

Prerequisites for Charge Transfer in Quantum Dots Functionalized by Metal-organic Complexes

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Semiconductor quantum dots (QDs) functionalized by metal-organic dyes are promising materials for energy conversion and lighting technologies. However, their photoexcited dynamics is strongly affected by dot-dye interactions, information on which is scarce. We have developed time-domain non-adiabatic dynamics based on density functional theory to determine conditions that govern the mechanisms of a charge and energy transfer in photoexcited QDs passivated by various Ru(II)-polypyridine complexes. Substantial differences in dot-dye binding energies and in frequencies between symmetric and asymmetric C-O vibrations of the carboxyl, serving as a linkage group, point on the exclusive attachment of the Ru(II)-complex to the QD sites predominantly via a bridging geometry. Independent on its attachment and the QD type (CdSe, PbSe, or ZnO), however, all complexes introduce additional states near the edge of the QD conduction band. These states are mainly localized on bipyridine ligands and govern the direction of electron transfer from the excited dye to the QD. However, orbitals associated with Ru(II) are deep inside in the QD's valence band making the hole transfer from the photoexcited QD to the complex energetically unfavorable. Change in a transition metal of the complex insignificantly affects the alignment of the electronic levels of the dye versus the QD's states. In contrast, substitutions of bipyridine to thiocyanate ligands results in a shift of Ru(II)-associated orbital towards the very edge of the QD valence band and provides the preferential conditions for the hole transfer from the QD to the dye. Thus, our calculations may be useful for rational design of organic and metal-organic dyes to improve the direction and mechanism of charge transfer – a key process in QD-based solar cells and photo-catalytic agents.