

Electronic Structure Contributions to Photoinduced Ground State Spin Polarization in Radical Elaborated Donor-Acceptor Molecules

Martin L. Kirk (1,2,3), *David A. Shultz* (4), *Patrick Hewitt* (4), *Ju Chen* (1), and *Art van der Est* (5)

(1) Department of Chemistry and Chemical Biology, The University of New Mexico, MSC03 2060, 1 University of New Mexico, Albuquerque, NM 87131-0001. (2) The Center for High Technology Materials, The University of New Mexico, Albuquerque, New Mexico 87106, United States. (3) Center for Quantum Information and Control (CQuIC), The University of New Mexico, Albuquerque, New Mexico 87131-0001. (4) Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204. (5) Department of Chemistry, Brock University, St. Catharines, Ontario, Canada L2S 3A1.
mkirk@unm.edu

Radical-Elaborated Donor-Acceptor chromophores of the general form (diimine)Pt(dioxolene-radical) [1-6] that possess ligand-to-ligand charge transfer (LL'CT) excited states are excellent platforms for the generation and study of ground state electron spin polarization (ESP). The nature of the dioxolene \rightarrow diimine LL'CT state is such that nearly a complete transfer of an electron is achieved, leading to $(L^{\bullet})Pt(L'^+)-R^{\bullet}$ three spin excited state configurations where each spin is localized on a different component of the molecule (Donor, Acceptor, and Radical). A combination of magnetic susceptibility measurements on $Tp^{Cum,Me}Zn(SQ-B-NN)$ (B = organic bridge, NN = nitronyl nitroxide) and related molecules, coupled with detailed magnetic circular dichroism studies of (bpy)Pt(CAT-B-NN) [7], have revealed the nature of the pairwise excited state exchange interactions that are critical to the control of electron spin polarization. The *Reversed Quartet Mechanism (RQM)* [8], which requires rapid mixing between excited trip-doublet and trip-quartet exchange coupled excited states, forms the basis for our understanding of photoinduced ESP in these radical elaborated chromophores. We have effectively expanded the *RQM* to include the presence of localized radical states (e.g. 2NN , 4NN) in order to explain the sign and the magnitude of the photoinduced ESP. These localized radical states can mix with the trip-doublet and trip-quartet exchange coupled excited states by an energy transfer mechanism, which is made efficient due to the close proximity of the donor, acceptor, and radical components of these molecules. Select examples of how this revised *RQM* explains the observed photogenerated ESP in these systems will be discussed.

References

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