Fine-Tuning of Spin-Dependent Optical Properties of Mo(0) and Mo(VI) Complexes

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Transition-metal complexes (TMCs) have shown a great promise in design of optically addressable (OA) qubit candidates for quantum information science (QIS). To realize optical initialization and read-out signals, TMCs must have a triplet ground state, T_0, featuring weak zero-field splitting to enable coherent manipulations of spin sublevels via electron paramagnetic resonance (EPR). The lowest lying excited state should be a singlet, S_1, that is well separated from subset of other states and radiatively decays to T_0 ground state. Such conditions have been found only in a few TMCs with V(III), Cr(IV), and Ni(II) centers. However, a vast synthetic space is available through the choice of both the metal center and ligand structure to improve the OA-qubit performance. Quantum chemistry calculations could establish relationships between excited properties and chemical structure of TMCs, which help to navigate design of new highly efficient OA-qubits. With this goal, we have performed calculations based on density functional theory (DFT) for the ground and excited states of zero-valent and VI-valent Mo complexes with carbonyl and diimine ligands varying in the π-conjugation length and electron withdrawing/donating abilities of their substituting groups. Our calculations show that complexes with Mo(0) coordinated to diimine-based ligands provide the triplet ground state (T_0) and $S_1 \rightarrow T_0$ optical transitions with predominant metal-to-ligand charge transfer (MLCT) character for most substituting groups, independent on the density functional choice. Thus, these complexes are potential candidate for OA-qubits. In contrast, Mo(VI) complexes tend to have singlet ground state (S_0) and phosphorescence energies at the near infrared (NIR) range at 750 nm-900 nm, depending on the substituents. These complexes are promising for applications in optical sensors, night-vision devises, and photodynamic therapy.