Magnetic exchange interactions 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 \( S = \frac{1}{2} \) nitronylnitroxide (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