Stephan Kupfer

Computational Photocatalysis

The effects of anthropogenic global warming are becoming increasingly apparent in everyday life, highlighting the now pressing need for a global switch to clean, renewable energies. A possible energy solution lies in solar power, however artificially replicating photosynthesis remains a significant scientific challenge. Research into photoactive molecules and materials for light-harvesting applications has greatly increased in recent years. However, the production of molecules for artificial photosynthesis is often an expensive, complicated and time-consuming task. Therefore, the ability to computationally build and assess the potential of new light-harvesting molecules, prior to their synthesis, is highly desirable. The power of quantum chemical methods in the analysis and prediction of the photophysical and photochemical properties of such molecules has been clearly demonstrated by several groups in recent years and is becoming an increasingly utilised analytical and predictive tool. Herein, we discuss the application of state-of-the art quantum chemical and quantum dynamical models for the prediction of photophysical properties and elucidation of both forward and back electron/energy transfer pathways as well as their respective rates in a variety of photoactive systems.

Our research has involved investigation into the kinetics and thermodynamics of excited-state electron and energy transfer processes in molecular photocatalysts using such computational approaches. In 2017 we assessed the electron transfer (ET) kinetics of a model intramolecular photocatalyst, containing a Ru(II) based photosensitizer (PS), a tetrapyridophenazine (tpphz) based bridging ligand (BL) to separate and accumulate charge and a metal based catalytic center (CC; Figure 1) [1].

Diabatic potential energy curves (PECs) were constructed for a range of donor and acceptor states and rate constants for the charge-separation (CS) processes were calculated using both semi-classical Marcus theory and quantum dynamics (QD) which showed excellent agreement in the given parameter range.

In subsequent studies published in 2018 and 2019, we utilised a similar methodology to investigate the mechanism responsible for some unusual experimental findings [2-4]. In summary, experimental studies compared the effect of changing the catalytic center in the intramolecular parent photocat-
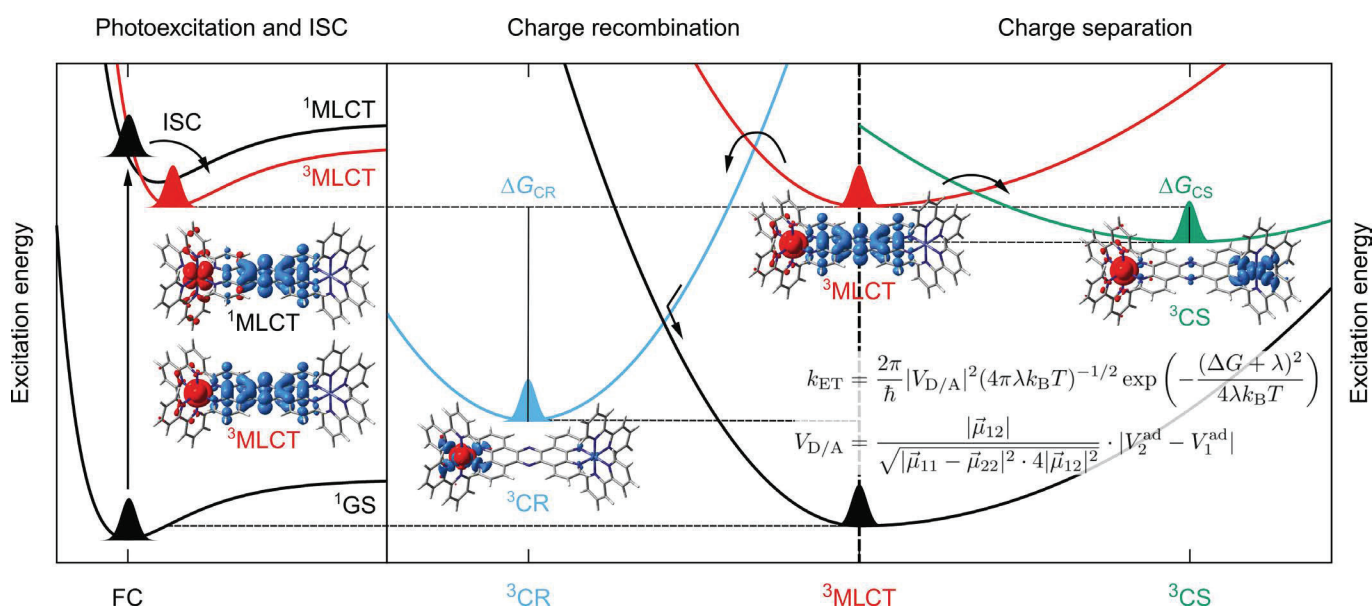
Fig. 1. Illustration of different electron transfer processes occurring in a model intramolecular photocatalyst. The leftmost panel depicts initial excitation in the Franck-Condon (FC) region, followed by either undesirable charge recombination (CR, blue curve, center panel) or charge separation (CS, green curve, rightmost panel). Kinetics of excited state processes associated with CR vs. CS can be assessed using semi-classical Marcus theory.

$$k_{\mathrm{ET}} = \frac{2\pi}{\hbar} |V_{\mathrm{D/A}}|^2 (4\pi\lambda k_{\mathrm{B}}T)^{-1/2} \exp\left(-\frac{(\Delta G + \lambda)^2}{4\lambda k_{\mathrm{B}}T}\right)$$

$$V_{\mathrm{D/A}} = \frac{|\vec{\mu}_{12}|}{\sqrt{|\vec{\mu}_{11} - \vec{\mu}_{22}|^2 \cdot 4|\vec{\mu}_{12}|^2}} \cdot |V_2^{\mathrm{ad}} - V_1^{\mathrm{ad}}|$$

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alyst, $[(tbbpy)_2Ru(tpphz)PdCl_2]^{2+}$ first published in 2006 [5], from Pd(II) to Pt(II) [2]. This resulted in an unexpected decrease in the turn-over number (TON) for H_2 production from 238 to 7. Furthermore, the formation of colloids was observed in the Pd(II) but not the Pt(II) containing complex. Our theoretical investigation demonstrated that the kinetics and thermodynamics of the light-induced reaction pathways differed between the

complexes, with the Pd(II) species postulated to exhibit energy transfer towards the CC. This was predicted to be accompanied by ligand dissociation (in agreement with the experimentally observed colloid formation) and the subsequent increased accessibility of a CS pathway, which is less readily populated in the Pt counterpart.

More recently, we have presented a theory-driven design strategy to direct light-driven charge transfer processes in a new series of molecules with photocatalytic potential, comprised of the same modular PS-BL-CC building blocks. We replaced the commonly used tbbpy coligand sphere of the parent complex with a series of electron rich biimidazole (bim) based ligands [6]. This structural modification allows panchromatic absorption of the photocenter throughout the visible region, with electron density directed exclusively towards the bridging ligand (singlet metal-to-ligand charge transfer, ^{1}MLCT$_{BL}$). Undesired MLCT transitions which photo-reduce the terminal coligand sphere are thereby shifted into the inaccessible UV region. At the same time, charge recombination (CR) processes via low-lying metal centered (^{3}MC) states of the Ru^{II}, which are well known to deactivate charge separated MLCT states in d^6 metals (see Figure 1, in blue), are quenched [7, 8]. As shown within the semi-classical Marcus picture, the underlying thermodynamic properties (driving force and reorganization energy) as well as the electronic coupling between the involved states of interest are also tailored by our design concept. To allow for a robust description of such potential couplings – originating from the typical breakdown of the Born-Oppenheimer approximation in the realm of excited-states – we rely on the Generalized Mulliken-Hush method, which allows one to predict and project such couplings along a particular reaction coordinate, based on the adiabatic energies as well as on the dipole and transition dipole moments of the associated adiabatic states (i.e., the so-called diabatization factor). Consequently, the rate constant for the undesirable ^{3}MLCT$_{BL}$→^{3}MC$_{Ru}$ deactivation is decreased by up to two orders of magnitude compared to the tbbpy parent complex. Notably, this deceleration

originates from the altered driving force but primarily from the decreased electronic coupling between the two diabatic states of interest. To assess efficient intramolecular excited-state reaction coordinates, we utilize our lately introduced external optimizer Pysisyphus, which is also aware of excited-states and linked to a plethora of quantum chemistry packages [9]. The unprotonated/non-alkylated bim ligand even allows this deactivation channel to be closed entirely, based on the strongly endergonic driving force. This approach therefore not only allows steering of the initial light-driven processes but also hampers undesirable charge recommendation cascades in d^6-based complexes, thus potentially enhancing both the quantum efficiency and the lifetime of the charge separated state. Therefore, such a concept is not limited to the investigated dyads in the frame of photocatalytic H$_2$ formation, but might also be of interest, e.g., in the scope of molecular sensors and photodynamic therapy.

Another key aspect involves the lifetime of the CS state. In typical transition metal-based photosensitizers there is a design tension between the creation of long-lived excited (triplet), e.g., ^{3}MLCT states and their successful population. Long-lived triplet states have low spin-orbit coupling (SOC) values and hence their population is low. Thus, a long-lived triplet state can be populated but inefficiently. If the SOC is increased, the triplet state population efficiency is improved – coming at the cost of decreasing the lifetime. In our most recent work, we employed a promising strategy to isolate the triplet excited state away from the metal after intersystem crossing (ISC) by combining a transition metal complex with an organic donor/acceptor group. These organic substituents introduce new excited states such as intra-ligand charge transfer (ILCT) and ligand-to-ligand charge transfer (LLCT) states into the already rich excited-state manifold.

We followed this design approach and presented a theoretical investigation of the photo-induced ET processes associated with CS in a series of five Ru(II)-based complexes that incorporate such photo-redox active organic groups.
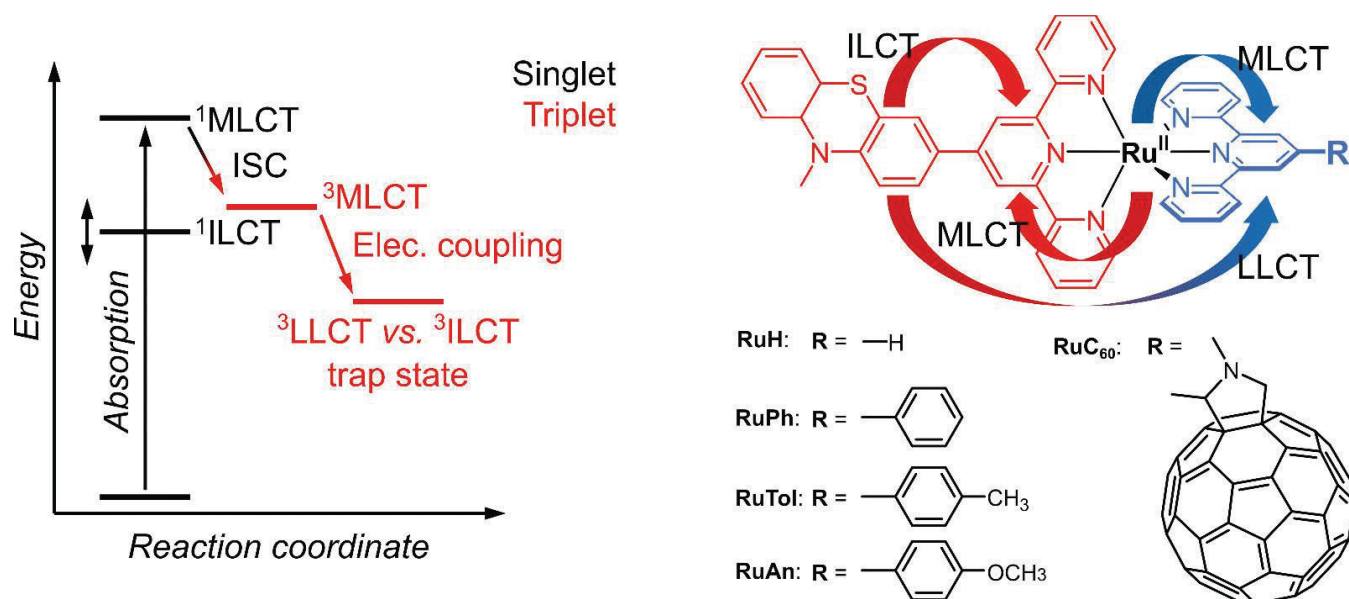
Fig. 2: Left: Jablonski scheme visualizing excited state processes associated with intersystem crossing and the subsequent population of long-lived 'trap states' by means of the associated electronic coupling (left). Right: Structures of the investigated Ru(II) photosensitizers (RuR) incorporating a phenothiazine-tpy donor ligand (red) as well as a tpy-based acceptor ligand (blue). Prominent electronic transitions are indicated [10].

These photosensitizers and their excited state relaxation processes were previously characterized by various spectroscopic techniques [11]. The measured ET rates as well as the underlying electronic couplings indicated a remote-control capability of the electronic coupling by means of structural modification. We were able to rationalize this effect by means of quantum chemical simulations [10].

Our computational study allowed for the elucidation of the Franck-Condon photophysics by scalar-relativistic (SR-)TDDFT and by multiconfigurational simulations. ISC channels along ^{1}MLCT/^{3}MLCT gateway states were found to function as efficient population transfer pathways to the triplet manifold. Subsequently, the excited-state relaxation processes were simulated – branching into two main channels from the thermally equilibrated lowest ^{3}MLCT state that involve low-lying ^{3}ILCT $vs.$ ^{3}LLCT states. The associated ET process, $i.e.$, along ^{3}MLCT-^{3}LLCT and ^{3}MLCT-^{3}ILCT channels, were investigated by means of semi-classical Marcus theory along excited-state reaction coordinates. Our simulations predict, in agreement with the experimental data, a modulation of the electronic coupling for the ^{3}MLCT-^{3}LLCT pathway. However, the overall small couplings lead to a slow MLCT deactivation along this channel. In contrast, significantly larger, yet mostly substitution-independent couplings, were simulated for the ^{3}MLCT-^{3}ILCT cascade, which led to a fast ET along this channel, $i.e.$, ~$4 \cdot 10^{12}$ s^{-1} (theory) $vs.$ ~$2 \cdot 10^{11}$ s^{-1} (experiment) for the parent compound. In summary, our theoretical investigation was able to assess the excited state ET kinetics in a series of Ru(II)-based complexes that incorporate organic donor/acceptor groups. Two main ET channels were identified and analyzed: $i)$ a slow ^{3}MLCT-^{3}LLCT and $ii)$ a fast ^{3}MLCT-^{3}ILCT. Ultimately, steering the population of such charge separated states that involve the organic chromophore provides a means by which to foster long-lived excited species with a multitude of applications in the field of photochemistry.

Computational chemistry provides a unique means by which the photophysical properties of complex molecular systems can be readily assessed. Through electronic tuning and modulation, promising candidate systems for applications in light-harvesting or photocatalysis can be identified computationally. Such calculations can provide fundamental insight into energy and electron transfer cascades and reaction mechanisms and thus can be utilized to steer synthetic design towards novel systems. Future projects will focus on extending Pysisyphus to allow a fully automated assessment of excited-state energy and electron transfer processes within the Marcus picture. Additionally and orthogonally, we aim to go beyond such a simple two-state Marcus picture to cover super-exchange phenomena and incomplete population transfer between the diabatic states of interest by means of dissipative quantum dynamics.

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Stephan Kupfer received his PhD in 2013 from the Friedrich-Schiller-University Jena, Germany, where he is currently a group leader in the Physical Chemistry Department. His research is focused on the theoretical modeling of photo-induced processes, i.e., in the fields of solar energy conversion and plasmonic hybrid systems. For light-harvesting applications, either in the scope of (dye-sensitized) solar cells or light-driven water-splitting, detailed understanding of the fundamental photophysics and photochemistry is of uttermost importance. Therefore, he aims to elucidate as well as to tune excited state relaxation dynamics in (supra)molecular photocatalysts and light-harvesting antenna associated to electron and energy transfer processes, i.e., charge separation, charge recombination and photodegradation.