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### Microscopic investigation of the emission efficiency of nanostructures

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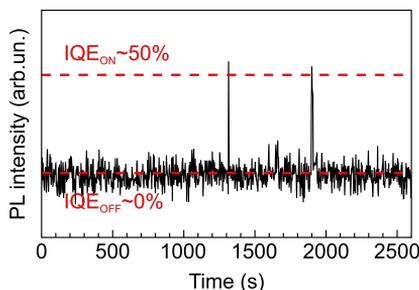
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## Discussion & outlook

Up to this point, we have demonstrated the different processes that determine the emission efficiency of QDs, by a detailed study of bu:Si-QDs. Importantly, we find that the IQE (Chapters 3) is more than a factor 10 larger than the QY. We critically re-examined the QY methodology itself (Chapter 2) and found that the QY method can lead to underestimation of the QY value. This occurs when the absorption of the sample is lower than  $\sim 10$  times the experimental uncertainties in the numbers of detected photons, e.g. for a relative uncertainty of  $\sim 1\%$ , samples with absorption below 10% are already affected. This is often the case for Si-QDs samples or low concentrated solutions. Nonetheless, even after corrections, the QY stayed very low. The much higher IQE thus suggests that, while in principle radiative processes can compete with non-radiative recombination, only a small fraction of QDs is optically active. Indeed, the presence of non-emissive QDs is commonly invoked to explain the discrepancy between QY and IQE in literature [9, 13, 20, 21, 36, 127]. As discussed in Chapter 1, the QY and IQE are related via [13]:

$$QY = \frac{1}{N} \sum_{i=1}^N QY_i = F_{br} \left[ \frac{1}{N_{br}} \sum_{i=1}^{N_{br}} IQE_i \delta_i \eta_i^{det} \right].$$

This shows that the discrepancy between the QY and IQE is the consequence of either a low fraction of permanently emissive QDs ( $F_{br}$ ) or due to a low fraction of temporarily emissive QDs, determined by the duty cycle ( $\delta$ ). In Chapter 4 by analysis of individual bu:Si-QDs we quantified the duty cycle and find that it is below 4%. The low duty cycle thus suggests that blinking is for the majority responsible for the low QY of bu:Si-QDs. This is schematically illustrated in Figure 6.1. Most of the time ( $\sim 96\%$ ), bu:Si-QDs are trapped in a long OFF state and only show short periods of high intensity, with an IQE of  $\sim 50\%$ . Only a limited fraction of the sample is permanently dark. The QY could thus be increased to values of at least the IQE, when the mechanisms that result in PL blinking can be suppressed. Most likely, this requires improved surface design, to prevent surface traps or defects likely to facilitate the charging and trapping of excited carriers in blinking [128, 129, 168]. Complete coverage of the surface of the small Si-QDs by



**Figure 6.1:** Proposed scheme to illustrate the emission efficiency of bu:Si-QDs. The QD is continuously excited, but this leads only to PL during brief periods of time. The brightness during these emissive periods is characterized by an IQE of  $\sim 50\%$ .

organic ligands, however, is prevented by steric hindrance [5], showing that alternative passivants should be explored for this.

A relevant consideration is that different types of surface passivation also affect the radiative and non-radiative recombination processes in the material. This makes it challenging to independently optimize the surface to suppress blinking for an improved ensemble QY. Especially for Si-QDs, where the surface has a critical influence on the transitions that are involved in radiative recombination, resulting in radiative rates that differ by orders of magnitude depending on the type of passivation [2, 5–7]. Importantly, via PL polarization anisotropy measurements (Chapter 3), we show that the emission TDM of bu:Si-QDs is static in nature, indicative of a localized state that is responsible for the emission. The static nature follows from the slow decay of the PL anisotropy compared to the PL lifetime of the material (Figure 6.2) and suggests the importance of localized states in radiative recombination. The long-lived PL anisotropy is observed also for other types of C:Si-QDs with visible range emission (Figure 6.2a and b). Potentially the localized states are introduced by the covalently bonded carbon atoms on the surface, which are expected to strongly contribute to the energy levels around the bandgap [2, 6, 7]. However, for C:Si-QDs with near-IR emission and microsecond lifetimes, we observe no PL anisotropy on time-scales comparable to the PL lifetime (Figure 6.2c and d). This indicates rather a degenerate radiative TDM, characteristic for band-to-band recombination [120]. The localized state involved in the visible range emission of Si-QDs thus seems not to significantly contribute to the radiative recombination in the near-IR emitting Si-QDs. This difference in PL anisotropy between the different types of C:Si-QDs illustrates that additional factors affect the nature of the TDM, e.g. the QD-size or the presence of oxygen, and requires further investigation.

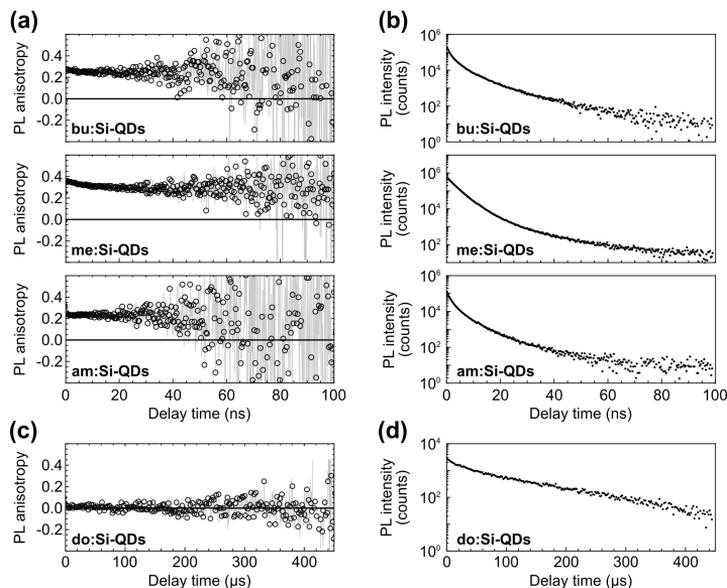
Without any optimization of the blinking dynamics, bu:Si-QDs seem at the current

<sup>4</sup>Samples courtesy of the group of Prof. Dr. H. Zuilhof (Wageningen University, The Netherlands)

<sup>5</sup>Samples courtesy of Dr. N. Licciardello and Prof. Dr. L. De Cola (Karlsruhe Institute of Technology, Germany)

<sup>6</sup>Samples courtesy of Dr. K. Kusova (Institute of Physics Czech Academy of Science, Czechia)

<sup>7</sup>Samples courtesy of MSc. S. Regli and Prof. Dr. J.G.C. Veinot, (University of Alberta, Canada)



**Figure 6.2:** (a,c) Decay of the PL anisotropy and (b,d) decay of the PL intensity after pulsed excitation with a linearly polarized 488 nm wavelength laser. (a,b) C:Si-QDs with a nanosecond PL lifetime, (c,d) C:Si-QDs with a microsecond PL lifetime: butyl-passivated Si-QDs (bu:Si-QDs)<sup>1</sup>, Amine-terminated Si-QDs (am:Si-QDs)<sup>2</sup>, methyl-passivated Si-QDs (me:Si-QDs)<sup>3</sup> and dodecane-passivated Si-QDs (do:Si-QDs)<sup>4</sup>. For more details on the samples see Appendix A.1.

stage most promising for applications in which low duty cycles are preferred, such as in super-resolution microscopy [139]. This technique is primarily aimed at the investigating of biological systems, for which Si-QDs already have many advantageous properties: a small size [169], bio-compatibility [31, 32, 170] and covalent surface functionalization options [33, 34, 171]. It remains to be explored, however, how the blinking dynamics of bu:Si-QDs are affected in the liquid cell environment and, more importantly, how the blinking can be controlled.

As an alternative to toxic and scarce material QDs, we investigated also the emission of carbon dots. The CDs have similarly advantageous properties to Si-QDs, but seem to be more versatile in terms of color engineering via surface groups. Nonetheless, for the CDs studied here, the ensemble QY is comparably low and also the duty cycle is limited, suggesting that this material suffers from similar surface related instabilities as the Si-QDs. The broad range of emission colors accessible via this benign material is otherwise very promising, but requires a more detailed study of the limitations of the emission efficiency, such as demonstrated here for Si-QDs.