TIME-RESOLVED SPECTROSCOPY OF SINGLE QUANTUM DOTS

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One well established class of nanomaterials is based on colloidal core/shell CdSe/ZnS quantum dots (QDs). Capping organic shells (including surfactants and ligands) have considerable impact on the surface structure, optical properties and exciton relaxation in QDs as has been successfully studied experimentally and theoretically for several systems [1–3]. Ensemble experiments on QDs are hampered by the fact that it is not immediately obvious whether an identified variation of parameters (such as PL energies or decay times) is related to a distribution of QDs with different properties (ensemble average) or, alternatively, whether each QD explores these parameters in course of observation time (time average).

To give more insight into this open question we have performed a series laser time-resolved experiments for single CdSe/ZnS QDs spin coated onto a quartz substrate at 293 K [4, 5]. It is well known that QDs show a strong photoluminescence (PL) intermittency (blinking) on time scales of ms to s [4–6]. We analysed blinking events by the change point analysis (CPA) [6] which allows detecting optical properties for each individual PL intensity of a single QD during a blinking time trace. As we have shown recently with an adequate time resolution [4] PL intensities vary continuously during a blinking time trace covering high, "dim" and low PL intensities. We also followed spectral diffusion (detected via energy jumps ΔE between 2 spectrally separated detection channels) of the PL of a single QD as a function of the intermittent PL intensity during a blinking time trace as is shown in Fig. 1 (top). Two observations immediately emerge. Firstly, the average PL energy at a given PL intensity (open circles) shifts (after an initial ≈ 10 meV "jump" to higher energies) by $\Delta E \approx$ 30 meV to lower energy with decreasing PL intensity between the 2 given (blue) lines in Fig. 1. The line on the right marks the maximum I_{max} of the PL intensity distribution given in the bottom part of Fig. 1. The line on the left marks 0.1 I_{max}. This latter intensity corresponds to the limit at which we can for sensitivity reasons discriminate between different spectral components in an ensemble experiment. Secondly, for a given PL intensity we obtain as is shown in Fig. 1 (middle) a Gaussian distribution σ of spectral energies (spectral diffusion) of $\sigma \approx$ 20–30 meV at a selected PL intensity during a blinking time trace which is considerably broader than the experimental error but narrower than the

typical FWHM of ≈ 130 meV observed in ensemble experiments [5]. Remarkably, σ becomes larger with decreasing intensity in the intensity range between the two blue lines in Fig. 1.

We additionally performed time resolved PL decay experiments on single QDs at 290 K as a function of PL intensity using also 2 spectrally separated ("blue" and "red") detection channels. This provides information on the spectral distribution of PL decay components.

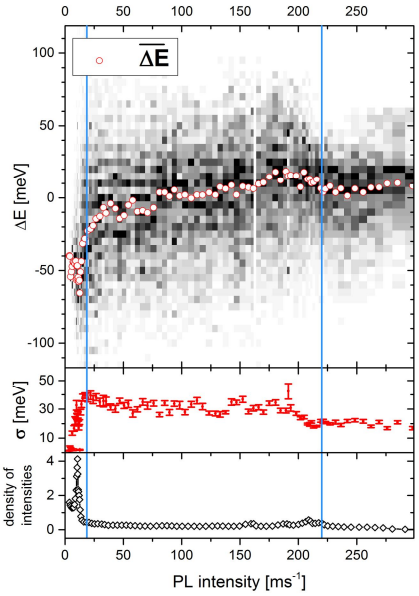

Fig. 1 Top: Spectral jumps (diffusion) Δ*E* with respect to the dichroic beam splitter at 567 nm during a blinking time trace as a function of the PL intensity (determined by CPA) of a single CdSe/ZnS QD. Circles correspond to the algebraic average of fluctuating Δ*E* at the respective PL intensity. Blue lines mark in the high intensity range the maximum of the intensity distribution (bottom) and at 1/10 of it. The latter corresponds to an intensity still detectable in cw PL spectra. The spectral shift between these two marks is typically ≈ 35 meV. Middle: σ corresponds to the Gaussian width of the spectral diffusion at a given PL intensity and is typically 20–40 meV in the intensity range between the 2 blue lines. Bottom: Density of intensities as a function of blinking (PL) intensity as determined during a blinking time trace of the PL of a single QD

Concluding, we find from single QD data 3 characteristic energies separated by typically 10 meV with 3 closely related PL decay times of about 1, 18, and 18 ns, respectively. PL decay times are increasing with decreasing PL energies. These findings are very close to those found for ensembles of QDs following deconvolution of PL spectra and decay times. In addition, we have shown that that despite weak ergodicity breaking *e.g.* blinking properties of single QDs can be closely mapped onto reversible photobleaching and PL decay of ensembles of QDs.

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