

Electronic Structure and Absorption Spectra of Semiconductor Quantum Dots Functionalized by Ru-bipyridine Complexes

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Semiconductor quantum dots (QDs) functionalized by metal-organic dyes promise great potentials in various emerging applications, including chemical sensing, photocatalysis, and photovoltaics. However, the electronic structure, optical response, and photoexcited dynamics, including energy and charge transfer, are strongly affected by dot-dye interactions, which are still not well understood in these complex systems. With the ultimate goal of understanding all of these processes, we utilize density functional theory (DFT) and time dependent DFT (TDDFT) to study magic size QD of different composites (CdSe, CdS, and PbSe) and Ru(II)-bipyridine-complex attached to the dot surface through the carboxyl groups. Substantial differences in the total energies and difference in frequencies between symmetric and asymmetric C-O vibrations of the carboxylic groups point on the exclusive attachment of the functionalized Ru-complexes to the QD sites predominantly via a bridging geometry. Independent on its attachment and the QD type, however, the adsorption of the complex on the QD surface leads to additional unoccupied states inside in the band gap of the QD close to the edge of the conduction band. These states are mainly localized on bipyridine ligands of the complex and govern the direction of charge/energy transfer in these systems. Our calculations confirm a possibility for efficient electron transfer from the photoexcited dye to the QD. In contrast, the hole transfer from the photoexcited QD to the complex is not preferable.