

Improving Near-Infrared Fluorescence Quantum Yield of *meso*-Aryldipyrroin Indium(III) Complexes via Annulation Bridging

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Abstract

Materials that absorb and emit light in the infrared (IR) and near IR range are of interest for various opto-electronic applications, such as sensors and luminescence sources. Finding materials with efficient luminescence in the IR region is known to be a challenging issue due to increased contributions from non-radiative recombination (NRR) with decreased bandgap (i.e. gap-law). Design of molecular structures which suppress vibrational modes which contribute to NRR can be exploited to thwart the ‘gap-law’. Here we explore the photo-physical response and photo-induced non-adiabatic (NAESD) for a series of In(III) dipyrroin-based complexes with functionalization schemes (i) substituting aryl groups with ‘strong’ ‘weak’ electron-withdrawing (EW) ability and (ii) saturated or unsaturated annulation of the pyrroin ligands. Annulation is predicted to provide structural rigidity by suppressing torsional vibrational modes and consequently improve the photoluminescence quantum yield (PLQY) of the complexes. For electronic structure it is observed that functionalizing with aryl groups of ‘weak’ and ‘moderate’ EW ability have primarily π - π^* character with a small admixture of intra-ligand charge transfer (ILCT) for their emitting states while ‘strong’ EW aryl groups have substantially increased ILCT. To determine the impact of structural changes on PLQY we implement NAESD where NRR rates are found from computing Redfield tensor elements corresponding to the lowest-excited state transition and RR are found from Einstein coefficients. From the NA excited-state dynamics we find that complexes with primarily π - π^* character show enhanced (reduced) PLQY with unsaturated (saturated) annulation. This correlates with unsaturated annulation providing a minima non-radiative recombination rate compared to the non-annulated and saturated annulation complexes. For complexes with primarily ILCT character we find that PLQY decreases with both annulation schemes due to decreased (increased) radiative (non-radiative) recombination rates. This study shows the promise for engineering the photo-physical properties of metal dipyrroin based complexes through functionalization schemes to provide structural rigidity for enhanced performance in NIR opto-electronic applications.

