

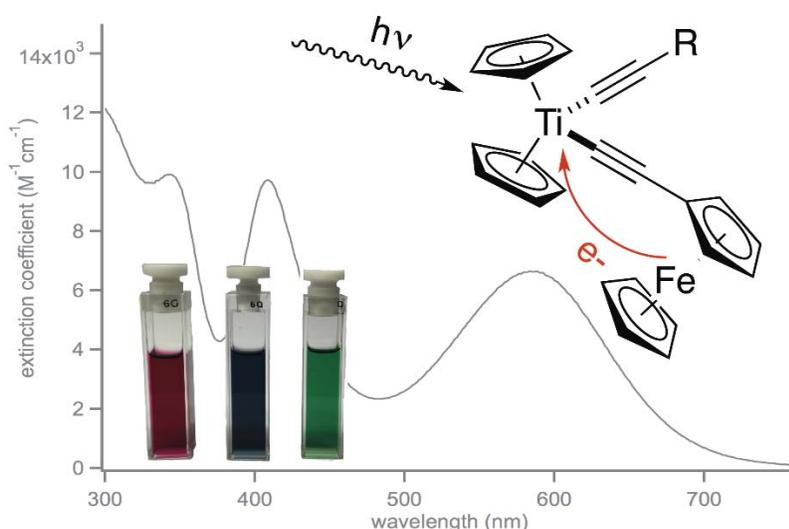
**Paul Wagenknecht Research Group**

**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 2 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. The other side of the coin is efficiently using that electricity – finding even 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- $\pi$ -bridge-acceptor complexes**

Iron(II)-to-titanium(IV) metal-to-metal-charge transfer (MMCT) is important in the photosensitization of  $\text{TiO}_2$  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  $\text{Ti}^{\text{IV}}$  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 that the excited state oxidation potential of the complexes is well-positioned to inject electrons into  $\text{TiO}_2$  and thus might be applicable to a new solar cell technology called dye-sensitized solar cells (DSSCs).



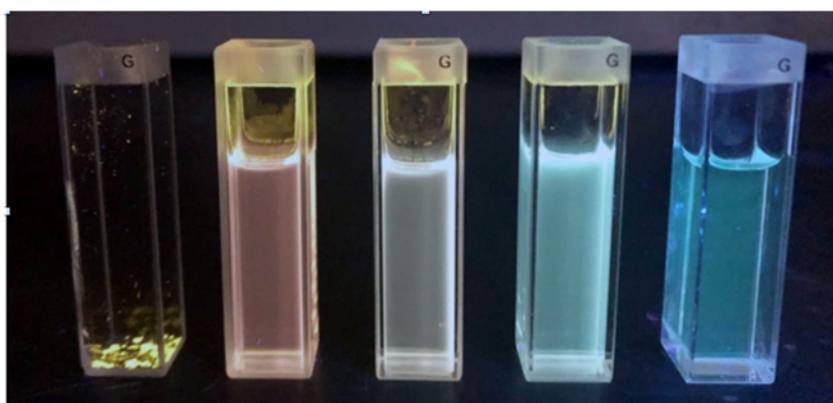
**Figure 1.** Adjusting the electron density at  $\text{Ti}^{\text{IV}}$  tunes the low energy absorption in a manner consistent with the assignment of this band as an  $\text{Fe}^{\text{II}}$  to  $\text{Ti}^{\text{IV}}$  MMCT. The MMCT is solvatochromic, shifting to lower energy with increased solvent polarizability. The reduction potential suggests the transient  $\text{Ti}^{\text{III}}$  species is appropriate for electron injection into  $\text{TiO}_2$ .

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  $\text{TiO}_2$  and ways to increase the photochemical and oxidative stability of these complexes. These investigations involve

collaborations with research groups all around the country (and world) who are experts in computational chemistry (right here at Furman), resonance Raman spectroscopy (New Zealand), ultrafast spectroscopy (New Mexico), and device chemistry (North Carolina).

### 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 ( $C_6F_5C\equiv C^-$ ). Our group is interested in even more electron deficient alkyne ligands and has turned to the trifluoropropynyl ligand ( $CF_3C\equiv C^-$ ). We have demonstrated that  $CF_3C\equiv C^-$  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.**  $Pt(Ph_2bpy)(C_2CF_3)_2$  in  $CH_2Cl_2$  under UV-irradiation. Concentration is increased from the far right (lowest concentration) to left. Intermediate concentrations result in white emission. The cuvette at the far left contains the compound in the solid state.