# CONTROLLING ELECTRON TRANSFER PHOTOREACTIVITY OF RUTHENIUM POLYPYRIDYL COMPOUNDS AT THE SEMICONDUCTOR INTERFACE AND IN SOLUTION

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## ABSTRACT

Evan E. Beauvilliers: Controlling Electron-Transfer Photoreactivity of Ruthenium Polypyridyl Compounds at the Semiconductor Interface and in Solution (Under the direction of Gerald J. Meyer)

The herein described work is motivated by the need to develop renewable energy sources. Given the magnitude of the growing global energy demand, solar energy will undoubtedly comprise a significant component of future renewable energy generation, necessitating the development of cheaper, more efficient solar technologies. Towards this end, this work describes the study of electron transfer reactions relevant to dye-sensitized solar cells (DSSCs).

Chapters 2 & 3 focus on electron transfer reactions at the semiconductor interface. Chapter 2 presents the study and simulation of intra- and intermolecular electron transfer reactions that may be useful for transporting charges to catalytic reaction centers for fuel production or for the design of new types of solid state DSSCs utilizing such charge transport mechanisms for sensitizer regeneration. Chapter 3 describes work in developing new types of sensitizer-semiconductor linkages to improve interfacial electron transfer kinetics, which is of critical importance for improving device efficiency. A new sensitizer is presented that has improved interfacial kinetics relative to a structurally similar compound bearing one of the "standard" semiconductor linkages.

The remaining chapters of this work study and utilize secondary coordination sphere interactions to manipulate the excited-state reactivity of molecular sensitizers. In Chapter 4, an iodide binding pocket is utilized to ion-pair an iodide ion with an excited state, and it is shown that the ion-paired iodide does not quench this excited state, but rather this excited state is quenched by a second iodide in solution. Such a mechanism may be useful in trying to access a concerted mechanism for iodide oxidation and I-I bond formation. Chapter 5 presents the study of Lewis acid-base interaction between carboxylates on sensitizers and metal cations in acetonitrile solutions. These interactions are shown to tune the photophysical properties of the sensitizers in a predictable way, and are furthermore shown to mediate excited-state electron transfer between sensitizers that do not undergo electron transfer in the absence of the cations.

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#### **1. Introduction**

### 1.1 Solar Energy Conversion & the Dye Sensitized Solar Cell

Meeting the increasing global demand for energy is one of the defining challenges of our time. The current global power consumption has been estimated at about 14 terrawatts (TW) by the International Energy Agency.<sup>1</sup> This is expected to increase by as much as 5 TW by 2030. What technologies we choose to implement to satisfy this increase will have profound consequences for the environment, human health, and the global economy.

In recent years, it has become widely recognized that human energy consumption, particularly the combustion of fossil fuels, has led to an increase in the average global temperature as a result of atmospheric greenhouse gases.<sup>2–5</sup> Higher global temperatures have been associated with more frequent and more violent major weather events, e.g. hurricanes, and lead to the melting of polar ice and consequently rising sea levels. This anthropogenic climate change has already been implicated in the extinction of at least one species and the loss of small islands and low-lying (previously) human inhabited lands.<sup>6,7</sup> Higher CO<sub>2</sub> concentrations also lead to ocean acidification, which has been implicated in the decline of many ocean species, most visibly corals.<sup>8</sup>

In order to meet the increasing global energy demand without causing catastrophic environmental damage, a paradigm shift in how energy is produced will be necessary, and is to some extent already underway. Environmentally benign energy production is not new. Hydroelectric, geothermal, wind, and solar electricity generation technologies have been utilized for decades. However, each has limitations that have prevented wide-spread adoption as primary electricity sources. Hydroelectric dams and geothermal power are geographically restricted by the availability of suitable locations. In recent years, wind and solar have seen a significant increase in demand. However, adoption of wind power has been stymied by aesthetic and noise concerns, and solar power remains cost-restrictive. Nuclear power also represents a reasonable source of "green" power, but growing concerns about nuclear waste and the potential for radiation leaks has caused a dramatic decrease in public support.

It is likely that the "solution" to the green power challenge will contain a mixture of energy sources, but solar stands out for several reasons. The first and foremost is the availability of solar energy. The average amount of solar irradiation reaching the Earth's surface is ~89,000 TW, or approximately 6,000 times the power required to meet current energy demands.<sup>9</sup> This means that a 20% efficient solar technology would require ~425,000 square kilometers of land area, roughly the size of California, to provide the total global energy demand. While this seems daunting, this is only about double the area currently covered by paved roadways. Furthermore, solar technologies with greater than 40% efficiencies have been developed, which could decrease this land area requirement.<sup>10</sup> Unlike fossil fuel burning power plants, solar energy generation can be achieved with approximately the same efficiency by many small installations (e.g. rooftop panels) as by large installations. However, while implementation on such a large scale is possible, it will necessarily be associated with considerable cost. As such, one of the primary challenges of solar technologies is to reduce the price of materials.

Towards this end, one potentially low-cost photovoltaic technology is the dye-sensitized solar cell (DSSC). The original idea of this device was to achieve solar electricity generation with a lower cost semiconductor than the high-purity silicon commonly used in current solar cells, which requires large amounts of energy to produce. One obvious target material is titanium

dioxide (TiO<sub>2</sub>). This wide band-gap semiconductor is produced in high purity on a massive scale as a white pigment and abrasive. However, being white, it does not absorb any visible light and is therefore not suitable by itself for solar energy conversion. To circumvent this, dye molecules called sensitizers were bound to the TiO<sub>2</sub> to absorb sunlight. The greatest leap forward in the development of DSSCs came in the 1991 report by Brian O'Regan and Michael Gratzel, that utilized mesoporous nanocrystalline TiO<sub>2</sub> thin films to increase light absorption by a factor of ~1,000 relative to a planar interface.

**Figure 1.1** shows the principles of DSSC operation. While all of the processes discussed below occur simultaneously under solar illumination, they are discussed below in sequence. First, a photon is absorbed by the sensitizer (1). The excited sensitizer then injects an electron into the  $TiO_2$  (2). The injected electron diffuses to the external circuit where it can perform useful work (3). The electron is then collected at a counter-electrode by a redox mediator, or "redox shuttle," (4), which reduces the sensitizer back to its original state (5). As such, a photon has been converted to electrical power, but no net chemistry has been performed. Regeneration of the sensitizer by the redox mediator and excited-state electron injection will be discussed further in sections below. The deleterious processes marked in red in **Figure 1.1**, back electron transfer, BET, and charge recombination, CR, are also discussed. It should be noted that the mesoporous  $TiO_2$  network is highly disordered, while for simplicity it is shown in **Figure 1.1** as a highly ordered array.



**Figure 1.1** Schematic representation of electron transfer processes in a dye-sensitized solar cell with a sensitizer, **S**, and redox mediator, **M**. Favorable electron transport processes are indicated by solid blue arrows. Deleterious electron transport processes are indicated by dashed red arrows. The left image is a cartoon representation of sensitizers (red dots) anchored to a mesoporous network of  $TiO_2$  nanocrystallites (gray spheres).

Each component of a DSSC must be optimized for its role, including matching its properties to each of the other components with which it interacts. For example, it is desirable to use a sensitizer that absorbs light throughout solar spectrum so that most solar photons are utilized. However, the sensitizer must simultaneously be a sufficiently strong photo-reductant to inject an electron into the semiconductor and a sufficient oxidant to be regenerated by the redox mediator. This places a lower limit on the photon energy that the sensitizer can absorb.

The maximum power that can be abstracted from the solar cell is the product of the voltage and the current. To a first approximation, the point where the maximum power is abstracted can be approximated by integrating the solar spectrum and multiplying by the energy of the lowest energy photon absorbed. Including corrections for various energy loss mechanisms, such an analysis gives the historical Shockley-Queisser limit, indicating that the optimum

efficiency for this type of solar cell is ~34% and occurs when the lowest energy photon absorbed is ~925 nm (1.34 eV).<sup>11,12</sup>

For all of the work described herein, and for much of the historical study of DSSCs, the sensitizers of choice are analogues of tris-(2,2'-bipyridine)-ruthenium(II), commonly abbreviated  $[Ru(bpy)_3]^{2+}$ , **Figure 1.2**. Such sensitizers have tunable absorption across the solar spectrum due to the presence of metal-to-ligand charge transfer (MLCT) transitions. There exists a great wealth of pre-existing knowledge of these MLCT excited states, rendering them uniquely suited for fundamental studies of DSSCs.



**Figure 1.2**. Structure of substituted  $[Ru(bpy)_3]^{2+}$ -type compounds. For  $[Ru(bpy)_3]^{2+}$ ,  $R_1 = R_2 = H$ . Note that the overall charge of the compound is dependent on the identities of  $R_1$  and  $R_2$ .

Upon light excitation of a ruthenium polypyridyl compound, an electron is transferred from the Ru center to one of the bpy ligands. The heavy Ru atom induces rapid intersystem crossing to a formally triplet MLCT state with a lifetime on the order of 1  $\mu$ s. In the absence of a quenching process, these excited states are emissive, with large Stokes shifts (> 150 nm) and quantum yields on the order of 0.01 – 0.10. The Ru center is redox active with a Ru(III/II)

reduction potential of around +1.5 V vs NHE. The bpy ligands can be reduced with the first ligand reduction potential around -1.1 V vs NHE.<sup>13</sup> Both the photophysical and electrochemical properties of these compounds can be significantly affected by substitutions on the bpy ligands. For example, for DSSC applications and in some of the studies described here, one ligand will have anchoring groups for binding to  $TiO_2$  (e.g.  $R_1 = COOH$  in **Figure 1.2**), while the other ligands will bear groups of various function, such as tuning reduction potentials or improving solubility.

Just as the sensitizer must be a strong enough photo-reductant to inject an electron into the semiconductor, the redox mediator must be a sufficiently potent reductant to reduce the oxidized sensitizer prior to back electron transfer. This can require tuning molecular-scale interactions between the mediator and sensitizer. The mediator must also be able to accept electrons from the counter-electrode, though this is not generally considered a limiting factor in device efficiency. The most commonly utilized mediator is the iodide/triiodide ( $\Gamma/I_3$ ) redox couple, which is described in Section 1.3 below.

A significant portion of this dissertation research is centered around Lewis acid-base interactions with ions in solution. As such, some discussion of the relevant DSSCs literature is warranted. A well-studied example is the influence Lewis-acidic cations present in the electrolyte have on the acceptor states of the  $TiO_2$  semiconductor films. The presence of Lewis-acidic cations enhances excited-state electron injection by a proposed mechanism in which Lewis acid-base adducts formed at the  $TiO_2$  interface induce a positive shift in the  $TiO_2$  acceptor states, rendering them easier to reduce.<sup>14</sup> Interestingly, the presence of Lewis bases in the electrolyte, such as pyridines, can similarly shift the  $TiO_2$  acceptor states, but in the opposite direction, which can increase the cells photovoltage.<sup>15</sup> A recently discovered role of cations has been

termed "charge screening."<sup>16</sup> Electron injection into  $TiO_2$  creates an electric field that induces a spectral shift in the ground state absorbance spectrum of the sensitizer, similar to that observed in Stark spectroscopy. Cations in the electrolyte respond to this electric field by diffusing towards the surface, which can reduce the electric field experienced by the sensitizers. There is now some evidence that screening influences charge recombination (CR, Figure 1.1).<sup>17</sup>

Besides serving as counter-ions for many sensitizers and for Lewis acid additives, anions play a prominent role in these devices primarily as the iodide/triiodide redox mediator. While the chemistry of iodide in these cells will be elaborated below, it is worth noting that these species are also ionic, and so will also be influenced by electric fields. The charge of iodide species provides a handle by which interactions with sensitizers may be tuned, as seen in Chapter 4.

### **1.2 Electron Transfer at the Semiconductor Interface**

As described above, following light absorption, a sensitizer can inject an electron into  $TiO_2$ . The factors that control the rate and efficiency of excited state injection are now understood in considerable detail. Many MLCT excited states inject electrons into  $TiO_2$  on the <50 ps timescale.<sup>18–21</sup> The efficiency of this process can be controlled experimentally through the sensitizer- $TiO_2$  electronic coupling. The influence of coupling becomes increasingly important as the sensitizer moves further from the surface. The use of long organic bridges that separate the sensitizer from the surface has provided a direct means by which the electronic coupling can be tuned. Quantitative injection is still observed in cases where the Ru center is quite distant from the surface and coupled through a conjugated or insulating bridge.<sup>22,23</sup> The rate constant for injection decreased as the length of the bridge unit increased, but injection remained in the <1 ns regime.

The energetic overlap between the TiO<sub>2</sub> acceptor states and the sensitizer excited-state reduction potential can be changed in at least three ways: 1) The excited state reduction potential of the sensitizer can be changed through synthetic modification; 2) the acceptor states in TiO<sub>2</sub> can be tuned through the introduction of Lewis acids/bases; and 3) these acceptor states can be tuned with an external bias. Generally, stronger photo-reductants inject more efficiently than structurally similar but weaker photo-reductants.<sup>24</sup> The introduction of Lewis acidic cations shifts the acceptor states to higher potentials, increasing the driving force and improving injection efficiency, while Lewis bases such as pyridines have the opposite effect.<sup>14,15</sup> Filling the acceptor states of TiO<sub>2</sub> with an external bias effectively decreases the maximum potential of available acceptor states, leading to less efficient injection.<sup>25</sup> While it is generally desirable to increase electron injection efficiency towards unity, doing so through tuning the TiO<sub>2</sub> acceptor states may also decrease the cell photo-voltage and hence the overall cell efficiency.

As indicated in **Figure 1.1**, injection is not the only electron transfer process that can occur at the semiconductor interface. There are also two deleterious processes: back electron transfer and recombination. The former refers to the photo-injected electron in TiO<sub>2</sub> recombining with the oxidized sensitizer before regeneration occurs. In full devices, the concentration of the mediator is generally quite high ( $\geq 0.5 \text{ M } \Gamma$ ), which was originally believed to mean that regeneration would outcompete back electron transfer, which generally occurs on the millisecond timescale.<sup>26</sup> However, at mediator concentrations used for spectroscopic studies, and in devices under operating conditions, it is now understood that recombination must be considered as it may compete with regeneration.<sup>27,28</sup> Back electron transfer should be minimized to optimize DSSC performance, and balancing this process with efficient injection is one focus of Chapter 3.

Charge recombination and back electron transfer kinetics do not obey a first-order kinetic model. This has been attributed to a distribution of  $TiO_2$  acceptor states<sup>29</sup> and/or a distribution of sensitizer orientations on the  $TiO_2$  surface. The function used in this dissertation to model such kinetic data is the Kolrausch-Williams-Watts model (KWW), sometimes called a stretched exponential, Equation 1.01:<sup>30,31</sup>

$$\Delta A_{t} = \Delta A_{0} e^{-(k_{KWW}t)^{\beta}}$$
(1.01)

where  $\Delta A_t$  is the change in absorbance at a given time, t,  $\Delta A_0$  is the initial absorbance change,  $k_{KWW}$  is a rate constant, and  $\beta$  is a stretching factor between 0 and 1. Note that at  $\beta = 1$ , the function simplifies to a single-exponential.

While a thorough discussion of the KWW model can be found elsewhere,<sup>32</sup> some discussion is warranted here. The  $\beta$  term is related to an underlying asymmetric distribution of rate constants. The k<sub>KWW</sub> value therefore does not have the same meaning as, and cannot necessarily be directly compared to, first-order rate constants. An "average" rate constant, k<sub>av</sub>, can be calculated per Equation 1.02:

$$k_{av} = \frac{k_{KWW}\beta}{\Gamma(\frac{1}{\beta})}$$
(1.02)

where  $\Gamma$  represents the gamma function. For comparative studies reported herein,  $\beta$  is held constant, allowing k<sub>KWW</sub> to be compared within a series of experiments.

Charge recombination between the photo-injected electron and an oxidized form of the redox mediator must be minimized to optimize DSSC performance. There has been considerable disagreement in the literature regarding what the primary electron acceptor is when the iodide/triiodide redox mediator is used. The complex equilibrium of iodide species present in the electrolyte of an operational DSSC makes determination of the primary acceptor difficult.<sup>33</sup>

During cell operation,  $\Gamma$ ,  $\Gamma$ ,  $I_2$ ,  $I_2^{-}$ , and  $I_3^{-}$  are all present. With the exception of  $\Gamma$ , any of these might serve as an acceptor of injected electrons. Tri-iodide,  $I_3^{-}$ , is present in the highest concentrations and its reduction is required for DSSC operation, **Figure 1.1**.



Figure 1.3. Redox potentials vs. NHE and equilibrium constants for iodide species in CH<sub>3</sub>CN.<sup>33–36</sup>

However, the one-electron reduction of  $I_3^-$  occurs at greater than -0.35 V vs. NHE, resulting in an unfavorable free energy change for recombination with injected electrons. There is no experimental evidence for recombination to  $I_2^-$  or  $I^{.37}$  Work by O'Regan indicates that  $I_2$  is the primary acceptor, despite its low equilibrium concentration.<sup>38</sup> Since both this process and back electron transfer limit device efficiency, methods for controlling these reactions are essential to DSSC optimization.

There is another electron transfer reaction that occurs at the semiconductor interface in DSSCs, sometimes called "hole-hopping." In this context, hole-hopping refers to the isoenergetic,  $\Delta G^{\circ} = 0$ , transfer of holes by intermolecular electron transfer between sensitizers anchored to the TiO<sub>2</sub> surface. Following photo-induced electron injection into TiO<sub>2</sub>, hole-hopping between sensitizers allows the location of the oxidized sensitizer to change. In fact, when a sensitized TiO<sub>2</sub> thin film is oxidized electrochemically, hole-hopping is required to oxidize the entire film since there are no redox active TiO<sub>2</sub> states to mediate the reaction. This

results in a percolation threshold for complete film oxidation that represents the minimum sensitizer surface coverage required.<sup>39,40</sup> Below this threshold,  $\sim 2/3$  of the maximum surface coverage, most sensitizers are too distant to be oxidized through hole hopping.<sup>40,41</sup> In exotic cases, electron hopping can also be studied and is relevant to charge transport as described in Chapter 2 of this dissertation.

#### 1.3 Photo-Oxidation of Iodide

Photo-excitation of the sensitizer in a DSSC leads to injection of an electron into the TiO<sub>2</sub> semiconductor, which leaves the sensitizer in an oxidized state. Before the sensitizer can repeat this process, it must be reduced back to the ground state, or regenerated, by the redox mediator. When the iodide/triiodide redox couple is used, regeneration can occur by two possible pathways, one bimolecular, and one termolecular. In the bimolecular pathway, the oxidized sensitizer is reduced by  $\Gamma$ , generating an iodine atom,  $\Gamma$ , shown in Equation 1.03 for a  $[Ru(bpy)_3]^{2+}$  sensitizer. This  $\Gamma$  then reacts with a second equivalent of  $\Gamma$  to generate the diiodide radical anion,  $I_2^{-}$ , Equation 1.04. Two of the  $I_2^{--}$  radical anions disproportionate to form  $\Gamma$  and  $I_3^{--}$ , Equation 1.05.

$$[\operatorname{Ru}^{\operatorname{III}}(\operatorname{bpy})_3]^{3+} + \Gamma \rightarrow [\operatorname{Ru}^{\operatorname{II}}(\operatorname{bpy})_3]^{2+} + \mathbf{I}^{\bullet}$$
(1.03)

$$\mathbf{I}^{\bullet} + \mathbf{I}^{\bullet} \rightarrow \mathbf{I}_{2}^{\bullet}$$
(1.04)

$$2 I_2 \xrightarrow{\cdot} \rightarrow I + I_3 \xrightarrow{\cdot} (1.05)$$

Equilibrium constants and relevant potentials are shown above in Figure 1.3.

In the termolecular mechanism, electron transfer has been proposed to occur in the same kinetic step as I-I bond formation, Equation 1.06. As shown in **Figure 1.3**, this reaction requires ~300 mV less driving force than the bimolecular reaction. However, termolecular reactions are often kinetically slow due to the statistical frequency of three-way collisions.

$$[Ru^{III}(bpy)_3]^{3+} + 2 \Gamma \rightarrow [Ru^{II}(bpy)_3]^{2+} + I_2^{-}$$
(1.06)

The concerted mechanism was first proposed by Stanbury<sup>42</sup> and Nord<sup>43</sup> based on stopped-flow studies. It was observed that the  $\Gamma$  concentration dependence went from first-order at low  $\Gamma$  concentrations to second-order at higher  $\Gamma$  concentrations. The concerted mechanism was evoked to explain the transition to second-order kinetics, though the concerted formation of  $I_2^{-}$  has never been directly observed. Note that this reaction is followed by the same disproportionation chemistry, Equation 1.05.

Since the termolecular pathway is energetically less demanding, it would be potentially beneficial if DSSCs could access such a concerted mechanism. However, the slow kinetics expected for a termolecular reaction must first be overcome. One strategy is to utilize ion-pairing or other non-covalent interactions in which a single  $\Gamma$  forms an adduct with the sensitizer, Equation 1.07. Since this adduct now acts kinetically as a single molecular entity, reaction with a second equivalent of  $\Gamma$  can now be considered a bimolecular reaction, Equation 1.08 (note that photo-excitation and electron injection are assumed between Equations 1.07 and 1.08).

$$[\operatorname{Ru}^{\mathrm{II}}(\operatorname{bpy})_{3}]^{2+} + I^{-} \rightarrow [\operatorname{Ru}^{\mathrm{II}}(\operatorname{bpy})_{3}, I^{-}]^{+}$$
(1.07)

$$[\operatorname{Ru}^{\operatorname{III}}(\operatorname{bpy})_3, \Gamma]^{2+} + \Gamma \rightarrow [\operatorname{Ru}^{\operatorname{II}}(\operatorname{bpy})_3]^{2+} + I_2^{\bullet}$$
(1.08)

Similar reaction chemistry can occur with the molecular excited state, rather than the oxidized sensitizer. In solution experiments without the TiO<sub>2</sub> semiconductor, photoexcitation of  $[\text{Ru}(\text{bpy})_3]^{2+}$  can lead to  $\Gamma$  oxidation, now called photo-oxidation, Equations 1.09 – 1.11. However, in this case, reduction by  $\Gamma$  does not revert the sensitizer back to the ground state, but rather generates its reduced form, Equation 1.10.

 $[Ru^{II}(bpy)_{3}]^{2+} + h\nu \rightarrow [Ru^{III}(bpy^{-})(bpy)_{2}]^{2+}$ (1.09)

$$[\operatorname{Ru}^{\operatorname{III}}(\operatorname{bpy}^{-})(\operatorname{bpy})_{2}]^{2+} + I^{-} \rightarrow [\operatorname{Ru}^{\operatorname{II}}(\operatorname{bpy}^{-})(\operatorname{bpy})_{2}]^{+} + I^{\bullet}$$
(1.10)

$$[\operatorname{Ru}^{\operatorname{III}}(\operatorname{bpy}^{-})(\operatorname{bpy})_{2}, \Gamma]^{+} + \Gamma \rightarrow [\operatorname{Ru}^{\operatorname{II}}(\operatorname{bpy}^{-})(\operatorname{bpy})_{2}]^{+} + I_{2}^{-}$$
(1.11)

Investigation of photo-oxidation is aided by understanding the reaction driving force. To a first approximation, the Gibbs free energy change for any electron transfer process,  $\Delta G_{eT}$ , is the difference in the reduction potentials of the reacting species.

For electron transfer from I<sup>-</sup> to the oxidized sensitizer, Equation 1.03, the driving force can be estimated by Equation 1.12:

$$\Delta G_{eT} = E^{\circ}(Ru^{II/II}) - E^{\circ}(I^{\bullet/-})$$
(1.12)

where  $E^{\circ}$  is the standard reduction potential for the indicated redox states. In this case, the Ru<sup>III/II</sup> reduction potential can be directly measured and literature values for the I<sup>+/-</sup> reduction potential exist. For the excited state reaction, Equation 1.10, the excited-state reduction potentials were not directly measured but were instead estimated using thermodynamic cycles similar to those proposed by Rehm and Weller,<sup>44</sup> Equation 1.13:

$$E^{\circ}(Ru^{III}*^{II}) = E^{\circ}(bpy^{0-}) + \Delta G_{ES}$$
(1.13)

where  $E^{\circ}(Ru^{III_{*}/II})$  is the Ru centered excited state reduction potential,  $E^{\circ}(bpy^{0/-})$  is the ligand centered ground state reduction potential, and  $\Delta G_{ES}$  is the free energy stored in the excited state.<sup>45</sup> It should be noted that the reduction potentials are in units of voltage, while Gibbs free energies are in units of energy. Using V and eV respectively allows a one-to-one comparison for the one electron processes being discussed. The first approximation of the driving force for the excited state reaction therefore becomes Equation 1.14.

$$\Delta G_{eT} = E^{\circ}(bpy^{0/-}) + \Delta G_{ES} - E^{\circ}(I^{-/-})$$
(1.14)

There are at least two corrections to  $\Delta G_{eT}$  called "work terms." One term results from a change in the donor and acceptor geometry accompanying electron transfer and is most relevant to covalently linked molecules.<sup>46</sup> The second work term, here called the "coulombic work term,"

is the change in the coulombic potential energy during electron transfer.<sup>46</sup> This can be conceptually understood if one considers the present case of electron transfer from  $\Gamma$  to  $[Ru(bpy)_3]^{2+}$ . Prior to electron transfer, a coulombic attraction between the negatively charged  $\Gamma$  and positively charged  $[Ru(bpy)_3]^{2+}$  exists with an associated coulombic potential energy. After electron transfer, the neutral iodine atom product is no longer charged and has no coulombic attraction to the  $[Ru(bpy)_3]^+$  product. The lost coulombic potential energy is therefore part of the driving force for the electron transfer. The coulombic potential energy is determined by Coulomb's Law, and the change in this energy is the coulombic work term,  $\Delta G_w$ , Equation 1.15:<sup>46</sup>

$$\Delta G_{\rm w} = -\frac{k_{\rm e}}{\epsilon r} \Delta (Z_+ Z_-) \tag{1.15}$$

$$\Delta G_{eT} = E^{\circ}(bpy^{0/-}) + \Delta G_{ES} - E^{\circ}(\mathbf{I}^{+/-}) + \Delta G_{w}$$
(1.16)

where  $k_e$  is Coulomb's constant,  $\varepsilon$  is the relative permittivity of the solvent, r is the donoracceptor distance, and  $Z_+Z_-$  is the product of the donor and acceptor charges. The full estimation of  $\Delta G_{eT}$  is therefore given by Equation 1.16. It can be seen from this expression that for any system in which the product of charges becomes more positive, e.g. for a negatively charged donor and positively charge acceptor,  $\Delta G_w$  makes the reaction more favorable.

A simple calculation of  $\Delta G_w$  can be performed in which the donor and acceptor are considered to be point charges at their centers of mass. However, a more thorough analysis involves summing the work term over every atom of the donor and acceptor. Such an analysis requires the use of theoretical calculations, specifically Natural Bond Orbital analysis<sup>47,48</sup> to determine the partial charges (and optimized positions) of all atoms in the donor and acceptor. In the case of  $\Gamma$ , only the acceptor requires such a calculation, and this allows  $\Delta G_w$  to be readily calculated for any desired position of  $\Gamma$ . The study of the photo-oxidation of iodide including calculations of the coulombic work terms is the focus of Chapter 4.

### 1.4 The Secondary Coordination Sphere

Generally, the primary coordination sphere of a redox active center is defined as any ligand directly coordinated to the center. The "classical" definition of the secondary coordination sphere is any species directly coordinated to the primary coordination sphere. In the present work, we will only be considering coordination of redox inactive metals to the primary coordination sphere, and as such, the classical definition is sufficient. However, a more inclusive definition of the secondary coordination sphere proposed by Harry Gray should be noted:<sup>49</sup> "…those groups that in any way influence the orientation and/or electronic properties of ligands directly coordinated to a metal center." This definition is particularly useful for metalloproteins in which reactivity and selectivity is controlled at least in part through steric control of geometry and redox properties are tuned by various weak interactions with amino acids.

The redox properties of metal centers are generally tuned through synthetic modification of the primary coordination sphere, but they can also be significantly influenced by the secondary coordination sphere. Two examples that fit readily into the classical definition of the secondary coordination sphere are the formation of Lewis acid-base adducts with a carbonyl<sup>50</sup> or pyridyl nitrogen<sup>51</sup> of a ligand with a boronic acid to tune the potential of a metal center. Other examples include the incorporation of crown ethers which can bind Lewis acidic cations, perturbing the reduction potential of a nearby metal center.<sup>52</sup>

Secondary coordination effects can influence the reactivity of metal centers in other ways as well. The incorporation of hydrogen bond donors into ligand architecture can aid in substrate binding.<sup>53–55</sup> The use of hemilabile ligands that grant access to catalytic sites upon binding of

Lewis acids also allows reactivity to be tuned.<sup>56</sup> Proteins make prominent use of secondary coordination sphere effects, including the highly studied oxygen evolving complex (OEC) of photosystem II. In the OEC, the presence of a redox-inactive calcium ion helps maintain the cubic structure. However, replacement of this ion with other Lewis acids, notably strontium, can maintain the structure, but results in considerable loss of activity, indicating that the calcium ion is also responsible for tuning the reduction potentials of the nearby manganese centers.<sup>57,58</sup> In many proteins, amino acids can serve as donors or acceptors of protons in proton coupled electron transfer reactions. The protein scaffold can also hold reaction centers in geometries between those optimal for different oxidation states, thereby lowering the previously mentioned reorganization energy for electron transfer to/from the center.<sup>49</sup>

In the context of  $[Ru(bpy)_3]^{2^+}$ -type compounds, there has been little intentional use of secondary coordination sphere effects to tune potentials or reactivity. Of particular interest for this thesis is the use of secondary coordination sphere effects to tune the photo-reactivity of these compounds. In fact, while the use of secondary coordination sphere effects is widely recognized and used in the development of many catalyst systems, surprisingly little has been done to incorporate these effects into excited state chemistry, e.g. photo-catalysis. However, it cannot be stated that these effects have never been studied, though perhaps not explicitly, as it could readily be argued that the interaction of sensitizers with TiO<sub>2</sub> or other substrates is a secondary coordination sphere interaction. Furthermore,  $[Ru(bpy)_3]^{2^+}$ -type compounds have been used in the development of photoluminescent ion sensors,<sup>59,60</sup> which is based on excited-state secondary coordination sphere interactions. Chapters 5 reports on secondary coordination sphere effects on the excited states of  $[Ru(bpy)_3]^{2^+}$ -type compounds.

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# 2. Intramolecular- and Lateral Intermolecular-Hole Transfer at the Sensitized TiO2 Interface<sup>1</sup>

## **2.1 Introduction**

Molecules with two or more redox-active groups have provided insights into interfacial electron transfer reactions at semiconductor interfaces that could not have been obtained from molecules with a single redox-active group.<sup>2–9</sup> A relatively common motif used for solar energy conversion in dye-sensitized solar cells is shown generically in Scheme 2.1. A sensitizing dye molecule S absorbs a photon to create an excited state that initiates two charge transfer reactions: (1) electron transfer to a TiO<sub>2</sub> nanocrystallite, and (2) intramolecular hole transfer to a covalently linked donor.<sup>10</sup> The net result is an interfacial charge-separated state comprising an injected electron and an oxidized donor. Here we report a study of 10 electron donor–acceptor compounds where the quantum yield for intramolecular hole transfer was systematically controlled.

Scheme 2.1 Excited-State Electron Injection and Intramolecular Hole Transfer for a Sensitizer–Linker–Donor Compound Anchored on a TiO2 Surface.



Previous studies have shown that intramolecular hole transfer can lead to a dramatic enhancement of the lifetime of the electron that was injected into the semiconductor.<sup>2,5</sup> However, hole transfer comes at the expense of a significant loss in free energy for which the longer

lifetime does not always compensate. It is therefore of interest to examine whether the driving force for hole transfer can be reduced without a loss in lifetime. Under such conditions, an "equilibrium" like that shown in Scheme 2.2 would be expected. This is not a true equilibrium, as recombination of the injected electron with the dye molecule is necessarily thermodynamically favored. Nevertheless, this recombination reaction is known to require milliseconds for completion<sup>10</sup> while intramolecular electron transfer occurs on a sub-nanosecond time scale,<sup>3</sup> so a quasi-equilibrium is expected on intermediate time scales and under steady-state illumination. Quantification of such a redox equilibrium is further complicated by the nonideal behavior of molecules anchored to conductive surfaces.<sup>11,12</sup> To our knowledge, with the one exception described below, no previous studies have characterized such interfacial equilibria and examined how they influence recombination or the free energy stored in the interfacial charge separated state as reported by the open-circuit photovoltage.





In a recent communication,<sup>9</sup> electron transfer studies of three ruthenium terpyridyl compounds with a tridentate cyclometalated ligand conjugated to a triaryl amine donor located at TiO<sub>2</sub> interfaces were reported (Scheme 2.3). Light excitation of these sensitized materials led to rapid excited-state injection with hole transfer yields that could be qualitatively predicted on the basis of the solution reduction potentials. Surprisingly, the charge recombination rates were insensitive to the location of the oxidizing equivalent (i.e., Ru<sup>III</sup> or NAr<sub>3</sub><sup>++</sup>), while the open circuit photovoltages were consistently larger for the compound that had undergone hole transfer. The

coincidence of redox potentials and charge recombination kinetics suggested that the interfacial dipole moment contributed to the measured open circuit photovoltage. Herein, DFT calculations have been employed to quantify the dipole moments before and after light excitation. A total of 10 donor–acceptor compounds with a broad range of  $Ru^{III/II}$  and  $NAr_3^{++/0}$  reduction potentials have been characterized so that the redox equilibrium in Scheme 2.3 could be systematically probed. In situ spectroelectrochemical results showed non-Nernstian behavior that provided new insights into the factors that control nonideality at semiconductor interfaces. In addition, a novel remote excited-state injection from a NAr<sub>3</sub> donor was observed under conditions where the ruthenium center was in the formal +III oxidation state. This excited-state injection was followed by rapid back electron transfer that was fast enough to compete with iodide oxidation. A lateral intermolecular hole hopping process was identified and modeled by Monte Carlo simulations.

Scheme 2.3 Molecular Structures of the Compounds with the Indicated  $Ru^{III/II}$  (blue) and  $NAr_3^{+/0}$  (red) Reduction Potentials



#### **2.2 Experimental**

*Materials*. Acetonitrile (Burdick & Jackson, spectrophotometric grade), methanol (Sigma Aldrich, spectrophotometric grade, >99.9%), tert-butanol (Fisher Scientific), lithium perchlorate

(Aldrich, 99.99%), tetra-n-butylammonium hydroxide (TBAOH) (1 M in methanol, Sigma Aldrich), argon gas (Airgas, >99.998%), oxygen gas (Airgas, industrial grade), titanium(IV) isopropoxide (Sigma-Aldrich, 97%), fluorine-doped SnO<sub>2</sub> (FTO)-coated glass (Hartford Glass Co., Inc., 2.3 mm thick, 15  $\Omega$ /sq), and glass microscope slides (Fisher Scientific, 1 mm thick) were used. The sensitizers in this study (C1–C5 in Scheme 2.3) and their methyl ester derivatives (abbreviated similarly as E1–E5) were available from previous studies.<sup>13</sup>

Sensitized Metal Oxide Thin Films. Mesoporous nanocrystalline TiO<sub>2</sub> thin films were prepared as previously described.13 The films were then immersed in C1–C5 dye solutions in methanol with 1 equiv of TBAOH to help solubility or in E1–E5 dye solutions in 50:50 (v/ v) acetonitrile/tert-butanol. Films were then washed with neat CH<sub>3</sub>CN and diagonally positioned in a standard 1 cm<sup>2</sup> quartz cuvette containing LiClO<sub>4</sub> solution (0.5 M in acetonitrile). The electrolyte solutions were purged with argon gas for at least 30 min prior to experimentation.

*UV–Vis Absorption*. Steady-state UV–vis absorption spectra were obtained on a Varian Cary 50 spectrophotometer. The experiments were performed at room temperature unless mentioned otherwise.

*Transient Absorption Spectroscopy*. Nanosecond transient absorption measurements were obtained with an apparatus similar to that previously described.<sup>14</sup> Samples were photoexcited by a frequencydoubled, Q-switched, pulsed Nd:YAG laser [Quantel USA (formerly Big Sky Laser Technologies) Brilliant B, 532 nm, 5–6 ns full width at half-maximum (fwhm), 1 Hz, ~10 mm in diameter] directed 45° to the film surface. A 150 W xenon arc lamp coupled to a 1/4 m monochromator (Spectral Energy Corp., GM 252) served as the probe beam (Applied Photophysics), which was aligned orthogonally to the excitation light. For detection at sub-100 µs time scales, the lamp was pulsed with 80 V. Detection was achieved with a monochromator

(Spex 1702/04) optically coupled to an R928 photomultiplier tube (Hamamatsu). Transient data were acquired on a computer-interfaced digital oscilloscope (LeCroy 9450, dual 350 MHz). Typically 30–50 laser pulses were averaged at each observation wavelength over the range 380–800 nm for full spectrum generation, and 120–200 laser pulses were averaged for single wavelength measurements. For the low-temperature studies (–45 °C), the sample temperature was maintained to  $\pm 0.1$  °C using a liquid nitrogen cryostat (UniSoku CoolSpek USP-203-B).

Infrared Absorption Spectroscopy. Attenuated total reflectance (ATR) spectra were obtained using a Thermo Scientific Nicolet Nexus 670 spectrophotometer. The measurements were made under a flow of N2 gas, and the spectra were averaged over 128 scans with  $1 \text{ cm}^{-1}$  resolution.

*Electrochemistry*. A potentiostat (BAS model CV-50W) was employed for measurements in a standard three-electrode arrangement with a sensitized TiO<sub>2</sub> thin film deposited on an FTO substrate working electrode, a platinum disk counter electrode, and a Ag/AgCl reference electrode (Bioanalytical Scientific Instruments, Inc.) in acetonitrile containing 0.5 M LiClO<sub>4</sub>. All potentials are reported versus the normal hydrogen electrode (NHE). The ferrocenium/ferrocene (Fc<sup>+</sup>/Fc) half-wave potential was measured at room temperature before and after each experiment and was used as an external standard to calibrate the reference electrode. A conversion constant of -630 mV from NHE to Fc<sup>+</sup>/Fc was used in acetonitrile at 25 °C.<sup>15</sup>

Spectroelectrochemistry. Steady-state UV-vis absorption spectra were recorded in concomitant with bulk electrolysis of a standard three-electrode cell. External biases were applied to the sensitized  $TiO_2$  thin film deposited on an FTO substrate working electrode positioned diagonally in a 1 cm cuvette. Each potential step was held for around 2 to 3 min until the spectrum was invariant with time and the next potential was applied.

*Data Analysis*. Kinetic data fitting was performed in Origin 8.5, and least-squares error minimization was accomplished using the Levenberg–Marquardt iteration method. For the transient absorption spectral modeling and spectroelectrochemical determination of concentrations of redox-active states, a method for the standard addition of known spectra, written in Wolfram Mathematica 8.0, was implemented to realize least-squares error minimization.

Intermolecular Hole Hopping Kinetics Simulation. Monte Carlo simulations to model the lateral hole hopping process for  $C1^+/TiO_2$  at variable laser fluences were performed with Wolfram Mathematica 8.0 and 9.0 on a personal computer (PC). Monte Carlo runs were repeated 1000 times for a single TiO<sub>2</sub> particle simulation (S/N  $\geq$  1000) while 50 runs were implemented for TiO<sub>2</sub> particle arrays (S/N  $\geq$  1350). The TiO<sub>2</sub> particle arrays were set to be 2  $\times$  2  $\times$  2 or 3  $\times$  3  $\times$  3, as larger arrays could not be minimized in a reasonable time period with a PC equipped with 16 GB of RAM.

*DFT Calculations*. The geometry optimizations and properties calculations of the groundstate and oxidized complexes were performed using the ADF2010.01 code.<sup>16</sup> The calculations were carried out using the ZORA Hamiltonian incorporating scalar (sc.) relativistic corrections<sup>17– <sup>20</sup> and the triple- $\zeta$  Slater basis set plus one polarization function (STO-TZP).<sup>20,21</sup> The molecular structures were fully optimized without symmetry constriction via analytical energy gradient techniques as implemented by Versluis and Ziegler,<sup>22</sup> employing nonlocal correction of exchange and correlation (XC) incorporated via the general gradient approximation (GGA) within the BP86 functional, which is composed of the exchange functional of Becke<sup>23</sup> and the correlation functional of Perdew.<sup>24</sup> Solvation effects were modeled by the conductor-like</sup> screening model for real solvents (COSMO)<sup>25,26</sup> using acetonitrile as the solvent for all of the calculations.

### **2.3 Results**



Figure 2.1 Visible absorption spectra of the indicated sensitized thin films immersed in 0.5 M  $LiClO_4/CH_3CN$  solutions.

The carboxylic forms of the compounds anchored to mesoporous anatase TiO<sub>2</sub> thin films with high surface coverages (> $3 \times 10^{-8}$  mol/cm<sup>2</sup>) within reaction times of 1 h in methanol solutions at room temperature. The ground-state absorption of these sensitized thin films immersed in 0.5 M LiClO<sub>4</sub>/CH<sub>3</sub>CN are shown in Figure 2.1a. The methyl ester forms of the compounds (**E1–E5**) displayed much slower kinetics for surface binding, requiring tens of hours to achieve the same surface coverage. The visible absorption spectra of the TiO<sub>2</sub> thin films sensitized with the ester forms of the compounds measured in 0.5 M LiClO<sub>4</sub>/CH<sub>3</sub>CN are shown in Figure 2.1b. In both cases, the visible absorption spectra of the sensitized thin films, abbreviated **C#**/TiO<sub>2</sub> or **E#**/TiO<sub>2</sub>, were very similar to those observed for the compounds in neat acetonitrile, indicating that the molecules anchored to the surface without measurable degradation.



**Figure 2.2** UV–vis–NIR absorption spectra of (a) C1/TiO<sub>2</sub> and (b) C5/TiO<sub>2</sub> measured at variable applied potentials in 0.5 M LiClO<sub>4</sub>/CH<sub>3</sub>CN solutions. The arrows indicate the direction of absorption changes with increased positive applied potential. The insets show the fraction (x) of dye molecules present in the C1/TiO<sub>2</sub> or C5/TiO<sub>2</sub> (black solid squares), C1<sup>+</sup>/TiO<sub>2</sub> or C5<sup>+</sup>/TiO<sub>2</sub> (red solid squares), and C1<sup>2+</sup>/TiO<sub>2</sub> or C5<sup>2+</sup>/TiO<sub>2</sub> (green solid squares) states. Overlaid on the data are fits to a modified Nernst equation.

Cyclic voltammetry of the sensitized thin films showed significant overlap of two redox waves with peak-to-peak splittings greater than 200 mV at a scan rate of 100 mV/s. Therefore, spectroelectrochemistry was carried out to estimate the reduction potentials and assign the redox processes. Figure 2.2 shows representative UV-vis-NIR spectral changes upon oxidation for  $C1/TiO_2$  and  $C5/TiO_2$ . Other data are shown in Figure S2.01 in Appendix 1. Initial oxidation of C1/TiO<sub>2</sub> to C1<sup>+</sup>/TiO<sub>2</sub> showed an absorption increase at 470 nm. Bleaches of the metal-to-ligand charge transfer (MLCT) bands at 433 and 531 nm indicated that oxidation occurred at the ruthenium metal center. The weak absorption band in the red and near-infrared region was attributed to ligand-to-metal charge transfer (LMCT). Further oxidation beyond 1035 mV vs NHE resulted in the loss of the initial isosbestic points and the formation of new ones at 423 and 526 nm. A marked absorption band around 980 nm characteristic of NAr3<sup>++</sup> absorption was observed that served as a probe of hole transfer in transient absorption studies. In the case of  $C5/TiO_2$ , the order of the redox chemistry was reversed. The immediate appearance of a strong absorption band from  $\sim$ 580 nm to the near-infrared region indicated that the first oxidation was NAr<sub>3</sub><sup>-</sup> centered.<sup>2</sup> This was followed by the ruthenium-centered oxidation at more positive

potentials. The standard addition method based on global modeling was used to calculate the fraction of each species present at each applied potential, and representative values are shown as the insets in Figure 2.2. Overlaid on the data are sigmoidal fits, given by  $x = 1/[1 + 10 \exp(\text{Eapp} - \text{E}^\circ)/a \times 59 \text{ mV}]$ , where x is the fraction of molecules present at a given applied potential, a is the nonideality factor, and  $\text{E}^\circ$  is the formal reduction potential of  $\text{Ru}^{\text{III/II}}$  or  $\text{NAr}_3^{\bullet+/0}$ , taken as the applied potential where the concentrations of the oxidized and reduced forms were equal. These data are summarized in Table 2.1.

 Table 2.1 Electrochemical and Photophysical Data for the Sensitized Thin Films

	$E_{1/2}^{\circ}(\operatorname{Ru}^{\operatorname{III/II}})^{a}(a_{1})^{b}$	$E_{1/2}^{\circ}(\mathrm{NAr_3}^{\bullet+/0})^a \ (a_2)^b$	$K_{eq}^{c}$	$\Phi_{ m ht,calc}$	$\Phi_{\mathrm{ht},a}$	$\Phi_{\rm ht,meas}$	$E^\circ_{1/2}(\mathrm{Ru}^{\mathrm{III/II}_{\circledast}})$ (V)	$\Delta G_{\rm es} \; ({\rm eV})^d$	abs max (nm)
<b>C</b> 1	$890 \ (1.45 \pm 0.04)$	$1155 (1.22 \pm 0.04)$	$3.31 \times 10^{-5}$	< 0.01	0.02	< 0.02 <sup>e</sup>	-0.76	1.65	435, 534
C2	945 (1.30 $\pm$ 0.04)	$1150 \ (1.21 \pm 0.04)$	$3.42 \times 10^{-3}$	0.02	0.04	< 0.02 <sup>e</sup>	-0.72	1.65	431, 529
C3	$1010 (1.44 \pm 0.03)$	$1150 (1.24 \pm 0.02)$	$4.30 \times 10^{-3}$	0.06	0.12	0.05 <sup>e</sup>	-0.67	1.68	427, 519
C4	$870 \ (1.33 \pm 0.03)$	960 (1.11 $\pm$ 0.03)	$3.01 \times 10^{-2}$	0.15	0.19	0.25	-0.81	1.68	439, 532
C5	$1060 (1.33 \pm 0.04)$	940 (1.04 $\pm$ 0.03)	$1.07 \times 10^{2}$	0.91	0.88	0.74	-0.62	1.68	431, 520
$^{a}E^{\circ}_{a}$ , given in mV vs NHE b <sub>2</sub> , and a, are the nonideality factors in Equations 2.3 and 2.4 $^{c}K_{a}$ is defined in									

<sup>a</sup>E  $_{1/2}$  given in mV vs NHE. <sup>b</sup> $a_1$  and  $a_2$  are the nonideality factors in Equations 2.3 and 2.4. <sup>c</sup>K<sub>eq</sub> is defined in Equation 2.3. <sup>d</sup> $\Delta G_{es}$  was estimated from the corrected photoluminescence spectrum measured for sensitized ZrO<sub>2</sub>. <sup>e</sup>Estimated from the absorption amplitude at 720–750 nm relative to C5/TiO<sub>2</sub>.

Theoretical characterization of three representative compounds (C2, C4, and C5) by density functional theory (DFT) was completed for the compounds in the ground and oneelectron oxidized states in the fully protonated form and with one of the carboxylic acid groups deprotonated. These calculations were performed to assess the molecular orbitals involved in the electron transfer chemistry and to quantify the change in dipole moment accompanying sensitizer oxidation. The frontier molecular orbitals are shown in Figures S2.02 and S2.03 in Appendix 1. The HOMOs of the oxidized compounds are located over the phenyl rings of the NAr<sub>3</sub> donor, while the LUMOs are composed of orbitals on the terpyridyl rings with contributions from the Ru d orbitals. Shown in Figure 2.3 are the calculated dipole moment vectors for the ground and one-electron-oxidized states of C2, C4, and C5 in the diprotonated form. The calculated dipole moment ( $\mu$ ) components are reported in Table S2.01 in Appendix 1. It was found that the magnitudes of  $\mu$  for the ground states of **C2**, **C4**, and **C5** were 27.4, 28.1, and 30.1 D, and after one-electron oxidation the dipole moments increased to 46.3, 50.8, and 55.5 D, respectively. The 9.2 D larger value for **C5**<sup>+</sup> relative to **C2**<sup>+</sup> resulted from the "hole" in **C5**<sup>+</sup> being localized on the NAr<sub>3</sub> donor group rather than the metal center.



**Figure 2.3** Calculated dipole moment vectors for (a) C2, (b) C4, (c) C5, (d) C2<sup>+</sup>, (e) C4<sup>+</sup>, and (f) C5<sup>+</sup>. The table in each image shows the percentage contributions of ruthenium (Ru), the terpyridine (Tp), and the triarylamine (NAr<sub>3</sub>) to the HOMO and LUMO.

Nanosecond transient absorption spectroscopy was used to quantify the interfacial charge recombination between TiO<sub>2</sub>(e<sup>-</sup>) and the oxidized compound. Figure 2.4 shows absorption difference spectra of the sensitized materials in an acetonitrile electrolyte at 100 ns delay time after 532 nm laser excitation. A single product was observed after laser excitation, consistent with excited-state injection and hole transfer occurring on a sub-10 ns time scale. At early observation times, evidence of a faster component was observed for C5/ TiO<sub>2</sub>, and measurements at -45 °C revealed a ~5 ns rise time for the appearance of the oxidized NAr<sub>3</sub><sup>++</sup> (Figure S2.04 in Appendix 1). This process was within the instrument response time but indicated that hole transfer occurs on a time scale from hundreds of picoseconds to a few nanoseconds. A progressive increase in the absorption band in the red region attributed to NAr<sub>3</sub><sup>++</sup> was observed in going from C1 to C5 or from E1 to E5 that was correlated with the increase in

the value of  $[E^{\circ}(Ru^{III/II}) - E^{\circ}(NAr_{3}^{*+/0})]$ . The kinetics measured for charge recombination between the injected electrons and the oxidized dye molecules were in good agreement with the results for C2<sup>+</sup>/TiO<sub>2</sub>(e<sup>-</sup>), C4<sup>+</sup>/TiO<sub>2</sub>(e<sup>-</sup>), and C5<sup>+</sup>/TiO<sub>2</sub>(e<sup>-</sup>) reported in an earlier communication.<sup>8</sup> In the present work, with an additional two sensitized films, it was again found that within experimental error there was no difference in the charge recombination rate constants, indicating that recombination was insensitive to the identity of the compound (Figure S2.05 in Appendix 1). The influence of surface coverage was also quantified (Figure S2.06 in Appendix 1). Decreasing the surface coverage from the saturation value (6 × 10<sup>-8</sup> mol/cm<sup>2</sup>) to values of ~1/5 saturation resulted in only a very minor change in the charge recombination kinetics.



**Figure 2.4** Absorption difference spectra measured at 100 ns delay time after pulsed 532 nm excitation of (a)  $C1/TiO_2-C5/TiO_2$  and (b)  $E1/TiO_2-E5/TiO_2$  immersed in 0.5 M LiClO<sub>4</sub>/CH<sub>3</sub>CN solution. Regions highlighted in pink are where NAr<sub>3</sub><sup>++</sup> absorbs light strongly.

Addition of sulfuric acid at concentrations as low as  $1.0 \times 10^{-4}$  M to a C4/TiO<sub>2</sub> thin film immersed in 0.5 M LiClO<sub>4</sub>/ CH<sub>3</sub>CN induced a noticeable bathochromic shift and increase in the

MLCT absorption band throughout the visible region (Figure 2.5). The spectral changes were preserved even after the C4/TiO<sub>2</sub> thin film was reimmersed in fresh 0.5 M LiClO<sub>4</sub>/ CH<sub>3</sub>CN. Laser excitation of the acid-exposed C4/TiO<sub>2</sub> thin film in 0.5 M LiClO<sub>4</sub>/CH<sub>3</sub>CN resulted in rapid excited-state electron injection to TiO<sub>2</sub> ( $k_{inj} > 10^8 \text{ s}^{-1}$ ). A significant absorption increase in the red region indicated a larger extent of intramolecular hole transfer relative to that for untreated C4/TiO<sub>2</sub> (Figure 2.5 insets). Spectral modeling indicated that the sulfuric acid treatment increased the hole transfer yield from 0.25 to 0.51. The ATR-FTIR spectra showed that the acid treatment resulted in the appearance of an intense carbonyl stretch at 1712 cm<sup>-1</sup> that was at the same energy as that measured for a C4 powder in the solid state (Figure S2.07 in Appendix 1).



**Figure 2.5** UV–vis absorption spectra of C4/TiO<sub>2</sub> immersed in 0.5 M LiClO<sub>4</sub>/CH<sub>3</sub>CN (black) and immersed in 0.5 M LiClO<sub>4</sub>/ $(1.0 \times 10^{-4} \text{ M H}_2\text{SO}_4/\text{CH}_3\text{CN})$  (red). The upper inset shows the absorption difference spectra measured 45 ns after pulsed 532 nm excitation of C4/TiO<sub>2</sub>, and the lower inset shows the same data for an H<sub>2</sub>SO<sub>4</sub>-treated C4/TiO<sub>2</sub> thin film; overlaid in solid curves are simulations, and regions highlighted in pink are where NAr<sub>3</sub><sup>++</sup> absorbs strongly.

The presence of two stable oxidation states enabled studies where the Ru<sup>II</sup> or NAr<sub>3</sub> group was oxidized prior to light excitation. Because of the proximity of the Ru<sup>III/II</sup> and NAr<sub>3</sub> •<sup>+</sup>/0 reduction potentials for C2–C5, C1 was chosen for the study as the reduction potentials were the most separated. The absorption difference spectra of C1/TiO<sub>2</sub> displayed in Figure 2.6a,c,e were acquired in 0.5 M LiClO<sub>4</sub>/CH<sub>3</sub>CN at applied potentials of 890, 960, and 1035 mV after 532 nm

excitation. At these potentials, the ratios of sensitizers present prior to light excitation were calculated from the spectroelectrochemical data. Spectral modeling based on the measured absorption spectra of C1, C1<sup>+</sup>, and C1<sup>2+</sup> (Figure S2.08 in Appendix 1) and TiO<sub>2</sub>(e<sup>-</sup>) were necessary to simulate the measured spectra. Spectral shifts due to an underlying Stark effect were also evident, and inclusion of the first-derivative absorption spectrum of C1<sup>+</sup>/TiO<sub>2</sub> improved the spectral modeling as has been previously described.<sup>27,28</sup> The fractions of C1, C1<sup>+</sup>, and C1<sup>2+</sup> generated after 532 nm light excitation over the total number of molecules (C1 + C1<sup>+</sup> + C1<sup>2+</sup>) as functions of the delay time were deconvoluted from the time-resolved spectral data and are shown in Figure 2.6b,d,f. Because the concentration of each oxidation state was determined, the injection yield of C1<sup>+</sup>/TiO<sub>2</sub> was calculated to be ~0.1 at a delay time of 20 ns (Figure 2.6b).



Figure 2.6 (a, c, e) Absorption difference spectra measured after pulsed laser excitation ( $\lambda_{ex} = 532 \text{ nm}$ ) of C1/TiO<sub>2</sub> biased to (a) 890 mV vs NHE (C1/TiO<sub>2</sub>:C1<sup>+</sup>/TiO<sub>2</sub> = 50:50), (b) 960 mV vs NHE (C1/TiO<sub>2</sub>:C1<sup>+</sup>/TiO<sub>2</sub> = 15:85), and (c) 1035 mV vs NHE (C1/TiO<sub>2</sub>:C1<sup>+</sup>/TiO<sub>2</sub> = 0:100) at the indicated delay times. Overlaid in solid lines are simulations based on the absorption profiles of C1/TiO<sub>2</sub>, C1<sup>+</sup>/TiO<sub>2</sub>, and C1<sup>2+</sup>/TiO<sub>2</sub> (shown in Figure S2.08 in Appendix 1) and the first-derivative spectrum of C1<sup>+</sup>/TiO<sub>2</sub> using the corresponding fractional concentrations of C1/TiO<sub>2</sub> (black squares), C1<sup>+</sup>/TiO<sub>2</sub> (red circles), and C1<sup>2+</sup>/TiO<sub>2</sub> (green triangles) as functions of time, shown in (b), (d), and (f).

A single wavelength of 507 nm was chosen to monitor the interfacial charge recombination of  $TiO_2(e^-)$  with the oxidized sensitizers (Figure 2.7). The absorption changes as a function of time were satisfactorily described by the Kohlrausch–Williams–Watts (KWW) model, Equation 1.01.<sup>29,30</sup> with a fixed  $\beta_{KWW}$  value of 0.17 under all bias conditions. The rate of

this process was found to be dramatically increased when more oxidized compounds (i.e., more positive potentials) were generated on  $TiO_2$  surfaces.



**Figure 2.7** Absorption changes monitored at 507 nm after pulsed light excitation at the indicated applied potentials ( $\lambda_{ex} = 532 \text{ nm}, 1.4 \text{ mJ/ cm}^2$ ). Overlaid in yellow are the fits to the KWW model ( $\beta_{KWW} = 0.17$ ).

Shown in Figure 2.8 are time-resolved absorption data measured after pulsed laser excitation of a C1/TiO<sub>2</sub> thin film held at an applied bias of +1035 mV vs NHE. At this applied potential, the ruthenium center was oxidized to the formal oxidation state of +III and is therefore better formulated as C1<sup>+</sup>/TiO<sub>2</sub>. Excited-state injection was rapid and efficient ( $k_{inj} > 10^8 \text{ s}^{-1}$  and  $\phi_{inj} = 0.1$ ). The data were recorded at five different irradiances from 0.3 to 1.5 mJ/cm<sup>2</sup>. Two different Monte Carlo simulation methods were used to understand the lateral intermolecular hole hopping process that occurred after interfacial electron transfer to a second dye molecule. In the first method, 536 dye molecules were evenly distributed on a single 15 nm diameter sphere with an average intermolecular distance of 11.5 Å. The second method took 8 or 27 similar spheres and packed them into a 2 × 2 × 2 or a 3 × 3 × 3 cubic array with nearest-neighbor center-to center interparticle distances of 14.8 nm.

In these arrays, dye molecules in the necking regions between spheres were removed. In both methods, after excited-state electron injection, the injected electron quantitatively recombined with a different molecule to yield equal numbers of C1 and  $C12^+$  randomly

positioned on the surface. The random walk of each **C1** or **C1**<sup>2+</sup> was controlled by a pseudorandom number generator either to the six adjacent **C1**<sup>+</sup> sites with equal probability for one sphere or weighted exponentially ( $\beta = 0.35 \text{ Å}^{-1}$ )<sup>31,32</sup> by the distance to every other site. The Ru<sup>III/II</sup> and NAr<sub>3</sub><sup>++/0</sup> hopping rates were assumed to be the same, such that an "effective" hopping rate was calculated. This assumption was supported by the spectroelectrochemical data, which showed that the time required to oxidize 40% of the NAr<sub>3</sub> donors in **C5**/TiO<sub>2</sub> was only about 1.5 times shorter than that required to oxidize the same percentage of Ru<sup>II</sup> sites in **C1**/TiO<sub>2</sub>, implying that the hopping rates were indeed very similar. Hole transfer from **C12**<sup>+</sup> to **C1** to yield two **C1**<sup>+</sup> compounds was assumed to be quantitative when the two were adjacent.

For both methods, the initial number of **C1** and **C1**<sup>2+</sup> molecules created with light was an important parameter that influenced the kinetic behavior for lateral hole hopping. Hole-hopping simulations for cases where one, two, three, four, or five charge separated pairs were created on each TiO<sub>2</sub> particle as well as 27, 54, 81, 108, or 135 pairs for each 27 particle array were performed. The best fits of the simulation data to the experimental data as determined by  $\chi^2$  analyses (Figure S2.12 in Appendix 1) are shown as the solid curves overlaid on the transient data in Figure 2.8. Hopping rates of (160 ns)<sup>-1</sup> for the single particle case and (130 ns)<sup>-1</sup> for the particle arrays were found. Simulations based on the nanoparticle arrays gave rise to a more well-defined minimum and were found to be in better agreement with the experimental data, particularly those data measured on the longer time scales (Figures S2.11 and S2.12 in Appendix 1).



**Figure 2.8** Absorption changes monitored at 540 nm after pulsed light excitation with five irradiances ( $\lambda_{ex} = 532$  nm and 0.3–1.5 mJ/cm2) of C1/ TiO<sub>2</sub> immersed in 0.5 M LiClO<sub>4</sub>/CH<sub>3</sub>CN and biased at 1035 mV vs NHE. Overlaid as solid lines are absorption profiles abstracted from Monte Carlo simulations of (a) 1 and (b) 27 nanoparticles.

### **2.4 Discussion**

The redox and photoinduced electron transfer properties of  $TiO_2$  thin films sensitized with five different cyclometalated ruthenium compounds with conjugated triarylamine donor groups were quantified. The presence of two redox-active portions of these compounds,  $Ru^{II/II}$ and  $NAr_3^{*+/0}$ , provided new insights into interfacial redox reactions that could not have been obtained with a single chromophoric sensitizer. In the discussion below, emphasis is placed on published literature on solar energy conversion that relates to (1) the non-Nernstian nature of the interfacial redox chemistry, (2) intramolecular hole transfer, (3) dipole moment contributions to the stored Gibbs free energy, and (4) lateral intermolecular hole transfer across the  $TiO_2$  surface.

*Non-Nernstian Redox Chemistry*. The Nernst equation predicts that for a one-electron transfer process at room temperature, a 59 mV shift in potential should arise when the ratio of the concentrations of the reduced and oxidized forms are changed by a factor of 10.<sup>33</sup> This relation has been phenomenally successful in fluid electrolyte solutions, particularly when activities are used in place of concentrations.<sup>33</sup> However, non-Nernstian behavior has been noted at chemically modified electrode surfaces and has been quantified by inclusion of a nonideality factor, a, into the Nernst equation.<sup>11,12,34–36</sup>

$$\mathbf{E} = \mathbf{E}^{\circ} + (\mathbf{aRT})/(\mathbf{nF}) \times \ln([\mathbf{Ox}]/[\mathbf{Red}])$$
(2.1)

When a = 1 in Equation 2.1, the Nernst equation results. Nonideality results when a > 1, behavior most often attributed to intermolecular interactions accompanying the redox chemistry as described by Frumkin.<sup>37,38</sup> The availability of two redox active groups in these compounds, namely, the Ru<sup>III/II</sup> center and the NAr<sub>3</sub><sup>\*+/0</sup> group, which is expected to be further from the TiO<sub>2</sub> surface, enabled interrogation of the origin of the nonideality by spectroelectrochemistry.

It was found that in order to achieve a factor of 10 change in concentration, more than 59 mV of applied potential was needed, and hence, nonideality factors had to be introduced to model all of the interfacial electrochemical data. For instance, a nonideality factor a = 1.45 was measured for Ru<sup>III/II</sup> of C1/ TiO<sub>2</sub>, indicating that an ~90 mV potential step was required for a factor of 10 change in concentration. Interestingly, the Ru<sup>III/II</sup> redox reactions for all five compounds revealed higher nonideality factors than those of the covalently linked NAr<sub>3</sub><sup>++/0</sup> groups (1.37 ± 0.08 vs 1.15 ± 0.09, respectively). The Ru<sup>III/II</sup> nonideality factors were larger than those of NAr<sub>3</sub><sup>++/0</sup> regardless of which redox center was oxidized first in the compound. For example, the ruthenium center was oxidized first in C2 and second in C5, yet both displayed nonideality factors of ~1.32. As counterions and solvent reorganize as a consequence of the redox chemistry, the insensitivity of the nonideality factors to the total oxidation state of the molecule implies that such interfacial reorganization was not the cause of the nonideality. It could well have been the case that the second group oxidized displayed the larger nonideality factors due to the higher charge on the molecule, but this was not observed.

The origin of the nonideality is instead consistent with either intermolecular interactions, as proposed by Frumkin,<sup>37,38</sup> or a surface electric field model.<sup>39</sup> The former seems less likely, as space-filling models indicate that the rigid thiophene linker results in similar Ru–Ru and

NAr<sub>3</sub>-NAr<sub>3</sub> intermolecular distances. Therefore, the surface electric field experienced by the redox-active group is most likely the origin of the nonideality, as such fields are known to decrease with distance from the semiconductor surface.<sup>34,39,40</sup> The only previously related literature report was a recent study of a cobalt porphyrin anchored to TiO<sub>2</sub>, where both Co<sup>III/II</sup> and Co<sup>II/I</sup> reactions were quantified.<sup>34</sup> While this chemistry was complicated somewhat by coordination number changes that accompany this redox chemistry, larger nonideality factors were observed for Co<sup>II/I</sup> relative to Co<sup>III/II</sup>. Like the Ru<sup>III/II</sup> and NAr<sub>3</sub><sup>+/0</sup> redox chemistry reported herein, the  $Co^{III/II}$  redox potentials occurred within the forbidden band gap of  $TiO_2$  and hence required a percolation pathway from the transparent conductive substrate to the molecules (see Intermolecular Hole Hopping below), while the direct reduction of TiO<sub>2</sub> accompanied the conversion of  $Co^{II}$  to  $Co^{I}$ . Electrons injected into  $TiO_2$  produce a large electric field, E = 3 MV/cm, that has been observed by electroabsorption spectroscopy (i.e., Stark spectroscopy) and reported to be distance-dependent.<sup>27,40-42</sup> Hence, the enhanced nonideality factors reported for Co<sup>II/I</sup> redox chemistry were also attributed to a surface electric field, consistent with the conclusions drawn here.

The appearance of nonideal redox chemistry raises the issue of what the true reduction potentials of the surface-anchored compounds are. This question is particularly relevant to operational solar cells when an electric field mechanism for nonideality is operative, as the reduction potentials would no longer be fixed values and would instead change with the solar flux. For the purposes of this study, the formal reduction potential was taken as the potential where the equilibrium concentrations of the oxidized and reduced forms were equal, with the understanding that these potentials likely do shift to more negative values with the  $TiO_2$  quasi-Fermi level under solar illumination. Comparisons of these "dark" potentials with those measured for the free compounds in fluid electrolytes were difficult because the carboxylic acid forms of the compounds were nearly insoluble in CH<sub>3</sub>CN. However, the ester derivatives were soluble, and the NAr<sub>3</sub><sup>\*+/0</sup> reduction potentials measured were in good agreement with the interfacial values. In contrast, the Ru<sup>III/II</sup> potentials were generally 70–90 mV more positive than those measured at the TiO<sub>2</sub> interface. This shift is consistent with an inductive effect where the electron-donating carboxylate binding groups yield less positive Ru<sup>III/II</sup> potentials than do the electron-withdrawing ester groups. Thus, the formal reduction potentials do not appear to be significantly altered upon surface binding once the change from carboxylic acid (or ester) to carboxylate that accompanies surface binding is taken into account. Nevertheless, the nonideality of the molecular redox chemistry at the TiO<sub>2</sub> interface perturbs the equilibrium for intramolecular hole transfer in a quantifiable manner as described below.

Intramolecular Hole Transfer. It was of interest to calculate the extent of hole transfer from the oxidized ruthenium center to the covalently linked triarylamine moiety on the basis of the spectroelectrochemical data, as these values can be compared to those measured experimentally after pulsed laser excitation. To account for the nonidealities and to be consistent with the spectroelectrochemical results, the Ru<sup>III/II</sup> and NAr<sub>3</sub><sup>\*+/0</sup> redox reactions were considered to be independent of each other even though these moieties were covalently linked (Equation 2.2).<sup>43</sup> The equilibrium constants and hole transfer yields were calculated with Equations 2.3 and 2.4, respectively. The hole transfer yields without and with the inclusion of nonideality factors ( $\Phi_{ht,calc}$  and  $\Phi_{ht,a}$ , respectively) were calculated, where a1 and a2 represent the nonideality factors for Ru<sup>III/II</sup> and NAr<sub>3</sub><sup>\*+/0</sup>, respectively. The results are summarized in Table 2.1.

$$Ru^{III} + NAr_3 \rightleftharpoons Ru^{II} + NAr_3^{*+}$$
(2.2)

$$K_{eq} = \frac{[Ru^{II}]^{a_1} [NAr_3^{\bullet+}]^{a_2}}{[Ru^{III}]^{a_1} [NAr_3^{\bullet}]^{a_2}}$$
(2.3)

$$\Phi_{\rm ht,calc} = \frac{[\rm NAr_3^{\bullet+}]}{[\rm NAr_3^{\bullet}] + [\rm NAr_3^{\bullet+}]} = \frac{K_{\rm eq}^{1/(a_1+a_2)}}{1 + K_{\rm eq}^{1/(a_1+a_2)}}$$
(2.4)

The inclusion of nonideality factors in essence broadens the potential range over which  $Ru^{III/II}$  and  $NAr_3^{++/0}$  redox chemistry occurs. This is conveniently depicted through the chemical capacitance as first suggested by Murray (Scheme 2.4).35 Three different scenarios are possible for the hole transfer reaction under study. In the first, the driving force for hole transfer is small and  $K_{eq} \ll 1$ . This is the case for C3/TiO<sub>2</sub> ( $K_{eq}=4.3 \times 10^{-3}$ ), and the inclusion of nonideality factors increases the overlap region and hence the fraction of  $Ru^{III}$  that can oxidize the NAr<sub>3</sub> group (Scheme 2.4a). Hence, nonideality is expected to increase the yield of hole transfer after excited-state injection when  $K_{eq} \ll 1$ . For C3/TiO<sub>2</sub> the magnitude of the effect was about a factor of 2. The second scenario occurs when  $K_{eq}=1$ , where little change in the yield of hole transfer is expected provided that the nonideality factors are similar. The third scenario occurs when the driving force for hole transfer is large and  $K_{eq} \gg 1$ , as was found to be the case for C5/TiO<sub>2</sub> ( $K_{eq}=1.1 \times 102$ ). Here the inclusion of nonideality factors results in a larger fraction of NAr<sub>3</sub> groups that cannot be oxidized by  $Ru^{III}$  (Scheme 2.4b). As a result, the expected hole transfer quantum yield decreases, by about 16% in the case of C5/TiO<sub>2</sub>.





<sup>a</sup>The solid curves represent best fits to the experimental data with the indicated nonideality factors. The dashed curves represent ideal Nernstian behavior. The overlap of the chemical capacitance represents potentials where both triarylamine and ruthenium redox chemistry occurs.

The quantum yields for hole transfer measured after pulsed laser excitation of the sensitized thin films were in better agreement with the calculated values when the nonideality factors were included, particularly for  $C4/TiO_2$  and  $C5/TiO_2$ , which displayed hole transfer yields greater than 0.25. Therefore, as shown through steady-state equilibrium measurements and transient kinetic studies, nonideal redox behavior is detrimental for hole transfer when the Gibbs free energy change for the reaction is favorable. It should be kept in mind that the hole transfer yields were calculated from data measured in the absence of injected electrons while the experimental data were measured after excited-state electron transfer, where the injected electron itself was expected to give rise to nonideal behavior. Had the nonideality resulted from intermolecular interactions (i.e., Frumkin-like behavior), one might anticipate that it would be absent in the photoinduced charge separation studies, where the number of oxidized dye molecules is small, on average less than five per nanocrystallite. Therefore, this suggests that nonidealities need to be taken into account for prediction of hole transfer yields and that the nonideality is likely due to the surface electric field.

The yield for photoinduced intramolecular hole transfer measured experimentally was highly sensitive to the interfacial conditions, as both increased proton concentration and the presence of ester groups resulted in enhanced hole transfer yields. The methyl ester derivatives of the sensitizers were found to anchor to the  $TiO_2$  surface with a pronounced ATRFTIR absorption peak at 1730 cm<sup>-1</sup> indicative of unhydrolyzed methyl ester groups. Enhanced hole transfer yields were measured for thin films sensitized with these compounds relative to the corresponding carboxylic acid derivatives. This can be rationalized by the inductive electronwithdrawing nature of the unhydrolyzed ester groups relative to the electron donating carboxylate groups present on the TiO<sub>2</sub> surface. Indeed, the same behavior was observed after protonation of free carboxylate groups by a dilute H2SO4/CH<sub>3</sub>CN solution. For example, light excitation of acid-treated C4/TiO<sub>2</sub> resulted in a factor of 2 increase in the hole transfer yield. These data show that the hole transfer yield was highly sensitive to environmental conditions such as the interfacial pH.

The Role of Dipole Moments. Charge recombination from TiO<sub>2</sub>(e<sup>-</sup>) to the oxidized comp unds was insensitive to whether the hole was localized on Ru<sup>III</sup> or NAr<sub>3</sub><sup>\*+</sup>. Therefore, for these compounds there was no kinetic advantage gained by hole transfer from Ru to the NAr<sub>3</sub> group. An explanation for this behavior remains unknown, but it may emanate from the conjugated thiophene bridge that links the triarylamine to the cyclometalated ligand, which provides delocalized LUMO with metal d and NAr<sub>3</sub> orbital character for all of the compounds studied. Back electron transfer to the Ru center may hence always occur. This would also be expected to occur when the redox equilibrium shown in Scheme 2.2 is established on the electron transfer time scale: the injected electron reduces Ru<sup>III</sup>, shifting the equilibrium to the left, and hence more Ru<sup>III</sup> is generated. Kinetic evidence that the quasiintramolecular redox equilibrium was established on the time scale before back interfacial electron transfer comes from the fact that the hole transfer rate constant for Ru<sup>III</sup>  $\rightarrow$  NAr<sub>3</sub> occurred on a time scale shorter than k<sub>ht</sub>  $\geq 1 \times 10^8$  s<sup>-1</sup> for all of the sensitized materials while recombination required milliseconds. Regardless of the mechanism, charge recombination of the injected electron with the oxidized sensitizer was remarkably insensitive to the sensitizer employed. At the same time, the open-circuit voltage ( $V_{OC}$ ) measured in the absence of a redox mediator was approximately 100 mV larger for C5/TiO<sub>2</sub>, which displayed the highest quantum yield for hole transfer to the amine donor. This was unexpected, as the spectroelectrochemical data showed that the acceptor states in TiO<sub>2</sub> were insensitive to the identity of the dye molecules present on the surface and hole transfer results in a loss in free energy. Therefore, if anything, hole transfer should have given rise to a smaller V<sub>OC</sub> for C2/TiO<sub>2</sub> than for C5/TiO<sub>2</sub>. In many previous studies, a decrease in the charge recombination rate constant compensated for this loss in free energy, as predicted by the diode equation.<sup>10</sup> However, an ~100 fold diminution of this rate constant would be needed to account for the measured V<sub>OC</sub> values, and this simply was not observed. Other factors such as inefficient sensitizer regeneration,<sup>7,28,44</sup> acid–base chemistry,<sup>45</sup> and/or interfacial dipole moments of the ground-state dyes are also known to influence  $V_{OC}$ .<sup>46-48</sup>

It is asserted that the enhancement in  $V_{OC}$  reported here results from the increased dipole moment that accompanies hole transfer. This assertion comes in part from an elimination of all other possibilities such as the recombination kinetics described above. Furthermore, spectroelectrochemical studies showed that the TiO<sub>2</sub> density of acceptor states was insensitive to the identity of the dye molecule and hence that specific sensitizer effects, such as the protonation state of the dye molecule as reported by Nazeeruddin and co-workers,<sup>45</sup> were not operative in this homologous series of dye molecules. In addition, it has previously been shown that the orientation of molecular dipole moments at the TiO<sub>2</sub> surface influences V<sub>OC</sub> through the electrostatic field generated.<sup>49,50</sup> Dipoles oriented toward the surface increase V<sub>OC</sub> because of the upshift of the quasi-Fermi level of the  $TiO_2$  nanoparticle, while those directed away decrease  $V_{OC}$ .

Before comparing these experimental data to the results of previous studies, it is important to point out a key experimental detail: the open-circuit photovoltage data reported here was measured against a pseudoreference electrode in the absence of redox mediators, while most other literature reports are for an operational solar cell with a redox mediator present, typically  $I/I_3$ . For this reason, previous workers used the inherent dipole of the surface anchored dye molecule, or coadsorbed nonchromophoric dipolar molecules, and attributed the measured Voc to the ground state, that is, the nonilluminated thin film.<sup>46–49</sup> This was reasonable as the steady state concentrations of excited and oxidized sensitizers were thought to be vanishingly small and hence would not contribute to the measured Voc values. In contrast, the data reported here were very sensitive to the concentration of the oxidized dye molecules as no regenerator was present. When the sensitized thin films were illuminated in such a nonregenerative cell, oxidized dye molecules were formed along with injected electrons that raised the TiO<sub>2</sub> quasi-Fermi level toward the vacuum level. These oxidized states had dipole moments that were almost twice as large as those of their ground states, as shown by DFT calculations. In addition, the calculated dipole moments were largest when the hole was predominantly localized on the NAr<sub>3</sub> group. For example,  $Ru^{III} \rightarrow NAr_3$  hole transfer in C5<sup>+</sup>/TiO<sub>2</sub> gave rise to a 9.2 D increase in dipole moment relative to  $C2^+/TiO_2$ , where the hole was predominantly localized on the  $Ru^{III}$  center.

The dipole moment data can be used to calculate the dipole moment-induced electrostatic potential drop ( $\Delta \phi_{dipole}$ ), Equation 2.5.

$$\Delta \phi_{\rm dipole} = \frac{N\Delta(\mu \cos\theta)}{\epsilon\epsilon_0} \tag{2.5}$$

This equation predicts that the Voc should be dependent on the change in the surface dipole moment that accompanies excitedstate injection,  $\Delta(\mu \cos \theta)$ , and the surface coverage of oxidized molecules, N, assuming that the permittivity of the molecular layer  $\varepsilon = 5.48$  At most about 10% of the dye molecules injected electrons at the highest irradiance employed, so N would be  $\sim 7 \times 10^{16}$  molecules/m2. When the full range of tilt angles and dipole moments of different protonation states of the dye molecule were considered (see Table S2.01 in Appendix 1), a  $\Delta \phi_{dipole}$  range of 40–60 mV was calculated to accompany hole transfer, which is in reasonable agreement with the value of 100 mV measured experimentally.

One could rightly argue that the Voc data reported here have little relevance to an operat onal dye-sensitized solar cell, which necessarily contains a redox mediator. With some organic dye molecules, however, compelling evidence was found that inefficient sensitizer regeneration lowers Voc.27 Hence, some fraction of the injected electrons leak back to the oxidized dye molecule under conditions where the number of injected electrons is large. More recently, Wang and co-workers reported clear evidence that this also occurs for highly optimized dye molecules like Ru(dcbH2)(dnb)(NCS)2 (Z907), where dcbH2 is 4,4'-(CO2H)2-2,2'-bipyridine and dnb is 4,4'-dinonylbipyridine.43 In one previous comparative study of donor-acceptor-sensitized thin films where the charge recombination kinetics was correlated with the kinetics for back interfacial electron transfer to the oxidized donor, the enhanced Voc that accompanied hole transfer was measured in the presence and absence of the redox mediator.1 Taken together, these results indicate that one cannot rule out the possibility that dipole moment measurements made without a redox mediator do have some relevance to operational solar cells. In any event, measurements of Voc in the absence of redox mediators are the most useful for fundamental studies of the interfacial dipole moment changes that follow excited-state injection.

Intermolecular Hole Hopping. It has long been known that molecules with formal reduct on potentials that lie within the forbidden band gap, where  $TiO_2$  is expected to be an insulator, can be reversibly oxidized in these mesoporous thin films.<sup>51</sup> The established mechanism is that oxidation is initiated at the transparent conductive oxide (TCO) substrate and proceeds by lateral intermolecular hole hopping throughout the film provided that a percolation threshold has been achieved.<sup>52,53</sup> Recently, lateral hole hopping has also been observed to occur after excited-state injection by time-resolved anisotropy spectroscopic measurements.<sup>32</sup> The sensitized interfaces under study here enabled lateral hole hopping reactions to be induced with light and monitored by transient absorption spectroscopy (Scheme 2.5). Such reactions are important in photoelectrosynthetic cells as they provide a means for translating oxidizing equivalents to a catalyst after excited-state injection.

**Scheme 2.5** Electron Transfer and Hole Hopping Processes Observed after 532 nm Laser Excitation of C1<sup>+</sup>/TiO<sub>2</sub>: (a) Excited-State Electron Injection; (b) Interfacial Charge Recombination; (c) Lateral Intermolecular Hole Hopping



When the Ru<sup>II</sup> center in C1/TiO<sub>2</sub> was electrochemically oxidized to yield C1<sup>+</sup>/TiO<sub>2</sub> (i.e., Ru<sup>III</sup>–NAr<sub>3</sub>), a new visible absorption band centered at 470 nm was observed that was assigned to be an intraligand charge transfer band from the triarylamine donor to the substituted terpyridine ligand (NAr<sub>3</sub>  $\rightarrow$  terpy<sup>\*</sup>). This band is very similar in energy and bandwidth to that

observed for organic D– $\pi$ –A molecules with triarylamine donors.<sup>28</sup> In addition, DFT calculations of the one-electron-oxidized forms of these compounds revealed that the HOMO is largely centered on the NAr<sub>3</sub> group and the LUMO on the terpyridyl ligand (Figure S2.03 in Appendix 1). Light excitation into this band resulted in the immediate appearance of the doubly oxidized sensitizer (i.e., where both Ru and NAr<sub>3</sub> were oxidized), confirming excited-state electron injection into TiO<sub>2</sub> from C1<sup>+</sup> (Scheme 2.5a and Equation 2.6).

$$TiO_2|Ru^{III}-NAr_3 \xrightarrow{h\nu} TiO_2(e^{-})|Ru^{III}-NAr_3^{\bullet+}$$
(2.6)

The interfacial electron injection yield measured by comparative actinometry on a 50 ns time scale was 0.1. It was unclear whether this low yield resulted from rapid back electron transfer or from intramolecular reductive quenching by the proximate Ru<sup>III</sup> center followed by rapid back electron transfer.

Excited-state electron injection was followed by interfacial back electron transfer to a neighboring  $C1^+$  molecule (Equation 2.7).

$$TiO_2(e^{-})|Ru^{III}-NAr_3 \rightarrow TiO_2|Ru^{II}-NAr_3$$
(2.7)

This process was investigated as a function of applied bias, which created different concentrations of singly oxidized **C1**. It was found that charge recombination rates were much larger when oxidized compounds were present. Kinetic modeling did not show a simple relationship between the rate constants abstracted from a KWW analysis and the concentration of the oxidized dye molecules. However, at one extreme where all of the compounds were oxidized, the KWW rate constants were 3 orders of magnitude larger than those under the conditions where no dye molecules had been electrochemically oxidized. The increased charge recombination was due to a higher probability of the injected electron to encounter a  $C1^+/TiO_2$ .

Quantitative interfacial back electron transfer in principle yielded C1/TiO<sub>2</sub> and C1<sup>2+</sup>/TiO<sub>2</sub> in equal concentrations.

Hole transfer from  $C1^{2+}/TiO_2$  to  $C1/TiO_2$  (Equation 2.8) was favored by 270 mV of Gibbs free energy and occurred after lateral intermolecular  $Ru^{III/II}$  and  $NAr_3^{+/0}$  hole hopping across the TiO<sub>2</sub> surface brought the two reactants close to each other.

$$TiO_{2}|Ru^{III}-NAr_{3}^{*+}+TiO_{2}|Ru^{II}-NAr_{3} \rightarrow 2(TiO_{2}|Ru^{III}-NAr_{3})$$
(2.8)

A significant absorption change accompanied this recombination reaction process that could not be adequately described by first- or second-order kinetic models. Instead, the data were fit to a random walk model based on Monte Carlo simulations. Scheme 2.6a shows a representative Monte Carlo simulation of three C1 molecules (small blue spheres) and three doubly oxidized  $C1^{2+}$  molecules (small red spheres) randomly positioned on a 15 nm diameter TiO<sub>2</sub> nanocrystal (large sphere). Time-dependent concentrations were calculated as the intermolecular hopping rate was varied, and the results were compared to experimental data measured at five different excitation irradiances. The simulations agreed with experiment when an effective intermolecular hole hopping rate of  $(160 \text{ ns})^{-1}$  was used. The experimental and simulated data were in best agreement on the microsecond and shorter time scales that represented greater than 70% of the recombination. The poor agreement on longer time scales might arise from cases where interparticle hopping occurred.<sup>54</sup> The necking regions could allow lateral hole hopping from one TiO<sub>2</sub> nanoparticle to another, thus decreasing the recombination rate. To test this hypothesis, an array of eight or 27 particles was used in a similar simulation that allowed for interparticle hopping (Scheme 2.6b). The best fit of the simulation data to the experiment was achieved with an effective hopping rate of  $(130 \text{ ns})^{-1}$ . A  $\chi 2$  error analysis of the respective fits showed significant improvement of the multiparticle simulation over the single-particle simulation, and the residuals revealed that it was the longertime- scale data where the fit to experimental data was most improved (Figure S2.12 in Appendix 1). On average, the hole hopped about 16 nm before encountering a reduced compound. Because of the random nature of the walk, a total distance of  $\sim$ 1800 nm would be reached if the path could be directed in a single direction.

**Scheme 2.6** Monte Carlo Simulations of Lateral Intermolecular Hole Hopping on Spherical TiO<sub>2</sub> Nanocrystallites: (a) Single TiO<sub>2</sub> Particle; (b) Array of 27 TiO<sub>2</sub> Particles<sup>a</sup>



<sup>a</sup>Black dots represent the  $C1^+$  sites that are evenly distributed on the surface. Red spheres are  $C1^{2+}$  and blue spheres are C1. Thirty steps of random walks are shown.

The  $(130 \text{ ns})^{-1}$  hopping rate recovered has relevance to photoelectrosynthetic watersplitting cells where accumulation of oxidizing equivalents at catalytic sites is required.<sup>55–58</sup> In one embodiment of such cells, the hole must hop to an oxidation catalyst after excited-state injection. This hole hopping is kinetically competitive with back electron transfer. At the lowest irradiance conditions studied, and with an average charge recombination rate constant of  $2 \times 105$ s<sup>-1</sup>, a single oxidizing equivalent could circumnavigate a single nanocrystallite once in search of a catalyst before recombination. Unfortunate for this goal was the finding that charge recombination occurred on the same time scale as did hole hopping when every sensitizer had been oxidized by one electron. In this case, back electron transfer and efficient accumulation at a catalyst would not be expected. This finding emphasizes the need to isolate the catalyst from the TiO<sub>2</sub> surface for the realization of efficient photoelectrosynthetic cells.

### **2.5 Conclusions**

The characterization of  $TiO_2$  sensitized to visible light with molecules possessing two redox-active groups has provided new insights into the kinetics and thermodynamics of interfacial electron and hole transfer reactions. The redox chemistry was non-Nernstian, behavior reasonably attributed to the electric field present at the interface, and accounted for the hole transfer yields measured after pulsed laser excitation. The charge recombination kinetics and the density of  $TiO_2$  acceptor states were the same for all of the sensitized materials that were characterized, while the open-circuit photovoltage was largest for the sensitizer that displayed the highest yield for hole transfer, demonstrating the importance of the dipole moment of the oxidized sensitizer. Finally, a novel photoinitiated intermolecular hole transfer process occurred with a hole hopping rate of  $(130 \text{ ns})^{-1}$  that was sufficient to translate the hole a considerable distance from the site of excited-state injection, provided that the concentration of holes was small.

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# 3. Alcohol-Based Sensitizer-Semiconductor Linkages Towards Improved Interfacial Electron Transfer Kinetics

## **3.1 Introduction.**

Modified electrodes in which redox active species have been anchored to the electrode surface have been studied in great detail. Gold-thiol linkages in particular have been used extensively to study electron transfer between the electrodes and surface-bound species,<sup>1</sup> including more recent work studying single-molecule conductivity.<sup>2</sup> Modified electrodes are of interest in solar energy conversion applications as photoanodes and photocathodes for the production of solar electricity and solar fuels.<sup>3–5</sup> In these applications, redox active chromophores are anchored to wide band gap semiconductors where they sensitize the semiconductor to visible light by injecting either holes or electrons into the semiconductor. These electron transfer reactions are essential to the operation of dye-sensitized solar cells (DSSCs).<sup>6</sup>

While considerable work has been done on the fundamental investigation of these reactions, it is of continuing interest to develop new methods for anchoring sensitizers to electrode surfaces to improve device performance and stability. For example, phosphonates have been developed as alternatives to carboxylic acids for aqueous sensitization of metal oxides like TiO<sub>2</sub>.<sup>7</sup> Previous work has studied the use of several other functional groups for surface anchoring including silanes, ethers, amides, esters, and acetylacetonate.<sup>8</sup> However, issues of long term photochemical and electrochemical stability remain.

The greater the sensitizer surface coverage, the more light can be absorbed at a given film thickness, increasing light-to-current efficiency. Light absorption is generally not a limiting factor in state-of-the-art DSSCs. Higher surface coverages would allow thinner semiconductor films to be used that may reduce deleterious back electron transfer reactions and hence optimize DSSC performance.<sup>9</sup>

In the work described herein, the synthesis, surface attachment, and surface stability of a series of four alcohol bearing ruthenium polypyridyl sensitizers of the form  $[Ru(dtb)_2(LL)]^{2+}$ , where dtb is 4,4'-di-*tert*-butyl-2,2'-bipyridine is described and compared to a "standard" sensitizer bearing carboxylic acids, Scheme 3.1. It is shown that systematic changes in the binding group can be directly related to changes in stability and photo-induced electron transfer kinetics. Of particular interest is that the kinetics for interfacial electron transfer were sensitive to the nature of the anchoring group. For example, sensitizer **4** had a greater injection quantum yield, and slower back electron transfer kinetics compared to sensitizer **5**. Unfortunately, none of the sensitizers studied had universally better surface stability than sensitizer **5**, with the more photostable sensitizers suffering from decreased electrochemical stability. While alcohols show promise for semiconductor surface anchoring, further work is necessary to achieve improved performance.

Scheme 3.1 Sensitizers Used in This Study, [Ru(dtb)<sub>2</sub>(LL)](PF<sub>6</sub>)<sub>2</sub>, LL =



## 3.2 Experimental.

*Materials*. All materials were reagent grade or better. Acetonitrile (CH<sub>3</sub>CN, Fisher), chloroform (Fisher), dioxane (Sigma), methanol (Fisher), ammonium hexafluorophosphate (NH<sub>4</sub>PF<sub>6</sub>, Sigma), lithium perchlorate (LiClO4, Sigma), sodium perchlorate hydrate (Sigma), magnesium perchlorate (Sigma), calcium perchlorate tetrahydrate (Sigma), aluminum perchlorate nonahydrate (Sigma), tetrabutylammonium perchlorate (TBAClO<sub>4</sub>, Sigma), 2-amino-2-methyl-1-propanol (Sigma), 2-amino-2-methyl-1,3-propanediol (Sigma), 2-amino-2hydroxymethyl-propane-1,3-diol (Sigma), argon (Airgas,  $\geq$ 99.998%), oxygen (O<sub>2</sub>, Airgas,  $\geq$ 99.998%), and fluorine-doped tin(IV) oxide (FTO; Hartford Glass Co., Inc., 2.3 mm thick, 15  $\Omega/\square$ ) were used as received. 4,4'-dimethylester-2,2'-bipyridine, [Ru(dtb)<sub>2</sub>((HOMe)<sub>2</sub>-bpy)](PF<sub>6</sub>)<sub>2</sub> (**4**), and [Ru(dtb)<sub>2</sub>(dcb)](PF<sub>6</sub>)<sub>2</sub> (**5**) were prepared as previously described.<sup>10-12</sup>

*Synthesis. N*,*N*'-bis(1-hydroxy-2-methylpropan-2-yl)-2,2'-bipyridine-4,4'dicarboxamide (LL1). To 1 g of 4,4'-dimethylester-2,2'-bipyridine was added 5 g of 2-amino-2-methyl-1-propanol. The reactants were mixed and then heated to 150 °C for 10 minutes under microwave irradiation. Addition of water gave a suspension which was filtered on a glass frit then washed with water and chloroform to yield 880 mg (63%) of white powder. <sup>1</sup>H NMR  $\delta$  (d<sub>6</sub>- DMSO): 8.82 (2H, d), 8.69 (2H, s), 8.04 (2H, s), 7.78 (2H, d), 4.89 (2H, t), 3.55 (4H, d), 1.34 (6H, s).

## *N,N'*-bis(1,3-dihydroxy-2-methylpropan-2-yl)-2,2'-bipyridine-4,4'-dicarboxamide

(**LL2**). To 1 g of 4,4'-dimethylester-2,2'-bipyridine was added 5 g of 2-amino-2-methyl-1,3propanediol. The reactants were mixed and then heated to 110 °C for 40 minutes under microwave irradiation. Addition of water gave a suspension which was filtered on a glass frit then washed with water and chloroform to yield 600 mg (40%) of white powder. <sup>1</sup>H NMR  $\delta$  (d<sub>6</sub>-DMSO): 8.83 (2H, d), 8.70 (2H, s), 7.83 (2H, s), 7.78 (2H, d), 4.78 (4H, t), 3.63 (8H, m), 1.30 (6H, s).

#### N,N'-bis(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)-2,2'-bipyridine-4,4'-

dicarboxamide (LL3). To 1 g of 4,4'-dimethylester-2,2'-bipyridine in 25 mL of methanol was added 5 g of 2-amino-2-hydroxymethyl-propane-1,3-diol. The mixture was refluxed overnight. Water was added and the resulting suspension was filtered on a glass frit and washed with water followed by chloroform to yield 960 mg (58%) of a white powder. <sup>1</sup>H NMR  $\delta$  (d<sub>6</sub>-DMSO): 8.95 (2H, d), 8.72 (2H, s), 7.79 (2H, d), 7.69 (2H, s), 4.69 (6H, t), 3.73 (12H, d).

[**Ru**(**dtb**)<sub>2</sub>(**LL1**)](**PF**<sub>6</sub>)<sub>2</sub> (1). Ru(dtb)<sub>2</sub>Cl<sub>2</sub> (100 mg, 0.140 mmol) and LL1 (62 mg, 0.148 mmol) were added to 50 mL of dioxane and refluxed for 24 hrs. Water (20 mL) was added to the reaction mixture which was subsequently filtered on a sintered glass frit. Aqueous NH<sub>4</sub>PF<sub>6</sub> was added to the filtrate, which was subsequently filtered on a sintered glass frit and washed with water to yield 94.8 mg (51 %) of orange powder. <sup>1</sup>H NMR δ (d<sub>6</sub>-DMSO): 9.12 (2H, s), 8.86 (4H, s), 8.14 (2H, s), 7.84 (2H, d), 7.75 (2H, d), 7.56 (6H, m), 7.48 (2H, d), 4.84 (2H, t), 3.54 (4H, s), 1.39 (18H, s), 1.38 (18H, s), 1.34 (12H, s). <sup>13</sup>C NMR δ (CD<sub>3</sub>CN): 164.3, 163.7, 158.4, 157.5, 152.9, 151.8, 144.1, 126.1, 125.6, 122.9, 122.5, 68.7, 57.3, 36.3, 30.4, 23.8. HRMS (ESI-MS)

m/z:  $[M - PF_6]^+$  Calcd for  $C_{56}H_{74}N_8O_4RuPF_6$  1169.451; Found 1169.456,  $[M - 2PF_6]^{2+}$  Calcd for  $C_{56}H_{74}N_8O_4Ru$  512.243; Found 512.244.

[**Ru**(**dtb**)<sub>2</sub>(**LL2**)](**PF**<sub>6</sub>)<sub>2</sub> (2). Ru(dtb)<sub>2</sub>Cl<sub>2</sub> (100 mg, 0.140 mmol) and LL2 (57 mg, 0.148 mmol) were added to 50 mL of dioxane and refluxed for 24 hrs. Water (20 mL) was added to the reaction mixture which was subsequently filtered on a sintered glass frit. Aqueous NH<sub>4</sub>PF<sub>6</sub> was added to the filtrate, which was subsequently filtered on a sintered glass frit and washed with water to yield 91.5 mg (48.5 %) of dark orange powder. <sup>1</sup>H NMR δ (d<sub>6</sub>-DMSO): 9.10 (2H, s), 8.87 (4H, s), 7.95 (2H, s), 7.83 (2H, d), 7.75 (2H, d), 7.56 (6H, m), 7.48 (2H, d), 4.74 (4H, t), 3.65 (8H, m), 1.39 (18H, s), 1.38 (18H, s), 1.30 (6H, s). <sup>13</sup>C NMR δ (CD<sub>3</sub>CN): 164.9, 163.8, 158.5, 157.4, 153.0, 151.8, 143.9, 126.0, 125.6, 123.0, 122.5, 66.0, 60.9, 36.3, 30.4, 19.1. HRMS (ESI-MS) m/z:  $[M - PF_6]^+$  Calcd for C<sub>56</sub>H<sub>74</sub>N<sub>8</sub>O<sub>6</sub>RuPF<sub>6</sub> 1201.441; Found 1201.445,  $[M - 2PF_6]^{2+}$  Calcd for C<sub>56</sub>H<sub>74</sub>N<sub>8</sub>O<sub>6</sub>Ru 528.238; Found 528.239.

[**Ru(dtb)**<sub>2</sub>(**LL3**)](**PF**<sub>6</sub>)<sub>2</sub> (3). Ru(dtb)<sub>2</sub>Cl<sub>2</sub> (166 mg, 0.23 mmol) and LL3 (110 mg, 0.24 mmol) were added to 50 mL of dioxane and refluxed for 24 hrs. Water (20 mL) was added to the reaction mixture which was subsequently filtered on a sintered glass frit. Aqueous NH<sub>4</sub>PF<sub>6</sub> was added to the filtrate, which was subsequently filtered on a sintered glass frit and washed with water to yield a dark brown solid. The crude material was purified by column chromatography on neutral alumina using first 10% methanol in acetonitrile followed by 2/2/1 acetonitrile/methanol/water to yield 143 mg (45%) of dark red-purple powder. <sup>1</sup>H NMR  $\delta$  (d<sub>6</sub>-DMSO): 9.39 (2H, s), 8.86 (4H, s), 7.92 (2H, s), 7.87 (2H, d), 7.79 (2H, d), 7.56 (6H, m), 7.49 (2H, d), 4.65 (6H, t), 3.75 (12H, s), 1.39 (18H, s), 1.38 (18H, s). <sup>13</sup>C NMR  $\delta$  (CD<sub>3</sub>CN): 165.5, 163.8, 158.5, 157.5, 153.0, 151.8, 143.46, 126.2, 125.6, 123.0, 122.5, 64.3, 62.9, 36.3, 30.4.

HRMS (ESI-MS) m/z:  $[M - PF_6]^+$  Calcd for  $C_{56}H_{74}N_8O_8RuPF_6$  1233.431; Found 1233.437,  $[M - 2PF_6]^{2+}$  Calcd for  $C_{56}H_{74}N_8O_8Ru$  544.233; Found 544.235.

*Preparation of TiO*<sub>2</sub> *Thin Films*. Nanocrystalline TiO<sub>2</sub> paste was made by a previously reported sol-gel method.<sup>13</sup> Thin films were prepared by doctor blading this paste onto either glass microscope slides or transparent FTO using scotch tape as a spacer. The films were annealed at 450 °C under a flow of O<sub>2</sub> for 30 min and stored at ~70 °C in a dark oven until use. Sensitized films were prepared by immersing these films into a CH<sub>3</sub>CN solution of the desired sensitizer for 24 hrs, after which the sensitized film was washed with CH<sub>3</sub>CN and stored in neat CH<sub>3</sub>CN and in the dark until use.

*NMR*. NMR spectra were taken on a Bruker Avance III 400 MHz (<sup>1</sup>H) and 600 MHz (<sup>13</sup>C, 150 MHz) spectrometer. All NMR spectra were acquired at room temperature and referenced to the solvent residual peaks.

*ESI-MS*. High resolution electrospray ionization mass spectrometry data were collected with a Thermo LTQ FT hybrid mass spectrometer using a micro-electrospray source at a flow rate of  $3 \mu L/min$ .

UV-Vis Absorption. UV-visible spectra were taken with a Cary 60 spectrometer.

*Photolysis*. Photolysis experiments were performed on  $TiO_2$  thin films sensitized with sensitizers **1-5** by illuminating the slides in a quartz cuvette filled with neat  $CH_3CN$  using a 150 W Cole Palmer Illuminator set at 2/3 of the maximum power. The slide was set at a 45° angle to incident illumination, and the cuvette was sealed with a rubber septum. The UV-visible absorbance spectrum of each sample was taken before illumination and at 60 min increments following illumination up to 6-7 hrs, and after 24 hrs.

*Electrochemistry.* Solution and TiO<sub>2</sub> thin film square wave voltammetry was performed with a Pine WaveNow potentiostat in a three-electrode arrangement. A Pt disk (solution) or the sensitized TiO<sub>2</sub> thin film on FTO (TiO<sub>2</sub>) were used as the working electrode with a Pt disk (solution) or Pt mesh (TiO<sub>2</sub>) counter electrode and a non-aqueous Ag wire pseudo-reference electrode. The reference electrode was calibrated against an external  $Fc^+/Fc^0$  standard (assumed 630 mV vs. NHE).

Overnight electrolysis experiments were performed on an Epsilon Electrochemical Analyzer with the same three electrode arrangement described for  $TiO_2$  thin films above. A potential of ~1.7 V vs. NHE was applied for 960 min followed by 0 V for 10 min. Square wave voltammetry was performed on the sample before and after electrolysis to ensure there was minimal drift in the reference electrode during the experiment. All electrochemical measurements were made in 100 mM TBACIO<sub>4</sub> CH<sub>3</sub>CN solution.

Steady-State Photoluminescence. Steady-state photoluminescence (PL) spectra were taken on a Horiba Fluorolog 3 fluorometer and corrected by calibration with a standard tungstenhalogen lamp. PL quantum yields were measured by the optically dilute method with  $[Ru(bpy)_3][PF_6]_2$  in acetonitrile ( $\Phi = 0.062$ ) as a quantum yield standard.<sup>14</sup> Samples were purged with CH<sub>3</sub>CN saturated Ar for at least 30 min.

*Time-Resolved Photoluminescence*. Time-resolved PL decays were obtained with a nitrogen dye laser with excitation centered at 445 nm. Pulsed light excitation was achieved with a Photon Technology International (PTI) GL-301 dye laser that was pumped by a PTI GL-3300 nitrogen laser. The PL was detected by a Hamamatsu R928 PMT optically coupled to a ScienceTech Model 9010 monochromator terminated into a LeCroy Waverunner LT322 oscilloscope. Samples were purged with CH<sub>3</sub>CN saturated Ar for at least 30 min.

*Transient Absorption*. Nanosecond transient absorption data were acquired with 532 nm laser excitation using a previously described apparatus.<sup>15</sup> Samples were placed at 45° to both the laser pulse and probe lamp in a quartz cuvette containing a 100 mM LiClO<sub>4</sub> CH<sub>3</sub>CN solution. The laser power was adjusted using a polarizer such that the change in absorbance after 5  $\mu$ s was ~ -0.012 for all samples. For TiO<sub>2</sub> back electron transfer kinetics, data were collected at an isosbestic point between the sample in neat CH<sub>3</sub>CN and in 100 mM LiClO<sub>4</sub> using multiple time intervals ranging from 10  $\mu$ s to 50 ms. Data were averaged over 120 laser pulses. All samples were purged with CH<sub>3</sub>CN saturated Ar for at least 30 min.

Injection Quantum Yield ( $\Phi_{inj}$ ). Injection quantum yields were determined by transient absorption using the optically dilute method, equation 3.1. A solution of  $[Ru(bpy)_3](PF_6)_2$  in CH<sub>3</sub>CN was used as the actinometer ( $\Delta \epsilon_{450} = -1.0 \times 10^4 \text{ M}^{-1} \text{cm}^{-1}$ ).<sup>16</sup> Data were collected at the isosbestic point between the ground and excited state ( $\lambda$ ), and averaged over 90 laser pulses. The  $\Delta \epsilon$  at this wavelength was determined by spectroelectrochemistry. Laser power was maintained at 3.0 ± 0.1 mJ/pulse.

$$\Phi_{\rm inj} = \frac{\left(\frac{\Delta A_{\lambda}}{\Delta \varepsilon_{\lambda}}\right)_{1-5}}{\left(\frac{\Delta A_{450}}{\Delta \varepsilon_{450}}\right)_{Ru(bpy)_3}} \frac{\left(1 - 10^{-A_{532}}\right)_{Ru(bpy)_3}}{\left(1 - 10^{-A_{532}}\right)_{1-5}}$$
(3.1)

Data Analysis. Data analysis for all experiments was performed using Mathematica version 11. All fits utilized the Levenberg-Marquardt fitting algorithm.

### **3.3 Results**

Three new sensitizers (1-3) were prepared from readily accessible ligands synthesized by the condensation reaction of primary amines with a bpy di-ester. The sensitizers were synthesized in moderate yields (~50%) by the reflux of the  $Ru(dtb)_2Cl_2$  precursor with >1 equiv.

of the lignd in 1,4-dioxane. Sensitizer **4** has been previously synthesized, but a crystal structure was not obtained and the sensitizer was not significantly characterized.<sup>11</sup> Large crystals of **4** suitable for X-ray diffraction were obtained by dissolving a sample of **4** in methanol and allowing the solvent to evaporate slowly over several days, Figure 3.1. X-ray diffraction gave average Ru-N distances of 2.070 and 2.058 Å for the (HOMe)<sub>2</sub>-bpy and (*tert*-butyl)<sub>2</sub>-bpy ligands respectively, with bite angles of 78.5 and 78.3°. The other average N-Ru-N angles were 98.8 and 173.0°. Additional crystallographic data are available in Table 3.1.



**Figure 3.1** Displacement ellipsoid plot (50% probability level) for **4** obtained from single-crystal x-ray crystallography. The  $PF_6^-$  counter-ions are omitted for clarity. Color code: green, Ru; blue, N; red, O; white, C.

#### **Table 3.1 Crystal Parameters for 4**

Empirical formula	$C_{48}H_{58}N_6O_2Ru \cdot 2(F_6P)$
Formula weight	1142.01
Temperature/K	110
Crystal system	Triclinic
Space group	<i>P</i> -1
a/Å	10.8384 (2)
b/Å	13.1395 (2)
c/Å	19.1391 (3)
α/°	84.7664 (13)
β/°	85.3961 (15)
γ/°	84.0724 (14)
Volume/Å <sup>3</sup>	2692.83 (8)
Z	2
$\mu/\text{mm}^{-1}$	3.66
Crystal size/mm3	$0.60 \times 0.38 \times 0.36$
Radiation	CuKa ( $\lambda = 1.54178$ )
Final R indexes [I>= $2\sigma$ (I)]	R1 = 0.049, wR2 = 0.138

Steady-state absorption spectra of sensitizers 1-5 in CH<sub>3</sub>CN are shown in Figure 3.2. All the sensitizers had broad absorption features in the 400 to 500 nm range that were assigned as metal-to-ligand charge-transfer (MLCT) transitions. An intense band at 295 nm was also observed and assigned as a ligand centered  $\pi \rightarrow \pi^*$  transition. Sensitizers 1-3 and 5 had similar absorbance spectra all of which displayed a broad MLCT absorption with two distinct maxima while 4 had only one distinct maximum. Sensitizers 1-3 and 5 also had a shoulder on the red edge of the  $\pi \rightarrow \pi^*$  region that sensitizer 4 lacked.



Figure 3.2 Absorbance spectra (solid) and PL spectra (dashed) for sensitizers 1-5 in CH<sub>3</sub>CN. The PL spectra are normalized by the relative photoluminescence quantum yield of each sensitizer.

Laser excitation of all five sensitizers resulted in room temperature photoluminescence (PL) visible to the unaided eye, Figure 3.2. Pulsed light excitation of these sensitizers resulted in PL decays that were well described by a first-order kinetic model, which yielded characteristic lifetimes for these sensitizers. These data are summarized in Table 3.2.

Sensitizer	$\lambda_{abs}$ (nm), $\mathcal{E} (M^{-1}cm^{-1})/10^3$	$\lambda_{PL}$ (nm)	$\tau (\mu s)^b$	$\Phi_{ m PL}$	$k_r$ (s <sup>-1</sup> /10 <sup>4</sup> )	$k_{nr}$ (s <sup>-1</sup> /10 <sup>4</sup> )	E <sub>Ru(III/II)</sub> (V vs. NHE)	E <sub>LL(0/-)</sub> (V vs. NHE)	E <sub>LL(-/2-)</sub> (V vs. NHE)	E <sub>LL(2-/3-)</sub> (V vs. NHE)
1	440, 12.5; 477, 12.5; 288, 69.2	680	0.71	0.041	5.8	135	1.47 1.45 <sup>a</sup>	-0.95 <sup>c</sup>	-1.38	-
2	430, 12.6; 479, 12.4; 287, 71.2	684	0.85	0.040	4.7	113	1.46 1.46 <sup>a</sup>	-0.93 <sup>c</sup>	-1.38	-
3	430, <i>13.0</i> ; 484, <i>13.3</i> ; 287, 69.7	689	0.86	0.037	4.3	112	1.47 1.46 <sup>a</sup>	-0.92 <sup>c</sup>	-1.38	-
4	460, <i>16.1</i> ; 289, 87.7	637	1.00	0.068	6.8	93	1.37 1.41 <sup>a</sup>	-1.21	-1.40	-
5	430, <i>14.9</i> ; 482, <i>15.2</i> ; 288, <i>71.8</i>	681	1.06	0.054	5.1	89	1.49 1.47 <sup>a</sup>	-1.23	-1.43	-1.70

Table 3.2 Photophysical and Electrochemical Data for Sensitizers 1-5

<sup>a</sup>Values obtained from dye adsorbed on TiO<sub>2</sub> (all others were obtained from CH<sub>3</sub>CN solutions). <sup>b</sup>Estimated error  $\sim$ 5%. <sup>c</sup>Irreversible.

Square wave voltammetry was used to determine the Ru(III/II) potential and ligand reduction potentials for **1-5** in a 100 mM TBACIO<sub>4</sub> CH<sub>3</sub>CN solution (Figure S3.1 in Appendix 2)

and the Ru(III/II) potential for TiO<sub>2</sub> thin films sensitized with **1-5**. Sensitizers **1-3** and **5** had similar Ru(III/II) potentials in the range of 1.46 to 1.49 V vs. NHE, while **4** had a Ru(III/II) potential of 1.37 V. However, the first ligand reduction, LL(0/-), of **4** was similar to that of **5**, - 1.21 and -1.23 V vs. NHE respectively, while those of **1-3** were in the range of -0.92 to -0.95 V. It is worth noting that **1-3** showed significant irreversibility for the first ligand reduction while **4** and **5** were quasi-reversible. All five sensitizers had quasi-reversible second ligand reductions in the range of -1.38 to -1.43 V. A third ligand reduction was obtained only for **5** of -1.70 V vs. NHE. These data are summarized in Table 3.2.

Soaking TiO<sub>2</sub> thin films in solutions of sensitizers **1-5** at concentrations between 1.0  $\mu$ M and 1.0 mM produced thin films with maximum MLCT absorbance dependent on both the concentration of the dyeing solution and the identity of the sensitizer. Plots of the MLCT absorbance versus this concentration were fit with a Langmuir-type binding isotherm to yield binding constants, K<sub>b</sub>, for these sensitizers on TiO<sub>2</sub>. These fits are shown in Figure 3.3, with the binding constants reported in Table 3.3. Sensitizer **5** had an order of magnitude larger binding constant than any of the other sensitizers. Interestingly, within the homologous series **1-3**, the binding constant decreased with the number of alcohols despite an increase in the maximum absorbance obtained.



Figure 3.3 Maximum MLCT absorbance of a TiO<sub>2</sub> thin film sensitized with sensitizers 1-5 at various concentrations. Overlaid on the data are fits to a Langmuir-type binding model of the form  $(a_0 \times K_b \times [Ru]) / (1 + K_b \times [Ru])$ .

The photostability of  $TiO_2$  thin films sensitized with sensitizer **1-5** was studied by white light illumination and intermittent monitoring of the MLCT absorption. For sensitizer **4**, illumination resulted in a red shift of the MLCT peak maximum from 460 nm to 475 nm and a change in the peak shape. For the other sensitizers, a decrease in absorbance was observed, but no significant spectral shifts were observed, Figure S3.2 in Appendix 2. The spectrum of **4** after 60 min of illumination showed remarkable similarity to that of **5**, as shown in Figure 3.4 with the spectrum of **1** after 60 min of illumination for comparison.



**Figure 3.4** Comparison of the normalized absorbance of a  $TiO_2$  thin film sensitized with sensitizers 1, 4, and 5 after 60 min of white light illumination (red and blue, respectively).

A plot of the maximum MLCT absorbance of the films versus the time illuminated yielded data that could be fit with a first-order kinetic model that decayed to a non-zero value, Figure 3.5. These fits allowed for a comparison of the photo-induced absorbance loss rate as well as the percent loss extrapolated to infinite time. These values can be found in Table 3.3 (hv Loss). Sensitizers **1** and **5** displayed the smallest rate constants and the smallest overall absorbance loss. Sensitizers **2** and **3** displayed approximately the same kinetics and the largest rate constants while sensitizer **4** displayed an intermediate rate constant and had the largest absorbance loss. Experiments repeated in either air or argon saturated CH<sub>3</sub>CN showed that both the kinetics and maximum absorbance loss were insensitive to the presence or absence of oxygen.



**Figure 3.5** Normalized absorbance of TiO<sub>2</sub> thin films sensitized with the indicated chromophores after white light illumination. The absorbance was measured at the wavelength corresponding to the MLCT maximum prior to illumination. Overlaid on the data are fits to a single exponential decay of the form  $c_1 \times \exp[-k \times t] + c_2$ .

Electrochemical stability was probed by applying 1.7 V vs. NHE in  $CH_3CN$  to completely oxidize the sensitized films for 16 hrs followed by a 10 min period with an applied 0 V bias. The absorbance of the films was measured before and after this potential step, Figure S3.3 in Appendix 2. All five sensitizers showed a significant loss of absorbance and a change in the MLCT absorbance spectra. Sensitizers **1-4** exhibited a red shift and shared a similar peak shape. The resulting spectra for sensitizers **1**, **4**, and **5** are shown in Figure 3.6 for comparison. The percentage of absorbance lost for each sample is given in Table 3.3 (Echem Loss).



Figure 3.6 Normalized absorbance of  $TiO_2$  thin films sensitized with the indicated chromophores after holding the films at ~1.7 V vs. NHE for 960 min.

TiO<sub>2</sub> thin films sensitized with **1-5** were soaked in 1 M CH<sub>3</sub>CN solutions of Li<sup>+</sup>, Na<sup>+</sup>,  $Mg^{2+}$ , Ca<sup>2+</sup>, and Al<sup>3+</sup> perchlorate salts for 16 hrs, which led to a loss in film absorbance. However, any cation induced spectral shifts were reversed by washing with neat CH<sub>3</sub>CN, as observed previously.<sup>16</sup> Sensitizer **4** was much more sensitive to cations than the other dyes, with a 33% loss of absorbance in the Na<sup>+</sup> solution while the other sensitizers showed no greater than a 9% loss. Within the homologous series **1-3**, the percentage of absorbance lost increased with the number of alcohols. These data are summarized in Table 3.3 (M<sup>n+</sup> Loss).

Table 3.3 Select Properties of 1-5 on TiO<sub>2</sub><sup>a</sup>

Sensitizer	$\begin{array}{c} K_b TiO_2 \\ M^{-1} / 10^3 \end{array}$	${{TiO_2}e^- k_{bet}^{\ \ b}} \over {s^{^{-1}}}/{10^3}$	$\Phi_{inj}^{c}$	M <sup>n+</sup> Loss (Li/Na/Mg/Ca/Al) % loss <sup>d</sup>	hv Loss k s <sup>-1</sup> /10 <sup>-5</sup> , <sup>b</sup> % loss <sup>e</sup>	Echem Loss <sup>f</sup> % loss
1	$180 \pm 70$	1.9	0.13	3/3/14/23/64%	3.5, 36%	33%
2	$16 \pm 4$	3.9	0.20	6/0/23/35/73%	6.3, 43%	43%
3	$11 \pm 2$	9.0	0.26	16/9/37/43/85%	6.3, 52%	39%
4	$170 \pm 40$	7.2	0.57	45/33/23/30/93%	5.2, 61%	20%
5	$2,700 \pm 600$	26.4	0.45	2/2/17/20/94%	3.0, 37%	62%

<sup>&</sup>lt;sup>a</sup>See text for an explanation of the column headings. <sup>b</sup>Estimated relative error ~20%. <sup>c</sup>Estimated relative error ~5%. <sup>d</sup>Estimated absolute error  $\pm$  20%. <sup>e</sup>Estimated absolute error  $\pm$  10%. <sup>f</sup>Estimated absolute error  $\pm$  5%. Estimated errors are the maximum standard deviation calculated from repeat experiments in a given column.

Pulsed laser excitation of TiO<sub>2</sub> thin films sensitized with sensitizers **1-5** immersed in a 100 mM LiClO<sub>4</sub> CH<sub>3</sub>CN solution resulted in electron transfer from the excited sensitizer to the TiO<sub>2</sub> substrate. Comparative actinometry by transient absorption allowed the quantum yield for this electron injection,  $\Phi_{inj}$ , to be determined, Table 3.3. Sensitizer **4** was determined to have the largest  $\Phi_{inj}$  of 0.57 while **1** had the smallest, 0.13. In the homologous series **1-3**, the injection yield increased with the increasing number of alcohol groups. Sensitizer **5** was intermediate between **4** and **3**.

After electron injection, transfer of the electron back to the oxidized sensitizer was monitored by the return of the ground state spectrum. Representative data is shown in Figure 3.7 for **1**. The initial decay (t < 1  $\mu$ s) is due to the excited state. The decay after 1  $\mu$ s could not be fit with a single exponential model and required the use of a stretched exponential function,  $a_0 \times$ exp[-( $k_{bet} \times t$ )<sup> $\beta$ </sup>]. The value of  $\beta$  was held constant between the different sensitizers and was found to fit well with a value of 0.24. The rate constants for back electron transfer determined from this fit,  $k_{bet}$  is given in Table 3.3 for sensitizers **1-5**. Sensitizer **5** was found to have a significantly larger  $k_{bet}$  than the other sensitizers,  $26.4 \times 10^3$  s<sup>-1</sup>, with **3** having the next largest at  $9.0 \times 10^3$  s<sup>-1</sup>. Within the series **1-3**, this rate increased with an increasing number of alcohols. Sensitizer **4** was found to be intermediate between **2** and **3**.



**Figure 3.7** Back electron transfer kinetics of a TiO<sub>2</sub> thin film sensitized with sensitizer 1 after 532 nm excitation, monitored at 481 nm. The different colors represent data collected using different time intervals. The data after 1  $\mu$ s are overlaid with a fit to a stretched exponential of the form  $a_0 \times \exp[-(k \times t)^{\beta}]$ , where  $\beta$  was fixed at 0.24.

### 3.4 Discussion.

A series of alcohol bearing sensitizers was synthesized and each was shown to sensitize  $TiO_2$  to visible light. The sensitization properties of the sensitizers were shown to change systematically with the anchoring group. Of particular interest was the discovery that a methyl alcohol binding group produced a sensitizer that simultaneously improved injection and slowed back electron transfer relative to structurally similar carboxylic acid bearing sensitizer. The relative stability of all the sensitizers with respect to photochemistry, electrochemistry, and the presence of high salt concentrations were uncorrelated, and no single anchoring group was found to be universally more stable than the others. Another notable result from this work is the determination that the electrochemical and photochemical instability was the result of different pathways. These conclusions are discussed in greater detail below.

Anchoring to  $TiO_2$ . Adsorption isotherms for all the sensitizers with  $TiO_2$  revealed considerable equilibrium binding constants,  $K_b \sim 10^4 - 10^6 \text{ M}^{-1}$ . However, the  $K_b$  values for the alcohols were one or two orders of magnitude smaller than that of the carboxylic acids. While the exact binding mode of carboxylic acids is ambiguous,<sup>8</sup> there is some evidence for the formation of ester-like linkages or carboxylate binding to the surface.<sup>15,17</sup> One explanation for the

decreased alcohol binding constants may be the considerably larger  $pK_a$  of the alcohols relative to carboxylic acids limiting the formation of this type of adduct.

However, a lower binding constant does not necessarily translate into lower maximum surface coverages, as is evident from this series of sensitizers. Within the homologous series 1-3, the binding constant decreased with the increasing number of alcohols, yet the surface coverage, proportional to the film absorbance, increased. It must be noted that the use of a Langmuir-type binding model is counterintuitive, since the surface binding is irreversible (no desorption is evident if sensitized films are immersed in neat  $CH_3CN$ ). The Langmuir model, and in fact any model that employs equilibrium binding implies a reversible reaction. This makes interpretation of the determined binding constants ambiguous. It is possible that surface anchoring is actually a multi-step process, and perhaps the binding constant is reporting on an initial, reversible step (which must eventually be followed by an irreversible step).

If this is the case, then the decreased binding constant with added alcohol groups may be the result of hydrogen bonding between alcohol groups on the sensitizer. Sensitizers 1 and 4, which both have two alcohol groups have, within error, the same binding constant. The decreased binding constant of 2 and 3 may be due to hydrogen bonding between alcohols, which may render the alcohols less available for surface binding. The increased maximum surface coverage of 4 relative to 1 may be due to the greater steric bulk of 1.

Interfacial Electron Transfer. The sensitizers studied were all able to inject electrons into  $TiO_2$  in a LiClO<sub>4</sub> CH<sub>3</sub>CN solution following pulsed 532 nm laser excitation with measureable efficiencies. Sensitizer **4** was found to have the greatest injection quantum yield. It has been previously shown that intimate electronic communication between the sensitizer and  $TiO_2$  surface is not necessary for efficient injection,<sup>13</sup> a result confirmed here. The excited state

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reduction potential,  $E^{\circ}([Ru]^{3+/2+})$ , is expected to be approximately the same within the series **1**-**3** since they have approximately the same  $E^{\circ}(Ru^{III/II})$  potential and PL energy.<sup>18</sup> The increased injection quantum yield within the series **1**-**3** may result from enhanced coupling between the surface and the sensitizer. The alcohol groups increase orbital density between the sensitizer and the surface, potentially increasing coupling despite the presence of two sp<sup>3</sup> hybridized carbons. On the basis of the PL spectra and  $E^{\circ}(Ru^{III/II})$ , sensitizer **4** is expected to have a ~150 mV larger driving force for injection than sensitizer **5** consistent with the increased injection quantum yield of **4** compared to **5**.

The rate constants for back electron transfer between the injected electrons and oxidized sensitizers may be understood by consideration of the electronic coupling with the TiO<sub>2</sub> surface. All of the sensitizers except 4 have approximately the same  $E^{\circ}(Ru^{III/II})$ . Hence, assuming that surface binding does not influence the energy levels of  $TiO_2$ , sensitizers 1-3 and 5 have the same driving force for back electron transfer, while sensitizer 4 should have a smaller driving force. There is evidence that this back electron transfer reaction falls within the Marcus inverted region for similar sensitizers to those studied here.<sup>19</sup> If this were the case, sensitizer 4 would have the largest rate constant for back electron transfer. Instead, sensitizer 5 has the largest rate constant for back electron transfer by a factor of  $\sim 2$ , indicating that other parameters, such as electronic coupling, are important considerations. Within the series 1-3, rate constants increase with the number of alcohol binding groups, again suggesting that the added alcohols lead to greater electronic coupling with the surface. An important finding was that sensitizer 4 simultaneously had a greater quantum yield for injection and slower back electron transfer compared to sensitizer 5, meaning solar devices made with this sensitizer would likely be more efficient than those made with **5**.

*Photo-, Electrochemical, and Electrolyte Stability.* In order to be used in a solar device, a sensitizer must be stable for long periods of light exposure, electrochemical gradients, and concentrated electrolyte solutions. To study these properties for sensitizers **1-5**, experiments were devised in which  $TiO_2$  thin films sensitized with each of the sensitizers were exposed to light, oxidizing potentials, or concentrated electrolytes overnight, with the absorbance spectrum of the films being measured before and after exposure. Unfortunately, no universal stability trends were observed, i.e. no one sensitizer was most stable under all three conditions. Both losses in absorbance, and changes in the MLCT absorbance spectra were observed, complicating analysis of these data. Furthermore, the chemical changes resulting in spectral shifts were not identified, limiting the conclusions that can be drawn from the experiments. However, comparison between the sensitizers allows for some useful discussion.

It has been previously shown that Lewis acidic cations can interact with sensitizers in solution<sup>20</sup> and on the TiO<sub>2</sub> surface.<sup>21,22</sup> The long term stability of sensitized TiO<sub>2</sub> was determined by soaking the sensitized films in CH<sub>3</sub>CN solutions containing 1 M Lewis-acidic cation perchlorate salts overnight. No spectral shifts were observed; the normalized absorbance spectra of the films were unchanged with cation exposure, but these high salt concentrations did lead to considerable loss of MLCT absorbance, likely due to surface desorption, Table 3.3, and Figure 3.8. Increased charge density resulted in enhanced sensitizer desorption for all sensitizers except **4**, which was unusually sensitive to Li<sup>+</sup> and Na<sup>+</sup>. One question that is raised is whether the desorption primarily stems from cation interactions with the sensitizer or with TiO<sub>2</sub>. The peculiar sensitivity of **4** to the monovalent cations suggests the primary interaction of interest is between the cation and the sensitizer. Within the series **1-3**, more alcohol groups led to greater desorption, which again suggests that desorption results from interaction with the sensitizer, since more

alcohols may result in a chelate effect for cation interactions or may allow simultaneous interaction with multiple cations.



Figure 3.8 Fraction of the MLCT absorbance of  $TiO_2$  thin films sensitized with 1-5 after soaking in 1 M cation perchlorate  $CH_3CN$  solutions for 16 hrs.

Illumination of sensitized TiO<sub>2</sub> films led to a decrease in maximum absorbance and for **4** a shift of the MLCT absorbance spectrum. The spectral shift implies some degree of net photochemistry of the sensitizer, hereafter termed degradation. The decrease in maximum absorbance of **4** may be the result of a combination of degradation and sensitizer desorption from the TiO<sub>2</sub>. The absorbance loss for all of the sensitizers was found to follow a single-exponential model, which allowed rate constants for this absorbance loss to be determined and compared, as well as the post-illumination spectra. Only sensitizer **4** showed a considerable shift in its absorbance spectrum, suggesting the other sensitizers only desorbed with illumination, rather than undergoing degradation chemistry. It is possible that illumination of the TiO<sub>2</sub> film of **4** led to oxidation of the methylene carbon resulting in the formation of a carboxylic acid. This is supported by comparison of the absorbance spectru of **4** was approximately the same as that of **5**, allowing for differences in the background TiO<sub>2</sub> absorbance. This type of chemistry has been suggested to occur for other sensitizers with similar methylene groups under oxidizing electrochemical conditions.<sup>7</sup>

The rate constants for desorption were similar for **1** and **5**, each of which have only two binding groups. The rate constants for **2** and **3** were similar to each other and larger than those of **1** and **5**. Furthermore, the first-order kinetic model included an added constant, indicating that at long time scales some sensitizers would remain on the surface. The percent of sensitizer lost (or remaining) extrapolated to infinite time was the same for **1** and **5**, and the same for **2** and **3**. The reason for this is unclear, but may be related to the hydrogen bonding between alcohols on **2** and **3** previously mentioned, since there appears to be a correlation between photostability and the measured binding constants.

The electrochemical stability of the oxidized sensitizers **1-5** on TiO<sub>2</sub> was studied by applying a potential of 1.7 V vs NHE for 16 hrs. The absorbance spectra of the films were recorded before and after the potential step. Significant loss of absorption was observed for all of the sensitizers, and sensitizers **1-4** also exhibited significant changes in the MLCT absorption spectra. Sensitizer **4** showed the smallest change in absorbance. Square wave voltammetry was performed on the films before and after the electrochemical treatment to ensure no drift in the reference electrode. No new peaks were observed in the voltammetry. Similar studies on phosphonate-based sensitizers in aqueous electrolytes showed electrochemical instability resulting in new redox reactions that were attributed to anation, i.e. loss of a coordinated pyridyl group and coordination of a  $ClO_4$ <sup>-.23</sup> However, there was no evidence of such chemistry here.

In contrast to the photostability experiments, where the absorbance spectrum of a film sensitized with **4** became similar to that of **5**, the spectra of films of sensitizer **4** following electrochemical treatment were similar to those of sensitizers **1-3** suggesting they formed the same degradation product(s). Furthermore, since sensitizer **4** was not similar to **5** after electrochemical treatment, the aforementioned possible oxidation to a carboxylic acid can be

discounted, as this would convert sensitizer **4** into sensitizer **5**. Unfortunately, no further information was obtained on the possible degradation mechanisms or products.

## **3.5 Conclusions.**

Several sensitizers bearing alcohol groups for surface anchoring have been synthesized and characterized in solution and on  $TiO_2$ . The stability of these sensitizers on  $TiO_2$  and their interfacial electron transfer properties were determined and compared to a similar sensitizer bearing carboxylic acids for surface binding. All of these sensitizers could be irreversibly anchored to  $TiO_2$  with most of them capable of achieving surface coverages comparable to the reference sensitizer. The sensitizer bearing two methanol groups was found to have more efficient electron injection and slower back electron transfer than the reference sensitizer. Systematic changes in the anchoring groups could, in some case, be correlated with stability and electron transfer properties. However, no single binding group was found to have increased surface stability under all the conditions studied. Further study is required to determine degradation pathways and products.

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# 4. Redox Active Ion-Paired Excited States Undergo Dynamic Electron Transfer<sup>1</sup>

## **4.1 Introduction**

Excited-state electron transfer reactions are of general importance as they provide a means to convert solar energy into stored potential energy in the form of redox equivalents. Bimolecular reactions generally occur by two mechanisms.<sup>2</sup> The first has been termed *dynamic* electron transfer wherein the excited state diffuses to a redox active species before electron transfer occurs. In an alternative *static* mechanism, a ground-state adduct between the chromophore and the redox active species gives rise to a non-emissive species that undergoes light-driven electron transfer without a diffusional step. Ground-state adduct formation is often enhanced by Coulombic attraction and ion-pair formation. This manuscript reports the first example of an ion-pair that undergoes diffusional excited-state electron transfer that does not occur in the absence of ion-pairing.

Ion-pairs are comprised of oppositely charged ions that share all or part of their solvation shell and possess a binding energy greater than the thermal energy. It is generally accepted that ion-pairs are able to adopt a variety of structures in fluid solution.<sup>3–6</sup> For example, a *contact ion-pair* (sometimes called a tight or intimate ion-pair) is formed when no solvent molecules are located between the ions, like that reported here, **Scheme 4.1**. Likewise, a *solvent separated ion-pair* is formed when solvent molecules exist between the ions that decrease the donor-acceptor electronic coupling for redox active ion-pairs.





It has also been recognized that ion-pairing can be enhanced by the presence of functional groups that form specific adducts with the ions. The halide receptor on the dea ligand of  $C1^{2+}$ utilizes hydrogen bonding alcohol and amide functional groups that have been previously used to recognize halide ions.<sup>7-12</sup> Visible spectroscopy and <sup>1</sup>H NMR data reported herein demonstrate that chloride, bromide, and iodide all form strong 1:1 adducts with this ruthenium complex that are well formulated as contact ion-pairs. The equilibrium in dichloromethane fell so far to the right that the precise values could not be determined while equilibrium constants in the range of  $K_{ip} = 10^4 - 10^6 M^{-1}$  were measured in more polar acetonitrile solutions. Interestingly, these adducts had longer lived excited states and stored more free energy in their excited states than did the non-ion-paired complex. Furthermore, there was no evidence of static electron transfer reactivity in the 1:1 ion-pairs. Instead, the ion-pair underwent efficient dynamic iodide photo-oxidation that did not occur in the absence of the ion-pair. To our knowledge, this represents the first example of diffusional excited-state electron transfer enabled by ion-pair formation between redox active donors and acceptors. The relevance of these findings to emerging classes of 'third generation' solar cells that utilize iodide is discussed.

#### **4.2 Experimental**

Materials. Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, Fisher, 98 %, Certified ACS Plus), methanol (Fisher, Certified ACS), chloroform (Fisher, Certified ACS), ethanolamine (Sigma-Aldrich,  $\geq 98$  %), acetone (Sigma-Aldrich, Certified ACS), acetonitrile (CH<sub>3</sub>CN, Burdick and Jackson, 99.98 %), and dichloromethane (CH<sub>2</sub>Cl<sub>2</sub> Burdick and Jackson, 99.98 %) were used as received. Argon gas (Airgas, 99.998 %) was passed through a Drierite drying tube before use. Ammonium hexafluorophosphate (NH<sub>4</sub>PF<sub>6</sub>, Sigma-Aldrich,  $\geq$  98 %), tetrabutylammonium chloride (TBACl, Sigma-Aldrich, purum  $\geq$  97 %), tetrabutylammonium bromide (TBABr, Acros Organics, 99+ %), tetrabutylammonium iodide (TBAI, Sigma-Aldrich,  $\geq$  99 %), tetrabutylammonium perchlorate (TBAClO<sub>4</sub>, Sigma-Aldrich, for electrochemical analysis, 99 >%). tetrabutylammonium triiodide (TBAI<sub>3</sub> Sigma-Aldrich,  $\geq$  97 %), ruthenium trichloride hydrate (Oakwood Chemicals, 97 %), and tri-*p*-tolylamine (TCI America,  $\geq$  98 %) were used as received. NMR solvents were purchased from Cambridge Isotope Laboratories, Inc. Ru(dtb)<sub>2</sub>Cl<sub>2</sub>•2H<sub>2</sub>O and 2,2'-bipyridine-4,4'-dicarboxylic acid were synthesized according to a literature procedure.<sup>37</sup> All solutions were sparged with argon for at least 30 minutes before all titration and transient absorption experiments.

*Synthesis.* **4,4'-dimethylester-2,2'-bipyridine:** The 4,4'-dimethylester-2,2'-bipyridine was synthesized by a modified literature procedure.<sup>13</sup> Briefly, to a mixture of 10 mL of  $H_2SO_4$  and 90 mL of methanol was added 5.0 g (20.5 mmol) of 2,2'-bipyridine-4,4'-dicarboxylic acid. The mixture was refluxed until there was no visible solid. The cooled pink solution was poured into chloroform and extracted with water until no color was apparent. The organic fraction was then evaporated under reduced pressure to yield 5.3 g (95%) of a microcrystalline white solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 8.96 (2H, dd), 8.86 (2H, dd), 8.80 (2H, dd), 4.00 (6H, s).

**4,4'diethanolamide-2,2'-bipyridine, (dea):** To 1.0 g (3.7 mmol) of 4,4'-dimethylester-2,2'-bipyridine in 20 ml of methanol was added 5 mL (5.1 g, 83 mmol) of ethanolamine. The mixture was refluxed for 4 hours. After cooling, ~25 mL of acetone was added to the resulting mixture that was then filtered on a sintered glass frit. The precipitate was washed with a copious amount of acetone and dried in an evacuated oven overnight at 150 °C to yield 1.1 g (92%) of a white powder. <sup>1</sup>H NMR (d<sub>6</sub>-DMSO, 600 MHz): 8.95 (2H, t), 8.87 (2H, d), 8.81 (2H, s), 7.87 (2H, dd), 4.8 (2H, t), 3.55 (4H, m), 3.38 (4H, m). <sup>13</sup>C NMR (d<sub>6</sub>-DMSO, 600 MHz): 164.70, 155.52, 150.05, 142.98, 122.00, 118.30, 59.51, 42.37.

[**Ru**(**dtb**)<sub>2</sub>(**dea**)](**PF**<sub>6</sub>)<sub>2</sub>, (**C1**<sup>2+</sup>): To a 10 mL glass microwave vial was added 100 mg (0.14 mmol) of Ru(dtb)<sub>2</sub>Cl<sub>2</sub>•2H<sub>2</sub>O, 49 mg (0.15 mmol) of **dea**, and ~5 mL of water. The mixture was heated under microwave radiation by an Anton Paar Monowave 300 at 150 °C for 10 minutes. The resulting mixture was filtered on a sintered glass frit. The filtrate was then treated with an excess of aqueous NH<sub>4</sub>PF<sub>6</sub> and precipitated an orange solid that was filtered on a sintered glass frit and washed with a copious amount of water. The precipitate was then dried under vacuum to give the desired product in a 78% yield. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 600 MHz): 8.88 (2H, s), 8.27 (4H, d), 7.82 (2H, dd), 7.77 (2H, d), 7.57 (2H, d), 7.55 (2H, d), 7.51 (2H, t), 7.46 (2H, dd), 7.44 (2H, dd), 3.78 (4H, m), 3.58 (4H, m), 2.72 (2H, bs) 1.42 (18H, s), 1.40 (18H, s). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 600 MHz): 164.38, 163.14, 163.05, 157.35, 156.32, 156.18, 151.54, 150.75, 150.52, 143.08, 125.97, 125.78, 125.50, 121.72, 120.79, 61.46, 50.46, 43.28, 35.54, 35.52, 30.63, 29.99, 29.95. Elem anal. Calcd for RuC<sub>52</sub>H<sub>66</sub>N<sub>8</sub>O<sub>4</sub>P<sub>2</sub>F<sub>12</sub> (1258.13): C, 49.64; H, 5.29; N, 8.91. Found: C, 48.23; H, 5.21; N, 8.60. HRMS (ESI-MS) m/z: [M]<sup>2+</sup> Calcd for C<sub>52</sub>H<sub>66</sub>N<sub>8</sub>O<sub>4</sub><sup>96</sup>RuPF<sub>6</sub> 1107.3925; Found 1107.3963.

*Nuclear Magnetic Resonance*. Characteristic NMR spectra were obtained at room temperature on a Bruker Avance III 400 or 600 MHz spectrometer. Solvent residual peaks were used as internal standards for <sup>1</sup>H ( $\delta$  =7.26 ppm for CDCl<sub>3</sub>, 2.50 ppm for DMSO) and <sup>13</sup>C ( $\delta$  = 77.16 ppm for CDCl<sub>3</sub>, 39.52 ppm for DMSO) chemical shift referencing. NMR spectra were processed using MNOVA.

*Mass Spectrometry*. Samples were analyzed with a hybrid LTQ FT (ICR 7T) (ThermoFisher, Bremen, Germany) mass spectrometer. Samples were introduced via a microelectrospray source at a flow rate of 3 µL/min. Xcalibur (ThermoFisher, Breman, Germany) was used to analyze the data. Each mass spectrum was averaged over 200 time domains. Electrospray source conditions were set as: spray voltage 4.7 kV, sheath gas (nitrogen) 3 arb, auxiliary gas (nitrogen) 0 arb, sweep gas (nitrogen) 0 arb, capillary temperature 275 °C, capillary voltage 35 V and tube lens voltage 110 V. The mass range was set to 150-2000 m/z. All measurements were recorded at a resolution setting of 100,000. Solutions were analyzed at 0.1 mg/mL or less based on responsiveness to the ESI mechanism. Low-resolution mass spectrometry (linear ion trap) provided independent verification of molecular weight distributions.

Elemental Analysis. Elemental analysis was performed by Atlantic Microlabs, LLC.

UV-Vis Absorption. UV-vis absorption spectra were recorded on a Varian Cary 60 UV-vis spectrophotometer with a resolution of 1 nm. The extinction coefficients were determined by diluting a stock solution of complex  $C1^{2+}$  and represent averages of at least three independent measurements.

*Steady-State PL*. Steady-state PL spectra were recorded on a Horiba Fluorolog 3 fluorimeter and corrected by calibration with a standard tungsten-halogen lamp. Samples were excited at 450 nm. The intensity was integrated for 0.1 s at 1 nm resolution and averaged over 3

scans. The PL quantum yields were measured by the optically dilute method using  $[Ru(bpy)_3][PF_6]_2$  in acetonitrile ( $\Phi = 0.062$ ) as a quantum yield standard.<sup>38</sup>

*Time-Resolved Photoluminescence*. Time-resolved PL data were acquired on a nitrogen dye laser with excitation centered at 445 nm. Pulsed light excitation was achieved with a Photon Technology International (PTI) GL-301 dye laser that was pumped by a PTI GL-3300 nitrogen laser. The PL was detected by a Hamamatsu R928 PMT optically coupled to a ScienceTech Model 9010 monochromator terminated into a LeCroy Waverunner LT322 oscilloscope. Decays were monitored at the PL maximum and averaged over 180 scans. Nonradiative and radiative rate constants were calculated from the quantum yields,  $\Phi = k_r/(k_r + k_{nr})$  and lifetimes,  $\tau = 1/(k_r + k_{nr})$ .

*Electrochemistry.* Square wave voltammetry was performed with a BASi Epsilon potentiostat in a standard three-cell in  $CH_2Cl_2$  electrolytes. The cells consisted of a platinum working electrode and a platinum mesh as an auxiliary electrode. A non-aqueous silver/silver chloride electrode (Pine) was used as a reference electrode that was referenced to an internal decamethylferrocene (Me<sub>10</sub>Fc) standard (250 mV vs. NHE).<sup>19</sup>

*Halide Titrations*. UV–vis, PL, and time-resolved measurements were performed in  $CH_2Cl_2$  or  $CH_3CN$  using 10 µM of  $C1^{2+}$ . Titration measurements were performed for each of the spectroscopies with TBACl, TBABr, or TBAI through additions of 0.25 equivalents. Throughout all titrations the concentration of  $C1^{2+}$  remained unchanged. In order to do so, a stock solution of  $C1^{2+}$  with an absorbance of ~0.1 at 450 nm in the desired solvent was prepared. The stock solution was transferred into a spectrophotometric quartz cuvette (5 mL). A titration solution was then prepared with 25 mL of the  $C1^{2+}$  stock solution. TBACl, TBABr, or TBAI were added to

the stock solution to obtain the desired concentration of halide. These solutions were then titrated to the quartz cuvette.

The <sup>1</sup>H NMR titrations were performed using Bruker Avance III 500 MHz spectrometer equipped with a broadband inverse (BBI) probe using 1 mM ruthenium complex in 600  $\mu$ L of deuterated solvent and 0.25 equivalent additions of TBACl or TBAI were added in 10  $\mu$ L additions. The ruthenium concentration was kept unchanged through preparation of a titration solution that contained both C1<sup>2+</sup> and the desired halide. Each spectrum was averaged over 16 scans.

*Data Analysis*. Data analysis for all experiments was performed using OriginLab, version 9.0. Data fitting was preformed using a Levenberg-Marquardt iteration method. Benesi-Hildebrand type analysis was performed in Mathematica, version 10.

*Transient absorption*. Nanosecond transient absorption measurements were acquired on a setup published previously.<sup>39</sup> Briefly, a Q-switched, pulsed Nd:YAG laser (Quantel U.S.A. (BigSky) Brilliant B 5-6 ns full width at half-maximum (fwhm), 1 Hz,  $\sim$ 10 mm in diameter) doubled to 532 nm. The laser irradiance at the sample was attenuated to 3 mJ/pulse. The probe lamp consisted of a 150 W xenon arc lamp and was pulsed at 1Hz with 70 V during the experiment. Signal detection was achieved using a monochromator (SPEX 1702/04) optically coupled to an R928 photomultiplier tube (Hamamatsu) at a right angle to the excitation laser. Transient data were acquired with a computer-interfaced digital oscilloscope (LeCroy 9450, Dual 330 MHz) with an overall instrument response time of  $\sim$ 10 ns. An average of 30 laser pulses was acquired averaged at each wavelength of interest over the 370-800 nm range. Intervals of 10 nm were used for wavelength between 370 and 600 nm and intervals of 20 nm were used between 600 and 800 nm. Time-resolved PL data were also acquired at the same laser intensity at 532 nm.

Diiodide Extinction Coefficient. The extinction coefficient for diiodide in  $CH_2Cl_2$  was calculated from the transient absorption spectra of a 4 µM TBAI<sub>3</sub>, 20 µM TBAI solution. A tripled Nd:YAG laser (355 nm) was used to excite the triiodide that produced one equivalent of iodine atoms and one equivalent of  $I_2^{\bullet}$  anions, Equation 4.01. The produced iodine atoms further react with the I<sup>-</sup> anions to produce I<sub>2</sub><sup>-</sup>, Equation 4.02. Therefore, the overall reaction involves the loss of one equivalent of triiodide and the gain of two equivalents of I2<sup>•</sup>, Equation 4.03. Immediately after laser excitation (~30 ns) the observed products are one equivalent of iodine atoms and one equivalent of  $\Gamma$ , Equation 4.01. After 10  $\mu$ s the produced iodine atoms have fully reacted to form a second equivalent of  $I_2^{\bullet}$ . The transient absorbance spectrum at 30 ns then is the linear combination of the loss of triiodide and the diiodide produced, Equation 4.03, and the TA spectrum at 10  $\mu$ s is the linear combination of the loss of triiodide and the two equivalents of diiodide produce, Equation 4.04. Solving the equations for the absorbance of  $I_3^-$  and  $I_2^{--}$  and utilizing the known extinction coefficient for  $I_3^-$  allows the extinction coefficient of  $I_2^{\bullet-}$  to be calculated, Equations 4.05-4.07. The calculated extinction coefficient of diiodide is shown in Figure S4.27 in Appendix 3.

$$I_3 + hv (355 nm) \rightarrow I' + I_2^{-1}$$

$$(4.01)$$

$$\mathbf{I}^{\bullet} + \mathbf{I}^{\bullet} \rightarrow \mathbf{I}_{2}^{\bullet}$$

$$(4.02)$$

$$I_3 + I^- \rightarrow 2I_2^{--} \tag{4.03}$$

$$Abs(I_3) = (2) - 2x(1)$$
 (4.04)

$$Abs(I_2^{\bullet}) = (2) - (1)$$
 (4.05)

$$[I_3] = Abs(I_3)/\varepsilon(I_3) = [I_2]$$
(4.06)

$$\varepsilon(\mathbf{I}_{2}^{\bullet}) = \operatorname{Abs}(\mathbf{I}_{2}^{\bullet})/[\mathbf{I}_{2}^{\bullet}]$$
(4.07)

Diiodide Formation Rate Constant. Separate  $CH_2Cl_2$  solutions of TBAI<sub>3</sub> (5 µM) in a quartz cuvette and TBAI (0.67 mM) in a 20 mL scintillation vial were prepared. Approximately 1 equivalent, 40 µL, aliquots of the  $\Gamma$  solution were added to the triiodide solution to a total of 4 equivalents of iodide. The formation of  $I_2^{\bullet}$  after excitation by a tripled Nd:YAG laser (355 nm) was monitored at 410 nm, near an isosbestic point between the absorbance of  $I_2^{\bullet}$  and triiodide. The growth of the diiodide transient signal was well modeled by a single exponential function which yielded the observed formation rate. A second-order rate constant for diiodide formation was then calculated from the slope of the observed rate constants vs. the iodide concentration. This procedure was repeated at TBAClO<sub>4</sub> concentrations of 1, 10, and 100 mM.

Determination of the reduced complex extinction coefficient. The absorption spectrum of the singly reduced complex ( $C1^+$ ) was determined using a procedure adapted from literature.<sup>17</sup> A 10 µM solution of  $C1^{2+}$  with 10 mM tri-*p*-tolylamine (TPA) was irradiated with 532 nm light (1.5 mJ/cm<sup>2</sup>). Laser excitation of  $C1^{2+}$  resulted in electron transfer from the TPA to  $C1^{2+*}$ . Transient absorption spectra were recorded, normalized at 680 nm, and the normalized spectrum of the oxidized TPA was subtracted from it to give the difference spectrum between the reduced  $C1^+$  and the ground state. The concentration of reduced complex formed was calculated as the extinction coefficient of the oxidized TPA is known.<sup>17</sup> Division of the difference spectrum by the concentration of reduced complex gave the delta extinction coefficient. Linear addition of this delta extinction coefficient to the ground state  $C1^{2+}$  extinction coefficient yielded the reduced complex extinction coefficient, Figure S4.27 in Appendix 3.

Spectral Modeling. Transient absorption spectra of  $C1^{2+}$  in the presence of 4 equivalents of iodide resulted in the formation of the reduced complex and diiodide. At any given time, the spectra consisted of the ground state loss, excited states, the reduced compound, and diiodide,
Equation 4.08. The kinetics monitored in the 380-560 nm range wavelength range were modeled through use of the ground state  $(C1^{2+})$  and reduced complex  $(C1^{+})$  extinction coefficients and the absorbance difference between the excited state and ground state. This allowed the formation of diiodide and the reduced compound to be analyzed as concentration instead of absorbance.

$$\Delta Abs = Abs(C1^{2+*}) - Abs(C1^{2+}) + Abs(C1^{+}) + Abs(I_2^{\bullet-})$$
(4.08)

*Cage Escape Yield.* Cage escape yields of the photoinduced iodide oxidation by  $C1^{2+}$  were determined through transient absorption experiments utilizing Equations 4.09 and 4.10. Actinometry with a Ru(bpy)<sub>3</sub><sup>2+</sup> standard was performed between each sample measurement, assuming a unity quantum yield of intersystem crossing to the <sup>3</sup>MLCT excited state. The  $\Delta\epsilon_{450}$  between the ground state Ru(bpy)<sub>3</sub><sup>2+</sup> and the excited state Ru(bpy)<sub>3</sub><sup>2+</sup> was -1.5 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>,<sup>40</sup> and  $\Delta\epsilon_{520}$  between the ground state C1<sup>2+</sup> and the reduced C1<sup>+</sup> was  $1.25 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup> for C1<sup>2+</sup>. The slope of a plot of  $\phi$  vs. % of PL quenched gave the cage escape yield.<sup>31</sup>

$$\Phi_{\rm CE} = \phi \, \frac{1}{\% \, PL \, Quenched} \tag{4.09}$$

$$\phi = \frac{\left(\frac{\Delta A_{\lambda 1}}{\Delta \varepsilon_{\lambda 1}}\right)_{C1}}{\left(\frac{\Delta A_{\lambda 2}}{\Delta \varepsilon_{\lambda 2}}\right)_{Ru(bpy)_3}} \frac{(1-10^{-A_{532}})_{Ru(bpy)_3}}{(1-10^{-A_{532}})_{C1}}$$
(4.10)

Debye-Hückel Analysis. Quenching rates constants from Stern-Volmer analysis were measured with solutions whose ionic strength varying from 0 to 1 mM TBAClO<sub>4</sub>. The quenching rate constant was found to be dependent on ionic strength, a trend that was analyzed by the extended Debye-Hückel theory according to Equation 4.16.<sup>31</sup> In this equation,  $\mu$  is the ionic strength, A and  $\beta$  are constants (taken to be 15.3 L<sup>1/2</sup> mol<sup>1/2</sup>, and 1.02 10<sup>-8</sup> L<sup>1/2</sup> mol<sup>1/2</sup>, respectively),<sup>41</sup>  $\alpha$  is the effective size parameter, here assumed to be 5.5 Å, k<sub>q,0</sub> is the quenching constant at  $\mu = 0$ , and  $z_{+}$  and  $z_{-}$  are the charges of the two species involved in the quenching

process. Plotting Log(k<sub>q</sub>) vs. (2 A  $\mu^{1/2}$ ) / (1 +  $\alpha \beta \mu^{1/2}$ ) gives a line with a slope equal to the product of Z<sub>+</sub> and Z<sub>-</sub>.<sup>31</sup>

Density Functional Theory. Quantum mechanical calculations were carried out using the Gaussian 09 program package.<sup>42</sup> The structure of  $C1^{2+}$  was optimized to a minimum energy and frequency calculations were performed to verify there were no imaginary frequencies. All calculations utilized the B3LYP functional<sup>43-46</sup> with the 6-311++G\*\*<sup>47</sup> basis set applied to chloride, LANL2DZ<sup>48-50</sup> with an added f-polar function applied to ruthenium,<sup>51</sup> and 6-311G\*<sup>52</sup> applied to all other elements. Parameters for the LANL2DZ basis set were obtained from the ESML basis set exchange.<sup>53,54</sup> Second-order perturbations analysis of intermolecular interactions and of natural atomic charges used for coulombic work term calculations were performed with the NBO 3 program, as implemented in the Gaussian software package.<sup>55-62</sup> All calculations were performed in the gas phase and an ultrafine integration grid was used for all calculations. When convergence was not otherwise achieved, two quadratic convergence steps were added through the SCF=XQC command.

## 4.3 Results

The synthesis of complex  $C1^{2+}$ ,  $[Ru(dtb)_2(dea)][PF_6]_2$  where **dea** is 4,4'-diethanolamide-2,2'-bipyridine and **dtb** is 4,4'-di-*tert*-butyl-2,2'-bipyridine, is presented in Scheme 4.2. The 2,2'-bipyridine-4,4'-dicarboxylic acid was esterified by a modified literature procedure with a 95% yield.<sup>13</sup> Substitution of 4,4'-dimethylester-2,2'-bipyridine by ethanolamine was achieved in methanol to yield the desired **dea** ligand in a 92% yield. Coordination to ruthenium was achieved under microwave irradiation in water and afforded  $C1^{2+}$  with a 78% yield. Scheme 4.2 Synthesis of complex C1<sup>2+</sup>



The photophysical properties of complex  $C1^{2+}$  were studied in both acetonitrile (CH<sub>3</sub>CN) and dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>). The steady-state UV-vis absorption spectrum in neat CH<sub>2</sub>Cl<sub>2</sub>, showed in Figure 4.01, displayed the characteristic ground state absorption features of ruthenium polypyridyl complexes. The low energy absorption between 420 and 500 nm were attributed to typical metal-to-ligand charge-transfer (MLCT) transitions (Equation 4.11), whereas the higher energy absorbance was attributed to ligand centered (LC)  $\pi \rightarrow \pi^*$  transitions.

$$[\operatorname{Ru}^{\mathrm{II}}(\mathrm{dtb})_2(\mathrm{dea})]^{2+} + \mathrm{hv} \to [\operatorname{Ru}^{\mathrm{III}}(\mathrm{dtb})_2(\mathrm{dea})]^{2+}$$
(4.11)

Light excitation of  $C1^{2+}$  resulted in photoluminescence (PL) with a maximum at 670 nm that could be observed by the unaided eye. Time-resolved PL decays generated with pulsed laser excitation of  $C1^{2+}$  were well described by a first-order kinetic model, from which excited-state lifetimes were abstracted, 745 ns and 1.32 µs in CH<sub>3</sub>CN and CH<sub>2</sub>Cl<sub>2</sub> respectively. The photophysical properties of  $C1^{2+}$  in neat solution and with added halides are reported in Table 4.1. Addition of the tetrabutylammonium (TBA<sup>+</sup>) salts of chloride, bromide, or iodide to CH<sub>3</sub>CN solutions of  $C1^{2+}$  resulted in measureable changes in the steady-state absorbance spectra. These absorbance changes are shown in Figure 4.01 for Cl<sup>-</sup> addition to a solution of  $C1^{2+}$  in CH<sub>2</sub>Cl<sub>2</sub>. Ion-pair equilibrium constants (K<sub>IP</sub>) abstracted from a modified Benesi-Hildebrand analysis were greater than  $10^6$  M<sup>-1</sup> for all the halides in CH<sub>2</sub>Cl<sub>2</sub>, but were about two order of magnitude smaller in CH<sub>3</sub>CN decreasing in the order Cl<sup>-</sup>>Br<sup>-</sup>>I<sup>-</sup>.<sup>14,15</sup>



**Figure 4.01** Absorption changes of  $C1^{2+}$  upon titration of chloride from 0 to 15 equivalents in  $CH_2Cl_2$ . Inset shows the difference between the absorption spectrum after each addition of chloride and the initial spectrum. Arrow indicates the direction of change in the spectra with increasing chloride concentration.

Solvent	Species	K <sub>IP,GS</sub> (M <sup>-1</sup> )	K <sub>IP,ES</sub> (M <sup>-1</sup> )	λ <sub>max</sub> PL (nm)	τ (ns)	$\Phi_{ m PL}$	$\frac{k_{\rm r}(\times10^4}{{\rm s}^{-1})}$	$\frac{k_{\rm nr}(\times10^6}{{\rm s}^{-1})}$
CH <sub>3</sub> CN	C1 <sup>2+</sup>			685	745	0.044	6.0	1.32
	$+ Cl^{-}$	$85  imes 10^4$	> 10 <sup>6 a</sup>	675	960 <sup>b</sup>	0.063 b	6.5 <sup>b</sup>	0.97 <sup>b</sup>
	$+ Br^{-}$	$9.0  imes 10^4$	$5.5  imes 10^4$	678	945 <sup>b</sup>	0.058 b	6.2 <sup>b</sup>	0.99 <sup>b</sup>
	$+\Gamma$	$1.7  imes 10^4$	$0.6  imes 10^4$	681	820 <sup>b</sup>	0.051 b	6.2 <sup>b</sup>	1.16 <sup>b</sup>
CH <sub>2</sub> Cl <sub>2</sub>	C1 <sup>2+</sup>			670	1320	0.083	6.3	0.70
	$+ Cl^{-}$	$> 10^{6 a}$	$> 10^{6 a}$	645	1830 <sup>b</sup>	0.165 b	9.0 <sup>b</sup>	0.46 <sup>b</sup>
	$+ Br^{-}$	$> 10^{6 a}$	с	647	1790 <sup>b</sup>	0.122 b	6.8 <sup>b</sup>	0.49 <sup>b</sup>
	$+ \Gamma$	$> 10^{6 a}$	с	650	1550 <sup>b</sup>	0.095 b	6.1 <sup>b</sup>	0.58 <sup>b</sup>

**Table 4.1** Equilibrium constants and photophysical properties of  $C1^{2+}$  and  $[C1^{2+}, X^{-}]^{+}$ 

<sup>a</sup> Equilibrium constant was too large to be measured, therefore a minimum is given. <sup>b</sup> Measured after the addition of 1 equivalent of the halide. <sup>c</sup> Could not be measured due to quenching induced by halide addition.



**Figure 4.02** <sup>1</sup>H NMR titration of  $C1^{2+}$  with tetrabutylammonium iodide in  $CD_2Cl_2$  (left). Job plot analysis for the NMR titration data (right). Inset represents the observed change in chemical shift of selected protons upon addition of iodide.

Chloride and iodide <sup>1</sup>H NMR titrations were performed in CD<sub>3</sub>CN and CD<sub>2</sub>Cl<sub>2</sub> with representative data given in Figure 4.02. Significant downfield shifts of the amide protons, the protons on the bipyridine 3,3' carbons, and the hydroxyl protons of the **dea** ligand were observed. Interestingly, in CD<sub>2</sub>Cl<sub>2</sub>, the hydroxyl protons were shifted the furthest ( $\Delta$ ppm of 1.96) with the addition of chloride and the least for iodide ( $\Delta$ ppm of 0.52), Figures S4.13-S4.21. Protons on the **dtb** ligands were not appreciably affected by the halide additions. The ion-pairing equilibrium stoichiometry was determined by the method of continuous variation through a Job plot<sup>16</sup> that revealed a 1:1 Ru:X<sup>-</sup> ratio (Figure 4.02).



**Figure 4.03** Steady-state PL titration of TBAI into a  $CH_2Cl_2$  solution of  $C1^{2+}$ . Inset shows the Stern-Volmer plot starting after one equivalent of  $\Gamma$  (solid spectra).

The addition of one equivalent of Cl<sup>-</sup>, Br<sup>-</sup>, or  $\Gamma$  to a CH<sub>2</sub>Cl<sub>2</sub> solution of Cl<sup>2+</sup> resulted in an increase of the PL intensity concomitant with a blue shift in the peak maximum that followed the trend Cl<sup>-</sup>>Br<sup>-</sup>>\Gamma. The magnitude of this shift was between 25 and 20 nm, which corresponded to ~60 meV. The excited-state lifetime also increased from 1.32 to 1.83, 1.79, and 1.55 µs upon the addition of one equivalent of chloride, bromide, and iodide respectively. Representative steady-state PL data for the addition of  $\Gamma$  in CH<sub>2</sub>Cl<sub>2</sub> are shown in Figure 4.03. A less intense increase and blue shift were also observed in CH<sub>3</sub>CN that followed the same halide trend.

The PL spectral changes saturated at a high halide concentrations in CH<sub>3</sub>CN and for chloride in CH<sub>2</sub>Cl<sub>2</sub> that enabled the excited state ion-pairing equilibrium constants,  $K_{IP,ES}$ , to be abstracted, Table 4.1. The absorbance and PL maximum of the ion-paired species are reported in Table 4.1 with the abstracted ion-pairing constants. The UV-vis and PL spectra of the ion-pairs are shown in Figures S4.06-S4.12. With the exception of chloride, when the solution ionic strength was increased by the addition of 100 mM TBAClO<sub>4</sub>, the absorbance and PL spectral shifts associated with iodide ion-pairing and excited-state quenching were lost, Figure S4.22-S4.25 in Appendix 3.

The addition of  $\Gamma$  or Br<sup>-</sup> beyond one equivalent led to excited-state quenching in CH<sub>2</sub>Cl<sub>2</sub>. Stern-Volmer analysis of the steady-state or the time resolved PL data yielded a Stern-Volmer constant,  $K_{SV}$ , of 4.0 x10<sup>5</sup> M<sup>-1</sup>, Equations 4.12 and 4.13. This provided a quenching rate constant,  $k_q = 2.6 \pm 0.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ , Equation 4.14, indicating that only dynamic quenching was operative. There was no evidence of excited state electron transfer when halide titrations were performed in CH<sub>3</sub>CN. The equilibrium constant for iodide and bromide with C1<sup>2+</sup> could not be accurately determined by PL measurements in CH<sub>2</sub>Cl<sub>2</sub> due to the observed quenching.

$$I_0/I = 1 + K_{SV}[X^-]$$
(4.12)

$$\tau_0 / \tau = 1 + K_{\rm SV} [X^-] \tag{4.13}$$

$$k_{\rm q} = \mathbf{K}_{\rm SV} \,/\, \boldsymbol{\tau}_0 \tag{4.14}$$



**Figure 4.04** Transient absorption spectrum of  $C1^{2+}$  in  $CH_2Cl_2$  with 20 equivalents of  $\Gamma$  (a), single wavelength transient absorption traces at 402 nm and 519 nm (b), and observed rate at these wavelengths at various concentrations of TBA iodide overlaid with linear fits (c). All experiments were performed at a  $C1^{2+}$  concentration of 70  $\mu$ M in  $CH_2Cl_2$  with a laser fluence of 3 mJ/pulse.

Transient absorption spectroscopy was performed in  $CH_2Cl_2$  solutions of  $C1^{2+}$ , Figure 4.04. The transient absorption spectrum of  $C1^{2+}$  in neat  $CH_2Cl_2$  following 532 nm pulsed laser excitation showed two isosbestic points at 402 nm and 519 nm, Figure S4.28 in Appendix 3. Upon the addition of iodide, two new features centered at 400 nm and 520 nm were observed and assigned to the growth of diiodide,  $I_2^{-}$ , and the singly reduced complex ( $C1^{+}$ ) respectively. The extinction coefficient spectrum of  $C1^{+}$ , i.e. [Ru(dtb)<sub>2</sub>(dea<sup>-</sup>)]<sup>+</sup>, was obtained by transient

absorption measurements after pulsed laser excitation of  $C1^{2+}$  in the presence of tri-*p*-tolylamine (TPA) as a reductive quencher. Subtraction of the known TPA<sup>+</sup> absorption spectrum yielded the desired spectrum.<sup>17</sup> The  $C1^+$  extinction coefficient spectrum showed maximums around 520 nm and 380 nm with minimal absorbance at 402 nm, Figure S4.27 in Appendix 3.

The absorbance spectrum of diiodide was obtained in CH<sub>2</sub>Cl<sub>2</sub> by direct excitation of TBAI<sub>3</sub> and was found to be very similar to the spectrum previously reported in CH<sub>3</sub>CN.<sup>18</sup> The I<sub>2</sub><sup>•</sup> radical anion has absorption maxima centered at 370 nm and 750 nm. The rate constant for I<sup>•</sup> +  $\Gamma \rightarrow I_2^{-}$  in CH<sub>2</sub>Cl<sub>2</sub> was determined to be  $1.7 \pm 0.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ , Figures S4.29-S4.30. Single wavelength kinetics data obtained at 402 nm reported primarily on the formation of I<sub>2</sub><sup>•</sup> while those obtained at 519 nm primarily reported on the mono-reduced complex. Figure 4.04a shows typical data with an initial C1<sup>2+</sup> concentration of 70 µM.

Single wavelength transient absorption data were used to determine the rate constant for formation of C1<sup>+</sup> and I<sub>2</sub><sup>-</sup>,  $5.9 \pm 0.4 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> and  $6.2 \pm 0.1 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> respectively (Figure 4.04b and c). Time-resolved PL data collected during the transient absorption experiment yielded a quenching rate constant of  $5.5 \pm 0.2 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>.

The kinetic measurements were repeated at a ruthenium concentration of 10  $\mu$ M. In addition, the absorption changes were converted to concentration changes using Beer's law (Figure 4.05a). At 10  $\mu$ M, a larger rate constant for the appearance of C1<sup>+</sup>, 1.5  $\pm$  0.04  $\times$ 10<sup>10</sup> M<sup>-1</sup> s<sup>-1</sup> and for I<sub>2</sub><sup>-</sup>, 1.5  $\pm$  0.05  $\times$ 10<sup>10</sup> M<sup>-1</sup> s<sup>-1</sup> were measured, Figure 4.05. The excited state also yielded a quenching rate constant of 1.5  $\pm$  0.10  $\times$  10<sup>10</sup> M<sup>-1</sup> s<sup>-1</sup>. Hence the rate constants in these highly ion-paired and unbuffered solutions increased upon decreasing the solution strength.



**Figure 4.05** (a) Time dependent concentration changes of  $I_2^{\bullet}$  (black),  $C1^{2+}$  (red) and the excited state decay (blue). (b). Observed rate constant for the formation of the mono-reduced complex and  $I_2^{\bullet}$  at various concentrations of TBAI. Measurements were performed at a  $C1^{2+}$  concentration of 10  $\mu$ M in CH<sub>2</sub>Cl<sub>2</sub>. The laser fluence was 3 mJ/pulse.

Competition experiments were performed in which one equivalent of chloride was initially added to a CH<sub>2</sub>Cl<sub>2</sub> solution of C1<sup>2+</sup>. Iodide was then titrated into the solution and quenching was observed by steady-state PL with a quenching rate constant of  $1.9 \pm 0.2 \times 10^{10}$  M<sup>-1</sup> s<sup>-1</sup>, Figure 4.06. This value is similar in magnitude to that determined by the titration of iodide alone, i.e.  $2.6 \pm 0.1 \times 10^{10}$  M<sup>-1</sup> s<sup>-1</sup>.



**Figure 4.06** Steady-state PL of  $C1^{2+}$  upon titration of up to one equivalent of TBACl (dashed spectra) followed by the addition of up to five equivalents of TBAI (solid spectra). Inset shows the Stern-Volmer plot for the addition of TBAI.

Square wave voltammetry of  $C1^{2+}$  and the complex ion-paired with chloride,  $[C1^{2+}, C\Gamma]^+$ , was performed using decamethylferrocene (250 mV vs. NHE)<sup>19</sup> as an internal standard, Figure 4.07.



**Figure 4.07** Square wave voltammograms of  $C1^{2+}$  (1.1 mM) in  $CH_2Cl_2$  with 0.1 M TBAClO<sub>4</sub> electrolyte before (black) and after (red) the addition of 5.1 mM TBACl.

In a 100 mM TBACIO<sub>4</sub> CH<sub>2</sub>Cl<sub>2</sub> solution, the Ru<sup>III/II</sup> potential E<sup>o</sup>(C1<sup>3+/2+</sup>) was 1.68 V vs. NHE. With the addition of ~5 equivalents of TBACl, this potential shifted to 1.72 V. The first ligand reduction, C1<sup>2+/+</sup>, shifted from -0.82 to -0.86 V with the addition of chloride. This gives an estimated increase of ~ 80 mV in the electrochemical HOMO-LUMO gap. Note that the broad shoulder for the [C1<sup>2+</sup>, Cl<sup>-</sup>]<sup>+/0</sup> redox chemistry was due to chloride as was demonstrated by control experiments performed in the absence of the metal complex. We note also that similar chloride redox chemistry has been reported in the literature.<sup>20,21</sup>

The excited state reduction potentials were calculated from the first  $\mathbf{C1}^{2+/+}$  reduction potential and the Gibbs free energy of the excited state,  $\Delta G_{ES}$ , that was estimated from the x-intercept of a linear extrapolation of the blue edge of the PL corrected spectra,<sup>22</sup> Equation 4.15, where *F* is Faraday's constant. The reduction potentials was estimated to be  $\mathrm{E}^{\mathrm{o}}(\mathbf{C1}^{2+*/+}) = +1.27$  and for the chloride ion-pair  $\mathrm{E}^{\mathrm{o}}([\mathbf{C1}^{2+},\mathbf{C\Gamma}]^{+*/0}) = +1.25$  vs. NHE.

$$E^{o}(C1^{2+*/+})/F = E^{o}(C1^{2+/+})/F + \Delta G_{ES}$$
(4.15)

### **4.4 Discussion**

Control of halide ion-pairing was effected through the design of  $C1^{2+}$ , which bears the 4,4'-diethanolamide-2,2'-bipyridine (dea) ligand. Ion-pairing between  $C1^{2+}$  and  $C\Gamma$ , Br<sup>-</sup>, and  $\Gamma$  did not result in excited-state quenching. Instead, the ion-paired excited-state stored more free energy, was longer lived, and initiated excited-state iodide oxidation through a dynamic mechanism. Static, i.e. non-diffusional, electron transfer between redox active ion-pairs is commonly observed, but dynamic electron transfer is unusual with little if any precedence. This new halide photo-oxidation mechanism is described below, preceded by a discussion of the nature of the ion-pairs. A systematic analysis of the mechanistic data provides compelling evidence that iodide photo-oxidation yields an iodide atom and provides new insights into how such ion-pairing influences the thermodynamics for excited state electron transfer.

*Ion-Pair structure*. The **dea** ligand design was inspired by the work of Beer et al. who have previously employed amides for halide recognition. Indeed, ruthenium polypyridyl complexes bearing similar 4,4'-di-amide-2,2'-bipyridine ligands displayed halide ion-pairing behavior in DMSO that did not occur in the absence of the amides, highlighting the importance of this functional group for ion-pairing.<sup>7</sup> The spectroscopic data reported herein provides compelling evidence for the presence of a 1:1  $C1^{2+}$  to halide contact ion-pair. This ion-pair has photophysical properties distinct from the non-ion-paired chromophore.

The <sup>1</sup>H NMR titrations provided insight into the ion-pair equilibrium and the specific halide binding sites (Scheme 4.1). The <sup>1</sup>H NMR resonance shifts were consistently larger in the lower dielectric constant solvent  $CH_2Cl_2$ . The presence of halides induced significant shifts in the proton resonances associated with the **dea** ligand, Table 4.2. Job plots indicated a 1:1 halide to

complex stoichiometry with anion dependent spectral changes. The most pronounced shift induced by chloride was the hydroxyl proton resonance while the most pronounced shift induced by iodide was the amide N-H resonance.

**Table 4.2** Change in <sup>1</sup>H NMR chemical shifts upon the addition of iodide or chloride, in dichloromethane and acetonitrile.

	H <sub>3,3</sub> ,	HOH	H <sub>NH</sub>
<b>Дррт CH<sub>2</sub>Cl<sub>2</sub>, Г</b>	1.05	0.52	1.33
Δppm CH <sub>2</sub> Cl <sub>2</sub> , Cl <sup>-</sup>	1.42	1.96	1.68
Δppm CH <sub>3</sub> CN, I <sup>-</sup>	0.70	0.25	0.92
Δppm CH <sub>3</sub> CN, Cl <sup>-</sup>	1.23	1.36	1.36

The halide binding site precludes solvent separation between the halide and the amide hydrogens and leads to the assignment of  $[C1^{2+}, X^{-}]^{+}$  as a *contact ion-pair*, Figure 4.08. Furthermore, the observed trend in the chemical shifts upon titration are consistent with expectations based on the halide radii. The small size of chloride ( $r_{ion}$  1.81 Å) allows the ethanol side chains to achieve a more favorable geometry in which the hydroxyl H atom points directly towards chloride, whereas the ethylene spacer is not long enough to wrap around the larger iodide ( $r_{ion}$  2.20 Å).<sup>23</sup> This hinders hydrogen binding with iodide as was manifest in the smaller <sup>1</sup>H NMR shifts and equilibrium constants than that measured for chloride.



**Figure 4.08** The left-hand side is the proposed structure of  $[C1^{2+}, X^{-}]^{+}$  contact ion-pair with chloride (green sphere) and iodide (purple dashed circle). Color code is blue (nitrogen), blue-green (ruthenium), grey (carbon), red (oxygen) and white (hydrogen). The right-hand side illustrates the difference in H-bonding between the chloride case (green sphere) and iodide case (purple sphere). The arrow in the left image indicates the point of view for the right images. The arrows in the right images emphasize the direction of the O-H bonds. Note that the dtb ligands were omitted for clarity.

For  $C1^{2+}$ , halide titrations performed in both  $CH_3CN$  and  $CH_2Cl_2$  led to an increase in the PL intensity and a blue-shift in the PL maximum. Titrations in  $CH_2Cl_2$  showed complete conversion to the ion-paired species that precluded the determination of the equilibrium binding constant,  $K_{IP}$ , values. The PL intensity increases were remarkable for chloride, which approximately doubled the quantum yield. As excited-state quenching was observed with Br<sup>-</sup> and  $\Gamma$ , the enhanced lifetimes and yields represent best estimates of the 1:1 stoichiometry ion-pairs.

In CH<sub>3</sub>CN, the equilibrium binding constant,  $K_{IP}$ , determined from both absorbance and PL data increased with the size-to-charge ratio of the halides,  $CI^- > Br^- > \Gamma$ . The excited state absorption spectra were independent of the identity of the halide or of its presence indicating that the blue shift was not due to localization of the excited state on the **dtb** ligand. In other words, the metal-to-ligand charge transfer (MLCT) excited state  $C1^{2+*}$  was well formulated as  $[Ru^{II}(dtb)_2(dea^-)]^{2+*}$  under all experimental conditions. Interestingly in CH<sub>3</sub>CN, a larger  $K_{IP}$  for chloride was abstracted from the PL data relative to the absorbance data whereas a smaller one was determined when bromide or iodide were used. These observations indicated that the excited state of  $C1^{2+}$  binds chloride more strongly than the ground state whereas the opposite was true for bromide and iodide. One might have expected that localization of an electron on the **dea** ligand would result in unfavorable excited-state electrostatics, but this was not the case for CI<sup>-</sup> and may result from increased planarity of the **dea** ligand that was absent for Br<sup>-</sup> and  $\Gamma$  due to steric crowding.<sup>24,25</sup>

The increased excited-state lifetime that resulted from ion-pairing can be understood as the result of at least two effects. The blue shift in the PL spectra with ion-pairing indicates an increased ground-excited state energy gap and a longer lifetime is therefore expected based on Jortner's energy gap law.<sup>26</sup> It is also reasonable to expect that the halide brings the amide moieties into greater planarity with the bipyridine  $\pi$  system, increasing delocalization of the excited electron along the ligand  $\pi$  system.<sup>27,28</sup> This hypothesis is supported by Density Functional Theory (DFT) calculations that predict a decrease in the angle between the amide moiety and the pyridyl rings upon chloride ion-pairing, Figure S4.31 in Appendix 3.

*Excited State Ion-Pair Electron Transfer Mechanism.* The experimental data clearly identifies the reaction products as the reduced Ru complex  $C1^+$  and  $I_2^-$ . Cage escape yields determined on a nanosecond time scale indicated that these photoproducts were produced with a quantum yield of 0.34. It is worthwhile to consider the possible mechanism(s) for this excited state iodide oxidation. A static electron transfer mechanism, involving a non-luminescent ion-pair, was immediately ruled out as the ion-pairs are more highly luminescent and showed no evidence of electron transfer. Hence only dynamic mechanisms were considered and four possibilities are shown in Figure 4.09.

A "concerted" mechanism has been proposed in thermal stopped-flow iodide oxidation studies by Stanbury and Nord,<sup>29,30</sup> in which electron transfer and I-I bond formation occur in one step, Figure 4.09A. It has also been proposed to be operative in dye-sensitized solar cells. The termolecular nature of the reaction has prompted researchers to speculate that it occurs through ion-paired intermediates. This mechanism has been rigorously tested by quantifying the appearance of the C1<sup>+</sup> and I<sub>2</sub><sup>-</sup> products after pulsed laser excitation. A concerted mechanism cannot be fully ruled out based on kinetic measurements, but is not believed to be operative as is discussed below.

Transient absorption measurements revealed that excited state electron transfer rate constants decreased as the solution ionic strength increased, behavior consistent with the reaction

of a cationic ion-paired excited state and an iodide donor. For example, with 70  $\mu$ M C1<sup>2+</sup>, the formation of the C1<sup>+</sup> and I<sub>2</sub><sup>--</sup> occurred with second-order rate constants of 6.2 ± 0.1 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> and 5.9 ± 0.4 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> respectively, that were within experimental error the same and well below the expected diffusion limit. The excited state quenching constant was within experimental error the same, consistent with C1<sup>+</sup> and I<sub>2</sub><sup>--</sup> being primary photochemical products. However, the rate constant for the reaction  $\Gamma + 1^{\bullet} \rightarrow I_2^{\bullet-}$  was determined to be  $1.7 \pm 0.2 \times 10^{10}$  M<sup>-1</sup> s<sup>-1</sup> under these conditions, and hence in the excited state reaction the I-I bond formation step may be rate limited by the appearance of iodine atoms. This interpretation was born out in measurements with a much lower 10  $\mu$ M C1<sup>2+</sup> concentration where excited state decay and both products occurred with the same rate constant of  $1.5 \pm 0.05 \times 10^{10}$  M<sup>-1</sup> s<sup>-1</sup>, which is approximately that expected for a diffusion limited reaction. Hence the kinetic data are consistent with either a concerted electron transfer mechanism or one that involves iodine atom formation as the rate limiting step.



**Figure 4.09** Plausible dynamic quenching of  $C1^{2+*}$  by iodide. The presence of the electron on the dea ligand in  $C1^{2+*}$  and  $C1^{+}$  is emphasized by the orange colored bipyridine. Purple spheres represent iodine species whereas green spheres represent chloride. Ancillary **dtb** ligands are omitted for clarity.

The concerted mechanism would require I-I bond formation with a freely diffusing iodide and the ion-paired iodide in the  $[C1^+, \Gamma]^{+*}$  excited state. This follows from the quenching data that was consistently first-order in the iodide concentration. By analogy, iodide quenching of the chloride ion-paired  $[C1^{2+}, C\Gamma]^{+*}$  excited state would yield the iodine monochloride radical, ICl<sup>\*</sup>, and there was no spectroscopic evidence for such inter-halogen bond formation. Instead the transient data were fully consistent with the formation of  $I_2^{-*}$ . This indirect measurement represents the most compelling evidence that the reaction between an ion-paired excited state and iodide generates a single iodine atom.

Two possible iodine atom pathways were considered in Figure 4.09, one that involved the  $C1^{2+*}$  excited state and the other that involved ion-paired  $[C1^{2+}, X^{-}]^{+*}$ . The former mechanism can be eliminated as the sole electron transfer process since it would imply decreased reactivity as the iodide concentration increased. Furthermore, chloride ion-paring is stronger in the

excited state than in the ground state indicating that dissociation of the ion-pair by light is not operative. Nevertheless, the cage escape yields were less than unity and multiple pathways are possible so a Debye-Hückel analysis was performed at various ionic strengths to distinguish whether the iodide reaction took place with a dicationic or a monocationic excited-state.

$$Log(k_q) = k_{q,0} + \frac{2 A Z_+ Z_- \mu^{1/2}}{1 + \alpha \beta \mu^{1/2}}$$
(4.16)

Equation 4.16 relates the quenching constant  $k_q$  to the ionic strength  $\mu$  and the charges of the reactants, Z<sub>+</sub>Z. The identities of the constants are explained in the Experimental Section.<sup>31</sup> A plot of log(k<sub>q</sub>) vs the properly formulated ionic strength revealed a slope of -0.92 that was most consistent with the reaction of iodide and a monocationic ion-paired [C1<sup>2+\*</sup>, X<sup>-</sup>]<sup>+</sup> species. Furthermore, at high 100 mM ionic strength with an inert salt, iodide ion-pairing with C1<sup>2+</sup> was completely suppressed and there was no evidence for excited-state electron transfer. Therefore, pathway B is not operative and the mechanism is identified as one in which iodide reacts with an ion-paired excited state, pathways C and D in Figure 4.09.

*Thermodynamic Considerations.* It remains unclear why electron transfer was only observed from the ion-paired excited state and only in dichloromethane. Prior work has shown that iodide oxidation occurs with rate constants greater than  $10^9 \text{ M}^{-1}\text{s}^{-1}$  for related dicationic MLCT excited states in CH<sub>3</sub>CN solutions with similar driving forces.<sup>32</sup> Yet this was not observed here, requiring a deeper look into the thermodynamics for ion-pair formation and excited-state iodide oxidation.

The significant blue shift in the PL spectra that occurs with halide ion-pairing suggests that the excited state would be a stronger oxidant than the non-ion-paired excited state, but electrochemical data reveals that this is almost equally offset by a shift in the ground state reduction potential. The inherent uncertainties in the free energy stored in the excited state, and its small dependency on the halide identity lead to the conclusion that the oxidation potential of  $[C1^{2+}, X^{-}]^{+*}$  and  $C1^{2+*}$  are within experimental error the same,  $1.26 \pm 0.2$  V, and cannot account for the remarkable reactivity turn-on induced by ion-pairing, Table 4.3.

	$\Delta G_{ES}$ (eV) <sup>a</sup>	E <sup>o</sup> (C1 <sup>2+/+</sup> ) (V vs NHE)	E <sup>o</sup> (C1 <sup>2+*/+</sup> ) (V vs NHE)	$\Delta G_w$ (eV) <sup>b</sup>	$\frac{\Delta G_{rxn}}{(eV)^c}$
C1 <sup>2+</sup>	2.09	-0.82	1.27	-0.39	-0.43
[C1, Cl <sup>-</sup> ] <sup>+</sup>	2.11	-0.86	1.25	-0.25	-0.27

Table 4.3 Electrochemical and free energy data for the photo-oxidation of iodide by C1.

The Gibbs free energy change for iodide oxidation,  $\Delta G_{rxn}$ , is related to the formal reduction potentials and the coulombic work term,  $\Delta G_w$ , associated with the change in donor-acceptor electrostatic interactions upon electron transfer, Equation 4.17 where F is Faraday's constant.<sup>33–35</sup> The  $\Delta G_w$  term is often neglected as in polar solvents the contributions are generally small. However, this is not necessarily the case in organic solvents where ion-pairing is evident.

$$\Delta G_{\rm rxn} = E^{\rm o} (C1^{2+*/+})/F - E^{\rm o} (I^{/-})/F + \Delta G_{\rm w}$$
(4.17)

$$\Delta G_{\rm w} = \frac{k_{\rm e}}{\epsilon} \Delta \sum_{j=1}^{N} \frac{Z_{\rm I} Z_{\rm j}}{r_{\rm Ij}}$$
(4.18)

The work term has been calculated directly through Equation 4.18, where  $k_e$  is Coulomb's constant,  $\varepsilon$  is the relative permittivity of CH<sub>2</sub>Cl<sub>2</sub> (~9), Z<sub>I</sub> is the charge of iodide, Z<sub>j</sub> is the partial charge of atom j of C1<sup>2+</sup> or [C1<sup>2+</sup>, Cl<sup>-</sup>]<sup>+</sup>, and r<sub>Ij</sub> is the distance between the iodide and atom j of C1<sup>2+</sup> or [C1<sup>2+</sup>, Cl<sup>-</sup>]<sup>+</sup>. Since the iodine atom is not charged, the coulombic potential energy after the electron transfer is zero.

<sup>&</sup>lt;sup>a</sup> Extrapolated from the corrected PL spectra as the abscissa intercept. <sup>b</sup> Calculated from **Equation 8** assuming an iodide position of 7.2 Å from the Ru center. <sup>c</sup> From **Equation 7**.

To our knowledge previous studies of excited-state electron transfer have not attempted to assign partial charges to each atom. Instead, the overall charge was placed at the center of mass of each ion.<sup>33–35</sup> This simplified approach reveals a  $-\Delta G_w$ , and hence an increased driving force, of 390 mV for C1<sup>2+</sup> and 250 mV for [C1<sup>2+</sup>, CI]<sup>+</sup>, Table 3. This relative permittivity would give rise to work term that are almost 4 times smaller for CH<sub>3</sub>CN ( $\varepsilon$  = 37.5) than for CH<sub>2</sub>Cl<sub>2</sub> ( $\varepsilon$  = 8.9) which begins to explain why no such quenching was observed in CH<sub>3</sub>CN. These values were calculated at an r<sub>Ij</sub> = 7.2 Å, yet the point charge approximation is most valid when the ions are much further away. As an iodide ion and the complex diffuse toward each other, the atomic contours of the electrostatic fields must begin to play a critical role.

To gain insights into the electrostatic interactions of the individual atoms in  $C1^{2+}$  and  $[C1^{2+}, C\Gamma]^+$ , the natural atomic charge of each individual atom was calculated through natural bond order analysis.<sup>36</sup> Shown in Figure 4.10 are contour plots of the calculated work terms over the plane containing the **dea** ligand in both the absence and presence of an ion-paired chloride.



**Figure 4.10** Contour plots of the calculated coulombic work term,  $\Delta G_w$ , in eV over the plane containing the **dea** ligand in the absence, A, and presence, B, of the chloride ion-pair. All atoms within 1 Å of this plane are shown as small colored dots. The **dea** ligand is superimposed in white.

Figure 4.10A shows the coulombic incentive for ion-pair formation in the proposed binding site. Indeed, the values range from -100 meV when the halide anion was located 20 Å

from the ruthenium center and reached a value close to -500 meV in the binding site provided by the **dea** ligand. Furthermore, the magnitude of the coulombic work term was substantially decreased at all locations after ion-pairing induced a unit decrease in the overall complex charge. Interestingly a halide anion approaching the chloride-paired **dea** binding site from a distance up to 20 Å give rises (up to -240 meV) to only unfavorable work terms while approach on the **dtb** side gives rise to favorable work terms and hence less coulombic repulsion. A preference for halide association remote to the ion-paired dea ligand should be even more pronounced in the MLCT excited state and suggests that iodide oxidation occurs in the dark green regions near the **dtb** ligands, Figure 4.10B.

These electrostatic considerations do not address the questions raised at the beginning of this section. Indeed they indicate that the thermodynamic driving force for iodide photo-oxidation decreased upon ion-pairing which is at odds with the turn-on in reactivity. To explain this phenomenon, we propose that ion-pairing competes kinetically with electron transfer *and* an ion-paired iodide stabilized in the **dea** ligand that is no longer a sufficiently potent reductant to react with the excited state. The kinetics for ion-pairing are unknown, but quenching rate constants of ~  $6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  imply a barrier to electron transfer that the electrostatically driven ion-pairing could outcompete. The free energy change for ion-pairing is tremendous with K<sub>IP</sub> values of  $10^4 \text{ M}^{-1}$  in CH<sub>3</sub>CN and immeasurably high >  $10^6 \text{ M}^{-1}$  in dichloromethane. These values do not directly address the formal E<sup>o</sup>(T<sup>'</sup>) reduction potential of the ion-paired iodide as it is conceivable that the Ru complex is stabilized to such a great extent that the iodide is destabilized. However, this seems highly unlikely when one considers the magnitude of the equilibrium constants and the Lewis basic nature of iodide that should render it more difficult to oxidize in the ion-pair.

A conclusion therefore is that  $C1^{2+*}$  traps iodide on the **dea** ligand and thus prevents its oxidation. Such behavior is ideal for iodide sensing, but not for solar energy conversion applications where iodide oxidation is desired. These applications include dye-sensitized and perovskite solar cells as well as HI splitting. The observed ion-pairing consumes an iodide ion and decreases the driving force for electron transfer. Hence, ligands that destabilize iodide yet retain or increase the coulombic attraction charge are expected to be the most ideal when photoredox chemistry is desired.

### **4.5 Conclusions**

In this work, the interaction of a ruthenium polypyridyl complex bearing a 4,4'diethanolamide-2,2'-bipyridine ligand, with chloride, bromide, and iodide was studied in both acetonitrile and dichloromethane. A 1:1 ion-paired halide complex was identified and characterized by standard spectroscopic and electrochemical techniques. The use of DFT computations to quantify the work terms for electron transfer in all the atoms of the complex provided electrostatic contour plots for the first time. The ion-pair formed was shown to photooxidize iodide, whereas the non-ion-paired species did not. This reactivity was not simply due to the ion-paired complex being a stronger oxidant or having a longer excited state lifetime. Instead, it was concluded that iodide ions were trapped and stabilized more rapidly than was excited state electron transfer. Ligands such as **dea** are desirable for anion sensing while alternative ligands that provide coulombic attraction yet destabilize the anion are more suitable for photoredox chemistry and solar energy conversion applications.

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# 5. Evidence for Cation Controlled Excited State Localization in a Ruthenium Polypyridyl Compound<sup>1</sup>

## **5.1 Introduction**

The metal-to-ligand charge-transfer (MLCT) excited states of Ru polypyridyl compounds are of considerable interest for both fundamental and practical application in solar energy conversion.<sup>2</sup> The prototypical example is  $[Ru(bpy)_3]^{2+}$ , where bpy is 2,2'-bipyridine. In fluid solution, the photoluminescent excited state can formally be viewed as an electron localized on a single bipyridine ligand and an oxidized metal center.<sup>3–6</sup> Radiative recombination is hence formally a ligand-to-metal charge transfer transition, Equation 5.1. Heteroleptic Ru compounds that contain one or more unique bipyridine ligands are generally of greater practical utility. A classic example is  $[Ru(dcbH_2)(bpy)_2]^{2+}$ , where  $dcbH_2$  is  $4,4'-(CO_2H)_2-2,2'-bpy$ , where the carboxylic acid groups have been utilized for surface oxide binding<sup>2</sup> and for covalent attachment to biomolecules<sup>7,8</sup> or polymers<sup>9</sup> through amide or ester linkages. The question of which ligand the excited state localizes upon in heteroleptic compounds of this type naturally arises. This question has been directly addressed by time-resolved resonance Raman (TR3) spectroscopy, which provides the vibrational spectra of the excited state.<sup>5,10</sup> A large body of electrochemical data has also indirectly revealed that the excited state localizes upon the ligand that is most easily reduced.<sup>11</sup> Chemical intuition leads one to conclude that two electron withdrawing carboxylic acid groups will render the dcbH<sub>2</sub> ligand more easily reduced than bpy, an expectation consistent with experiment, Equation 5.2.<sup>12</sup> For the first time, compelling evidence is provided herein that excited state localization can be directed toward a specific ligand through Lewis acid-base adduct formation in fluid solution.

$$[\operatorname{Ru}^{\operatorname{III}}(\operatorname{bpy})_2]^{2+*} \rightarrow [\operatorname{Ru}^{\operatorname{II}}(\operatorname{bpy})_3]^{2+} + \operatorname{hv}$$
(5.1)

$$[\operatorname{Ru}^{\operatorname{III}}(\operatorname{dcbH}_{2})(\operatorname{bpy})_{2}]^{2+*} \rightarrow [\operatorname{Ru}^{\operatorname{II}}(\operatorname{dcbH}_{2})(\operatorname{bpy})_{2}]^{2+} + \operatorname{hv}'$$
(5.2)

Many dcbH<sub>2</sub> containing Ru polypyridyl compounds have been anchored to metal oxide surfaces<sup>13</sup> or reacted to form metal organic frameworks (most commonly with the 5,5'-(CO<sub>2</sub>H)<sub>2</sub>-2,2'-bpy ligand).<sup>14–16</sup> In the final materials, the carboxylic acids are fully deprotonated to their conjugate base forms that are herein abbreviated as  $dcb = 4,4'-(CO_2)_2-2,2'-bpy$ . It remains unclear whether the excited state remains localized on a dcb ligand as it does in the carboxylic acid form, Equation 5.2. This is unfortunate as the nature of the excited state in these sensitized materials is of critical importance for applications where vectorial electron or energy transfer is generally desired. However, excited states are not easily characterized in these materials. For example, rapid excited state electron transfer makes TR3 experiments on TiO<sub>2</sub> surfaces difficult and the ligand reductions are usually obscured by much larger currents associated with reduction of the semiconducting material itself. The insulating<sup>17</sup> and light scattering<sup>14–16</sup> properties of metal-organic frameworks also provide significant experimental challenges. Inductive reasoning familiar to chemists is challenging for compounds like [Ru(dcb)(bpy)<sub>2</sub>] as the carboxylate functional group and the H atom have identical Hammett parameters.<sup>18</sup> In addition, with ligand orbitals that are expected to be energetically proximate, theoretical calculations at any level may not fully take into account the influence of solvation, ion-pairing, or more subtle outer-sphere interactions.

Herein is reported a modified synthetic pathway to the neutral ruthenium carboxylate compounds shown in Scheme 5.1. A comparative absorption and photoluminescence (PL) study

of these compounds is described in fluid solutions with added Lewis acidic Li<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Zn<sup>2+</sup>, Al<sup>3+</sup>, Y<sup>3+</sup>, and La<sup>3+</sup> cations. In methanol solutions, no evidence for interactions between these cations and the Ru compounds was obtained. In acetonitrile solutions, where solubility restricted detailed studies to [Ru(dcb)(bpy)<sub>2</sub>] (**B2B**) and [Ru(dcbq)(bpy)<sub>2</sub>],(**D2Q**), a significant stabilization of the MLCT excited states observed at higher cation concentrations was attributed to Lewis acid-base adduct formation, most likely between the metal cation and the carboxylate groups present on the diimine ligand. A noteworthy finding was made for the excited state of **B2B**, abbreviated **B2B**\*; the experimental data indicate that adduct formation leads to localization of the excited stated on the dcb ligand, while the excited state is localized on the bpy ligand in the absence of these adducts. To our knowledge such behavior has not previously been reported in the literature.





# **5.2 Experimental**

*Materials*. Ethanol (EtOH, Fisher), reagent grade methanol (MeOH, Fisher), acetone (Sigma), spectroscopic grade methanol (Sigma) and acetonitrile (Burdick & Jackson) were used

as received. Argon (Airgas, 99.995%) was used as received. Lithium Perchlorate (Sigma, 99.99%), Sodium Perchlorate Hydrate (Sigma, 99.99%), Magnesium Perchlorate (Sigma, ACS Reagent Grade), Calcium Perchlorate Tetrahydrate (Sigma, 99%), Zinc Nitrate Hexahydrate (Strem, 98%), Aluminum Perchlorate Nonahydrate (Sigma, 98%), Yttrium Nitrate Hexahydrate (Strem, 99.9%), Lanthanum Nitrate Hexahydrate (Strem, 99.9%), and Tetrabutylammonium Perchlorate (Sigma,  $\geq$  99.0%) were used as received. The 4,4'-dicarboxylato-2,2'-bipyridine disodium salt (dcb(Na)<sub>2</sub>) and 4,4'-dicarboxylato-2,2'-biquinoline disodium salt (dcbq(Na)<sub>2</sub>) were prepared as previously reported.<sup>13</sup> Ru(bpy)<sub>2</sub>Cl<sub>2</sub>•2H<sub>2</sub>O and Ru(dtb)<sub>2</sub>Cl<sub>2</sub>•2H<sub>2</sub>O were prepared by literature methods.<sup>19,13</sup>

*Synthesis.* [**Ru(bpy)<sub>2</sub>(dcb)**] (**B2B**). Ru(bpy)<sub>2</sub>Cl<sub>2</sub>•2H<sub>2</sub>O (540 mg, 1.0 mmol) and dcb(Na)<sub>2</sub> (580 mg, 2.0 mmol) were added to 50 mL of 1:1 (v/v) EtOH:H<sub>2</sub>O and refluxed for 8 hrs. The EtOH was removed under reduced pressure and then acetone was added to precipitate a red/orange solid which was filtered on a sintered glass frit and washed with acetone. Washing with EtOH yielded a pale orange precipitate and a bright orange solution which was subsequently evaporated under reduced pressure to yield a red precipitate. Recrystallization by slow evaporation of MeOH gave a white solid and red crystals suitable for single crystal XRD which could be separated by physical means to yield the pure product (390 mg, 53%). <sup>1</sup>H NMR  $\delta$  (d<sub>4</sub>-MeOD): 9.07 (2H, s), 8.71 (4H, dd), 8.14 (4H, m), 7.83 (8H, m), 7.50 (2H, m). <sup>13</sup>C NMR  $\delta$  (d<sub>4</sub>-MeOD): 170.1, 158.9, 158.7, 158.5, 152.9, 152.7, 152.6, 149.1, 139.3, 129.1, 129.0, 128.0, 125.7, 125.6, 125.0. HRMS (ESI-MS) m/z: [M + 2H]<sup>2+</sup> Calcd for C<sub>32</sub>H<sub>24</sub>N<sub>6</sub>O<sub>4</sub>Ru 329.045; Found 329.044, [M - CO<sub>2</sub> + H]<sup>+</sup> Calcd for C<sub>31</sub>H<sub>23</sub>N<sub>6</sub>O<sub>2</sub>Ru 613.092; Found 613.091, [M<sub>2</sub> + 2H]<sup>2+</sup> Calcd for C<sub>64</sub>H<sub>46</sub>N<sub>12</sub>O<sub>8</sub>Ru<sub>2</sub> 657.082; Found 657.082, [M<sub>3</sub> + 2H]<sup>2+</sup> Calcd for C<sub>96</sub>H<sub>68</sub>N<sub>18</sub>O<sub>12</sub>Ru<sub>3</sub> 984.615; Found 984.619.

[**Ru(dtb)**<sub>2</sub>(**dcb**)] (**D2B**). Ru(dtb)<sub>2</sub>Cl<sub>2</sub>•2H<sub>2</sub>O (750 mg, 1.0 mmol) and dcb(Na)<sub>2</sub> (580 mg, 2.0 mmol) were added to 50 mL of 1:1 (v/v) EtOH:H<sub>2</sub>O and refluxed for 8 hrs. The EtOH was removed under reduced pressure and the mixture was refrigerated overnight. The mixture was filtered on a sintered glass frit and washed with H<sub>2</sub>O, yielding an orange powder (790 mg, 86%). <sup>1</sup>H NMR δ (d<sub>4</sub>-MeOD): 9.05 (2H, s), 8.72 (4H, dd), 7.80 (4H, m), 7.69 (4H, d), 7.54 (4H, m), 1.47 (18H, s), 1.45 (18H, s). <sup>13</sup>C NMR δ (d<sub>4</sub>-MeOD): 168.6, 162.9, 157.4, 156.9, 156.8, 150.8, 150.7, 150.4, 147.1, 126.3, 124.8, 124.7, 123.3, 121.4, 121.3, 35.2, 29.2. HRMS (ESI-MS) m/z:  $[M + 2H]^{2+}$  Calcd for C<sub>48</sub>H<sub>56</sub>N<sub>6</sub>O<sub>4</sub>Ru 441.170; Found 441.169,  $[M + H + Na]^{2+}$  Calcd for C<sub>48</sub>H<sub>55</sub>N<sub>6</sub>O<sub>4</sub>RuNa 452.161; Found 452.160,  $[M + 2Na]^{2+}$  Calcd for C<sub>48</sub>H<sub>54</sub>N<sub>6</sub>O<sub>4</sub>RuNa<sub>2</sub> 463.152; Found 463.151,  $[M - CO_2 + H]^+$  Calcd for C<sub>47</sub>H<sub>55</sub>N<sub>6</sub>O<sub>2</sub>Ru 837.342; Found 837.341,  $[M_2 + 2H]^{2+}$  Calcd for C<sub>96</sub>H<sub>106</sub>N<sub>12</sub>O<sub>8</sub>Ru<sub>2</sub> 881.332; Found 881.331,  $[M_2 + 2Na]^{2+}$  Calcd for C<sub>96</sub>H<sub>108</sub>N<sub>12</sub>O<sub>8</sub>Ru<sub>2</sub> 903.314; Found 903.313.

[**Ru(bpy)**<sub>2</sub>(**dcbq**)] (**B2Q**). Following a previously reported preparation,<sup>13</sup> Ru(bpy)<sub>2</sub>Cl<sub>2</sub>•2H<sub>2</sub>O (540 mg, 1.0 mmol) and dcbq(Na)<sub>2</sub> (700 mg, 1.8 mmol) were added to 50 mL of argon purged H<sub>2</sub>O and refluxed for 8 hrs. The reaction mixture was filtered on a sintered glass frit yielding a red precipitate that was washed with water then acetone (750 mg, 95%). <sup>1</sup>H NMR  $\delta$  (d<sub>6</sub>-DMSO): 8.79 (2H, d), 8.74 (4H, t), 8.62 (2H, s), 8.12 (4H, t), 7.91 (4H, t), 7.49 (6H, m), 7.12 (2H, t), 6.99 (2H, d). <sup>13</sup>C NMR  $\delta$  (d<sub>4</sub>-MeOD): 171.3, 160.7, 157.5, 157.4, 153.4, 151.3, 151.0, 150.1, 138.2, 138.0, 130.8, 128.4, 128.1, 127.6, 127.4, 125.9, 124.5, 124.2, 124.1, 117.8. HRMS (ESI-MS) m/z: [M – CO<sub>2</sub> + Na]<sup>+</sup> Calcd for C<sub>39</sub>H<sub>27</sub>N<sub>6</sub>O<sub>2</sub>RuNa 735.105; Found 735.104, [M + Na]<sup>+</sup> Calcd for C<sub>40</sub>H<sub>26</sub>N<sub>6</sub>O<sub>4</sub>RuNa 779.095; Found 779.094.

[**Ru**(dtb)<sub>2</sub>(dcbq)] (D2Q). Ru(dtb)<sub>2</sub>Cl<sub>2</sub>•2H<sub>2</sub>O (750 mg, 1.0 mmol) and dcbq(Na)<sub>2</sub> (780 mg, 2.0 mmol) were added to 50 mL of 1:1 (v/v) EtOH:H<sub>2</sub>O and refluxed for 8 hrs. The EtOH

was removed under reduced pressure and the mixture was refrigerated overnight. The mixture was filtered on a sintered glass frit and washed with H<sub>2</sub>O yielding a dark red/purple powder (940 mg, 95%). <sup>1</sup>H NMR  $\delta$  (d<sub>4</sub>-MeOD): 8.78 (2H, s), 8.61 (4H, dd), 8.46 (2H, d), 7.73 (4H, d), 7.54 (2H, t), 7.50 (4H, m), 7.16 (2H, t), 7.10 (2H, d) 1.41<sub>4</sub> (18H, s), 1.41<sub>0</sub> (18H, s). <sup>13</sup>C NMR  $\delta$  (d<sub>4</sub>-MeOD): 171.3, 163.7, 163.1, 160.7, 157.3, 157.2, 152.7, 151.1, 150.6, 149.7, 130.5, 128.3, 128.1, 125.9, 124.8, 124.6, 124.5, 121.4, 121.3, 117.7, 35.2, 29.2. HRMS (ESI-MS) m/z: [M + H]<sup>+</sup> Calcd for C<sub>56</sub>H<sub>59</sub>N<sub>6</sub>O<sub>4</sub>Ru 981.364; Found 981.362.

*NMR*. NMR spectra were taken on a Bruker Avance III 400 MHz (<sup>1</sup>H) and 600 MHz (<sup>13</sup>C, 150 MHz) spectrometer. All NMR spectra were acquired at room temperature and referenced to the solvent residual peaks.

*ESI-MS*. High resolution electrospray ionization mass spectrometry data were collected with a Thermo LTQ FT hybrid mass spectrometer using a micro-electrospray source at a flow rate of 3  $\mu$ L/min. **B2B** and **D2Q** were analyzed as acetonitrile solutions. **B2Q** and **D2B** were analyzed as methanol solutions.

*ATR-IR*. Transmission infrared measurements were performed with a Bruker Alpha ATR FT-IR spectrometer however the low solubility in CH<sub>3</sub>CN precluded reliable measurements.

UV-Vis Absorption. UV-visible spectra were taken with a Cary 60 spectrometer.

Steady-State Photoluminescence. Steady-state PL spectra were taken on a Horiba Fluorolog fluorometer and corrected by calibration with a standard tungsten-halogen lamp. PL quantum yields were measured by the optically dilute method with  $[Ru(bpy)_3][PF_6]_2$  in acetonitrile ( $\phi = 0.062$ ) as a quantum yield standard.<sup>20</sup>

*Time-Resolved Photoluminescence*. Time-resolved PL decays were obtained with a nitrogen dye laser with excitation centered at 445 nm. Pulsed light excitation was achieved with

a Photon Technology International (PTI) GL-301 dye laser that was pumped by a PTI GL-3300 nitrogen laser. The PL was detected by a Hamamatsu R928 PMT optically coupled to a ScienceTech Model 9010 monochromator terminated into a LeCroy Waverunner LT322 oscilloscope. Nonradiative and radiative rate constants were calculated from the quantum yields,  $\phi = k_r/(k_r + k_{nr})$  and lifetimes,  $\tau = 1/(k_r + k_{nr})$ .

Spectroelectrochemistry. Spectroelectrochemistry was performed using a Pt honeycomb working electrode with a Pt counter electrode (Pine) and non-aqueous Ag/AgCl reference electrode. The reference electrode was calibrated against an external ferrocenium/ferrocene ( $Fc^+/Fc$ ) standard ( $E^o = 630$  mV vs. NHE in CH<sub>3</sub>CN). Spectra were collected after the solution was allowed to equilibrate at each potential for 45-60 seconds with an Avantes StarLine AvaSpec-2048 UV/Visible spectrometer synchronized to a Pine Wavenow potentiostat utilizing the Aftermath software package (Pine).

*Cation Titrations.* UV-vis and PL titrations were performed on **B2B** and **D2Q** in CH<sub>3</sub>CN. Two solutions were prepared: **1**) a **B2B** (or **D2Q**) solution with a maximum MLCT absorption of 0.10 - 0.11; and **2**) a cation solution prepared by first dissolving a weighed sample of the desired cation salt in a 10 mL volumetric flask with solution **1**, from which a 50 µL aliquot was added to another 10 mL volumetric flask that was filled to a total volume of 10 mL with solution **1**. In this manner the chromophore concentration was held constant. In the titration experiments, a 5.0 mL portion of solution **1** was pipetted into a standard cuvette and was purged with CH<sub>3</sub>CN saturated argon for  $\geq$  30 minutes, after which an initial measurement (UV-vis and/or PL) was taken. Then a 100 µL glass syringe (Hamilton) was used to transfer 25 – 100 µL aliquots of solution **2** to the cuvette. After each addition, the cuvette was purged with argon for  $\sim$ 1 minute, after which a measurement was taken. A solution made from 25  $\mu$ L of **2** and 5.0 mL of **1** contained ~1/20 as much cation as chromophore.

UV-vis spectra were averaged over 3 scans. For **B2B**, steady-state PL spectra were an average of 3 scans, with 5 or more scans averaged for **D2Q**. In both cases, excitation wavelengths were chosen that had the minimum change in absorbance upon addition of cations. Time resolved PL decays were averaged over 180 - 300 laser pulses. **B2B** emission was monitored at 624 nm with **D2Q** monitored at 780 nm. **B2Q** and **D2B** were insufficiently soluble in CH<sub>3</sub>CN for titrations to be performed in this solvent. Data analysis for all experiments was performed using *Mathematica* version 10. Spectral modelling of UV-vis titration data was performed by the method of least squares.

## **5.3 Results**

A modified literature procedure for the preparation of the neutral compounds was utilized in which cis-Ru(LL)<sub>2</sub>Cl<sub>2</sub> and the sodium salt of a carboxylate bearing diimine ligand were refluxed together in water-ethanol, the ethanol removed, and the product filtered from the reaction mixture.<sup>13</sup> The isolated yield of **B2B** was 53% and > 85% for the other three compounds. Large crystals suitable for single crystal X-ray diffraction were obtained by dissolving **B2B** in methanol and allowing the solvent to evaporate slowly, Figure 5.1. Methanol present in the crystal was not well resolved and was omitted from Figure 5.1. There was no evidence of an anion present in the structure. The average Ru-N distances were 2.067 and 2.063 Å for the dcb and bpy ligands respectively, with bite angles of 79.80° and 79.05°. The other average N-Ru-N angles were 93.60° and 171.1°. Additional crystallographic data are available in Table 5.1.



**Figure 5.1** Displacement ellipsoid plot (50% probability level) for  $[Ru(dcb)(bpy)_2]$ , B2B, obtained from singlecrystal x-ray crystallography. Methanol has been omitted. Color code: green, Ru; blue, N; red, O; gray, C, and white, H.

Table 5.1 Crystal Parameters for B2B

Empirical formula	$C_{32}H_{22}N_6O_4Ru$
Formula weight	655.62
Temperature/K	100
Crystal system	monoclinic
Space group	C2
a/Å	22.771(4)
b/Å	13.1530(14)
c/Å	15.402(2)
a/°	90
β/°	130.597(8)
$\gamma/^{\circ}$	90
Volume/Å <sup>3</sup>	3502.6(9)
Z	4
$\rho_{calc}g/cm^3$	1.243
$\mu/\text{mm}^{-1}$	3.956
Crystal size/mm3	$0.241\times0.146\times0.132$
Radiation	$CuK\alpha (\lambda = 1.54178)$
Final R indexes [I>= $2\sigma$ (I)]	R1 = 0.0319, wR2 = 0.0804
Final R indexes [all data]	R1 = 0.0327, wR2 = 0.0809

Steady-state absorption spectra of the compounds in CH<sub>3</sub>OH and CH<sub>3</sub>CN are shown in Figure 5.2. Each compound displayed two absorption bands in the 400 to 600 nm range that were assigned as metal-to-ligand charge-transfer (MLCT) transitions and an intense band at 290 nm that was assigned as a ligand localized  $\pi \rightarrow \pi^*$  transition. Both **B2Q** and **D2Q** displayed an additional broad, structured absorption feature with an onset at ~390 nm assigned as a dcbq centered  $\pi \rightarrow \pi^*$  transition.



**Figure 5.2** A: Absorbance (solid) and PL (dashed) spectra of neutral sensitizers in CH<sub>3</sub>OH. B: Absorbance (solid) and normalized PL (dashed) spectra in CH<sub>3</sub>CN.

Light excitation into the MLCT absorption bands of all four compounds resulted in room temperature photoluminescence, PL, Figure 5.2. For **B2B** and **D2B**, this PL was visible to the unaided eye. Pulsed light excitation of **B2B** and **D2Q** resulted in PL decays that were well described by a first-order kinetic model. The compounds **D2B** and **B2Q** were not sufficiently soluble for characterization in  $CH_3CN$  and were not studied further. Photophysical data for the four compounds are summarized in Table 5.2.

Compound	MLCT $\lambda_{abs}$ (nm), $\varepsilon (M^{-1}cm^{-1})/10^{3}$	$\lambda_{PL}$ , nm	$\tau, \mu s^b$	$\phi_{\rm PL}$	$k_r,  {\rm s}^{-1}/10^4$	$k_{nr},  {\rm s}^{-1}/10^4$
B2B	455, 13.8 430, 11.2 (454, 13.7) (430, 11.8)	624 (630)	$1.3 \pm 0.1$ (1.2 ± 0.3)	0.072 (0.095)	5.5 (7.9)	71 (75)
D2B	460, <i>13.6</i> 430, <i>11.2</i>	644	$1.2 \pm 0.1$	0.092	7.7	76
B2Q	529, 9.1 445, 7.5	757	$0.21 \pm 0.02$	0.0027	1.3	480
D2Q	543, 9.2 445, 8.7 (532, 11.0) (452, 10.9)	776 (761)	$0.13 \pm 0.01$ (0.40 ± 0.07)	0.0021 (0.0056)	1.6 (1.4)	770 (250)

Table 5.2 Photophysical Properties of Neutral Ru Compounds<sup>a</sup>

<sup>a</sup>Values in parentheses were acquired in CH<sub>3</sub>CN; other values were acquired in CH<sub>3</sub>OH. <sup>b</sup>Standard deviations were determined from a statistical analysis of multiple experiments.

All titration experiments were performed in CH<sub>3</sub>CN. Figure 5.3 shows the absorption and PL spectra of **D2Q** in CH<sub>3</sub>CN as Mg(ClO<sub>4</sub>)<sub>2</sub> was titrated into the solution. With the addition of Mg<sup>2+</sup>, the MLCT transition centered at ~532 nm red shifted to 552 nm while the absorption centered near 452 nm blue shifted to 440 nm. A red shift was also observed in the onset of the  $\pi \rightarrow \pi^*$  transition of dcbq. No isosbestic points were apparent. The PL maxima shifted from 761 nm in neat CH<sub>3</sub>CN to ~800 nm at the highest Mg<sup>2+</sup> concentration. This change was concomitant with a 30% decrease in intensity, while the absorbance change at the 540 nm excitation wavelength was < 6%. The addition of Mg<sup>2+</sup> to **D2Q** decreased the lifetime from 0.33 µs to 0.20 µs by a Ru:Mg ratio of 1.5:1. In all cases, satisfactory fits to a first-order kinetic model were obtained throughout the titration. However, the data could also be fit to a bi-exponential kinetic model by setting the two lifetimes as the lifetime in neat CH<sub>3</sub>CN and at high cation concentration. Studies with the other Lewis acidic cations showed similar behavior. In all cases, the spectral changes were found to saturate at high cation concentrations beyond which increased cation concentration had little influence on the measured spectra or lifetimes.


**Figure 5.3** The UV-vis absorbance spectra (A) and PL spectra (B) of **D2Q** with the addition of  $Mg(ClO_4)_2$  to the CH<sub>3</sub>CN solution. Arrows indicate the direction of change with increasing  $Mg^{2+}$  concentration.

Figure 5.4 shows the absorption and PL spectra of **B2B** in neat CH<sub>3</sub>CN as Mg(ClO<sub>4</sub>)<sub>2</sub> was titrated into the solution. Addition of up to 1/3 equivalent Mg<sup>2+</sup> enhanced the MLCT absorbance and increased the PL intensity by 90%. The excited state lifetime increased from 0.9  $\mu$ s to 1.6  $\mu$ s. Addition of Mg<sup>2+</sup> beyond 1/3 equivalent caused a red shift and a 30% decrease in the PL intensity with maintenance of an isosbestic point at 471 nm. Addition of up to 100  $\mu$ M TBA<sup>+</sup> to **B2B** resulted in no measureable changes in either absorption or PL spectra. However the other divalent and trivalent Ca<sup>2+</sup>, Zn<sup>2+</sup>, Al<sup>3+</sup>, Y<sup>3+</sup>, and La<sup>3+</sup> cations also induced a red shift in the MLCT and PL, similar to Mg<sup>2+</sup> (Figures S5.3 and S5.5). Titration with Na<sup>+</sup> and Li<sup>+</sup> cations induced a smaller increase in the PL intensity and only a very slight red shift at higher cation concentrations.



**Figure 5.4** The UV-vis absorbance spectra (A) and PL spectra (B) of **B2B** in CH<sub>3</sub>CN with the addition of  $Mg(ClO_4)_2$  solution. The inset magnifies the peak of the MLCT region. Arrows indicate the direction of change with increasing  $Mg^{2+}$  concentration.

Modelling the **D2Q** or **B2B** absorption spectra obtained during titration experiments required the linear combination of no fewer than three spectra, as depicted by Equation 5.3:

$$\mathbf{S} = \mathbf{c}_1 \times \mathbf{S}_1 + \mathbf{c}_2 \times \mathbf{S}_2 + \mathbf{c}_3 \times \mathbf{S}_3 \tag{5.3}$$

where S was the measured spectrum and  $c_1$ ,  $c_2$ , and  $c_3$  were the fractions of spectra  $S_1$ ,  $S_2$  and  $S_3$ , required to simulate the measured spectra at each Mg<sup>2+</sup> concentration. The spectrum  $S_1$  was constrained to be that of **B2B** or **D2Q** in neat CH<sub>3</sub>CN.  $S_3$  was that measured beyond the saturation point of the titration, where additional Mg<sup>2+</sup> did not influence the measured spectra.



**Figure 5.5** Fractional contributions of the three spectra,  $S_1$ ,  $S_2$ , and  $S_3$  plotted against the ratio of  $Mg^{2+}$  to Ru. The concentrations of **D2Q** and **B2B** were ~ 8  $\mu$ M. The vertical lines show where the [**D2Q**]/[Mg<sup>2+</sup>] ratio is 3:1 and 1.5:1 and where the [**B2B**]/[Mg<sup>2+</sup>] ratio is 3:1 and 1:1.

 $S_2$  was identified as the spectrum that best fit the titration data at intermediate cation concentrations. Visual inspection and least squares analysis revealed that this spectrum was measured at a 3:1 Ru:Mg<sup>2+</sup> molar ratio (Figure S5.1). The coefficients  $c_1$ ,  $c_2$ , and  $c_3$  were plotted against the total Mg<sup>2+</sup> concentration, Figure 5.5. For **D2Q**, the growth of the final spectrum was found to begin saturating at a 1.5:1 Ru:Mg<sup>2+</sup> molar ratio while for **B2B** the final spectrum saturated more sharply at a 1:1 Ru:Mg<sup>2+</sup> molar ratio. Similar analysis was performed with all the cations under investigation and the results are given in the Supporting Information. This analysis showed that the spectral changes with the monocations were simply too small for meaningful analysis. The other cations have "turning points" at approximately the same ratios (3:1 and 1:1 Ru:M<sup>n+</sup>), with the notable exception of Zn<sup>2+</sup>, which appeared at 2:1 and 1:1 ratios for both **B2B** and **D2Q**, and Al<sup>3+</sup> with **B2B** that had turning points at 4:1 and 1:1.

The UV-vis absorption and steady state PL titrations of **B2B** and **D2Q** solutions were repeated with Li<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Zn<sup>2+</sup>, Al<sup>3+</sup>, Y<sup>3+</sup>, and La<sup>3+</sup>. All of these cations induced a measureable red shift in the MLCT absorption and PL maximum that saturated at high cation concentrations; the energy of the MLCT absorption or PL maximum was subtracted from the maximum measured in neat acetonitrile,  $\Delta E$ , and was plotted against the cation charge-to-size ratio,<sup>19</sup> Figure 5.6. These data showed that cations with greater charge density induced larger spectral shifts attributed to stabilization of the MLCT excited state.



**Figure 5.6** The MLCT absorption and the PL spectral shift,  $\Delta E$  for **D2Q** (left) and **B2B** (right) plotted against the cation charge-to-size ratio.  $\Delta E$  represents the energy of maximum absorption or maximum PL measured in neat CH<sub>3</sub>CN subtracted from that measured with an excess of the indicated cation. Error bars indicate  $\pm 1$  nm converted to cm<sup>-1</sup> at the relevant wavelengths.

The low solubility of **B2B** and **D2Q** frustrated attempts to measure formal reduction potentials by cyclic voltammetry or square wave voltammetry, but spectroelectrochemical data for **B2B** were obtained in the presence of either 1 mM TBA<sup>+</sup> or Mg<sup>2+</sup> perchlorate acetonitrile electrolytes (Figure S5.4). The bleach of the MLCT absorption consistent with Ru<sup>II</sup>  $\rightarrow$  Ru<sup>III</sup> was quantified as well as the more intense transitions in the ultraviolet region. In the TBA<sup>+</sup> solution, the Ru(III/II) potential of **B2B** was E<sup>o</sup> = 1.20 ± 0.08 V vs. NHE and increased to 1.67 ± 0.06 V vs. NHE when an excess of Mg<sup>2+</sup> was present. The presence of Mg(ClO<sub>4</sub>)<sub>2</sub> increased the solubility of **B2B**. Therefore a second measurement of a more concentrated **B2B** solution in 100 mM Mg<sup>2+</sup> was performed. Under these conditions, a Ru(III/II) potential of 1.63 ± 0.02 V vs. NHE was obtained, indicating that uncompensated solution resistance in the 1 mM salt solutions was not a significant factor. Attempts to quantify the Ru(III/II) potential for **D2Q** or the ligand reduction potentials of either compound were unsuccessful.

The time-resolved PL decay from **B2B**<sup>\*</sup> in an acetonitrile solution that contained a 2:1 molar ratio of **B2B** to **D2Q** required bi-exponential kinetics when  $Mg^{2+}$  was added. The longlived component maintained a lifetime similar to that measured in the absence of **D2Q**, while the other had a much shorter lifetime, 10 - 45 ns, Figure 5.7. The PL decays were insensitive to a further increase in the  $Mg^{2+}$  concentration once a ~1:1 Ru:Mg<sup>2+</sup> ratio was established. The lifetime of **D2Q**<sup>\*</sup> underwent approximately the same decrease as was described for **D2Q**<sup>\*</sup> in the absence of **B2B**. Time-resolved PL measurements of 2:1 **B2B** to **D2Q** solutions in the presence of the other polyvalent metal cations (Ca<sup>2+</sup>, Zn<sup>2+</sup>, Al<sup>3+</sup>, Y<sup>3+</sup>, and La<sup>3+</sup>) resulted in bi-exponential kinetics with approximately the same lifetimes as with  $Mg^{2+}$ , but the PL remained single-exponential with the monovalent cations, Li<sup>+</sup> and Na<sup>+</sup>.



**Figure 5.7.** Time-resolved PL monitored at 624 nm after pulsed light excitation of a 2:1 **B2B:D2Q** CH<sub>3</sub>CN solution with added Mg(ClO<sub>4</sub>)<sub>2</sub>, The arrow indicates the direction of change with increasing Mg<sup>2+</sup> concentration. The inset shows the PL decays on a shorter time scale in neat CH<sub>3</sub>CN and at the highest Mg<sup>2+</sup> concentration.

## **5.4 Discussion**

The synthetic procedure described herein provides a general method for the high yield synthesis of neutral Ru diimine compounds directly from reaction of *cis*-Ru(LL)<sub>2</sub>Cl<sub>2</sub> and the sodium salt of a dicarboxylate diimine ligand. The spectroscopic properties were fully consistent with the assignment of neutral compounds with carboxylate functional groups. Titrations with Lewis acidic cations induced characteristic changes in the absorption and photoluminescence properties of the Ru compounds in acetonitrile solutions that were absent in methanol solutions. Taken together the spectroscopic data provide compelling evidence that these Lewis acidic cations form adducts with the Ru compounds, stabilize the excited states, and in one case result in a change in excited state localization. These conclusions are discussed in more detail below within the context of relevant literature reports. Some implications of these findings for solar energy conversion are also discussed.

*Evidence for Adduct Formation.* Decades of research on organic acids have shown that substituent effects of a carboxylic acid are in fact best understood as an electric field effect, rather than an inductive effect.<sup>21,22</sup> The difference being that the field effect is transmitted directly through space rather than along bonds. Hence the cation induced spectral changes described herein may be due to the field created by the charged ion, the extent of charge redistribution in the proposed Lewis acid-base adduct(s), or, most probably, some combination of the two. In this study like those before, it was difficult if not impossible to rationally separate the relative contributions of the two effects. In the text below the inductive contributions are described, but it should be emphasized that substantial electric fields are also present and it is their combined action that is most relevant to this acid-base chemistry.

The addition of metal cation salts to acetonitrile solutions of the neutral Ru(II) diimine compounds resulted in significant shifts of the absorption and PL spectra. Titration experiments showed that the magnitude of the spectral shift was correlated with the cation charge-to-size ratio. At these same ion concentrations, no significant spectral changes were observed with the tetrabutylammonium cation that lacked Lewis acidity. Taken together this behavior was consistent with the formation of adducts between the cations and the neutral Ru compounds. Attempts to abstract equilibrium constants from the titration data were frustrated by small spectral changes for weaker Lewis acids like Li<sup>+</sup> and Na<sup>+</sup> and by what appeared to be nearly stoichiometric reactions with the more Lewis acidic cations like  $Mg^{2+}$ ,  $K_{eq} > 10^6 M^{-1}$ , seen as sharp transitions in the titration curves (Figure 5.5). It is interesting to note that the time-resolved PL decays remained single-exponential as cations were titrated into the solutions even though two emitting species were expected. Our inability to kinetically resolve this likely results from the similarity of the two lifetimes. A further challenge was that clean isosbestic points were rarely observed suggesting the presence of several Lewis acid-base adducts. Indeed, full spectral modelling revealed that at least three species with unique absorption spectra were required to model the titration data with a given cation. The observed saturation points of 3:1 and 1:1  $Ru:M^{n+}$  may be indicative of the empirical formulas of the major adduct(s) present at these points in the titration.

Kinetic evidence for adduct formation was discovered in PL experiments of a 2:1 B2B:D2Q mixture. The MLCT excited state of B2B was significantly quenched when polyvalent cations were added to the solution. The short-lived B2B\* excited state,  $\tau < 45$  ns, was not observed unless both D2Q and a Lewis acidic cation were present, allowing diffusional quenching to be ruled out. Hence the B2B and D2Q must be in close proximity, most likely through a cation carboxylate bridge. The quenching mechanism(s) is unknown, however, as energy transfer (B2B\*-D2Q  $\rightarrow$  B2B-D2Q\*) and electron transfer (B2B\*-D2Q  $\rightarrow$  B2B<sup>+</sup>-D2Q) are both thermodynamically favorable. Energy transfer would lead to the rapid formation of D2Q\* that was not observed by PL, therefore the electron transfer pathway is favored. Electron transfer through H-bonded carboxylate compounds has been reported,<sup>23,24</sup> as has electron transfer between cation bridged compounds on a semiconductor surface.<sup>25</sup> To our knowledge this is the first evidence for electron transfer through a metal cation salt-bridge in solution, and furthermore, between compounds that do not undergo electron transfer in the absence of the bridge. It is interesting that the same appearance of bi-exponential kinetics and PL quenching was not observed with Na<sup>+</sup> or Li<sup>+</sup> addition, implying that these cations do not form salt bridges. This may be explained by the local neutrality of a carboxylate – monovalent cation adduct, for which there is less coulombic incentive for the inclusion of another carboxylate.

The spectroscopic data reported herein does not provide direct information on the structure of the Lewis acid-base adducts present in solution. There is literature precedence for Lewis acidic cations forming adducts with the  $\pi$  electrons of aromatic compounds<sup>26</sup> and with carboxylates.<sup>27–32</sup> Although speculative, the data reported here are most consistent with expectations based on hard-soft acid base chemistry and the presence of cation–carboxylate adducts. There are indeed a tremendous number of metal carboxylates known in the synthetic and biological literature.<sup>33,34</sup> For example, there are known crystal structures of Mg<sup>2+</sup> carboxylates containing arrangements of many Mg<sup>2+</sup> ions bridged by multiple different carboxylate binding modes.<sup>32</sup>

Direct detection of such adducts by solution IR or NMR spectroscopies was unsuccessful due to the low solubility of the neutral Ru diimine compounds. Indeed their solubility in acetonitrile was a significant issue and restricted measurements to UV-visible absorption and PL spectroscopy of **B2B** and **D2Q**. Electrospray ionization mass-spectrometry was also attempted but gave no evidence for the presence of adducts. All four of the synthesized compounds showed much greater solubility in more polar solvents like methanol, however no evidence of adduct formation was garnered from cation titration studies in this solvent. Presumably methanol solvation of the cations, and perhaps the carboxylates, disfavors a measureable equilibrium concentration of the metal-carboxylate adducts.

*Cation Induced Excited State Stabilization and Localization*. The titration data with **D2Q** were particularly informative of how the proposed Lewis acid-base chemistry influences the excited state. The absorption properties of the neutral **D2Q** was similar to that of the fully protonated compound where resonance Raman experiments have previously demonstrated that the low energy metal-to-ligand charge transfer (MLCT) absorption band was  $Ru \rightarrow dcbq$  in nature and the higher energy MLCT band was  $Ru \rightarrow bpy$ .<sup>13</sup> Adduct formation with Lewis acidic cations caused the lower energy band to red shift while the higher energy MLCT absorption underwent a blue shift. A red shift of the PL spectra was also observed that was accompanied by a decreased PL intensity and excited state lifetime. Taken together the data are most consistent with cation induced stabilization of the emissive dcbq-based excited state and a destabilization of the higher energy dtb-based MLCT transition. The spectral shifts can be rationalized based on expectation of charge redistribution in the Lewis acid-base adducts. Electron donation from the carboxylate groups on dcbq to the cations lowers electron density on the Ru center resulting in a more positive Ru<sup>III/II</sup> formal reduction potential. The dtb based  $\pi^*$ orbitals are not greatly influenced by this adduct formation, and a blue shift in the Ru  $\rightarrow$  dtb MLCT absorption band results. The dcbg ligands, on the other hand, are stabilized by adduct

formation with cations to a much greater extent than the positive shift in the Ru<sup>III/II</sup> reduction potential and a red shift results. These changes are summarized pictorially in Scheme 5.2 below. Note that for **B2B** a significant 450 mV shift in the Ru(III/II) potential was observed when the TBAClO<sub>4</sub> electrolyte was replaced with Mg(ClO<sub>4</sub>)<sub>2</sub>, consistent with the expectation in Scheme 5.2. As the energy gap between the dcbq  $\pi^*$  orbitals and the metal d orbitals decreased through cation stabilization in the Lewis acid-base adducts, the decreased excited state lifetimes observed were expected based on Jortner's energy gap law.<sup>35</sup>



The photophysical behavior of **B2B** in neat acetonitrile with low concentrations of the Lewis acidic cations was particularly interesting. The addition of any Lewis acidic cation resulted in a significant increase in the MLCT absorption, the PL intensity, and the excited state lifetime. This behavior was observed with  $Mg^{2+}$  even when 100  $\mu$ M tetrabutylammonium cations were present. For all the cations except Li<sup>+</sup> and Na<sup>+</sup>, the continued addition of Lewis acidic cations resulted in a red shift and a decrease in the PL intensity like that observed for **D2Q**, (Figure S5.5). It is the initial increase in absorptivity and PL intensity that are of particular interest. This behavior is attributed to a cation-induced change in the nature of the lowest lying MLCT excited state as described below and shown qualitatively in Scheme 5.3.

Scheme 5.3 Excited State Localization of B2B in the Absence and Presence of Lewis Acidic Cations.



As described in the Introduction section, it is well established that the MLCT excited states of heteroleptic Ru diimine compounds are localized on the ligand that is most easily reduced. A comparison of 4,4'-(CO2)2-2,2-bipyridine (dcb) with 2,2-bipyridine (bpy) centers around whether  $-CO_2^-$  is more electron withdrawing or donating then -H. Carboxylate has an identical Hammett parameter to the H atom which is defined as zero.<sup>18</sup> This suggests that the reduction potentials of the coordinated dcb and bpy ligands are similar and that subtle changes in the environment may influence the nature of the MLCT excited state. As an electron is formally localized on a single diimine ligand in the MLCT excited state, the anionic nature of the dcb ligand may provide unfavorable coulombic interactions that could be overcome by adduct formation with Lewis acidic cations. Adduct formation with the mono-, di-, and tri-valent cations under study lowers Coulombic repulsion and, at the same time, the Lewis acid-base interaction transfers some charge from the carboxylate to the cation that stabilizes this excited state. Ruthenium polypyridyl compounds with excited states localized on dcb ligands are known to be more emissive than those localized on unsubstituted or alkyl-substituted bipyridine ligands. This has been attributed to a mesomeric effect where enhanced conjugation between the carboxylate and the pyridine ring results in greater delocalization of the excited state and a longer lifetime.<sup>36</sup> In a recent pH dependent study, excited states localized on dcb ligands were

about a factor of two more emissive than those localized on alkyl disubstituted bipyridines, which is in good agreement with the ~ 90% enhancement observed here.<sup>12</sup> Hence the increase in PL intensity with a negligibly small spectral shift observed at low cation concentrations is completely consistent with a change in the location of the excited state, bpy in neat acetonitrile and dcb in acetonitrile solutions with Lewis acidic cations.

Decreased coulombic repulsion and stabilization of the dcb based MLCT excited state induced by Lewis acid-base interactions thus readily explain the measured **B2B** spectra during titration experiments. The data reported do not address the dynamics of these processes. For example, if a **B2B**\* were to form an adduct with a Lewis acidic cation in the excited state, would the excited state reorient? The titration data and the interpretation imply yes, the excited state would indeed reorient. One can envision that light absorption influences the ground state equilibrium and that a new quasi-equilibrium is established in the long-lived MLCT excited states. When the cations are protons, this gives rise to the well-documented photo-acid and photo-base properties of excited states where **B2B** is well known to be a photo-base, i.e. more basic in the excited state than in the ground state.<sup>12,37</sup> The data reported here suggest that cations with Lewis acidity, in addition to Brønsted acidity, may also be detected, released and/or collected by luminescent excited states.

Implications for Solar Energy Conversion. One feature of Ru polypyridyl compounds that makes them ideal for solar applications is their ability to rectify charge at interfaces. Excited state electron transfer occurs from an electron formally localized in the bipyridine  $\pi^*$  orbitals while the unwanted recombination reactions involve electron transfer to the metal d-orbitals. Hence in dye-sensitized solar cells and emerging forms of solar cells based on metal organic frameworks and other materials, it is desirable to locate the electron acceptor proximate to the ligand on which the excited state will localize.

In metal organic framework materials, the 5,5'-(CO<sub>2</sub>H)<sub>2</sub>-2,2'-bipyridine ligand is most commonly used due to the nearly linear orientation of the carboxylate groups that results in the crystalline solid state.<sup>13-15</sup> Cations are generally divalent with Zn<sup>2+</sup> being most relevant to these studies. Redox active metals like  $Cu^{2+}$  have also been utilized in MOFs, although  $Cu^{2+}$  is expected to significantly shorten the excited state lifetime.<sup>38</sup> Interestingly, the  $\pi^*$  acceptor levels of 5,5'-disubstituted bipyridine compounds are at lower energy than are the corresponding 4,4'disubstitited bipyridine compounds. This is evident in their visible absorption spectra where the 5,5'- compounds absorb light at longer wavelengths and also in the electrochemistry where the ligands are 200 - 300 mV more easily reduced.<sup>39</sup> The largest spectral shift reported here was ~1200 cm<sup>-1</sup> (~150 meV) with Al<sup>3+</sup>, which would further stabilize the 5,5'- ligand localized excited state, so it is unlikely that adduct formation with cations would influence excited state localization like that observed for **B2B**. Such changes in the excited state localization may instead be observed in the layer-by-layer approach of assembling molecules at interfaces based on the interactions of Zr(IV) and other metal cations with phosphonate groups.<sup>25,40–44</sup> With phosphonate groups conjugated to bipyridine rings, the Lewis acid-base chemistry described here would be expected. Indeed in both metal organic frameworks and for interfaces synthesized in the layer-by-layer approach, the cations are expected to influence the  $\pi^*$  levels of the diimine ligand to an extent predicted by the cation charge-to-size ratio.

Ruthenium compounds with the dcb ligand are directly relevant to many studies of dyesensitized solar cells. Indeed Goodenough proposed the carboxylic acid form of **B2B** for dye sensitization studies back in the 1970s.<sup>45</sup> It was also shown that **B2B** anchored to the

mesoporous  $TiO_2$  thin films had a very low quantum yield for excited state injection in neat acetonitrile,  $\phi < 0.01$ , that increased to 0.51 when 1.0 M LiClO<sub>4</sub> was present.<sup>46</sup> This behavior was reasonably attributed to a lowering (i.e. away from the vacuum level) of the TiO<sub>2</sub> acceptor states induced by Li<sup>+</sup> adsorption to the oxide surface.<sup>47</sup> Other alkali and alkaline earth cations were reported to enhance the excited state injection yields in a similar manner. The results provided herein indicate that the location of the excited state may have been an additional factor. If surface anchoring to TiO<sub>2</sub> did not appreciably influence energetics, the excited state would be localized on a remote bpy ligand in neat acetonitrile that was not strongly coupled to the semiconductor surface. The addition of cations would yield a dcb localized excited state better oriented for excited state injection. Similarly, long chain hydrocarbons or bulky t-butyl groups have been placed in the 4 and 4'positions of biypridine to sterically block unwanted electron transfer with the redox mediators,<sup>48</sup> and the results here suggest that an additional benefit of these substitutions is that they force the excited state to remain localized on the dcb ligand in compounds of the type, cis-Ru(dcb)(bpy')(NCS)<sub>2</sub>, resulting in a higher excited state injection yield.

The chemical nature of cations present in the external electrolyte of dye-sensitized solar cells is known to influence many aspects of the cells. These include the aforementioned excited state injection yields, as well as the transport of the injected electrons to the external circuit, dye 'regeneration' through iodide oxidation, and screening of the electric fields created by excited state injection.<sup>49</sup> In some regards, the titration data reported here can be viewed as control experiments that show such behavior is unique to the mesoporous TiO<sub>2</sub> thin film. Control experiments of this type have appeared, but are often focused on the protonated from of the

ligand, i.e. dcbH<sub>2</sub>. It is now understood that Lewis acidic cations may also interact with the dye molecule and that control experiments are best performed with the carboxylate forms of the dye.

## **5.5 Conclusions**

The acid-base chemistry of four neutral, carboxylate containing ruthenium diimine compounds with Lewis acidic cations were characterized by absorption and PL spectroscopies. In polar methanol solution, the spectral properties of the compounds were unaffected by the presence of the cations. In acetonitrile, compelling evidence for adduct formation was garnered from titration experiments where the magnitude of the spectral shifts were correlated with the cation charge-to-size ratio. For  $[Ru(dcbq)(bpy)_2]$ , the low energy  $Ru \rightarrow dcbq$  metal-to-ligand charge transfer (MLCT) absorption shifted to lower energy with adduct formation, while the Ru  $\rightarrow$  bpy MLCT shifted to higher energy; behavior rationalized by the inductive nature of Lewis acid-base cation-carboxylate adducts. Cation titration experiments with  $[Ru(dcb)(bpy)_2]$ provided compelling evidence that the MLCT excited state was localized on the bpy ligand in neat CH<sub>3</sub>CN and on the dcb ligand when a significant concentration of cations were present. The data show that Lewis acid-base adduct formation has a strong influence on the energetics of charge transfer excited states that need be taken into account for applications in dye-sensitized mesoporous materials, metal-organic frameworks, layer-by-layer deposited thin films, and emerging classes of solar cells.

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## **APPENDIX 1. SUPPORTING INFORMATION FOR CHAPTER 2.**

**Figure S2.01.** UV-vis absorption spectra of (a) C2/TiO<sub>2</sub> (b) C3/TiO<sub>2</sub> (c) C4/TiO<sub>2</sub> measured at different applied potentials in 0.5 M LiClO<sub>4</sub> CH<sub>3</sub>CN solutions. The insets show the fraction (x) of dye molecules present in the fully reduced state (black squares), singly oxidized state (red squares) and doubly oxidized state (green squares). Overlaid are sigmoidal fits,  $x=1/(1+10\exp((Eapp-E^{\circ}1/2)/a\times59mV))$ , where a is the non-ideality factor.

**Table S2.1** Calculated dipole moment vector components, orientation with respect to the  $TiO_2$  surface normal, and electrostatic potential drop for C2, C4, and C5 in their two protonation studied states (a, triprotonated and b, diprotonated) and in their two oxidation states (Ru(II) and Ru(III)).

			μ <sub>x</sub>	μ	μ <sub>z</sub>	μ	θ (°)	<b>¢</b> <sub>dipole</sub> (m∨)	$\Delta \phi_{dipole}$ (mV)
Ground State	C2	a	1.61	2.64	-4.29	5.3	27.61	-25	
		b	0.88	23.84	-13.44	27.4	43.63	-105	
	C4	a	1.87	3.91	-3.15	5.4	40.49	-22	
		b	9.15	23.70	-12.05	28.1	41.96	-110	
	C5	a	1.30	4.74	-5.74	7.6	43.07	-29	
		b	10.36	24.44	-14.11	30.1	39.58	-122	
<b>Oxidized State</b>	<b>C2</b> <sup>+</sup>	a	17.56	4.09	-9.86	20.5	9.54	-107	-82
		b	35.10	26.98	-13.60	46.3	26.05	-220	-115
	C4 <sup>+</sup>	a	29.57	7.48	-6.15	31.1	-0.85	-164	-142
		b	43.55	23.29	-11.69	50.8	17.38	-256	-146
	C5 <sup>+</sup>	a	29.81	7.34	-11.75	32.9	-4.62	-173	-144
		b	47.93	24.16	-14.18	55.5	18.28	-278	-156



Figure S2.2. Frontier molecular orbitals for the three studied complexes in their ground states.



Figure S2.03. Frontier Molecular Orbitals for the three studied complexes in their oxidized state with one carboxylic acid group deprotonated.



**Figure S2.04.** Absorption change monitored at 640 nm after 532 nm light excitation for C5/TiO<sub>2</sub> immersed in 50 mM LiClO<sub>4</sub> CH<sub>3</sub>CN at -45 °C. The data correspond to intra-molecular Ru<sup>III</sup>  $\rightarrow$  NAr<sub>3</sub> hole transfer with an overlaid fit to a first-order kinetic model.



**Figure S2.05.** Absorption change monitored at 550 nm after pulsed light excitation (532 nm) of C1-C5/TiO<sub>2</sub> immersed in 0.5 M LiClO<sub>4</sub> CH<sub>3</sub>CN. Overlaid in yellow is the best fit to the KWW kinetic model.



**Figure S2.06.** Absorption change monitored at 740 nm after pulsed light excitation (532 nm) of C5/TiO<sub>2</sub> immersed in 0.5 M LiClO<sub>4</sub> CH<sub>3</sub>CN at 1/5 saturation surface coverage (black) and saturation surface coverage (red).



**Figure S2.07.** The ATR-FTIR spectra of C4/TiO<sub>2</sub> (blue),  $H_2SO_4$  treated C4/TiO<sub>2</sub> (red) and C4 powder (black). The green dashed line serves as a guide line for the peaks appearing at 1712 cm<sup>-1</sup>.



Figure S2.08. The UV-vis absorption of C1/TiO<sub>2</sub>, C1<sup>+</sup>/TiO<sub>2</sub> and C1<sup>2+</sup>/TiO<sub>2</sub>



Figure S2.09. ATR-FTIR spectrum of E4/TiO<sub>2</sub>



Figure S2.10. Plot of open circuit voltages of C2/TiO<sub>2</sub>, C4/TiO<sub>2</sub> and C5/TiO<sub>2</sub> in 0.5 M LiClO<sub>4</sub> CH<sub>3</sub>CN non-regenerative electrolyte versus steady state irradiances.



**Figure S2.11.** Absorption changes monitored at 540 nm after pulsed light excitation with five irradiances ( $\lambda_{ex} = 532$  nm 0.3-1.5 mJ/cm<sup>2</sup>) of **C1**/TiO<sub>2</sub> immersed in 0.5 M LiClO<sub>4</sub> CH<sub>3</sub>CN and biased at 1035 mV versus NHE. Overlaid as solid lines are absorption profiles abstracted from Monte Carlo simulations of 8 TiO<sub>2</sub> nanoparticles (2×2×2 array).



**Figure S2.12.** Chi-Squared analysis (a) and residuals for the highest S/N data (b) of Monte Carlo simulations for lateral hole transfer reactions occurring on a single nanocrystal (black), an 8 nanocrystal array (red) and a 27 nanocrystal array (blue). Chi-squared values were calculated using 1000 points evenly spaced on a logarithmic scale. Experimental values were a 21-point moving average of the raw data.



**Figure S3.1**. Square wave voltammetry of compounds 1-5 in a CH<sub>3</sub>CN solution containing 100 mM TBAClO<sub>4</sub> using an internal  $Fc^+/Fc^0$  standard (630 mV vs. NHE).



**Figure S3.2.** Absorbance of a  $TiO_2$  thin film sensitized with the indicated chromophore after white light illumination. The red spectrum is prior to illumination, with subsequent spectra after 60 min increments except the final (purple) spectrum, after 1400 min.



**Figure S3.3**. Absorbance spectra of  $TiO_2$  thin films sensitized with compounds **1-5** before (solid) and after (dashed) holding the films at ~1.7 V vs. NHE for 960 min. The spectra are normalized such that the maximum MLCT absorbance is 1 before the application of a potential.





**Figure S4.01**: <sup>1</sup>H NMR of 4,4'-diethanolamide-2,2'-bipyridine (dea) in DMSO-d<sub>6</sub> at 600 MHz and 298K.



Figure S4.02: <sup>13</sup>C NMR of 4,4'-diethanolamide-2,2'-bipyridine (dea) in DMSO-d<sub>6</sub> at 600 MHz and 298K.



Figure S4.03: <sup>1</sup>H NMR of  $[Ru(dtb)_2(dea)](PF_6)_2$  in  $CD_2Cl_2$  at 600 MHz and 298K.



Figure S4.04: <sup>13</sup>C NMR of [Ru(dtb)<sub>2</sub>(dea)](PF<sub>6</sub>)<sub>2</sub> in CD<sub>2</sub>Cl<sub>2</sub> at 600 MHz and 298K.



Figure S4.05: High-resolution mass spectrum of [Ru(dtb)<sub>2</sub>(dea)](PF<sub>6</sub>)<sub>2</sub>.



Figure S4.06: Difference absorption spectra upon titration of  $C1^{2+}$  (concentration of 10  $\mu$ M) in acetonitrile with tetrabutylammonium chloride.



Figure S4.07: Difference absorption spectra upon titration of  $C1^{2+}$  (concentration of 10  $\mu$ M) in acetonitrile with tetrabutylammonium bromide.



Figure S4.08: Photoluminescence increase upon titration of  $C1^{2+}$  in acetonitrile with tetrabutylammonium bromide.



Figure S4.09: Difference absorption spectra upon titration of  $C1^{2+}$  (concentration of 10  $\mu$ M) in acetonitrile with tetrabutylammonium iodide.



Figure S4.10: Photoluminescence increase upon titration of  $C1^{2+}$  in acetonitrile with tetrabutylammonium iodide.



Figure S4.11: Difference absorption spectra upon titration of  $C1^{2+}$  (concentration of 10  $\mu$ M) in dichloromethane with tetrabutylammonium bromide.



**Figure S4.12**: Difference absorption spectra upon titration of  $C1^{2+}$  (concentration of 10  $\mu$ M) in dichloromethane with tetrabutylammonium iodide. Triiodide, in a concentration smaller than 3 $\mu$ M, is produced in dichloromethane during titration.



**Figure S4.13**: <sup>1</sup>H NMR titration (aromatic region) of  $C1^{2+}$  in CD<sub>3</sub>CN with tetrabutylammonium iodide at 500 MHz and 298K.



**Figure S4.14**: <sup>1</sup>H NMR titration (aliphatic region) of  $C1^{2+}$  in CD<sub>3</sub>CN with tetrabutylammonium iodide at 500 MHz and 298K.



**Figure S4.15:** Job plot analysis of the interaction between  $C1^{2+}$  and iodide in acetonitrile. Inset represents the observed chemical shift for selected protons after each addition of tetrabutylammonium iodide.


**Figure S4.16**: <sup>1</sup>H NMR titration (aromatic region) of  $C1^{2+}$  in CD<sub>3</sub>CN with tetrabutylammonium chloride at 500 MHz and 298K.



Figure S4.17: <sup>1</sup>H NMR titration (aliphatic region) of  $C1^{2+}$  in CD<sub>3</sub>CN with tetrabutylammonium chloride at 500 MHz and 298K.



Figure S4.18: Job plot analysis of the interaction between  $C1^{2+}$  and chloride in acetonitrile. Inset represents the observed chemical shift for selected protons after each addition of tetrabutylammonium chloride.



**Figure S4.19**: <sup>1</sup>H NMR titration (aromatic region) of  $C1^{2+}$  in  $CD_2Cl_2$  with tetrabutylammonium chloride at 500 MHz and 298K.



**Figure S4.20:** <sup>1</sup>H NMR titration (aliphatic region) of  $C1^{2+}$  in  $CD_2Cl_2$  with tetrabutylammonium chloride at 500 MHz and 298K.



**Figure S4.21**: Job plot analysis of the interaction between  $C1^{2+}$  and chloride in dichloromethane. Inset represents the observed chemical shift for selected protons after each addition of tetrabutylammonium chloride.



Figure S4.22: Titration of  $C1^{2+}$  in dichloromethane with tetrabutylammonium iodide with 0.1 M TBAClO<sub>4</sub> electrolyte.



Figure S4.23: Titration of  $C1^{2+}$  in dichloromethane with tetrabutylammonium iodide with 1 mM TBAClO<sub>4</sub> electrolyte. Inset represents the Stern-Volmer analysis using the lifetime data as well as the emission data.



Figure S4.24: Photoluminescence increase upon titration of  $C1^{2+}$  in 0.1 M TBAClO<sub>4</sub> in acetonitrile with tetrabutylammonium chloride.



**Figure S4.25**: Normalized photoluminescence intensity increase of  $C1^{2+}$  upon titration of tetrabutylammonium chloride in neat acetonitrile (red circles) and in 0.1 M TBAClO<sub>4</sub> (black squares).



**Figure S4.26**:  $\triangle$ Absorption spectra between ground and excited state of C1<sup>2+</sup> in dichloromethane.



**Figure S4.27**: Extinction coefficient and absorption spectra used to model transient absorption data. Extinction coefficient of diiodide (black), change in extinction coefficient of  $C1^+$  vs.  $C1^{2+}$  (red) and absorbance difference between the excited state and the ground state (blue).



Figure S4.28: Rate constant for the quenching of the excited state of  $C1^{2+}$  by iodide in dichloromethane vs. the concentration of  $C1^{2+}$ . Dashed line represent the diffusion controlled rate constant of formation of diiodide in acetonitrile (green) and in dichloromethane (red).



Figure S4.29: Determination of the rate constant of formation of diiodide in dichloromethane using a triiodide concentration of 5  $\mu$ M.



Figure S4.30: Determination of the rate constant of formation of diiodide in dichloromethane using a triiodide concentration of 50  $\mu$ M.



**Figure S4.31**: Optimized structure of  $C1^{2+}$  (top) and  $[C1^{2+}, C\Gamma]$  (bottom).



Figure S4.32: Debye-Huckel analysis to establish the dependence of the quenching constant versus the ionic strength



Figure S4.33: Determination of the cage escape yield of  $C1^{2+}$  and iodide in dichloromethane. Each color represents a different experiment.

## **APPENDIX 4. SUPPORTING INFORMATION FOR CHAPTER 5.**



**Figure S5.1**. The UV-vis absorbance spectra utilized in the spectral modelling of the titration data in Figures 5.3 & 5.4.



**Figure S5.2**. The UV-vis absorbance spectra of **D2Q** in CH<sub>3</sub>CN with the addition of the indicated cation solution and the fractional concentrations of the species, c1, c2 and c3 plotted against the total  $M^{n+}$  concentration. The UV-vis spectra go from red in neat CH<sub>3</sub>CN to purple at the highest concentration of cation. The vertical lines in the spectral modelling show where the [D2Q]/[ $M^{n+}$ ] ratio is 3:1 and 1:1 (2:1 and 1:1 for Zn<sup>2+</sup>).



**Figure S5.3**. The UV-vis absorbance spectra of **B2B** in CH<sub>3</sub>CN with the addition of the indicated cation solution and the fractional concentrations of the species, c1, c2 and c3 plotted against the total  $M^{n+}$  concentration. The UV-vis spectra go from red in neat CH<sub>3</sub>CN to purple at the highest concentration of cation. The vertical lines in the spectral modelling show where the [B2B]/[ $M^{n+}$ ] ratio is 3:1 and 1:1 (2:1 and 1:1 for Zn<sup>2+</sup>; 4:1 and 1:1 for Al<sup>3+</sup>).



**Figure S5.4**. Spectroelectrochemistry of **B2B** in A) 100 mM Mg(ClO<sub>4</sub>)<sub>2</sub>, B) 1 mM TBA(ClO<sub>4</sub>), and C) 1 mM Mg(ClO<sub>4</sub>)<sub>2</sub> plotted as the normalized change in absorbance,  $\theta$ , at the indicated wavelength vs. the applied potential. These data are overlayed with the fits to the linear portions used to determine  $E_{1/2}$  values as well as fits to a sigmoidal curve. The  $E_{1/2}$  values from the linear fits are 1.63 ± 0.02, 1.20 ± 0.08, and 1.67 ± 0.06 V vs. NHE, respectively.



**Figure S5.5**. PL spectra of **B2B** in CH<sub>3</sub>CN with the addition of the indicated cation solution. The spectra are normalized such that the PL maximum in neat CH<sub>3</sub>CN is 1. The spectra go from red in neat CH<sub>3</sub>CN to purple at the highest concentration of cation.