Supporting Information for “Colloidal Nanoparticles for Intermediate Band Solar Cells”

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In this Supporting Information we first show the density of states for several $\text{Cd}_{33}\text{Se}_{33}$ NP models. We then show the computed inverse participation ratios (IPRs) for larger nanoparticles. Finally, we provide details on the computation of oscillator strengths.

Figure S1 shows the electronic density of states (DOS) of several different $\text{Cd}_{33}\text{Se}_{33}$ NP models. The formation of the intra-gap state (IGS) is a persistent feature: all choices of initial configurations for the atomic positions lead to the formation of a well separated state.

Figure S1: Electronic density of states (DOS) of several $\text{Cd}_{33}\text{Se}_{33}$ NP models, obtained at the DFT-PBE level of theory.

The IPR was computed as:

$$\text{IPR}_i = \frac{\int |\psi_i(\mathbf{r})|^4 d^3r}{\left(\int |\psi_i(\mathbf{r})|^2 d^3r\right)^2}. \quad (1)$$

The IPR measures the localization of the wave function ψ_i : the larger the IPR, the higher the degree of localization. Figure S2 shows the computed IPRs for the $\text{Cd}_{15}\text{Se}_{15}$ NP, and one of the $\text{Cd}_{33}\text{Se}_{33}$ and $\text{Cd}_{45}\text{Se}_{45}$ NPs. It can be noticed that the IPR for the IGS (blue) is comparable to other conduction states (black) and smaller than states close to HOMO (red). For the $\text{Cd}_{45}\text{Se}_{45}$ NP it can also be noticed that the some states in the close vicinity to the HOMO are also separated from the rest of the valence states and are highly localized. Although not shown, we obtained similar IPRs for the rest of the $\text{Cd}_{33}\text{Se}_{33}$ and $\text{Cd}_{45}\text{Se}_{45}$ NPs.

Oscillator strengths were computed using the matrix elements of the position operator:

$$f_{i \rightarrow j} = \frac{2E_{i \rightarrow j}}{3} \sum_{\mu=1}^3 \left| \int \psi_i^*(\mathbf{r}) r_{\mu} \psi_j(\mathbf{r}) d^3r \right|^2, \quad (2)$$

where $E_{i \rightarrow j}$ is the single particle energy difference of the transition from the Kohn-Sham state ψ_i to state ψ_j and $r_{\mu} = x, y, z$ is the position operator. The absorption (or photoabsorption cross section) is proportional to the imaginary part of the dipole polarizability,¹ which translates to:

$$\text{Absorption}(E) \propto \sum_{ij} f_{i \rightarrow j} \delta(E - (E_{i \rightarrow j})). \quad (3)$$

The absorption was obtained by convoluting Eq. 3 with a Gaussian function with standard deviation of 0.1 eV.

Figure S2: Red, blue, black diamonds represent the IPR of occupied states, the IGS and the rest of the unoccupied states, respectively. The zero of the energy scale was set to the energy of the highest occupied state.

References

1. Ullrich, C. *Time-Dependent Density-Functional Theory: Concepts and Applications*; Oxford Graduate Texts; OUP Oxford, 2012.