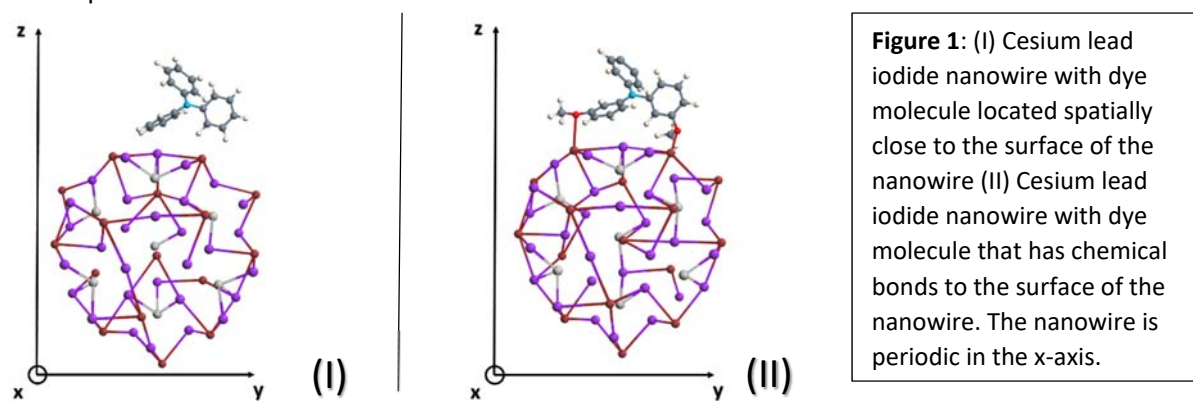# Morphology Influence on Hole Transfer - Spatial Locality versus Explicit Ligand Coordination: Case Study of Dye-Sensitized Lead Halide Perovskite Solar Cells

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Lead halide perovskites have gained attention as an active material in solid state dye-sensitized photovoltaics due to its high absorption of visible light and long charge transport lengths[1]. In perovskite based dye-sensitized photovoltaic architectures, the perovskite material is paired with a dye molecule, such as spiro-OMeTAD, which extracts a hole from the photo-excited perovskite to generate free charge carriers. In this study we explore how the interfacial bonding between donor/acceptor pairs influence charge transfer dynamics in photo-induced chemical processes. Two atomistic models where studied and compared (shown in Figure 1 below): (I) A periodic cesium lead iodide perovskite nanowire, $Cs_{16}Pb_7I_{30}$, that is paired with Benzenamine, $N(C_6H_5)_3$, which is not covalently adsorbed to the surface of the nanowire and (II) A periodic cesium lead iodide perovskite nanowire, $Cs_{16}Pb_7I_{30}$, paired with Benzenamine, 3-methoxy-N-(3-methoxyphenyl)-N-phenyl-, $C_{20}H_{19}NO_2$, where the oxygen atoms coordinate bond to the surface of the nanowire at various sites. Ground state electronic structure and geometry are computed using DFT with PBE functional[2] in a plane-wave basis set along with PAW pseudopotentials[3] in VASP software. K-point sampling was done along the x-axis of the nanowire. Charge transfer dynamics, providing rates of electron/hole relaxation and relaxation pathways, are calculated using Reduced Density Matrix formalism. Adiabatic molecular dynamics with on-the-fly non-adiabatic couplings between nuclear and electronic degrees of freedom provide components for the Redfield tensor followed by propagating the electronic populations with Redfield equations[4,5]. The role of momentum dispersion onto non-adiabatic couplings is explored. Comparison of charge transfer rates though chemical bonds versus though physical space matches the expectation that charge transfer rates though bonds are quicker than through space. This work influences material design considerations for future hole transfer materials in lead halide perovskite photovoltaics.

Figure 1: (I) Cesium lead iodide nanowire with dye molecule located spatially close to the surface of the nanowire (II) Cesium lead iodide nanowire with dye molecule that has chemical bonds to the surface of the nanowire. The nanowire is periodic in the x-axis.

References: [1]Cui, J. et al. (2015). Recent progress in efficient hybrid lead halide perovskite solar cells. *Science and Technology of Advanced Materials*, *16*(3), 036004.| [2]J. P. Perdew, K. Burke, and M. Ernzerhof. Generalized gradient approximation made simple. Phys. Rev. Lett., 77:3865, 1996. | [3]G. Kresse and D. Joubert, Phys. Rev. 59 , 1758 (1999). | [4]Kilina, S.et al. (2015). Light-driven and Phonon-Assisted dynamics in organic and semiconductor Nanostructures. *Chemical Reviews*, *115*(12), 5929–5978.| [5]Micha, D. A. (2010). Relaxation of Photoexcited electrons at a Nanostructured Si(111) surface. The Journal of Physical Chemistry Letters, 1(7), 1073–1077. doi:10.1021/jz100122f