Adventures in Transition Metal Photophysics

State-of-the-art phosphorescent materials are integral to devices such as flat screen displays and modern energy efficient lighting. Such materials efficiently convert electricity to light. The reverse process, the conversion of light into electricity, is perhaps even more technologically desirable. Our group studies complexes of metals such as iron, titanium, ruthenium, chromium, iridium, and rhodium as possible materials to improve these technologies.

MMCT in donor-π-bridge-acceptor complexes

Iron(II)-to-titanium(IV) metal-to-metal-charge transfer (MMCT) is important in the photosensitization of TiO_2 by ferrocyanide, charge transfer in solid-state metal-oxide photocatalysts, and has been invoked to explain the blue color of sapphire, blue kyanite, and some lunar material, yet molecular examples of this phenomenon have not been investigated. We have prepared a series of complexes with alkynyl linkages between ferrocene (Fc) and Ti^{IV} and investigated the charge transfer by UV-Visible spectroscopy, electrochemistry, TRTAS, and TD-DFT. All of the complexes with both Fe and Ti show an intense absorption between 540 and 630 nm that is absent in complexes lacking a suitable donor. TD-DFT and Marcus-Hush type analysis of the electrochemical and spectroscopic data are consistent with the assignment of the low energy absorption as a MMCT band. This class of compounds has now been extended to include complexes where arylamine donors are connected to a titanocene acceptor via an alkynyl bridge. The electrochemical and spectroscopic data suggest that the excited state oxidation potential of the complexes is well-positioned to inject electrons into TiO_2 and thus might be applicable to a new solar cell technology called dye-sensitized solar cells (DSSCs).

Our group is interested in further understanding these complexes and testing whether or not they can be utilized in DSSCs. We are studying ways of coupling them to the surface of TiO_2 and ways to increase the photochemical stability of these complexes. These investigations involve collaborations with research groups all around the world who are experts in computational chemistry (Virginia and Turkey), resonance Raman spectroscopy (NZ), and ultrafast spectroscopy (NM).

Photophysics of complexes with electron deficient alkyne ligands

Many transition metal complexes with alkynyl ligands are investigated for their luminescent properties. Of particular interest is adjusting the electronic properties of the metal/ligands, as this provides for the variation of colors observed in many complexes used in organic light emitting diodes (OLEDs). One common alkynyl ligand used to diminish the electron density at the metal is the pentfluorophenylethynyl ligand (C_6F_5C≡C−). Our group is interested in even more electron deficient alkyne ligands and has turned to the trifluoropropynyl ligand (CF_3C≡C−). Electronically, this ligand behaves much like the cyano ligand. However, emission from a Rh(III) complex with this ligand, trans-[Rh(cyclam)(C_2CF_3)2]^+ shows intense metal centered luminescence (Figure 2). We are presently investigating the relative electronic properties of C_6F_5C≡C− and CF_3C≡C− through spectroscopic, voltammetric, and computational methods.