

Electronic Structure of Janus Pbse/Cdse QDs Functionalized By Ru(II) N719 Dye and its Tunability via Dye Attachment and Solvent Polarity

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Colloidal quantum dots (QDs) represent a highly promising material for light harvesting, energy conversion, and light emitting devices. Additional control over the electronic and optical properties can be obtained through heterostructures, so called Janus QDs, where a half of the QD is made from one semiconductor (CdSe) and another half is from another semiconductor (PbSe) forming an interface along a specific crystalline direction. The charge transfer – the key processes for both solar-to-electrical and solar-to-chemical energy conversion processes – can be further improved via organic-inorganic interfaces by functionalization of the QD surface with dye molecules, such as derivatives of Ru(II) bipyridine. However, challenges remain in controlling complicated surface and interface chemistry of Janus QDs and the QD-dye interaction, which fundamental understanding is still far from completion. Using density functional theory (DFT) and linear response time dependent DFT (TDDFT) methods, we have studied the effect of the binding configuration of Ru(II) N719 dye on the electronic structure and optical properties of Janus PbSe/CdSe QDs of 2 nm in size. Calculations show that attachment of the dye to either PbSe or CdSe surface by two carboxylic groups leads to shrinking of the energy gap, compared to the attachment by a single carboxylic group. This is because the attachment via two carboxylic groups shifts the occupied dye's orbitals to the energy gap of the QD and provides favoring conditions for a hole transfer from the photoexcited QD to the dye. Additionally, the alignment of the dye's orbitals with respect to the QD's states is sensitive to the solvent media, with more polar solvent shifting the occupied dye's orbitals deeper inside in the QD's valence band. Also non-polar solvent results in charge-transfer character of lowest energy optical transitions, where the hole is localized on the dye and the electron is localized on the CdSe part of the QD. Thus, our calculations confirm that the photophysics of Janus PbSe/CdSe QDs is adjustable by the dye attachment and media/solvent polarity allowing for favorable conditions for the hole transfer from the excited QD to the dye.