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 $\Delta E$ 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 $\approx 10$ 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 $I_{\text{max}}$ of the PL intensity distribution given in the bottom part of Fig. 1. The line on the left marks 0.1 $I_{\text{max}}$. 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 $\sigma$ 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 \( \approx 130 \) meV observed in ensemble experiments [5]. Remarkably, \( \sigma \) 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](image)

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 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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