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Transition Metal Polypyridine Complexes: Studies of Mediation in Dye-Sensitized Solar Cells and Charge Separation

The Elliott group has long been supported by DOE for studies of cobalt(II/III) trisbypiridine (DTB) mediator complexes in dye sensitized solar cells. Previous work demonstrated that Co(II/III) chemistry is sensitive to the environment, showing unprecedented electrode-surface and electrolyte dependant voltammetry. In electrolytes that have large lipophilic cations, voltammetry of the $[Co(DTB)_3]^{2+/3+}$ couple is nearly Nernstian in appearance on nominally oxide-free metal surfaces. In contrast, on semiconductor electrodes in electrolytes with small, hard cations such as Li^+, the electron transfer rates are so slow that it is difficult to measure any Faradaic current even at overpotentials of ±1 V. These studies are of direct relevance to the operation of cobalt-based mediators in solar cells. The research has also shown that these mediators are compatible with copper phenantroline based dyes, in contrast to I^- due to the insolubility of CuI.

Proposed Research:

My colleague, C. M. Elliott, originally wrote this proposal. After his death I assumed the role of PI with the goal of graduating the two students supported by this proposal. This is the final report on this work.

Prof. Elliott's original proposal suggested a work plan that consisted of two parts. The first considered photoinduced charge separation within the context of discrete molecular assemblies composed of a chromophore simultaneously linked to an electron donor(s) and an electron acceptor(s). The second considered photoinduced charge separation in dye-sensitized solar cells. Each concerns the fundamental aspects of photoinduced charge separation in molecular systems designed to undergo long-lived, photoinduced charge-separation.

The first part was focused on the design of supramolecular assemblies of Cu(I) bis-phenantroline, $[Cu(I)P_2]^+$, as chromophore (C) with covalent attachments of electron donor (D) and acceptor (A) groups to facilitate unidirectional electron transfer. The proposed design of copper-based D-C-A triads and C-A diads complexes was based on the following criteria: (i) ligands with an appended electron acceptors that will oxidatively quench the excited state efficiently (such are ^{R}4OMV and ^{R}4OMQ); (ii) donors that are sufficiently strong reductants to re-reduce weakly oxidizing $[Cu(II)P_2]^{2+}$ (such are TPZ and POZ); (iii) ligands with appended donors that will facilitate the same type of π-π association between the $[Cu(I)P_2]^+$ chromophore and donor as is critical to efficient charge-separated state (CSS) formation in the ruthenium based assemblies; and (iv) D- and A-containing phenanthroline ligands with different steric bulk in the 2,9-positions such that the heteroleptic complex is highly thermodynamically favored. The proposed research included syntheses and studies of recombination kinetics of CSS using time-resolved transient absorption spectroscopy. By studing the effect of magnetic field on recombination kinetics, the question whether the electron transfer in proposed complexes is dictated by spin chemistry will be address. This work was very successful, and resulted in a Ph.D. dissertation for Dr. Megan Lazorski (with related references).

The second part focused on integrated systems of dye sensitized solar cells using cobalt polypyridine complexes, $[CoL_3]^{2+/3+}$, as redox shuttle mediators to replace I^-/I_3. The proposed work included synthesis of cobalt complexes chemically tuned in a way to achieve larger open circuit voltage, V_{OC}, while maintaining high short-circuit photocurrent, J_{SC}. Substituting bipyridine with electron deficient polypyridine ligands (having electron withdrawing groups) was proposed to result in cobalt complexes with highly positive potential. Another suggested strategy in achieving large V_{OC} was transferring the responsibility of attaining weak $[CoL_3]^{3+}/TiO_2$ electronic coupling from the cobalt complex to the dye. Two types of dyes were prepared and investigated: ones based on traditional ruthenium bipyridine chromophores and ones based on Cu(I) chromophores. In both cases, the dyes incorporated a secondary electron donor. The purposes of the donors were to transfer the hole away from the metal center after photoinjection and to contribute to the barrier for recombination, so that the recovery of sensitizer is not limited by the diffusion of mediator**.**

Technical Progress since Prof. Prieto became PI

Current progress has been focused on Part B of the proposed project objectives: using Cobalt Polypyridine Complexes as Electron-Transfer Mediators in Dye-Sensitized Photoelectrochemical Cells. Continuing studies fall under Part B, Section C and E of the proposal, investigating dyes with donor appended ligands, in order to mediate electron transfer between the oxidized dye and the cobalt complexes in solution. Additional studies fall under Part B, Section D of the proposal, investigating high-potential cobalt mediator complexes with the goal of improving the open-circuit potential of dye-sensitized photoelectrochemical cells.

Ligands and subsequent sensitizers as outlined in Part B, Sections C and E have been prepared and evaluated in solar cells. Addressing first the Ru(II) complexes referred to as RD1 and RD2 in the proposal (Figure 8), it was found that after further purification these compounds were exemplary dyes without the need for addition of "imperfections" in the dye layer introduced by way of dye mixing. In fact, RD1 appears to exhibit lipophilic effects (similar to Z-907) as well as a modest photovoltage increase due to increased electron-hole distance. Interestingly, although these two effects are not mutually exclusive, they appear to work best cooperatively. Further studies are ongoing to separate the two components and better understand the interplay between them. A manuscript is currently being prepared disseminating these results. In addition, the ligands in Figure 12 have been obtained or synthesized and various Cu(I) sensitizers have been prepared from them. The dye prepared from the ^{Me}4OTPZ donor ligand and mdcb binding ligand appears to be particularly promising. This dye exhibits higher stability and photocurrent than any other combination of donor and binder, including the case of CD1 which we have already published. In the next six months we will complete the testing of this dye, and will publish these results in a manuscript as well as a Ph.D. dissertation.

Our own work, as well as recent literature, has shown promising results by separating the task of blocking recombination from shifting the potential of the $[Co(L)_3]^{2+/3+}$ mediator complex. This is accomplished specifically by incorporating steric blocking groups on the dye rather than the mediator, allowing the use of smaller electron-withdrawing groups on the cobalt complex ligands in order to minimize mass transport limitations. Therefore, we have synthesized many of the electron deficient bipyridine ligands shown in Table 4 of the proposal and characterized their cobalt complexes as mediators in dye sensitized solar cells. A major finding is that, as predicted, the highest-potential complexes show significant instability with regard to ligand substitution, giving rise to very high recombination currents and poor performance in solar cells. A manuscript discussing these results has been submitted to the Journal of Physical Chemistry C. These findings have redirected our focus towards the development of cobalt mediators employing clathrochelating ligands, such as those shown in Figure 10 of the proposal. Progress towards the synthesis of such ligands is underway, and the characterization of these complexes will be completed as the final goals of the grant. Dr. Lance Ashbrook successfully defended his dissertation in the fall of 2015, and continued on as a postdoctoral fellow to help clear out Prof. Elliott's labs. Prof. Elliott's final student, Josh Thomas, will be defending this June.

References since 2014 (two manuscripts in preparation)

Lance N. Ashbrook and C. Michael Elliott “Sulfide Modification of Dye-Sensitized Solar Cell Gold Cathodes for Use with Cobalt Polypyridyl Mediators” *J. Phys. Chem. C,* **2014**, *130* (30), 16643-16650.
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Joel Kirner and C. Michael Elliott “Are High-Potential Cobalt Tris(bipyridyl) Complexes Sufficiently Stable to be Efficient Mediators in Dye-Sensitized Solar Cells?: Synthesis, Characterization, and Stability Tests” .
Phys. Chem. C, **2015**, *119* (31), pp 17502–17514
DOI: 10.1021/acs.jpcc.5b02513