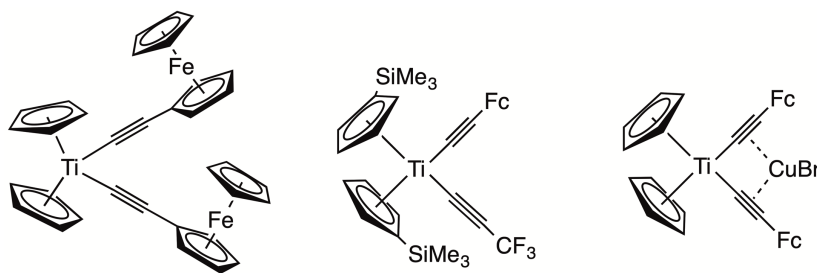


Manipulation of Iron(II) to Titanium(IV) Metal-to-Metal Charge-Transfer State Lifetimes

Maksim Y. Livshits, Postdoctoral Fellow, University of New Mexico; Michael D. Turlington, Undergraduate Student, Furman University; Carl O. Trindle, Emeritus Professor, University of Virginia; Zikri Altun, Professor, Marmara University; Jeffrey J. Rack, Professor, University of New Mexico; and Paul S. Wagenknecht*, Professor, Furman University

Understanding and manipulating charge-transfer (CT) excited states is important in solar energy conversion and photoredox catalysis. We have prepared a series of complexes with alkynyl linkages between ferrocene (Fc) and Ti^{IV} and investigated the Fe^{II} to Ti^{IV} MMCT by UV-Vis spectroscopy, electrochemistry, time-resolved transient absorption spectroscopy (TRTAS), and time dependent density functional theory (TD-DFT) calculations. Complexes with two ferrocene substituents include $\text{Cp}_2\text{Ti}(\text{C}_2\text{Fc})_2$, $\text{Cp}^*\text{Ti}(\text{C}_2\text{Fc})_2$, and $\text{Me}^{\text{OOC}}\text{Cp}_2\text{Ti}(\text{C}_2\text{Fc})_2$. Complexes with a single ferrocene include $\text{TMS}\text{Cp}_2\text{Ti}(\text{C}_2\text{Fc})(\text{C}_2\text{R})$, where $\text{R} = \text{C}_6\text{H}_5$, and CF_3 . All complexes with both Fc and Ti show an intense absorption between 540 and 630 nm that is absent in complexes lacking a ferrocene donor. Marcus-Hush type analysis of the electrochemical and spectroscopic data are consistent with the assignment of the low energy absorption as a MMCT band. TD-DFT analysis also supports this assignment, but suggests some admixture of Fc centered d-d states. Fitting of TRTAS experiments results in transient lifetimes between 18 and 41 ps. Spectroelectrochemical data are consistent with this transient being the MMCT state, suggesting that these lifetimes are measuring back-electron transfer (BET). Though Marcus-Hush analysis is consistent with BET being in the Marcus inverted region ($\lambda < -\Delta G^\ddagger$) the rate constants for BET increase with increasing driving force, thus showing normal behavior. We propose that the lifetime is significantly decreased by the degree of admixture of the short-lived (< 10 ps) Fc d-d state into the MMCT state, and the extent of this mixing increases as the energy of the MMCT state increases. This is supported by calculations of the Ciofini CT index. Lastly, we demonstrate that the excited state lifetime increases by three orders of magnitude upon coordination of CuBr between the alkynes.



References

Pienkos, J. A.; Webster, A. B.; Piechota, E. J.; Agakidou, A. D.; McMillen, C. D.; Pritchett, D. Y.; Meyer, G. J.; Wagenknecht, P. S. "Oxidatively stable ferrocenyl- π -bridge titanocene D- π -A complexes: an electrochemical and spectroscopic investigation of the mixed-valent states" *Dalton Trans.* **2018**, 47, 10953-10964.

Pienkos, J. A.; Agakidou, A. D.; Trindle, C. O.; Herwald, D. W.; Altun, Z.; Wagenknecht, P. S. "Titanocene as a New Acceptor (A) for Arylamine Donors (D) in D- π -A Chromophores" *Organometallics* **2016**, *35*, 2575-2578.

Michael D. Turlington, Jared A. Pienkos, Elizabeth S. Carlton, Karlee N. Wroblewski, Alexis R. Myers, Carl, O. Trindle, Zikri Altun, Jeffrey J. Rack, Paul S. Wagenknecht "Complexes with Tunable Intramolecular Ferrocene to Ti(IV) Electronic Transitions: Models for Solid State Fe(II) to Ti(IV) Charge Transfer" *Inorg. Chem.* **2016**, *55*, 2200 – 2211.

Presentation Keywords – solar energy conversion, transient absorption spectroscopy