Photophysical properties of radical elaborated donor-acceptor Pt complexes.

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Square planar donor-acceptor platinum complexes have garnered considerable interest due to their rich photochemical properties and their photoluminescence behavior. These complexes possess a low energy Donor → Acceptor ligand-to-ligand charge transfer transition that effectively creates charge separated singlet biradicals in the electronic excited state. Herein, we describe a new molecular framework to probe the effects of excited state lifetimes as a function of radical elaboration. Importantly, these new complexes will allow for detailed interrogation by magnetic circular dichroism (MCD) spectroscopy to understand their electronic structure and time-resolved spectroscopies to understand their excited state lifetimes and dynamics. Understanding these complex excited state interactions is crucial for the further development of improved solar cells, molecular electronics applications, and spintronics. The excited states of these complexes are emissive and indicate long-lived excited states can be achieved. In this presentation, we will discuss our latest photophysical results, which have been interpreted in the context of quantum chemical computations.

Key words: donor, acceptor, radical, platinum

Ground State Nuclear Magnetic Resonance Chemical Shifts Predict Charge-Separated Excited State Lifetimes

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ABSTRACT: Dichalcogenolene platinum(II) diimine complexes, (LE,E′)Pt(bpy), are characterized by charge separated dichalcogenolene donor (LE,E′) → diimine acceptor (bpy) ligand-to-ligand charge transfer (LL′CT) excited states that lead to their interesting photophysics and potential use in solar energy conversion applications. Despite the intense interest in these complexes, the chalcogen dependence on the lifetime of the triplet LL′CT excited state remains unexplained. Three new (LE,E′)Pt(bpy) complexes with mixed chalcogen donors exhibit decay rates that are dominated by a spin−orbit mediated nonradiative pathway, the magnitude of which is proportional to the anisotropic covalency provided by the mixed-chalcogen donor ligand environment. This anisotropic covalency is dramatically revealed in the 13C NMR chemical shifts of the donor carbons that bear the chalcogens and is further probed by S K-edge XAS. Remarkably, the NMR chemical shift differences also correlate with the spin−orbit matrix element that connects the triplet excited state with the ground state. Consequently, triplet LL′CT excited state lifetimes are proportional to both functions, demonstrating that specific ground state NMR chemical shifts can be used to evaluate spin−orbit coupling contributions to excited state lifetimes.

Model studies address the geometric and electronic structure of a key dimethyl sulfoxide reductase (DMSOr) enzyme intermediate

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Dimethyl sulfoxide reductase (DMSOr) catalyzes the reduction of DMSO to volatile dimethyl sulfide (DMS), playing a vital role in geochemical sulfur cycles. The product, DMS, is a compound of increasing environmental importance that facilitates cloud formation and albedo. The paramagnetic Mo(V) “high-g split” intermediate has been studied by electronic absorption, magnetic circular dichroism, and electron paramagnetic resonance spectroscopies with the data being interpreted as deriving from a 6-coordinate low-symmetry intermediate along the electron transfer half reaction of the enzyme. However, a recent EXAFS study has suggested that this intermediate is 5-coordinate and is off the catalytic pathway. To resolve these issues, we have synthesized new 6-coordinate model compounds for the DMSOr “high-g split” intermediate. A combination of electronic absorption, EPR, and XAS spectroscopic studies have been performed on these models and interpreted in the context of all available enzyme data. We conclude that a 6-coordinate structure is most likely for this intermediate. An interesting inverted bonding scheme is proposed that addresses the electron transfer reactivity of this site in the reductive half reaction of the enzyme.

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Probing the Active Site of a Novel Molybdenum Enzyme

Molybdoenzymes possess a unique molybdopterin cofactor and they catalyze a large number of different reactions that are important for the biogeochemical cycles of the most abundant elements of the Earth, such as N, S, C, Cl, as well as playing critical roles in metabolic cycles. YedY is a novel bacterial molybdoenzyme; a putative methionine sulfoxide reductase capable of rescuing proteins damaged by reactive chlorine species. Although YedY exhibits several commonalities with other molybdoenzymes, it has characteristic differences in its electronic structure that make it distinct. Despite structural similarities to sulfite oxidase (SO), YedY cannot catalyze the same reactions and functions as a sulfoxide reductase *in vitro*. It is the only molybdoenzyme known that is isolated in the paramagnetic Mo(V) oxidation state. YedY possesses an atypical axial EPR spectrum at X-band frequencies that displays an unusually high g_1 value for a molybdoenzyme. Unlike other molybdoenzymes that oxidize and reduce substrates through mechanisms that cycle Mo through its Mo(IV), Mo(V), and Mo(VI) oxidation states, there is no evidence that YedY can be oxidized to the Mo(VI) oxidation state observed for all other SO family enzymes in their catalytic cycles. It has been proposed that YedY instead employs a unique mechanism by which oxidation state changes occur on the ubiquitous pyranopterin dithiolene (PDT) ligand; the Mo ion remaining in the reduced Mo(IV) oxidation state throughout the catalytic cycle. In this work, we utilize a combination of spectroscopy, site-directed mutagenesis of various active site residues, and computations to address these ambiguities.

Keywords: molybdoenzyme, EPR, spectroscopy, mutagenesis