

Magnetic Exchange Interactions in Both Ground- and Excited States: Evaluation of Electronic Coupling Parameters and Photoinduced Electron Spin Polarization

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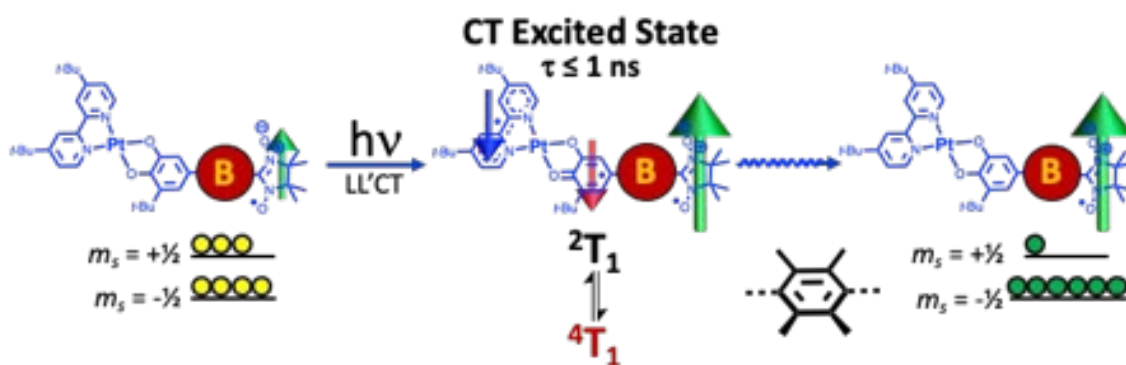
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Magnetic exchange interactions (J) between unpaired spins play a crucial role in molecule-based magnetic-, electronic-, and spintronic materials, as well as photophysics, and quantum information science. This presentation will describe our research efforts focused on understanding exchange coupling in donor-acceptor biradical ligand complexes, and how this leads to control of ground-state electron spin polarization in radical-substituted donor-acceptor complexes of (primarily) platinum(II).

Metal complexes of donor-acceptor biradical ligands comprised of $S = \frac{1}{2}$ semiquinonate (SQ, donor) and $S = \frac{1}{2}$ nitronyl nitroxide (NN, acceptor), offer a unique molecular platform to evaluate bridge-dependent electronic- and magnetic exchange coupling (H and J , respectively) in the context of a valence bond-type configuration interaction model.¹⁻³ These molecules serve as ground-state analogs of charge-transfer (CT) excited states, affording us the ability to predict the relative energies of multi-spin CT excited states. In solvent glasses, equilibria between an excited doublet (2T_1) and closely-spaced quartet states (e.g., 4T_1) provides a pathway for non-Boltzmann populations of the 2T_1 state via the reversed quartet mechanism.⁴ Rapid nonradiative decay of the 2T_1 state transmits this spin polarization to the ground state where it is detected as a time-resolved EPR signal. Our results show that the magnitude and sign of the spin-polarized EPR signal is correlated with the exchange parameter between SQ and NN (J_{SQ-NN}) in the CT excited state.⁵⁻⁷ Moreover, J_{SQ-NN} can be tuned through rational synthetic design.



References

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