Electronic Supplementary Information: Size-dependent Exciton Substructure in CdSe Nanoplatelets and its Relation to Photoluminescence Dynamics

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SAMPLE SYNTHESIS AND CHARACTERIZATION

CdSe core NPLs with the first exciton absorption bands around 512 nm (4.5 ML) were synthesized as described in Ref.[1]. Absorption and PL spectra as well as TEM images and results of a TEM size analysis of several nanoplatelet sizes are shown in Fig. S1 of the Supporting Information. Core-only CdSe NPLs with 21x7 nm^2 lateral extensions were synthesized as in Ref.[2] In line with results of She et al.[3] we assume our NPLs to be Cd terminated on both basal planes. The particles were redissolved in toluene forming a dilute dispersion, freed from aggregates by centrifugation and embedded in PMAO polymer (from Aldrich), then coated on on thin fused silica substrates and mounted in a Cryovac Conti IT cryostat (3.5-300 K). The volume fraction in the polymer was kept below 1% to avoid any aggregation or FRET effects.[4] A similar method has proven effective prevention of aggregation.[5]

Our experimental PL setup allows for the measurement of time-integrated and -resolved fluorescence of a sample with confocal excitation (SHG of a titanium sapphire laser at 420 nm (Coherent Mira 900F, FWHM 130 fs, 75.4 MHz)) and detection (N.A.=0.4) through an objective. A spectrometer with an attached CCD (Roper Spec10) for time-integrated or a streak camera (Hamamatsu C5680) for time-resolved measurements are used.

The excitation density was held below moderate CW equivalent 0.2 W/cm^2 (pulse peak irradiance 25 kW/cm^2) to avoid any heating, ground state saturation and the presence of higher order processes such as biexcitons or trions. Using the absorption cross sections of the CdSe NPLs reported in Achtstein et al.[6] we calculate only < 0.1 percent of the platelets to be excited within one laser pulse (average number of excitons per platelet per pulse below 10^{-3}). The probability that a platelet undergoes two subsequent photoexcitations or two excitations within one pulse is < 10^{-6} and thus negligible. Therefore biexcitonic effects are unlikely.

A detailed discussion ruling out the presence of bie excitons and ground state saturation and powerdependent PL analysis is found in the supporting material of Ref.[7]

Figure S1. Room temperature photoluminescence (red) and absorption (blue) spectra and corresponding TEM images of several 4.5 ML CdSe core NPLs. The average lateral sizes are noted for each NPL population. We remark that the TEM micrographs were taken from the conventionally drop casted and dried dispersions, not from the same in polymer embedded, isolated nanoplatelets used in experiments. Hence the TEM images are not indicative for stacking in the used samples for PL experiments.