Supplementary Material: Optimized long-range corrected density functionals for electronic and optical properties of bare and ligated CdSe quantum dots

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In the following we compare the fundamental gap and electronic excitation spectra for two different geometries. First, the optimized B3LYP geometry of Ref.[1] used in the present study (labeled QC). Second, the geometry obtained in Ref.[2] by Molecular Dynamics using plane-wave DFT with the PW91 functional and Vanderbilt pseudopotentials (labeled MD).

From Fig. S1 we find a strong dependence of the onset of the absorption spectrum on geometry. For LC-BLYP the difference is as much as ∼0.8 eV. Incidentally, the structure MD-LC-BLYp spectrum looks rather close to experiment, which usually shows a rather

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sharp feature at the onset. This must be considered fortunate, since the MD structure is considerably less stable than the QC for all functional used one as can be seen from Table T1. This table also points to the strong dependence of the fundamental gap on geometry. However, the general observation that the fundamental gap for LC-BLYP is larger than for B3LYP/PBE and thus closer to experimental still holds true.

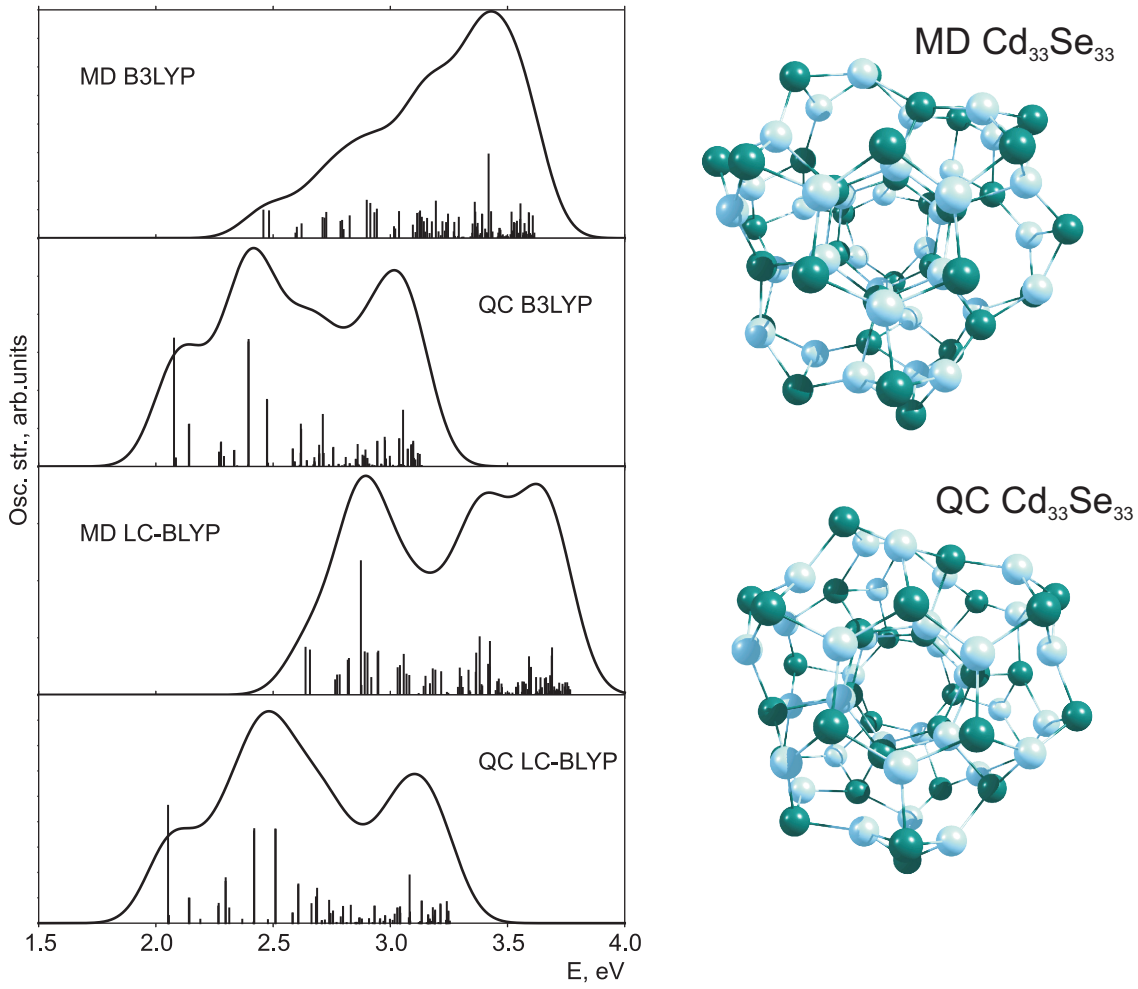

Figure 1: (S1) B3LYP and tuned LC-BLYP absorption spectra of pure $Cd_{33}Se_{33}$ for two different geometries. The 100 lowest transitions are taken into account. The spectra are broadened with a Gaussians of 0.1 eV half-width and scaled by a factor of 0.5 to facilitate the presentation of stick and broadened spectra in one graph. In the right panel, the top views of both structures are provided.

In order to investigate temperature effects on the onset of the absorption spectrum,

Table 1: (T1) Values of the fundamental gap, Δ, and conformer energy difference ΔE (in eV) of pure QDs. For the meaning of the geometry notation, see Fig. S1.

	PBE	B3LYP	LC-BLYP
Δ MD-$Cd_{33}Se_{33}$	1.73	2.80	4.42
Δ QC-$Cd_{33}Se_{33}$	1.43	2.46	4.04
ΔE (MD-QC)	2.26	1.98	1.41

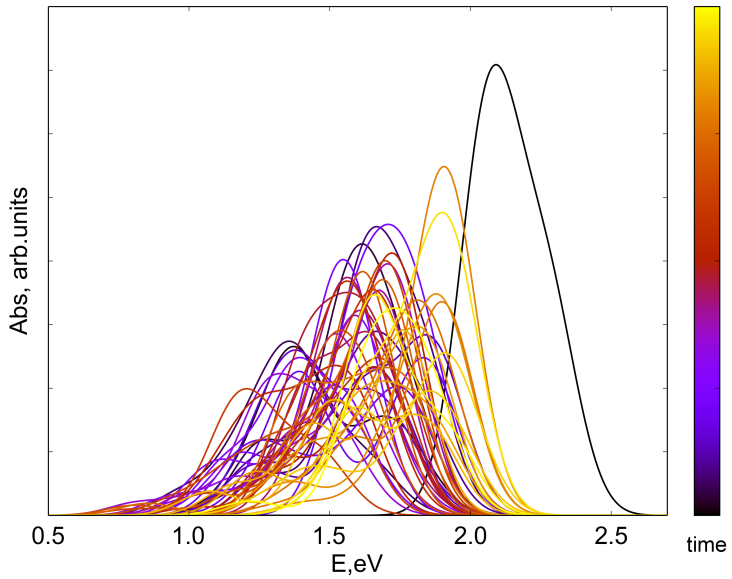

Figure 2: (S2) Tuned LC-BLYP absorption spectra of pure $Cd_{33}Se_{33}$ for 50 selected geometries sampled from a canonical ensemble at $T = 50°C$. The color code indicates the time along the sampling trajectory.

molecular dynamics sampling of a canonical ensemble has been performed as described in the main text. Spectra for randomly selected geometries are shown in Fig. S2.

References

(1) Wu, S. W. A First-Principles Study of Thiol Ligated CdSe Nanoclusters. Ph.D. thesis, The Graduate School, Stony Brook University, Stony Brook, NY, 2012.

(2) Kilina, S.; Ivanov, S.; Tretiak, S. *J. Am. Chem. Soc.* **2009**, *131*, 7717–7726.