

Review

Using computational chemistry to design Ru photosensitizers with directional charge transfer

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ABSTRACT

Recent developments in computational chemistry offer an attractive opportunity to design new photosensitizers with suitable properties. A number of theoretical techniques can be exercised to tune the optical and electrochemical properties required to optimize the efficiency of solar energy conversion schemes. In this contribution, it is illustrated how computational chemistry hand-in-hand with experimental results can aid the design of photosensitizers. To this aim, computational methods with emphasis on recent developments in density functional theory (DFT), as the “work horse” of computational coordination chemistry, are reviewed in the light of explaining how ground and excited properties can be related to different physical observables relevant to design photosensitizers with particular properties. A case study based on a family of [Ru(dqp)₂]²⁺ complexes is used in a tutorial fashion to exemplify the different properties that can be obtained from theory, including nuclear geometries, electronic transitions and mechanistic aspects of photodeactivation, in order to optimize directional charge transfer in photosensitizers.

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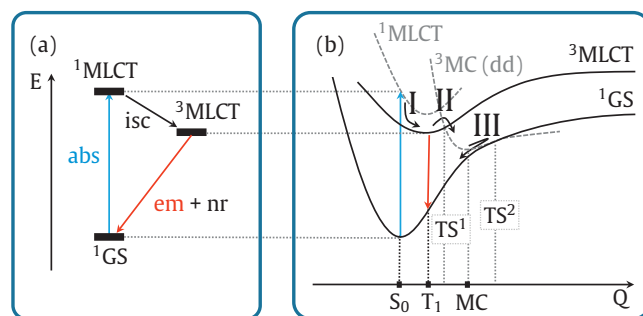
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1. Introduction

One major societal challenge is the generation of sufficient amounts of energy, which is to date primarily provided by the combustion of fossil fuels. Irrespective of the projected abundance of such fuels, i.e. oil, gas and coal resources, severe environmental concerns arise from their extensive use, particularly from the production process itself and from the release of green-house gases that contribute to climate change. In this respect, sunlight provides an abundant and cheap energy source, although this energy is dispersive and therefore requires affordable materials to process it. The process of converting photon energy has been mastered by nature [1], ultimately creating organic matter that also forms the basis of the fossil fuels consumed today. During the last decades, a number of technologies have matured to efficiently generate electricity (photovoltaics) and/or to generate fuels by coupled catalytic processes (photo-electrochemical or photosynthetic devices) [2–4]. Given their importance for our future society, different strategies are pursued to qualitatively fulfill this task, and lead to diverse discussions that concern their current and anticipated application potential, creating a vibrant interdisciplinary field ranging from chemical synthesis and catalysis to material science.

Photovoltaic devices follow a common working principle, which resembles also the primary steps of natural photosynthesis: Photon absorption and exciton migration, primary charge separation, charge transport. Hence, current work is devoted to maximize the overall power conversion efficiency (PCE; power = voltage \times current) by minimizing the losses, either in form of excessively spent driving forces, which lowers the open-circuit voltage, or by recombination of charge carriers, reducing the short-circuit current. For example, research in material science focuses on the advancement of processing techniques and engineering of the devices, particularly in silicon-based solar cells, perovskite-based solar cells, quantum dots cells, while the advances in synthetic chemistry allow preparation of molecular components and materials with improved optical and electrochemical properties, e.g. in dye-sensitized solar cells (DSSCs) or organic solar cells. In the latter cases, systematic improvement of PCEs relies on a modular strategy to assemble the functional components (light absorber, conductive domain etc.) and thereby precisely control their interaction. For example, the photophysical and electrochemical properties of a photosensitizer determine its efficiency for charge separation, while its interaction with charge-transporting components, including inorganic semiconductors [5], controls the rates of forward charge transfer vs. undesired processes, e.g. charge trapping and ultimately recombination.

Polypyridyl-based ruthenium complexes, e.g. archetypal $[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy is 2,2'-bipyridine), constitute an attractive class of photosensitizers not only for solar energy conversion schemes [6–10], but also for use in optoelectronic/photonic devices [11–14], as optomechanical actuators [15], molecular sensors [16] and switches [17,18], in photoredox catalysis [19–22], and with particular interest in medical and biochemical applications, such as diagnostics and photo-therapy [23–25]. Their broad practical application originates from the widely adjustable photophysical and electrochemical properties, both in the ground and excited states [26–29]. The photophysical processes of Ru-polypyridyl complexes have been studied experimentally in great depth during the last decades [28]. The most important states and associated processes are depicted in the simplified Scheme 1. They will serve as the starting point for the discussion of design strategies to tailor specific properties of photosensitizers (vide infra). After photon absorption in the ground state (GS) of a Ru polypyridyl complex (Scheme 1a), the initially populated singlet metal-to-ligand charge transfer ($^1\text{MLCT}$) state undergoes ultrafast intersystem crossing (ISC), typically in or very close to the Franck–Condon region, then



Scheme 1. (a) Simplified Jablonski diagram illustrating the most relevant states (GS=ground state, MLCT=metal-to-ligand-charge transfer) and principle photo-physical processes (abs=photon absorption (blue), isc=intersystem crossing, em=emission (red), nr=non-radiative decay) of Ru polypyridyl complexes. (b) Schematic associated potential energy curves illustrating the population and deactivation pathways of the $^3\text{MLCT}$ states as a function of the nuclear coordinates (Q): (I) intersystem crossing and relaxation from $^1\text{MLCT}$ to $^3\text{MLCT}$ state, (II) thermally activated surface crossing from $^3\text{MLCT}$ to ^3MC (metal-centered or dd transition) state, and (III) surface crossing with intersystem crossing to ^1GS .

populating a triplet MLCT ($^3\text{MLCT}$) state or a triplet manifold. The $^3\text{MLCT}$ excited state can decay to the ground state via radiative decay – so-called emission – and non-radiative pathways, whereby the excited state lifetime and the emission quantum yields are determined by the individual rate constants.

A typical scenario is depicted in Scheme 1b, where the dominant non-radiative deactivation occurs via thermally activated population of a triplet metal-centered (^3MC) state. This state can populate the ground state efficiently, as usually dictated by the energy gap law [28]. The activation barrier to the transition state (TS^1), that ultimately determines the $^3\text{MLCT}$ lifetime, can be as low as 1500 cm^{-1} (0.19 eV) for $[\text{Ru}(\text{tpy})_2]^{2+}$ (tpy = 2,2':6',2''-terpyridine), leading to very short $^3\text{MLCT}$ lifetime of 0.2 ns and low quantum yield [30], while this barrier is significantly higher for $[\text{Ru}(\text{bpy})_3]^{2+}$ and leads to long excited state lifetimes (~ 800 ns) and moderate quantum yields (0.06) [27]. Long excited state lifetimes are crucial for an efficient energy transfer to an acceptor. For example, in homogenous photocatalysis, the excited state lifetimes should be as long as possible to enable efficient diffusional encounter with a suitable electron donor or acceptor; whereas in DSSCs lifetimes of several nanoseconds are considered sufficient for charge injection into TiO_2 , where panchromatic absorption and energy level alignment with respect to the semiconductor valence band are of high current interest [31]. In addition to the excited state lifetime, the versatility of a photosensitizer for charge transfer depends further on the redox properties, which are commonly derived from the emission energy and the ground state redox potentials [28].

The photophysical properties of ruthenium complexes can be widely tailored by the choice of the ligand sphere. Generally, undesired photodissociation and photodegradation is effectively diminished by chelating ligands, for example, by tridentate cyclometalating ligands vs. monodentate isocyanates in DSSC applications [31,32] or by the significantly enhanced photostability of *tris*-bidentate vs. *bis*-tridentate coordination, i.e. $[\text{Ru}(\text{bpy})_3]^{2+}$ vs. $[\text{Ru}(\text{dqp})_2]^{2+}$ [33]. Historically, the ligand modifications by functional groups allowed to fine-tune the electron transfer properties [27], and/or to prolong the excited state lifetime in case of tpy-based complexes (Scheme 2) [34]. Alternatively, replacement of the pyridine-rings by alternative (hetero)cycles, including (carb)anionic [35–37] and/or carbene [38–42] donors, has stimulated intensive research in the last years. The use of strong σ -donating ligands causes an increased ligand-field splitting, e.g. by carbenes, which raises the relative energy of the ^3MC state vs. the $^3\text{MLCT}$ and thereby increasing the thermal activation barrier for

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