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

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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 Cp$_2$Ti(C$_2$Fc)$_2$, Cp*$_2$Ti(C$_2$Fc)$_2$, and MeOOC$_2$Ti(C$_2$Fc)$_2$. Complexes with a single ferrocene include TMS$_2$Ti(C$_2$Fc)(C$_2$R), where R = C$_6$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 ($\lambda < -\Delta G^*$) 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


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