

Research Group of Paul Wagenknecht
Sustainable energy production and usage

Cheap, abundant, renewable, portable energy holds the promise to solve significant world health issues such as the availability of potable water and the lack of health care facilities in remote areas. It would also address concerns about our dependence on fossil fuels. The amount of energy from the sun that strikes the surface of the earth in two hours exceeds the total amount of energy consumed by the world in one year. Solar photovoltaic (PV) technology (the conversion of solar energy to electricity) is a promising means by which to tap into this cheap, abundant, and renewable energy source and is one of the major technological challenges being addressed by chemists and material scientists. Another challenge is finding more efficient means by which to convert electricity to light. State-of-the-art phosphorescent materials are integral to devices such as flat screen displays and modern energy efficient lighting.

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 using UV-Visible spectroscopy, electrochemistry, TRTAS, and TD-DFT. All of the complexes with both Fc 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 been extended to include complexes where arylamine donors are connected to a titanocene acceptor via an alkynyl bridge. The electrochemical and spectroscopic data suggest 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).

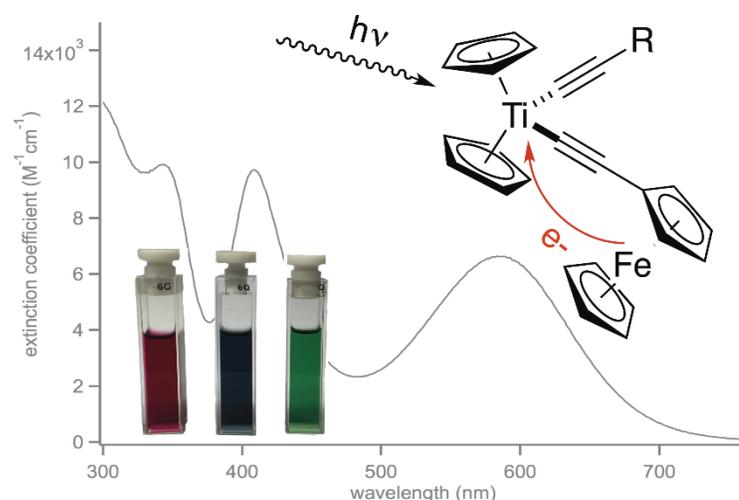


Figure 1. Adjusting the electron density at Ti^{IV} tunes the low energy absorption in a manner consistent with the assignment of this band as an Fe^{II} to Ti^{IV} MMCT. The MMCT is solvatochromic, shifting to lower energy with increased solvent polarizability. The reduction potential suggests the transient Ti^{III} species is appropriate for electron injection into TiO_2 .

The Wagenknecht group seeks to further understand these complexes and test whether or not they can be utilized in DSSCs. We are studying ways of coupling them to the surface of TiO_2 and to increase the photochemical and oxidative stability of these complexes. These investigations involve collaborations with research groups around the world with expertise in computational chemistry (Turkey and Virginia, U.S.), resonance Raman spectroscopy (New Zealand), and ultrafast spectroscopy (New Mexico, U.S.).

Photophysics of complexes with electron deficient alkyne ligands

Many transition metal complexes with alkynyl ligands have been 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 pentafluorophenylethynyl ligand ($\text{C}_6\text{F}_5\text{C}\equiv\text{C}^-$). Our group is interested in even more electron deficient alkyne ligands and has turned to the trifluoropropynyl ligand ($\text{CF}_3\text{C}\equiv\text{C}^-$). We have demonstrated that $\text{CF}_3\text{C}\equiv\text{C}^-$ as a ligand has ideal characteristics for coaxing high-energy (blue) emission from transition-metal complexes. We are now working on preparing Pt^{II} complexes with this ligand and investigating their emission. The trifluoropropynyl ligand has indeed resulted in blue-shifted emission, and the emission color is dependent on concentration. We are presently investigating this phenomenon.



Figure 2. $\text{Pt}(\text{Ph}_2\text{bpy})(\text{C}_2\text{CF}_3)_2$ in CH_2Cl_2 under UV-irradiation. Concentration is increased from the far right (lowest concentration) to the cuvette with the orange solution. In the cuvette at the far left is the compound in the solid state.