Electronic Supplementary Material (ESI) for Nanoscale.

# Electronic Supplementary Information

## Strain-Induced Exciton Transition Energy Shift in CdSe Nanoplatelets: The Impact of the Organic Ligand Shell

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## Infrared Spectroscopy:

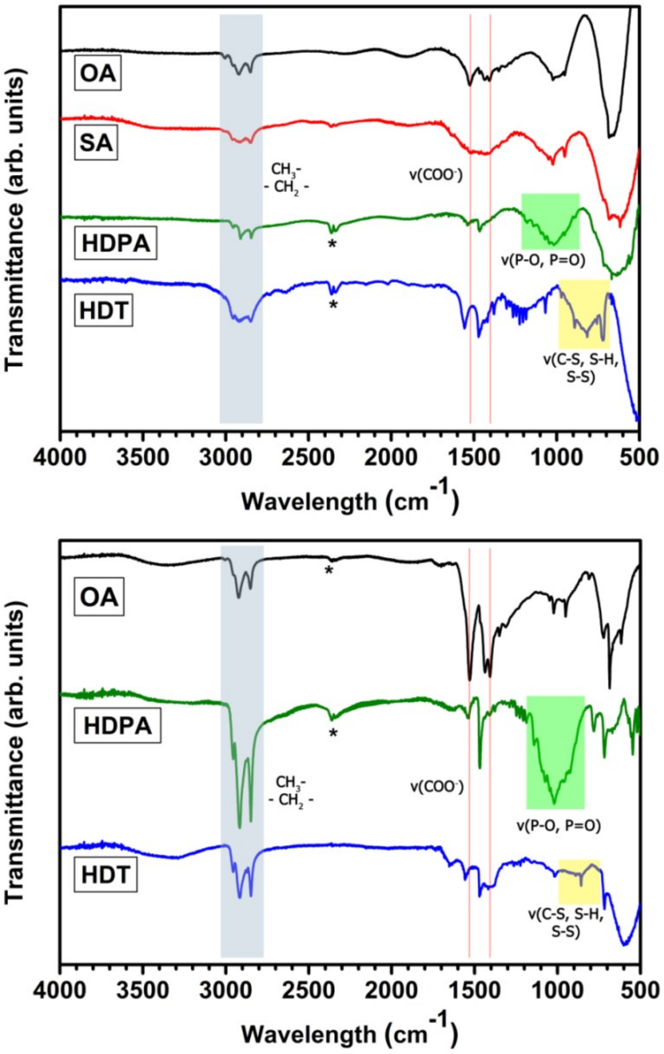

**Figure S1.** IR-spectra of 3.5 ML (top) and 4.5 ML-thick (bottom) NPls capped with different ligands. Asterisks indicate vibrations of $CO_2$ molecules.

## TEM Characterization:

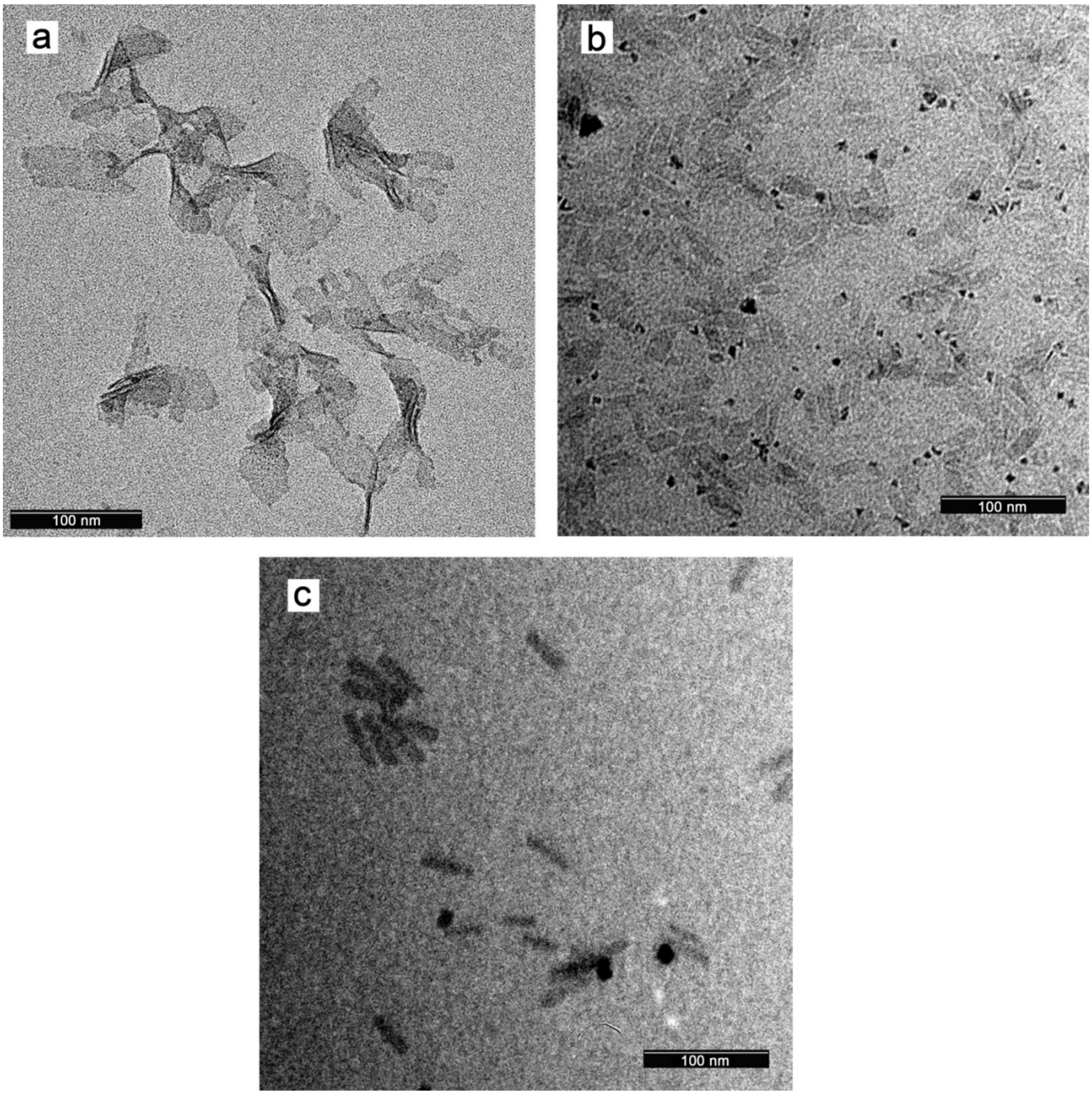

**Figure S2.** TEM images of 3.5 ML (a), 4.5 ML (b) and 5.5 ML (c) CdSe NPls capped with oleic acid.

**Table S1.** Size of 3.5 ML, 4.5 ML and 5.5 ML CdSe NPls capped with oleic acid.

| Thickness | Length, nm | Width, nm |
|---|---|---|
| **3.5 ML** | 64 ± 6 | 33 ± 4 |
| **4.5 ML** | 30 ± 1 | 12 ± 1 |
| **5.5 ML** | 42 ± 4 | 12 ± 1 |

## PL and Absorption Spectra:

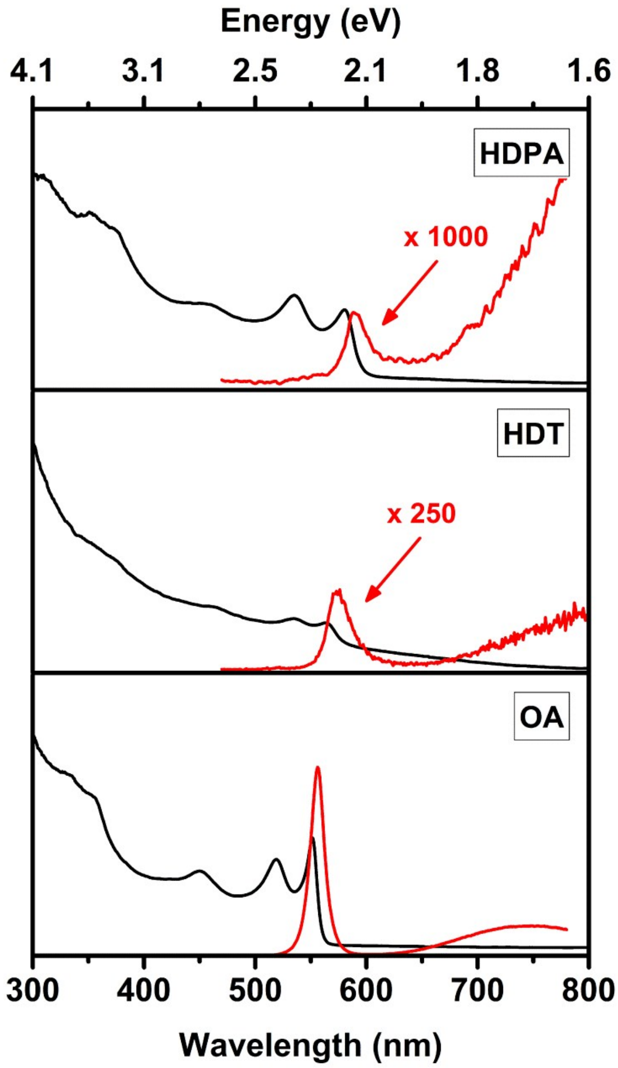

**Figure S3.** Absorbance (black) and PL (red) spectra of 5.5 ML-thick CdSe NPls capped with oleic acid (OA), hexadecanethiol (HDT) and hexadecylphosphonic (HDPA) acid.

## XRD Evaluation:

The lattice distortion by the ligands can be considered equal in both lateral directions but not in the thickness direction. So the symmetry of the initially cubic unit cell is reduced to a tetragonal type. The evaluation of the lattice parameters was performed for the ligand-coated NPls shown in Figure 3 according to:

$$\frac{1}{d^2}=\frac{h^2+k^2}{a^2}+\frac{l^2}{c^2} \tag{S1}$$

Since the (220) reflexes consist of two peaks representing different planes with respect to the NPl orientation (Figure 3), lattice cell parameters can be calculated by using only one set of reflections of the same family. Also, since NPl thickness is in [001] direction, it is possible to assign lattice planes perpendicular to basal planes of NPls to the (220) plane. Further, because NPls are anisotropic (i.e.

lateral dimensions are much greater than thickness) and FWHM of XRD-peak sharpens as number of lattice planes in that directions increases, the sharp component of the peak is attributed to (220) planes and the broad component of the peak – to the sum of the diffraction on (022) and (202) planes in the originally cubic system (see Figure 3). Thus the lattice parameters were calculated by solving the equation system:

$$\begin{cases} \dfrac{1}{d_{lateral}^{2}} = \dfrac{2^2 + 2^2}{a^2} + \dfrac{0^2}{c^2} \\ \dfrac{1}{d_{thickness}^{2}} = \dfrac{2^2 + 0^2}{a^2} + \dfrac{2^2}{c^2} \end{cases} \qquad \text{(S2)}$$

where *a* is the lattice parameter in lateral direction and *c* is the parameter in thickness direction.

In order to characterize lattice transformation upon ligand exchange quantitatively, we also calculated relative lattice parameter change ε with respect to OA-capped NPls in lateral ($\Delta\varepsilon_{x,y}$, Equation 3) and thickness ($\Delta\varepsilon_z$, equation 4) directions:

$$\Delta\varepsilon_{x,y} = \frac{(a_x - a_{OA})}{a_{OA}} \cdot 100\ \% \quad , \qquad \text{(S3)}$$

$$\Delta\varepsilon_{z} = \frac{(c_x - c_{OA})}{c_{OA}} \cdot 100\ \% \quad , \qquad \text{(S4)}$$

where $a_x$ and $c_x$ are corresponding lattice parameters for NPls capped with ligand *x*, $a_{OA}$ and $c_{OA}$ are lattice parameters for OA-capped NPls.

**Table S2.** Structural data of 3.5 ML CdSe nanoplatelets capped with stearic acid (SA): interplane distance as obtained from the (220) reflexes, tetragonal lattice parameters, relative parameter change (with respect to OA-capped NPls) and unit cell volume

| **Sample** | **$d_{220}$, Å lateral** | **$d_{220}$, Å thickness** | **a, Å** | **c, Å** | **a/c** | **$\varepsilon_{x,y}$, %** | **$\varepsilon_z$, %** | **V, Å$^3$** |
|---|---|---|---|---|---|---|---|---|
| 3.5 ML SA | 2.179 | 2.154 | 6.164 | 6.025 | 1.023 | - 0.13 | 0.02 | 228.9 |

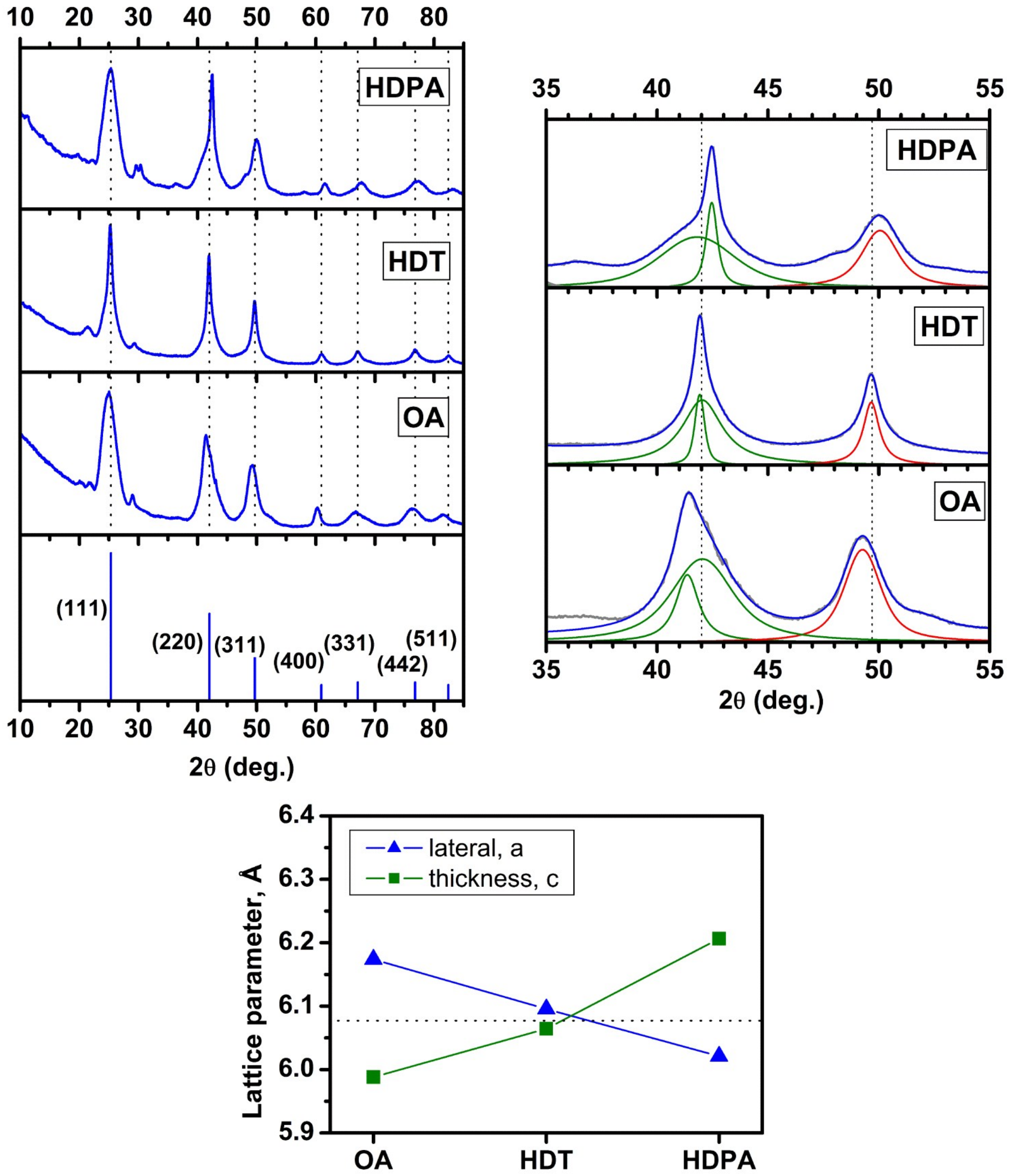

**Figure S4.** Wide-angle XRD diffractograms of 5.5 ML CdSe NPls capped with oleic acid (OA), hexadecanethiol (HDT) and hexadecylphosphonic acid (HDPA) (top left), results of the fitting of (220) and (311) XRD peaks for 5.5 ML-thick NPls (grey curve – experimental data, green – fitted peaks for (220) reflexes, red – fitted peaks for (311) reflexes, blue – cumulative curve) (top right) and variation of lattice parameters in different directions for 5.5 ML-thick NPls treated with different ligands (bottom). Dotted lines indicate values for bulk ZB CdSe phase.

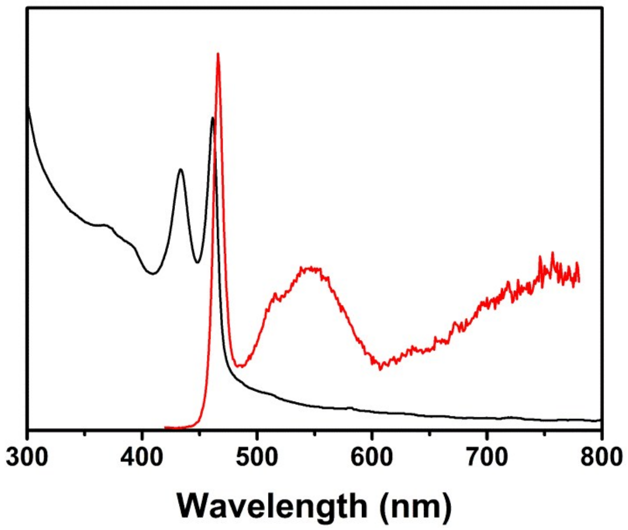

**Figure S5.** Absorbance (black) and PL (red) spectra of 3.5 ML-thick NPls capped with stearic acid.

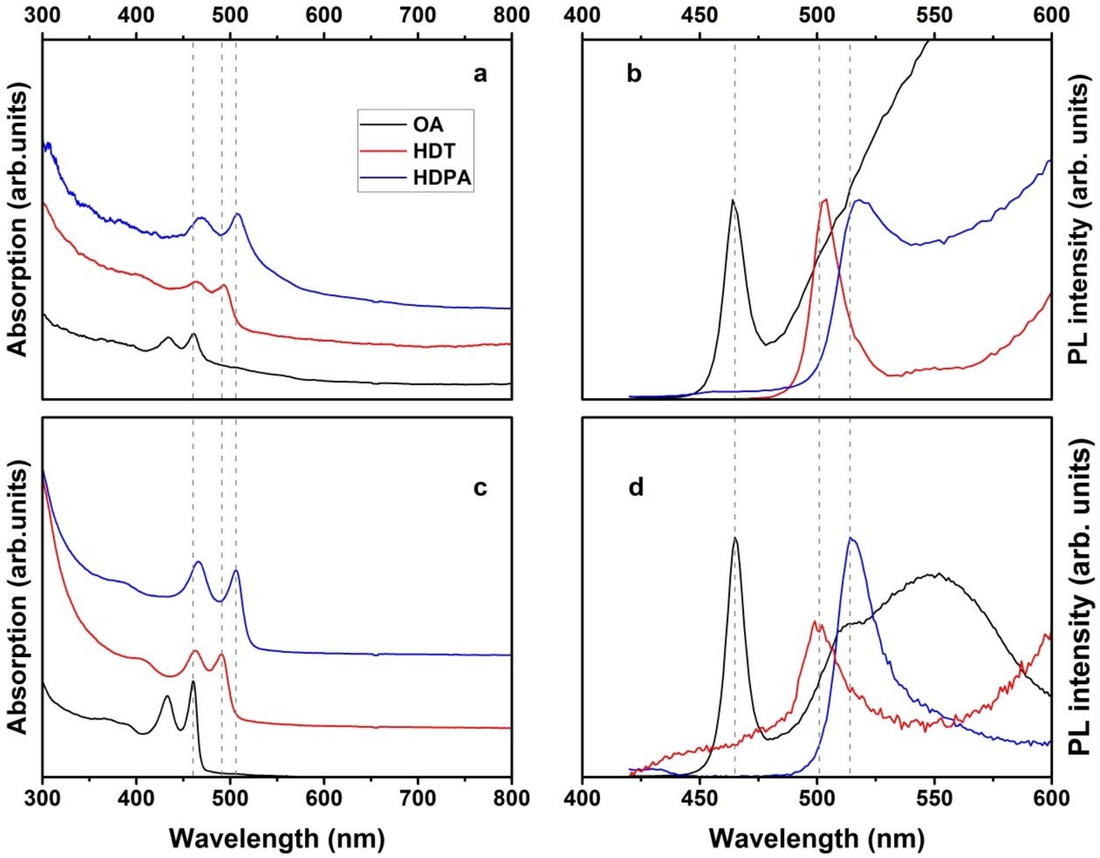

**Figure S6.** Absorption (a, c) and PL (b, d) spectra of 3.5 ML-thick NPls capped with oleic acid (OA, black), hexadecanethiol (HDT, red) and hexadecylphosphonic acid (HDPA, blue) in powder (a, b) and in solution (c, d). The absorption spectra of powdered samples were made from their slurry in the commercial silicon-based immersion oil for microscopy. The immersion oil was a standard silicon-based liquid from Sigma widely used for microscopy and spectroscopy. A powder of NPls mixed with immersion oil has been gently grinded in a mortar and the resultant slurry was sandwiched between two quartz substrates. The results show that there is negligible spectral shift between the platelets in solution and in ~ 100 micron sized, dry aggregates embedded in immersion oil both for PL and absorption. Hence PL and absorption data of our samples in solution and dry form exhibit the same strain induced shifts, and both data complement each other and can be used for our analysis in the main text.

## Deformation potential models:

Using the definition of the (hydrostatic) deformation potential α connecting the change in band gap of a semiconductor

$$dE = \alpha \cdot\ dln(V) = \alpha \cdot \frac{dV}{V} \tag{S5}$$

to a change in volume dV, we can approximate the strain-induced energy shift in NPls by integration of the differential equation.[1] The strain-induced energy shift of the absorption ΔE is then related to the deformation potential by:

$$\Delta E = \alpha \cdot ln\frac{V}{V_0}, \tag{S6}$$

where V is the strained unit cell volume and $V_0$ is the unstrained unit cell volume. However Table 1 shows only slight changes of the platelet volume across the different ligand types. As unstrained unit cell crystallographic data are not available for ZB CdSe NPls because the phase is not macroscopically stable and epitaxially grown epilayers of ZB CdSe are always strained to some extent, we relate the ligand-induced volume changes of the platelets to OA-capped NPls so that $V_0$=$V_{OA}$. The bulk hydrostatic deformation potential constant is α = -2.7 eV for ZB CdSe and hence a blue shift is expected upon reduction of the unit cell volume.[1] This is in clear contradiction to the trend observed in Table 1, where a regular decrease of the unit cell volume with respect to OA for the other ligands is accompanied with a redshift of the exciton transition in the CdSe NPls. Hence it cannot account for our findings.

Following Gindele et al.[2] a strained (ZB) CdSe quantum well shows beyond the above mentioned hydrostatic energy shift of the heavy hole exciton transition also a shear contribution to the total shift:

$$\Delta E = E_{hyd} - E_{shear} = 2\tilde{\alpha}\frac{C_{11} - C_{12}}{C_{11}}\epsilon_{xx,yy} - b\frac{C_{11} + 2C_{12}}{C_{11}}\epsilon_{xx,yy} \tag{S7}$$

Using the elastic moduli $C_{ij}$ (taken from Ref. 3), $\tilde{\alpha}$ and b from Ref. 2 and the in-plane strain $\epsilon_{xx,yy} = \epsilon_{xx} = \epsilon_{yy} = \Delta\varepsilon_{x,y}$ relative to oleic acid from Table 1, we obtain $2\tilde{\alpha}\frac{C_{11} - C_{12}}{C_{11}}$ = α = -2.87 eV and $b\frac{C_{11} + 2C_{12}}{C_{11}}$ = -1.81 eV, so that ΔE = -1.06 eV · $\Delta\varepsilon_{x,y}$ (α = -2.87 eV is in a good agreement with the above mentioned value of -2.7 eV from literature). Calculation results are given in Table 2 in the main text.Ananalysis of the calculation results shows, that a blue shift is still predicted in contrast to the observed red shift. Moreover, its absolute value is ~ 4-8 times smaller than the actual experimental value. Hence, deformation potentials can account only for ~ 12-20 % of the observed shift, and are hence a small perturbation.

Additionally we calculated deformation-induced spectral shifts using an approach employed by Zhou et al.[4] according to the following equation:

$$\Delta E =- \ \alpha \cdot \Delta \varepsilon_z \cdot Y, \tag{S8}$$

where α is the band-gap pressure coefficient (27.5 meV/GPa)[3], $\varepsilon_z$ is relative parameter change in the thickness direction and $Y$ is the Young's modulus (61.2 GPa).[3] Calculated energy shifts ($\Delta E^{(S8)}_{calc}$) are presented in Table 2 (main text). However, the resulting values show the same trend as the experiments, but the values of the predicted shifts according to equation S8 are considerably too low to explain the experimental findings.

## References

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3 E. Deligoz, K. Colakoglu and Y. Ciftci, *Phys. B Condens. Matter*, 2006, **373**, 124–130.

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