Enhanced Photoluminescence Quantum Yield in Lead Halide Perovskite Quantum Dots through Doping with Manganese Ion – A Computational Study

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Fully inorganic lead halide perovskite quantum dots (QDs) are of interest for optoelectronic and light emitting devices due to their photoluminescence (PL) emission properties which can be tuned/optimized by (I) surface passivation and (II) doping. (I) Surface passivation of the QD has shown to be a major factor in PL properties, as a poorly passivated surface can introduce trap states which ultimately reduce PL quantum yields (QY) [1]. (II) Historically, doping quantum dots with transition metal impurities to obtain d-d optical transitions has been a method to evade this issue[2]. Recently, it has been found that doping perovskite QDs with Mn^{2+} ions results in d-d optical transitions in addition to the intrinsic QD emission[3]. Here we use *ab initio* methodology to investigate the roles of surface passivation and doping on PLQY of perovskite quantum dots. Two models are investigated: (i) an intrinsic QD ($Cs_8Pb_{27}Br_{54}$) terminated with amines and carboxylic acids with overall charge 2^+ (ii) a QD doped with Mn^{2+} ion ($Cs_8Pb_{26}Mn_1Br_{54}$) terminated with amines and carboxylic acids and has overall charge 2^- (shown in Figure 1 below). Ground state electronic structure was determined using non-collinear DFT with PBE functional[4] in a plane-wave basis set along with PAW pseudopotentials[5] in VASP software[6]. Non-radiative relaxation of excited states are computed with spinor nonadiabatic couplings [7] using Reduced Density Matrix formalism. Radiative relaxations are computed from oscillator strengths to generate time resolved PL[8]. Atomistic treatment identifies the nature of most the intense optical transitions in the doped model: metal-ligand charge transfer (CT), ligand-metal CT, metal-metal excitation facilitated by spin flip. It is found that the Mn^{2+} 3d-orbitals experience weak crystal field splitting within the perovskite QD resulting a high spin state being most energetically favorable. Consequently, this requires the use of spin-orbit coupling (SOC) interaction to adequately describe the metal-metal spin-flip transition. Interestingly, it was computed that with the inclusion of SOC the PLQY of the intrinsic HOMO-LUMO transition of the perovskite QD increased four-fold. This indicates that the spin-orbit effect enhances radiative transitions within perovskite materials, which to our knowledge has not been reported in the literature.

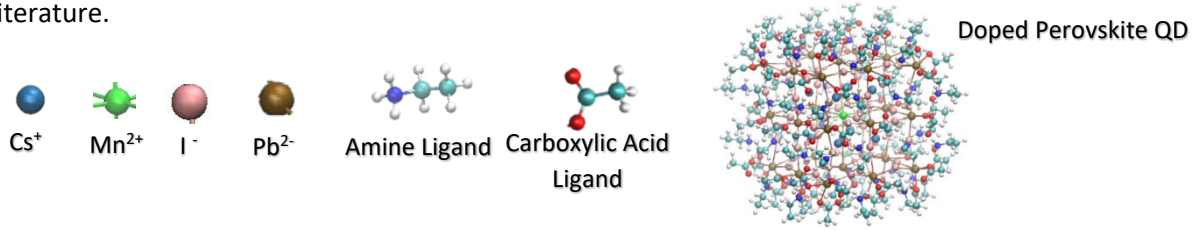

Figure 1: Chemical components that make up the doped perovskite QD (left) and the 2x2x2 unit cell doped perovskite QD (right)

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