

Valentine I. Vullev
University of California, Riverside

Metal-halide perovskites, with composition $A^+B^{2+}X_3^-$, have exerted one of the biggest impacts in the development of photovoltaics (PVs). The unique electronic structure of the $[BX_6]^{4-}$ octahedrons ensures not only long exciton lifetimes, but also separate transport pathways for electrons and holes. The latter feature, along with the small exciton binding energy has made these perovskites practically the “perfect” materials for photovoltaics. The ionic bonding in the $A^+B^{2+}X_3^-$ crystalline structures is relatively weak, allowing for a certain level of plasticity of the metal-perovskite lattices. This softness of the ionic structure, along with the “looseness” of the large counterion, A^+ , is key for the beneficial optoelectronic properties of the metal-halide perovskites. As regularly used organic ions for A^+ , methylammonium and formamidinium are charged species with permanent electric dipoles. Conversely, large alkaline cations, such as Cs^+ , are spherically symmetric with no permanent dipole, but highly polarizable. This propensity of A^+ to induce electronic and orientational polarization aids the formation of positive and negative polarons. The polarons keep the holes spatially separated from the electrons, which is crucial for impeding undesired charge recombination. As important as the lattice softness is for the optoelectronic properties of the metal-halide perovskites, it also is an underlying reason for one of its biggest demises: i.e., the lack of stability and photostability in polar or humid environments. Despite the success in the efforts to address this challenge, it still remains an issue. All-inorganic metal-halide perovskites, such as $CsPbBr_3$, have gained attention in recent years for applications in LEDs, PVs, lasers, and photodetectors, due to their strong optical absorptions, narrow line widths, high photoluminescence quantum yields (ϕ_{PL}) and increased thermal stability relative to the organic-inorganic perovskite. While they have not matched yet the performance of their hybrid counterparts, PVs of all-inorganic perovskites have recently gained momentum, showing an increase in η from about 10% to 19%. Most of the early work on $CsPbBr_3$ focuses on films, and recently research with suspensions of all-inorganic perovskite nanocrystals (NCs) gained traction. The inherent lack of stability of these materials in polar solvents and moisture, however, proves especially pronounced for NCs, even with $CsPbBr_3$ composition. We focus on interfacial photoinduced hole transfer (PHT) from $CsPbBr_3$ NCs to an external electron donor in a hydrocarbon solvent medium. An amine derivative of the electron donor, allows us to examine the role of surface binding for achieving efficient interfacial CT. The donor without an amine hardly affects the photoluminescence (PL) of the NCs. At μM concentrations, on the other hand, the amine derivative substantially quenches the PL of the NCs. Despite the dynamic nature of the surface binding of the amines, their affinity for the NCs ensures strong enough electronic coupling of the donor with the $CsPbBr_3$ inorganic phase within the timescales of the CT process. Increasing the concentrations of the amine increases the number of donor moieties per NC and hence, increases the probability for PHT. Such an increase in the amine concentration above 1 mM, however, causes etching of the NCs and a drastic change in their morphology, placing a limit on the feasibly attainable number donor ligands per a NC. Analysis of the results from the time-resolved-spectroscopy studies reveals 1- μs inherent PL lifetimes of the $CsPbBr_3$ NCs that is drastically shortened by features of the materials itself, which are ascribed to traps in analogy with other semiconductor nanoparticles. The rate constant, k_{PHT} , of hole transfer from a NC to the surface-bound donor is about $10^8 s^{-1}$, which is consistent with the electronic coupling pathway through three covalent bonds of the linker. Most importantly, binding of the amine-donor to the NCs eliminates some of the traps responsible for shortening the exciton lifetime, which increases the efficiency of the nanosecond interfacial CT. While the non-polar media limits the choices of electron donors and acceptors, lowering the polarity of the environment keeps the perovskite structures intact and enhances the ionic binding interactions. Anchoring of amine-derivatized redox species to perovskite surfaces: (1) ensures through-bond electronic coupling for efficient interfacial CT; and (2) eliminates sites responsible for undesirable non-radiative deactivation of the excitons. This dual benefit from using redox-active species with surface-binding groups for efficient extraction of charge carriers, demonstrates a crucially important paradigm for pursuing unexplored optoelectronic properties of metal-halide perovskites.