

From Spin-Orbit Coupling to Coherences: Shedding Light on the Intricate Photodynamics of $[\text{Pt}(\text{ppy})(\mu\text{-}^t\text{Bu}_2\text{pz})_2]$

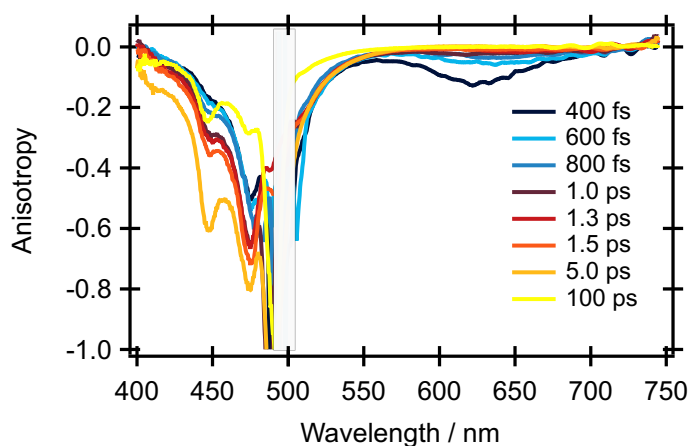
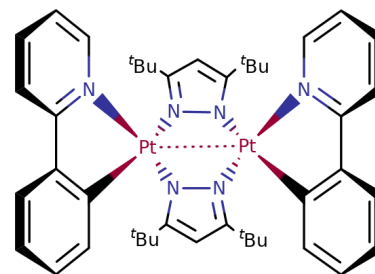
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Tuning electronic properties through deliberate structural modification of chemical species is the long-standing goal of rational molecular design. To do this requires a detailed understanding of the influence of specific structural and geometric features on the overall electronic structure of the molecular system. For photochemical processes, this relationship is particularly complex as the breakdown of the Born-Oppenheimer approximation means that the electronic dynamics of a molecule are intimately linked to its nuclear dynamics.[1]



By using a series of time-resolved spectroscopic techniques and complementary *ab initio* calculations, we have investigated the relationship between the electronic and nuclear dynamics in a prototypical dimeric Pt(II) complex, $[\text{Pt}(\text{ppy})(\mu\text{-}^t\text{Bu}_2\text{pz})_2]$ in toluene. In this work, we show that, by combining state-of-the-art electronic structure strategies alongside time-resolved techniques such as fluorescence up-conversion and broadband anisotropy measurements, it is possible to disentangle complex photoinduced dynamics for species that

show heavily convoluted transient electronic absorption spectra. With this, we can identify the role of specific electronic states, nuclear motions and resulting vibrational coherences in the energetic deactivation mechanisms of this system. This combination of tools could prove a powerful approach for characterisation and identification of metal complex properties for subsequent rational design applications.

[1] W. Domcke and D. R. Yarkony, *Annu. Rev. Phys. Chem.*, **2012**, *63*, 325–52.