatalysts for light-induced hydrogen generation. This class of complexes adopts a general structure involving a Ru(II) center coordinated to two peripheral ligands and one bridging ligand, which bonds to a catalytic metal center as schematically shown in Figure 1. Photoexcitation of the complexes leads to intra-molecular electron transfer processes, which are investigated by using ultrafast time-resolved spectroscopic techniques. The excited state photodynamics are systematically studied considering the individual building blocks of the complexes (i.e. peripheral/bridging ligands and the catalytic moiety). The knowledge obtained in this thesis facilitates interpreting the structure-reactivity relationship, allowing the photophysical exploration of other analogous complexes, and guiding the optimization of new photocatalysts with improved photocatalytic efficiency.

Figure 1. General structure of the Ru/M (M = Pd or Pt) bimetallic photocatalysts studied in this thesis (A), and a simplified representation illustrating the excited state evolution studied by using the pump-probe method (B).

This thesis is organized in the following way:

- Chapter 1 provides a general background of photocatalytic hydrogen generation, coordination complexes, and time-resolved spectroscopy. In particular, the prototype complex $[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy = 2,2'-bipyridine) is introduced in detail to provide key concepts which are frequently referred to in later chapters.
- Chapter 2 discusses the methodological aspects of transient absorption, which is the main technique used in this thesis.
- Chapter 3 explores the impact of the bridging ligand on the excited state properties of two analogous Ru/Pd complexes.
- Chapter 4 investigates the critical role played by the catalytic moiety in the early-time photodynamics of two analogous Ru/Pd and Ru/Pt complexes.

- Chapter 5 studies the influence of the peripheral ligands on the photodynamics for a series of Ru/Pt complexes.
- Chapter 6 focuses on the photodynamics of a new Ru/Pt complex whose design is based on the knowledge obtained in previous chapters.
- Chapter 7 extends the discussion of Chapter 4 by applying time-resolved X-ray absorption spectroscopy to investigate the catalytic Pt center of a Ru/Pt complex.
- Chapter 8 summarizes the main conclusions obtained from the previous chapters, and presents an outlook overview.

Chapter 1. Introduction

The present chapter provides a general background of photocatalytic hydrogen generation, coordination complexes, and time-resolved spectroscopy. In particular, the prototype complex $[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy = 2,2'-bipyridine) is introduced in detail to provide key concepts which are frequently referred to in later chapters.

1.1. Light-induced H_2 generation: a clean way to utilize solar energy

No one doubts the significance of sunlight to life on Earth. The sun has been constantly providing energy to our planet for at least several billions of years, whereas our human civilizations are known to have appeared only approximately five thousand years ago. Actually the fossil fuels on which our modern society relies also represent solar energy collected by life forms for at least several millions of years. It is the sun that directly and indirectly powers our life and society on Earth.

The rapid industrialization and modernization since the mid-18th century has boosted the global energy consumption to approximately 14 TW (1 TW = 10^{12} W) today. The profligate burning of fossil fuels results in serious environmental problems such as air pollution and global warming. To combat such problems, the development of clean and renewable energy conversion systems is under high demand.¹ Direct harvesting of solar energy is an attractive approach because the sun delivers energy to the Earth with an average rate on the order of 10^5 TW, far beyond our current 14 TW usage.²

There are various approaches to utilize solar energy by conversion into other energy forms such as electricity and heat. An inevitable drawback associated with these approaches is the lack of a feasible and efficient energy storage method. On the other hand, direct use of solar energy for the production of fuels or chemical feedstocks eliminates this drawback because energy is stored automatically and locally in chemical bonds.

Among many forms of solar fuels, the production of solar hydrogen (H_2) by light-induced water splitting is highly attractive because of several advantages:

- (1) Abundance. Water covers approximately 70% of the Earth's surface.
- (2) Enormous energy supply by the sun.
- (3) Sustainability. H_2 is photolytically produced from water, and is subsequently recovered into water upon conversion in a fuel cell or combustion engine.
- (4) Environmental friendliness. No emission of greenhouse gasses (e.g. CO_2) or any toxic species.
- (5) High energy density. Hydrogen is the lightest element, giving rise to a high

energy density (142 MJ/kg). For comparison, gasoline has a typical energy density of 44.4 MJ/kg.³

Solar hydrogen is hence a promising solution to the increasing demand for energy supply and environmental protection, putting its development high on the agenda.⁴

One straightforward way to produce solar hydrogen is to combine an electrolyzer with external photovoltaic solar cells. In this way, the electricity power generated by the solar cells is used to drive the water splitting reaction in the electrolyzer. In order to achieve solar water splitting in a cost-effective way, enormous research efforts have been put in developing fully integrated photoelectrochemical (PEC) cells using various solid state semiconductors, and energy conversion efficiencies close to or exceeding 10% have been achieved.⁵⁻⁷ Alternatively, solid state semiconductors can be combined with molecular photosensitizers or photocatalysts to realize a hybrid dye-sensitized PEC system, similar to the concept of dye-sensitized solar cells.^{8,9} An advantage of this hybrid approach is the tunability of the individual components, allowing amenable mechanistic studies and therefore ample room for further improvement.¹⁰

Generally speaking, the overall efficiency of a PEC (molecular) device is determined primarily by three processes: light-harvesting processes; charge generation and separation processes; and catalytic reaction processes.¹¹ From a thermodynamical point of view, the splitting of water into molecular hydrogen and oxygen (reaction 1) is an up-hill reaction, meaning a positive Gibbs free energy change ($\Delta G^0 = 237$ kJ/mol).¹² This energy represents the minimum amount of energy to be supplied by the sun for the water splitting reaction to proceed, and can also be considered as the energy stored locally as chemical energy:

Reaction 1 can be split into two half reactions (2) and (3) as follows (NHE = normal hydrogen electrode):

The redox potentials shown in reactions (2) and (3) indicate that the minimum photon energy thermodynamically required for the overall water splitting is 1.23 eV, corresponding to a wavelength of approximately 1000 nm. However, in reality an overpotential is required to overcome an activation energy barrier for the reaction to proceed with a kinetically favorable speed. Therefore the development of efficient photocatalysts reducing this activation barrier (and overpotential) is of great importance for realizing a high solar-to-hydrogen conversion efficiency as shown in Figure 1. Various solid state and molecular photocatalysts have been

studied in the past 40 years,^{6,12-20} among which ruthenium-based coordination complexes have attracted broad interest. In the next section, a prototype ruthenium complex will be introduced, which has played and is still playing a key role in the development of efficient molecular photocatalysts for light-induced H₂ generation.

Figure 1. The role of photocatalyst in the light-induced water splitting reaction.

1.2. [Ru(bpy)₃]²⁺: a prototype ruthenium(II) coordination complex

Ruthenium(II) polypyridine compounds are a class of transition metal coordination complexes that have been intensively studied. The successful application of these complexes in the field of solar energy such as dye-sensitized solar cells, photocatalytic H₂ generation and water oxidation is attracting broad interest.^{14,21-23} Among many derivatives, the prototype [Ru(bpy)₃]²⁺ (bpy = 2,2'-bipyridine) is one of the most investigated complexes during the last 30 years. The reason for such great interest originates from a unique combination of excellent photophysical and photochemical properties which will be summarized in the present section. The knowledge obtained from this prototype complex will facilitate the discussion of a variety of Ru(II)-based photocatalysts in later chapters.

1.2.1. Bonding and electronic structure of [Ru(bpy)₃]²⁺

Coordination complexes, or metal complexes, are a class of molecules consisting of a central metal atom or ion (coordination center) and a surrounding array of ions or molecules (ligands) which are covalently bound to the metal center. The metal center and surrounding ligand are a Lewis acid and base, respectively, and therefore the bond is also called coordinate covalent bond or dative covalent bond to indicate that the coordinated ligand donates a pair of electrons to the metal center to form the chemical bond.²⁴ [Ru(bpy)₃]²⁺ is a typical coordination complex, whose structure is shown in Figure 2. The Ru(II) center is a d⁶ transition metal system, and the nitrogen atoms of the bpy ligands possess σ donor characteristics.²⁵

Figure 2. Chemical structure of $[\text{Ru}(\text{bpy})_3]^{2+}$.

In order to describe the bonding and electronic structure of $[\text{Ru}(\text{bpy})_3]^{2+}$, in the following discussion the Crystal Field Theory (CFT) is firstly applied to illustrate qualitatively the electronic interaction between the metal cation center and the electrons of the ligands in a simplified octahedral configuration. Afterwards CFT is extended to the more realistic Ligand Field Theory (LFT) for the discussion of $[\text{Ru}(\text{bpy})_3]^{2+}$, taking into account covalent interactions based on molecular orbitals (MOs).

In the CFT, the interaction between the metal core and the surrounding ligands is considered to be purely electrostatic, and the ligands are simplified as point charges. In an octahedral configuration, the point charges are placed along the Cartesian axes, imposing a symmetric electric field (crystal field) to the metal center, as shown in Figure 3A. Without this crystal field, the electronic structure of the metal core is described by atomic orbitals. The fully occupied s orbitals are spherically symmetric, and their interaction with the crystal field causes an energy raise of the orbitals due to the electrostatic repulsion between the negative point charges and the s orbital electrons. Similarly, the metal p orbitals lie along the Cartesian axes pointing directly towards the point charges, and their interaction with the crystal field also causes an increase in energy due to electrostatic repulsion. However, the degeneracy of p orbitals (p_x , p_y , p_z) is maintained because they have the same degree of interaction with the point charges representing the surrounding ligands.²⁶

Figure 3. (A) An octahedral crystal field defined by six point charges positioned along the Cartesian axes. The cation metal core is represented as M^{n+} . (B) The influence of an octahedral crystal field on the splitting of the metal d orbitals.

Contrary to the s and p orbitals, the crystal field has a different influence on the d orbitals of the metal center. In case the crystal field would be uniformly distributed around the metal core (i.e. a spherical field), its interaction with the d orbitals would only cause an increase in energy, but keep the orbital degeneracy, similar to the case of the s or p orbitals. In reality, however, the specific symmetry of the d orbitals and their relative orientation with respect to the octahedral point charge cage split the d orbitals into two groups as illustrated in Figure 3B. The d_{z^2} and $d_{x^2-y^2}$ orbitals have lobes pointing directly towards the point charges, resulting in a larger electrostatic repulsion. The d_{xy} , d_{xz} and d_{yz} orbitals have lobes pointing between point charges, resulting in a weaker electrostatic repulsion. Therefore the d orbitals are no longer degenerate. The two d orbitals which are higher in energy are often denoted as e_g , and the three lower-lying d orbitals are denoted as t_{2g} . The notations of e_g and t_{2g} are associated with specific symmetry properties derived from group theory. The letters e and t refer to double and triple degeneracy. The subscript g originates from the German word ‘gerade’, meaning a symmetric wavefunction through the center of inversion. The subscript 2 of t_{2g} indicates an asymmetric wavefunction with respect to a C_2 axis perpendicular to the principal axis. The energy difference between e_g and t_{2g} is described by the crystal field splitting Δ_o , where the subscript ‘o’ refers to ‘octahedral’. Because of energy conservation, e_g lays $0.6\Delta_o$ above the level before splitting, and t_{2g} is at $-0.4\Delta_o$.²⁶

While the CFT provides valuable insight into the splitting of d orbitals as discussed above, this simplified description is purely based on electrostatic interactions between the metal core and the surrounding point charges. A more advanced model involves the LFT which treats the chemical bonding on basis of MOs. In this manner, one or more ligand group orbitals overlap with one or more metal-based atomic orbitals in case these orbitals have similar energies and compatible symmetries. This orbital interaction produces a new set of bonding and anti-bonding MOs, which are often of σ or π character, depending on the bonding

interaction orientations. The concept of MOs has been developed to describe the multi-electron system (molecule) by treating its approximate electronic wavefunction as a combination of atomic orbitals. A MO represents a one-electron wavefunction in a molecule with a certain energy. The highest occupied MO is referred to as the HOMO, and the lowest unoccupied MO is as the LUMO. A schematic MO diagram of $[\text{Ru}(\text{bpy})_3]^{2+}$ simplified by assuming an octahedral symmetry is presented in Figure 4A. A more realistic and detailed representation based on the D3 symmetry is shown in Figure 4B.²⁶⁻²⁷

Figure 4. (A) MO diagram of $[\text{Ru}(\text{bpy})_3]^{2+}$ in a simplified octahedral symmetry. (B) Detailed representation of the MLCT transitions in D3 symmetry.

Ru(II) is a d^6 transition metal system, and the bpy ligands possess σ donor orbitals localized on the nitrogen atoms, and also π (π^*) donor (acceptor) orbitals delocalized over the aromatic ring. In an octahedral geometry, the MOs can be treated according to their predominant atomic (and ligand group) orbital contributions:²⁵

(1) σ_L , which are strongly bonding. The subscript L means that the orbitals are predominantly ligand-based.

(2) π_L , which are bonding, and also predominantly based on the ligands.

(3) π_M , which are essentially nonbonding and based on the Ru(II) metal center. These orbitals are analogous to the t_{2g} orbitals derived from CFT as discussed above.

(4) σ_M^* , which are antibonding and predominantly based on the Ru(II) center. These orbitals are analogous to the e_g orbitals derived from CFT as discussed above.

(5) π_L^* , which are antibonding and ligand based.

For $[\text{Ru}(\text{bpy})_3]^{2+}$ in the ground state, the σ_L , π_L and π_M orbitals are all completely filled, whereas the π_L^* and π_M^* orbitals are empty. Therefore the HOMO is mainly based on the d orbitals of Ru, and the LUMO is predominantly ligand-based. As a result, the transition between the HOMO and LUMO gives rise

to a metal-to-ligand charge transfer (MLCT) character. Similarly, transitions between π_L and π_L^* are mainly ligand-centered (LC), and transitions between π_M and σ_M^* are often called metal-centered (MC) d-d transitions.²⁸

In fact, the π_M and π_L^* orbitals are known to further split based on detailed studies of $[\text{Ru}(\text{bpy})_3]^{2+}$ with D3 symmetry, which is more realistic than the simplified octahedral geometry. As shown in Figure 4B, the HOMOs are composed of three Ru-based orbitals, and the LUMOs consist of three bpy-based orbitals.²⁸ The additional notations of a_1 , a_2 and e are derived from the character table of the D3 point group, reflecting certain symmetry properties.²⁹ As a result, the lowest excited state of $[\text{Ru}(\text{bpy})_3]^{2+}$ is a cluster of closely positioned MLCT levels.

1.2.2. Ground and excited states properties of $[\text{Ru}(\text{bpy})_3]^{2+}$

Figure 5 shows the steady state absorbance spectrum of $[\text{Ru}(\text{bpy})_3]^{2+}$ and the proposed assignments.²⁸ The sharp band at ca. 285 nm is due to LC transitions. The two bands centered at ca. 240 nm and 450 nm are widely accepted as MLCT transitions. The weak absorption around 350 nm might be associated with spin-allowed but Laporte forbidden MC d-d transitions.

Figure 5. Steady state absorbance spectrum (normalized) of $[\text{Ru}(\text{bpy})_3]^{2+}$ in acetonitrile at room temperature.

In the ground state, the π_M orbitals (HOMOs) are completely filled by six electrons ($\pi_M e^4 \pi_M a_1^2$) with paired spins, resulting in a singlet state. Photoexcitation of the MLCT band promotes an electron from π_M to π_L^* , and in the excited state $[\text{Ru}(\text{bpy})_3]^{2+}$ can exhibit either singlet or triplet character. In fact, it is known for $[\text{Ru}(\text{bpy})_3]^{2+}$ that intersystem crossing (ISC), a singlet-to-triplet transition process, occurs within 100 fs with a yield near unity.³⁰⁻³³ This efficient ISC process results in the formation of long-lived $^3\text{MLCT}$ states whose lifetimes are on the order of several hundreds of ns in various solvents at room

temperature.³⁴ The superscript 3 in ³MLCT indicates the triplet character, distinct to a singlet situation denoted as ¹MLCT. Detailed investigations estimated a singlet character less than 10% for the ³MLCT states of [Ru(bpy)₃]²⁺.^{35,36}

Photoexcitation of [Ru(bpy)₃]²⁺ also leads to luminescence emission with a quantum yield between 0.06 and 0.1 in various solvents at room temperature.³⁷ Studies based on temperature dependent emission lifetimes and quantum yields show that photoluminescence originates from a cluster of three closely positioned and thermally equilibrated ³MLCT states.²⁸ These three ³MLCT states may be in equilibrium with a fourth ³MLCT state slightly higher in energy.^{28,38} In the excited state, this ³MLCT manifold can undergo a thermally activated surface crossing to higher ³MC states, from where fast deactivation to the ground state (recombination) occurs due to a strong geometry displacement.²⁸

While a MLCT transition promotes an electron from π_M to π_L^* , the same π_L^* orbital is also involved in reducing [Ru(bpy)₃]²⁺ to [Ru(bpy)₃]¹⁺ (at -1.28 V vs. SCE in aqueous solution, SCE = saturated calomel electrode). Oxidation of [Ru(bpy)₃]²⁺ into [Ru(bpy)₃]³⁺ occurs at 1.26 V vs. SCE. In the ³MLCT state, *[Ru(bpy)₃]²⁺ (asterisk indicates excited state) is very reactive, capable of being an energy donor, an electron donor or an electron acceptor. It can undergo a quenching process (*[Ru(bpy)₃]²⁺ → [Ru(bpy)₃]²⁺) involving an energy transfer of 2.12 eV. Alternatively, *[Ru(bpy)₃]²⁺ can be oxidatively (reductively) quenched via electron transfer processes at a potential of 0.86 V (-0.84 V) vs. SCE in aqueous solution.²⁸ These photoelectrochemical properties allow derivatives of [Ru(bpy)₃]²⁺ to be used as photocatalysts for both proton reduction and water oxidation reactions.^{14,23}

Another important excited state property of [Ru(bpy)₃]²⁺ involves the (de)localization of the electron density. As discussed earlier, ISC occurs within 100 fs. In fact it is widely accepted that in the Franck-Condon region (before ISC), the photoexcited electron density is likely delocalized over the three bpy ligands in the ¹MLCT singlet manifold.²⁸ Accompanied by ISC, however, this delocalization vanishes. Consequently the ³MLCT states are spatially localized, meaning the electron density is localized on one of the three bpy ligands.^{27,39,40} This spatially localized electron probably undergoes inter-ligand hopping on a ps time scale.²⁸ Note that at this time scale vibrational cooling and/or solvent reorganization are also likely to occur.^{41,42} Recent research also suggests that the early-time photodynamics are probably more complex, and randomized inter-ligand hopping may also occur on a sub-ps time scale.⁴¹ Furthermore, it is even debatably argued that a spatially localized state is already formed during the photoexcitation process.⁴³

1.3. Basic principles of ultrafast spectroscopies to explore photodynamics

The knowledge about the unique combination of photophysical and photochemical properties of $[\text{Ru}(\text{bpy})_3]^{2+}$ discussed in the previous section is based on continuous research of more than 30 years, during which period time-resolved techniques emerged as powerful tools for the investigation of the excited state photodynamics. In this section two time-resolved techniques, i.e. transient absorption spectroscopy and time-resolved photoluminescence, will be briefly introduced. These two techniques are applied to study the photodynamics of other Ru(II)-polypyridyl derivatives discussed in later chapters.

1.3.1. Transient absorption spectroscopy

Transient absorption (TA) spectroscopy is a pump-probe technique to study excited state processes and their dynamics by measuring the differential absorbance induced by photoexcitation of the sample. Its principle can be explained as the following. Firstly, the absorbance of the sample in its ground state is defined by the optical density (OD) according to the Lambert-Beer law:

$$\text{OD} = \varepsilon cl = -\log_{10}\left[\frac{I(\lambda)}{I_0(\lambda)}\right] = -\log_{10}(T), \quad (4)$$

where ε is the molar absorptivity ($\text{M}^{-1}\text{cm}^{-1}$), c is the sample concentration (M), l is the sample thickness (cm), $I(\lambda)$ and $I_0(\lambda)$ are the transmitted light intensity (at wavelength λ) with and without the sample, and T is the transmittance. It is obvious that OD is a unitless quantity reflecting an exponential light attenuation. A fraction of the sample is excited by a pump laser pulse. Shortly after this photoexcitation, a weak probe pulse is sent through the sample, whose delay time with respect to the pump pulse is accurately controlled. The probe beam spatially overlaps with the pump beam at the sample, and is used to detect the sample absorbance in the excited state, given by the same Lambert-Beer law:

$$\text{OD}'(\Delta t) = \varepsilon^* c^* l + \varepsilon c(1 - f)l = -\log_{10}\left[\frac{I'(\lambda, \Delta t)}{I_0(\lambda)}\right] = -\log_{10}(T'), \quad (5)$$

where the asterisk indicates the excited state character, and the prime emphasizes the quantities after photoexcitation, Δt is the delay time between the pump and probe pulses, and f is the excitation fraction.

Although in a typical TA experiment $I_0(\lambda)$ is not necessarily recorded, it can be eliminated by taking the differential absorbance as shown in equation 6:

$$\Delta\text{OD}(\Delta t, \lambda) = \text{OD}' - \text{OD} = -\log_{10}\left[\frac{I_{\text{on}}(\lambda, \Delta t)}{I_{\text{off}}(\lambda)}\right], \quad (6)$$

where $I_{\text{on}}(\lambda, \Delta t)$ and $I_{\text{off}}(\lambda)$ are the transmitted probe light intensities with the pump pulse on (i.e. after excitation) and off (i.e. before excitation), respectively. Note that this differential absorbance can be measured at various time delays Δt , allowing the temporal information to be recorded as a series of transients. The spectral information can be simultaneously recorded by using a broad band probe.

The principle discussed above is illustrated in Figure 6A. A unique advantage of TA compared to steady state absorption is that the former can simultaneously provide both spectral and temporal features of the excited states, whereas the latter only gives a time-averaged absorption almost completely originating from the ground state. In general, TA spectra may possess contributions from various processes shown in Figure 6B:

(1) Ground state bleach (GSB): as described earlier, the pump pulse photoexcites a fraction of the sample. Consequently, the amount of molecules in the ground state decreases, resulting in less absorption based on the ground state. Due to this reason, the GSB contributes to negative signals in a ΔOD spectrum, and its shape normally resembles the mirror image of the steady state absorption.

(2) Stimulated emission: once the system is photoexcited into its excited state by the pump pulse, it can relax back into the ground state by emitting a photon when the probe pulse passes through the sample. This stimulated emitting photon travels exactly in the same direction as the probe photon, resulting in an effectively increased I_{on} signal and therefore a negative signal in the TA spectrum.

(3) Spontaneous emission: the photoexcited system may also undergo this process in absence of the probe beam. Analogous to stimulated emission, this type of signal is also negative.

(4) Excited state absorption (ESA): when the system is in its excited state, optical transitions to higher excited states become accessible. These extra absorptions can contribute to the positive signals observed in a TA spectrum.

(5) Product absorption: this type of signal may be detected if photoexcitation by the pump pulse leads to the formation of a photo-product due to possible photochemical reactions and electron (or energy) transfer processes.

Figure 6. (A) Schematic depiction of the basic principle of a TA measurement. (B) Various processes contributing to a TA spectrum. For simplicity vibrational sub-levels are not included. See main text for detailed discussion of processes 1–5.

As shown in Figure 6A, the key aspect of a TA measurement is the accurate control of the ultrashort pump and probe pulses. In practice these two pulses are generated differently. The pump pulse is typically in the UV-visible range, while the probe may also be in a different part of the electromagnetic spectrum, depending on the investigation purpose. For controlling Δt with ns or larger time steps, electronic triggering systems can be used. In order to control the time delay Δt with fs accuracy, an optical delay line (mechanical delay stage) is often used according to the following relationship:

$$\Delta t = \frac{\Delta L}{c}, \quad (7)$$

where ΔL is the beam path-length difference between the pump and probe pulses, and c is the speed of light ($\approx 2.998 \times 10^8$ m/s). It can be derived from equation (7) that a ΔL of 1 μm yields a Δt of ca. 3.34 fs. A detailed description of the transient absorption setup will be provided in the next chapter.

1.3.2. Time-resolved photoluminescence

Unlike TA, time-resolved photoluminescence (TRPL) is based on detecting the temporal decay of the spontaneous emission signal only, therefore this technique is only suitable to investigate excited state properties of emitting samples. Generally speaking, photoluminescence (PL) is divided into two categories: fluorescence and phosphorescence, depending on the electronic spin configurations of the excited

states as shown in Figure 7.

Figure 7. Schematic representation of two PL categories: fluorescence and phosphorescence. For simplicity vibrational sub-levels are not included.

When a molecular system, e.g. $[\text{Ru}(\text{bpy})_3]^{2+}$ as introduced earlier, absorbs a photon, the system is photoexcited from the ground state to an excited state. For simplicity, the ground state is assumed to be a singlet state (S_0). Since photon absorption does not change the spin of the photoexcited electron, the almost instantly formed ($\sim 10^{-15}$ s)⁴⁴ excited state is also a singlet state denoted as S_n . The subscript n emphasizes that this state is not necessarily the lowest excited state. Then the system may undergo an (or multiple) internal conversion (IC) process through transition from S_n to the lowest singlet excited state S_1 , from where the system can relax back to its ground state by emitting a photon. This emission originating from a singlet excited state is called fluorescence. Alternatively, the system may undergo an ISC process from the singlet state (e.g. S_1), leading to the formation of a triplet state (e.g. T_1). This phenomenon is often observed in $[\text{Ru}(\text{bpy})_3]^{2+}$ as discussed in section 1.2. Although the transition from T_1 to S_0 by emitting a photon is spin-forbidden, in reality this emission can sometimes be observed due to spin-orbit coupling and singlet-triplet mixing.^{25,28} However, this emission process generally occurs much slower than fluorescence, and is therefore called phosphorescence. For $[\text{Ru}(\text{bpy})_3]^{2+}$, the PL signal is dominated by phosphorescence due to the ultrafast and efficient ISC (Section 1.2). Note that photon emission does not necessarily originate from the lowest excited states (S_1 and T_1), but according to Kasha's rule⁴⁵ these lowest states mainly contribute to the total emission signal for most molecular systems. Irrespective of the nature of the PL signal (fluorescence or phosphorescence), the PL lifetime τ represents the characteristic time the system stays in the excited states. In other words, τ represents the excited state lifetime available for the system to emit prior to returning to its ground state. Note that τ differs from the intrinsic emission lifetime τ_i (*vide infra*).

As explained above, TRPL is only suitable to study emitting samples, either fluorescent or phosphorescent. In order to compare the emitting capability of different chromophores, a quantity called quantum yield (Φ) is defined as the ratio between the numbers of emitted and absorbed photons. For $[\text{Ru}(\text{bpy})_3]^{2+}$, the phosphorescence quantum yield equals 0.063 in water and 0.095 in acetonitrile under deaerated conditions at room temperature.³⁷

Considering an arbitrary two-level (level-0 and level-1) system and assuming that all processes between these two levels are first order with respect to the number densities n_0 and n_1 , then a rate equation gives:

$$\frac{dn_1}{dt} = k_A n_0 - (k_r + k_{nr}) n_1, \quad (8)$$

where n_0 (n_1) refers to the number of molecules in state 0 (1) per unit volume, k_A is the excitation rate, k_r is the radiative decay rate, and k_{nr} is the non-radiative decay rate. Under constant illumination and at steady state, n_1 should remain unchanged, yielding the following relationship:

$$n_1 = \frac{n_0 k_A}{k_r + k_{nr}}. \quad (9)$$

Considering the definition of the emission quantum yield Φ :

$$\Phi = \frac{k_r n_1}{k_A n_0}, \quad (10)$$

then equations (6) and (7) yield the following expression:

$$\Phi = \frac{k_r}{k_r + k_{nr}}. \quad (11)$$

The experimentally observed emission lifetime τ is a result of both radiative and non-radiative decay processes, and is therefore given by:

$$\tau = \frac{1}{k_r + k_{nr}}. \quad (12)$$

Note that τ determined from the above relationship is different from the so-called intrinsic emission lifetime τ_i , which is given by equation 13 assuming an emission quantum yield of unity:

$$\tau_i = \frac{1}{k_r}. \quad (13)$$

Since τ and Φ can be experimentally measured, the above equations are useful to calculate k_r and k_{nr} according to the following relationships:

$$k_r = \frac{\Phi}{\tau}, \quad (14)$$

$$k_{nr} = \frac{1 - \Phi}{\tau}. \quad (15)$$

To measure the PL lifetime, various techniques such as time correlated single photon counting (TCSPC) and streak camera detection can be used. The basic principle of TCSPC is illustrated schematically in Figure 8. Briefly, a pulsed light source triggers the timing electronics by sending an "on" signal, and also photoexcites the sample. Once a photon emitted by the sample is detected, the detector sends an "off" signal to stop the timing electronics. The time difference between these "on" and "off" signals is put into a histogram, which consists of many time "bins" with a fixed width δt . This measurement is repeated multiple times until a statistically well resolved histogram is obtained, which often exhibits exponential decay features. In practice, it is important to guarantee a low probability of having more than one photon per excitation cycle, because the TCSPC photodetector is designed to detect single photons. Note that the detector and other electronics unavoidably have a "dead" time after a photon event, during which period they cannot process another event. Many other factors influence the performance of TCSPC, such as the time "bin" width, the excitation pulse duration and the photodetector accuracy, resulting in a time resolution typically exceeding several tens of ps.

Figure 8. Simplified schematic representation of TCSPC.

Streak camera detection is another technique to measure the PL lifetime. Unlike TCSPC, a time resolution well below 10 ps can be achieved. A key feature of a streak camera is that it transforms the spectral and temporal PL information into a spatially resolved profile on a detector. Figure 9 illustrates the basic principles of this method. The incident photons (PL signal) on the photocathode are converted into an electron train proportional to the incident light intensity. The electron train then passes through a pair of electrodes, to which a high sweeping voltage is applied. During this fast electric field sweep, electrons arriving at different times are deflected into different directions. After deflection, the electrons go through a micro channel plate (MCP), from where the number of electrons is

multiplied to increase the signal intensity. The deflected electrons are then collected by a phosphor screen, and the brightness distribution of the formed streak can be analyzed to extract the temporal PL information. In practice, a streak camera is often operated together with a spectrograph, which is used to spectrally resolve the PL signal in the direction perpendicular to the sweep direction of the streak camera. In this way, both spectral and temporal PL features are obtained.

Figure 9. Simplified schematic representation of a streak camera.

In summary, both TCSPC and streak camera detection can be used to measure temporal PL decay features, which reflect the excited state lifetime and are characteristic of the system of interest. A combination of TRPL and TA can provide an extensive insight into the photodynamics of a molecular system such as $[\text{Ru}(\text{bpy})_3]^{2+}$ and its derivatives, which will be discussed in more detail in later chapters.

1.4. Thesis aim and overview

This thesis aims to provide a fundamental understanding of the early-time photodynamics of a series of Ru(II)-based molecular photocatalysts derived from the prototype $[\text{Ru}(\text{bpy})_3]^{2+}$, using time-resolved spectroscopic methods including TA and TRPL. As introduced in section 1.1, the overall efficiency of a photocatalytic conversion reaction is determined by the balance of thermodynamics and kinetics of multiple processes.¹¹ A complete study of all these processes is beyond the scope of this thesis. However, a detailed investigation of the early-time photophysical processes sets a starting point for the understanding of the subsequent photodynamical processes occurring at later time scales. The knowledge developed during this study facilitates the design and optimization of new molecular photocatalysts for light-induced H_2 formation with improved efficiency.

The general structure of the photocatalysts studied in this thesis is shown in Figure 10. A Ru(II)-based chromophore is covalently connected to a catalytic metal center via a bridging ligand. Upon light absorption, an electron is photoexcited from the HOMO based on the d orbitals of the Ru(II) core to a ligand-based orbital, described as a MLCT transition (Section 1.2). Subsequent ISC and IC processes also occur, which may induce a directional electron transfer towards the catalytic center where proton reduction can take place. This thesis focuses on the influences of the structure of the individual building blocks (peripheral ligands, bridging ligands, and catalytic metal centers) on the early-time photodynamics. Based on this systematic investigation, the early-time photodynamics and their influence on the H_2 evolution reactivity will be summarized, and directions for future research are identified.

Figure 10. General structure of the Ru(II)-based photocatalysts for light-induced H_2 generation.

Figure 11. An overview of the individual building blocks of the molecular photocatalysts discussed in this thesis.

In reality, the transfer and accumulation of two photoexcited electrons are required in order to achieve the overall H_2 formation at the catalytic center, as described by equation (3) in Section 1.1. Therefore sacrificial electron donors must

be used to regenerate the photocatalysts. This topic will not be discussed in this thesis due to several issues:

- (1) The photostability of the complexes in the presence of sacrificial electron donors.
- (2) The challenge to in-situ monitor H₂ formation at the catalytic metal center.
- (3) Technical difficulty to detect the second photoexcited electron.
- (4) The presence of large amounts of radicals may create side reactions by reacting with solvents, further complicating photophysical assessment.⁴⁶

As a result, all TA and TRPL measurements are performed in absence of sacrificial electron donors. In spite of the above limitations, however, knowledge of the early-time photodynamics investigated in this thesis provides a reference for future investigation of the role of electron donating sacrificial reagents or semiconductor surfaces, as will be introduced in Chapter 8.

This thesis is organized in the following way. Chapter 2 discusses the methodological aspects of TA, including technical and analytical details. Chapters 3–7 discuss the early-time photodynamics of various Ru/M (M = Pd or Pt) bimetallic photocatalysts with a general structure shown in Figure 10. The individual building blocks of these photocatalysts are shown in Figure 11. Chapter 8 summarizes and compares the photodynamical properties of all the photocatalysts discussed in previous chapters, and points out directions for future research.

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Chapter 2. Methodology of transient absorption spectroscopy

The basic principles of transient absorption (TA) and its capability of investigating the excited state processes have already been introduced in Chapter 1. The present chapter focuses on the technical aspects of TA. In particular, the theoretical background of key optical components are discussed. Afterwards, the photophysical modeling of TA data is described. The application of the modeling strategy on specific photocatalysts is discussed in later chapters.

2.1. An overview of the transient absorption setup

As discussed in Chapter 1, the heart of TA involves the generation and control of two ultrashort light pulses, i.e. the pump and probe pulses. In practice, the pump pulse is generated and spectrally tuned by a non-collinear optical parametric amplifier (NOPA, Clark-MXR Inc.) pumped by a Ti:Sapphire laser (Clark-MXR CPA-2001, 1004 Hz, 775 nm, ~100 fs pulse duration). A mechanical chopper wheel is placed at the NOPA output to modulate the on/off pump signal (*vide infra*). A prism pair is used to compress the pump pulse to (near-)transform limit characterized by an autocorrelator. The probe pulse is generated by pumping a calcium fluoride (CaF_2) crystal (Newlight Photonics Inc., 3 mm thickness, [001] cut) by part of the 775 nm fundamental, which is firstly guided through a mechanical delay line and a half-wave plate. This procedure yields a delayed white light continuum (WLC) probe with tunable polarization angle, ranging from the ultraviolet (340 nm) across the entire visible region, and is cut at 700 nm by a short-pass filter. The CaF_2 window is mounted on a continuously moving translational stage to prevent thermal damage. The pump and probe beams are focused and spatially overlapped at the sample. After passing through the sample the pump beam is blocked, whereas the probe beam is spectrally dispersed by a spectrograph (Acton SP150, 150 grooves/mm grating). A photodiode array consisting of 256 pixels is used to record the TA signals. The above setup arrangement is summarized in Figure 1.

Figure 1. Simplified representation of the TA setup. For details see text.

Because the NOPA is pumped by a 1004 Hz fundamental laser, its output also has the same frequency. Half of the pump pulses are cut by a chopper to allow an on/off modulation as shown in Figure 2. As a result, the sample is brought to its "on" state (photoexcited state) at a frequency of 502 Hz. On the other hand, the WLC is produced by pumping the CaF_2 crystal using the same fundamental, yielding a probe with a frequency of 1004 Hz. Half of the probe pulses are used to detect the "on" state of the sample, and the other pulses detect the "off" state (ground state), enabling measuring differential absorption spectra.

Figure 2. Schematic explanation of the signal modulation in a TA measurement.

As discussed above, the sample is photoexcited by the pump every ca. 2 ms. Therefore in principle the setup is capable of measuring TA of any sample with an

excited state lifetime significantly below 2 ms. For the various Ru(II)-based photocatalysts discussed in this thesis, the excited state lifetimes are below 10 μ s at room temperature, fulfilling this criterion. In the following section, the individual optical components in the setup are discussed in more detail.

2.2. Key optical elements in the transient absorption setup

2.2.1. White light generation

The phenomenon of WLC (also called supercontinuum) generation by pumping a crystal or glass with a pulsed laser was discovered in the 1970s,¹ and is still under development nowadays, as WLC is widely used in a diverse range of optical fields. Its mechanism is still not fully understood, as WLC generation is a result of several complex nonlinear processes occurring when an intense laser pulse passes through a medium. However, one of the main contributions is widely believed to be related to a process called self-phase modulation.¹

Briefly, when an ultrashort laser pulse travels through a medium, the high peak power of the pulse may induce a change in refractive index of the medium. This effect is called the optical Kerr effect.² The local refractive index change possesses a variation in time when the pulse propagates through the media, resulting in a shift in phase of the pulse. This phase shift leads to an instantaneous frequency shift. Note that dispersion (for more details see section 2.2.3) can simultaneously act on this self-phase modulation effect, causing a more complex WLC generation mechanism. Other possible contributions for WLC generation includes four-wave mixing, second harmonic generation and Raman scattering.³⁻⁵

In practice, the WLC is produced by pumping a CaF₂ crystal with a focused pulsed laser beam at 775 nm.⁶ The laser-induced change in refractive index results in an effective focusing lens, causing the so-called self-focusing effect.⁷ This effect can strongly influence the stability of the generated WLC, and can even damage the CaF₂ crystal due to overheating. Therefore the CaF₂ crystal is mounted on a continuously moving stage. Several parameters have to be carefully tuned in order to achieve a stable WLC output, such as the pump power and the focusing distance.

A WLC can be also generated by pumping sapphire.⁸ Generally speaking, a stable output can be achieved in an easier way as compared to CaF₂, due to sapphire's higher thermal conductivity. However, the generated WLC is spectrally limited down to 400 nm. For this reason sapphire is not used for probe light purpose in TA. It is though used inside the NOPA as discussed in the next section.

2.2.2. Noncollinear optical parametric amplification

Coordination complexes like $[\text{Ru}(\text{bpy})_3]^{2+}$ and its various derivatives discussed in this thesis have a typical MLCT absorption band below 600 nm. However, the fs laser system of the TA setup has an output at 775 nm. Therefore a NOPA is used to tune the pump wavelength to a desired position. This method is a special type of optical parametric amplification (OPA) arranged in a noncollinear geometry.

OPA (also called difference frequency generation) is a nonlinear process involving three light beams, which are often called pump, signal and idler with their respective frequencies ω_p , ω_s and ω_i ($\omega_p = \omega_s + \omega_i$). The pump and signal are spatially and temporally overlapped at a nonlinear crystal such as β -barium borate (BBO). As a result, the pump power is decreasing, simultaneously amplifying the signal and generating the idler.

One problem for a collinearly arranged OPA is that the matching of the phase velocities of the pump, signal and idler does not simultaneously assure an automatic matching of their group velocities, limiting the amplified signal pulse duration. This phenomenon is schematically illustrated in Figure 3A. While the signal pulse (green) is amplified by the pump pulse (violet) inside a BBO crystal, an idler pulse (red) is generated. A continuous amplification of both the signal and idler is achieved when they propagate through the crystal. Due to group velocity dispersion (GVD), the idler travels faster than the signal. As a result, newly generated signal photons are added to the signal pulse's leading edge, and similarly the newly generated idler photons are added to the trailing edge of the idler pulse. This phenomenon leads to a signal output stretched in time.

Figure 3. Simplified schematic representation of collinear (A) and noncollinear (B) OPA processes. For details see text.

The aforementioned problem can be avoided by adopting a noncollinear geometry as shown in Figure 3B. An angle between the pump and signal results in an angle between the signal and idler. The latter angle can be tuned in such a way

that the projection of the idler group velocity onto the signal's propagation direction matches the group velocity of the signal. In this way, the signal photons generated by amplification of the idler are produced at the same position as the photons generated by amplification of the signal itself.⁹

In practice, prior to noncollinear OPA, the signal is produced by WLC generation using a sapphire crystal. The generated WLC signal beam acts as a seed for the OPA. The pump beam is produced via second harmonic generation (SHG) by pumping a BBO crystal with the fundamental 775 nm laser. The WLC and ca. 20% of the pump are used for the first stage noncollinear OPA, producing a spectrally broad signal at a selected center wavelength. This signal beam is used as the seed for a second stage noncollinear OPA process using the remaining ca. 80% of the pump. Two optical delay lines are used for the first and second stage OPAs to control the time delay between the WLC signal (seed) and the pump, determining the wavelength of the amplified signal output. The output stability is strongly dependent on the WLC stability.

Limited by the fundamental laser pulse duration (ca. 100 fs), imperfect alignment and dispersion (*vide infra*), the amplified signal beam has a typical pulse duration exceeding 100 fs. A prism pair is therefore used to compress the NOPA output pulses. This method is introduced in the next section.

2.2.3. Pulse compression

When a light pulse travels through a transparent and dispersive media, the group velocity depends on the optical frequency ω or wavelength λ . This phenomenon is called group velocity dispersion (GVD), whose quantity is given by:

$$\text{GVD} = \frac{\partial}{\partial \omega} \left(\frac{1}{v_g} \right) = \frac{\partial}{\partial \omega} \left(\frac{\partial k}{\partial \omega} \right) = \frac{\partial^2 k}{\partial \omega^2}, \quad (1)$$

where v_g is the group velocity, and k is the frequency-dependent angular wavenumber ($k=2\pi/\lambda$).

The origin of GVD can be understood by expressing the spectral phase as a Taylor expansion at the carrier frequency ω_0 of the pulse as shown in the following expression. For simplicity, higher orders are neglected:

$$\varphi(\omega - \omega_0) = \varphi_0 + \varphi_1 \cdot \frac{(\omega - \omega_0)}{1!} + \varphi_2 \cdot \frac{(\omega - \omega_0)^2}{2!} + \dots \quad (2)$$

Given the following expression to account for the influence of the medium on the phase:

$$\varphi(\omega) = k(\omega)L, \quad (3)$$

where L is the thickness of the medium, the expansion coefficients φ_1 and φ_2 in equation (2) can be expressed as:

$$\varphi_1 = \left. \frac{d\varphi}{d\omega} \right|_{\omega=\omega_0} = L \cdot \left. \frac{dk}{d\omega} \right|_{\omega=\omega_0} = \frac{L}{v_g(\omega_0)}, \quad (4)$$

$$\varphi_2 = \left. \frac{d^2\varphi}{d\omega^2} \right|_{\omega=\omega_0} = L \cdot \left. \frac{d^2k}{d\omega^2} \right|_{\omega=\omega_0} = L \cdot \left. \frac{d}{d\omega} \left(\frac{1}{v_g} \right) \right|_{\omega=\omega_0}. \quad (5)$$

From the above expressions, it is clear that φ_1 is related to the time for the pulse to pass the media, and is called group delay. The parameter φ_2 is referred to as group delay dispersion (GDD), and is closely related to the GVD defined in equation (1). Since φ_1 only adds a delay to the pulse, it does not affect the pulse shape. On the other hand, GDD introduces a frequency dependent delay to the different spectral components of the pulse, causing a temporal change of the pulse shape.

Due to GVD, the group velocity decreases with increasing frequency for most dispersive media. Such dispersion is often called normal dispersion. In other words, the higher frequency components are lagging behind the lower frequency components. Such a pulse is often called a positively chirped pulse. In some cases, however, the opposite trend occurs, and the corresponding dispersion is referred to as anomalous dispersion (negative chirp).

The NOPA output is often positively chirped with a pulse duration exceeding 100 fs. In order to reduce the pulse duration, a negative chirp can be introduced to compensate the positive chirp. In practice, this strategy can be realized by using a prism pair as shown in Figure 4.

The angle between the incident beam and prism A is set at Brewster angle to minimize reflection losses. The beam is then refracted by prism A, after which prism B is placed to collimate the spatially dispersed beam. A mirror is placed to reflect the collimated beam. Due to optical reversibility, this arrangement is equivalent to a configuration with a second prism pair (prism A' and B') as shown in Figure 4, resulting in an effective organization of four prisms. Because the spectral component at a shorter wavelength (blue beam in Figure 4) is refracted stronger than that at a longer wavelength (red beam in Figure 4), these two beams travel different path lengths. This wavelength dependent path length depends on the distance L between the apexes of prisms A and B. Therefore by carefully tuning the position of these two prisms, an effective control of the GDD can be achieved.¹⁰

Figure 4. Geometric arrangement of a prism pair to introduce negative chirp to compress a positively chirped pulse.

A prism pair is only effective to correct the linear chirp originating from the quadratic term in equation (2). Fortunately, higher order nonlinear chirp is normally not very severe for pulses exceeding 50 fs.¹⁰ Note that a pulse cannot be compressed to be infinitely short. In fact, for a Fourier transform limited pulse with a Gaussian shape, the product of its spectral and temporal bandwidths is limited by:

$$\Delta\nu\Delta t \approx 0.441, \quad (6)$$

where $\Delta\nu$ is the full width at half maximum (FWHM) of frequency, and Δt is the FWHM of the pulse duration. The above relationship limits the pulse duration for a certain wavelength FWHM $\Delta\lambda$ as follows:

$$\Delta t = \frac{0.441\lambda^2}{c\Delta\lambda}, \quad (7)$$

where c is the speed of light and λ is the central wavelength.

2.2.4. Optical autocorrelation

While the previous section introduces an elegant way to compress pulses using a prism pair, in practice a technique to measure the pulse width is required. In this section, a method called optical autocorrelation is introduced. In short, this technique is based on measuring the pulse duration by using the pulse itself.

Given $I(t)$ as the time-dependent intensity function of a pulse, an intensity autocorrelation $A(\tau)$ is defined as:

$$A(\tau) = \int_{-\infty}^{+\infty} I(t)I(t - \tau)dt, \quad (8)$$

where $I(t-\tau)$ represents a delayed replica of $I(t)$. From this definition it is clear that $A(\tau)$ represents a correlation of $I(t)$ with its own past and future values. Therefore by measuring $A(\tau)$ and assuming a certain shape of $I(t)$ (typically Gaussian), the pulse width can be estimated.

The aforementioned strategy can be realized by using an intensity autocorrelator, whose arrangement is depicted in Figure 5. The collimated beam of interest is reflected on a half-mirror pair, producing two replicas (beam 1 and 2). One half mirror is driven by a piezoelectric translator to scan the optical delay between the two replicas, which are further reflected and focused by a parabolic mirror onto a BBO crystal with proper orientation and cut angle. Due to the high peak power of ultrashort pulses, at the BBO crystal beams 1 and 2 undergo a SHG process, producing frequency doubled photons travelling in the same directions as their fundamentals. In case beams 1 and 2 overlap both spatially and temporally, a third sum-frequency signal is generated, whose direction is determined by the phase-matching condition:

$$\vec{k}_3 = \vec{k}_1 + \vec{k}_2, \quad (9)$$

where $\vec{k}_1$, $\vec{k}_2$ and $\vec{k}_3$ are the wave vectors of beam 1, beam 2 and the generated sum-frequency beam, respectively. The fundamental and frequency-doubled beams are blocked by a combination of a short-pass filter and beam stoppers, allowing only the sum-frequency beam to be detected by a photodiode. The pulse duration is encoded in this sum-frequency signal $A(\tau)$. When beams 1 and 2 overlap perfectly in time, $A(\tau)$ reaches its maximum amplitude, whereas a loss of this overlap leads to a vanishing $A(\tau)$. Assuming a Gaussian shape of $I(t)$, the width of $A(\tau)$ exceeds the width of $I(t)$ by a factor of 1.414.¹¹

Figure 5. Schematic representation of an intensity-autocorrelator. The right panel depicts SHG and sum-frequency generation. For details see text.

Note that although the aforementioned intensity-autocorrelator can be used to estimate the pulse duration, no phase information can be extracted. In order to fully characterize a pulse, more sophisticated optical techniques such as frequency-resolved optical gating¹² has to be used, which is beyond the scope of this research.

2.3. Photophysical modeling of transient absorption data

2.3.1. Modeling assumptions

In the previous sections, the experimental aspects of TA are discussed. The present section, on the other hand, focuses on the photophysical modeling of TA data. For completeness, some assumptions are made prior to developing a mathematical model describing the TA data.

One of the most important assumptions is homogeneity. In case the properties of the system under study are homogeneous, a discrete set of parameters can be used to describe the system.¹³ On the other hand, inhomogeneity means that many subsystems exist, and a model with distributed parameters has to be used. Sometimes it can be assumed that a system with few sub-populations is represented by a weighted average of homogeneous subsystems.¹⁴ Homogeneity is the most common assumption for TA modeling, and is also adopted in this thesis to avoid over-modeling.

Separability is another important assumption. A typical TA dataset is a 2D matrix Ψ with the horizontal (x) axis denoting the wavelength and the vertical (y) axis denoting the time delay between pump and probe (or vice versa). Therefore an arbitrary matrix element $\Psi(x = \lambda, y = t)$ represents the ΔOD value at wavelength λ and time t . Separability means that such a matrix can be represented by a superposition of contributions from several individual components:

$$\Psi(\lambda, t) = \sum_{i=1}^{n_{\text{comp}}} c_i^T \otimes \varepsilon_i(\lambda), \quad (10)$$

where n_{comp} is the total number of individual components, $c_i^T(t)$ is a column vector denoting the time-dependent concentration of component i , $\varepsilon_i(\lambda)$ is the row vector denoting the spectrum of component i , and $\otimes$ refers to the outer product.

Equation (10) shows that modeling TA data is an inverse problem. Since the experimentally measurable Ψ is a superposition, the recovery of its individual components has multiple pathways, meaning there is no unique way to decompose the matrix. An immediate problem is that the number of components n_{comp} is unknown. Therefore a mathematic tool called singular value decomposition is often used to estimate n_{comp} . This method will be introduced in the next section.

2.3.2. Singular value decomposition

Singular value decomposition (SVD) is a frequently used technique to factorize a matrix. Given $\Psi_{m \times n}$ as an arbitrary $m \times n$ matrix, it can be written into the following form according to the SVD theorem:

$$\Psi_{m \times n} = U_{m \times m} S_{m \times n} W_{n \times n}^T, \quad (11)$$

where $U_{m \times m}$ and $W_{n \times n}$ are $m \times m$ and $n \times n$ orthogonal matrices, respectively. The columns of the former matrix contain the left singular vectors, and the latter matrix contains the right singular vectors. The symbol $S_{m \times n}$ denotes an $m \times n$ diagonal matrix, whose diagonal elements are called singular values.

Equation (11) represents a separable case of the matrix $\Psi_{m \times n}$, which can be written into a form that closely resembles equation (10):

$$\Psi_{m \times n} = \sum_i \Phi_i = \sum_i \sigma_i U_i \otimes W_i^T, \quad (12)$$

where Φ_i is a matrix separated from $\Psi_{m \times n}$, U_i and W_i are the i -th columns of $U_{m \times m}$ and $W_{n \times n}$ respectively, and σ_i is the corresponding singular value. The number of non-zero σ_i values is exactly equal to the rank of $\Psi_{m \times n}$.

By comparing equations (10) and (12), it is apparent that the number of individual components n_{comp} can be estimated from the number of singular values. In reality, due to noise perturbing $\Psi_{m \times n}$, n_{comp} can be estimated, as a first trial, to be the number of significantly different singular values obtained from SVD. In addition, since the left and right singular vectors reflect the temporal and spectral dependence of a particular component, inspection of these two vectors also facilitates physical interpretation of the TA data.

2.3.3. Global analysis

As the previous section introduces a mathematical way to estimate the number of components n_{comp} , the next step is to decompose these components from the TA dataset Ψ , taking into account the spectral and temporal properties simultaneously. As discussed in Section 2.3.1, this decomposition is an inverse problem, therefore in practice the extracted individual components must have a realistic physical meaning.

An important parameter for photodynamical modeling is the order of the kinetics. In case the concentrations are described by linear differential equations, the solution is given by a sum of exponential decays, meaning first-order kinetics. When concentration product terms are also included, the kinetics are of higher orders. This section is limited to the discussion of first-order kinetics.

From a modeling point of view, if the system under study contains a large degree of uncertainty and no priori knowledge about a detailed kinetic model exists, a 'trial' way to fit the TA data is to model with n_{comp} independent exponential decays and their amplitudes. These decays occur in parallel and the spectra of the individual components are called decay associated spectra (DAS). The model associated with this fitting pathway is referred to as a parallel model as shown in

Figure 6A.

Figure 6. Analysis schemes of (A) parallel model and (B) sequential model. The parameter k_n ($n = 1, 2, 3, \dots$) represents a specific rate constant.

Alternatively, if the decays occur sequentially, the obtained model is called a sequential model. In this case, the components are often referred to as compartments as shown in Figure 6B. In such models, the first compartment is populated by an input excitation function, and subsequently forms the second compartment, which then decays into a third one etc. until the last compartment decays back to the ground state. The spectra of these individual compartments are called evolution associated spectra (EAS). Note that unlike in a parallel model, in a sequential model the individual components are interconnected. For example, the formation of the third EAS is associated with the lifetime of the second EAS. Back transfers are not taken into account, meaning their rates are slow enough to be negligible.

The data analysis based on either parallel or sequential models is referred to as global analysis, in the sense that the rate constants are obtained from a global fit of the data at all wavelengths and times. In fact, a successful global analysis must return a physically meaningful DAS or EAS. On this basis, the number of modeling parameters should be kept as low as possible to avoid problems such as divergence and over-modeling.

2.3.4. Target analysis

The methods introduced in the previous section are often used without a priori knowledge of the photodynamical behavior of the system. In some cases, however, a formerly established interpretation is available, and therefore a specific photophysical or photochemical model can be tested. Such a model can be as simple as a single sequential or parallel model, but more often it is a linearly formed compartment model containing multiple sequential or parallel sub-models.

This modeling method is referred to as target analysis, and the corresponding model is called a target model, with kinetics described by the following linear differential equation:

$$\frac{d}{dt} \mathbf{c}^T(t) = \mathbf{K} \mathbf{c}^T(t) + \mathbf{j}^T(t), \quad (13)$$

where $\mathbf{c}^T(t) = [c_1(t) \ c_2(t) \ \dots c_{n_{comp}}(t)]^T$ is a concentration vector with n_{comp} compartments, $\mathbf{K}$ is a transfer matrix, and $\mathbf{j}^T(t)$ describes the input to the system. According to equation (13), the total decay rates of each compartments are exactly the diagonal elements of $\mathbf{K}$, whereas the transition rate constants between these compartments are the off-diagonal elements of the $\mathbf{K}$ matrix.

Equation (13) can be visualized by plotting an analysis scheme. For example, Figure 7 shows a target model. Compartment A is initially populated via an input function j_A . This compartment then evolves into two compartments B and C in a parallel way, with two specific rate constants k_1 ($A \rightarrow B$) and k_2 ($A \rightarrow C$). Compartment C directly decays to the ground state with a rate constant k_5 . Compartment B relaxes into compartment D with a rate constant k_3 , and compartment D finally decays to the ground state with a rate constant k_4 . In this specific complex target model, the initial branching process ($A \rightarrow B \& C$) is in fact a parallel sub-model, and the sequential process ($B \rightarrow C \rightarrow$ ground state) is a sequential sub-model.

Figure 7. Schematic plot of a target model example. For details see text.

The spectra of the associated compartments obtained from target analysis are called species associated spectra (SAS), similar to the concept of DAS or EAS in global analysis. Since target analysis is generally more complex than global analysis using a parallel or sequential model, special attention has to be paid to the photodynamical interpretation of the obtained SAS. In some cases different target models may even result in similar fits, and therefore the real challenge is to establish a good connection between the model and its physical meaning. Due to the complexity of TA modelling as discussed above, the open-source program

Glutaran is used for data analysis in the context of this thesis.¹⁵

In summary, the methods for photodynamical modeling introduced in this section, together with the experimental description of the TA setup explained in the previous sections, provide a basis for applying TA spectroscopy to study the photodynamics of various Ru(II)-based photocatalysts, as will be discussed in the following chapters.

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Chapter 3. The impact of the bridging ligand on the excited state properties

While the previous chapters introduced the fundamentals of light-induced H₂ generation and time-resolved spectroscopy, the present chapter focuses on the photodynamics of a model photocatalyst [Ru(bpy)₂(2,5-tpy)Pd(CH₃CN)Cl]²⁺ (**RuPd1**; bpy = 2,2'-bipyridine, 2,5-tpy = 2,2':5',2''-terpyridine). An inter-ligand electron transfer process is observed competing with vibrational cooling (VC), resulting in an effective ³MLCT_{bpy} → ³MLCT_{tpy} internal conversion process taking place on a ps time scale. Importantly, replacing the 2,5-tpy bridging ligand with an analogous 2,2':6',2''-terpyridine (2,6-tpy) ligand significantly reduces the excited state lifetime of the chromophore by three orders of magnitude, resulting in a completely vanished H₂ evolution reactivity. These insights highlight the importance of the bridging ligand, not only concerning its coupling with the peripheral ligands, but also regarding its influence on the overall excited state lifetime. The knowledge obtained in the present chapter supports the discussion of the excited state properties of other photocatalysts in later chapters of this thesis. The content of this chapter is based on work published in the following article:

- Pan, Q.; Mecozzi, F.; Korterik, J. P.; Sharma, D.; Herek, J. L.; Vos, J. G.; Browne, W. R.; Huijser, A. *J. Phys. Chem. C* **2014**, *118*, 20799.

3.1. Introduction

Light-induced H₂ formation from water is one of the primary targets in producing renewable green fuel by storing transient solar energy in chemical bonds.¹ Splitting of water requires the transfer and accumulation of multiple charges, and hence, directional electron transfer and long-lived charge separation are required in synthetic systems.² The search for molecular photocatalysts for efficient proton reduction has focused on Ru(II)-polypyridyl complexes, with [Ru(bpy)₃]²⁺ serving as a starting point, in large part due to their outstanding photophysical and photochemical properties as introduced in Chapter 1.

One photocatalytic approach for proton reduction is to physically mix the light-absorbing photosensitizers and catalytically active metal centers such as metal halides in solution. The photosensitizers may transfer electrons to the catalytic metal centers, where the proton reduction reaction could take place. Sacrificial electron donors such as triethylamine are added to regenerate the photosensitizers.³ An apparent drawback of this inter-molecular approach is that the electron transfer from the photosensitizers to the catalytic centers is diffusion limited.⁴

To overcome this limitation, an alternative strategy involves the intra-molecular approach by covalently connecting the photosensitizer and the catalytic metal center by a bridging ligand, which can mediate directional electron transfer. Based on this strategy, several model systems have been reported. Sakai et al. reported a series of Ru/Pt complexes, of which the structure-reactivity relationship and reaction mechanisms were studied.^{5,6} Rau and co-workers studied a Ru/Pd photocatalyst,⁷ and the fundamental photophysics were explored showing directional intra-molecular electron transfer towards the catalytic center.^{8,9} Fontecave et al. investigated several Ru/Co complexes, which were also found photoactive for H₂ generation.¹⁰ It should be noted that the reaction conditions (e.g. the sacrificial donor concentration, water percentage, irradiation power and wavelength, pH value) often differ, complicating direct comparison of the reported H₂ evolution turnover number (TON) values. In addition, the obtained TONs are the results of a sequence of complex photophysical and photochemical processes. Consequently, the photocatalytic performance cannot be judged from the reported TON alone. However, deeper insights can be obtained by studying the fundamental photodynamics of the complexes, providing essential routes for further improvement.

In this chapter, two related Ru-polypyridine-Pd complexes (**RuPd1** and **RuPd2**, Figure 1) with the same peripheral ligands but different bridging ligands are discussed. For **RuPd1**, a TON value of 130 over 18 h of irradiation at 470 nm was reported in earlier work.¹¹ Interestingly, the analogous **RuPd2** complex was found to be completely inactive for light-induced H₂ generation.¹¹ The underlying photodynamical reasons for this distinct photocatalytic behavior, and in particular the role of the bridging ligand, are explored by using a combination of different spectroscopic techniques. Firstly, resonance Raman (rR) spectroscopy is used to probe the localization of the initial excited states in the Franck-Condon (FC) region. This technique is only sensitive to the initial localization upon photoexcitation as only the modes in resonance with electronic transitions are enhanced and detected.^{12,13} The temporal evolution of the initially formed excited states is probed by ultrafast transient absorption (TA) spectroscopy, which provides kinetic information in a time window ranging from 100 fs to the sub-ns regime. The relaxation of the lowest excited states is studied by time-resolved photoluminescence (TRPL). Covering the complete time range over which excited state processes occur, a comparison of the behavior of the complexes enables the identification of the impact of the bridging ligand on the excited state properties, as will be discussed in the next section.

Figure 1. Molecular structure of **RuPd1** (left) and **RuPd2** (right). The mononuclear Ru precursors are denoted as **Ru-A** and **Ru-B**.

3.2. Results and discussion

3.2.1. Steady state characterization

The steady state absorption and photoluminescence (PL) properties of the complexes are shown in Figure S1 in the Supporting Information (SI) at the end of this chapter, and summarized in Table 1. Each complex exhibits a broad absorption band between 400 nm and 550 nm that is typical for Ru(II)-polypyridyl complexes as introduced in Chapter 1, and is therefore assigned to metal-to-ligand charge transfer (¹MLCT) transitions.^{11,14} The sharp absorption bands in the ultraviolet are due to ligand-centered (LC) $\pi-\pi^*$ transitions (SI).^{11,14} For **Ru-A** and **RuPd1**, the PL bands are comparable in terms of spectral shape and quantum yield Φ_{PL} , with the emission of **RuPd1** only slightly red-shifted. This result indicates that the energy gap between the ground state and the lowest excited states is not substantially perturbed by the presence of the Pd(II) moiety. **Ru-B** and **RuPd2** however exhibit a significantly reduced Φ_{PL} , suggesting the presence of an efficient non-radiative decay pathway and a resultant short excited state lifetime. This hypothesis is supported by both TA and TRPL as discussed in the next section.

Table 1. Steady state absorption and PL properties of the complexes.^{11,14}

Complex	Max. ¹ MLCT abs.	ϵ ($10^4 \text{ M}^{-1}\text{cm}^{-1}$)	Max. PL	Φ_{PL}
Ru-A	446 nm	1.18	629 nm	0.047
RuPd1	462 nm	1.33	632 nm	0.032
Ru-B	448 nm	1.88	618 nm	0.003
RuPd2	449 nm	1.72	635 nm	0.001

3.2.2. Excited state photodynamics

In this section the photodynamics of **Ru-A** and **RuPd1** are investigated in detail prior to the discussion of **Ru-B**. The localization of the initial $^1\text{MLCT}$ excited states upon photoexcitation has been studied by rR spectroscopy by identifying the various vibrational modes with strong resonance enhancement. This technique is a powerful tool to study the wave packet motion in the FC region for Ru-based complexes,^{8,13,15} providing information complementary to the results obtained from TA (*vide infra*) which has a time resolution of 100–150 fs.

Figure 2 shows the rR spectra of **Ru-A**, **RuPd1** and the reference $[\text{Ru}(\text{bpy})_3]^{2+}$ complex dissolved in acetonitrile. The peak positions are listed in Table 2. At $\lambda_{\text{exc}} = 473$ nm, which is close to the pump wavelength (480 nm) used in the TA experiments, the Raman scattering from the ligands associated with the $\text{GS} \rightarrow ^1\text{MLCT}$ (GS: ground state) transitions is enhanced through resonance.

Figure 2. Resonance Raman spectra of **Ru-A** (blue), **RuPd1** (red) and $[\text{Ru}(\text{bpy})_3]^{2+}$ (black) in acetonitrile recorded at $\lambda_{\text{exc}} = 473$ nm. Solvent contributions have been removed by scaled subtraction. The band at 1041 cm^{-1} (*) for $[\text{Ru}(\text{bpy})_3]^{2+}$ is due to imperfect subtraction of the solvent signal.

In all three spectra, the characteristic modes of $[\text{Ru}(\text{bpy})_3]^{2+}$ are readily resolved, consistent with the resonance with the $^1\text{MLCT}(\text{t}_{2\text{g}}\text{-Ru(II)} \rightarrow \pi^*\text{-bpy})$ electronic transitions at 473 nm. For simplicity reasons, these transitions will be denoted as $^1\text{MLCT}_{\text{bpy}}$ where the subscript denotes the localization of the excited state electron density, and the superscript emphasizes its singlet character. Resonance with the $^1\text{MLCT}_{\text{tpy}}$ transitions is also observed for **Ru-A**, in particular at 1606, ~ 1507 , ~ 1473 and 1318 cm^{-1} . In the case of **RuPd1**, an additional tpy

associated mode is observed at 1589 cm^{-1} under the influence of Pd(II) coordination. Note that some tpy and bpy associated modes overlap at 1606 and 1318 cm^{-1} . The assignment of the Raman bands based on deuteration experiments is given in the Supporting Information (SI). In summary, the rR data provide evidence for the initial population of both $^1\text{MLCT}_{\text{bpy}}$ and $^1\text{MLCT}_{\text{tpy}}$ states upon excitation at 473 nm for **Ru-A** and **RuPd1**.

Table 2. Comparison of rR bands [cm^{-1}] of **Ru-A** and **RuPd1** with those of $[\text{Ru}(\text{bpy})_3]^{2+}$.

$[\text{Ru}(\text{bpy})_3]^{2+}$	Ru-A	RuPd1
1028	1027	1027
1173	1173	1172
1274	1274	1274
—	—	1289
1318	1318	1317
—	—	1475
1489	1489	1489
—	—	1506
1561	1562	1561
—	—	1589
1606	1606	1606

The subsequent photodynamics in the fs and ps time window have been probed by TA spectroscopy. Figure 3A shows the TA spectra of **Ru-A** at several delay times between pump and probe pulses, together with the kinetic traces (ΔOD vs time) at key wavelengths (Figure 3B). Although spectral changes occur in the region above 500 nm related to ligand-to-metal charge transfer (LMCT) transitions,¹⁶ the most informative time dependent changes are observed in the blue-ultraviolet region, with two pronounced bands observed at ca. 370 nm and 420 nm. The former band is assigned to excited state absorption (ESA) of the bpy^- monoanion,^{16,17} while the latter is assigned to ESA of tpy^- .¹⁴ Therefore, allocation of the excited states can be realized by tracking the signal amplitudes of these two ESA bands in time. The possibility of solvated electrons is excluded, as the ESA bands in the 500–700 nm region do not show the characteristic solvated dimer anion features in the ps time domain.¹⁸

Figure 3. TA spectra (A) and kinetic traces at selective wavelengths (B) of **Ru-A**. Fits based on a target analysis model (*vide infra*) are presented by solid curves.

At 500 fs, the two ESA bands at ca. 370 nm and 420 nm have comparable intensities, indicating that both the bpy and tpy ligands are populated by the excited state electron density, in agreement with the rR results discussed earlier. Between 500 fs and 20 ps, the ESA signal amplitude at ca. 370 nm decreases, concomitant with an increase of the ESA signal amplitude at ca. 420 nm with an isosbestic point at ca. 375 nm. This observation provides strong evidence for electron density motion from the bpy to the tpy ligands, which is often referred to as the inter-ligand electron transfer (ILET). This result is consistent with a recent work reporting ILET occurring on a similar time scale in some analogous Ru(II)-based complexes based on bpy and 1,10-phenanthroline ligands.¹⁷ In addition, earlier research on a Ru(II)-polypyridyl complex anchored on TiO₂ also reported ILET occurring on a ps time scale.¹⁹ Notably, the ground state bleach (GSB) signal at ca. 450 nm shows no significant change in amplitude throughout the entire temporal window (probed till 700 ps), meaning recombination in **Ru-A** is irrelevant at this time scale. Furthermore, the observation of the bpy⁻ based ESA signal at 370 nm even 500 ps after excitation indicates that the bpy⁻ monoanion is present after finalization of the ILET process, suggesting a competing relaxation channel at the bpy ligands. This observation is consistent with ns transient Raman spectroscopic studies reported earlier, which showed the presence of characteristic features (1210 and 1282 cm⁻¹) of the bpy anion radical.¹¹ This phenomenon will be discussed in more detail in the next section.

The TA spectra and kinetic traces of **RuPd1** are shown in Figure 4A and 4B. The most notable difference between the TA spectra of **Ru-A** and **RuPd1** is that the tpy⁻ associated ESA band at 420 nm is much less intense for the latter complex, while the intensities of the bpy⁻ associated ESA band at 370 nm and the GSB signal are comparable. The less intense absorption around 420 nm may be caused by a decrease in oscillator strength of the tpy⁻ associated ESA band due to the close

proximity of the Pd atom. Alternatively, this phenomenon may be due to charge delocalization over the tpy ligand and the Pd moiety. Interestingly, the kinetic trace at 370 nm of **RuPd1** (Figure 4B) associated with the bpy ligand remains similar compared to that of **Ru-A** (Figure 3B). This observation suggests that the degree of electron transfer from bpy to tpy is comparable for **Ru-A** and **RuPd1**, presuming that the oscillator strength of the bpy^- associated ESA band at 370 nm is not significantly affected by Pd coordinated to the tpy ligand. A second difference between the TA spectra of **Ru-A** and **RuPd1** is that the broad ESA bands in the longer wavelength region (500–700 nm) are red-shifted for **RuPd1**. This difference is most likely due to the influence of Pd on the $^3\text{LMCT}$ transitions from the tpy ligand to the formerly oxidized Ru(III) center.

Figure 4. TA spectra (A) and kinetic traces at selective wavelengths (B) of **RuPd1**. Fits based on a target analysis model (*vide infra*) are presented by solid curves.

Despite the aforementioned differences, **RuPd1** shows a qualitatively similar evolution of the ESA bands as **Ru-A**. A decrease in absorbance at 370 nm and an increase in absorbance at 420 nm is again observed before ca. 20 ps, with an isosbestic point at ca. 385 nm. This observation shows that ILET in **RuPd1** also occurs on a ps time scale. No significant changes are observed for the GSB signal (e.g. at 475 nm), indicating slow recombination. Importantly, the bpy^- associated ESA band at 370 nm does not decrease further after 20 ps, indicating the presence of long-lived excited states based on the bpy ligand. This result is consistent with earlier ns transient Raman studies, similar to the case of **Ru-A**.¹¹

The decay of the relaxed excited states on the ns time scale has been studied by TRPL as shown in Figure 5. **Ru-A** shows a mono-exponential PL decay with a time constant of 790 ns. The PL decay of **RuPd1** is however bi-exponential with two time constants of 88 ns and 400 ns, with the faster component dominating (62%). The mono-exponential PL decay of **Ru-A** suggests a thermally equilibrated population of excited states. Alternatively, the bpy and tpy based excited states may decay with a similar time constant close to 790 ns. This issue will be

addressed in more detail in the next chapter by excitation wavelength dependent TA studies. For **RuPd1**, however, the bi-exponential PL decay strongly indicates the presence of two co-existing excited states that emit independently with distinct lifetimes. The 88 ns component is assigned to the emission from the $^3\text{MLCT}_{\text{tpy}}$ state to the GS, as coupling tpy to Pd(II) is likely to enhance the radiative decay rate as a result of the spin-orbital coupling effect.¹⁴ Alternatively, electron transfer from the tpy ligand to the Pd(II) moiety may also decrease the lifetime of the $^3\text{MLCT}_{\text{tpy}}$ state. This possibility is discussed in more detail in the next section. The observed 400 ns component is attributed to the emission from the $^3\text{MLCT}_{\text{bpy}}$ state to the GS, as the bpy ligand is relatively far from the Pd(II) center and is therefore less affected.¹⁴

Figure 5. PL decays of **Ru-A** and **RuPd1** obtained on excitation at 460 nm. Fits to mono-exponential (**Ru-A**) and bi-exponential (**RuPd1**) decays are represented by black solid curves.

Based on the above discussion, it is concluded that both $^3\text{MLCT}_{\text{bpy}}$ and $^3\text{MLCT}_{\text{tpy}}$ states are populated and long-lived for **Ru-A** and **RuPd1**. The next step is to compare this result with the excited state behavior of **Ru-B**, which is the chromophore of **RuPd2**. Figure 6A and 6B show the TA spectra and kinetic traces obtained for **Ru-B**. The negative GSB signal is readily observed around 450 nm. Interestingly, only one single ESA band is observed in the ultraviolet at ca. 375 nm, possibly due to overlap of the bpy-based and 2,6-tpy-based LC transitions. Both the GSB and ESA signals of **Ru-B** decay, in contrast to **Ru-A** and **RuPd1**, strongly indicating that the excited states of **Ru-B** are short-lived. Global analysis using a sequential model yields two decay time constants of 5.0 (± 0.4) ps and 62.7 (± 8.3) ps. Note that the TA signals are not completely vanished even beyond ca. 300 ps, suggesting the population of a longer-lived excited state. Therefore a fixed time constant of 726 ps (determined by fitting the PL decay, *vide infra*) is applied to

account for the residual TA signal beyond 300 ps. The obtained evolution associated spectra (EAS) are shown in Figure S4 (SI).

Figure 6. TA spectra (A) and kinetic traces at selected probe wavelengths (B) of **Ru-B**. Global fits based on a sequential model are presented by solid curves.

The TA data of **Ru-B** suggests its PL decay to be also ultrafast on a sub-ns time scale, which is confirmed by the data shown in Figure 7. A multi-exponential decay fit gives two time constants of $\tau_1 = 66 \pm 7$ ps (52.2%) and $\tau_2 = 727 \pm 27$ ps (43.3%). The value of τ_1 is in excellent agreement with the value obtained from TA (62.7 ± 8.3 ps), and τ_2 is applied to obtain a fit of the aforementioned long-lived TA signal beyond 300 ps. Note that the PL signal does not completely vanish even after 2 ns. Therefore a third time constant τ_3 of 33 ns (4.5%), adopted from an earlier ns TRPL study,¹¹ was fixed during fitting to account for the signal offset. The multi-exponential PL decay feature of **Ru-B** indicates the co-existence of multiple emitting excited states that are non-equilibrated. Based on the above discussion, both TA and TRPL show that the excited states of **Ru-B** are short-lived and recombination occurs on a (sub-)ns time scale, three orders of magnitude faster than the recombination rates observed for **Ru-A** and **RuPd1**.

Figure 7. PL decays of **Ru-B** integrated from 600 nm to 670 nm obtained by exciting at 532 nm. A fit to a tri-exponential decay function is represented by the solid curve. For details of the fit, see text.

Although the excited state properties of **RuPd2** have not been measured due to synthesis difficulties, the absence of any observable photocatalytic H₂ generation reactivity of **RuPd2** can be rationalized by the short excited state lifetime of its chromophore **Ru-B**. A metal-centered (³MC) triplet excited state (see Chapter 1 for its origin) is probably close in energy to the ³MLCT states, providing a fast recombination channel to the GS. The large steric encumbrance induced by the 2,6-tpy ligand is probably the reason for such a ³MC state to be relatively low in energy as compared to **Ru-A** and **RuPd1** based on the 2,5-tpy bridging ligand.

3.2.3. Photophysical modeling

As it is shown in the previous section that the 2,6-tpy ligand significantly reduces the excited state lifetime of the chromophore, this ligand is therefore not suitable as a bridging ligand, explaining the photocatalytic inactivity of **RuPd2**. The 2,5-tpy ligand is however more suitable as a bridging ligand, as it results in the formation of long-lived excited states, allowing essential photophysical and photochemical processes to occur (e.g. regeneration by sacrificial reagents). As ILET is observed for **RuPd1**, the next issue to address is the functionality of the 2,5-tpy bridging ligand. In particular, the ability of this bridging ligand to allow directional electron density motion from the peripheral bpy ligands to the catalytic Pd center is of high importance. Therefore this section focuses on the photophysical modeling of **RuPd2** by combining the results obtained from rR, TA and TRPL discussed above.

The rR data show that photoexcitation leads to population of both ¹MLCT_{bpy} and ¹MLCT_{tpy} manifolds. This conclusion is also supported by the observation of

ESA bands at both 370 nm and 420 nm in the TA spectra at 200 fs (Figure S8, SI). ISC in $[\text{Ru}(\text{bpy})_3]^{2+}$ is known to occur on a time scale of ~ 100 fs or even faster in acetonitrile (see Chapter 1).²⁰⁻²² It is therefore assumed that ISC processes occur similarly fast in **Ru-A** and **RuPd1**, and $^3\text{MLCT}_{\text{bpy}}$ and $^3\text{MLCT}_{\text{tpy}}$ triplet states are formed within the TA instrumental response time of 100–150 fs. On the triplet potential energy surfaces, ILET ($\text{bpy} \rightarrow \text{tpy}$) is observed to take place within ca. 20 ps as discussed in the previous section. Importantly, the presence of the bpy^- associated ESA band at 370 nm (representative of the $^3\text{MLCT}_{\text{bpy}}$ state) after 20 ps indicates that not all electron density moves towards the bridging tpy ligand. This phenomenon is likely related to a loss channel associated with the bpy ligands competing with this ILET process. Since VC after ISC is known to occur on a ps time scale,^{16,17,23,24} a VC process localized on the peripheral bpy ligands is likely competing with the ILET process. An alternative explanation for the observation of the long-lived $^3\text{MLCT}_{\text{bpy}}$ state involves an excited state equilibrium, which was recently observed for a series of Ru(II)-based complexes.¹⁷ However, the bi-exponential PL decay observed for **RuPd1** strongly supports a non-equilibrated population of excited states. Furthermore, as will be shown in Chapter 4, this equilibration hypothesis cannot explain the strong excitation wavelength dependent TA data. Therefore a model based on excited state equilibrium will not be adopted. Instead, the photophysical modeling will be based on ILET and VC.

As explained in Chapter 2, a global analysis based on a simple sequential model is often helpful for building a more complex target analysis model. Therefore a global analysis is firstly applied to **Ru-A** and **RuPd1**, yielding a time constant of 5.3 (± 0.5) ps for **Ru-A** and 7.0 (± 0.5) ps for **RuPd1**. These time constants represent an effective internal conversion (IC) process that shifts the excited state electron density from the peripheral bpy ligands towards the bridging tpy ligand. In other words, on the triplet potential energy surfaces, the $^3\text{MLCT}_{\text{bpy}} \rightarrow ^3\text{MLCT}_{\text{tpy}}$ transition occurs on a time scale of several ps. The obtained evolution associated spectra (EAS) based on this global analysis are shown in Figure S5 and S6 (SI).

Based on the above global analysis results, a more complex target analysis model is applied to **Ru-A** and **RuPd1**. In this model, the ILET and VC processes are decoupled from the overall IC process via the following relationship:

$$\frac{1}{\tau_{\text{IC}}} = \frac{1}{\tau_{\text{ILET}}} + \frac{1}{\tau_{\text{VC}}}, \quad (1)$$

where τ_{IC} , τ_{ILET} and τ_{VC} represent the time constants of effective IC, ILET and VC, respectively. As a unique determination of the two variables τ_{ILET} and τ_{VC} is not possible from applying equation (1) only, it is further assumed that the absorption profiles of the hot and relaxed $^3\text{MLCT}_{\text{bpy}}$ states are identical. This assumption is equivalent to the approximation that the electron density is localized in a similar

way on the peripheral bpy ligands for both of these two states, and therefore their excited state absorption should not differ significantly.

Figure 8. Simplified photophysical model for light-induced processes in **RuPd1**.

The photophysical model used for target analysis is shown in Figure 8. Photoexcitation leads to population of both the bpy- and tpy-based $^1\text{MLCT}$ states, followed by ultrafast ISC within the instrumental response time (100 – 150 fs). The population percentage of bpy- and tpy-based $^3\text{MLCT}$ triplet states is estimated by inspecting the shape and position of the obtained species associated spectra (SAS, *vide infra*). Two distinct bpy-based $^3\text{MLCT}$ states are distinguished, one is associated with a hot $^3\text{MLCT}_{\text{bpy}}$ state, and the other one to a relaxed state. Although these two states are assumed to have an identical absorption, ILET to the tpy ligand is only possible from the hot $^3\text{MLCT}_{\text{bpy}}$ state. Both ISC and ILET lead to the population of the $^3\text{MLCT}_{\text{tpy}}$ state, which is possibly delocalized over the tpy ligand and the Pd(II) moiety (*vide infra*). The decay time constants of the relaxed $^3\text{MLCT}$ states to the GS are obtained from the PL lifetimes. Note that no tpy-based VC process is considered in this model to avoid over-modeling.

Figure 9 shows the obtained SAS of **RuPd1** based on the photophysical model presented in Figure 8. SAS1 and SAS2 (blue curve, Figure 9) represent the spectra of hot and relaxed $^3\text{MLCT}_{\text{bpy}}$ states, whose absorption spectra are assumed to be identical. The negative GSB band around 460 nm resembles the scaled and inverted steady state absorption profile shown as a grey area in Figure 9. The broad ESA band above 500 nm is due to bpy-based LMCT transitions. The positive ESA band around 370 nm is associated with the bpy^- monoanion. The shape of SAS1 (and SAS2) closely resembles the TA spectrum of $[\text{Ru}(\text{bpy})_3]^{2+}$ published earlier.^{16,17} SAS3 (red curve, Figure 9) is the spectrum of the $^3\text{MLCT}_{\text{tpy}}$ state. The positive ESA band around 420 nm is associated with the tpy^- monoanion. The tpy-based LMCT

band (above 500 nm) is more intense than that based on the bpy ligands. The coupling between the tpy ligand and the Pd(II) center may lead to a strong LMCT absorption in this region. The SAS of **Ru-A** determined by applying an analogous model are provided in Figure S7 (SI).

Figure 9. Obtained SAS of **RuPd1**. The gray area represents the scaled and inverted steady state absorption.

Based on the above discussion, the obtained ILET time equals 8.8 ± 0.7 ps for **Ru-A** and 32.5 ± 1.5 ps for **RuPd1**. These values are close to the ~ 20 ps found by Sundström and co-workers for a Ru(II)-based photosensitizer on TiO_2 .¹⁹ The competing bpy-localized VC process occurs with a time constant of 13.4 ± 1.5 ps for **Ru-A** and 9.1 ± 0.4 ps for **RuPd1**. These results are in agreement with the values of 5–15 ps reported by various groups.^{16,17,23,24} The current work also suggests that coordinating Pd to the tpy ligand slows down the ILET process. One possible reason is that the ILET process is coupled to the rotation of the complexes and/or vibrational relaxation of the tpy ligand.²⁵ TA anisotropy measurements demonstrated a rotational decay constant of about 40–50 ps for $[\text{Ru}(\text{bpy})_3]^{2+}$ in acetonitrile at room temperature.^{16,26} As the Pd moiety likely slows down the molecular rotation and increases the rigidity of the tpy ligand, ILET may become slower and less competitive to VC at the bpy ligands.¹⁴

Another important aspect of this photophysical model involves the localization/delocalization nature of the $^3\text{MLCT}_{\text{tpy}}$ state. Assuming this state is localized on the tpy ligand, after its population an electron transfer process towards the Pd(II) moiety can be expected. The bi-exponential PL decay observed for **RuPd1** allows estimation of the time scale of this electron transfer process through the equation:

$$\tau_{\text{RuPd1}} = \frac{1}{k_r + k_{nr} + k_{et}} = 88 \text{ (ns)}, \quad (2)$$

where τ_{RuPd1} is the excited state lifetime of **RuPd1**, and k_r , k_{nr} and k_{et} represent the rate constants for radiative decay, non-radiative decay and electron transfer from tpy to Pd, respectively. Similarly, the excited state lifetime of **Ru-A** is given by:

$$\tau_{\text{Ru-A}} = \frac{1}{k_r' + k_{nr}'} = 790 \text{ (ns)}, \quad (3)$$

where k_r' and k_{nr}' are the rate constants for radiative and non-radiative decays for **Ru-A**.

Assuming the Pd(II) moiety does not significantly alter the radiative and non-radiative decay rates (i.e. $k_r = k_r'$ and $k_{nr} = k_{nr}'$), it can be expected from equations (2) and (3) that the rate constant for electron transfer from tpy to Pd is on the order of 10^7 s^{-1} , equivalent to a time constant of 100 ns. This value is much slower than the ps ILET time constant. Notably, a much faster (310 ps) electron transfer from the bridging ligand to the Pd center was reported earlier for an analogous Ru/Pd photocatalyst.⁸ Apparently, such fast electron transfer does not occur in **RuPd1**, as no significant changes in TA features are observed from ca. 20 ps to at least 700 ps.

Alternatively, it is possible that the $^3\text{MLCT}_{\text{tpy}}$ is delocalized over the tpy bridging ligand and the Pd(II) moiety. Such delocalization may explain the reduced ESA band brightness around 420 nm in the TA spectra of **RuPd1** as compared to **Ru-A**. In this case, the observed shorter $^3\text{MLCT}_{\text{tpy}}$ lifetime (88 ns) for **RuPd1** compared to that of **Ru-A** (796 ns) is caused mainly by a more efficient radiative decay pathway, rather than directional electron transfer to the Pd center (oxidative quenching). In other words, k_r is significantly larger than k_r' , possibly due to an enhanced spin-orbit coupling due to the Pd moiety. The non-radiative decay pathway may become less dominant, as Pd likely increases the rigidity of the complex. This phenomenon has been observed by Sakai and co-workers for a platinated Ru complex. In their case, the Ru/Pt dinuclear complex has an even longer excited state lifetime than the Ru mononuclear compound due to an increased ligand rigidity upon platination.²⁷ Based on these results, a delocalized $^3\text{MLCT}_{\text{tpy}}$ state over tpy and Pd is more likely than a localized state that slowly (~ 100 ns) transfers electron density towards the Pd center.

3.3. Conclusions

The impact of the bridging ligand on the ultrafast excited state properties has been studied by a combination of spectroscopic techniques including rR, TA and TRPL. The 2,6-tpy ligand is unable to function as a suitable bridging ligand, as it significantly reduces the excited state lifetime of the chromophore, possibly due to

a lowered ^3MC state caused by steric encumbrance. On the other hand, the 2,5-tpy ligand is more suitable as a bridging ligand, as it allows an excited state lifetime three orders of magnitude longer than that of the 2,6-tpy analogue.

The coupling between the 2,5-tpy bridging ligand and the peripheral bpy ligands in the excited state is also investigated. Optical excitation leads to the population of both bpy- and tpy-based $^1\text{MLCT}$ states. After ultrafast (~ 100 fs) ISC, the electron density localized on the peripheral bpy ligands subsequently flows to the bridging tpy ligand on a ps time scale. Importantly, not all electron density ends up at the bridging tpy ligand, but a part remains at the peripheral bpy ligands. This phenomenon is explained by the occurrence of a competing VC process localized at the bpy ligands, resulting in a non-equilibrated population of the $^3\text{MLCT}_{\text{bpy}}$ and $^3\text{MLCT}_{\text{tpy}}$ states.

The coupling between the bridging 2,5-tpy ligand and the Pd(II) moiety is likely to result in an $^3\text{MLCT}$ state where the electron density is delocalized over tpy and Pd. Less probably, a slow electron transfer (tpy $\rightarrow$ Pd) process may occur on a time scale of ~ 100 ns. Further investigation of the catalytic metal center is required, and an example is discussed in Chapter 7 for an analogous Ru/Pt bimetallic photocatalyst.

3.4. Experimental section

(1) Material synthesis and steady state characterization

The synthesis of the complexes was described elsewhere earlier.¹¹ ^1H NMR spectral data are provided in the Supporting Information of ref. 14. The complexes were dissolved in acetonitrile (Sigma-Aldrich, purity $>99.5\%$) in 1 cm path length quartz cuvettes for steady state measurements. UV-vis absorbance spectra were recorded using a SHIMADZU UV-1800 spectrophotometer. Steady state PL spectra were obtained using a Horiba Jobin Yvon FluoroMax-4 spectrofluorometer with excitation at 450 nm, with the same optical density (OD) at the excitation wavelength for all the complexes. Both absorbance and PL spectra were recorded at room temperature.

(2) Resonance Raman spectroscopy

Raman spectra were recorded at 473 nm excitation (Cobolt Lasers 50 mW) in 1 cm path length quartz cuvettes. The excitation beam was focused at the sample using a 10 cm focal length parabolic mirror at ca. 35° with respect to the collection axis. The Raman scattering was collected and collimated with a 2.5 cm diameter, 15 mm focal length plano convex mirror, filtered to remove Rayleigh scattering using a

Steep Edge long pass filter (Semrock), focused into a spectrograph (Shamrock 303, AndorTechnology, 1200 l/mm grating blazed at 500 nm), and imaged onto a Andor iDus-420-BEX2-DD CCD camera.

(3) Ultrafast transient absorption spectroscopy

Samples for transient absorption (TA) experiments were prepared by dissolving the compounds in anhydrous acetonitrile (Sigma-Aldrich, purity >99.9%) in 1 mm optical path length quartz cuvettes. All samples had the same OD (~0.45) at 480 nm (excitation wavelength). Photo-induced chemical degradation was excluded by comparison of the UV–vis absorption spectra recorded before and after the TA experiments. The TA setup was described earlier in Chapter 2. Briefly, the system consists of an amplified Ti:sapphire laser system (Clark MXR CPA-2001), which produces laser pulses at 775 nm at a 1 kHz repetition rate, with a pulse duration less than 120 fs. Part of this 775 nm output is directed into a noncollinear optical parametric amplifier (NOPA, Clark MXR), to generate a pump beam at 480 nm, and is compressed afterward by a SF10 prism pair, yielding a pulse duration around 50 fs, and a FWHM bandwidth of 7 nm. The remaining part of the fundamental 775 nm beam, after passing a mechanical delay stage, is focused onto a 3 mm thick CaF₂ window (001-cut, Newlight Photonics Inc.) to generate a white light continuum (345–700 nm) probe. The CaF₂ crystal is mounted on a continuously moving stage to avoid thermal damage. The polarization angle between the pump and probe beams is set at magic angle (54.7°).²¹ The pulse energy of the pump was ca. 1.5×10^{-4} J/cm² (3.7×10^{14} photons/cm²), and was verified to be in the linear regime. After passing through the sample, the pump beam is blocked and the probe beam is spectrally dispersed using a spectrograph (Acton SP-150, 150 grooves/mm grating). A photodiode array consisting of 256 pixels is used to record the data. TA data were numerically corrected for chirp by fitting the spectro-temporal traces of pure solvent coherent artifact peaks with a polynomial function, and by subsequent correction of the time axis based on that polynomial function. From the coherent artifact signals, the TA time resolution was determined to be 100–150 fs. The open-source software Glotaran²⁸ was used for data analysis.

(4) Time-resolved photoluminescence

Samples were prepared in a similar way as in the UV–vis absorbance experiments, and were deaerated by using dry N₂ gas. Nanosecond TRPL was measured by using a FluoroMax Spectrofluorometer extended for time-correlated single photon counting measurements (HORIBA JOBIN YVON, Fluoro- Max-4 TCSPC). A NanoLED-460 laser source (462 nm, 1.3 ns pulse duration) was used to excite the samples at a repetition rate of 250 kHz. The PL lifetime data were recorded at 630

nm for **Ru-A** and 635 nm for **RuPd1**. Picosecond TRPL was measured by using a Hamamatsu C10910 streak camera with a M10913 module for single sweep measurements. An Acton SP2300i spectrograph (150 grooves/mm grating, Princeton Instrument) was placed in front of the streak camera to spectrally disperse the signal. The sample was excited at 467 nm by using a PicoQuant LDH-P-C laser with a pulse duration less than 70 ps.

Supporting Information

Section S1 (steady state absorbance and PL spectra)

Figure S1 shows the normalized steady state absorbance and PL spectra of the complexes in acetonitrile recorded at room temperature. All complexes exhibit broad $^1\text{MLCT}$ absorption bands between 400 nm and 550 nm. The absorbance bands at ca. 280 nm for **Ru-A** and 290 nm for **RuPd1** correspond to the bpy LC $\pi\text{-}\pi^*$ transitions, and the shoulders at ca. 300 nm for **Ru-A** and 310 nm for **RuPd1** have been assigned earlier to the 2,5-tpy LC $\pi\text{-}\pi^*$ transitions on basis of rR spectroscopy.¹¹ The shift to longer wavelength for these latter bands compared with those of bpy is due to the increased conjugation present in the 2,5-tpy ligands. The observation of a single sharp absorbance band around 290 nm for **Ru-B** suggests that the bpy and 2,6-tpy LC $\pi\text{-}\pi^*$ transitions are close in energy. The PL band of **RuPd1** is only slightly redshifted by 3 nm compared to that of **Ru-A**. **Ru-B** exhibits a weak PL band around 618 nm. Due to sample impurity reasons, measurements on **RuPd2** were not performed.

Figure S1. Normalized steady state absorbance (solid curves) and PL (dashed curves) spectra of **Ru-A**, **RuPd1** and **Ru-B**.

Section S2 (resonance Raman spectra of deuterated compounds)

Resonance Raman spectra were recorded for the compounds with deuterated bpy ligands, and the results are shown in Figure S2. The peak positions are summarized in Table S1. Exclusive deuteriation of the bpy ligands is expected to shift the Raman bands associated with bpy, whereas the tpy-associated Raman bands are likely to be unaffected. Based on this assumption, the assignment of the Raman bands can be performed. In the case of **Ru-A**, the bands at 1604, ~1507, 1473, and ~1317 cm^{-1} are not affected by deuteriation of bpy, and are therefore assigned to tpy-based modes. The bands at 1604, 1561, 1489, 1317, 1274, 1172, 1064 and 1027 cm^{-1} are shifted, and are therefore assigned to the bpy-based modes. Note that some tpy-bands overlap with the bpy-bands, for instance, at 1604, 1489 and 1317 cm^{-1} . The assignment of the Raman bands of **RuPd1** is similar to that of **Ru-A**, with the bands at 1604, 1590, ~1506, ~1474, 1315 and 1112 cm^{-1} assigned to the modes of tpy, and those at 1604, 1561, 1487, 1315, 1274, 1172, 1064 and 1026 cm^{-1} are assigned to the modes of the bpy ligand.

Figure S3. Resonance Raman spectra ($\lambda_{\text{exc}} = 473 \text{ nm}$, solvent subtracted) of (deuterated) **Ru-A** (left) and (deuterated) **RuPd1** (right).

Table S1. Comparison of the Raman bands [cm^{-1}] of **Ru-A** and **RuPd1** with those of the corresponding deuterated compounds (marked with d).

Ru-A	Ru-A(d)	RuPd1	RuPd1(d)
–	1005	–	1007
1027	–	1026	–
–	1038	–	~1038
1064	–	1064	–
1172	1172	1112	1113
–	1200	–	1163
1274	–	1172	–
–	~1302	–	1200
–	~1310	1274	–
1317	–	–	1312
–	~1320	1315	–
–	1422	–	1422
~1473	1472	~1474	1472
1489	–	1487	–
–	1491	~1506	1508
~1507	–	–	1523
–	1523	1561	–
1561	–	–	1568
–	1567	1590	1590
1604	1604	1604	~1604

*Section S3 (EAS and SAS of **Ru-A**, **Ru-B** and **RuPd1**)*

Figure S4 shows the EAS of **Ru-B** obtained from global analysis by using a sequential model. A negative GSB band around 460 nm and a positive ESA band at ca. 375 nm are resolved. The GSB band resembles the mirror image of the steady state absorption shown as the gray area in Figure S4. EAS1 represents the spectrum of the initially formed triplet state (i.e. immediately after ISC). EAS1 evolves into EAS2 with a time constant of 5.0 ± 0.4 ps, which further evolves into EAS3 in 62.7 ± 8.3 ps. EAS3 is longer-lived with a lifetime of 727 ps (fixed for fitting the TA data) determined from the TRPL measurement. The decay of both the ESA and GSB signals indicates that the excited states of **Ru-B** are shorter-lived than those of **Ru-A** and **RuPd1**.

Figure S4. Obtained EAS of **Ru-B**. The gray area represents the scaled and inverted steady state absorption spectrum.

Figure S5. Obtained EAS of **Ru-A**. The gray area represents the scaled and inverted steady state absorption spectrum.

Figure S5 shows the EAS of **Ru-A** obtained from global analysis by using a sequential model. Similar to the case of **Ru-B**, EAS1 represents the spectrum of the initially formed triplet state (i.e., immediately after ISC). Two positive ESA bands around 370 nm and 420 nm contribute to EAS1, with the former band assigned to the bpy^- monoanion and the latter one assigned to the bpy^- monoanion as discussed in the main text. EAS1 evolves into EAS2 in 5.3 ± 0.5 ps, with EAS2 showing an enhanced ESA amplitude around 420 nm and a decreased signal amplitude below 370 nm. This result indicates a ${}^3\text{MLCT}_{\text{bpy}} \rightarrow {}^3\text{MLCT}_{\text{tpy}}$ IC process. The lifetime of EAS2 is 790 ns (fixed for fitting the TA data) determined from TRPL measurement.

The EAS of **RuPd1** obtained from global analysis using the same sequential

model of **Ru-A** are shown in Figure S6. EAS1 evolves into EAS2 in 7.0 ± 0.5 ps. This time constant is associated with a similar ${}^3\text{MLCT}_{\text{bpy}} \rightarrow {}^3\text{MLCT}_{\text{tpy}}$ IC process as observed in **Ru-A**. The lifetime of EAS2 is 88 ns (fixed for fitting the TA data) obtained from TRPL measurement.

Figure S6. Obtained EAS of **RuPd1**. The gray area represents the scaled and inverted steady state absorption.

Figure S7 shows the SAS of **Ru-A** obtained from target analysis using an analogous photophysical model as shown in Figure 7. SAS1 and SAS2 represent the spectra of hot and relaxed ${}^3\text{MLCT}_{\text{bpy}}$ states, whose absorption spectra are assumed to be identical. SAS3 denotes the spectrum of the ${}^3\text{MLCT}_{\text{tpy}}$ state.

Figure S7. Obtained SAS of **Ru-A**. The gray area represents the scaled and inverted steady state absorption.

Section S4 (TA spectra at 200 fs of **Ru-A** and **RuPd1**)

With the TA time resolution of 100-150 fs, the TA spectra of **Ru-A** and **RuPd1** at 200 fs are resolved, and are shown in Figure S8. Note that the ESA intensities at 370 nm and 420 nm reach 3-4 mOD, indicating that both bpy and tpy are occupied at least at 200 fs after photoexcitation.

Figure S8. TA spectra of **Ru-A** and **RuPd1** at 200 fs.

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Chapter 4. The effect of the catalytic moiety on the photodynamics

The present chapter extends the discussion of the previous chapter by comparing the ultrafast photodynamics of **RuPd1** with those of an analogous Ru/Pt bimetallic photocatalyst **RuPt1** (see Figure 1) by using ultrafast transient absorption (TA) spectroscopy. Although these two photocatalysts possess the same peripheral and bridging ligands, remarkably different photodynamics are observed. In comparison to **RuPd1** as discussed in Chapter 3, **RuPt1** 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 **RuPd1**. For **RuPt1** an additional lower-lying excited state is proposed to quench the hot higher-lying triplet metal-to-ligand charge transfer (3 MLCT) states. Furthermore, a strong excitation wavelength dependent population of excited states is observed for both **RuPd1** and **RuPt1**, indicating a non-equilibrated distribution even on the 10^2 ps timescale. These insights shed light on the significant impact of the catalytic moiety on the fundamental early-time photophysics of Ru-based photocatalysts. The content of this chapter is based on work published in the following article:

- Pan, Q.; Mecozzi, F.; Korterik, J. P.; Vos, J. G.; Browne, W. R.; Huijser, A. *ChemPhysChem* **2016**, *17*, 2654.

4.1. Introduction

Ru(II)-polypyridyl coordination compounds have attracted broad interest due to their unique combination of excellent photophysical and photochemical properties as introduced in Chapter 1. Their excited state redox properties and excellent stability as visible-light harvesting components are especially suited in photocatalysis.^{1,2} For example, bimetallic Ru(II) complexes have demonstrated both light-induced proton reduction and water oxidation,^{3,4} highlighting their potential in photocatalytic water splitting by using sunlight.⁵⁻⁸ 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.⁹ In particular, understanding the early-time photodynamics^{10,11} that follow photoexcitation is essential in addressing subsequent steps in the overall process of solar-to-fuel conversion.

For the proton reduction reaction, a variety of Ru/M (M = Pt or Pd) bimetallic

photocatalysts have been studied.¹²⁻¹⁴ The reason for selecting Pt or Pd as the catalytic center originates from these noble metal's low overpotential for electrochemical hydrogen evolution.¹⁵ This class of photocatalysts is in general based on a Ru-polypyridyl photosensitizer connected to a catalytic moiety via a bridging ligand as introduced in Chapter 1. Several recent studies have focused on the relation between the overall photocatalytic reactivity and the nature of the bridging and peripheral ligands.¹⁶⁻¹⁹ 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 and co-workers reported that the early-time photodynamics of two Ru/MCl₂ photocatalysts, where M = Pd or Pt, were similar, despite different photocatalytic reactivities of the complexes.²⁰ 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.²¹ 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.

On the other hand, Vos *et al.* have recently developed another series of photocatalysts (**RuPd1** and **RuPt1**, Figure 1) with 2,2'-bipyridine (bpy) peripheral ligands and a 2,2':5'2"-terpyridine (tpy) bridging ligand.^{17,22} Both complexes show comparable photocatalytic performance under similar reaction conditions with respect to turnover number (TON) and turnover frequency (TOF) for H₂ generation.^{17,22} 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 photodynamics of **RuPd1** observed upon photoexcitation at 480 nm have already been discussed in the Chapter 3. A photophysical model was established through target analysis of the TA data, in which rapid intersystem crossing (ISC) within 100 fs^{23,24} into triplet ³MLCT 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 (VC).²⁵ In the present chapter **RuPd1** and **RuPt1** are compared by using a generalized model, which combines ILET and vibrational cooling as ³MLCT_{bpy} → ³MLCT_{tpy} internal conversion (IC).²⁶ This model is equivalent to a sequential model in global analysis, and gives time constants of 5.3±0.5 ps for **Ru-A** and 7.0±0.5 ps for **RuPd1** as shown in the previous chapter.

Figure 1. Molecular structure of **RuPd1** and **RuPt1**. The mononuclear Ru precursor is denoted as **Ru-A**. S = solvent (acetonitrile).

In the present chapter, a similar sequential model from global analysis is applied to the TA data obtained by photoexciting **RuPt1** at 480 nm, allowing a direct comparison between **RuPd1** and **RuPt1**. Furthermore, detailed photodynamical knowledge on the impact of the catalytic moiety is obtained from pursuing studies at additional excitation wavelengths (516 nm and 527 nm).

4.2. Results and discussion

4.2.1. Steady state characterization

The steady-state UV-vis absorbance and photoluminescence (PL) spectra of **Ru-A**, **RuPd1** and **RuPt1** are shown in Figure 2 and summarized in Table 1. Although the absorbance of **RuPd1** or **RuPt1** is redshifted by approximately 10–20 nm as compared to that of **Ru-A**, the shape of the individual bands remains largely unchanged, suggesting that the cyclometalated Pt or Pd moiety does not significantly alter the electronic transition origins of these absorbance bands. Similar to the assignments in Chapter 3, each complex shows a broad absorbance band between 400 nm and 550 nm originating from the $^1\text{MLCT}$ transitions.²⁵ The sharp bands around 287 nm are due to ligand-centered (LC) $\pi-\pi^*$ transitions of the peripheral bpy ligands, and the shoulders at ca. 300 nm for **Ru-A** and 320 nm for **RuPd1** and **RuPt1** are assigned to the LC $\pi-\pi^*$ transitions of the bridging tpy ligand.¹⁷ Similarly, the PL bands of **RuPd1** and **RuPt1** are also redshifted as compared to that of **Ru-A**, indicating that the energy gap between the ground state and the lowest excited states is reduced upon cyclometalation with Pd or Pt.

Figure 2. Normalized steady state absorbance (solid curves) and PL (dashed curves) spectra of **Ru-A**, **RuPd1** and **RuPt1**.

Table 1. Steady state absorption and PL properties of the complexes.^{17,22}

Complex	Max. ¹ MLCT abs.	ϵ ($10^4 \text{ M}^{-1}\text{cm}^{-1}$)	Max. PL	Φ_{PL}
Ru-A	446 nm	1.18	629 nm	0.047
RuPd1	462 nm	1.33	632 nm	0.032
RuPt1	457 nm	1.05	644 nm	0.027

4.2.2. Excited state photodynamics of RuPt1

The TA spectra of **RuPd1** obtained upon 480 nm excitation have already been presented in Figure 4 of Chapter 3. For comparison, Figure 3A shows the TA spectra of **RuPt1** obtained by exciting at the same wavelength. The spectral features are qualitatively similar to those observed for **Ru-A** and **RuPd1**,²⁵ allowing for assignment of the individual bands by analogy. The negative signal between 440 nm and 520 nm is due to ground state bleach (GSB). The broad excited state absorption (ESA) band above 520 nm is associated with ligand-to-metal charge transfer transitions. The two ESA bands at ca. 420 nm and 375 nm are likely due to ligand-centered (LC) π - π^* transitions of the bpy⁻ and tpy⁻ radical anions, respectively.^{25,27,28} The kinetic traces of **RuPt1** (Figure 3B), however, illustrate that the temporal evolution of these bands is more complex than for **Ru-A** and **RuPd1**. 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 ca. 100 ps. Furthermore, the negative signal at 475 nm recovers, likely due to contributions from ESA overlapping with the GSB signal. The complex spectro-temporal behavior of **RuPt1** requires three time constants to achieve a global fit using a sequential model (Table 2). Note that these

observed processes proceed on the triplet, rather than the singlet, potential energy surfaces, as ISC in coordinated Ru(II) complexes is generally accepted to occur within 100 fs^{23,24} as introduced in Chapter 1.

Figure 3. TA spectra (A) and kinetic traces at key wavelengths (B) of **RuPt1** obtained upon 480 nm excitation. Global fits based on a sequential model are represented as solid curves.

Table 2. Overview of the obtained time constants and their assignment.

λ_{exc}		480 nm	516 nm	527 nm	Assignment
Ru-A	τ_1 (ps)	5.3 ± 0.5	4.5 ± 0.4	N.A.	$^3\text{MLCT}_{\text{bpy}} \rightarrow ^3\text{MLCT}_{\text{tpy}}$
RuPd1	τ_1 (ps)	7.0 ± 0.5	10.7 ± 0.7	N.A.	$^3\text{MLCT}_{\text{bpy}} \rightarrow ^3\text{MLCT}_{\text{tpy}}$
RuPt1	τ_1 (fs) ²⁹	865 ± 445	600 ± 398	980 ± 184	$^3\text{MLCT} \rightarrow \text{T}_3$
	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

The obtained evolution associated spectra (EAS) shown in Figure 4A provide insight into the nature of the overlapping TA bands. EAS1 is representative of the spectrum at early times, i.e. immediately after ISC. 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 a recent resonance Raman study.²² EAS1 evolves into EAS2 in 865 ± 445 fs (τ_1),²⁹ with the latter spectrum showing reduced absorption for both the bpy⁻ and tpy⁻ LC 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 nm and 450 nm and quenches these $^3\text{MLCT}$ states, as shown in Figure 5. 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 $^3\text{MLCT} \rightarrow \text{T}_3$ 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 in Chapter 3 for **RuPd1** (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 **RuPd1** (Figure 4, Chapter 3). However, as compared to **RuPd1** the tpy⁻ LC band at ca. 420 nm of **RuPt1** is relatively broad and overlaps with the GSB. As a result of the rise of this tpy⁻ LC band over time, the kinetic trace at 475 nm (Figure 3B) shows a decrease in amplitude over time. EAS3 develops into EAS4 with a time constant of 117 ± 11 ps (τ_3). The tpy⁻ LC band at ca. 420 nm increases concomitant with a decrease in ESA >520 nm. The origin of this spectral development will be discussed below.

Figure 4. EAS of **RuPt1** at (A) 480 nm and (B) 516 nm excitation obtained from a global fit of the TA data using a sequential model.

Figure 5. Overview of processes following intersystem crossing into the triplet manifold for **RuPt1**. 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.

The new T_3 state in **RuPt1** is likely associated with the Pt(II) moiety, as it is not observed in **Ru-A** and **RuPd1** (see Chapter 3). The T_3 state quenches the ${}^3\text{MLCT}_{\text{bpy}}$ and ${}^3\text{MLCT}_{\text{tpy}}$ states on a sub-ps timescale 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 S1, SI) 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 (see Table 2). The EAS obtained provide insight into the nature of overlapping TA bands. Comparison of the individual EAS shown in Figure 4A ($\lambda_{\text{exc}} = 480$ nm) and 4B ($\lambda_{\text{exc}} = 516$ nm) evidences changes in intensities, indicating a change in excited state population distribution with excitation wavelength. EAS1 in Figure 4B shows that for excitation at 516 nm the tpy^- LC band around 420 nm is more intense than the bpy^- LC band at ca. 375 nm, while EAS1 in Figure 4A shows that this order is reverse for excitation at 480 nm. This difference indicates that exciting **RuPt1** at longer wavelengths results in an increase in the initial $^3\text{MLCT}_{\text{tpy}}/^3\text{MLCT}_{\text{bpy}}$ population ratio directly after ISC.

The EAS1 $\rightarrow$ EAS2 developments shown in Figures 4A and 4B 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 TA data at 527 nm excitation (Figure 6A) clearly showing these features. The minor signal development <450 nm with $\lambda_{\text{exc}} = 527$ nm complicates global analysis. Nevertheless, tentative fitting³⁰ yields the EAS shown in Figure 6B 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 2). 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 Figures 4A ($\lambda_{\text{exc}} = 480$ nm) and 4B ($\lambda_{\text{exc}} = 516$ nm), indicating that the ~ 100 ps process is independent 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 ca. 660 nm due to equilibration between solvated electrons and solvated dimer anions³¹ should be observed. Furthermore, the decay time of the ESA band >530 nm (which matches the photoluminescence lifetime of **RuPt1** of ca. 300 ns at $\lambda_{\text{exc}} = 532$ nm³²) is not consistent with the presence of solvated electrons. The ~ 100 ps process observed for **RuPt1** only may be assigned to the T_3 state. Importantly, delocalization of the LUMO over the bridging ligand and the Pt moiety has been observed for a related Ru/Pt complex with a bipyridyl-based bridging ligand.³³ An analogous delocalization effect is likely also present in **RuPt1**, explaining the weak ESA signal <450 nm (see Figure 2 of Chapter 5). 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),

motivating the time-resolved X-ray absorption studies discussed in Chapter 7.

Figure 6. (A) TA spectra of **RuPt1** obtained upon 527 nm excitation. Fits are represented by solid curves. (B) Obtained EAS from global analysis.

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 only shows weak absorption below 450 nm. This state is more likely associated with the Pt moiety, as it is not observed for **Ru-A** and **RuPd1**. The Pt moiety will be investigated in more detail in Chapter 7 by transient x-ray absorption. A competing VC 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 ca. 100 ps independent of λ_{exc} .³⁴ A consequence of this non-equilibrated population is the bi-exponential photoluminescence (PL) decay (see Chapter 5).²² It was proposed earlier that the formation of two non-equilibrated emissive states can occur for certain combinations of ligands.³⁵ 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, i.e. the final population distribution of the excited states depends on the Franck-Condon states populated initially. It is of note that in earlier temperature-dependent ps transient Raman studies³⁶ by Hopkins et al., 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 the present work allows this conclusion to be extended, i.e. even though inter-ligand IC occurs at an early ps timescale, excited states can remain non-equilibrated at longer timescales.

4.2.3. Excited state photodynamics of RuPd1

The complex early-time photodynamics of **RuPt1** discussed in the previous section raise the question as to whether an excitation wavelength dependence is also present in **Ru-A** and **RuPd1**, prompting the measurements of TA for these two complexes with excitation at 516 nm as shown in Figures S2 and S3 (SI). The EAS of **RuPd1** (Figure 7A, $\lambda_{\text{exc}} = 480$ nm and Figure 7B, $\lambda_{\text{exc}} = 516$ nm) show an excitation wavelength dependence, though much less than for **RuPt1**. ESA1 represents the spectrum immediately after ISC from the Franck-Condon states. Therefore, comparison of the intensities of the tpy^- LC band at ca. 420 nm and the bpy^- LC band at ca. 370 nm provides insight into the initial $^3\text{MLCT}$ population, with a reduction in the initial $^3\text{MLCT}_{\text{tpy}}/^3\text{MLCT}_{\text{bpy}}$ population ratio upon increasing λ_{exc} , while this trend is opposite for **RuPt1** (see Figure 4). EAS2 represents the spectrum after $^3\text{MLCT}_{\text{bpy}} \rightarrow ^3\text{MLCT}_{\text{tpy}}$ IC. Comparison of the intensities at 370 nm and 420 nm in the individual EAS2 in Figures 7A and 7B 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 **RuPd1** 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 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 **RuPd1**, leading to a bi-exponential PL decay (see Chapter 3).²⁵ Note that a mono-exponential PL decay was observed for **Ru**,^{22,25} suggesting a thermally equilibrated population of the $^3\text{MLCT}$ states. However, the EAS at $\lambda_{\text{exc}} = 480$ nm and 516 nm are different as shown in Figure S4 (SI). This apparent discrepancy may be explained by a non-equilibrated population of $^3\text{MLCT}$ states with similar lifetimes.

Figure 7. EAS of **RuPd1** at (A) 480 nm and (B) 516 nm excitation.

The λ_{exc} dependent photodynamics for **RuPd1** may have a major impact on its $\Phi(\lambda)$ for photocatalytic H_2 generation, i.e. the wavelength dependent H_2 turnover number corrected for the molar absorptivity.¹⁷ 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 **RuPd1** showed an increase of $\Phi(\lambda)$ as λ_{exc} increases.¹⁷ It is worth noting that a similar $\Phi(\lambda)$ response is reported by Popp and co-workers for a related Ru/Pd bimetallic photocatalyst.³⁷ Resonance Raman studies on that Ru/Pd complex 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.³⁷ In a recent TA study on the same Ru/Pd photocatalyst, a long-lived (>1 ps) coherent vibrational motion was observed.³⁸ 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.³⁸ 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, it has been 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.^{14,16,22} The key question is hence to what extent the early-time population of the peripheral ligands affects the subsequent

photoelectrochemical processes occurring at longer timescales.

4.3. Conclusions

In summary, ultrafast TA studies on two analogous bimetallic photocatalysts **RuPd1** and **RuPt1** show that the catalytic moiety has a strong impact on the early-time photodynamics of the photosensitizer unit. A substantial dependence of the excitation wavelength is observed for both complexes, indicating that the population of the excited states has not equilibrated even 500 ps after photoexcitation. For **RuPd1**, 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 **RuPt1**, 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 **RuPd1**. 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 will be discussed in Chapter 7.

4.4. Experimental section

The synthesis and characterization of the compounds were published in ref. 25 and 22. The complexes were dissolved in acetonitrile (Sigma-Aldrich, purity >99.5%) in 1 cm path length quartz cuvettes for steady state measurements. UV-vis absorbance spectra were recorded using a SHIMADZU UV-1800 spectrophotometer. Steady state PL spectra were obtained using a Horiba JobinYvonFluoroMax-4 spectrofluorometer with excitation at 450 nm. Both absorbance and PL spectra were recorded at room temperature. The TA setup was described in detail in Chapter 2. TA samples were prepared by dissolving the complexes in anhydrous acetonitrile (Sigma-Aldrich, purity >99.9%) in 1 mm path length quartz cuvettes. The **RuPt1** concentration was 0.53 mM for TA using 480 nm excitation, corresponding to an optical density (OD) of 0.45. The **RuPt1** 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). **RuPd1** and **Ru-A** samples have similar OD values as compared to those of **RuPt1**. 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 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 Glotaran.³⁹

Supporting Information

Global analysis of the TA data has been performed based on a variety of sequential models for different complexes (GS = ground state):

- (1) One-component model (one fitted time constant τ_1):

In the above model species A evolves into species B with a time constant τ_1 , which is obtained from a global fit to the TA data. Species B returns to the GS with a fixed time constant determined from time-resolved PL measurements.

- (2) Two-component model (two fitted time constants τ_1 and τ_2):

In the above model species A evolves into species B with a time constant τ_1 . Species B further evolves into species C with a time constant τ_2 . The values of τ_1 and τ_2 are obtained by globally fitting this model to the TA data. Species C returns to the GS with a fixed time constant determined from time-resolved PL measurements.

- (3) Three-component model (three fitted time constants τ_1 , τ_2 and τ_3):

In the above model species A evolves into species B with a time constant τ_1 . Species B further evolves into species C with a time constant τ_2 . Furthermore, species C evolves into species D with a time constant τ_3 . The values of τ_1 , τ_2 and τ_3 are obtained by globally fitting this model to the TA data. Species D returns to the GS with a fixed time constant determined from time-resolved PL measurements.

Figure S1. TA spectra (A) and kinetic traces at key wavelengths (B) of **RuPt1** obtained upon 516 nm excitation. Global fits based on a three-component sequential model are represented by solid curves.

Figure S2. TA spectra at various time delays (A) and kinetic traces at key wavelengths (B) of **Ru-A** obtained upon 516 nm excitation. Global fits based on a one-component sequential model are represented by solid curves.

Figure S3. TA spectra at various time delays (A) and kinetic traces at key wavelengths (B) of **RuPd1** obtained upon 516 nm excitation. Global fits based on a one-component sequential model are represented by solid curves.

Figure S4. EAS of Ru-A at (A) 480 nm and (B) 516 nm excitation.

Figure S5. TA spectra (A) and kinetic traces at key wavelengths (B) of RuPt1 obtained upon 527 nm excitation. Fits based on a two-component sequential model are represented by solid curves. The deviation between early-time (<500 fs) data and fit is likely due to a coherent artifact signal.

Figure S6. TA spectra (A) and kinetic traces at key wavelengths (B) of RuPt1 obtained upon 527 nm excitation. Fits based on a one-component sequential model are represented by solid curves. The deviation between early-time (<500 fs) data and fit is likely due to a coherent artifact signal.

Figure S7. Comparison between the fits based on a two-component sequential model (A) and a one-component sequential model (B) at early time (500 fs).

Figure S8. PL decay of **RuPt1** obtained on excitation at 532 nm. A fit based on a mono-exponential decay is represented by the solid curve.⁴⁰

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Chapter 5. The influence of the peripheral ligands on the photodynamics

The present chapter focuses on the effects of the peripheral ligands on the photophysics of five Ru/Pt bimetallic photocatalysts. **RuPt1**, which has been discussed previously in Chapter 4, is compared with a related photocatalyst **RuPt2** bearing the same bridging ligand and catalytic moiety but different peripheral ligands. The significantly different H₂ generation performance of these two photocatalysts is explained based on the contrasting early-time photodynamics as a result of ester functionalization of the peripheral ligands. Afterwards, the photophysics of a series of structurally analogous complexes **RuPt3**, **RuPt4** and **RuPt5** are discussed, highlighting the important influences of the coupling between the peripheral and bridging ligands on the early-time photodynamics and the photocatalytic performance. The content of this chapter is based on research published in the following articles:

- Kowacs, T.; Pan, Q.; Lang, P.; O'Reilly, L.; Rau, S.; Browne, W. R.; Pryce, M. T.; Huijser, A.; Vos, J. G. *Faraday Discuss.* **2015**, *185*, 143.
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5.1. Introduction

Molecular photocatalysts that mimic natural photosynthesis have been studied intensively in recent years.¹⁻³ In these assemblies a photosensitizer is bound covalently to a catalytic center via a bridging ligand (see Figure 10, Chapter 1). While the effects of the bridging ligand and the catalytic moiety have been discussed in Chapters 3 and 4, a systematic investigation of the peripheral ligands is the main focus of the present chapter.

It has been shown in Chapter 4 that photoexcitation of **RuPd1** at longer wavelengths results in an enhanced population of the excited states based on the peripheral ligands.⁴ Surprisingly, the H₂ turnover number corrected for the molar absorptivity is found to increase upon reducing the excitation photon energy.⁵ These results imply the important role of the peripheral ligands on the photocatalytic H₂ generation reactivity.

However, the photocatalytic efficiency is the result of a sequence of

photophysical and photochemical processes occurring in a broad window of time scales. A sacrificial agent such as triethylamine (TEA) is required to regenerate the photosensitizer by electron donation to the formally oxidized Ru(III) center. This process however also results in the formation of radicals, which may lead to side reactions by reacting with the solvent.⁶ The presence of TEA, thus, prevents photophysical studies under catalytic conditions. However, earlier studies showed that the early-time (fs-ns) photodynamics under non-catalytic conditions provide important mechanistic insight into the photocatalytic performance. For instance, it was concluded that the electron density distribution of the initial photoexcited state determines the H₂ generation efficiency.⁷ Furthermore, the occurrence of intramolecular electron transfer in the ps time window was shown to be essential.⁸⁻¹⁰ Hence, understanding of the fundamental early-time photodynamics is an important first step towards the design of improved photocatalysts. Such knowledge also facilitates the investigation of subsequent processes occurring at later time scales.

In fact, the influence of the peripheral ligands on the early-time photodynamics and H₂ generation efficiency can be complex considering the coupling between the peripheral ligands and other functional components (i.e. the bridging ligand and the catalytic moiety). For instance, as discussed in Chapter 4, a lower-lying T₃ state likely originated from the catalytic Pt center quenches the ³MLCT (metal-to-ligand charge transfer, see Chapter 1) states associated with both the peripheral and bridging ligands for **RuPt1**.⁴ Furthermore, inter-ligand electron transfer from the peripheral ligands to the bridging ligand occurs on a ps time scale for **RuPd1** and **RuPt1** as discussed in Chapters 3 and 4.

In this chapter, the effect of the peripheral ligands is studied by firstly comparing **RuPt2** (see Figure 1) with **RuPt1** which is already discussed in Chapter 4. Note that these two complexes bear the same tpy (tpy = 2,2':5',2''-terpyridine) bridging ligand and Pt iodide catalytic moiety but different peripheral ligands. The bpy (bpy = 2,2'-bipyridine) ligands function as the peripheral ligands for **RuPt1**, whereas the ester-functionalized dceb ligands (dceb = 4,4'-diethoxycarbonyl-2,2'-bipyridine) act as the peripheral ligands for **RuPt2**. It has been recently reported that **RuPt2** shows a significantly improved H₂ generation turnover number (TON = 650 after 6 h of irradiation at 470 nm) as compared to **RuPt1** (TON = 80) in the same reaction conditions.¹¹

Figure 1. Molecular structure of the complexes discussed in this chapter. S = solvent (acetonitrile). The mononuclear Ru(II) precursors of **RuPt1** and **RuPt2** are denoted as **Ru-A** and **Ru-C**, respectively.

The beneficial effect of ester functionalization of the peripheral ligands has also been reported for a number of other complexes studied independently by Sakai and Vos. Two closely related bimetallic assemblies based on the same di(pyridine-2-yl)pyrazine (2,5-dpp) bridging ligand are both inactive for photocatalytic H_2 generation^{12,13}, suggesting that 2,5-dpp is not a suitable bridging ligand. Remarkably, functionalization of the peripheral bpy ligands with ester groups leads to a complex showing a TON of 400.¹³ A similar effect is also recently reported for another series of Ru/Pt complexes **RuPt3**, **RuPt4** and **RuPt5** (see Figure 1) with 2,3-dpp (2,3-dpp = 2,3-di(pyridine-2-yl)pyrazine) bridging ligand.¹⁴ **RuPt3** and **RuPt4** with the bpy peripheral ligands are inactive for photocatalytic H_2 evolution, whereas **RuPt5** with dceb peripheral ligands shows a TON of 44.¹⁴ Although H_2 generation depends on other parameters as well, it becomes clear that the peripheral ligands play a central role, as will be discussed in more detail in the next section.

5.2. Results and discussion

The steady-state absorbance and emission spectra recorded under normal and electrochemical reduction conditions are shown and discussed in Section 1 of the Supporting Information. The following sections focus on the excited state properties of the complexes.

5.2.1. Photodynamics of **RuPt1** and **RuPt2**

The excited state photodynamics of **RuPt1** have already been discussed in detail in Chapter 4. Briefly, photoexcitation leads to the population of both the bpy- and tpy-based $^3\text{MLCT}$ states, which are quenched by a lower-lying T_3 state on a sub-ps time scale.⁴ Due to the active involvement of vibrational cooling and possibly a

high energetic barrier for inter-ligand electron transfer, the thermalized excited states are non-equilibrated, giving rise to a bi-exponential decay of the photoluminescence signal.¹¹

This section extends the discussion of **RuPt1** by comparing it with **RuPt2**. Intersystem crossing (ISC) to the triplet manifold in Ru(II)-polypyridyl complexes is known to occur within 100 fs after photoexcitation^{15,16} and hence it is the energetics of the triplet states that determine the early-time photodynamics. The geometries and spin density distribution at the minima of the lowest ³MLCT states (see Figure 2) calculated by density functional theory (DFT), indicate that the order of the ³MLCT states changes upon ester functionalization of the peripheral ligands.⁶ For **Ru-A** and **RuPt1**, a tpy-based ³MLCT state is the lowest in energy, whereas for **Ru-C** and **RuPt2** a dceb-based state becomes the lowest. This trend is the same for the lowest unoccupied molecular orbitals calculated at the ground state geometry.⁶

The time evolution of the population of the dceb/bpy and tpy-localized ³MLCT states of **Ru-A** and **Ru-C** has been studied by transient absorption (TA). Figure 3A and 3B show the TA spectra of **Ru-A** and **Ru-C**, respectively. The TA spectrum of **Ru-A** shows two bands around 370 nm and 420 nm, with the first due to excited state absorption (ESA) of the bpy radical anion and the second related to the tpy radical anion.^{8,17,18} The ESA increase around 420 nm concomitant with a decrease at ca. 370 nm in time manifests internal conversion (IC) from a bpy-based to a tpy-based ³MLCT state occurring within ca. 20 ps. Vibrational cooling is likely competing with this process as discussed in Chapter 2.⁸

Figure 2. Spin densities of the lowest triplet states of **Ru-A**, **Ru-C**, **RuPt1** and **RuPt2** in acetonitrile.

Figure 3. TA spectra of **Ru-A** (A), **Ru-C** (B), **RuPt1** (C) and **RuPt2** (D) in acetonitrile. The fits for **RuPt2** and **Ru-C** are based on the photophysical models shown in Figures 4 and S5. The fits for **Ru-A** and **RuPt1** are obtained from global analysis using a sequential model as discussed in Chapter 4.⁴

The TA spectral features observed for **Ru-C** are different from those of **Ru-A**. An ESA band at ca. 350 nm increases in intensity within 1 ps, concomitant with a decrease of ESA at ca. 420 nm, as also evident from the kinetic traces provided in Figure S4. Since the DFT calculations show that the $^3\text{MLCT}_{\text{dceb}}$ state is lower in energy than the $^3\text{MLCT}_{\text{tpy}}$ state, the observed dynamics likely reflect $^3\text{MLCT}_{\text{tpy}} \rightarrow ^3\text{MLCT}_{\text{dceb}}$ IC. Based on this interpretation, the ESA bands at ca. 350 nm and 420 nm are assigned to the reduced dceb and tpy ligands, respectively. An additional ESA band is present at ca. 385 nm, which does not evolve in time significantly, likely due to the overlapping contributions from the nearby ESA bands around 350 nm and 420 nm. The observation of a similar band at ca. 385 nm for the homoleptic complex $[\text{Ru}(\text{dceb})_3]^{2+}$ in acetonitrile¹⁹ indicates that this ESA band is likely associated with a reduced dceb ligand. The assignment of the ESA bands at both 350 nm and 385 nm to the dceb ligands is consistent with the species associated spectra (SAS, see Figure S7) obtained from the photophysical model shown in Figure S5. Further indirect support is provided by the differential absorption spectra under electrochemical reduction conditions (Figure S2). The above

assignment suggests that, although ester functionalization of the bpy ligands does not significantly alter the ESA position of the tpy ligand at ca. 420 nm, the bpy-based ESA band is split, possibly due to coupling between different ligands. Note that the ESA features of related heteroleptic complexes are known to depend on the combination of ligands. An ESA band at ca. 350 nm was found for $[\text{Ru}(\text{dceb})_2\text{BTL}]^{2+}$ (BTL = 9'-[4,5-bis(cyanoethylthio)]-1,3-dithiol-2-ylidene]-4',5'-diazafuorene).²⁰ For $[\text{Ru}(\text{dceb})_2(2,3\text{-dpp})\text{PtI}_2]^{2+}$, an ESA band at ca. 385 nm has been observed,¹⁴ while $[\text{Ru}(\text{dceb})(\text{bpy})_2]^{2+}$ manifests a broad ESA band below ca. 400 nm.^{21,22} The absence of spectral changes at times beyond a few ps (up to at least 6 ns, Figure S6) indicates that the formed ³MLCT manifold is long-lived and excited state equilibration between ³MLCT_{dceb} and ³MLCT_{tpy} states in **Ru-B** is ultrafast (Figure S5).

The TA spectral features of **RuPt1** and **RuPt2** (Figure 3C and 3D) are similar to those of their mononuclear precursors. For **RuPt1**, an ESA band at ca. 370 nm becomes less intense in time concomitant with a growth of an ESA at ca. 420 nm, indicating IC from bpy-localized ³MLCT states to tpy-based ³MLCT states. Again, as observed for the two monometallic precursors, the direction of IC observed for **RuPt2** is opposite to that of **RuPt1**, indicating that cyclometalation by Pt does not change the direction of ultrafast intramolecular electron transfer.

A photophysical model of **RuPt2** established by target analysis of the TA data is shown in Figure 4. The obtained SAS are provided in Figure S8. Photoexcitation leads to the population of dceb and tpy-based singlet excited states, which undergo ultrafast ISC^{15,16} into dceb and tpy-Pt localized triplet states. The electron density at the bridge side moves on an ultrafast timescale to the dceb ligands (535±17 fs). The backward electron transfer from dceb to tpy-Pt occurs at >3 ps. This equilibration results in only a minor population of the bridge-based states.

The TA data discussed above allow interpretation of the time-resolved photoluminescence data as shown in Table S1 of the Supporting Information.¹¹ The excited state decay of **Ru-A** is mono-exponential ($\tau = 796 \pm 6$ ns), indicating that the various peripheral and bridging ligand based low-lying ³MLCT states are thermally equilibrated.²³ For **Ru-C** ($\tau = 1.05 \pm 0.01$ μs) and **RuPt2** ($\tau = 632 \pm 24$ ns), ultrafast excited state equilibration results in a major population of the ³MLCT_{dceb} states, yielding a mono-exponential emission decay. However, for **RuPt1** a bi-exponential decay ($\tau_1 = 122 \pm 55$ ns, 15 %; $\tau_2 = 661 \pm 16$ ns, 85 %) is observed. **RuPd1** shows analogous features with the fast component more pronounced (see Chapter 3).⁸ The fast component observed for **RuPt1** is possibly due to enhanced spin-orbit coupling caused by Pt increasing the radiative decay rate. Alternatively, it can be explained by an increased rigidity of the

bridging ligand upon coordination with the Pt center, possibly resulting in a lowering of the energy of the deactivating triplet metal-centered (^3MC) level at the Ru moiety. The increased rigidity may also reduce the vibrational freedom of the ligand, thereby increasing the difficulty of inter-ligand IC. This hypothesis is in agreement with DFT calculations showing that the root-mean-square deviation between the bpy and tpy structures increases upon bonding of the Pt center.⁶ As a result, both $^3\text{MLCT}$ states contribute to the photoluminescence, resulting in a bi-exponential decay.

Figure 4. Simplified photophysical model of light-induced processes in **RuPt2**.

5.2.2. Photodynamics of RuPt3, RuPt4 and RuPt5

As discussed in the previous section, an important effect of ester functionalization of the peripheral bpy ligands involves a lowering in $^3\text{MLCT}$ energy levels. A major consequence is an inversion in inter-ligand IC direction, causing an ultrafast population of the $^3\text{MLCT}_{\text{dceb}}$ states for **RuPt2**. However, it remains a question whether such an effect can be generalized for other Ru/Pt bimetallic complexes. i.e. **RuPt3**, **RuPt4** and **RuPt5** bearing 2,3-dpp (rather than tpy) as the bridging ligand. This question is of fundamental importance as the effect of the peripheral ligands on the photodynamics not only depends on the structure of the peripheral ligands, but may also depend on the coupling between the peripheral and bridging ligands. In other words, the properties of the bridging ligand may also influence the excited states based on the peripheral ligands.

A recent study based on resonance Raman spectroscopy has shown that photoexcitation of **RuPt3** and **RuPt4** at 473 nm mainly leads to an initial population of the $^1\text{MLCT}$ states based on the bridging 2,3-dpp ligand.¹⁴ However, for **RuPt5** both the dceb- and 2,3-dpp-based $^1\text{MLCT}$ states are populated.¹⁴ These results suggest that functionalization of the peripheral bpy ligands with ester groups alters the electronic structure of the complexes.

The evolution in excited state population on the triplet potential energy

surfaces is investigated by TA spectroscopy. Figure 5A and 5B show the TA spectra observed for **RuPt3** and **RuPt4** by photoexciting at 480 nm. Both complexes show similar spectral features, demonstrating that the differences brought about by a change from chloro to iodo ligands at the Pt(II) center are minor at sub-ns time scales, in agreement with a recent report by Rau and co-workers.²⁴ The TA spectra are dominated by the negative GSB signal.¹⁴ Similar to **RuPt1** and **RuPt2**, LMCT (ligand-to-metal charge transfer) transitions give rise to the positive signal above 570 nm.¹⁴ In the UV region a weak and broad ESA band centered around 375 nm is also observed for both complexes, and assigned to absorption by the reduced bpy and 2,3-dpp ligands, as their absorption bands overlap in the UV region.^{8,17,25} Furthermore, the low signal amplitude of the UV band approaches the detection limit.

Figure 5. TA spectra of **RuPt3** (A) and **RuPt4** (B), and kinetic traces at key wavelengths for **RuPt3** (C) and **RuPt4** (D). Fits based on a two-component sequential model from global analysis are presented as solid curves. Note that a dual-axis configuration is applied in (C) and (D).

An important observation is that the GSB signal increases in amplitude on a ~ 100 ps time scale, as shown from the kinetic traces at 510 nm (Figure 5C and 5D). This result suggests the presence of an additional ESA band overlapping with the GSB signal. The amplitude of this ESA band probably decreases on a ~ 100 ps time scale, effectively giving rise to the observed increasing GSB signal amplitude on

the same time scale. Interestingly, the kinetic traces observed at 420 nm shown in Figure 5C and 5D suggest that the excited state evolution is more complex. Two distinct dynamical components are observed: a fast ~ 3 ps process (further increasing the negative signal amplitude) and a subsequent slower ~ 100 ps process decreasing the signal amplitude. Note that although the absolute signal change is less than 1 mOD at 420 nm, the signal/noise ratio still allows distinguishing these two processes. The slower ~ 100 ps process observed at 420 nm is likely associated with the aforementioned process observed at 510 nm occurring at the same time scale. These results suggest complex sub-ns photodynamics involving multiple distinct excited states whose absorption bands strongly overlap. Consequently, detailed photophysical modelling based on target analysis is not realistic for **RuPt3** and **RuPt4**. Nevertheless, a sequential model based on global analysis is applied, yielding two time constants for each complexes (5.3 ± 1.2 ps and 148 ± 41 ps for **RuPt3**; 3.1 ± 1.1 ps and 101 ± 30 ps for **RuPt4**). These time constants reflect complex IC processes among multiple excited states. Importantly, these excited states are non-equilibrated, as bi-exponential photoluminescence decays have been observed for both complexes.¹⁴ The obtained evolution associated spectra (EAS) are shown in Figure S9.

Figure 6. TA spectra (A) and kinetic traces (B) at key wavelengths for **RuPt5**. Fits based on a sequential model from global analysis are presented as solid curves.

In contrast to **RuPt3** and **RuPt4**, significantly different photodynamics are observed for **RuPt5**. The TA spectra shown in Figure 6A exhibit an analogous negative GSB band around 460 nm, a positive ligand-based ESA band around 380 nm and a LMCT band above 600 nm.¹⁴ These three bands decrease in amplitude on a same ~ 100 ps time scale as shown by the kinetic traces (Figure 6B) indicating recombination. However, the GSB signal (i.e. at 460 nm) does not completely decay from -5.5 mOD to zero, but an offset of ca. -2.8 mOD remains. This observation indicates the existence of excited states with distinct lifetimes (~ 100 ps vs. >1 ns). Importantly, these excited states are non-equilibrated, as otherwise the

total lifetime would have been determined by the excited state with the shortest lifetime, i.e. ~ 100 ps. A global analysis yields a time constant of 105 ± 14 ps for this partial recombination process, representing the evolution from EAS1 to EAS2 as shown in Figure S10.

In short summary, although photophysical modeling by target analysis of **RuPt3**, **RuPt4** and **RuPt5** is not possible, it becomes clear that the effects of the (ester functionalized) peripheral ligands on the photodynamics differ significantly as compared to the complexes discussed in Section 5.2.1 (**RuPt1** and **RuPt2**). This result suggests that the photocatalytic H_2 evolution properties of these compounds may also differ remarkably, as will be discussed in the next section.

5.2.3. Influences of the excited state photodynamics on light-induced H_2 evolution

As shown in the previous sections, the role of the peripheral ligands in the excited state photodynamics not only depends on the structure of the peripheral ligands, but also involves the coupling between the peripheral ligands and the bridging ligand. In other words, the structure of the peripheral ligands is not an independent parameter in determining the excited state properties. Consequently, **RuPt1** and **RuPt2** are discussed separately from **RuPt3**, **RuPt4** and **RuPt5** in this section.

As outlined in the introduction section, **RuPt2** shows a significantly improved H_2 evolution TON value of 650 as compared to **RuPt1** (TON = 80).¹¹ Importantly, as discussed in Section 5.2.1, ester functionalization of the peripheral ligands leads to an inversion in inter-ligand IC direction, causing an ultrafast population of 3MLCT states localized on the peripheral ligands. This result seemingly indicates that electron density is moving in a disadvantageous direction. *A priori*, it could be anticipated that movement of electron density from the photosensitizer to the catalytic center by population of the bridging ligand would be beneficial for photocatalytic H^+ reduction, and it is commonly accepted that a favoring population of excited states localized on the bridging ligand is essential for efficient photocatalysis. As a result, the bridging ligand is generally designed to facilitate electron transfer from the photosensitizer to the catalytic center, and store the photo-generated electron prior to any subsequent photochemical reactions.⁷⁻²⁶ This strategy has been applied before by functionalizing the bridging ligand with an electron withdrawing CN group in a Ru/Pt photocatalyst (**RuPt-CN**), and improved electron transfer to the catalytic Pt moiety and hydrogen evolution were observed.¹⁰ However, for **RuPt2** the electron transfer direction is the opposite while at the same time a much higher efficiency is achieved for **RuPt2** compared to **RuPt1**.¹¹ Definitely, the observation shown in Section 5.2.1 provides the first photophysical evidence challenging the conventional design paradigm based on a

bridging ligand acting as electron density storage reservoir.

Establishing a connection between storage of electron density at the peripheral ligands at early-times and the high H₂ generation reactivity is not straightforward considering the multiple photochemical reactions occurring at later times. However, it is important to consider two key parameters required for efficient H₂ generation; a long excited state lifetime and efficient IC towards the bridging ligand. A long excited state lifetime is essential to allow multiple slow (diffusion controlled) processes to proceed. However, fast IC to the bridge does not guarantee a long lifetime. For instance, a negative side effect observed in **RuPt-CN** involved the recombination of 30-40 % of the excited states within ~1 ps.¹⁰ Deactivation induced by the cyclometalated Pt due to, *e.g.* strong spin-orbit coupling and additional nonradiative deactivation, is likely to reduce the bridge-based excited state lifetime.⁸ However, when the photoexcited electron is localized on the peripheral ligands, the relatively longer distance to the Pt center makes the Pt induced deactivation channels less accessible. Furthermore, functionalization of the peripheral ligands with ester groups stabilizes the ³MLCT states, increasing the gap with the deactivating ³MC state.²⁷ These effects result in a longer excited state lifetime. An analogous trend has been observed in Ru/Mn photocatalysts for oxygen evolution: the lifetime is reduced from 1400 ns to 23 ns upon Mn coupling for unsubstituted complexes, whereas for the ester substituted analogues the lifetimes remain almost independent of Mn coupling (>1000 ns).²⁸ Most interestingly, when the ester group is also present at the bridge, the improvement achieved by ester functionalization of the peripheral ligands is lost.²⁹ Besides an improved excited state lifetime, populating the peripheral ligands by the first photoexcited electron may also have a significant impact on the potential energy surfaces relevant for the second photoelectron, promoting future investigation of this fundamental aspect. Remarkably, a recent study shows that an additional charge localized on the bridging ligand of an electrochemically mono-reduced Ru/Pt photocatalyst prevents directional transfer of the second electron.³⁰

Generalization of the insights obtained for **RuPt2** and **RuPt1** to other complexes, *i.e.* **RuPt3**, **RuPt4** and **RuPt5**, is not straightforward. **RuPt3** and **RuPt4** are both inactive for light-induced H₂ generation, whereas a TON of 44 has been reported for **RuPt5**.¹⁴ The improved photocatalytic reactivity of **RuPt5**, however, is likely not directly related to the capability of the peripheral ligands to act as electron storage reservoirs as one would anticipate. On the contrary, a ~100 ps partial recombination process is observed for **RuPt5** as shown in Section 5.2.2. This fast recombination explains the low TON value of 44 obtained on **RuPt5**. However, the GSB offset signal observed for **RuPt5** also indicates the presence of a long-lived (>1 ns) excited state which is non-equilibrated with the short-lived (~100 ps) state. This long-lived excited state allows **RuPt5** to be active for

photocatalytic reactions. For **RuPt3** and **RuPt4**, the excited states photodynamics are more complex. As discussed in Section 5.2.2, multiple excited states are involved in the early-time photodynamics. Although allocation of these excited states is challenging considering the weak signal amplitude and strong overlap of the ESA bands, the IC processes between these excited states involves multiple steps occurring at different time scales from a few ps to ca. 100 ps. The photocatalytic inactivity observed for **RuPt3** and **RuPt4** remains elusive, as no sub-ns recombination is observed for these two complexes, motivating future investigation of the processes occurring at longer time scales.

5.3. Conclusions

In summary, the key observation for **RuPt1** and **RuPt2** is that ultrafast intramolecular equilibration resulting in storing the first photoexcited electron on the peripheral ligands at early times allows a considerable increase in photocatalytic reactivity. This observation cannot be explained within the traditional framework based on the bridging ligand acting as electron storage reservoir. An important advantage of ³MLCT states based on the peripheral ligands relative to those based on the bridging ligand is their lower susceptibility to excited state deactivation induced by the catalytic center.

However, a successful application of this strategy for enhanced photocatalytic H₂ evolution not only depends on the structure of the (ester functionalized) peripheral ligands, but also relies on their coupling with the bridging ligand. A complex photodynamical coupling between these ligands may result in multiple IC processes occurring at different time scales. Importantly, as shown for **RuPt5**, functionalizing the peripheral ligands with ester groups does not necessarily lead to a thermally equilibrated population of the excited states, but a partial recombination process takes place on a ~100 ps time scale, limiting the photocatalytic H₂ evolution efficiency. These results show that the structure of the peripheral ligands does not independently influence the photodynamics and consequently the performance of the photocatalyst.

5.4. Experimental section

Details regarding the synthesis, chemical characterization and light-induced H₂ generation are provided in ref. 11 for **RuPt1** and **RuPt2**, and ref. 14 for **RuPt3**, **RuPt4** and **RuPt5**. Details regarding the DFT calculations are provided in ref. 6.

The steady state absorbance and emission spectra under normal conditions were recorded by the same methods as discussed in Chapter 3. The samples for absorbance measurements under reduction conditions were prepared by dissolving

the compounds in dimethyl sulfoxide (DMSO; Roth, purity $\geq 99.5\%$, ≤ 200 ppm H_2O) with 0.5 M of tetra-n-butylammoniumtetrafluoroborate (TBABF_4 ; Merck-Schuchardt, purity $\geq 98\%$) added as the supporting electrolyte. The solution was purged with N_2 prior to and during the measurement. An ITO-covered glass substrate (Indium Tin Oxide; Delta Technologies, sheet resistance 8-12 Ω/sq) served as the working electrode. The ITO was covered with an uncoated glass (Roth) leaving a thin layer of electrolyte in front of it, which was lifted above the electrolyte level by capillary forces forming a transparent thin layer cell. A leak-free LF-2 reference electrode (Warner Instruments, 242 mV vs. NHE) and a platinum wire counter electrode (Aldrich, purity 99,99%) were used. A diode array spectrometer setup (LS-C H lamp, LOE-USB MMS 1 spectrometer from Tec5) was used to analyze transmission changes in the thin layer cell while the electrochemical measurement was performed using a IviumStat potentiostat (IVIUM Technologies). Various voltages were applied to the thin layer of the solution. The differential spectrum at each potential was recorded after applying the voltage for 10 minutes and corrected for the steady state absorbance at zero bias, assuming no changes in reflection during electrochemical reduction.³¹

TA experiments were performed in the same way as discussed in Chapters 2 and 3.^{6,14} Time-resolved photoluminescence data were recorded at room temperature using a FluoroMax Spectrofluorometer extended for time-correlated single photon counting (TCSPC) measurements (HORIBA JOBIN YVON, FluoroMax-4 TCSPC). Samples were dissolved in acetonitrile (Sigma-Aldrich, purity $>99.5\%$) in 1 cm path length quartz cuvettes and were degassed by dry N_2 gas for 20 min prior to the emission lifetime measurements. A NanoLED-460 laser (462 nm, 1.3 ns pulse duration) was used for excitation. The compounds **Ru-A**, **RuPt1** and **RuPt2** were excited at a repetition rate of 100 kHz. **Ru-C** was measured at 50 kHz. The wavelength-dependent emission lifetime measurements were performed in a "back and forth" sequence: λ_{em} (the wavelength of maximum emission intensity), 680, 640, 720, 600 and 760 nm, and lastly λ_{em} again to exclude the possibilities of oxygen leakage and parasitic drift.¹¹

Supporting Information

Section 1. Absorbance/emission under normal and reduction conditions

The steady state absorbance and emission spectra of **RuPt1**, **RuPt2** and their mononuclear Ru(II) precursor **Ru-A** and **Ru-C** under normal conditions are shown in Figure S1. The broad bands from 400 nm to 600 nm, common for Ru(II)-polypyridyl complexes, are described as the MLCT transitions³² as introduced in Chapter 1. For **Ru-A**, as assigned earlier in Chapter 3, the sharp band

around 280 nm and the shoulder at ca. 300 nm are due to ligand-centered (LC) π - π^* transitions of the bpy and tpy ligands, respectively.^{5,8} **Ru-C** shows an analogous broad MLCT band. However, a single LC band is present at ca. 305 nm close to the tpy-based LC band observed around 300 nm for **Ru-A**. This result suggests that the ester groups lower the energy levels of the bpy ligands, and the bpy- and tpy-based π - π^* transitions become close in energy.⁶ This conclusion is supported by the absorbance spectra recorded under electrochemically reduced conditions (Figure S2, *vide infra*). The absorbance spectrum of **RuPt1** is redshifted as compared to that of **Ru-A**. A similar effect has been observed for the analogous Ru/Pd complex **RuPd1** as discussed in Chapter 3.⁸ The MLCT band of **RuPt2** is also redshifted relative to **Ru-C**, reflecting the influence of Pt cyclometalation. However, the LC band around 305 nm remains mostly unaffected. This result suggests that this LC band is probably dominated by the transitions localized on the dceb ligands, which are not significantly influenced by the Pt center coordinated to the tpy ligand. This hypothesis is in agreement with the TA results showing minor differences between **Ru-C** and **RuPt2** (see Section 5.2.1).

The normalized steady state emission spectra shown in Figure S1 indicate that the bands of both **RuPt1** and **RuPt2** are redshifted by approximately 10-20 nm as compared to their corresponding mononuclear Ru(II) precursor **Ru-A** and **Ru-C**. A similar trend is observed of the Ru/Pd analogue **RuPd1** as shown in Chapter 3.⁸ These results indicate that Pt cyclometalation reduces the energy gap between the ground state and the lowest excited state.

Figure S1. Normalized steady state absorbance and emission ($\lambda_{\text{exc}} = 450$ nm) spectra of the Ru/Pt photocatalysts (solid curves) **RuPt1** and **RuPt2**, and their mononuclear Ru(II) precursors (dashed curves) **Ru-A** and **Ru-C**.

Figure S2 shows the differential absorbance spectra of **Ru-A** and **Ru-C** at various reduction potentials. For **Ru-A** two absorbance bands (one at ca. 360 nm

and another at ca. 420 nm) are well distinguishable when the complex is reduced. These bands are in agreement with the TA spectra for **Ru-A** shown in Chapter 3. The band at ca. 360 nm is due to the reduced bpy ligand (bpy⁻),³³ close to the ESA (excited state absorption) band around 370 nm observed in TA.^{8,17} Analogously, the band around 420 nm is due to the reduced tpy ligand (tpy⁻). Initially, at -1.07 V neither bpy nor tpy is reduced, and consequently no absorbance difference compared to the spectrum at 0 V exists. On moving towards more negative potentials (-1.36 V and -1.63 V) predominantly the tpy⁻ band starts appearing, while at -2.00 V the bpy⁻ band has become more intense than the tpy⁻ band. These results demonstrate that for **Ru-A**, reduction of the bpy ligand requires a more negative potential than for the tpy ligand, showing that the bpy-based π^* orbital is higher in energy than the tpy-based one. The situation for **Ru-C** is different. Differential absorbance features appear at less negative potentials as compared to **Ru-A**, suggesting that the ester groups lower the excited state energy levels. Throughout all applied negative potentials (down to -1.80 V) both dceb⁻ and tpy⁻ contribute to the differential absorbance. This result shows that the dceb and tpy require rather similar negative potentials to become reduced. In conclusion, functionalization of the bpy peripheral ligands with ester groups changes the energetics. For **Ru-A** the bpy⁻ level is higher in energy than the tpy⁻ level, whereas for **Ru-C** the energy levels for the peripheral and bridging ligands are rather close, suggesting the equilibrium discussed in Section 5.2.1 is feasible.

Figure S2. Differential absorbance spectra of **Ru-A** (A) and **Ru-B** (B) at various potentials (vs. Ag/AgCl) corrected for the steady state absorbance at zero bias.

The steady state absorbance spectra of **RuPt3**, **RuPt4** and **RuPt5** under normal conditions are shown in Figure S3. The absorbance features are nearly identical for **RuPt3** and **RuPt4**, indicating that changing from the chloro to iodo moieties does not significantly influence the electronic structure of the complexes. This result is in agreement with the TA results discussed in Section 5.2.2. The two absorbance bands around 420 nm and 520 nm are both of MLCT character, with

the latter band most likely related to the pyrazine based MLCT transition.^{14,34} The sharp bands at ca. 283 nm are due to LC π - π^* transitions of the peripheral bpy ligands, similar to the case of **RuPt1**.^{6,34} The bands between 300 nm and 360 nm is assigned to the LC π - π^* transitions of the bridging 2,3-dpp ligand.¹⁴ The absorbance of **RuPt5** is distinct from **RuPt3** or **RuPt4**. A broad MLCT transition is observed between 420 nm and 650 nm. The sharp band at ca. 308 nm is due to the LC π - π^* transitions of the dceb ligands. The band at ca. 350 nm is assigned to the LC transitions of the 2,3-dpp ligands and possibly also Pt $\rightarrow$ 2,3-dpp MLCT transitions.¹⁴ Unlike **RuPt1** and **RuPt2**, the photoluminescence signals from **RuPt3** and **RuPt4** are rather weak and possibly around 775 nm, and **RuPt5** is likely not emissive.¹⁴

Figure S3. Normalized steady state absorbance of **RuPt3** (red), **RuPt4** (green) and **RuPt5** (blue).

Section 2. Additional time-resolved data

Figure S4. Kinetic traces of **Ru-A** (A) and **Ru-C** (B). The fits for **Ru-A** are based on a sequential model from global analysis as discussed in Chapter 4. The fits for **Ru-C** are based on the photophysical model shown in Figure S5.

Figure S5. Simplified photophysical model of light-induced processes in **Ru-C**.

Figure S6. TA spectra of **Ru-B** at time delays of 20 ps and 6 ns.

Table S1. Photoluminescence lifetimes at various emission wavelengths (± 3 nm) measured with $\lambda_{\text{exc}} = 470$ nm at room temperature. The fit error is less than 5 ns.

	600 nm	640 nm	680 nm	720 nm	760 nm	λ_{max}^*
Ru-A	791 ns	794 ns	802 ns	794 ns	802 ns	790 ns
RuPt1	177 ns (15%)	151 ns (11%)	111 ns (12%)	100 ns (15%)	66 ns (17%)	136 ns (12%)
	677 ns (85%)	663 ns (89%)	653 ns (88%)	650 ns (85%)	645 ns (83%)	659 ns (88%)
Ru-C	1.06 μs	1.04 μs	1.06 μs	1.06 μs	1.05 μs	1.04 μs
RuPt2	656 ns	632 ns	620 ns	613 ns	607 ns	624 ns

* $\lambda_{\text{max}}(\text{Ru-A}) = 630$ nm; $\lambda_{\text{max}}(\text{RuPt1}) = 645$ nm; $\lambda_{\text{max}}(\text{Ru-B}) = 645$ nm; $\lambda_{\text{max}}(\text{RuPt2}) = 660$ nm.

The obtained SAS for **Ru-B** and **RuPt2** based on the photophysical models shown in Figure S5 and Figure 4 are presented in Figure S7-S8. The grey area represents the scaled and inverted steady state absorption. SAS1 (blue curve) is associated with the $^3\text{MLCT}_{\text{ipy}}$ state. The intense ESA band at ca. 420 nm is characteristic of the absorption of the tpy^- monoanion, analogous to the observation for **RuPt1** as shown in Chapter 4.^{6,8} The broad ESA band above 520 nm is due to LMCT transitions.¹⁷ SAS2 (red curve) is related to the $^3\text{MLCT}_{\text{dceb}}$ state. Two ESA bands in the UV region (at ca. 350 nm and 385 nm) are readily resolved likely due to the reduced dceb ligands.⁶ The shape of the negative band around 460 nm resembles the inverted steady state absorption, indicating the GSB origin of this negative band.

Figure S7. SAS of **Ru-C** based on the photophysical model presented in Figure S5.

Figure S8. SAS of **RuPt2** based on the photophysical model presented in Figure 4.

Figure S9. EAS of **RuPt3** (left) and **RuPt4** (right) from global analysis based on a sequential model.

Figure S10. EAS of **RuPt5** from global analysis based on a sequential model.

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Chapter 6. Extending the excited state lifetime for light-induced hydrogen generation

While the previous chapters discuss the individual components (i.e. the catalytic moiety, the bridging/peripheral ligands) of Ru/M (M = Pd or Pt) bimetallic photocatalysts, the design and photodynamical properties of a new photocatalyst **RuPt6** is presented in this chapter, showing a promising $>1\ \mu\text{s}$ excited state lifetime. A manuscript based on the content of this chapter is in preparation.

6.1. Introduction

The transition from fossil to renewable energy is one of the most important challenges our society is facing today. Solar devices are widely considered as a highly promising option. The energy provided by the sun to the earth by far exceeds global needs¹ and photovoltaic cells have been extensively investigated during last decades. A key disadvantage of photovoltaic cells and other renewable energy sources like wind and tidal energy involves the lack of effective storage approaches for excess energy. This limitation is driving a widespread interest in the realization of efficient solar-to-fuel conversion devices. The insights obtained from extensive studies on photosynthetic light-harvesting complexes are motivating the development of biomimetic molecular systems capable of producing solar fuel.²⁻⁶ In particular, ruthenium-based coordination complexes are attracting wide interest, in large part motivated by their strong visible light absorption, ultrafast intersystem crossing, long excited state lifetime, and excellent redox reversibility as introduced in Chapter 1.⁷⁻¹⁰

Within the framework of the Ru/M (M = Pt or Pd) bimetallic photocatalyst for photocatalytic H₂ generation as discussed in previous chapters, the general molecular structure involves two peripheral ligands coordinated to the Ru(II) center, and a bridging ligand connecting the Ru(II) atom and the catalytic metal center (see Figure 10 of Chapter 1). As the formation of H₂ requires the accumulation of two photoexcited electrons, a key aspect of the widely adopted traditional design strategy involves a bridging ligand acting as an electron storage reservoir for the first photoexcited electron.¹¹ The H₂ generation reactivity of such a supramolecular photocatalyst has been shown to depend on the structure of the individual components.¹²⁻¹⁵ Ideally, light-induced electron transfer from the Ru(II)-ligand photosensitizer to the catalytic moiety occurs with a quantum yield near unity to allow efficient photon-to-hydrogen conversion. However, it has been recently observed that photoexcitation of a series of Ru/Pd and Ru/Pt photocatalysts leads to the population of Franck-Condon states not only localized on the bridging ligand,

but also on the peripheral ligands.¹⁶⁻¹⁸ As a consequence, directional electron transfer from the peripheral ligands to the bridging ligand is essential to allow a major proportion of the electron density to reach the catalytic moiety. Importantly, ultrafast photophysical studies have showed that inter-ligand electron transfer (ILET) can occur in a broad time window, ranging from ps to sub-ns scales.^{16,19-21} Sakai *et al.* succeeded in accelerating ILET by functionalizing the bridging ligand of a Ru/Pt complex with an electron withdrawing CN group, improving the H₂ generation efficiency.²¹

Although the effect of this CN functionalization highlights the importance of fast ILET to the bridging ligand, it was also observed that 30-40 % of the excited states in that particular complex return to the ground state within ca. 1 ps.²¹ This ultrafast recombination process significantly limits the H₂ generation reactivity, highlighting the importance of a long excited state lifetime for efficient H₂ generation. However, fast ILET causing a major part of the electron density to become localized on the bridging ligand does not guarantee a long excited state lifetime. In fact, the close proximity of the bridging ligand to the catalytic moiety may decrease the excited state lifetime due to more efficient radiative decay caused by spin-orbit coupling and/or additional non-radiative decay channels.^{16,22,23} These effects may explain the reduction in excited state lifetime typically observed for Ru/Pt and Ru/Pd bimetallic complexes relative to their mononuclear Ru(II) precursors,^{13,17} emphasizing the importance of considering the balance between fast ILET and a long excited state lifetime, as discussed in Chapter 5.^{23,24}

Figure 1. Structure of **RuPt6**, the mononuclear Ru(II) precursor is denoted as **Ru-D**. S = solvent (acetonitrile).

While the research has focused on the optimization of the bridging ligand as electron storage reservoir, a number of exceptions violating this traditional design approach have also been observed.^{12,17} It has recently been reported that a substantial improvement in H₂ generation efficiency is achieved by functionalizing the peripheral ligands with electron withdrawing ester side groups, resulting in H₂ turn-over number (TON) and turn-over frequency (TOF) values amongst the highest reported to date for supramolecular Ru/Pt photocatalysts.²⁴ This

functionalization effect indicates a more important role of the peripheral ligands in realizing efficient photocatalytic H₂ generation than until now considered.²³ Utilization of the peripheral ligands instead of the bridging ligand as electron storage reservoir may provide an opportunity to tune the ILET/lifetime balance. The position of the electron storage reservoir may also influence accumulative charge separation processes²⁵ necessary for H₂ formation. Although direct probing of the second photoexcited electron is challenging, recent work by Dietzek *et al.* showed that electrochemical reduction of the bridging ligand impairs transfer of the photoexcited electron (mimicking the second electron) towards the bridging ligand.²⁶ These studies, highlighting the importance of the peripheral ligands, motivates the design of a new photocatalyst **RuPt6** (Figure 1) based on 4,7-diphenyl-1,10-phenanthroline (dpph) peripheral ligands. The dpph peripheral ligands can be expected to lead to long-lived triplet metal-to-ligand charge transfer (³MLCT) states,^{27,28} which may have an advantageous effect on the H₂ generation reactivity.

The complex **RuPt6** is designed to be structurally analogous to **RuPt1** and **RuPt2** (see Chapter 5) based on the same 2,2':5',2''-terpyridine (tpy) bridging ligand, since tpy generally outperforms alternatives like 2,2':6',2''-terpyridine¹³, 2,3-di(pyridine-2-yl)pyrazine (2,3-dpp)¹⁷ and 2,5-dpp^{12,29} in terms of inaccessibility to the deactivating Ru(II) metal-centered state and capability to accept electron density from the peripheral ligands.¹⁶ The structure of the catalytic moiety is motivated by recent work by Rau *et al.*^{14,15} indicating a superior photocatalytic reactivity and stability for photocatalysts based on a Pt iodide catalytic moiety compared to Pt chloride or Pd chloride equivalents. Importantly, as discussed in Chapter 4 for **RuPt1**, the coupling between the tpy bridging ligand and the Pt iodide moiety likely induces a lower-lying triplet state (denoted as T₃), which quickly quenches the ³MLCT states on a ~1 ps time scale. This T₃ state likely involves electron density delocalization over the tpy-Pt-I moiety via the backbonding effect.³⁰ An important question to address is whether a similar quenching process is also present in **RuPt6**.

6.2. Results and discussion

6.2.1. Absorption and emission properties

Figure 2A shows the steady state absorbance and emission spectra of **Ru-D** and **RuPt6**. As common for Ru(II)-polypyridyl complexes, **Ru-D** shows a broad singlet ¹MLCT absorbance band⁷ from ca. 380 - 550 nm. On basis of **Ru-A** and **RuPd1** (see Chapter 3),¹⁶ the shoulder around 300 nm is assigned to a tpy ligand-centered π - π^* transition. Analogously, the sharp band at ca. 275 nm is ascribed to a dpph

ligand-centered π - π^* transition. Unlike **RuPt1**²⁴ and **RuPd1**¹⁶ based on bpy instead of dpqh peripheral ligands, the absorption of **RuPt6** is not redshifted relative to **Ru-D**, indicating that cyclometalation with Pt does not significantly alter the light absorption properties of the Ru(II)-ligand photosensitizer. The photoluminescence reflects the decay of the lowest ³MLCT states to the ground states, with the redshift in maximum emission intensity from 629 nm for **Ru-D** to 639 nm for **RuPt6** indicating a minor reduction in energy gap induced by the Pt moiety.

As discussed above, the application of dpqh peripheral ligands is expected to lead to long-lived ³MLCT states, motivating the design of **RuPt6**. Figure 2B shows the photoluminescence decays of **Ru-D** and **RuPt6** at their emission maxima. Both complexes exhibit a mono-exponential decay, with a photoluminescence lifetime of 1.5 ± 0.1 μ s for **Ru-D** and 1.1 ± 0.1 μ s for **RuPt6**. For comparison, [Ru(dpqh)₂]Cl₂ shows a 2.1 ± 0.1 μ s mono-exponential decay (see Figure S1 of the Supporting Information), reflecting the long lifetime of the ³MLCT_{dpqh} state. The long excited state lifetime achieved for **RuPt6** suggests that this complex is a promising candidate for photocatalysis. For comparison, **RuPt1** and **RuPt2** show significantly shorter lifetimes (<700 ns).²⁴ However, as discussed above, a long excited state lifetime and fast ILET towards the bridging ligand are not necessarily reconcilable. In addition, fast quenching of ³MLCT states by a T₃ state (see Chapter 4) induced by the Pt moiety as recently observed for **RuPt1**³⁰ remains unexplored for **RuPt6**. These photodynamical aspects will therefore be discussed in the next section.

Figure 2. Steady state absorbance and photoluminescence spectra (A) and photoluminescence decays obtained upon excitation at 460 nm (B) for **Ru-D** and **RuPt6** in anhydrous acetonitrile. Fits to a mono-exponential decay function are included as black solid curves.

6.2.2. Photodynamics of **Ru-D** and **RuPt6**

The early-time (fs–ns) photodynamics have been characterized by ultrafast

transient absorption (TA) spectroscopy. Figure 3A shows the differential absorption spectra of **Ru-D** at various time delays, measured using an excitation wavelength (λ_{exc}) of 480 nm. As intersystem crossing in Ru(II)-based complexes is generally accepted to occur within 100 fs,^{8,9,31} the spectrottemporal changes observed are due to triplet rather than singlet excited states. Several features contribute to the TA spectra. The negative signal between 430 nm and 500 nm overlaps with the scaled and inverted steady-state absorption spectrum (included as grey area), and is therefore assigned to ground state bleach (GSB). In addition to the GSB signal, three excited state absorption (ESA) regions can be distinguished. The broad ESA band above 500 nm is likely due to ligand-to-metal charge transfer transitions typically observed for Ru(II)-based complexes,^{16,32} with contributions from both reduced tpy and dppe ligands. A second ESA band around 420 nm is likely due to ligand-centered transitions of the reduced tpy ligand, in agreement with earlier assignments for **Ru-A** and **RuPt1** (see Chapter 4).^{16,30} Note that this positive ESA signal is overlapping with the negative GSB. A third and intense ESA band below ca. 350 nm is only partially resolved, and likely due to ligand-centered transitions of the reduced dppe ligands.³³ These ESA bands indicate that, similar to **Ru-A** and **RuPt1**,^{16,30} ³MLCT states localized on both the peripheral and bridging ligands are populated after intersystem crossing.

Figure 3. TA spectra at various time delays for **Ru-D** in acetonitrile for excitation at (A) 480 nm and (B) 527 nm. The grey areas represent the scaled and inverted steady-state absorption. The corresponding kinetic traces are shown in (C) for excitation at 480 nm and (D) for excitation at 527 nm.³⁴ The solid lines indicate a global fit based on a one-component sequential model.³⁵

To identify whether the population of the $^3\text{MLCT}_{\text{tpy}}$ and $^3\text{MLCT}_{\text{dpph}}$ states is λ_{exc} dependent, TA experiments have also been performed using an excitation wavelength of 527 nm (Figure 3B). The similar spectrottemporal features shown in Figures 3A ($\lambda_{\text{exc}} = 480$ nm) and 3B ($\lambda_{\text{exc}} = 527$ nm) indicate a thermally equilibrated population distribution of the $^3\text{MLCT}_{\text{tpy}}$ and $^3\text{MLCT}_{\text{dpph}}$ states, explaining the mono-exponential photoluminescence decay observed for **Ru-D** (see Figure 2B). Note that although the signal amplitude decreases upon moving λ_{exc} to 527 nm due to the lower absorption of the $^1\text{MLCT}$ band, the relative amplitudes of the individual TA bands remain similar. An analogous excited state equilibrium has recently been reported for a series of heteroleptic Ru(II)-complexes based on bpy and 1,10-phenanthroline ligands.²⁰

Information regarding the time scale at which an equilibrium between the $^3\text{MLCT}_{\text{tpy}}$ and $^3\text{MLCT}_{\text{dpph}}$ states is reached can be obtained from the kinetic traces shown in Figures 3C ($\lambda_{\text{exc}} = 480$ nm) and 3D ($\lambda_{\text{exc}} = 527$ nm). No substantial decay in GSB around 470 nm is observed for both excitation wavelengths, indicating that

recombination is insignificant in the sub-ns time window, in agreement with the long photoluminescence lifetime (see Figure 2B). Importantly, the ESA signal <350 nm representative of the population of $^3\text{MLCT}_{\text{dpph}}$ states decreases on an early ps time scale, concomitant with an ESA signal increase at 420 nm originating from the $^3\text{MLCT}_{\text{tpy}}$ states. This trend indicates $^3\text{MLCT}_{\text{dpph}} \rightarrow ^3\text{MLCT}_{\text{tpy}}$ inter-ligand internal conversion (IC) occurring on a ps time scale. Note that the ESA signal at 600 nm likely contains contributions from both the tpy^{16} and dpph^{20} ligands, and is developing on a similar ps time scale. A global fit based on a one-component sequential model³⁵ yields time constants of 12.5 ± 2.6 ps for excitation at 480 nm and 8.6 ± 2.1 ps for excitation at 527 nm. The obtained evolution associated spectra (EAS) are provided in Figure S2 of the Supporting Information.

Figure 4. TA spectra at various time delays for **RuPt6** in acetonitrile for excitation at (A) 480 nm and (B) 527 nm. The grey areas represent the scaled and inverted steady-state absorption. The corresponding kinetic traces are shown in (C) for excitation at 480 nm and (D) for excitation at 527 nm.³⁴ The solid lines indicate a global fit based on a one-component sequential model.³⁵

The long-lived and equilibrated $^3\text{MLCT}$ states of **Ru-D** motivate exploring the photodynamical properties of **RuPt6** as a potential H_2 generating photocatalyst.

While the photoluminescence decays (Figure 2B) show that the long excited state lifetime is largely preserved upon introduction of the Pt moiety, a question remains regarding possible quenching of $^3\text{MLCT}$ states by a tpy-Pt-I delocalized T_3 state as observed for **RuPt1** (see Chapter 4). Note that the population of the T_3 state was observed to increase with the excitation wavelength for **RuPt1**.³⁰ A second issue to address is whether the excited state equilibrium between the $^3\text{MLCT}_{\text{dpph}}$ and $^3\text{MLCT}_{\text{tpy}}$ states observed for **Ru-D** is maintained for **RuPt6**. The TA spectra of **RuPt6** are shown in Figures 4A ($\lambda_{\text{exc}} = 480$ nm) and 4B ($\lambda_{\text{exc}} = 527$ nm), the corresponding kinetic traces are provided in Figures 4C and 4D. The spectral features are qualitatively similar to those observed for **Ru-D**, enabling assignment of the individual bands by analogy. A global fit of the TA data of **RuPt6** using a similar one-component sequential model³⁵ as used for **Ru-D** yields time constants of 7.1 ± 1.6 ps for $\lambda_{\text{exc}} = 480$ nm and 6.4 ± 1.1 ps for $\lambda_{\text{exc}} = 527$ nm, likely reflecting electron density motion from the dpph ligands to the tpy ligand (i.e. ILET). The obtained EAS are provided in Figure S3 of the Supporting Information.

An interesting difference between **Ru-D** and **RuPt6**, however, involves the TA amplitude change associated with the $\text{dpph} \rightarrow \text{tpy}$ ILET process. In particular the change in ESA signal around 420 nm associated with the tpy ligand decreases due to the introduction of the Pt moiety, as clearly illustrated in Figure S4 of the Supporting Information. This observation may be explained by delocalization of electron density over the tpy bridging ligand and the Pt moiety. A second important difference with **Ru-D** is that **RuPt6** shows an excitation wavelength dependence, as evident from comparison of Figures 4A ($\lambda_{\text{exc}} = 480$ nm) and 4B ($\lambda_{\text{exc}} = 527$ nm). Moving λ_{exc} from 480 nm to 527 nm leads to a substantial increase in amplitude of the ESA band >530 nm relative to the GSB signal. This phenomenon is unlikely due to an increase in population of the $^3\text{MLCT}_{\text{tpy}}$ state with λ_{exc} , since an increase in ESA around 420 nm with λ_{exc} (relative to the GSB) is absent. A similar increase in ESA >530 nm observed for **RuPt1** was assigned to an increase in population of the delocalized T_3 state.³⁰ Hence, the wavelength dependence observed for **RuPt6** is likely also due to a change in population of a state that is delocalized over the tpy bridging ligand and the Pt moiety. However, the nature of this delocalized state may differ from the T_3 state of **RuPt1**, as a ~ 100 ps process observed for **RuPt1** tentatively assigned to electron density redistribution over the tpy-Pt-I moiety accompanied by solvent reorientation³⁰ is absent for **RuPt6**. Furthermore, the T_3 state in **RuPt1** was observed to quench the $^3\text{MLCT}$ states on a ~ 1 ps time scale, while such quenching is not observed for **RuPt6**. Ultrafast intersystem crossing (<100 fs) in **RuPt6** hence likely not only leads to population of $^3\text{MLCT}_{\text{dpph}}$ states, but also of a state delocalized over the tpy bridge and the Pt moiety (Figure 5). This state is likely lower in energy than the $^3\text{MLCT}_{\text{dpph}}$ states, as its population increases with excitation wavelength. Inter-ligand IC between these states occurs on a time

scale of 5-9 ps, depending on λ_{exc} .

Figure 5. Simplified photophysical model involving a non-equilibrated population of the excited states. For simplicity the ground state is not shown.

The λ_{exc} dependence observed for **RuPt6** indicates the absence of a thermally equilibrated population of excited states, even at 200 ps after photoexcitation. This situation differs from **Ru-D** and 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 in ca. 100 ps independent of λ_{exc} .²⁰ This non-equilibrated population in **RuPt6** likely originates from a high energy barrier to IC and the involvement of vibrational cooling, similar to **RuPt1** and **RuPd1**.³⁰ In fact, vibrational cooling typically occurring in 5-15 ps^{16,32,36,37} likely proceeds simultaneously to the inter-ligand IC process. Such effect implies an increase in energy barrier to IC in time,²⁰ causing a part of the electron density to relax at the peripheral dpph ligands as local energetic minima. This non-equilibrated population of excited states is seemingly in contradiction to the mono-exponential photoluminescence decay observed for **RuPt6** (Figure 2B), as one would expect the number of non-equilibrated emitting excited states to be reflected by the order of the exponential decay.^{16,38,39} One possible explanation is that the observed photoluminescence is dominated by $^3\text{MLCT}_{\text{dpph}}$ states, due to a difference in photoluminescence quantum yield between emitting states. An alternative explanation is that the populated excited states indicated in Figure 5 have similar lifetimes.

As discussed above, the traditional design strategy of a H_2 generating bimetallic photocatalyst is based on realizing fast ILET towards the electron storing bridging ligand. Recent research however indicates that functionalizing the peripheral ligands with electron withdrawing groups improves the H_2 generation efficiency.^{12,17,23,24} Consequently, it is not straightforward to determine the

advantageous electron storage location (i.e. bridging/peripheral ligands) for efficient photocatalytic H₂ generation. The photodynamics of **RuPt6** demonstrate that excited states based on both the peripheral and bridging ligands are populated in a non-equilibrated way (Figure 5), while a promising >1 μ s long-lived excited state is realized by the use of dppe peripheral ligands. The consequences of these photophysical features measured in non-catalytic reaction conditions can be complex, as in catalytic conditions a variety of photophysical and photochemical processes accompanied by multiple side reactions can occur in a broad window of time scales.²³ For instance, the generation of molecular hydrogen requires the accumulation of two photoexcited electrons coupled by proton transfer, while the detection of the second electron is challenging. This fundamental process is currently extensively studied by Hammarström and co-workers.^{5,25} The photodynamics of the second electron depend on the storage location of the first electron, as recently shown by Dietzek *et al.*²⁶ The detection of the key intermediate Pt-H species also remains challenging.^{21,40} An additional complexity arises from potential inter-molecular interactions. For instance, an adduct pre-equilibrium between the sacrificial reagent and a Ru/Pt photocatalyst has been proposed by Sakai and co-workers, and a bi-photocatalyst interaction has also been suggested.²⁹ Another important parameter is the photostability of the complexes. Recent work by Rau *et al.* shows decomposition of a Ru/Pd complex into Pd colloids in catalytic conditions, whereas the Ru/Pt analogue remains stable.¹⁴ These studies emphasize the complexity of the H₂ generation pathways following the excited state processes studied in the present work. As a next step, it is however important to investigate the H₂ generation reactivity of **RuPt6**.

6.2.3. Photocatalytic H₂ evolution

The photocatalytic H₂ generating reactivity of **RuPt6** has been measured using triethylamine as a sacrificial agent, in similar reaction conditions as recent studies on **RuPt1**.²⁴ No H₂ generation was observed in the dark, whereas illumination **RuPt6** at 470 nm leads to a H₂ TON of 134 within the first reaction hour (preliminary data⁴¹). The initial H₂ TOF of **RuPt6** of 1.9 min⁻¹ significantly outperforms **RuPt1** (TOF = 15 h⁻¹)²⁴. This remarkable improvement illustrates the potential of extending the excited state lifetime by the use of dppe peripheral ligands to realize efficient H₂ generation. The stability of **RuPt6** is however limited to ca. 1.5 h, as shown in Figure 6, possibly due to the interaction with the sacrificial agent. As a result, the overall H₂ TON value stabilizes and reaches a value of ca. 180 after 6 h of illumination. Improving the stability is hence a key challenge to be overcome to realize a long-term H₂ output.

Figure 6. Time-dependent H₂ evolution TON for **RuPt6** (preliminary data) and **RuPt1** (adopted from ref. 24).

6.3. Conclusions

In summary, the present chapter focuses on the photodynamics of a novel H₂ generating photocatalyst **RuPt6**, designed and synthesized on basis of recent progress in developing efficient Ru/Pt bimetallic photocatalysts. The application of dpph peripheral ligands results in a promising long photoluminescence lifetime of $1.1 \pm 0.1 \mu\text{s}$, which significantly exceeds the value of the bpy analogue **RuPt1** ($< 700 \text{ ns}$).²⁴ The early-time photodynamics of **RuPt6** and its mononuclear Ru(II) precursor **Ru-D** have been studied by ultrafast TA spectroscopy. An equilibrated excited state population has been observed for **Ru-D**, whereas cyclometalation with Pt leads to a non-equilibrated population for **RuPt6**, resulting in excitation wavelength dependent TA features. Ultrafast intersystem crossing leads to population of $^3\text{MLCT}_{\text{dpph}}$ states based on the peripheral ligands, and in addition a state delocalized over the tpy bridging ligand and the Pt moiety. This state likely differs from the T_3 state observed for **RuPt1** discussed in Chapter 4. The population of this delocalized state increases with λ_{exc} . This state is likely lower in energy than the $^3\text{MLCT}_{\text{dpph}}$ states. Inter-ligand IC occurs on a 5–9 ps time scale, rebalancing the excited state population in time. Vibrational cooling likely occurs simultaneously to this IC process, causing a part of the electron density to relax at the peripheral dpph ligands as local energetic minima. Preliminary data suggest that the initial photocatalytic H₂ generation reactivity of **RuPt6** significantly outperforms that of **RuPt1**. The stable H₂ output is however limited to ca. 1.5 h, possibly due to a limited photostability of the photocatalyst in catalytic conditions, motivating the identification of the various photochemical pathways in relation to H₂ generation as future research.

6.4. Experimental section

Details regarding material synthesis, characterization and H₂ evolution experiments will be provided in a future publication. Steady-state UV–vis absorption spectra were recorded using a Shimadzu UV-1800 spectrophotometer. Steady-state photoluminescence spectra were measured upon excitation at 450 nm using a Horiba JobinYvon FluoroMax-4 spectrofluorometer. Both absorption and photoluminescence spectra were recorded at room temperature. The transient absorption setup is described in detail in Chapter 2.¹⁶ Samples were prepared by dissolving the complexes in anhydrous acetonitrile (Sigma-Aldrich, purity >99.9 %) in 1 mm path length quartz cuvettes. The samples were either excited at 480 nm or at 527 nm, and had optical density (OD) values of 0.35 and 0.10, respectively. The 480 nm pump pulse had a full width at half maximum (FWHM) bandwidth of 7 nm and a 50 fs pulse duration. The 527 nm pump pulse had a FWHM bandwidth of 7 nm and a 68 fs pulse duration. The excitation power was kept sufficiently low (2.4×10^{14} photons/(cm² pulse) for $\lambda_{\text{exc}} = 480$ nm and 5.2×10^{14} photons/(cm² pulse) for $\lambda_{\text{exc}} = 527$ nm) and verified to be in the linear regime. The angle between the polarizations of the pump and probe beams was set at magic angle (54.7°). Data were numerically corrected for chirp and analyzed using the open-source program Glotaran.⁴² Time-resolved photoluminescence data were recorded using a FluoroMaxSpectrofluorometer extended for time-correlated single photon counting (TCSPC, Horiba Jobin Yvon, FluoroMax-4). Samples were dissolved in anhydrous acetonitrile and degassed by using dry N₂. A NanoLED-460 laser (462 nm, 1.3 ns pulse) was used to excite the samples at a repetition rate of 50 kHz. The TCSPC data were recorded at emission wavelengths of 630±3 nm for **Ru-D** and 640±3 nm for **RuPt6**.

Supporting information

Figure S1. photoluminescence decay obtained by exciting $[\text{Ru}(\text{bpph})_2]\text{Cl}_2$ at 460 nm. A fit to a mono-exponential decay function is included as black solid curve.

Figure S2. EAS obtained from a global analysis of the TA data for **Ru-D** (A) and **RuPt6** (B) with an excitation wavelength of 480 nm.

Figure S3. EAS obtained from a global analysis of the TA data for **Ru** (A) and **RuPt6** (B) with an excitation wavelength of 527 nm.

Figure S4. Kinetic traces recorded at 420 nm for **Ru-D** and **RuPt6** ($\lambda_{\text{exc}} = 480$ nm). Note that the signal change for **Ru-D** exceeds that of **RuPt6** by approximately a factor of two.

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Chapter 7. Probing the optically dark site of a H₂-generating photocatalyst

While the early-time photodynamics of **RuPt1** have been discussed in Chapter 4, the nature of the T₃ state quenching higher-lying ³MLCT (metal-to-ligand charge transfer, see Chapter 1 for more details) states remains elusive. However, this T₃ state is most likely associated with the cyclometalated Pt center. The present chapter hence exclusively focuses on the excited state properties related to the Pt moiety in **RuPt1** by using time-resolved X-ray absorption spectroscopy (TR-XAS) based on synchrotron radiation.¹ The motivation for applying TR-XAS to understand photo-induced processes in **RuPt1** will be discussed, followed by a short introduction to the basic principles, advantages and limitations of TR-XAS. The data analysis and interpretation are still in progress and are therefore not discussed in detail. However, directions for future research are identified in the outlook section. The work described in this chapter is based on the collaboration with Argonne National Laboratory, Lund University, University of Groningen and Technical University of Denmark.

7.1. Motivation

Transient absorption (TA) spectroscopy based on visible pump and probe pulses have been proven as a powerful technique to study ligand-based excited states (e.g. ³MLCT states), as shown in the previous chapters for a variety of Ru/Pd and Ru/Pt photocatalysts. However, the catalytically active center, e.g. the Pt moiety, is sometimes optically dark and therefore cannot be directly probed by using the supercontinuum generated by a CaF₂ window in a standard TA setup (see Chapter 2 for details). Therefore a different TA technique based on a visible pump and an X-ray probe is required. The motivation for using an X-ray probe originates from its interactions with the catalytic metal centers, generating characteristic absorption features which are sensitive to the oxidation state and the local chemical structure of the metal center (an introduction to these features is provided in Section 7.2). Therefore TR-XAS offers a unique opportunity to selectively probe electronic and structural photodynamics associated with the catalytic metal moiety. These insights are complementary to the results obtained from other investigation methods such as visible TA, TRPL and DFT calculations.

Recently, TR-XAS have been successfully applied to study a variety of molecular systems relevant for artificial synthesis.² For instance, high resolution (ps or even fs) TR-XAS has been applied to study the photodynamics of a Ru/Co bimetallic model complex.^{3,4} In addition, the key Co(I) intermediate species formed

from a Co(II)-based catalyst has also been recently probed by μs TR-XAS.⁵ Furthermore, highly accurate (± 0.008 Å) determination of the excited-state structure of an Os(II)-based photosensitizer has also been achieved.⁶ These studies have demonstrated that TR-XAS is an outstanding tool to investigate the optically dark site of coordination complexes, motivating its application to investigate the Pt moiety in **RuPt1**.

As discussed in Chapter 4, **RuPt1** exhibits complex excited state photodynamics with a strong dependence on the excitation wavelength λ_{exc} . In particular, for $\lambda_{\text{exc}} = 527$ nm, the T_3 state is likely substantially populated.⁷ Importantly, a ~ 100 ps process possibly related to electron density redistribution over the *tpy*-Pt-I moiety accompanied by solvent reorientation is expected to change the platinum bond lengths, through changes in backbonding effects.⁷ As the T_3 state is not observed for the mononuclear Ru(II) precursor **Ru** and the Ru/Pd analogue **RuPd1** (see Chapter 4), it has been tentatively assigned to the cyclometalated Pt center. This assignment is supported by DFT calculations⁸ showing that the electron density is delocalized over the *tpy* bridging ligand and the Pt center in the lowest triplet state (see Figure 2 of Chapter 5). Therefore a detailed investigation exclusively of the Pt moiety is of key importance in order to understand the nature of the T_3 state and the ~ 100 ps process.

Another unresolved key question for **RuPt1** is associated with the local structure of the catalytic Pt moiety. In the ground state, the cyclometalated Pt is most likely in its 2+ oxidation state, i.e. Pt(II), as Pt(I) species are less common and unstable.⁹ Pt(II) has a d_6 configuration and is well-known to form a square-planar coordination complex.¹⁰ As shown in Figure 1, Pt is coordinated to one C atom and one N atom at the bridge side. Upon dissolving in acetonitrile (CH_3CN), a solvent molecule likely becomes coordinated to the Pt center as proposed for **RuPt1** and other analogous Ru/Pt and Ru/Pd complexes.^{11,12} The fourth coordination site is likely occupied by an iodide anion (I^-) as the ligand, as evident from NMR and elementary analysis.¹² However, under the joint influence of the visible pump and the X-ray probe, the complex may gradually decompose, leading to the formation of triiodide anions (I_3^-) which may also coordinate to the Pt center. Further complexity arises from the relative position of the (tri)iodide ligand with respect to the solvent molecule (*cis-trans* isomerism). DFT calculations show that in the ground state the *cis*- and *trans*-forms are close in energy ($\sim kT$),⁸ and therefore both forms likely co-exist, as illustrated in the right panel of Figure 1.

Figure 1. Molecular structure of **RuPt1**. The right panel shows the possible local structure of the catalytic Pt moiety.

The oxidation state of the Pt center especially in the excited state is also an important aspect to explore. This parameter is of fundamental importance for photocatalysis, as Pt is likely the active site where the proton reduction reaction occurs. Intra-molecular electron transfer from the Ru-based photosensitizing part of the photocatalyst to the catalytic Pt center results in an increased electron density on Pt, effectively causing Pt to become reduced in an equivalent view. Analogously, back electron transfer or recombination leads to an electron density deficiency at the Pt center, effectively causing oxidation. These reduction and oxidation processes can be monitored directly by TR-XAS.

In summary, TR-XAS is a unique technique to investigate **RuPt1** with high selectivity to the catalytic Pt center, providing fundamental insights into the nature of the T_3 state, the local chemical structure, and the oxidation state of the catalytic Pt center. These insights are complementary to the results obtained from standard TA as discussed in Chapter 4. The basic principles of TR-XAS and preliminary data obtained on **RuPt1** will be discussed in the next section.

7.2. Principle of time-resolved X-ray absorption spectroscopy and its application to study RuPt1

Generally speaking, when an X-ray photon is absorbed by a core electron, the electron is excited to a higher orbital simultaneously producing a core hole. The linear absorption coefficient $\mu(E)$ can be expressed by equation (1) by applying the well-known Fermi's golden rule:¹³

$$\mu(E) \propto \sum_f |\langle \psi_f | \mathbf{p} \cdot \mathbf{A}(\mathbf{r}) | \psi_i \rangle|^2 \delta(E_f - E_i - E), \quad (1)$$

where $\mathbf{p}$ is the momentum operator, $\mathbf{A}(\mathbf{r})$ is the vector potential of the incident electromagnetic field (X-ray) with photon energy E , ψ_i denotes the initial state before transition with energy E_i , and ψ_f denotes the final state after transition with energy E_f . The quantity $\mathbf{A}(\mathbf{r})$ can be taken into a classical wave form $\mathbf{A}(\mathbf{r}) \approx \boldsymbol{\varepsilon} A_0 e^{i\mathbf{k} \cdot \mathbf{r}}$

where $\boldsymbol{\varepsilon}$ is the polarization vector that is perpendicular to the wave vector $\mathbf{k}$.¹³ Under the dipole approximation, i.e. $e^{i\mathbf{k}\cdot\mathbf{r}} \approx 1$, and considering the commutating relationship between $\mathbf{p}$ and $\mathbf{r}$,¹⁴ equation (1) can be written from its momentum form into an equivalent position form as shown by equation (2):

$$\mu(E) \propto \sum_f |\langle \psi_f | \boldsymbol{\varepsilon} \cdot \mathbf{r} | \psi_i \rangle|^2 \delta(E_f - E_i - E). \quad (2)$$

If the photon energy E is sufficient to excite the core electron from its initial orbital to a higher unoccupied orbital, an absorption line is often observed. In case of high-density of lines (i.e. continuum), a sharp rise in $\mu(E)$ is often observed and is referred to as an absorption edge. More specifically, the principal quantum numbers $n = 1, 2, 3$ for the initial ψ_i state correspond to the K-, L- and M-edges, respectively.¹⁵ Note that these absorption edges are element selective.¹⁶ For instance, the Ru K-edge (transition from the 1s orbital) has an energy of ~ 22.12 keV, whereas for Pt the K-edge energy is at ~ 78.39 keV. The discussion of **RuPt1** in the present chapter is based on the Pt L_{III} edge (~ 11.56 keV), corresponding to the transition from the 2p ($J = 3/2$) orbital of Pt. Figure 2 shows the obtained X-ray absorption spectrum of **RuPt1**. Note that the Pt L_{II} edge, i.e. the transition from the 2p ($J = 1/2$) orbital, is at ~ 13.27 keV which is at much higher energy (>1.5 keV) than the L_{III} edge, and is therefore not shown in Figure 2.

Figure 2. X-ray absorption spectrum of **RuPt1** dissolved in anhydrous acetonitrile.

In addition to the absorption edge, several other features contribute to the spectrum shown in Figure 2. The sharp absorption edge leads to an intense peak which is often called the "white line". This name originates from the historic use of photographic plates to record X-ray absorption spectra. The strong absorption at a certain wavelength leads to a stripe region of the plate that is not exposed to X-ray. This region appears white after developing, resulting in the name of "white line".

The absorption features near the absorption edge are often referred to as the X-ray absorption near-edge structure (XANES), reflecting the transition from a core electronic orbital to higher orbitals. The absorption features observed at higher energy beyond the XANES region are often referred to as the extended X-ray absorption fine structure (EXAFS). The transition from the XANES region to the EXAFS region is loosely defined, but conventionally XANES is within 50-100 eV near the absorption edge, whereas EXAFS can extend to 1 keV or more beyond the absorption edge.¹⁷

The aforementioned features are useful to investigate the catalytic moiety of **RuPt1**. For instance, information regarding the Pt oxidation state can be extracted by inspecting and modeling the absorption edge positions in the XANES region. An increased electron density at Pt, i.e. reduction in an equivalent view, leads to an enhanced shielding of the positively charged nucleus. Consequently, the electrons are less bound to the nucleus, reducing the energy required to excite an electron from the positive core. Conversely, in case the Pt center is oxidized, the outer electrons are more strongly bound to a less effectively shielded nucleus, and therefore more energy is required to excite an electron from its orbital. This effect may cause the absorption edge energy to increase with increasing oxidation state.

In the EXAFS region, the high excitation photon energy can cause photo-emission of an electron (i.e. ionization). In a simplified view, the outgoing wave of the emitted (ionized) electron from the Pt metal core may constructively or destructively interfere with the photoelectron waves that are backscattered from the neighboring atoms (e.g. I and N), causing a modulation of the absorption probability as compared to that of a free Pt atom. This effect allows an accurate determination of the local chemical structure (e.g. the bond length and ligand type) near the Pt metal center by analyzing the EXAFS data. A significant advantage of an EXAFS measurement over X-ray crystallography is that the former technique does not necessarily require crystal order to determine the local structure of the element of interest.¹⁷

The successful application of synchrotron radiation to generate pulsed X-ray beam allows the detection of XANES and EXAFS spectra in a time-resolved manner (i.e. TR-XAS). The theory of synchrotron radiation is well established and the reader is referred to ref. 1 for extensive discussions. For the present work, TR-XAS experiments on **RuPt1** were performed at the Advanced Photon Source (APS) at the Argonne National Laboratory. Figure 3 shows the basic principles of the TR-XAS experiments at APS. A more detailed description of the setup can be found elsewhere.¹⁸ Briefly, a frequency-doubled Nd:YFL (neodymium-doped yttrium lithium fluoride) laser was applied as the pump (5 ps pulse duration) to excite **RuPt1** at 527 nm. The X-ray probe pulses at a certain delay time with respect to the pump pulses were extracted from the synchrotron ring. In total 24

electron bunches are distributed around the synchrotron ring with an equal time interval (24 bunches per orbit), generating X-ray pulses (60 ps full width at half maximum) at a 6.5 MHz repetition rate. TR-XAS experiments with time resolution limited to ~ 60 ps³ were recorded by using a single-bunch X-ray pulse as the probe with an electronically tunable time delay between the pump and probe. For probing the sample at longer time scales (>154 ns), multiple bunches were used as the probe pulses. Note that although the bunch-to-bunch intensity fluctuation can be as high as 10%, it can be corrected by using a reference detector to record air scattering signals for the pulse-to-pulse intensity normalization.¹⁸

Figure 3. Basic principles of TR-XAS experiments at APS.

Figure 4 shows the obtained time-resolved differential X-ray absorption spectrum of **RuPt1** recorded at 120 ps after photoexcitation ($\lambda_{\text{exc}} = 527$ nm). Importantly, a lowering of the binding energy (i.e. redshift of the absorption edge) is likely present. As discussed in Chapter 4, exciting **RuPt1** at 527 nm predominantly leads to the population of the T_3 state. Although the $^3\text{MLCT}$ states (and possibly other excited states) may also be populated, the present TR-XAS result suggests that the net effect of populating these states is an increased excited state electron density at the Pt catalytic center at least at 120 ps after excitation. In order to investigate how fast this reduction process occurs, TR-XAS was also recorded at 30 ps as shown in Figure 5. The appearance of similar differential absorption features shown in Figures 4 and 5 suggests that reduction of the Pt center probably occurs at an even earlier time scale (i. e. <30 ps, within the instrumental response of ca. 60 ps). As also evident from Figure 5, the Pt center likely remains reduced at 1 ns after photoexcitation.

Figure 4. Time-resolved differential X-ray absorption spectrum of **RuPt1** in anhydrous acetonitrile, recorded at 50 ns after photoexcitation and averaged over 70 individual scans. The absorption edge is also plotted for reference (right vertical axis).

Figure 5. Time-resolved differential X-ray absorption spectra of **RuPt1** in anhydrous acetonitrile, recorded at various time delays between the pump and probe pulses.¹⁹ The absorption edge is also plotted for reference (right vertical axis).

The above interpretation is in agreement with the conclusion of ultrafast (within 1 ps, see Chapter 4) population of the T_3 state which is likely associated with the Pt moiety, provided that the observed TR-XAS features reflect the population of the T_3 state. Further investigation is required for the TR-XAS modeling, which is challenging and the following aspects need to be carefully considered:

(1) The high X-ray energy flux may cause permanent damage to the sample, and the degraded sample may also contribute to the measured spectra, complicating data analysis. Figure 6 shows the differential spectrum measured at 120 ps for a

degraded **RuPt1** sample, showing dramatically different features as compared to Figure 4. Note that the pump and probe repetition rates were at 1 kHz and 6.5 MHz, respectively. Therefore an elegant way to minimize the damage is to chop the probe reducing the X-ray flux. Alternatively, the damage problem can be circumvented by applying ultrashort (tens of fs) X-ray pulses as the probe. Within this short time, the probing event is completed prior to decomposition of the sample, known as the “probe-before-destroy” approach.²⁰ The Linear Coherence Light Source (LCLS) at the Stanford Linear Accelerator Center (SLAC) and the FemtoMAX at Lund University are capable to generate such ultrashort X-ray pulses.

Figure 6. Time-resolved differential X-ray absorption spectrum of **RuPt1** (photodegraded) in anhydrous acetonitrile, recorded at 120 ps after photoexcitation and averaged over 14 individual scans. The absorption edge is also plotted for reference (right vertical axis).

(2) In the experiment, the sample was flowed in order to reduce the damage. However, caution has to be taken when analyzing the data at long time scales, as the pump and probe beams need to be spatially overlapped on a flowing sample rather than a still sample. Assuming a flow speed of 1 m/s, then a time delay of 100 μ s between the pump and probe corresponds to a “walk-off” of 100 μ m, which is on the order to the focal diameter of the pump beam. This effect needs to be considered for interpreting the TR-XAS data at long time delays ($\sim$ 100 μ s). Note that sometimes a pump-flow-probe configuration is intentionally applied to measure TR-XAS with a time resolution of tens of μ s. In that case, the time delay is determined by the distance between the laser and X-ray beams and the flow velocity of the sample.²¹

(3) Diffusion controlled inter-molecular processes also need to be considered. Assuming a typical diffusion coefficient of 2×10^{-10} m²s⁻¹ for Ru complexes in acetonitrile at 20 °C,²² a mean-square displacement $>10^2$ nm² is expected within 1 μ s. This value is comparable to the mean distance of ca. 15 nm between two

neighboring **RuPt1** molecules for samples with high concentration (~ 0.5 mM) for a typical TR-XAS measurement. As a result, TR-XAS data at time delays > 1 μ s require the consideration of inter-molecular interactions. Note that as discussed in Chapter 1, $[\text{Ru}(\text{bpy})_3]^{2+}$ in its excited state can act both as a strong oxidant and as a strong reductant. **RuPt1** is likely to have analogous redox properties considering its photosensitizing Ru(II)-polypyridyl structure.

(4) Complexity also arises when modeling the XANES and EXAFS spectra. For instance, scattering atoms with a small difference in atomic number (e.g. C and N) are difficult to distinguish.¹⁷ Furthermore, the degree of freedom is sometimes difficult to determine, as multiple conformers may co-exist, requiring careful statistical analysis. The limited signal-to-noise (S/N) ratio due to small signal amplitude changes ($\sim 1\%$) also complicates the analysis.

(5) The lack of a reference system for **RuPt1** further complicates the analysis of the TR-XAS data, as Pt(I) species are known to be less stable than the Pt(II) species.⁹

Due to the challenges and limitations as discussed above, the TR-XAS modelling which is still in progress, is not presented in this chapter. An outlook of this research will be provided in the next section.

7.3. Outlook

As discussed in the previous sections, TR-XAS provides an elegant opportunity to investigate the local structure and the oxidation state of Pt, and possibly the T_3 state in **RuPt1**. Although the complexes may decompose under the joint influence of a visible laser pump and high-energy X-ray probe, in practice the spectra obtained from each individual scan are compared with the spectra recorded on fresh samples in order to eliminate contributions from damaged samples. Chemical analysis of the degraded complexes may facilitate the interpretation of the recorded spectra. Further support can be obtained from DFT calculations which provide a starting point for the structural modeling. Aside from the concerns about damage, the following aspects may need consideration for improved data analysis/interpretation and for future research:

(1) Lifetime broadening

As discussed in the previous section, absorption edge shifts are likely associated with oxidation state changes. However, considering the short lifetime of the generated core hole (i.e. depletion of an electron from the inner shell orbital), the edge region is also influenced by the lifetime broadening effect,²³ resulting a wide edge. Consequently, multiple near-edge transitions may also contribute to an edge shift. It has been shown for transition metals that careful investigation of the

generated core hole can provide deep electronic and structural insights.²⁴

(2) Combining TR-XAS with ns-TA and TRPL

While TA results for **RuPt1** obtained by using a UV/visible probe in the fs-ps time window have been discussed in detail in Chapter 4, an extension to the ns- μ s window is still required for establishing a complete connection between the spectra obtained with a UV/visible probe and an X-ray probe. Such extension studies are still in progress, while ns-TA measurements on **RuPt1**²⁵ show similar spectral features ($\lambda_{\text{exc}} = 532$ nm) as compared to the results shown in Chapter 4, with an excited state lifetime of ca. 350 ns. This lifetime value is of the same order of magnitude as the lifetime (ca. 250 ns) obtained from TRPL ($\lambda_{\text{exc}} = 532$ nm) measurement.²⁶ The difference of these obtained lifetimes (i.e. ~ 350 ns from ns-TA and ~ 250 ns from TRPL) may be due to different degassing conditions.²⁷ The analysis of these data is still in progress.

(3) Monitoring the Ru center

As the experiments focused on the Pt L_{III} edge, the recorded spectra were sensitive to the Pt moiety of **RuPt1**. For future investigations, it is helpful to also monitor the Ru center, providing complementary information of the electron density motion inside the **RuPt1** complex. A directional intra-molecular electron transfer process from the Ru center to the Pt center is expected to result in an electron density decrease and increase at the former and latter metal centers, respectively. Note that the absorption edges for Ru are far from the Pt edges, i.e. the K edge is at 22.12 keV, whereas the energy of L edges is below 3.5 keV.¹⁶ As a result these experiments will have to be performed in entirely different X-ray probe windows.

(4) Improving the S/N ratio and time resolution

For the investigation of the T₃ state, the limited S/N ratio and time resolution in the present work need to be improved in order to spectrally and temporally track the formation and evolution of the T₃ state. Note that it has been shown in Chapter 4 that this T₃ state quenches the ³MLCT states of **RuPt1** on a sub-ps time scale.⁷ Experiments with fs X-ray pulses at SLAC or FemtoMAX may be required for further investigation of the T₃ state.

(5) Measuring TR-XAS in catalytic conditions

In catalytic conditions (i.e. including sacrificial electron donors and water), the photodynamics may be different from the results obtained in pure anhydrous acetonitrile in the present study. In particular, the detection of the key intermediate Pt-H species remains challenging,^{28,29} although the synthesis of mononuclear Pt dihydrides is well known.³⁰ The limited stability of **RuPt1** in catalytic conditions implies the need for a large quantity of sample, posing a major challenge for

synthetic chemistry.

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Chapter 8. Conclusions and outlook

This chapter summarizes the early-time (fs – ns) photodynamics of the various Ru/M (M = Pd or Pt) bimetallic complexes discussed in the previous chapters. In particular, the influences of the individual components (i.e. the bridging ligands, peripheral ligands and catalytic moieties) on the excited state photodynamics are addressed, providing an overview of the structure-photodynamics relationship. A comparison of the photodynamical behaviors of these complexes in relation to their photocatalytic H₂ generation reactivity facilitates the design of new photocatalysts with improved efficiency. Furthermore, the opportunities and challenges of extending the application of Ru(II)-based complexes to develop efficient dye-sensitized solar cells (DSSCs) and hybrid photoelectrochemical (PEC) water-splitting devices are discussed in the outlook section.

8.1. Summary of the excited state photodynamics of the photocatalysts discussed in this thesis

As introduced in Chapter 1, the general structure of the molecular photocatalysts discussed in this thesis involves a covalent connection between a Ru(II)-based photosensitizer and a catalytic metal center. Key individual components of such a photocatalyst include the bridging/peripheral ligands and the catalytic moiety, as illustrated in Figures 10 and 11 of Chapter 1. Importantly, the structure of these building blocks strongly influences the overall H₂ generation efficiencies of these bimetallic complexes, as measured in terms of both turnover numbers (TON) and turnover frequencies (TOF). A complete mechanistic understanding of these obtained TON and TOF values is highly challenging, as these values are the results of complex photophysical and photochemical processes occurring in a broad window of time scales. However, detailed investigation of the fundamental early-time (fs – ns) photodynamics is an essential first step towards the design of improved photocatalysts. The knowledge obtained from such studies also facilitates the investigation of subsequent processes occurring at later time scales. For the above reasons, the previous chapters focus on the early-time photodynamics of various Ru/M (M = Pd or Pt) bimetallic complexes in relation to their molecular structure.

Figure 1 shows the structures of the various complexes discussed in the previous chapters. The complexes **RuPd1** and **RuPd2** bear the same 2,2'-bipyridine (bpy) peripheral ligands and Pd-chloride catalytic moiety. The bridging ligand is however different, and consists of 2,2':5',2''-terpyridine (tpy) for **RuPd1** and 2,2':6',2''-terpyridine (2,6-tpy) for **RuPd2**. These two complexes are discussed in Chapter 3, highlighting the important role of the bridging ligand in the

excited state lifetime. Chapter 4 extends the discussion of Chapter 3 by comparing **RuPd1** with a structurally analogous complex **RuPt1**, which bears the same bpy peripheral ligands and tpy bridging ligand, but has a different catalytic moiety (Pt-iodide rather than Pd-chloride for **RuPt1**). Complex photodynamics are observed for **RuPt1**, with a lower-lying T_3 state been proposed, which is not observed in the mononuclear Ru(II) precursor **Ru-A** and the dinuclear complex **RuPd1**. This T_3 state is likely associated with the cyclometalated Pt center, and time-resolved X-ray absorption spectroscopy allows to selectively investigate processes at the Pt moiety in **RuPt1**, as introduced in Chapter 7. The photodynamical behavior of **RuPt1** is also compared to a series of other Ru/Pt complexes (**RuPt2**, **RuPt3**, **RuPt4** and **RuPt5**), as discussed in Chapter 5. An important conclusion is that the structure of the peripheral ligands does not independently influence the photodynamics. Consequently, the coupling between the peripheral and bridging ligands is essential in optimizing the photocatalyst structure. Motivated by the insights discussed in Chapters 3–5, a new photocatalyst **RuPt6** has been designed and studied, showing a long ($>1\ \mu\text{s}$) excited state lifetime as discussed in Chapter 6. Table 1 provides an overview of the individual complexes discussed in the previous chapters.

Figure 1. Molecular structures of the complexes discussed in the previous chapters. S = solvent (acetonitrile).

Table 1. Overview of the various complexes discussed in the previous chapters.

Complexes	Chapter 3	Chapter 4	Chapter 5	Chapter 6	Chapter 7
RuPd1	√	√			
RuPd2	√				
RuPt1		√			√
RuPt2			√		
RuPt3			√		
RuPt4			√		
RuPt5			√		
RuPt6				√	
Ru-A	√	√			
Ru-B	√				
Ru-C			√		
Ru-D				√	

For a detailed discussion of the individual complexes shown in Figure 1, the reader is referred to the corresponding previous chapters. The theoretical and methodological backgrounds are introduced in Chapter 1 and 2, respectively. The main conclusions regarding the photodynamics of these complexes are summarized below.

(1) Photoexcitation of the MLCT band leads to initial population of ¹MLCT states based on both the peripheral and bridging ligands.

As discussed in Chapter 3, resonance Raman isotope studies of **RuPd1** and **Ru-A** show that both the peripheral-ligand-based and bridging-ligand-based ¹MLCT states are populated upon photoexcitation of the MLCT bands. This conclusion can be generalized to various other Ru/M (M = Pd or Pt) bimetallic complexes.¹⁻³ Importantly, the population percentage of the ¹MLCT states based on the different ligands is likely dependent on the excitation wavelength.¹ Note that the MLCT bands of Ru(II) complexes are generally broad (ca. 400 – 600 nm) and consist of a variety of transitions.⁴

(2) On the triplet potential energy surfaces, internal conversion (IC) between various triplet states can occur on a (sub-)ps time scale.

It is assumed that intersystem crossing (ISC) occurs ultrafast (≤ 100 fs) for the complexes discussed in this thesis. This assumption is generally adopted for Ru(II) complexes as ISC of the prototype complex $[\text{Ru}(\text{bpy})_3]^{2+}$ is known to occur in ~ 100 fs or even faster.⁵⁻⁷ The population of the initially formed singlet ¹MLCT states

hence likely quickly vanishes and the triplet $^3\text{MLCT}$ states are populated within the TA instrumental response time (~ 100 fs). As a result, the observed (sub-)ps photodynamics discussed in previous chapters reflect IC between triplet rather than singlet excited states. In particular, IC between $^3\text{MLCT}$ states based on different ligands can be equivalently viewed as electron density motion between different ligands, i.e. inter-ligand electron transfer (ILET). This ILET process is essential to realize directional electron transfer towards the catalytic metal center.⁸

(3) Vibrational cooling (VC) can be in competition with ILET, resulting in a non-equilibrated population of the individual $^3\text{MLCT}$ states.

An example of this phenomenon is discussed in Chapter 3 for the complex **RuPd1**. The non-equilibrated population of $^3\text{MLCT}$ states is confirmed by the excitation wavelength dependent TA results discussed in Chapter 4. Consequently, a bi-exponential photoluminescence (PL) decay is observed. This non-equilibrated population of $^3\text{MLCT}$ states is also observed for **RuPt1** and **RuPt6** as discussed in Chapters 4 and 6, respectively.

(4) The ligand structure can strongly influence the excited state lifetimes of the mononuclear Ru(II) chromophores.

For the series of mononuclear Ru(II) chromophores discussed in this thesis, their excited state lifetimes vary from ~ 65 ps to >1 μs , depending on the structure of the ligands. For instance, although **Ru-A** and **Ru-B** have the same peripheral bpy ligands, the excited state lifetime of **Ru-B** is only ~ 65 ps, possibly due to the large steric encumbrance induced by the 2,6-tpy ligand. For comparison, **Ru-A**, which bears a 2,5-tpy ligand, exhibits an excited state lifetime of ca. 790 ns, which is three orders of magnitude longer than the lifetime of **Ru-B**. Importantly, functionalizing the peripheral bpy ligands of **Ru-A** with carboxyethyl ester groups further increases its excited state lifetime to ca. 1.05 μs , as shown for **Ru-C** in Chapter 5. A long (~ 1.5 μs) lifetime is also obtained on **Ru-D**, which bears 4,7-diphenyl-1,10-phenanthroline (dpph) ligands as shown in Chapter 6.

(5) The excited state lifetimes of the dinuclear Ru/M ($M = \text{Pd}$ or Pt) complexes are in general shorter than those of their mononuclear Ru(II) precursors.

A trend observed for the various complexes discussed in this thesis is that the dinuclear complexes generally exhibit shorter excited state lifetimes as compared to their mononuclear Ru(II) precursors. This phenomenon is directly reflected by the PL decay kinetics. For instance, as shown in Chapter 3, the PL decay of **RuPd1** is bi-exponential with two time constants of 88 ± 1 ns and 400 ± 1 ns, with the faster component dominating (62%). Analogously, **RuPt1** shows a bi-exponential PL decay ($\tau_1 = 124 \pm 58$ ns, 15 %; $\tau_2 = 658 \pm 19$ ns, 85 %). For comparison, the

mononuclear Ru(II) precursor **Ru-A** shows a mono-exponential PL decay with a lifetime of 790 ± 5 ns. This reduction in lifetime is also related to the reduction in emission quantum yield, as shown in Chapter 4. Coupling the Ru(II) precursor **Ru-A** to a Pd(II) or Pt(II) metal center may cause an increase in radiative decay rate due to an enhanced spin-orbit coupling effect. The Pd(II) or Pt(II) metal center may also introduce additional non-radiative decay channels, reducing the excited state lifetime.^{4,8}

(6) The catalytic moieties may or may not influence the early-time (fs–ns) photodynamics.

Recent TA studies on a series of Ru/Pd and Ru/Pt complexes show that modifying the catalytic moiety does not significantly influence the early-time photodynamics of the photocatalysts.^{9,10} This conclusion can be extended to **RuPt3** and **RuPt4** as discussed in Chapter 5. However, two analogous complexes violating this conclusion are **RuPt1** and **RuPd1** as discussed in Chapter 4. In particular, a lower-lying T_3 state is observed to quench the higher-lying $^3\text{MLCT}$ states on a sub-ps time scale in **RuPt1**. Importantly, this T_3 state is not observed in **RuPd1** and the mononuclear Ru(II) precursor **Ru-A**. Time-resolved X-ray absorption spectroscopy provides an elegant approach to selectively investigate the cyclometalated Pt center, as introduced in Chapter 7.

(7) The excited state electron density may delocalize over the catalytic metal center and the conjugated bridging ligand.

As shown in Chapter 5, the electron density in the lowest triplet excited state of **RuPt1** is likely delocalized over the tpy bridging ligand and the catalytic Pt center. A similar delocalization effect is likely also present for the analogous complex **RuPd1**,¹¹ and has also been reported in the literature for a different Ru/Pt complex with a bridging ligand bearing a bpy unit.¹² Electron density delocalization is also suggested for **RuPt6** as discussed in Chapter 6. These results indicate that in case the catalytic metal center is coupled to a conjugated bridging ligand, the excited state electron density may become delocalized over these two components.

(8) The peripheral and bridging ligands do not independently influence the photodynamics.

As discussed in Chapter 5, functionalizing the peripheral bpy ligands of **RuPt1** with ester side groups results in electron density storage reservoirs based on the peripheral ligands with a superior excited state lifetime (~ 625 ns) for **RuPt2**. However, applying the same functionalization method to **RuPt4** does not lead to an improved excited state lifetime for **RuPt5**. On the contrary, a partial recombination process occurs on a ~ 100 ps time scale. Since **RuPt2** and **RuPt5** bear the same

peripheral ligands but a different bridging ligand, the contrasting ester functionalization effects observed for these complexes indicate that the peripheral ligands do not independently influence the photodynamics. In other words, the role of the peripheral ligands in determining the excited state photodynamics not only depends on the structure of the peripheral ligands, but also depends on the coupling between the peripheral and bridging ligands.

(9) Storing the first photogenerated electron on the peripheral ligands at early times provides a new design strategy for efficient hydrogen generating photocatalysts.

Although the bridging ligands are generally designed to store the photogenerated electrons prior to subsequent photochemical reactions, the balance between a long excited state lifetime and a high ILET rate to the bridging ligand (and catalytic center) may limit the photocatalytic performance. However, this limitation may be circumvented by utilizing the peripheral ligands as temporal electron storage reservoirs at early times, as shown for **RuPt2** in Chapter 5. An excited state equilibrium may play an important role for benefiting from this new design strategy. The lack of this equilibrium for **RuPt6** in the early times might explain its lower TOF for H₂ generation as compared to **RuPt2**, as discussed in Chapter 6.

Note that the above conclusions are based on photodynamical studies in non-reaction conditions, i.e. without sacrificial electron donors such as triethylamine (TEA) to regenerate the formally oxidized Ru(III) center. As outlined in Chapter 1, the addition of sacrificial reagents leads to the formation of radicals and side reactions, which prevent detailed photophysical studies. However, photodynamical studies in non-catalytic conditions are still relevant for understanding the photocatalytic performance of various photocatalysts.^{1,12,13} In addition, the early-time photodynamical insights summarized above provide the first step towards understanding the subsequent (diffusion controlled) photochemical processes. Moreover, the knowledge obtained from previous chapters facilitates the development of hybrid photocatalytic systems that do not require sacrificial reagents. These issues will be discussed in the following sections.

8.2. Towards efficient homogeneous photocatalytic H₂ generation

The photocatalytic H₂ generation performance of the series of complexes discussed in this thesis are summarized in Table 2, providing a structure-reactivity overview. Note that the TON and TOF values have been obtained in comparable reaction conditions. The excited state lifetimes obtained from ultrafast (<1 ns) TA are also

included. These lifetime values have been determined by monitoring the ground state bleach (GSB) signals in the TA spectra, therefore directly reflecting recombination processes. Note that TA of **RuPd2** is not directly measured. However, the excited state lifetime of its Ru(II) precursor **Ru-B** is shorter than 100 ps (see Chapter 3). Since dinuclear complexes generally exhibit shorter excited state lifetimes as compared to their Ru(II) precursors as discussed in the previous section, the excited state lifetime of **RuPd2** is likely also shorter than 100 ps.

Although the complexes listed in Table 2 have related chemical structures as illustrated in Figure 1, establishing a direct connection between the chemical structure and the photocatalytic reactivity is not straightforward. However, the photophysical insights gained from previous chapters allow interpretation of the reactivity. In particular, a correlation between the excited state lifetime and the photocatalytic reactivity is observed, meaning that deactivation of the excited states (i.e. recombination) is one of the limiting factors that strongly influence the H₂ generation efficiencies of these complexes.

Table 2. Overview of the photocatalytic H₂ generation performance and excited state lifetime of the various complexes discussed in the previous chapters.

Complex	TON ^{2,3,11}	Initial TOF (h ⁻¹) ^{2,3,11}	TA lifetime
RuPd1	130 (8 h)	27 ^a	> 1 ns
RuPd2	0	0	Likely < 100 ps
RuPt1	80 (6 h)	15	> 1 ns
RuPt2	650 (6 h)	200	> 1 ns
RuPt3	0	0	> 1 ns
RuPt4	0	0	> 1 ns
RuPt5	44 (18 h)	N.A.	$\tau_1 = 105$ ps $\tau_2 > 1$ ns
RuPt6	179 (6 h)	114 (preliminary data)	> 1 ns

^a Estimated from the reported TON data.

On one hand, fast recombination generally leads to less efficient or even inactive complexes. For instance, around 80 % of the GSB signal is recovered within 100 ps for the Ru(II)-polypyridyl photosensitizing unit of **RuPd2**, explaining its inactivity for H₂ generation. In addition, a partial recombination process causes a loss of around 50 % of the excited states over ca. 100 ps for **RuPt5**, limiting its photocatalytic reactivity.² Note that although the excited state lifetimes of **RuPt3** and **RuPt4** exceed 1 ns, these complexes are both inactive for H₂ generation. The PL decays of these two complexes are bi-exponential with the dominating component faster than 30 ns.² Importantly, a PL lifetime of 33 ns has

been reported for the inactive complex **RuPd2**.¹¹ Note that both radiative and nonradiative processes contribute to the PL decay (see equation 12 in Chapter 1), and therefore these PL lifetimes are correlated to the excited state lifetimes. Importantly, the PL lifetime values obtained for inactive complexes are significantly shorter than those obtained for photoactive complexes.

On the other hand, a longer excited state lifetime favors a higher photocatalytic efficiency. Remarkably, throughout all the eight complexes listed in Table 1, **RuPt6** exhibits the longest PL lifetime of ca. 1.1 μ s while showing the second highest initial TOF (preliminary data). However, the TON of **RuPt6** is only limited to 179 due to stability issues. For comparison, both **RuPd1** and **RuPt1** show bi-exponential PL decays with the faster components shorter than 150 ns. Importantly, both complexes exhibit significantly lower initial TOF values as compared to **RuPt6**. The most efficient complex **RuPt2** shows an initial TOF of 200 h^{-1} . This complex exhibits a mono-exponential PL decay with a lifetime of ca. 625 ns. A comparison between **RuPt2** and **RuPt6** seemingly violates the correlation between a long excited state lifetime and a high photocatalytic reactivity. However, a balance between a long excited state lifetime and a high electron transfer rate to the catalytic center (*vide infra*) should also be considered.

Ideally, it is preferred that all photoexcited electrons are transferred to the catalytic metal center, and consequently these electrons can be fully utilized for proton reduction reactions. Based on this motivation, the bridging ligands are generally designed to favor directional electron transfer from the peripheral ligand (i.e. ILET), and store the electron for subsequent photochemical reactions. Note that the electron density is likely delocalized over the bridging ligand and the catalytic center, as outlined in the previous section. Unfortunately, a high electron transfer rate to the bridging ligand (and the catalytic center) does not guarantee a long excited state lifetime. In fact, the close proximity of the bridging ligand to the catalytic metal center may increase the recombination rate due to enhanced spin-orbit coupling and additional non-radiative decay channels.⁴ As a result, the excited state lifetime is limited by storing the photoexcited electron density on the bridging ligand.

The above limitation may be circumvented by a new design strategy based on utilization of the peripheral ligands, rather than the bridging ligand, as temporal electron storage reservoirs at early times, as discussed in Chapter 5 and summarized in the previous section. The high photocatalytic H_2 generation efficiency observed for **RuPt2**, which bears electron withdrawing ester groups on the peripheral ligands, is a successful example of this strategy. Importantly, an excited state equilibrium between the ³MLCT excited states based on the peripheral and bridging ligands is proposed. This equilibration process is essential to realize electron transfer in the direction of the catalytic center for **RuPt2**. The lack of such

equilibration in **RuPt1** and **RuPt6** may limit their photocatalytic reactivity. Based on the above discussion, it is proposed that the coupling between the peripheral and bridging ligands is an important parameter to optimize in order to achieve inter-ligand equilibration and at the same time to maintain a long excited state lifetime.

In addition to the photophysical insights discussed above, the optimization of efficient molecular photocatalysts also requires future investigation of the complexes in reaction conditions, i.e. in the presence of sacrificial reagents such as triethylamine (TEA). The directions for such studies are proposed below.

(1) Investigating the radical formation process

In reaction conditions, TEA can donate an electron to regenerate the formally oxidized Ru(III) center back to its 2+ oxidation state. This radical formation process may proceed in competition with recombination processes. Consequently, the PL signal can be quenched.¹⁴ In other words, once the radical is formed, recombination is impaired as the formerly depleted LUMO of the photocatalyst is already filled by an electron donated by TEA. As a result, the donation of an electron by TEA likely prevents back electron transfer from the reduced catalytic moiety to the Ru(III) center. A key aspect for future investigation is therefore to determine the rate of this radical formation process, which is diffusion controlled and consequently dependent on the TEA concentration. Note that the TON and TOF values shown in Table 2 are obtained for solution samples with high TEA concentration (~2 M),^{2,3,11} suggesting that TEA might not behave as an efficient electron donor. Under such a high TEA concentration, an iron-pair adduct¹⁴ of TEA and the Ru(II) complex in its ground state may be formed, requiring further investigation. TRPL measurements in the presence of TEA of variable concentrations can be performed to estimate the radical formation rate.

(2) Investigating the H₂ formation mechanisms

Since the net reaction of proton reduction into molecular H₂ requires two photoexcited electrons, it is important to investigate the mechanisms of this H₂ formation process. One possible mechanism involves the accumulation of two photoexcited electrons at the catalytic moiety of a single photocatalyst.² Although TA spectroscopy is widely used to investigate the first photoexcited electron, the detection of the second photoexcited electron remains a challenge. Nevertheless, recent work on a Ru/Pt photocatalyst has shown that when the electron density is localized on the bridging ligand in an electrochemically mono-reduced situation, directional transfer of the photoexcited electron (to mimic the second electron) to the catalytic Pt site is impaired.¹⁵ This observation implies that it might be advantageous to store the first photoexcited electron on the peripheral ligands,

leading to high TON and TOF as observed for **RuPt2**.⁴ An alternative mechanism for photocatalytic H₂ formation involves a bi-molecular approach. In this approach, the two electrons needed for H₂ formation are supplied by two individual photocatalysts.¹² Consequently, the H₂ generation rate (i.e. the initial TOF) is expected to be linearly dependent on the excitation photon flux.

(3) Investigating the decomposition pathways

One of the factors complicating photophysical and photochemical studies in the presence of TEA is the limited stability of the synthesized Ru(II) complexes. For instance, although **RuPt6** shows a high initial TOF, its total TON is limited to only 179 as the complex decomposes within a few hours in catalytic reaction conditions. It is therefore important to address the decomposition pathways and develop approaches to avoid these processes in order to achieve a stable H₂ output. Controlled experiments in combination with in-situ spectroscopic methods can provide information about the stability of the photocatalyst. For instance, a recent in-situ X-ray absorption study on a Ru/Pt photocatalyst indicates that the Pt chloride catalytic moiety is well maintained during photocatalysis. On the contrary, for a structurally analogous Ru/Pd complex, the Pd chloride moiety decomposes to form Pd colloids in reaction conditions.⁹

The complex involvement of sacrificial reagents in homogeneous photocatalysis motivates the development of hybrid PEC systems, which are free of sacrificial reagents. Such concepts will be discussed in the next section.

8.3. Extending the application of Ru(II) complexes to develop dye-sensitized solar cells and hybrid photoelectrochemical water-splitting devices

The concept of hybrid PEC cells for water splitting is analogous to that of DSSCs. Ru(II)-based complexes are widely used in these two types of systems to sensitize semiconductors with wide band gaps, forming solid/molecular hybrid systems. Note that the knowledge obtained in previous chapters is based on homogeneous solution samples, and might not be directly applicable to hybrid systems. However, the intrinsic excited state properties in solution provide a reference platform to facilitate the design of hybrid systems, and more importantly, to allow photodynamical interpretations by analogy (*vide infra*). In the following discussion, the basic principles of the intensively studied DSSCs will be introduced firstly, followed by the discussion of hybrid PEC systems, which are less widely investigated as compared to DSSCs. Recent photodynamical studies on these hybrid systems in relationship to the insights gained in this thesis will also be

discussed in the end of this section.

Generally speaking, DSSCs can be categorized into three main types, i.e. n-type, p-type and tandem systems. Figure 2 shows the simplified working principles of these three types of systems. For an n-type DSSC (Figure 2A), photoexcited molecular photosensitizers (P^*) inject electrons into the conduction band (CB) of an n-type semiconductor (e.g. TiO_2) where electrons (e^-) are the majority charge carriers. The injected electron flows through an external load (providing power) and reaches the counter electrode (cathode) of the DSSC, where a redox couple (e.g. I^-/I_3^-) is applied to mediate electron transfer to regenerate the formally oxidized photosensitizers, completing the electric circuit. The maximum open circuit voltage (V_{oc}) for such a device is determined by the Fermi level (E_F) of the semiconductor and the potential of the redox mediator. In practice, a transparent conductive oxide (TCO) glass is coated onto the semiconductor to facilitate charge transport and collection. The working principle of p-type DSSCs is analogous to that of the n-type, as shown in Figure 2B. Note that in this p-type DSSC a p-type semiconductor (e.g. NiO) is applied, where holes (h^+) are the majority charge carriers. A tandem DSSC combines both n-type and p-type semiconductor electrodes into one tandem system, as shown in Figure 2C. Note that in such a tandem device, the total maximum V_{oc} is the sum of the voltages individually generated on the n and p sides. In other words, the maximum V_{oc} is determined by the Fermi level difference of the individual n-type and p-type semiconductors. A high V_{oc} exceeding 1 V has been realized for a tandem DSSC, however, its efficiency is limited to ca. 2% due to a low current density.¹⁶ Power conversion efficiencies over 10% have been achieved for n-type DSSCs.¹⁷⁻¹⁹ The efficiencies of p-type DSSCs remain lower than those of the n-type, and are largely limited by the valence band (VB) edge position of the commonly used NiO semiconductor.²⁰

Figure 2. Simplified schematic representation of the working principles of n-type (A), p-type (B) and tandem (C) DSSCs.

The concept of hybrid water-splitting PEC cells is shown in Figure 3, which is analogous to that of DSSCs discussed above. However, in a PEC cell, the photogenerated power is not applied to an external load. Instead, the power is utilized to drive proton reduction and water oxidation reactions at the photocathode and photoanode, respectively. Since the potential difference of these two reactions is 1.23 V as introduced in Chapter 1 (and also illustrated in Figure 3), PEC cells

convert solar energy directly into chemical energy, which is determined by the product of this voltage (i.e. 1.23 V) and the generated current density. Note that no sacrificial reagents are required because the H_2 and O_2 evolving half reactions are coupled.

Figure 3. Simplified schematic representation of the working principles of n-type (A), p-type (B) and tandem (C) hybrid PEC cells.

A second difference between hybrid PEC cells and DSSCs is that the photosensitizers are generally connected to catalysts to form photocatalysts (PCs). The performance of these photocatalysts is crucial for the efficiency of the PEC cells, as these photocatalysts cover both the catalysis and light absorption functionalities of the devices. As a result, optimization of these photocatalysts is at the research frontier. Some prototype hybrid PEC cells have been demonstrated by utilizing Ru(II)-based photocatalysts.^{21,22} However, the solar-to-fuel conversion efficiencies of these cells are still lower than 1%, motivating investigating of the fundamental photodynamics of these devices.

Ru(II) complexes are widely used both in DSSCs and hybrid PEC cells owing to their excellent photophysical and photochemical properties as introduced in Chapter 1. Insight into the photodynamical properties investigated in the present thesis facilitates the interpretation of the photodynamical results obtained for some solid/molecular hybrid systems. For instance, ILET occurring on a ps time scale has also been observed in a Ru(II)-polypyridyl complex anchored onto a TiO₂ surface, providing an important channel for excited state electron injection into the sensitized TiO₂ film.²³ This phenomenon is analogous to the ILET process observed in **Ru-A** occurring on a similar time scale as discussed in Chapter 3.

Importantly, it has recently been reported that on the triplet potential energy surfaces, electron injection from Ru(II)-polypyridyl dyes into TiO₂ occurs via two distinct channels.²⁴ One channel is associated with the thermally equilibrated excited states (i.e. the so-called THEXI states), leading to slow (~100 ps) electron injection. A second injection pathway is from ³MLCT states which are higher in energy than the THEXI states, leading to relatively fast (~10 ps) injection. This ~10 ps time scale is close to the time scale of vibrational cooling as determined for **Ru-A** in Chapter 3, suggesting that vibrational cooling may play an important role in controlling electron injection dynamics. Note that the TA experiment in that particular study was performed with a pump wavelength (λ_{exc}) of 420 nm, which is at the high energy end of the MLCT band. As discussed in Chapter 4, the formed ³MLCT states may stay non-equilibrated even at 500 ps after photoexcitation when photoexciting at the low energy tail of the MLCT band (i.e. $\lambda_{\text{exc}} > 480$ nm). Therefore it might be of interest to further investigate the λ_{exc} dependent injection kinetics of the complexes studied in ref. 24. Note that it has been shown in early work that the photodynamics of hybrid systems can be strongly dependent on the excitation wavelength and pump power intensity,²⁵⁻²⁷ while the TA experiments for the solution samples discussed in this thesis were performed in the linear regime, i.e. the TA signal scales linearly with the excitation power.

As discussed in Chapter 5, an important conclusion is that functionalizing the peripheral bpy ligands with carboxyethyl groups (to form the di(carboxyethyl)-2,2'-bipyridine ligand, denoted as dceb) significantly stabilizes

the dceb-based ³MLCT states, and ILET towards the dceb ligands is accelerated. This conclusion suggests that Ru(II) complexes containing dceb as the peripheral ligands may allow directional hole injection into the VB of NiO. The reason is that the excited state electron density (at the dceb ligands) is relatively far away from NiO, which is in direct contact with the anchoring ligand. Such expectation is confirmed by a recent ultrafast spectroscopic work showing hole injection for a Ru(II) complex containing dceb peripheral ligands.²⁸ Remarkably, a Ru(II) analogue containing bpy peripheral ligands does not inject holes into NiO.²⁸

The above discussion indicates that a correlation of the photodynamics between the solution phase and the hybrid phase can be obtained. However, it must be noted that the solid surface may strongly influence the excited state properties of the molecular complexes. For instance, it has been observed that some Ru(II) complexes immobilized onto ZrO₂ show an excited state relaxation process occurring on a 100 ps time scale, while such process is absent in solution.²⁴ It has also been shown in earlier work that the photodynamics strongly depend on the preparation method of the solid film.²⁷ Importantly, trap states in the solid film can also influence recombination processes, as recently shown for a Ru(II) dye anchored onto NiO.²⁹ In addition, the orientation of the attached dyes relative to the solid surface also requires careful consideration.³⁰ As a result, it is important in future research to use the photodynamics observed in solution phase as a reference to systematically investigate the hybrid systems.

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Summary

Throughout this dissertation the fundamental photodynamical properties of a series of ruthenium-based hydrogen generating photocatalysts have been presented. This thesis focuses on the early-time (i.e. 10^{-15} – 10^{-6} s) photodynamics, because they determine all the subsequent photophysical and photochemical processes occurring at later time scales. The early-time photodynamics of various molecular photocatalysts have been systematically investigated considering their molecular structure. In particular, the role of the individual building blocks (i.e. the peripheral/bridging ligands and the catalytic moiety) in the photodynamics has been studied. There are still a number of questions that are under investigation or need to be investigated in the future. However, the aim of this thesis is to provide a starting point not only to understand the complexes discussed herein, but also to guide and inspire the design of new photocatalysts with improved performance.

Followed by a general introduction of photocatalytic hydrogen generation, ruthenium-based coordination complexes and ultrafast spectroscopy in Chapter 1, Chapter 2 discusses in more detail the methodology of transient absorption spectroscopy, which is the main experimental tool used in this research to explore the early-time photodynamics of the various complexes. The overall setup arrangement and the involved key optical elements are introduced. The theoretical background of photophysical modeling of transient absorption data is also discussed.

Chapter 3 explores the impact of the bridging ligand on the excited state properties of two analogous Ru/Pd bimetallic complexes bearing the same peripheral ligands and catalytic moiety. Modifying the structure of the bridging ligand is found to have a strong influence on the excited state lifetime of the photosensitizing Ru(II) chromophore. It is suggested that steric encumbrance needs to be avoided in order to achieve a long excited state lifetime, which is one of the key parameters for efficient photocatalysis. Another important observation is the occurrence of inter-ligand electron transfer, which can be alternatively interpreted as an internal conversion process between the excited states based on the peripheral and bridging ligands. Importantly, vibrational cooling may limit the inter-ligand internal conversion efficiency.

Chapter 4 extends the discussion of Chapter 3 by comparing the effect of the Pd-based and Pt-based catalytic moieties on the photodynamics for two analogous complexes. A key observation is that the Pt-based catalytic moiety can introduce a lower-lying triplet state (T_3), which is absent for the Pd-based complex. The origin

of this state is probably related to electron density delocalization over the bridging ligand and the Pt moiety, motivating further investigation currently in progress. By applying excitation wavelength dependent transient absorption measurements, it has also been shown that the excited states of these two photocatalysts remain non-equilibrated even 500 ps after photoexcitation, indicating the importance of vibrational cooling in controlling the internal conversion efficiency as already suggested earlier.

Chapter 5 further extends the discussion of the Ru/Pt complex described in Chapter 4 by comparing it with four related Ru/Pt complexes. The essential influences of the peripheral ligands on the photodynamics are addressed. A key conclusion is that the structure of the peripheral ligands does not independently influence the photodynamics and consequently the photocatalytic performance. As a result, the coupling between the peripheral and bridging ligands needs to be considered carefully. Another important conclusion is that utilizing the peripheral ligands as a temporal storage reservoir for the first photoexcited electron could be beneficial for photocatalytic hydrogen generation, as the peripheral ligands may be less susceptible to excited state deactivation induced by the catalytic center relative to the bridging ligand.

Chapter 6 introduces a new Ru/Pt photocatalyst whose design has been inspired by the knowledge described in the previous chapters. The development of this complex has been motivated by an expected long excited state lifetime, and a high value ($\sim 1.5 \mu\text{s}$) has indeed been successfully achieved for the Ru(II) photosensitizing chromophore. Evaluation of the performance of the Ru/Pt bimetallic complex is still in progress, but preliminary results suggest a remarkable initial photocatalytic efficiency. However, the overall performance of this complex is likely limited by the photostability.

Chapter 7 focuses on the application of time-resolved X-ray absorption. This technique has been used to investigate the lower-lying T_3 triplet state, which has preliminarily been assigned to the catalytic Pt center as discussed in Chapter 4. An absorption change near the Pt L_{III} edge ($\sim 11.56 \text{ keV}$) has been monitored by pumping at 532 nm and probing with a synchrotron-based X-ray pulse. An edge shift is likely present, indicating a change in Pt oxidation state. Data analysis and interpretation are still in progress.

The field of photocatalytic hydrogen generation, also known as artificial photosynthesis, is currently developing rapidly. Though the future looks bright, challenges still remain. In particular, there is a need to accelerate the understanding

of the fundamental photophysical/photochemical processes and hydrogen formation mechanisms. This knowledge is essential in order to design new photocatalytic systems with improved efficiency. This thesis has elaborated on the relationship between the early-time photodynamics and the molecular structure of the photocatalysts, providing a central stage for extending the exploration into later time scales. Furthermore, it must be noted that the future of artificial photosynthesis is not limited to molecular photocatalytic systems only. Solid-state semiconductors and/or a combination of molecular and semiconducting materials can also provide numerous opportunities. Though the research should not be limited to one single type of photocatalytic system, the knowledge we have gained, however, should always inspire the research for the optimal design in the future.

Samenvatting

Dit proefschrift beschrijft de fundamentele fotofysica van een reeks ruthenium-gebaseerde waterstof producerende fotokatalysatoren. Er wordt in het bijzonder ingegaan op de processen die plaatsvinden op vroege tijdschalen na lichtabsorptie, omdat deze de daaropvolgende fotofysische en fotochemische processen bepalen. Dit onderzoek richt zich vooral op de invloed van de structuur van de fotokatalysator op de vroege fotodynamica. Er wordt in het bijzonder ingegaan op de rol van de individuele bouwstenen (de perifere en brugvormende liganden en de katalytisch actieve groep) op de ultrasnelle fotodynamica. Hoewel er nog diverse vragen zijn die in de toekomst in meer detail bestudeerd dienen te worden, beschrijft dit proefschrift de basis om het gedrag van deze fotokatalysatoren te begrijpen en geeft het ook richtlijnen om de fotokatalytische efficiëntie te verbeteren.

Hoofdstuk 1 geeft een algemene introductie van fotokatalytische waterstofproductie, ruthenium-gebaseerde coördinatieverbindingen en ultrasnelle spectroscopie. In hoofdstuk 2 wordt de ultrasnelle transient absorptie spectroscopie methode verder uitgewerkt. In het bijzonder deze techniek is gebruikt voor het bestuderen van de ultrasnelle fotodynamica van de verschillende fotokatalysatoren. Ook de opbouw van de experimentele opstelling en de belangrijkste optische elementen worden beschreven. Verder wordt ingegaan op de theoretische achtergrond van het fotofysisch modelleren van de transient absorptie data.

In hoofdstuk 3 wordt ingegaan op de invloed van de structuur van de brugvormende ligand op de eigenschappen van de aangeslagen toestanden van twee gerelateerde Ru/Pd fotokatalysatoren met identieke perifere liganden en katalytisch actieve groep. Het modifieren van de structuur van de brugvormende ligand van de Ru(II) chromofoor blijkt een grote invloed te hebben op de levensduur van de aangeslagen toestand. Dit effect wordt waarschijnlijk verzwakt door sterische hindering te reduceren, wat het mogelijk maakt een lange levensduur van de aangeslagen toestand te realiseren, essentieel voor efficiënte fotokatalyse. Een tweede belangrijke observatie is een elektronoverdrachtproces tussen de liganden, ofwel interne conversie tussen aangeslagen toestanden gebaseerd op de perifere en de brugvormende liganden. De efficiëntie van dit proces is echter beperkt, waarschijnlijk doordat er tegelijkertijd ook vibrationele relaxatie plaatsvindt.

Hoofdstuk 4 borduurt verder op hoofdstuk 3 en gaat in op het effect van de katalytisch actieve groep op de ultrasnelle fotodynamica van twee gerelateerde

fotokatalysatoren, met een actieve groep gebaseerd ofwel op Pd of op Pt. Een belangrijke conclusie is dat de Pt-gebaseerde katalytisch actieve groep een nieuwe triplettoestand introduceert, welke afwezig is in het Pd-gebaseerde complex. Deze triplettoestand is mogelijk gerelateerd aan een delocalisatie van elektrondichtheid over de brugvormende ligand en de Pt-gebaseerde katalytisch actieve groep, hetgeen op dit moment in meer detail bestudeerd wordt. Door ultrasnelle metingen te doen bij verschillende excitatie golflengtes blijkt dat de populatie van deze aangeslagen toestanden van deze twee fotokatalysatoren zelfs 500 ps na excitatie nog niet in evenwicht is. Deze waarneming bevestigt dat vibrationele relaxatie een belangrijke rol speelt bij het beïnvloeden van de efficiëntie van interne conversie processen, zoals al eerder gesuggereerd is.

Hoofdstuk 5 bouwt voort op de inzichten in de fotodynamica van het Ru/Pt complex beschreven in hoofdstuk 4, door het te vergelijken met vier gerelateerde Ru/Pt fotokatalysatoren. De sterke invloed van de perifere liganden op de ultrasnelle fotodynamica wordt ook besproken. De belangrijkste conclusie is dat de structuur van de perifere liganden geen onafhankelijke parameter is die de fotodynamica en de fotokatalytische efficiëntie beïnvloedt. Als gevolg hiervan is het essentieel ook de koppeling tussen de perifere en brugvormende liganden te beschouwen. Een tweede belangrijke conclusie is dat het gebruik van perifere liganden als tijdelijk reservoir voor het eerste geëxciteerde elektron de fotokatalytische efficiëntie verbeterd. Perifere liganden zijn minder gevoelig voor deactivatie van de aangeslagen toestand door de katalytisch actieve groep vergeleken met het brugvormende ligand, hetgeen leidt tot deze verbetering.

In hoofdstuk 6 wordt een nieuwe Ru/Pt fotokatalysator geïntroduceerd waarvan het design is geïnspireerd op de fotofysische inzichten beschreven in de eerdere hoofdstukken. Het ontwerp van deze fotokatalysator is gebaseerd op een verwachte lange levensduur van de aangeslagen toestand, inderdaad is een hoge waarde (~ 1.5 μ s) gerealiseerd voor de Ru(II) chromofor. De evaluatie van de fotokatalytische efficiëntie van het Ru/Pt bimetallische complex is nog gaande. De eerste resultaten suggereren een behoorlijk goede initiële fotokatalytische efficiëntie. De stabiliteit van dit complex lijkt echter beperkt te zijn, hetgeen de activiteit beperkt.

Hoofdstuk 7 bespreekt de toepassing van een zeer innovatieve ultrasnelle X-ray transient absorptie techniek. Deze methode is gebruikt voor het bestuderen van de nieuwe triplettoestand, die onder voorbehoud gedeeltelijk is toegeschreven aan de katalytisch actieve Pt groep zoals besproken in hoofdstuk 4. De verandering in X-ray absorptie rond de Pt L_{III} edge (~ 11.56 keV) is bestudeerd door het complex te exciteren met een 532 nm laser en vervolgens te monitoren met een in een

synchrotron gegenereerde X-ray puls. De Pt L_{III} absorptie edge blijkt te verschuiven, wat een verandering in oxidatietoestand van het Pt atoom aangeeft. Geavanceerde data analyse en interpretatie zijn op dit moment gaande.

Het onderzoeksveld van fotokatalytische waterstofproductie, ofwel kunstmatige fotosynthese, ontwikkelt zich snel. Hoewel de toekomst er veelbelovend uitziet, zijn er ook grote uitdagingen. Wat vooral belangrijk is, is het ontwikkelen van fundamenteel begrip van de fotofysische en fotochemische processen en de mechanismes waarmee waterstofproductie plaatsvindt. Deze kennis is essentieel om nieuwe fotokatalysatoren met een hogere efficiëntie te realiseren. Dit proefschrift richt zich op het verband tussen de vroege fotodynamica en de moleculaire structuur van de fotokatalysator, hetgeen essentieel is om processen leidend tot waterstofvorming op latere tijdschalen te begrijpen en te beïnvloeden. Verder moet opgemerkt worden dat de toekomst van kunstmatige fotosynthese niet beperkt is tot alleen moleculaire systemen. Halfgeleiders en/of een combinatie van moleculaire en halfgeleider materialen bieden ook vele mogelijkheden. Hoewel onderzoek aan een breed scala aan systemen aan te bevelen is, kan de in dit onderzoek opgebouwde kennis als inspiratie dienen voor toekomstig onderzoek met als uiteindelijk doel de realisatie van de optimale waterstof producerende fotokatalysator.

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Thank you,

Qing PAN
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List of publications

Journal publications covered in this thesis

- Pan, Q.; Freitag, L.; Kowacs, T.; Falgenhauer, J.; Korterik, J. P.; Schletwein, D.; Browne, W. R.; Pryce, M. T.; Rau, S.; González, L.; Vos, J. G.; Huijser, A. *Chem. Commun.* **2016**, 52, 9371.
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Articles in preparation

- Pan, Q.; Das, N.; O'Reilly, L.; Korterik, J. P.; Vos, J. G.; Pryce, M. T.; Huijser, A. "Improving hydrogen generating Ru/Pt bimetallic photocatalysts by the use of phenyl-phenanthroline peripheral ligands extending the excited state lifetime".
- Uhlig, J.; Pan, Q.; van Duinen, D.; Laursen, M.; Kong, Q.; Zhang, X.; El-Nahas, A.; Browne, W. R.; Haldrup, K.; Huijser, A. "Shedding light on dark excited states in a hydrogen generating photocatalyst using ultrafast x-ray spectroscopy".

Other peer-reviewed publications

- Valdueza-Felip, S.; Mukhtarova, A.; Pan, Q.; Altamura, G.; Grenet, L.; Durand, C.; Bougerol, C.; Peyrade, D.; González-Posada, F.; Eymery, J. *Jpn. J. App. Phys.* **2013**, 52, 08JH05.
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Oral presentations

- CHAINS 2015: annual Dutch conference in chemistry, “A new photophysical insight into high turnover numbers for hydrogen generation in Ru(II)-polypyridine-Pt(II) photocatalytic complexes”, November 30th – December 2nd (2015), Veldhoven, The Netherlands.
- New trends and faces II, spectroscopy of organic materials: internal PhD and postdoc symposium, “Photocatalytic water splitting: from solar energy conversion to spectroscopy”, October 20th – 24th (2014), Stellenbosch, South Africa.
- IPS-20, the 20th International Conference on Conversion and Storage of Solar Energy, “The crucial role of the bridging ligand in Ru/Pd complexes for long-lived charge separation and photocatalytic activity”, July 27th – August 1st (2014), Berlin, Germany.
- NWO study group meeting: chemistry in relation to physics and materials sciences, “Spectroscopic Studies on the Intramolecular Charge Transfer Dynamics: the Role of Bridging Ligands in the Ru/Pd Complexes”, February 10th – 11th (2014), Veldhoven, The Netherlands.
- EU/COST Action CM1202 PERSPECT-H₂O meeting: spin-effects on the ultrafast dynamics of photoactive transition metal complexes, “Spectroscopic Studies on the Intramolecular Charge Transfer Dynamics: the Role of Bridging Ligands in the Ru/Pd Complexes”, November 18th – 19th (2013), Vienna, Austria.

Poster presentations

- FOM annual Dutch conference in physics, “The capacity of peripheral ligands to act as electron storage reservoir and their effect on enhanced photocatalytic hydrogen generation”, January 19th – 20th (2016), Veldhoven, The Netherlands.
- MESA+ symposium 2014, “Ultrafast optical sciences: real-time detection of light-induced processes in materials for energy”, September 28th (2015), Enschede, The Netherlands.

- ISF-1: 1st International Solar Fuels Conference, “Photodynamics of hydrogen-evolving Ru/Pd and Ru/Pt photocatalysts”, April 26th – May 1st (2015), Uppsala, Sweden.
- FOM annual Dutch conference in physics, “Directionality of ultrafast electron transfer in a hydrogen evolving Ru-Pd based photocatalyst”, January 20th – 21th (2015), Veldhoven, The Netherlands.
- EU/COST Action CM1202 PERSPECT-H₂O symposium: current challenges in supramolecular artificial photosynthesis, “Ultrafast electron transfer in Ru(II)-polypyridine complexes”, March 9th – 13th (2014), Jena, Germany.
- ICP 2013: 26th International Conference on Photochemistry, “Spectroscopic studies on the intramolecular charge transfer dynamics: the role of bridging ligands in the Ru/Pd complexes”, July 21st – 26th (2013), Leuven, Belgium.
- EU/COST Action CM1202 PERSPECT-H₂O symposium: supramolecular photocatalytic water splitting, “A preliminary case study: the role of bridging ligands in the photodynamics of Ru/Pd assemblies for photocatalytic hydrogen generation”, February 21th – 22nd (2013), Prague, Czech Republic.

Awards

- EU/COST Action CM1202 PERSPECT-H₂O grant for a short-term scientific mission (STSM) to Dublin City University, June 15th – July 6th (2015), Dublin, Ireland.
- David Reinhoudt poster award, MESA+ symposium 2014.

PHOTOPHYSICAL MODELING EXCITED STATE RUTHENIUM
RAMAN FEMTOSECOND ELECTRON PHOTOPHYSICS
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LIFETIME ULTRAFAST
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NON-EQUILIBRIUM PLATINUM
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