LEVERAGING THE PHOTOPHYSICS OF FIRST-ROW TRANSITION METAL COMPLEXES FOR SUSTAINABILITY AND SELECTIVITY IN PHOTOREDOX CATALYSIS

JAMES K. MCCUSKER[*]

[*]*Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, USA*

Photoredox: The Merging of Organic and Physical-Inorganic Chemistries

Photoredox catalysis represents a vibrant and growing area of chemistry both in academia and industry. Launched in its modern form with the near simultaneous publications by MacMillan [1] and Yoon [2] in 2008, the field owes its success to the leveraging of well-known photophysical properties of certain classes of chromophores to carry out organic transformations that are difficult if not impossible to perform under thermal conditions. The use of light to drive these otherwise endothermic processes has revolutionized synthetic organic chemistry [3] while at the same time providing unprecedented opportunities for collaborative efforts across various sub-fields to achieve transformative results that the individual teams could not have foreseen nor realized on their own.

A critical developmental aspect of the field that allowed for its rapid and widespread utility was the initial use of transition metal-based charge-transfer chromophores such as $[Ru(bpy)_3]^{2+}$ (where bpy is 2,2'-bipyridine). Irradiation of this compound in the visible region creates a so-called metal-to-ligand charge-transfer (MLCT) excited state that is characterized by the transfer of an electron from the metal center to the bpy ligand.[4] The ca. 2 V of energy stored in this excited state coupled with its ~1 μs lifetime in fluid solution predisposes it to engage in a wide variety of both energy and electron transfer reactions. While this behavior was first identified by Gafney and Adamson in 1972 [5], no one had thought to apply these properties to synthetic organic chemistry. Since the initial reports in 2008, many researchers have now gone on to develop a range of photocatalysts based on the charge-transfer excited states of Ru(II), Ir(III), Os(II), and Re(I) compounds to name a few.[6]

Despite the enormous success that has been realized with the use of these chromophores, there are certain aspects of these photocatalysts that together make for a compelling argument to look beyond these systems for alternatives. For one, light capture is the most material-intensive aspect of any light-to-chemical energy conversion process due to the relatively low energy density associated with either sunlight or light in a laboratory setting. Accordingly, the scalability of processes reliant on the absorption of light is tied directly to the elemental scarcity of the chromophore's components. While compounds based on the elements just listed are undeniably successful in terms of carrying out the desired chemistry, they are also among the least abundant elements on Earth. Scaling up desirable processes – even when the compounds are being utilized at levels appropriate for a catalyst – will nevertheless become subject to concerns surrounding cost and elemental availability. A second issue of great importance to the synthetic organic community in particular centers on the question of selectivity. As mentioned above, the MLCT excited state of $[Ru(bpy)_3]^{2+}$ stores ~2 V of energy; this energy is split up roughly equally in terms of the oxidizing and reducing power associated with the Ru(III) and bpy^- moieties, respectively, that comprise the excited state. Put another way, the MLCT excited state of $[Ru(bpy)_3]^{2+}$ can, in principle, react indiscriminately as either an oxidant or a reductant. Selectivity of one process versus another will therefore rely, at least in part, on tuning the thermodynamics of the reaction in question and/or introducing other design features that will help drive the system along the desired pathway. These two issues – sustainability and selectivity – therefore present significant challenges as the field of photoredox catalysis continues to develop.

Our contribution to the field: Photofunctionality in the First Transition Series.

We would argue that both issues raised above can be partly if not wholly addressed if one could develop photoredox catalysts based on elements of the first transition series.[7] Fe(II), for example, is valence isoelectronic with Ru(II), sitting just above the latter in Group 8. Iron is present in the Earth's crust at a level in excess of 10^7-fold greater than that of ruthenium, essentially taking the elemental availability and cost questions off the table. Despite possessing the same electronic excited states as $[Ru(bpy)_3]^{2+}$, $[Fe(bpy)_3]^{2+}$ fails to carry out any of the same photo-induced processes endemic to the excited-state chemistry of $[Ru(bpy)_3]^{2+}$. The reason for this was first intimated in the work of Creutz and Sutin in 1980 [8] and expanded upon by McCusker and Hendrickson in the early 1990s [9], but it was not established by a definitive experiment until 2000 when we published the first femtosecond time-resolved absorption data on an Fe(II) polypyridyl complex.[10] That study revealed a sub-100 fs decay of the compound's MLCT excited state; subsequent work filled in the details of these initial observations and created a picture of ultrafast formation of a metal-centered, ligand-field excited state as the lowest energy excited state in this class of compounds.[11] Many researchers have expanded on our findings, marshalling a wide range of optical and computational methods to characterize this remarkable photophysical process and generalizing it to complexes across the first row of the transition series. Figure 1 depicts the picture that has emerged, one in which the relative energies of the charge-transfer and metal-centered ligand-field excited states undergo an inversion upon moving from the second- or third-row of the transition series up to the first. The consequences regarding applications in photoredox catalysis are immediately obvious: whereas the ^{3}MLCT state of $[Ru(bpy)_3]^{2+}$ persists 1000-fold longer than diffusion times in solution, the corresponding state in $[Fe(bpy)_3]^{2+}$

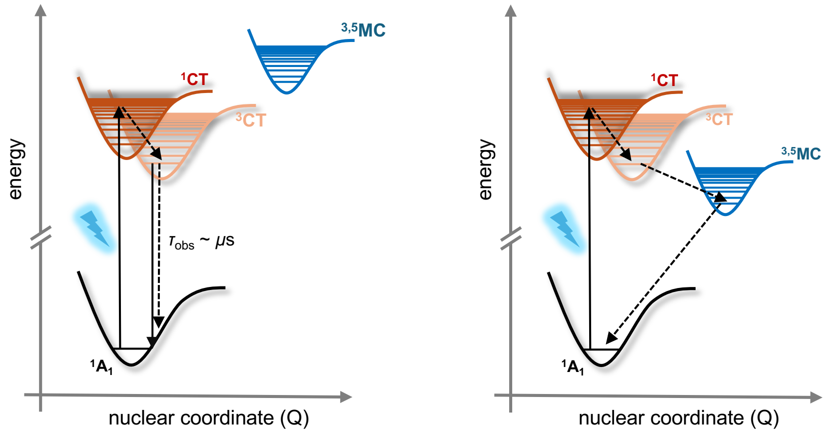

Fig. 1. Simplified potential energy surface (PES) diagrams depicting the electronic landscape typical of chromophores based on Ru(II) and Ir(III) (left) versus that encountered in the first transition series (*e.g.*, Fe(II) and Co(III), right). The energetic inversion between the charge-transfer (CT) and metal-centered (MC) excited states represents a fundamental challenge associated with the use of earth-abundant elements of the first transition series in light-to-chemical energy conversion strategies, including photoredox catalysis.

disappears 10,000-fold faster than a bimolecular reaction can occur. This situation, the origin of which is linked to the so-called primogenic effect [12], represents a fundamental challenge that must be overcome in order to leverage the advantages that chromophores based on first-row transition metals present. Appreciation of this issue has catalyzed the chemical community into finding ways to circumvent this problem, efforts have resulted in tremendous advances both in terms of the synthesis of new ligand platforms that present stronger ligand fields to the metal [13] as well as the development of novel complexes based on first-row elements in unusual oxidation states such as Cr(0) [14] and Mn(I).[15, 16]

In addition to pursuing novel ligand constructs, our group has focused primarily on two research thrusts: (1) using ultrafast spectroscopy to identify the reaction coordinate(s) that drives the MLCT-to-ligand-field state relaxation process with the goal of feeding that information back into synthetic design, [17] and (2) exploring whether ligand-field states themselves are viable for applications in photoredox catalysis. This second approach has resulted in significant progress, particularly in the case of Co(III). Complexes of this ion are iso-electronic with their Fe(II) counterparts but possess important differences in terms of their excited-state energetics. First, the increase in charge relative to Fe(II) causes an increase in ligand-field strength, which in turn can result in changes in the relative energies of the various excited states within the ligand-field manifold. Second, the oxidation state change gives rise to changes in charge-transfer absorption features in terms of both their nature (LMCT instead of MLCT) and energy (ultraviolet instead of visible); the latter provides direct optical access to metal-centered transitions in the visible [18] and allows for elucidating the properties of this class of excited states.

The photophysics of Co(III) complexes had received relatively little attention as compared to complexes of other first-row metal complexes, so we undertook a comprehensive study of their ground-state recovery dynamics. In particular, our use of variable-temperature time-resolved ultrafast absorption spectroscopy has proven to be extremely useful at elucidating details concerning structure-property relationships necessary for the development of novel compounds with synthetically tailored physical and photophysical characteristics. In the case of Co(III) polypyridyl complexes, our studies established two important features of their excited-state properties: (1) the lowest energy excited state corresponds to a metal-centered $^3T_1$ ligand-field state (as opposed to the $^5T_2$ state found for corresponding Fe(II) complexes), and (2) the ground-state recovery dynamics associated with relaxation from this $^3T_1$ excited state occurs in the Marcus inverted region (again, in contrast to the normal region behavior exhibited by Fe(II)-based systems).[19] It is this inverted region behavior that is particularly important when considering their potential use in photoredox catalysis: in contrast to normal region behavior, where the excited-state lifetime decreases as the energy of the excited state is increased, the lifetimes of Co(III) complexes become more and more amenable to diffusional reaction chemistry the more energy one stores in its excited state.

At the time we were working out the fundamentals of Co(III) photophysics, the MacMillan group had been exploring photochemical approaches for achieving oxidative C(sp^2)-N bond formation and had, on a parallel track, begun looking at simple Co(III) polypyridyl complexes as potential photoredox agents. We quickly realized that what we were learning about Co(III) photophysics could tie in perfectly with the chemistry the MacMillan group was pursuing. An absence of charge separation and their generally non-emissive behavior presents a challenge when trying to quantify redox properties of metal-centered excited states that might be exploited for photoredox catalysis. Nevertheless, time-resolved absorption measurements on solutions of $[Co(Br_2bpy)_3]^{3+}$ (where Br_2bpy is 4,4'-dibromo-2,2'-bipyridine) with a series of substituted arenes allowed us to establish that the compound's $^3T_1$ ligand-field excited state is a potent oxidant: its potential of ca. -1.25 V exceeds that of the MLCT excited states of $[Ru(bpy)_3]^{2+}$ as well as most commonly employed Ir(III)-based photocatalysts.[20] Moreover, since formation of Co(IV) is significantly endothermic, the excited state of Co(III) can only be reduced, i.e., it will be intrinsically selective as a photooxidant.

The collaboration resulted in the process summarized in Figure 2.[21] The basic reaction involves the coupling of an aryl amide with an aryl boronic acid, where oxidation of the amide to its corresponding amidyl radical sets the system up for a dark reaction that ultimately results in the C(sp^2)-N coupled product. The reaction does not proceed thermally due to the energy required to create the radical, but single electron transfer to an excited state with sufficient oxidizing power was proposed as a means of creating the amidyl radical. A variety of both transition metal-based (e.g., Ru(II) and Ir(III)) as well as organic photoredox agents were tested: none of them produced reactions where the yield exceeded 10%. In contrast, when $[Co(Br_2bpy)_3]^{3+}$ was used we

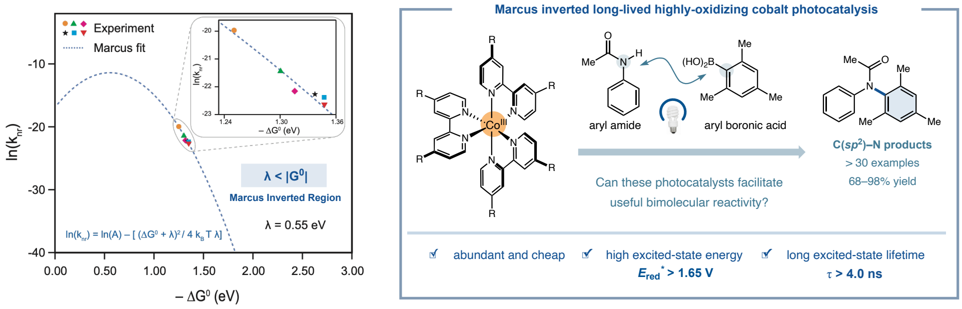

Fig. 2. *Left.* Marcus curve (i.e., natural log of the rate constant as a function of driving force) describing the ground-state recovery dynamics of Co(III) polypyridyl complexes. The data indicate behavior in the inverted region, where an increase in excited-state energy leads to a lengthening of the excited-state lifetime that makes it amenable for bimolecular reaction chemistry. *Right.* Summary of the photo-driven coupling of aryl amides with aryl boronic acids. The Co(III) polypyridyl complex shown outperformed both organic photocatalysts as well as charge transfer-based photocatalysts based on Ru(II) and Ir(III). Adapted from ref. 21.

found it to be highly successful, giving rise to reactions whose yields ranged from 65 – 95% across a wide range of substrates. Efforts are continuing with new ligand designs that are leading to increases in the absorption cross-section of the photocatalysts, shifting their absorption profiles toward the red region of the visible spectrum, as well as increasing the ligand-field strength which, due to the inverted region behavior these compounds exhibit, will increase the energy content of the excited state while simultaneously making the system more amenable to bimolecular reaction chemistry.

Outlook. There are enormous opportunities for leveraging metal-centered excited states for photoredox catalysis that go beyond their Earth-abundant nature. Inherent selectivity was already alluded to: excited-states based on Co(III), for example, will be preferentially oxidative in nature whereas those based on isoelectronic Fe(II) complexes will be reductive due to an inability to form a Fe(I)-based photoproduct. Another as yet untapped opportunity exists due to the fact that a substrate must interact with the metal center directly to undergo metal-based reactivity. This implies that significant stereochemical control – including enantioselectivity – through judicious ligand design is endemic to reactions associated with metal-centered excited states to a degree that would be more difficult to achieve with other types of photocatalysts. Given all this, we believe that the possibilities associated with the use of Earth-abundant metals for photoredox catalysis are just beginning to be explored.

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