Observing Electron Charge Transfer in Manganese Doped Perovskite Quantum Dots using Marcus Theory

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Perovskite Quantum Dots (QD) have improved a variety of technologies including, solar photovoltaics and light emission applications, due to their light absorption and emission properties. However, Perovskite QDs often fall short with respect to stability; degrading rapidly and being easily damaged. Our research attempts to solve this issue by analyzing radiative and non-radiative transitions between electronic states of Manganese doped Cesium Lead Bromide ($CsPbBr_3$) quantum dot (QD). The doping process causes induces polarization of surrounding environment that affect transition energy and transition probability (**Figure 1**), which promises improvement in properties but also produces challenges to the modeling. Our method includes a combination of (i) first principles calculation by density functional theory (DFT), in both spin-polarized and non-collinear spin versions, and (ii) a quantized nuclear dynamics approach to account for the effects of nuclear reorganization; physically achieved and demonstrated through the use of quantum evolution operator technique. Atomistic modeling (i) provides parameters for quantized vibronic dynamics modeling (ii). First principles modeling of the doped QD allows to specify energies and geometries, and to identify type of an excitation (i.e., metal to ligand CT, ligand to metal CT, metal to metal, etc.). For each geometry and electronic configuration, values of Mn-Br distances are recorded to form intersection potential energy surfaces. The quantum dynamics of a vibronic excitation created by a short pulse is propagated in time to explore how amplitude of quantized nuclear motion affects rate of nonradiative electronic transitions. The results are compared to predictions of Marcus theory. The knowledge of rates and pathways of nonradiative transitions allows to estimate lifetimes of the excited states and to estimate influence of nuclear motion onto quantum yield of photoluminescence. This research reports the trends that transition metals like Manganese impose onto optical properties of lead halide perovskite QDs. One expects to find optimal morphology of doped perovskite QD that stabilizes the optical properties.

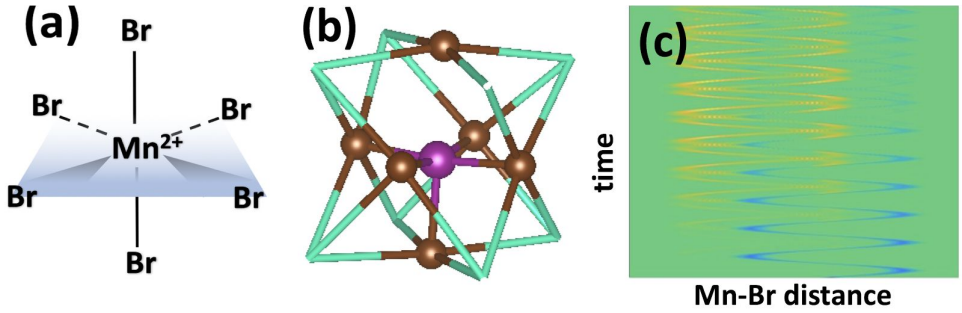

Figure 1. (a) schematic diagram of Mn^{2+} coordination; **(b)** fragment of atomistic model in the vicinity of Mn ion (purple), bromine (brown), cesium (green); **(c)** probability distribution of quantum electron nuclear dynamics for excited (blue) and ground (orange) electronic configurations. Distribution of Br-Mn distance in the excited and ground states oscillate about different equilibrium values, the probability migrates between excited to the ground state due to nonadiabatic transition mechanism.