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Microscopic investigation of the emission efficiency of nanostructures

Bart van Dam
MICROSCOPIC INVESTIGATION OF THE EMISSION EFFICIENCY OF NANO STRUCTURES
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<th>Description</th>
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<tr>
<td>AFM</td>
<td>Atomic force microscope</td>
</tr>
<tr>
<td>AM</td>
<td>Analytical model</td>
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<tr>
<td>APD</td>
<td>Avalanche photodiode</td>
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<tr>
<td>CCD</td>
<td>Charge coupled device</td>
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<tr>
<td>CD</td>
<td>Carbon dot</td>
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<tr>
<td>CMOS</td>
<td>Complementary metal oxide semiconductor</td>
</tr>
<tr>
<td>EBPVD</td>
<td>Electron beam physical vapor deposition</td>
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<tr>
<td>EDX(S)</td>
<td>Energy-dispersive X-ray (spectroscopy)</td>
</tr>
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<td>EMCCD</td>
<td>Electron-multiplying CCD</td>
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<tr>
<td>FTIR</td>
<td>Fourier-transform infrared spectroscopy</td>
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<tr>
<td>FOV</td>
<td>Field of view</td>
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<td>GFP</td>
<td>Green fluorescent protein</td>
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<tr>
<td>IQE</td>
<td>Internal quantum efficiency</td>
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<td>IR</td>
<td>Infrared</td>
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<td>IRF</td>
<td>Internal response function</td>
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<td>IS</td>
<td>Integrating sphere</td>
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<tr>
<td>LDOS</td>
<td>Local density of optical states</td>
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<td>LED</td>
<td>Light emitting diode</td>
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<tr>
<td>MLE</td>
<td>Maximum likelihood estimation</td>
</tr>
<tr>
<td>NA</td>
<td>Numerical aperture</td>
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<tr>
<td>PL</td>
<td>Photoluminescence</td>
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<td>QD</td>
<td>Quantum dot</td>
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<td>QY</td>
<td>Quantum yield</td>
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<td>STEM</td>
<td>Scanning transmission electron microscopy</td>
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<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
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<tr>
<td>TDM</td>
<td>Transition dipole moment</td>
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<tr>
<td>UV</td>
<td>Ultraviolet</td>
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<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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Introduction

1.1 Emission efficiency of nanomaterials

Fluorescent nanomaterials, such as proteins and molecules, but also semiconductor quantum dots (QDs) enable the manipulation of the wavelength of light through the absorption and re-emission of photons. The emission color is determined by the electronic energy levels of the material, which result in general from the material’s atomic composition and structure (symmetry). However, in contrast to dyes and rare earth ions, the emission of QDs also strongly depends on the size and shape of the particles. This results from the confinement of the electron and hole wavefunctions within the nanometer-sized particle, giving rise to an increase in the bandgap energy compared to the bulk value. This broadens the range of emission colors that can be achieved with a single material. For materials such as silicon (Si) and germanium (Ge) this range even spans from the ultra-violet (UV) to near-infrared (IR) spectral region [1, 2]. The emission properties arising from the QD core can be further modified via surface engineering. For II-VI class semiconductor QDs significant progress has been made by adding a shell of a different compound around the core, which allows further control over the emission properties and, moreover, can significantly improve the surface quality of the QD, through passivation of surface defects [3]. For Si based QDs, the type of surface passivation was shown not only to influence the emission wavelength [2, 4], but also the emission rate [2, 5–7], enabling to partially overcome the indirect bandgap nature of silicon.

The versatility of nanomaterials makes them of great interest for many lighting applications: As phosphors for light emitting diodes (LEDs), as the active material in solid state lasers, as a solar shaper for photovoltaics and for bio-medical applications, such as bio-imaging and drug delivery. For such applications, the most crucial characteristic is the emission efficiency of the emitter, i.e. the efficiency with which excitation energy can be converted into emission photons. In this thesis, we discuss important factors that determine the emission efficiency of fluorescent nanomaterials. This we do by quantifying the emission efficiency on different levels, starting from the efficiency on a macroscopic
scale, i.e. from a collection of nanoparticles, to the emission efficiency on a microscopic scale, from individual nanoparticles. While the methods described here are generally applicable to any type of emitter, here we use them to investigate carbon and silicon based nanoparticles. These materials exhibit in general advantageous properties, such as bio-compatibility, resource abundance, covalent functionalization options etc, but for which application is blocked by their limited emission efficiency. For Si-QDs this especially concerns emission in the visible spectral range as shown in Figure 1.1, where the ensemble emission efficiency is typically below 20%.

![Figure 1.1: Emission efficiency of Si-QDs. Overview of the quantum yield (QY) (filled symbols) and internal quantum efficiency (IQE) (open symbols) of values found in literature for different types of Si-QDs (black symbols). IQEs from Miura et al. [8] and Walters et al. [9] and QYs from Dohnalova et al. [2], Jurbergs et al. [10], Kusova et al. [11], Mastronardi et al. [12], Sangghaleh et al. [13] and Tu et al. [14]. The shaded area indicates the emission wavelength range for which high QYs and IQE have been reported.]

1.2 Microscopic origin of the emission efficiency

1.2.1 Quantum yield

The efficiency with which an emitter converts excitation photons into emission photons, can be quantified by the photoluminescence (PL) quantum yield (QY), given by the ratio of the number of emitted ($N_{em}$) and absorbed photons ($N_{abs}$):

$$QY = \frac{N_{em}}{N_{abs}}.$$  

The QY determines the fraction of light that is converted into photons that can be harvested and hence is for practical purposes an important parameter. It is commonly used to characterize ensembles of emitters, in which case the QY gives the average efficiency of the individual emitters and impurities that form the ensemble. This depends on the their internal quantum efficiency (IQE) and duty cycle ($\delta$) and on the out-coupling
1.2. Microscopic origin of the emission efficiency

The efficiency ($\eta$) of emission into the far-field [13]:

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

where $N_{br}$ and $F_{br}$ are the number of bright emitters and the fraction of bright emitters in the sample and $N$ the total number of emitters. The QY considers all losses within the ensemble, including those arising from non-emissive but absorbing (‘dark’) emitters with an IQE close to zero, and due to inefficient coupling of the emission towards the detector. Therefore the QY gives the lowest estimate of the emission efficiency, which could still be considerably improved by e.g. filtering the sample from impurities or via improved surface passivation.

### 1.2.2 Internal emission efficiency

The internal quantum efficiency (IQE) is determined by the competition between radiative and non-radiative recombination pathways available to the photo-excited electron-hole pair. The probability of both processes is given by their recombination rates $\gamma_r$ and $\gamma_{nr}$, respectively, from which the IQE is defined:

$$IQE = \frac{\gamma_r}{\gamma_r + \gamma_{nr}},$$

i.e. the ratio between the radiative recombination rate $\gamma_r$ and the total decay PL decay rate $\gamma_{PL} = \gamma_r + \gamma_{nr}$. Unlike the QY, which quantifies the emission efficiency via comparison of the number of emitted and absorbed photons by the sample, the IQE is determined solely from the PL of the studied material. This is typically done in time-resolved PL measurements, in which the rate ($\gamma_{PL}$) is probed at which carriers relax from the excited state back to the ground state. Since only bright emitters contribute to the PL signal, the IQE gives the average emission quantum efficiency of the bright subset of the ensemble of emitters only. As such, it provides insight into the most efficient emitters and gives the upper bound for the emission efficiency, provided that the non-radiative rate cannot be further improved (e.g. by removing trap states through surface passivation). Ultimately, in the absence of non-radiative channels, the IQE reaches 100%.

### 1.2.3 Duty cycle

For almost all quantum emitters it is generally observed that they do not emit continuously [15], but switch between ON periods during which the emitter is optically active, and dark OFF periods where the brightness is significantly reduced and close to zero. This so called PL intermittency or ‘blinking’ is observed over a broad range of time scales ranging from microseconds to minutes and results from different states of the emitter, which are characterized by a different IQE. The OFF-state occurs either due to change in the radiative probability, e.g. due to inter-system crossing of the emitter from a singlet to a triplet state, from which radiative recombination is inhibited, or
from the activation of a non-radiative channel. For QDs, blinking is most commonly interpreted in terms of charging of the QD [16, 17], e.g. as a result of the trapping of the photo-excited electron or hole on the QD surface. This leaves the core charged so that subsequent excitation will be efficiently quenched by Auger recombination. In most cases, the quenched OFF state of the emitter is optically inactive and considered dark ($IQE_{OFF} \sim 0$). In that case, the efficiency of the blinking process can be quantified by its duty cycle:

$$\delta = \frac{T_{ON}}{T_{ON} + T_{OFF}},$$ (1.1)

i.e. the fraction of time during which the QD is emissive. However, even in the OFF state radiative recombination can be sufficiently efficient to compete with the non-radiative recombination, resulting in a ‘gray’ state [18, 19] for which the $IQE > 0$.

### 1.2.4 Dark QDs

In addition to temporary switched off emitters, the ensemble might also contain permanently dark species [20, 21] or impurities. These species absorb excitation light but do not emit, as energy is dissipated via non-radiative channels. In contrast to the OFF state resulting from blinking, the non-emissive state is permanent and dark QDs are generally thought to be responsible for the low QY in poly-disperse ensembles of QDs [8, 20, 21]. For QDs, these dark species are expected to arise from poor surface passivation, which results in dangling bonds at the surface of the nanoparticles. The missing bonds break the crystal symmetry and contribute energy levels within the bandgap of the material, which constitute efficient non-radiative channels. Already a single dangling bond results in the full quenching of the emission of Si-QDs in an oxide matrix [22], demonstrating the importance of surface passivation.

For Si-QDs, the highest surface coverage can be obtained with hydrogen, which, however, is not stable in ambient conditions and makes the surface prone to oxidation. Alternatives are passivation by SiO$_2$, potentially followed by a hydrogen post-treatment to further decrease the amount of dangling bonds [23]. Passivation using organic ligands is also explored, although with the decreasing QD-size it becomes increasingly difficult to achieve full surface coverage due to steric hindrance.

### 1.2.5 Out-coupling efficiency

The QY concerns the efficiency with which excitation can be converted into harvested photons, which for most applications concerns photons ending up in the far-field. In addition to the excitation that is lost via non-radiative channels, however, not all radiative recombination transitions result in photons that couple to the far field: Photons can be trapped in the embedding medium via internal reflection, or can couple to surface plasmon polaritons (SPPs) or lossy surface waves in nearby metal interfaces [24, 25]. Moreover, the photonic environment also affects the directionality of the emission, which can be strongly anisotropic for emitters in an anisotropic environment. As a result, the observed brightness (and QY) is reduced. This was demonstrated for Si-QDs above a
1.3 Benign luminescent nanoparticles

1.3.1 Silicon quantum dots

Silicon has become the cornerstone of CMOS technologies, implemented in microelectronics, photovoltaics and photodetector technologies. However, as an active emitter in lighting or photonic applications, silicon is hindered by its indirect bandgap. The indirect bandgap is characterized by an inefficient band-edge absorption and low radiative rates, which result in impractically low photon fluxes and emission efficiencies in the presence of non-radiative channels. The limitations of the indirect bandgap can be partly overcome with silicon QDs (Si-QDs) via quantum confinement [1, 5, 27]. Si-QDs show room temperature size-tunable luminescence and have many advantages when compared to typically used phosphors, such as direct bandgap QDs, organic dyes or rare earth ions: Si-QDs are photo-chemically robust and stable due to covalent bonding of ligands [28, 29], they offer spectrally broad PL, tunable from the infrared (IR) to the ultraviolet (UV) [1, 5, 30], are non-toxic (bio-compatible and bio-degradable [31, 32]) and can be (bio-)functionalized by a large diversity of covalently bonded ligands [33, 34].

While the emission efficiency of Si-QDs remains comparatively low with respect to direct band gap materials and dyes, it has been significantly improved since their discovery [27]. E.g. for Si-QDs emitting in the near-IR spectral region, QYs exceeding 60% [10, 35, 36] have been reported, which could see even further improvement as the IQE has been reported to reach unity [8, 13, 36]. This shows that bright subsets within the ensemble of QDs exist for which non-radiative channels are already completely suppressed and suggests a promising future for the application of Si-QDs.

For emission in the visible spectral region the situation is very different. The QY of intrinsic PL is only sparsely reported on and have not exceeded 20% [5]. This is typically argued to be the consequence of the non-radiative contribution due to the increased number of surface defects for smaller Si-QDs [5, 12, 37, 38]. Furthermore, tunability of the PL by the size of the Si-QD through the visible spectral range seems inaccessible for Si-QDs in the presence of oxygen defect states [4], rendering the most commonly studied oxide passivated Si-QDs (O:Si-QDs) unsuitable for this spectral range. Potentially, these limitations can be overcome with a class of Si-QDs capped with organic molecules (C:Si-QDs), which extend emission into the visible spectral region [1, 2, 5, 11, 39, 40]. The emission rates in C:Si-QDs have been shown to approach those of direct bandgap materials [2, 6, 7, 11, 39, 40], suggesting significant enhancement of the radiative recombination rates by 2-3 orders of magnitude compared to hydrogen or oxide passivated Si-QDs [2, 5–7, 11]. Unfortunately, despite the greatly enhanced radiative rates in C:Si-QDs, the QY remains comparatively low in the visible range (<20%) [5, 11, 39], with the most probable cause being the low degree of surface passivation by organic
molecules.

1.3.2 Carbon dots

Carbon dots (CDs) are a promising class of carbon-based fluorescent nanoparticles that consist of a mixture of sp$^2$ and sp$^3$ hybridized carbon atoms [41]. Since their discovery in 2004 [42], CDs have drawn much attention due to their facile synthesis [43], bio-compatibility [44–47] and the large natural abundance of carbon. Even more interestingly, some synthetic routes yield CDs with excitation-dependent PL that spans the entire visible spectral region. This broad PL allows for flexible ‘tuning’ of the light emission from blue to red via changes in excitation wavelength [48–51], offering new opportunities for emission color engineering with a single material. Owing to the great application potential, many studies have been devoted to unraveling the mechanism behind the PL of CDs, providing evidence for emission controlled by the CD core size [49], emission from functional groups on the CD surface [52] and a combination of both [50, 53, 54]. The emission tunability has been most prominently ascribed to selective excitation of subsets of CDs within the CD ensemble [55–57]. Indeed, multiple studies have shown that it is possible to tune the emission by using different types of CDs that are themselves excitation-independent [58–60]. On the other hand, Pan et al. [51] and Fu et al. [61] have suggested that different emission sites within individual CDs are responsible for the excitation-dependent emission. Establishing a generic model for the excitation-dependent PL of CDs has proven to be challenging [62], due to the great variety of chemical and structural compositions resulting from the different synthetic routes [63] and even observed within one and the same CD ensemble. Until now, the majority of studies is focused on ensemble spectroscopy techniques that provide only limited insight into the microscopic distribution of different emission mechanisms within CD ensembles and within a single CD. Spectroscopic investigations of the single CDs provide significant insight, but these are scarce [64, 65], while the improved understanding of the origin of the PL is a prerequisite for the understanding and optimization of the emission efficiency. Hence, there is an active debate regarding the microscopic origin of the PL, motivated by the possibility of excitation-dependent single CD emission.

1.4 Synergy of this thesis

In this thesis, different factors that critically affect and determine the emission efficiency of fluorescent nanomaterials are investigated. This is demonstrated in great detail in Part I on C:Si-QDs, for which the limited emission efficiency is the major limitation of this otherwise promising material. This is divided into three chapters, starting with the ensemble emission efficiency in Chapter 2, which is quantified by the QY. Here, the reliability of the methodology most commonly used to measure the QY is assessed and shown to yield underestimated values for low-absorbing materials. By comparison with theoretical simulations, a corrected QY method is proposed and applied to evaluate the QY of different types of C:Si-QDs. In Chapter 3, the emission efficiency limit of Si-QDs
emitting in the visible range is investigated, by measurement of the IQE through a Drexhage-type setup. This gives the emission efficiency of the emissive subset of QDs and therefore the maximum QY that could potentially be achieved with this material. Finally, in Chapter 4 the emission efficiency of individual C:Si-QDs is studied, by employing single-dot microscopy. In addition to Si-QDs, an alternative group-IV nanomaterial is explored in Chapter 5: carbon based nanoparticles. Using single-dot spectroscopy, the microscopic organization of different emission mechanisms within these complex materials is investigated. This shows that CDs have versatile PL properties, as additional emissive channels can be introduced via nitrogen and oxygen containing surface groups. The thesis is concluded in Chapter 6 where the insights obtained through the emission efficiency measurements are combined. The factors that limit the efficient emission of C:Si-QDs are identified and the potential of C:Si-QDs and CDs for lighting applications is discussed.
PART I

Microscopic origin of the emission efficiency
Chapter 2

Quantum yield

PL QY offers a simple and robust way to assess the emission efficiency of light emitting materials, such as fluorescent proteins, dyes and semiconductor QDs, and is defined by the ratio of the numbers of emitted and absorbed photons. Common methods of QY measurement employ an integrating sphere (IS) technique that has been standardized and is used commercially and for research. In this chapter we test the validity of this method, both experimentally (Section 2.3) and theoretically (Section 2.4) and show that the QY methodology suffers from an artifact. This artifact results in an underestimation of the QY and depends on the absorption of the studied sample. The effect is present already under common experimental conditions and is therefore highly relevant for a number of published studies, which employ the QY methodology. To correct for the intrinsic absorption-dependence of the QY determination, in Section 2.5 we propose a dedicated calibration protocol, enabling the correct evaluation and interpretation of the QY of samples with varying absorption. These findings are applied to determine the QY of different types of Si-QDs.

2.1 Introduction

As generally for lighting applications, a crucial property for fluorescent materials is the emission efficiency, which can be quantified by the PL QY, defined as the ratio of emitted to absorbed photons:

\[ QY = \frac{N_{em}}{N_{abs}}. \]  

(2.1)

To measure this ratio, various techniques exist [66, 67], many of which rely on the comparison with a calibration standard of which the QY is known. Since this requires a QY standard which has similar absorption and emission as the sample of interest and of which the QY must be precisely known, finding a suitable calibration material is challenging, especially when the sample scatters and when emission is anisotropic or spectrally broad. A direct optical method, originally introduced by de Mello et al. [68] in 1997, avoids the problems associated with the comparative methods by implementing an
integrating sphere (IS) (Figure 2.1a). The IS, a reflectively scattering cavity, allows the direct determination of the absolute number of emitted and absorbed photons. Originally implemented as a three-step measurement [68], this method was later simplified into a two-step measurement [69], and involves the comparison of the calibrated emission and absorption spectra of the studied sample to a suitable blank.

The IS technique gained popularity in the research and development of new fluorescent materials. Moreover, it has been employed to study the size-dependent [12, 37, 70], excitation-energy-dependent [71–74] and concentration-dependent properties [71, 75] of QD systems. However, the broad application of the IS methodology in literature raises questions on the validity of the determined QY values. Several guidelines exist for QY measurements [76, 77], discussing e.g. the effects of re-absorption [78] and excitation geometry [79, 80]. In this work we study the validity of the IS methodology, over a broad range of excitation wavelengths and for different sample concentrations. Specifically, we focus on the effect of low sample absorption which is typically encountered for Si-QDs. We show both theoretically and experimentally that the IS methodology suffers from an experimental artifact that gives rise to underestimated QY values. We propose a correction procedure and quantitative guidelines for more reliable QY determination. Finally we apply these findings to quantify the emission efficiency of Si-QDs.

### 2.2 Integrating sphere methodology

In the implementation of the QY method described by Mangolini et al. [69], a sample (e.g. a cuvette containing a solvent in which emitting nanoparticles are dispersed) is suspended inside an IS (Figure 2.1a). The sample is excited from the entrance port, where a fraction $F$ of the excitation beam impinges directly on the sample. The IS’ highly reflective coating ensures that all the transmitted excitation and emission photons are captured and distributed over the IS’ interior. After multiple reflections and scattering events within the IS, the excitation and emission photons are ultimately detected, (re-)absorbed in the sample or lost (e.g. absorbed by the coating). The detected spectrum is compared to that of a blank reference sample (e.g. the cuvette with solvent) as shown in Figure 2.1b for the QY calibration dye Rhodamine 6G (R6G). From the difference (Figure 2.1c) in the detected photons intensities at the excitation ($\lambda_{exc}$) and emission wavelength ($\lambda_{em}$), $I$ and $I^*$ respectively, the numbers of absorbed and emitted photons can be evaluated:

\[
QY = \frac{N_{em}}{N_{abs}} = \frac{N^*_S - N^*_Ref}{N_{Ref} - N_S} = \frac{\int_{\lambda_{exc}}^{\lambda_{em}} [I^*_S(\lambda) - I^*_Ref(\lambda)] C(\lambda) d\lambda}{\int_{\lambda_{exc}}^{\lambda_{em}} [I_{Ref}(\lambda) - I_S(\lambda)] C(\lambda) d\lambda},
\]

where subscripts $S$ and $Ref$ refer to the sample and reference measurements and $N$ and $N^*$ to the total number of photons at the excitation and emission wavelength, respectively. The factor $C(\lambda)$ corrects for the spectral sensitivity of the detector and IS, for which an additional calibration measurement is performed using an empty IS and a calibration source with a known spectrum.
2.3. Experimental limitations of the IS methodology

To study the experimental range in which the IS method yields reliable QY estimates, we measure the QY of three very different materials (an organic dye and two types of inorganic QDs) in a wide range of excitation wavelengths and for various material concentrations commonly encountered in literature. For this we use a standard IS geometry (shown schematically in Figure 2.1a), with the excitation provided by a stabilized Xenon lamp coupled via a double-grating monochromator into a spectrally broad optical fiber. Light is detected using a second spectrally broad optical fiber coupled to a spectrometer equipped with a charge-coupled device (CCD) camera (for a detailed description, see QY setup 1 in the Materials & methods section). Moreover, additional measurements were carried out in an independent QY setup in a different laboratory (see QY setup 2 in the Materials & methods section).

**Rhodamine 6G**

First we study R6G in ethanol (for details, we refer to Section A.1), which is a well-known fluorescent dye that is commonly used as a calibration standard for comparative QY measurements and has a reported QY of about 95% [81]. We prepared several solutions of R6G in ethanol, with concentrations between $\sim 120$ and $6 \mu$M. Within this range, the shape of the absorption coefficient spectrum is unaltered (Figure 2.2a), indicating the absence of clustering effects or other material changes [82]. Moreover, the PL lifetime in the studied range is independent of excitation wavelength and concentration (Figure 2.2b), showing that the internal emission efficiency is constant. The PL spectra show a strong dependence on the concentration as a result of re-absorption effects (Figure 2.2c). This is commonly encountered for materials with overlapping emission and absorption spectra (see e.g. [78, 82]). We corrected our results for re-absorption using the procedure...
described in detail by Ahn et al. [78].

QYs obtained at various R6G concentrations excited between 300 and 520 nm are shown in Figure 2.3. For the highest concentration of 120 μM, we find a QY of ~83-89 % that is almost constant over the whole spectral range, which is expected due to the Kasha-Vavilov rule. We note that the absolute QY value is somewhat lower than that found in literature [81], which will be discussed in Section 2.5. Interestingly, as the concentration decreases and hence also the sample’s absorption, the determined QY drops significantly, at some points to as low as 38 %. The same drop in QY is observed when the concentration is fixed and the excitation wavelength is lowered below ~460 nm, for which the absorption coefficient of R6G decreases significantly. In contrast, no decrease is observed for higher absorption ranges, such as near the resonant absorption peak at 530 nm.

The effect of the sample absorption becomes even more apparent when plotting the QY in a different manner, against the single-pass absorption\(^1\) of the sample, showing that the QY decreases significantly at low absorption, independently whether the absorption is lowered via the sample concentration or via the excitation wavelength (Figure 2.3b). At around a critical absorption value (\(A_{\text{crit}}\)) of 10-15% there is an abrupt change in the behavior of the QY, where for absorption above \(A_{\text{crit}}\) the QY is constant and close to the literature value, but decreases continuously with the absorption for \(A < A_{\text{crit}}\). The same decrease is observed when we fix the concentration and excitation wavelength and decrease the single-pass absorption of the R6G solution by only changing the optical path length through the sample by using a thinner cuvette, as shown in Figure 2.4. This shows that the effect is

\[^1\]In this thesis the single-pass absorption is defined as the fraction of absorbed light upon a single passage through the sample, i.e. similar to the absorptivity or absorptance.
2.3. Experimental limitations of the IS methodology

not intrinsic to the studied material and seems to depend only on the sample’s absorption.

**Figure 2.3:** QY of R6G. (a) Determined QY values as a function of the excitation wavelength for different sample concentrations between 120 and 6 µM. Data are corrected for re-absorption effects using the procedure described in [78]. Dashed black lines serve as guides to the eye, the solid lines represents the single-pass absorption of the highest and lowest concentration sample (right axis). For comparison with literature, the QY values as determined by Faulkner et al. [79] for a 100 µM (the higher QY value) and 1 µM (the lower QY value) solution of R6G in ethanol are plotted in blue. (b) QY values from (a) plotted against the single-pass absorption to illustrate the dependence of QY on absorption. Red points represent QY values obtained for different concentrations under 380 nm excitation wavelength. Blue points are from Faulkner et al. [79], where the single-pass absorption has been estimated from the concentration assuming an optical path length of 10 mm. The vertical dashed line indicates the critical absorption, $A_{\text{crit}}$, below which QY is underestimated.

To check if the effect is caused by our specific implementation of the IS method, we measure the QY also under indirect excitation conditions ($F = 0$). Interestingly in this case, the QY approaches 95% at high sample absorption, as expected for R6G. However, similarly to under direct excitation conditions ($F = 1$), the QY is underestimated for decreasing absorption (Figure 2.5a and b).

**Figure 2.4:** (a) QY versus excitation wavelength of R6G in ethanol (black: $\sim$260 µM, gray: $\sim$22 µM) for a 10 and 2 mm optical path length through the sample. For one and the same sample lower QY values are obtained when the path length is reduced. Solid line shows the single-pass absorption of the samples. (b) QY plotted against the single-pass absorption. A similar trend is observed as in Figure 2.3b.

We carefully confirmed this effect also in an independent experimental configuration. For this we use an IS with a different internal geometry, a laser-driven light source which
gives improved stability and a liquid nitrogen-cooled CCD camera to reduce the detection noise (for more details, see QY setup 2 in the Materials & methods section). Again, both under indirect (Figure 2.5c and d) and direct excitation (Figure 2.6) the QY is underestimated, although we note that the critical absorption ($A_{\text{crit}}$) below which this occurs varies slightly between the different setups (vertical dashed lines).

**Figure 2.5:** (a) QY versus excitation wavelength of R6G in ethanol ($\sim 14 \mu\text{M}$) with the sample under direct ($F = 1$, blue) and indirect ($F = 0$, red) illumination conditions. The solid line shows the single-pass absorption of the sample. (b) QY from (a) plotted against the single-pass absorption. (c) Comparison of the QY of R6G in ethanol under indirect excitation conditions measured in two independent experimental setups: The red symbols show the same data as in panels a and b (red), the green data show the QY measured in a different setup (QY setup 2). (d) QY from (c) plotted against the single-pass absorption. The vertical dashed lines in b and d indicate $A_{\text{crit}}$.

**QD materials**

In addition to R6G, we demonstrate the effect also on dispersions of two types of semiconductor QDs - Si-QDs and CdSe QDs (for sample details see Appendix A.1) - in Figure 2.7. Both materials have very different optical properties from each other and from those of R6G, such as emission efficiency, single-pass absorption and emission spectra (Figure 2.7a). The most notable difference is the broad absorption spectrum, resulting from the band-like dispersion relation in semiconductors. Also, Si-QDs have a larger Stokes shift and a less abrupt absorption onset than CdSe QDs due to the indirect band-structure. Nevertheless, independently of the differences with R6G, the QY of both types of QDs decreases with longer excitation wavelengths (Figure 2.7b), when absorption drops below $A_{\text{crit}}$. Again, the effect is more pronounced for lower concentrations.
2.3. Experimental limitations of the IS methodology

Figure 2.6: QY of a $\sim 60 \mu$M (black) and $\sim 6 \mu$M (gray) solution of R6G in ethanol under direct excitation plotted against the excitation wavelength (a) and single-pass absorption (b). The vertical dashed line indicates $A_{\text{crit}}$. The measurements (courtesy of J. Valenta, Charles University) are carried out in an independent experimental setup (QY setup 2).

One might argue that the process of emission and absorption is more complex for QDs than for organic dyes such as R6G, and that therefore the validity of the Kasha-Vavilov rule might be weaker or not hold at all [71, 84]. With that line of reasoning, the observation of explicit QY dependence on various parameters could be interpreted in terms of novel effects [12, 37, 70–73, 75]. Another alternative - more conservative - explanation of the dependence would be that the size-polydispersity of QD ensembles can lead to a broadening of the emission spectrum [8], which in turn could lead to excitation wavelength dependent QY via excitation of different subsets of the QD ensemble. Additionally, the concentration of QD dispersions is expected to affect QD interactions [71, 85], which strongly depend on the inter-particle distance. Nonetheless, when plotting the QY of the QDs versus their absorption (Figure 2.7c), the resemblance with the trend observed for R6G is striking in terms of the shape of the QY-dependence and the value of $A_{\text{crit}}$, suggesting that the excitation- and concentration-dependence is for the largest part described by the presented effect.

Figure 2.7: (a) Absorption coefficients and PL spectra (dashed lines) for three types of samples: R6G in ethanol (black), Si-QDs in toluene (red) and CdSe QDs in hexane (blue). (b) QY against the excitation wavelength of CdSe QDs and Si-QDs. The QY of Si-QDs below 360 nm is omitted because the solvent is non-transparent in this spectral region. (c) The QY of the CdSe and Si-QDs from (b) and of R6G (Figure 2.3) against the single-pass absorption. The dashed lines serve as guides to the eye, showing a similar trend of the QY independent of the studied material. The critical absorption is indicated by the vertical dashed line.
Conclusion

In summary, we have shown that we observe the same decrease of the QY when the single-pass absorption of the sample is lowered, either by lowering the sample’s concentration, excitation wavelength or by shortening the optical path and which shows independently of the experimental conditions, studied material and particular setup. Hence we conclude that it is an experimental artifact that manifests itself independently of the particular setup geometry or implementation of the IS methodology. The artifact generally occurs for materials with absorption in the range $A < A_{\text{crit}}$, where the QY value becomes critically underestimated as the absorption decreases. To the best of our knowledge, this artifact has not been noticed in the literature until now, despite the fact that, as we demonstrate here, it also occurs for well-known materials such as R6G in ethanol, which is commonly used as a calibration standard for QY measurements. For R6G, the artifact could have passed unnoticed due to the absence of broad studies in which the absorption is considerably varied through the excitation wavelength or concentration, such as reported here. Studies reporting on the QY of R6G typically probe only the excitation maximum situated around 530 nm wavelength [82, 86, 87], or show the QY only for a few concentrations [79], from which the artifact is not directly apparent. Hence, the absorption-dependence of the QY has not been identified as an artifact of the QY methodology and could have been misinterpreted in terms of physical effects. Nevertheless, when we add literature values obtained by Faulkner et al. [79] for two concentrations of R6G to our results in Figure 2.3, we find excellent agreement. This shows that while the artifact is not identified, it is present in other studies as well. Hence, even more for other materials that are not expected to fulfill the Kasha-Vavilov rule such as QD systems [12, 37, 70–73, 75], this effect has passed unnoticed. Therefore, it could have affected the conclusions drawn based on the excitation wavelength, concentration and QD-size dependence of the QY, all cases in which also the sample’s absorption is varied.

2.4 Theoretical model of the QY methodology limitations

2.4.1 Analytical model

For a detailed analysis of the artifact described in Section 2.3, we simulate the QY experiment in the IS setup using an analytical model (AM). For this we express the measured photons intensities $I$ in Equation 2.2, used to compute the QY, in terms of the probability that emission and excitation photons reach the detector port via multiple reflections within the IS.

To obtain an analytical expression, we generalize the IS and model it as a cavity with two small openings: an entrance port from which excitation light enters and an exit port equipped with a detector, as shown in Figure 2.8. The sample or reference is modeled as a spherical object in the center of the sphere with an absorption $A$, reflection $R$ and
transmission $T$, where $A + R + T = 1$. The interior of the IS is covered by a coating that is highly reflective over a broad spectral range $R_w$ (usually $> 97\%$) and acts as an ideal scatterer, i.e. the directionality of the light is lost after a single reflection from the walls. We model this by assigning a probability $p$ that a photon impinges on an object inside the IS, by the relative area of the object to the area of the IS interior. For example the probability of hitting the wall ($p_w$), loss channel ($p_l$), detector ($p_d$) or sample ($p_s$), with $1 = p_l + p_d + p_s + p_w$. Since the ideally scattering walls ensure the spatially homogeneous distribution of the photons, we assumed for our generalized geometry that these probabilities do not depend on the exact location in the IS at which the photon scatters from the wall. However, the directionality of the light, which starts from a single point (i.e. excitation from the entrance port and emission from the sample) is not lost before it reflects of the ideally scattering coating. To account for this in our simulations, we separate the first round before the light reflects of the wall ($n = 1$) from the consequent ones ($n \geq 2$) (see Figure 2.8). We do this by assigning modified probabilities $p_{0x}$ of hitting objects inside the IS, given by their visibility from the entrance port and sample. Again, $1 = p_{0l} + p_{0d} + p_{0s} + p_{0w}$ and $1 = p_{sw} + p_{sw} + p_{sw}$. $p_{0s}$ represents the fraction of the initial excitation light intensity, $I_{0}^{exc}$, that hits the sample directly, a parameter that is commonly varied in literature [68, 79, 80]. To separate this parameter from the other probabilities, we set $p_{0s} = F$, where $F = 1$ for direct or $F = 0$ for indirect excitation conditions. Furthermore, in accordance with the standard IS methodology, direct detection of the excitation and emission photons is prevented by an inserted baffle, simulated by setting $p_{0sd} = p_{sd} = p_{sd} = p_{sd} = 0$ (dashed lines in Figure 2.8). For completeness, we finally assume that the measurement is in a regime in which the QY is independent of the excitation photon flux.

From the light paths illustrated in Figure 2.8 and their probabilities $p_x$, we simulate the transmitted excitation intensities during the first ($n = 1$) up to the $n$-th reflection:

\[
I_1^{exc} = I_0^{exc}[p_{0w} + F(1 - A)p_{0sw}]R_w
\]
\[
I_2^{exc} = I_1^{exc}[p_{w} + p_{s}(1 - A)p_{sw}]R_w
\]
\[
I_3^{exc} = I_2^{exc}[p_{w} + p_{s}(1 - A)p_{sw}]R_w
\]
\[
\vdots
\]
\[
I_n^{exc} = I_{n-1}^{exc}[p_{w} + p_{s}(1 - A)p_{sw}]R_w
\]
\[
= I_0^{exc}[p_{0w} + F(1 - A)p_{0sw}]R_w
\]
\[
\cdot \{(p_{w} + p_{s}(1 - A)p_{sw}]R_w\}^{n-2}.
\]

Here, $p_{0sw}$ and $p_{sw}$ indicate the probabilities of light passing through the sample and hitting the wall for the first and consecutive reflections, respectively. Similarly, we evaluate the absorbed intensity ($I^{abs}$) by the sample/reference and the intensity recorded
by the detector ($I_{\text{det}}$) at the exit of the IS by:

$$I_{\text{abs}}^1 = I_{0}^{\text{exc}} FA$$
$$I_{\text{abs}}^n = I_{n-1}^{\text{exc}} p_s A$$
$$I_{\text{det}}^1 = I_{0}^{\text{exc}} [p_{0d} + F(1 - A)p_{0sd}]$$
$$I_{\text{det}}^n = I_{n-1}^{\text{exc}} [p_d + p_s (1 - A)p_{sd}]$$.

Figure 2.8: Schematics of the generalized IS setup used for our model. The IS cavity has a small entrance on the left side and an exit on the bottom side, where a detector is placed. The sample/reference is modeled as a spherical object suspended in the center. Lines represent the light paths between different objects inside the IS - wall (w), loss channel (l), detector (d) and sample (s). The parameters $p_{xy}$ represent the probabilities associated with each specific light path. Light paths shown in dashed lines are prevented by baffles. The light paths before the first reflection from the IS wall ($n = 1$) are considered separately to account for the inhomogeneity of the light field in that instance. This differs for excitation light (entering from outside) and emission (originating from the center). Emission (red lines) is assumed separately from the excitation (blue lines) due to different spectral ranges, where the reflectivity of the sphere and the sample’s absorption differ.

For the emitted light intensity ($I^{\text{em}}$) and its fraction recorded by the detector ($I_{\text{det}}^*$), we consider a different reflectivity of the IS coating $R_w^*$ and an effective sample absorption $A^*$:

$$I_{1}^{\text{em}} = I_{0}^{\text{em}} p_{0w} R_w^*$$
$$I_{n}^{\text{em}} = I_{n-1}^{\text{em}} R_w^* [p_w + p_s (1 - A^*)p_{sw}]$$
To account for re-absorption and subsequent re-emission, $A^*$ is defined as $A^* = A(\lambda_{em}) \cdot (1 - \eta)$. Here, $\eta$ is the ‘real’ QY of the sample, i.e. the intrinsic QY unaffected by the measurement method, so that $A^*$ gives the fraction of emission light that is absorbed by the sample, but not re-emitted. The initial emission intensity originating from the sample is given by $I_{em}^0 = I_{em}^{abs} c \eta$, where $I_{em}^{abs}$ is the total excitation intensity absorbed in the sample and $c$ is the fraction of light absorbed by the emitters in the sample (i.e. $c < 1$ when the emitters are dispersed in an absorbing matrix or solvent). The total absorbed intensity by the sample during the measurement is calculated by summation of $I_{n}^{abs}$ over all reflection-steps. Using the geometric series, $\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$, we obtain:

$$I_{tot}^{det} = \sum_{n=1}^{\infty} I_{n}^{det}$$

$$= I_0^{exc} \left\{ p_{od} + F(p_{od} + R_w[p_{0w} + F(1 - A)p_{0sw}]) \frac{p_d + p_s(1 - A)p_{sd}}{1 - R_w[p_w + p_s(1 - A)p_{sw}]} \right\}$$

$$I_{tot}^{abs} = \sum_{n=1}^{\infty} I_{n}^{abs}$$

$$= I_0^{exc} A \left\{ F + R_w[p_{0w} + F(1 - A)p_{0sw}] \frac{p_s}{1 - R_w[p_w + p_s(1 - A)p_{sw}]} \right\}$$

$$I_{tot}^{det^*} = \sum_{n=1}^{\infty} I_{n}^{det^*}$$

$$= I_0^{em} \left\{ p_{0d} + p_{0w}^* R_w^* \frac{p_d + p_s(1 - A^*)p_{sd}}{1 - R_w^*[p_w + p_s(1 - A^*)p_{sw}]} \right\}.$$

To evaluate the spectral sensitivity correction factors $C$ and $C^*$ we assume an empty sphere ($A = 0$) and compare the theoretical intensity, equal to the input intensity at the sphere entrance $I_0^{exc}$, with the detected intensity at the sphere exit. This is done separately for excitation and emission wavelengths, where in the latter case we replace $R_w$ by $R_w^*$:

$$C = \frac{I_0^{exc}}{I_{tot}^{det}(A = 0)}$$

$$= \left[ p_{od} + F p_{0sd} + R_w(p_{0w} + F p_{0sw}) \frac{p_d + p_s p_{sd}}{1 - R_w(p_w + p_s p_{sw})} \right]^{-1}.$$

For common IS conditions, such as a non-absorbing reference ($A_r = 0$), no re-absorption ($A^*_S = 0$) and inserted baffles ($p_{0d} = p_{0sd} = p_{0w}^* = p_{sd} = 0$), the number of emitted $N_{em}$
and absorbed $N_{abs}$ photons in Equation (2.2) can be expressed as:

$$N_{em} = I_0^{exc} [F + (p_{0w} + F(1 - A_S)p_{0sw})M_p] A_S \eta \frac{p_{0w} M^* p_d}{(p_{0w} + F p_{0sw})M_{cal} p_d}$$  \hspace{1cm} (2.7)$$

$$N_{abs} = I_0^{exc} \left[ 1 - (p_{0w} + F(1 - A_S)p_{0sw})M_p \right]$$  \hspace{1cm} (2.8)$$

$M$ and $M^*$ are "sphere-multipliers", defined as $M = R_w (1 - R_w[p_{sw} + p_s(1 - A)p_{sw}]^{-1}$ and $M^* = R_w^* (1 - R_w[p_{sw} + p_s(1 - A)p_{sw}]^{-1}$ and describe how light is distributed over the IS interior and the objects inside it [77]. For the calibration measurements, $M_{cal} = M(A = 0)$ and $M^*_{cal} = M^*(A = 0)$. Assuming that loss channels are small, $p_{0w} = 1 - F - p_{0l} \sim 1 - F$, Equations 2.7 and 2.8 reduce to the QY descriptions found elsewhere [68, 77, 79], which justifies the described approach. Our model enables one to express the measured QY in terms of the intrinsic QY of the studied material.

2.4.2 Ray-tracing simulations

In collaboration with the Computer Graphics Group from the Charles University\textsuperscript{2} we verify our AM using numerical ray-tracing simulations (RTS), described in Appendix A.2. In contrast to the AM, different photon paths are individually considered in the RTS approach, thus yielding solutions even for non-uniform photon distributions and IS geometries. Although the RTS approach is computationally more demanding, it enables us to model the setup more precisely.

We simulate the QY for an IS setup for a sample with a QY of $\eta = 45\%$ and for a non-absorbing and non-emitting reference sample, i.e. $N_{Ref}^* = 0$. The results are shown in Figure 2.9a. Both models give QY estimates that are in excellent agreement with the input emission efficiency $\eta = 45\%$, for single-pass absorption values between 1 and 100\%. Moreover, the QY estimate is independent of the reflectivity of the IS in the range between 0.9 and 1.0, which is properly accounted for through the spectral sensitivity correction.

The simulated number of absorbed ($N_{abs}$) and emitted ($N_{em}$) photons used to compute the QY, normalized to the total number of excitation photons ($N_{0}^{exc} = \int I_0^{exc} dt$), are shown in Figure 2.9b and c. The fraction of absorbed photons decreases roughly proportional to the single-pass absorption of the sample as shown in Figure 2.9b (solid lines). However, it is slightly increased with respect to the single-pass absorption, as a consequence of the multiple light passages through the sample, which shows especially when the reflectivity of the sphere is high (second term in Equation 2.7). The fraction of emitted photons (dashed lines) have a similar dependence on the single-pass absorption, but start at a lower value due to the QY used for these simulations ($\eta = 45\%$). Again, there is good agreement between the AM and RTS, from which we conclude that the generalizations made to derive the AM are well justified. Nevertheless, neither of the simulation approaches appears to exhibit an explicit bias in the QY for low absorption.

\textsuperscript{2}Courtesy of MSc. I. Kondapaneni, Dr. A. Wilkie and Dr. J. Krivanek (Charles University, Prague Czechia)
2.4. Theoretical model of the QY methodology limitations

values. This is further investigated in the following section.

Figure 2.9: (a) Simulated QY against the single-pass absorption, using the RTS approach (symbols) and the AM approach (solid line) for a sample with a QY, $\eta = 45\%$. For the simulations, we used an IS with a diameter of 10 cm and set the diameter of the sample, input port and output to 1 cm, 4 mm and 1 mm respectively. Different values of the reflectivity of the IS are shown by colors for the RTS approach. For the AM approach these curves overlap perfectly and only a single value is plotted. (b,c) Simulated number of absorbed (b) and emitted (c) photons, normalized by the number of excitation photons $N_{\text{exc}}^0$, against the single-pass absorption. The solid black lines indicate a linear dependence. RTS courtesy of MSc. I. Kondapaneni and co-workers (Charles University, Prague, Czechia).

2.4.3 Bias resulting from experimental uncertainty

In our theoretical description so far the photon fluxes exiting the IS are described relative to the input photon flux $I_{\text{exc}}^0$ provided by the excitation source. In such a theoretical framework, the experimental uncertainties $\alpha$ associated with the detected number of emitted and absorbed photons ($N_{\text{em}}, N_{\text{abs}}$) are usually assumed to contribute proportionally to the uncertainty in the determined QY [77, 88]:

$$\alpha_{\text{QY}}^2 = \alpha_{N_{\text{em}}}^2 + \alpha_{N_{\text{abs}}}^2,$$

where $\alpha$ is the relative uncertainty of the variable. However, this approach might not reflect the uncertainty of a multi-variable function with a skewed, asymmetric distribution function, e.g. as a result of the distribution of the input variables [89].

To investigate the distribution function of the QY, we account for the measurement uncertainties associated with the number of detected excitation and emission photons in Equation 2.2. To do so, we describe those variables by a distribution function centered at the expected values predicted by our AM approach (Equations 2.3 and 2.5) as illustrated in Figure 2.10. The peak of the distribution indicates the most-likely sampled value of the variable (also known as the ‘mode’), whereas the standard deviation of the distribution $\sigma$ indicates its fluctuations.

We study the error propagation in a our QY geometry described in Section 2.3, where we assume the reference sample to be non-absorbing and non-emitting ($A_R = 0$ and $N_{\text{Ref}}^* = 0$). We investigate two types of distributions to cover commonly encountered measurement uncertainties: a Poisson and normal distribution. The Poisson distribution is used to describe shot noise, which arises from the discrete nature of photons. This type of noise will show especially for low flux signals since the signal-to-noise ratio
increases with $\sqrt{N}$. For high $N$ the Poisson distribution can be well described by a normal distribution, which we use to model additional measurement uncertainties that arise e.g. from mechanical/electronic stability of the detection and excitation chains. The normal distribution thus describes a more general situation in which the relative uncertainty can be set independently of the flux.

![Figure 2.10](image)

**Figure 2.10:** Normalized histograms of the detected number of emission ($N_{em}$) and excitation photons $N_S$ and $N_{Ref}$ for a sample absorption of 6%. The vertical dashed lines indicate the expected, noiseless quantities. A total number of $\sim 10^7$ excitation photons was used for the simulations.

**Poisson distribution**

First, we study the effect of Poissonian distributed variables, given by $P(\mu, k) = \frac{\mu^k e^{-\mu}}{k!}$, where $\mu$ is the expected (mean) value and $P(\mu, k)$ the probability of measuring a value $k = 0, 1, 2, 3, \ldots$. We add this noise to the simulated numbers of detected photons (Equation 2.2) $N_S$, $N_S^*$ and $N_{Ref}$ by drawing semi-randomly from a Poisson distribution, $P(N_S, k)$, $P(N_S^*, k)$ and $P(N_{Ref}, k)$, as illustrated in Figure 2.10. We vary the relative uncertainty in the variables $\alpha = \sigma/\mu$, which goes with $\sim 1/\sqrt{N}$ for a Poisson distribution, via the single-pass absorption of the sample ($A_S$) and the total number of excitation photons ($N_{exc}^0$). The resulting QY distributions are shown in Figure 2.11 and 2.12a. For a relative uncertainty of 1% and for high sample absorption, the simulated QY distribution lies symmetrically around the expected QY value as shown in Figure 2.11 (dashed vertical line). The peak of the distribution, i.e. the value that will be most likely sampled in a single QY measurement, is in good agreement with the expected QY. Upon decreasing absorption, however, the distribution broadens and becomes asymmetric. The most-likely QY value shifts towards lower, underestimated values with respect to the expected mean QY value. For absorption of 1%, the most-likely QY is underestimated by more than a factor of 2, i.e. 200%. The absorption value for which a QY measurement yields underestimated values strongly depends on the relative uncertainty of the measurement, as shown in Figure 2.12a. For $\alpha = 0.1\%$, obtained under a high number of excitation photons ($N_{exc}^0 \sim 10^9$), the most-likely QY agrees very well with the expected QY, independently of the absorption of the sample. However, already for relative uncertainties of 0.5% ($N_{exc}^0 = 5 \cdot 10^7$), the QY estimate agrees with the expected QY only for absorption above $\sim 5\%$. For even higher uncertainties of 1% ($N_{exc}^0 \sim 10^7$), the absorption limit is as high as $\sim 15\%$. 

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2.4. Theoretical model of the QY methodology limitations

**Figure 2.11:** Simulated effect of shot noise on the QY: Normalized histograms of simulated QY values for different sample absorption. When absorption is high, the distribution of obtained QY values lies symmetrically around the noiseless QY value of 80% (dashed line). For decreasing absorption, the distribution shifts towards lower QY values and becomes asymmetric. A total number of $\sim 10^7$ excitation photons was used for the simulations.

To investigate if the noise affects mainly the estimated number of emitted or absorbed photons, we break down the QY estimate and compute the fraction of emitted $N_{em}/N_0^{exc}$ and absorbed photons $N_{abs}/N_0^{exc}$, used to evaluate the most-likely QY value. The dependence of the fraction of emitted photons on the single-pass absorption is retained in the presence of measurement uncertainty and is in excellent agreement with the noiseless value (dashed colored lines in Figure 2.12b). In contrast, the fraction of absorbed photons is unaffected by the noise only when the single-pass absorption value is high with respect to the relative uncertainty (solid colored lines) and is overestimated compared to the noiseless estimate when the single-pass absorption is low. The overestimation in the absorption coincides with the underestimation of the QY. This suggests that the denominator in the QY definition, i.e. the number of absorbed photons, is critically affected by the measurement uncertainty and leads to the QY underestimation. Conversely, our findings show that the ‘noisiness’ of the nominator, i.e. the number of emitted photons, is not relevant.

**Normal distribution**

Next, we investigate normally distributed variables, given by $G(\mu, k, \sigma) = \frac{e^{-\frac{(k-\mu)^2}{2\sigma^2}}}{\sqrt{2\pi\sigma}}$. Here $\mu$ is the expected (mean) value and $\sigma$ the standard deviation as before. The results for a typical range of experimental uncertainties between 0.1 and 1% are shown in Figure 2.12c and d. Again, when the relative uncertainty is small ($\alpha \sim 0.1\%$) the simulated most-likely QY is in good agreement with the predicted value for a noiseless ‘ideal’ measurement. However, already for a relative uncertainty of $\alpha \sim 1\%$, the QY is underestimated (Figure 2.12c). Like in the case of the Poissonian distribution, this is accompanied by an overestimation of the number of absorbed photons (Figure 2.12d), whereas the number of emitted photons is determined correctly. Analysis of both types of variable distributions shows that the QY estimation depends on the relative uncertainty of the measured photon intensities, but not on the specific type of noise (Figure 2.12). Indeed, for sufficiently high counts, a Poisson distribution can be well approximated by a normal distribution: $P(\mu, k) \sim G(\mu, k, \sqrt{\mu})$. Hence for a fixed
value of $\alpha$, any differences in our simulations between both distributions are expected to disappear. Only for $\mu \ll 50$, the Poisson distribution is clearly asymmetric, from which an additional bias could arise as was shown by Park et al. [89] for quantities defined by a ratio $X/Y$. However, in typical QY experiments the recorded counts $N_{\text{Ref}}$ and $N_S$ are usually very high ($10^5$ counts or more) and can otherwise easily be increased, either by extending the measurement time or by multiple runs of the same measurement. Therefore, the scenario where (Poissonian) shot noise dominates the signal is unlikely in practice.

Regarding the source of the bias, Figure 2.12 suggests that it arises purely from the relative uncertainty $\alpha = \sigma/\mu$ of the distribution, since the QY is underestimated especially when the fluctuations are high (i.e. comparable to the absorption of the sample, $\alpha \sim A_S$). The full dependence of the QY on the relative uncertainty is shown in Figure 2.13a for a sample with a single-pass absorption $A_S = 5\%$. When $\alpha$ is small compared to the absorption $\alpha/A_S < 10\%$, the QY is in good agreement with the unbiased result. However, for $\alpha/A_S$ larger than 10\% (yellow area) the QY is increasingly underestimated. For $\alpha$ equal to the sample’s single-pass absorption, the QY is already underestimated to 50\% of the unbiased value. A nearly identical curve is obtained for an arbitrary absorption value, even for absorption close to 100\% (green curve). This shows that it is the ratio of the relative uncertainty and the sample absorption that plays a crucial role in the
2.5. Comparison of model and experiment

underestimation of the QY and in the overestimation of the fraction of the number of absorbed photons \( N_{abs}/N_{exc}^0 \) (Figure 2.12b and d).

**Figure 2.13:** (a) Simulated most-likely QY against the relative measurement uncertainty, normalized to the sample’s single-pass absorption (\( A_S =5\% \), black line; \( A_S =100\% \), green line). The measurement uncertainty is introduced by assuming a normal distribution of the variables. The arrows indicate the QY values corresponding to a relative uncertainty of \( \alpha = 0.1\% \) (red) and \( \alpha = 2\% \) (black). The shaded area indicates the FWHM and the horizontal black line indicates the noiseless QY value. For a relative noise level larger than 10% of the single-pass absorption value, the QY is underestimated as indicated by the yellow area. (b) Simulated distribution of \( N_{Ref} \) and \( N_S \) for a single-pass absorption of \( 5\% \) and a relative measurement uncertainties of 2% (black) and \( \sim 0.1\% \) (red). The vertical dashed lines indicate the noiseless values.

Importantly, in the ideal case, in which noise is absent, the IS methodology itself does not yield biased results. Only when we account for measurement uncertainty in the simulated numbers of detected photons, predicted by Equations 2.3 and 2.5, the bias arises. This is illustrated in Figure 2.13b, where we show the simulated detected number of excitation photons \( N_{Ref} \) and \( N_S \) for a sample with single-pass absorption of \( \sim 5\% \). When the uncertainty in both variables is small (red curves), the number of absorbed photons \( N_{abs} = N_{Ref} - N_S \) can be precisely determined and the measurement yields a precise QY estimate (red arrow in Figure 2.13a). However, when the uncertainty in \( N_{Ref} \) and \( N_S \) approaches the difference between them, the distribution of \( N_{abs} \) broadens (black curves in Figure 2.13b) and the most-likely obtained QY value becomes underestimated (black arrow in Figure 2.13a). Hence, we conclude that the bias results purely from the relation from which the QY and, in particular the absorption part of the QY, is determined: \( QY \propto 1/(N_{Ref} - N_S) \). The bias is thus not specific to the QY methodology, but will show for any similarly defined quantity. This general impact of our findings will be discussed further in the next sections.

**2.5 Comparison of model and experiment**

We now combine our experimental and theoretical findings and use the AM and RTS approaches to simulate our specific experimental setup used to measure the QY of R6G in Section 2.3. First we compare the experimentally determined QY with the simulated values under ideal conditions, i.e. in the absence of experimental uncertainty (Figure 2.14a). The AM approach yields a flat QY dependence for single-pass absorption between 1 and 100%, preserving the input value of the material’s QY of 95% expected
for R6G [81]. The RTS approach yields also a flat QY dependence, but with a slightly underestimated QY of \( \sim 87\% \). This predicted lower value for R6G is in good agreement with our experimentally determined values for absorption above 15% (Figure 2.14a), showing the strength of the RTS approach for modelling of the IS set-up. From detailed analysis using RTS, it appears that the slight underestimation is related to the specific geometry of our IS setup, which contains home-built aluminum parts that serve as holders for the cuvette and the fibers. Indeed, when we replace the aluminum in our RTS by a Lambertian scatterer, we obtain a QY of 95% (blue empty triangle in Figure 2.14a). Nonetheless, neither of the two simulations approaches shows a dependence of the QY on the sample’s absorption and, hence, the artifact cannot be explained by the standard IS theory.

**Figure 2.14:** (a) Comparison of the experimental dependence of the QY of R6G on the single-pass absorption (black) with simulated values by the AM (red) and RTS (blue) approaches. The shaded region serves as a guide to the eye. The vertical dashed line (in all panels) indicates the critical absorption value. The empty blue triangle shows the simulated QY where we replaced the aluminum parts in the IS setup with a Lambertian scatterer. (b) Comparison of the experimentally determined dependence of the absorbed (black symbols, left axis) and emitted (green symbols, right axis) fractions on the single-pass absorption of the sample with the simulated dependence using the AM (red lines). The AM is compared to the RTS approach in the inset of the figure within the same plot range (blue circles: fraction of absorbed photons, blue triangles: fraction of emitted photons) and show excellent agreement. (c) Simulated most-likely measured QY in the presence of measurement uncertainty (blue line: relative uncertainty \( \alpha_{N\text{Ref}} = 0.1\% \), black line: relative uncertainty of \( \alpha_{N\text{Ref}} = 1.1\% \)). Shaded areas indicate the full-width at half-maximum of the obtained QY distribution. (d) Simulated fraction of absorbed (black) and emitted (green) photons, corresponding to the QY estimate in panel (c) for a relative measurement uncertainty of 1.1%. Red lines show the simulated fraction of absorbed and emitted photons in the absence of measurement uncertainty, as in panel (b).

We then separately analyze the measured fractions of emitted and absorbed photons which are used to evaluate the QY (Equation 2.2). Both fractions decrease roughly linearly proportional to the single-pass absorption of the sample, as shown in Figure 2.14b. This linear dependence holds over the full studied single-pass absorption range for the
emitted fraction (green symbols), whereas it deviates from the linear dependence for the absorbed fraction (black symbols), when the single-pass absorption drops below \( \sim 15\% \). This value coincides with the critical absorption \( A_{\text{crit}} \), below which we observe a decrease in the QY (dashed vertical line in Figure 2.14). Since the experimentally observed fraction of absorbed photons deviates from the simulated fraction (red line Figure 2.14b), whereas it is in good agreement for the emitted fraction (dashed red line), we conclude that the absorption is overestimated with respect to the IS theory, which gives rise to the underestimated QY values.

The dependence of the QY on the sample’s absorption is very similar to the behavior of the QY in the presence of experimental uncertainties, observed in our simulations (Section 2.4). Therefore, we compare the experimental QY values to the simulated results, where we take into account the effect of measurement uncertainties on the estimated QY value (Figure 2.14c and d)). For this we assume normally distributed variables, with a relative uncertainty of \( \alpha \sim 1\% \), a magnitude that is reasonable when compared to the typical uncertainties estimated for our setup (Figure 2.15a). The normal distribution of the measured variables is justified by the limited dependence of the measured QY on the detected number of photons (Figure 2.15b), showing that Poissonian distributed shot noise is not the dominant source of the experimental uncertainty.

Unlike the simulations with noiseless quantities (red lines in Figure 2.14a and b), incorporation of the measurement uncertainty in our simulations gives good quantitative agreement with the observed experimental QY values (black curve in Figure 2.14c and d). This applies not only above the critical absorption \( A_{\text{crit}} \sim 15\% \) where the standard approach holds, but also below \( A_{\text{crit}} \) where the artifact is strongly present (Figure 2.14a and b). It also separately describes very well the overestimation of the fraction of absorbed photons (Figure 2.14d) as the cause of the QY underestimation and confirms the negligible influence of the fraction of emitted photons and its associated uncertainty.

**Figure 2.15:** (a) Estimated relative uncertainty \( \alpha = \sigma/\mu \) against the excitation wavelength for the two different experimental setups used in Section 2.3. The measurement uncertainty has been estimated from multiple measurements of the total number of detected excitation photons in the reference measurement (\( N_{\text{Ref}} \)) and from the fluctuations in the lamp intensity between different measurements (red squares). (b) Measured QY of R6G in ethanol (\( \sim 1.6 \mu\text{M} \)) against the detected number of excitation photons \( N_{\text{Ref}} \) under 440 nm wavelength excitation. \( N_{\text{Ref}} \) is changed by varying the acquisition time between 5 and 180 seconds. The measured QY is independent of \( N_{\text{Ref}} \), as indicated by the shaded guide area.
Furthermore, in the limit of disappearing uncertainties, the model converges to the ideal flat QY-dependence (Figure 2.14c, blue curve), where the assumption of proportionally increasing uncertainty in the QY estimate holds \([77, 88]\). We conclude that the non-linear propagation of error is indeed the source of the underestimated QY artifact. Importantly, as shown in Section 2.4, the bias resulting from the experimental uncertainty is purely a consequence of the definition of the QY, i.e. \(QY = N_S^*/(N_{Ref} - N_S)\). Hence, the presented experimental artifact is not limited to the IS implementation of the QY methodology, but applies to the QY methodology in general. We thus predict the artifact also for comparative and relative measurements, where the QY is obtained from separate measurement of the number of emitted and absorbed photons, the latter of which is determined by comparison of a sample with a blank reference (such as Equation 2.2). Our findings thus demonstrate the urgent need for a remedy.

### 2.6 Corrected QY methodology

For reliable QY determination first the critical absorption value \(A_{crit}\) needs to be quantified for each specific QY setup. It is determined by the absorption of the sample and the uncertainty in the detected number of photons as shown in Figure 2.16, where we plot the general dependence of the QY on the fraction of absorbed photons \((N_{Ref} - N_S)/N^0_{exc}\) and relative measurement uncertainty \(\alpha\). The critical absorption, below which the QY estimate becomes unreliable, is designated by the white dotted line in Figure 2.16. Based on the relative uncertainty associated with each specific experimental setup, the critical absorption can be easily estimated. As a rule of thumb \(A_{crit}\) is roughly given by 10 times the value of the measurement uncertainty. As we have stressed before, the same dependence holds for any quantity in the general form \(Z/(X - Y)\), when the uncertainty in \(X\) and \(Y\) becomes larger than \(\sim10\%\) of the value of \((X - Y)\) (Figure 2.16).

![Figure 2.16: QY (color bar) as a function of the absorption of the sample \((N_{Ref} - N_S)/N^0_{Ref}\) and relative uncertainty in the \(N_{Ref}\) and \(N_S\) estimates. The dashed white line indicates the threshold below which the QY is unreliable. This holds for any quantity given by the general relation \(Z/(X - Y)\) where \((X - Y)/X^0\) is compared to the uncertainties associated with \(X\) and \(Y\).](image-url)
2.6. Corrected QY methodology

The critical absorption can also be determined experimentally, by measuring the QY of a reliable QY calibration standard, such as a high purity R6G dissolved in ethanol, in a wide range of absorptions reaching below and above $A_{\text{crit}}$, such as shown in Figure 2.14a. Our results in Section 2.3 show that $A_{\text{crit}}$ can be expected to be around 5-15% in a typical IS setup, so that the measured range should be for absorption between 1 and 30%. This absorption range can be accessed either by varying (i) the excitation wavelength, (ii) the standard’s concentration and/or (iii) the standard’s optical thickness, or even by a combination of the above since the artifact manifests itself independently of how the absorption is changed. Separately, one needs to ensure that the internal properties of the used standard remain unaffected within the measured range, by testing it for constant emission lifetime and absorption spectrum. The setup-characteristic critical absorption $A_{\text{crit}}$ is given by the absorption for which the measured QY deviates from the expected constant value, such as shown in Figure 2.14a. In the next step, the QY of the sample of interest ($QY_{\text{meas}}^S$) is measured, from which a more reliable QY estimate ($QY_{\text{cor}}^S$) can be obtained in the range $A < A_{\text{crit}}$, by comparison of the obtained QY dependence of the calibration standard $QY_{\text{Cal}}(A)$, with the unbiased value $QY_{\text{Cal}}(A > A_{\text{crit}})$:

$$QY_{\text{cor}}^S(A) = QY_{\text{meas}}^S(A) \frac{QY_{\text{Cal}}(A > A_{\text{crit}})}{QY_{\text{Cal}}(A)} (2.9)$$

We applied this correction procedure to the QY measurements presented previously in Figure 2.17. Indeed, the vast majority of the observed spectral and concentration dependence of the QY in Figure 2.7 can be explained by the described artifact. Our proposed procedure corrects for this, and therefore ensures reliable QY estimates in a much broader range of experimental conditions and sample variations. Alternatively, as follows from the statistical nature of this effect, the artifact might be resolved by taking a taking higher number of QY measurements, the average value of which will tend more towards the expected value of the unbiased QY.

![Figure 2.17: QY versus excitation wavelength, before (a) and after (b) correction for the absorption dependence of the QY methodology using Equation 2.9. Different symbols represent different sample concentrations (see Figure 2.3 and 2.7). After correction, the QY of the Si-QDs is constant at ~ 45% and independent of the sample concentration. Part of the excitation and concentration dependence of the QY of the CdSe QDs persists after correction, potentially related to the ligands on the surface [74, 75, 90, 91]. The correction function was obtained by taking a moving average of the QY versus single-pass absorption dependence of R6G in Figure 2.14b. For reference, the corrected QY for the R6G is also shown.](image-url)
2.7 QY of Si-QDs

We apply the corrected QY methodology to different types of organically passivated Si-QDs, shown in Figure 2.18. For C:Si-QDs emitting below 600 nm wavelength the QY is limited to \( \sim 20\% \), whereas for Si-QDs emitting in the near-IR the QY is much higher, between 45 and 65\%. For intrinsic PL of Si-QDs, the increase of the QY with emission wavelength is commonly observed in literature (for an overview, see Dohnalova et al. [5]), which is typically argued to be the consequence of the increased number of surface defects with smaller Si-QDs [5, 12, 37, 38]. Our results are in good quantitative agreement with this trend (illustrated by the shaded area in Figure 2.18). In the next chapters, we will elaborate on the emission efficiency limit for the visible range emitting Si-QDs.

![Figure 2.18: Corrected QY estimates against the peak emission wavelength of different types of organically passivated Si-QDs samples: Allylamine-terminated Si-QDs (am:Si-QDs), butyl (bu:Si-QDs) and methyl-passivated Si-QDs (me:Si-QDs), methyl undecanoate passivated Si-QDs (me-un:Si-QDs) and dodecane-passivated Si-QDs (do:Si-QDs). For more details on the samples we refer to Appendix A.1. The measured QY values are compared to literature values (gray symbols): Dohnalova et al. [2], Jurbergs et al. [10], Kusova et al. [11], Mastronardi et al. [12], Sangghaleh et al. [13] and Tu et al. [14]. The shaded area indicates the emission wavelength range for which high QYs are found.](image)

2.8 Conclusion

In conclusion, we report on a critical artifact generally present in the QY methodology, leading to the underestimation of the QY value under common experimental conditions and which depends on the absorption of the studied material. This effect is critical
not only for studies where QY is evaluated as an important material characterization, but also in studies where materials with different absorption are compared, or a single material is studied in a broad range of excitation wavelengths, concentrations or other parameters that are directly or indirectly linked to the material’s absorption. The effect manifests itself independently of the type of material and of the specific geometry of the experimental setup. By comparison with theoretical simulations, we show that the effect is due to a bias resulting from the experimental uncertainty in the detected photon intensities that are used to compute the QY. The critical absorption under which the artifact shows is roughly ten times the relative measurement uncertainty: e.g. for only 1% of experimental uncertainty materials with absorption below 10% are already affected. This leads even for calibration standards such as R6G to a strongly underestimated QY, when excited non-resonantly or studied at an insufficient concentration. The artifact described here passed undetected for a long time, due to the common assumption that the error in the measured number of photons ($N$) propagates in a linear manner and that therefore low photon fluxes, obtained when measuring low-absorption or emission materials, merely result in a larger uncertainty in the obtained QY value [77, 88]. We show that is assumption is not justified and the QY, given by $QY = N_S/(N_{Ref} - N_S)$, is biased towards lower values when the uncertainty in the measured variables $N_{Ref}$ and $N_S$ exceeds 10% of the difference $(N_{Ref} - N_S)$ between them. Our findings apply to any methodology where a quantity with the general form $Z/(X - Y)$ is evaluated and hence we anticipate that, not only the absolute QY, but also relative and comparative QY methods suffer from this effect, as these methods rely on similar definitions [67].

The QY is frequently used also to characterize novel materials such as semiconductor QDs, to study the emission efficiency dependence, e.g., on size [12, 37] and density [70] of the QDs, excitation energy [71, 84] or to show ligand instability [75]. A critical assessment of these results and of the methodology is therefore needed, since the size, density and excitation energy are intimately linked to the magnitude of the absorption of the studied samples. To eliminate the artifact, we propose a dedicated calibration procedure that corrects for the intrinsic absorption-dependence of the QY determination. In this way it possible to establish robust and reliable QY measurements for materials developed for e.g. bio-imaging, bio-sensing or optoelectronic devices.

2.9 Materials & methods

Samples

Rhodamine 6G (Sigma-Aldrich) was dissolved in UV-grade ethanol (Merck KGaA, Uvasol), from which different concentrations were prepared by dilution. The concentration was estimated by comparison of the measured absorption coefficients with the value specified by Birge [92]. For all optical measurements, $\sim 1.5$ mL of solution is contained in a UV spectroscopy-grade quartz cuvette (Hellma Analytics, 111-QS). CdSe/ZnSe/ZnS core/shell/shell QDs (CANdots Series A CSS) in hexane were purchased from the Center for Applied Nanotechnology (CAN) GmbH. High efficiency Si QDs were obtained
from the group of Prof. Dr. J.G.C. Veinot (University of Alberta, Canada), prepared following the synthesis described in References [93, 94]. The concentration was estimated from the measured absorption coefficient and the absorption cross-sections reported in Reference [95].

**QY setup 1**

The sample is illuminated by a stabilized Xenon lamp (Hamamatsu, L2273) coupled to a double-grating monochromator (Solar, MSA130). The excitation beam is split using a spectrally broad bifurcated fiber (Ocean Optics, BIF600-UV-VIS), where one part is used to monitor the fluctuations of the excitation intensity using a power-meter (Ophir Photonics, PD300-UV) and the other part to excite the sample. A collimator lens is used to reduce the spot-size at the sample position to enable purely direct excitation of the sample (\( F = 1 \)). The samples are suspended using an aluminum holder in the center of the IS (Newport, 70672) with a diameter of 10 cm. The use of such type of holder is verified using ray-tracing simulations (see Section A.2). Light is detected using a second spectrally broad optical fiber (Ocean Optics, QP1000-2-VIS-BX), coupled to a spectrometer (Solar, M266) equipped with a CCD (Hamamatsu, S7031-1108S). All measurements are corrected for the spectral response of the detection system determined by illuminating the IS via the excitation port with a tungsten halogen calibration lamp (Oriel, 63358) for the visible range and a deuterium lamp (Oriel, 63945) for the UV range (<400 nm). From the ratio between the theoretical (\( I_{\text{cal}}^{\text{th}} \)) and measured calibration spectrum, the correction function is determined:

\[
C(\lambda) = \frac{I_{\text{cal}}^{\text{th}}(\lambda)}{I_{\text{exp}}^{\text{cal}}(\lambda)},
\]

where the measured calibration spectrum is corrected for the spectrometer’s stray-light contribution.

For all measurements, \( \sim 1.5 \text{ mL} \) of solution is contained in a UV spectroscopy-grade quartz cuvette (Hellma Analytics, 111-QS).

**QY setup 2**

Independent QY measurements, courtesy of Prof. Dr. J. Valenta (Charles University, Prague, Czechia) are carried out using an IS with a diameter of 10 cm and an inner surface covered by the Spectraflect coating. The excitation is provided by a laser-driven light source (LDLS, Energetiq, EQ-99X) coupled to the 15 cm monochromator (Acton SpectraPro SP-2150i). The monochromatized light (bandwidth of about 10 nm) is guided to the IS via a silica fiber bundle. The output signal from the IS is collected by another fused-silica fiber bundle placed in the direction perpendicular to the excitation axis and is shielded by baffles against the direct visibility of both the LED excitation source and the sample. The end of the fiber bundle (which has a stripe-like shape) is imaged to the input slit of an imaging spectrograph (30 cm focal length) and a liquid-nitrogen-cooled CCD camera is used for detection. The spectral sensitivity of the complete apparatus is calibrated over the broad UV-NIR spectral range (300-1100 nm) using two radiation standards (Newport Oriel): A 45 W tungsten halogen lamp (above 400 nm) and a deuterium lamp (below 400 nm). Again, special attention is paid to avoid stray-light effects in the spectrometer.
Data analysis

QY is evaluated using Equation 2.2. Re-absorption effects were corrected for using the procedure described by Ahn et al. [78] by comparing the measured PL spectrum with that of low concentration sample for which re-absorption is negligible. Error estimates are obtained following procedures found e.g. in References [84, 88].

Time-resolved PL

Time-resolved PL was measured using an inverted confocal microscope (Olympus, FV1000) equipped with a TCSPC module (Picoquant, Picoharp). For excitation, we used a pulsed 440 or 485 nm wavelength laser diode (Picoquant, LDH-P-C-440B or LDH-P-C-485) operated at 20 MHz (∼2.7µW or 0.4µW) focused to diffraction limited spot by a 60x water immersion objective (Olympus, UPLS Apo, NA = 1.2). Light is collected by the same objective lens, filtered through a 562 ± 20 nm band-pass filter and detected using an avalanche photon detector (MPD, PDM). For the measurements the R6G solutions were contained in a 96-well plate.

Single-pass absorption

Transmission of the sample (TS) and reference (TRef) was measured using a dual-beam spectrophotometer (Perkin Elmer, Lambda 950), from which the sample’s single-pass absorption, i.e. the fraction of absorbed light upon a single passage through the sample, was evaluated: AS = 1 − TS/TRef. For this it is assumed that the reflection of the sample and reference is the same.
Internal quantum efficiency

The IQE gives the emission efficiency of the bright fraction of emitters in an ensemble and hence the upper limit of the material’s emission efficiency when non-radiative recombination pathways cannot further be improved. The IQE can be extracted from the PL recombination rate, through control of the LDOS. For this we use a Drexhage-type method that employs a spherical mirror. We apply this method to study, for the first time, the radiative rate and IQE of organically passivated Si-QDs (C:Si-QDs) emitting in the visible spectral region below 600 nm, a range which is inaccessible for most types of Si-QDs. By carefully considering the dipole nature of C:Si-QDs, we show that they have high direct bandgap-like radiative rates, which enable a high IQE of over \( \sim 50\% \). In this way, we demonstrate that Si-QDs can be a competitive candidate for a phosphor in lighting applications and medical imaging, also in the visible spectral range.

3.1 Introduction

The IQE is determined by the competition between the radiative \( (\gamma_r) \) and non-radiative \( (\gamma_{nr}) \) decay rates:

\[
IQE = \frac{\gamma_r}{\gamma_r + \gamma_{nr}}.
\]

(3.1)

The radiative decay rate is determined by the electronic coupling between the initial \( |i\rangle \) and final \( |f\rangle \) states [24], as given by Fermi’s Golden rule:

\[
\gamma_r = \frac{2\pi}{\hbar^2} \sum_f \left| \langle f | \hat{H} | i \rangle \right|^2 \delta(E_i - E_f).
\]

(3.2)

Here, the initial and final states have energies \( E_i \) and \( E_f \), respectively, and are coupled via the interaction operator \( \hat{H} = -\hat{p} \cdot \hat{E} \), i.e. the product of the dipole moment operator and electric field operator. \( |i\rangle \) and \( |f\rangle \) involve the emitter’s electronic states, i.e. the electronic excited \( |e\rangle \) and ground state \( |g\rangle \), but also the photonic states \( |\omega_k\rangle \) available to the emitted photon: \( |i\rangle = |e, \{0\}\rangle \) and \( |f\rangle = |g, \{1, \omega_k\}\rangle \) [24]. The electronic and photonic
contributions can be separated, yielding [24, 96]:

\[ \gamma_r \propto |p|^2 \rho(\omega, r), \]  

(3.3)

where \( p \) is the transition dipole moment (TDM) between the electronic excited and ground state and \( \rho \) the local density of optical states (LDOS).

The non-radiative decay rate, arising e.g. from vibrational relaxation, recombination through defects and traps or energy transfer to neighboring emitters [85, 97], is usually assumed to be an intrinsic property of the particle and its immediate surroundings, unaffected by the LDOS [98]. Hence, the total PL decay rate can be written as:

\[ \gamma_{PL} = \gamma_{nr} + \gamma^{vac}_r \rho \rho^{vac}, \]  

(3.4)

where \( \gamma^{vac}_r \) and \( \rho^{vac} \) are the radiative decay rate and LDOS in vacuum respectively.

Hence, through the LDOS the radiative and non-radiative contributions can be uncoupled, as was first done by Drexhage [99] and which is typically done by placing the emitters of interest in close proximity to a metal or dielectric interface [100–104]. Control over LDOS enables extraction of the IQE, but can also be exploited to increase the radiative rate, e.g. by coupling emitters to an antenna [105, 106]. However, since not all photonic modes that are introduced via a reflective interface radiate into the far-field [24, 25], this does not necessarily enhance the QY of the material.

From the above definition, it is clear that the IQE gives the upper limit of the material’s emission efficiency in case the non-radiative rate cannot be further reduced and gives the emission efficiency of the emitting particles within an ensemble. For Si-QDs, Miura et al. [8] used wedge-shape samples to modify the LDOS, expanding on the work of Walters et al. [9], and showed that the IQE can reach 100% for emission above 800 nm. Such high IQE values have also been observed via independent methods based on the PL decay kinetics [13, 36] and clearly demonstrate the possibility of highly efficient emission with Si-QDs. Moreover, comparison with the QY enabled identification of the losses in large Si-QDs, being primarily ascribed to non-emissive QDs in the ensemble [20, 21].

For Si-QDs emitting in the visible spectral range, below 700 nm, the radiative recombination rate and IQE have been studied only theoretically [2, 6, 7, 107]. Hence, little is known about the factors that limit the QY, e.g. efficient non-radiative channels or non-emissive QDs in the ensemble. In this chapter we study the IQE of Si-QDs emitting in the visible spectral range, by means of LDOS modifications in a Drexhage-type experiment, and establish their emission efficiency limit.

### 3.2 Methods

#### 3.2.1 Controlling the LDOS

To study the radiative recombination rate and the IQE, the LDOS can be modified by precisely controlling the separation between the studied emitters and a reflective
3.2. Methods

material, for which different geometries have been employed [8, 9, 99–104]. Here we use Lunnemann et al.’s implementation of the Drexhage-type method, which employs a spherical lens coated with an optically thick layer of silver [108], placed on top of the sample (Figure 3.1). The advantage of this implementation is that it does not require specific sample fabrication to control the LDOS as the mirror can simply be added on top of any spin- or drop-casted thin layer of emitters [108].

![Figure 3.1: Schematic of the experimental setup used for IQE measurements.](image)

The decay dynamics of the sample are studied using an inverted scanning confocal microscope as shown in Figure 3.1. The PL is excited from the emitter layer with a ps-pulsed laser focused to a diffraction limited spot and the arrival times of the emitted photons are detected using an avalanche photodiode (APD). By scanning the area around the point where the silver-coated lens contacts the sample, different emitter-mirror separations, $d$, are probed. The mirror that is used has a large radius of curvature (2 mm), which ensures that at each scanning position emitters effectively experience an almost flat mirror and enables an exquisite resolution over the separation $d$. A large in-plane scan range of $\sim 60 \mu m$ leads to a substrate-mirror separation of only $\sim 1 \mu m$. Thereby the LDOS, $\rho(d)$, is controllably varied. The IQE can be extracted from the dependence of the decay rate on the emitter-mirror separation ($d$) and the LDOS corresponding to the relevant dipole orientation ($\rho$), which follows from Equations 3.1 and 3.4:

$$\gamma_{PL}(d) = \gamma_{PL}(\infty) \left\{ 1 + IQE \left[ \frac{\rho(d)}{\rho(\infty)} - 1 \right] \right\}, \quad (3.5)$$

where $\gamma_{PL}(\infty)$ and $\rho(\infty)$ are the decay rate and LDOS in the absence of the mirror.

3.2.2 LDOS calculations

To extract the IQE from Equation 3.5, the LDOS is calculated using Amos and Barnes’ implementation [103] of the methodology introduced by Chance, Prock and Silbey [109]. For this we assume that the emitters are located within a stack of parallel layers as shown in (Figure 3.2a). The LDOS results from the electric field at the emitter position
(embedded in medium 1), which is given by the sum of the source’s dipole field and the source’s field that is reflected by the substrate (medium 2) and the mirror (medium 3) [25]. To calculate this, the dipole field is expressed as the sum of plane waves, each characterized by the parallel component $k_\parallel$ of its wave-vector, normalized to the wave-vector in medium 1:

$$u = \frac{k_\parallel}{k_1}.$$ 

Integrating over $u$ yields the LDOS for the two principal dipole orientations, perpendicular and parallel to the plane of the layered medium (Figure 3.2a) [103]:

$$\rho_\perp = n_1 \frac{3}{2} \text{Im} \left[ \int_{0}^{\infty} \frac{(1 - r_{12}^p e^{-2\beta_{12}}) (1 - r_{13}^p e^{-2\beta_{13}}) u^3}{1 - r_{12}^p r_{13}^p e^{-2(\beta_{12} + \beta_{13})}} \left( 1 - r_{12}^s e^{-2\beta_{12}} \right) \left( 1 + r_{13}^s e^{-2\beta_{13}} \right) \text{du} \right]$$

$$\rho_\parallel = n_1 \frac{3}{4} \text{Im} \left[ \int_{0}^{\infty} \left\{ (1 - u^2) \frac{(1 + r_{12}^p e^{-2\beta_{12}}) (1 + r_{13}^p e^{-2\beta_{13}})}{1 - r_{12}^p r_{13}^p e^{-2(\beta_{12} + \beta_{13})}} \right. \right.$$

$$+ \frac{(1 + r_{12}^s e^{-2\beta_{12}}) (1 + r_{13}^s e^{-2\beta_{13}})}{1 - r_{12}^s r_{13}^s e^{-2(\beta_{12} + \beta_{13})}} \left( 1 - r_{12}^s e^{-2\beta_{12}} \right) \left( 1 + r_{13}^s e^{-2\beta_{13}} \right) \text{du} \right] \text{l}_1.$$

Here, $n_1$ is the refractive index of the layer in which the emitters reside and $l_1 = -i \sqrt{1 - u^2}$ is related to the perpendicular component of the wavevector. $r^s$ and $r^p$ are the reflection coefficients for s- and p-polarized light, for reflections at the interface below ($r_{12}$) and above ($r_{13}$) the emitter. The phase shift due to the traveled distance from the emitter to the interface and back, is given by $2\beta$, where the subscripts denote the involved media. From these principle orientations, the LDOS can be calculated for a dipole with an arbitrary angle $\theta$ from the plane normal to the sample:

$$\rho(\theta, d, z) = \rho_\perp (d, z) \cos^2(\theta) + \rho_\parallel (d, z) \sin^2(\theta),$$

where $d$ and $z$ are the substrate-mirror and emitter-substrate separation, respectively. The integration runs from $u = 0$ to $u = \infty$, where we can distinguish two regimes: The ordinary part of the LDOS ($\rho_{\text{ord}}$), which results from wave-vectors that couple to the far-field ($0 \leq u \leq 1$) and the extraordinary part of the LDOS ($\rho_{\text{ext}}$), corresponding to wave-vectors that are evanescent in nature ($u > 1$). The evanescent field can couple to surface modes, such as surface plasmon polaritons (SPPs) or lossy surface waves at the metal interface [25].

The reflection coefficients $r_{12}$ and $r_{13}$ are calculated using Fresnel’s equations, taking into account both the phase and amplitude of the reflected field. We use the transfer matrix approach to calculate the net reflection and phase shift that result from the multiple layers in the upper (mirror) and lower (substrate) half-spaces. To carry out the integration we furthermore use the complex-plane integration technique described by Paulus et al. [110]. All calculations were carried out using a script (courtesy of Prof. Dr. A.F. Koenderink, AMOLF, The Netherlands) ran in Wolfram Mathematica 10 and were verified by comparison with the geometries and LDOS values found in Urbach and Rikken [111] and Novotny and Hecht [24] for geometries involving dielectrics and metals, respectively.
3.3 Method testing

The LDOS calculated for the two principal dipole orientations in front of the mirror is shown in Figure 3.2b, corresponding to two static orientations of the emission transitions dipole moment (TDM). The LDOS for dipoles oriented parallel or perpendicular to the substrate shows a different dependence on the substrate-mirror separation due to a different interaction with the mirror. The isotropic LDOS ($\rho_{iso}$) is also shown, which describes the LDOS experienced by an individual dipole that rotates quickly compared to the PL lifetime ($\kappa < \tau_{PL}$), in which case all dipole orientations are sampled and the LDOS is given by $\rho_{iso} = \frac{2}{3}\rho_\parallel + \frac{1}{3}\rho_\perp$ [25].

Figure 3.2: (a) Sketch of the stratified medium specific to our experimental setup that is assumed for LDOS calculations. (b) The LDOS calculated for our geometry for emitters with dipole oriented parallel (red) and perpendicular (black) to the interface, against the air gap normalized to the emission wavelength. Green curve shows the isotropic LDOS. The parameters assumed for these LDOS calculations are shown in Table 3.2

3.3 Method testing

To test the setup, we measure two commercially available reference materials, CdSe QDs and Alexa 488 fluorophores (see Appendix A.1 for details), both drop-casted from a solution onto a cleaned quartz substrate. Using an inverted scanning confocal microscope we excite the PL from the emitting layer with a 488 nm wavelength ps-pulsed laser and detect the arrival times of the emitted photons using an APD. By scanning the area of the sample around the point $r_0$ where the silver-coated lens touches the sample, we obtain the time-resolved PL intensity $I_{PL}(t, r)$ for different sample positions $r$. By integrating the time-resolved intensity recorded at each scanning position, we acquire a PL image as shown in Figure 3.3. For both samples, the PL images clearly show concentric rings of similar intensity, which result from positions on the sample characterized by the same distance $d$ to the spherical mirror, given by the radius of the mirror $R$:

$$d = \sqrt{|r - r_0|^2 + R^2} - R. \tag{3.9}$$

By summation of the time-resolved PL of pixels lying on concentric rings (dashed white line in Figure 3.3a and b) we obtain the average PL decay at different distances from the
CHAPTER 3. INTERNAL QUANTUM EFFICIENCY

mirror, $I_{PL}(t, d)$. Examples are shown in Figure 3.3a and b. The PL decays are fitted by a multi-exponential decay, where we use a maximum entropy method (MEM) [112] to determine the number of distinct lifetime components in the signal. The MEM enables one to estimate the contribution of different lifetime components to a PL decay, without a priori assumptions on their distribution.

![Figure 3.3: Detected number of emitted photons obtained by a confocal scan of CdSe QDs (a) and Alexa 488 Fluor (b) with a spherical mirror placed on top. Examples of pixels characterized by the same substrate-mirror separation ($d = 300$ nm) are indicated by the dashed circles. (c,d) Examples of the time-resolved PL intensity for different substrate-mirror separations $d$, for the CdSe QDs (c) and Alexa Fluor (d). The PL decays are obtained by summing the PL decays of pixels lying within concentric rings around the points where the mirror contacts the substrate, as illustrated by the circles in panel a and b.](image)

The PL decay rate of the CdSe QDs is best described by a bi-exponential function (Figure 3.16 in the S.I.), which we use to extract the decay rates as a function of the distance from the mirror (Figure 3.4). For the slower decay component (bottom), we obtain clear oscillations in the PL decay rate. At distances below $d \sim 100$ nm the decay rate is strongly enhanced, indicating the coupling of the emitters to surface plasmon polariton modes. These modes do not couple to the detector, which is confirmed by the decreased PL intensity around the contact point of the mirror (Figure 3.3a). The quenching of the emission is characteristic for an isotropic dipole orientation (Figure 3.2b). The faster decay component (top curve in Figure 3.4) shows no clear dependence on the emitter-mirror separation.

The PL decay of the Alexa Fluor is well described by a mono-exponential function (Fi-

\[ MEM \text{ script courtesy of Dr. M. Postma (University of Amsterdam, The Netherlands) } \]
3.3. Method testing

Figure 3.4: (a) Measured decay rate as a function of the substrate-mirror separation for CdSe QDs and (b) Alexa 488 Fluors under 488 nm excitation wavelength. The green line represents a fit assuming the mean isotropic LDOS, whereas the red line represents a fit assuming the mean parallel LDOS. Shaded areas show the uncertainty in the fits resulting from uncertainties in the refractive indices and dimensions of the system and from the width of the detected emission wavelengths (see Table 3.3).

gure 3.17 in the S.I.). Similarly to the CdSe QDs the decay rate shows clear oscillations with the distance from the mirror (Figure 3.4b). However, in contrast to the CdSe QDs, the drop-casted layer of the Alexa dye shows no decay rate enhancement at close proximity to the mirror, characteristic for a parallel dipole orientation with respect to the substrate (Figure 3.2b).

To confirm that the radiative component is modified by the proximity of the mirror, we performed Fourier analysis and compare the frequency of the observed PL decay rate oscillations to the frequency of the LDOS modulations and excitation wavelength (Figure 3.5). Modulations in the non-radiative rate caused by Auger recombination as a result of the inhomogeneity of the pump intensity, arising due to interference of the pump laser and its reflected field by the mirror, would oscillate with a frequency correlated with the excitation wavelength. Fourier analysis shows that the frequency of the decay rate oscillations is in good agreement with the oscillation frequency of the LDOS and not with the frequency expected for the pump field (Figure 3.5). This confirms that the radiative component is modified by the varied LDOS in proximity of the mirror. The high amplitude of the observed decay rate modifications (Figure 3.4) is thus indicative of a significant radiative contribution to the PL decay rate, which is expected for these high efficiency emitters. Moreover, it shows that the faster component of the PL decay of the CdSe QDs is mainly of non-radiative character as it shows no clear dependence on the LDOS.

The difference in the decay rate modifications obtained for the CdSe QD and the Alexa Fluor reference materials (Figure 3.4) can be explained in terms of the orientation of the emission TDM of both emitters (Figure 3.2b). This follows from the fact that the experimentally determined decay rate depends not only on the decay rate of each individual emitter but also on the number of photons that each orientation contributes to the total PL signal [113, 114]. In particular for a static emission TDM, the brightness of the
emitter strongly depends on its orientation. This results from the orientation-dependent excitation $A(\theta, \phi)$ and detection efficiency $F(\theta, \phi, d, z)$ and from the orientation-dependent LDOS that the dipole experiences (Equation 3.8) [113]. The measured PL decay of an ensemble of emitters is given by integration over the intensity of all dipole orientations (see e.g. [100, 113, 114]):

$$
\langle I_{PL}(t, d, z) \rangle = \int_0^{2\pi} \int_0^\pi A(\theta, \phi) F(\theta, \phi, d, z) D(\theta, \phi) \gamma_{PL}(\theta, \phi, z) e^{-(\gamma_r(\theta, \phi, z) + \gamma_{nr})t} \sin \theta \, d\phi \, d\theta,
$$

(3.10)

where $D(\theta, \phi)$ is the distribution of dipole orientations within the detected volume and the angles $\theta$ and $\phi$ are defined in Figure 3.6a. It follows from Equation 3.10 that the decay rate of the total PL intensity is determined mainly by the emitters with TDM orientations that are efficiently excited and that couple well to modes that radiate into the far field detector (i.e. that are not quenched). Furthermore, as the LDOS depends on the position within the emitter layer, the total PL intensity is obtained by averaging over the layer with thickness $d_{layer}$:

$$
I_{PL}(t, d) = \frac{1}{d_{layer}} \sum_{z=0}^{z=d_{layer}} \langle I_{PL}(t, d, z) \rangle.
$$

(3.11)

Danz et al. [113] showed that for particular geometries, this ensemble averaging effect can lead to the preferential observation of only the parallel or perpendicular oriented subset of dipoles in a randomly oriented ensemble. The dipole orientation that was
most dominantly observed strongly depended on the numerical aperture (NA) of the excitation and detection system [113]. To investigate how this effect influences the detected ensemble decay rate in our setup, we use Equations 3.10 and 3.11 and simulate the decay rate. The excitation efficiency for an emitter with a TDM orientation as shown Figure 3.6 is given by [113]:

$$A(\theta, \phi) = \int_0^\alpha \int_0^{2\pi} [p(\theta, \phi) \cdot E(\theta', \phi')]^2 \sin \theta \, d\phi' \, d\theta'. \quad (3.12)$$

The integration runs over all angles up to the angular aperture $\alpha$ of the objective lens. The electric field distribution $E$ of the excitation light in the focal volume can be calculated using the equations derived by Richards and Wolf [115]. $A(\theta, \phi)$ is shown for a high and low NA in Figure 3.6b. As expected, dipoles aligned with the excitation field (along the X-axis) are preferentially excited, although part of the linear polarization is lost to the Z-axis when using a high NA objective lens. We approximate the number of photons contributed to the detected signal by the fraction of excited carriers that recombine radiatively, into modes with k-vectors (angles) that can be collected by the objective lens ($\gamma_{\text{NA}}(\theta, \phi, z)$), i.e. modes for which $u < \text{NA}/n_2$):

$$F(\theta, \phi, d, z) = \frac{\gamma_{\text{NA}}r(\theta, \phi, d, z)}{\gamma_{\text{PL}}r(\theta, \phi, d, z)}. \quad (3.13)$$

The detection efficiency is shown for the principal dipole orientations in front of a mirror in Figure 3.7. The intensity emitted towards the detector is not constant, but fluctuates as a result of the LDOS enhancement. In close proximity of the mirror, 0 < $d$ ≤ 200 nm, dipoles oriented perpendicular to the substrate are quenched by the metal interface. In this region dipoles aligned with the substrate contribute the strongest to the measured PL intensity.
To investigate the effect of the detection bias on the extracted IQE, we use Equation 3.10 to simulate the decay rate modifications of an ensemble of randomly oriented emitters $(D = \text{constant})$, with an IQE in an homogeneous medium of 80%. Firstly, we study an ensemble comprised of emitters that each individually experience an isotropic LDOS as a result of a quickly rotating TDM (green symbols in Figure 3.8). The decay rate modifications of such an ensemble are well described by the average isotropic LDOS $\rho_{iso} = 2/3\rho_\parallel + 1/3\rho_\perp$, as the emitter’s brightness does not depend strongly on its orientation or position in the focal volume. Fitting Equation 3.5 gives excellent agreement with the IQE (80%) used for these simulations. For an ensemble of randomly oriented emitters with a static emission TDM (black symbols, right axis), the amplitude of the decay rate is significantly reduced for $d < 100$ nm compared to that of the quickly rotating TDM case. For our geometry, this shows as a reduced contribution of the perpendicular dipole orientation to the PL decay rate as a result of their reduced brightness (Figure 3.7) and hence a large contribution of the parallel component, which comprises up to 92% of the radiative decay rate (top panel). As a result, the IQE that is extracted using the isotropic LDOS for $d > 100$ nm, is slightly overestimated (IQE $\sim 86\%$), whereas it is underestimated when assuming a parallel LDOS (IQE $\sim 50\%$) with respect to the input value of 80%. The quantitative ramifications of this orientation-selectivity strongly depend on the setup, i.e. the numerical aperture (NA) of the excitation and detection system [113], on the emitter’s absorption and emission TDM and on the refractive indices of the different layers within the geometry.

We apply these insights to our measurements in Figure 3.4. The Alexa 488 Fluor is known to have a static TDM that is locked to its molecular structure and well aligned with the absorption dipole moment [116]. Following the above discussion, we thus expect (Figure 3.8) a higher visibility of parallel dipole orientations in our experiment. This is congruent with the decay rate modifications observed in Figure 3.4b, which are mainly of parallel LDOS character. Although our simulations do not justify the observation of purely parallel dipole orientations, we note that the Alexa molecule is structurally flat. Drop-casting might therefore lead to preferential arrangement of dipoles parallel to the substrate, $D(\theta, \phi) = D(\pi/2, \phi)$, which will further attribute to the mainly parallel LDOS contribution to the PL decay. Hence, the IQE is obtained by fitting the PL decay rate.
3.3. Method testing

with the parallel LDOS, yielding IQE = 55%. For the CdSe QDs, which are expected to have a quickly rotating dipole [117], the average decay rate is well described by the isotropic LDOS (Figure 3.4a) in accordance with our simulations and yields IQE = 82%.

![Figure 3.8](image)

**Figure 3.8:** Bottom panel: Simulated measured decay rate of an ensemble of emitters in proximity of an metal interface for emitters with a static (black) and quickly oscillating (green) TDM. The y-axis is shifted for presentation purposes. Solid lines are fits using Equation 3.5, assuming isotropic (green) and parallel (red) LDOS. For the quickly rotating dipoles, isotropic LDOS fits the data very well, yielding an IQE of 79% which is close to the input value used for the simulations (IQE=80%). For the static dipole orientation, both parallel and isotropic LDOS are fitted yielding 48% and 86% respectively. Top panel: Fraction of the radiative decay rate resulting from dipoles oriented parallel to the substrate ($\sin^2(\theta)$). For the simulations, we assume a linearly polarized laser (485 nm wavelength) focused through a NA=1.2 objective lens. The emitters are positioned at an air-glass interface in front of a mirror, with the PL wavelength and decay rate set to 537 nm and 0.25 ns$^{-1}$, respectively.

We conclude that the decay rate can be modified by controlling the LDOS in the presented setup. To extract the IQE, ensemble averaging effects should be taken into account, which critically depend on the emitter’s absorption and emission TDM. In particular for emitters with a static TDM, the decay rate and brightness is strongly orientation-dependent (Figure 3.1c) and the average decay rate is determined by the brightest emitters with dipole orientations that most efficiently radiate towards the detection system. This depends on the numerical aperture (NA) of the excitation and detection system of the used setup [113]. For emitters with a quickly rotating dipole the average decay rate is well described by the isotropic LDOS, as such an ensemble is characterized by a narrow distribution of decay rates.
3.4 Efficiency limit of Si-QDs in the visible spectral range

3.4.1 Sample: bu:Si-QDs

To investigate the emission efficiency limit of Si-QDs emitting below $\sim 650$ nm we study a class of Si-QDs passivated by organic ligands (C:Si-QDs). These QDs show emission in the visible spectral region [1, 2, 5, 11, 39, 40] and emission rates that approach those of direct bandgap materials [2, 6, 7, 11, 39, 40]. Specifically, we study butyl passivated Si-QDs (bu:Si-QDs)\(^2\) synthesized using a wet-chemical method described in detail in Appendix A.1 \[34\]. The synthesis yields bu:Si-QDs with a core size of $2.2 \pm 0.5$ nm, as determined from transmission electron microscopy (TEM, Figure A.1) \[2, 39\]. Bu:Si-QDs show PL that is smoothly tunable between 350 and 650 nm as shown in Figure 3.9a and b, with a high PL recombination rate, evident from the PL intensity which decays within $\sim 3$ ns (Figure 3.10).

\[ \text{Figure 3.9:} \ (a) \text{ Schematic of the structure bu:Si-QDs (top) and real-color photos of the PL of bu:Si-QDs in ethanol under 350, 400 and 460 nm pulsed excitation (bottom).} \ (b) \text{ PL spectra of bu:Si-QDs in ethanol for different excitation wavelengths, indicated by the arrows. The sharp peak on top of the spectrum excited by 490 nm likely results from Raman-scattered excitation light. The black line shows the PL spectrum for a drop-casted film of bu:Si-QDs under 445 nm excitation.} \]

To measure the IQE, we prepare a thin layer of bu:Si-QDs by drop-casting a dispersion of bu:Si-QDs in ethanol onto a cleaned quartz substrate. We confirm that the PL spectra (Figure 3.9b) and PL dynamics of the dried thin layer and dispersion are very similar (Figure 3.10), indicating that the emissive processes are not considerably influenced by both environments. The PL decay can be well described by a bi-exponential as has been done previously \[39\], but can also be fitted well with a stretched-exponential function. This applies for bu:Si-QDs dried on a substrate, dispersed in ethanol as well as for a single bu:Si-QD (Figure 3.10). Furthermore, in agreement with results in literature on similar materials, the QY is very low and is below 6% (Figure 3.18 in the S.I.).

\[ ^2 \text{Samples courtesy of Dr. C.P. Umesh, Dr. J.M.J. Paulusse and Prof. Dr. H. Zuilhof (Wageningen University, The Netherlands)} \]
3.4. Efficiency limit of Si-QDs in the visible spectral range

![Figure 3.10](image)

**Figure 3.10:** (a) Time-resolved PL of bu:Si-QDs dispersed in ethanol and dried on a substrate under ~450 nm pulsed laser excitation. The curves are shifted along the horizontal axis for presentation purposes and fitted using a bi-exponential (green) and stretched-exponential (red) function. The gray curve shows the internal response function (IRF) of the detection system used for the dispersion. The IRF for the dried sample measurement has a similar temporal width. Inset: Normalized PL decay of an individual bu:Si-QD (~3.5 kcounts at peak) taken from [39]. (b) Standardized residuals of fits in (a).

3.4.2 Decay rate modifications

The PL image of the layer of bu:Si-QDs is shown in Figure 3.11. Similarly to the CdSe and Alexa measurements, we observe clear rings in the image as a result of the spherical mirror that is placed on top. In addition, we observe irregular regions with an enhanced PL intensity, potentially arising from damage of the mirror’s coating. Indeed, when the mirror is removed, these areas are absent (Figure 3.11b), showing that they are not in the QD layer itself. The mirror shows damage also at around the area where it contacts the sample and the imprint that remains after removal is larger than expected for a thin layer (<30 nm, Figure 3.11). We correct for the resulting offset in the substrate-mirror separation as explained in the supporting information (Section 3.7) and we exclude the bright areas from our analysis by excluding pixels that have a high intensity compared to other pixels lying within the same ring. We verified that the exact value of this intensity threshold level does not have a significant influence on the observed decay rate modifications.

The PL decay rate of bu:Si-QDs is shown in Figure 3.12c and d, obtained by fitting the PL decay by a bi-exponential and stretched-exponential function. Both decay models result in satisfactory fit residuals (Figure 3.10), but convey a different physical mechanism underlying the PL. The bi-exponential decay suggests the overlapping signal from two sub-populations of QDs in the sample, whereas the stretched exponential decay is characteristic for a single population that is broadened e.g. due to an intrinsic size-distribution or a variable environment. Nevertheless, for both models the decay
rate components show well-defined oscillations with a high amplitude (Figure 3.12). Interestingly, when assuming bi-exponential decay dynamics, the high amplitude of the oscillations shows that both components have a strongly radiative character. This is unexpected, as the faster decay component could be anticipated to result from a strong non-radiative decay, as observed for the CdSe QDs where the fast decay rate component is unaffected by the proximity to the mirror (top curve in Figure 3.4a). This surprising result for bu:Si-QDs suggests that the observed two PL decay components, also observed in dispersion and for a single bu:Si-QD (Figure 3.10), correspond to two separate emissive states of a bu:Si-QD. It is, however, unlikely to have two distinct emissive states with such a similar IQE value, rather suggesting that these states are closely related. We therefore expect that the stretched-exponential model describes the physics more accurately. The choice of a distribution of lifetimes rather than two distinct values is further supported by MEM analysis (Figure 3.19 in the S.I.).

For both models, the decay rates are best fitted to Equation 3.5 for a static parallel...
dipole orientation (red curve in Figure 3.12b), which yields values for the IQE of $\sim 41\%$ and $\sim 57\%$ and radiative rates of $0.44 \pm 0.03 \text{ ns}^{-1}$ and $0.11 \pm 0.01 \text{ ns}^{-1}$ for the faster and slower decay components of the bi-exponential decay respectively. For the stretched-exponential model we obtain a very similar IQE of $\sim 48\%$ and a mean decay rate of $0.45 \pm 0.03 \text{ ns}^{-1}$. Assuming an isotropic dipole orientation instead, (green curve in Figure 3.12b), typically expected for emitters with a band-like energy level dispersion, yields higher values for the IQE of $\sim 53\%$ and $\sim 76\%$ with radiative rates of $0.13 \pm 0.02 \text{ ns}^{-1}$ and $0.49 \pm 0.05 \text{ ns}^{-1}$ for the bi-exponential model and $\sim 64\%$ with a radiative rate of $0.60 \pm 0.06 \text{ ns}^{-1}$ for the stretched-exponential model, but provides a poorer fit at short distances ($d < 100 \text{ nm}$). We conclude that the already very high IQE values fitted by the parallel dipole orientation case are in fact conservative estimates of the IQE.

### 3.4.3 Orientation of the emission TDM

The detection bias towards parallel dipole orientations only applies to emitters with a static emission TDM (Section 3.3). Indeed, for molecules like the Alexa 488 Fluor the static TDM is well established [116, 118], but for Si-QDs the situation is less clear. There have been reports of a static TDM orientation, resulting in polarized emission in porous-Silicon [119], for Si-QDs where emission is governed by defect centers [120], and for alkylamine-passivated Si-QDs [121]. Other studies, however, presented evidence for a degenerate TDM [120, 122] and moreover, early IQE studies of Si-QDs embedded in SiO$_2$ assumed an isotropic dipole orientation [8, 9].

To resolve the nature of the TDM of bu:Si-QDs, we investigate their emission with PL anisotropy measurements. For this, the sample is excited with a linearly polarized laser and the PL intensity is detected through linear polarizer filters oriented parallel and perpendicular to the polarization of the excitation source (Figure 3.13). The PL anisotropy $\psi$ is defined from the intensities measured in the parallel ($I_\parallel$) and perpendicular ($I_\perp$) polarization directions, normalized to the total intensity [123]:

$$\psi = \frac{I_\parallel - G I_\perp}{I_\parallel + 2 G I_\perp}.$$  \hspace{1cm} (3.14)

Here $G$ is a factor which corrects for the difference in the detection efficiency of both polarization directions. The decay of the PL anisotropy over time enables one to quantify the time $\kappa_{pol}$ that the polarization, induced by the selective excitation of emitters with their absorption TDM $p$ aligned with the pump field $E$ (Equation 3.12), is maintained [123]:

$$\psi = \psi_0 e^{-t/\kappa_{pol}}.$$  \hspace{1cm} (3.15)

Here, $\psi_0$ is the initial anisotropy, given by the angle $\beta$ between the excitation and emission TDMs $\psi_0 = \frac{3}{8} \frac{3 \cos^2 \beta - 1}{2}$ [123], and $\kappa_{pol}$ is the depolarization time.
Using the setup described in Figure 3.13, we measure the PL anisotropy of a drop-casted layer CdSe QDs and Alexa 488 Fluor (Figure 3.14). For the CdSe QDs we observe an initial anisotropy close to zero, which indicates depolarization faster than the time resolution of our system, $\kappa_{pol} < 0.16$ ns, as expected for a degenerate TDM, previously reported for CdSe QDs [117]. Less likely, this could result from an angle between absorption and emission TDM being exactly equal to the magic angle $\beta = \arctan(\sqrt{2})$. For the Alexa dye, we observe an initial anisotropy of $\sim 0.35$, which is in good agreement with literature values ($\sim 0.37$) [116] and a depolarization time in the order of tens of ns. Interestingly, for the bu:Si-QDs we observe a similar initial anisotropy ($\sim 0.3$) and a depolarization time of $\sim 60$ s. This is surprising, as we would rather expect a quickly rotating TDM orientation like observed for the CdSe QDs due to the assumed band-to-band recombination that is typically degenerate. The static nature of the TDM of bu:Si-QDs could suggest that emission is governed by localized states around the bandgap, contributed by the covalently bonded organic ligands [2, 6, 7]. Alternatively this could be due to a slightly anisotropic shape of the Si-QD [124]. In any case, comparison with the PL lifetime shows that both for the Alexa Fluor and bu:Si-QDs $\kappa_{pol} > \tau_{PL}$, so that the emission TDM can be considered static for LDOS effects. This is in good agreement with the LDOS character observed in Figure 3.4 and 3.12.

In addition, we performed PL anisotropy measurements in solution (Figure 3.14d and e). In this case, apart from intrinsic depolarization effects, depolarization is also driven by the rotational diffusion of the emitters. For a spherical particle, the diffusion time $\kappa_d$ depends on its radius $r$ and is given by the Stokes-Einstein relation [123]:

$$\kappa_d = \frac{4\pi \eta r^3}{3k_bT},$$

(3.16)

where $\eta$ and $T$ are the viscosity and temperature of the dispersion respectively and $k_b$ is Boltzmann’s constant. The PL anisotropy of bu:Si-QDs in ethanol is shown in Figure 3.14e. Fitting the anisotropy decay with an exponential function yields $\kappa_d \sim 1.9$ ns, corresponding to a hydrodynamic radius of $1.13 \pm 0.02$ nm, which is in good agreement with the diameter of $2.2 \pm 0.5$ nm estimated from TEM (Figure A.1). For comparison, also the rotational diffusion of the enhanced green fluorescent protein (eGFP) in water...
3.4. Efficiency limit of Si-QDs in the visible spectral range

is shown. Both the initial anisotropy \( \sim 0.37 \) and rotational diffusion time \( \sim 16 \) ns are in good agreement with values found in literature [125, 126].

Figure 3.14: Time-resolved PL anisotropy, after excitation with a linearly polarized pulsed laser under 488 nm excitation. (a,b,c) Emitters drop-casted on a substrate and (d,e) in solution. The solid lines are mono-exponential fits.

3.4.4 Discussion

Using a Drexhage-type experiment, we have investigated the IQE and radiative rates of bu:Si-QDs and two reference materials, CdSe QDs and the Alexa 488 Fluor. Measurements on the reference materials reveal that decay rate modifications induced by the changing LDOS strongly depend on the orientation of the TDM of the emitter. For the Alexa Fluor, characterized by a static TDM, we observe modifications congruent with a parallel LDOS. For CdSe QDs, characterized by a degenerate TDM, we observe decay rate modifications governed by the isotropic LDOS. Surprisingly, we have confirmed the observed static nature of the TDM in the LDOS measurements of bu:Si-QDs by means of polarization anisotropy measurements.

Although we verified the static nature of the TDM of bu:Si-QDs, it is debatable whether the same explanation for the predominant observation of the parallel LDOS as for the Alexa 488 Fluor can be applied. The detection bias towards parallel oriented dipoles alone is not sufficient to justify observation of only TMDs oriented parallel to the substrate, because we used a high NA objective (NA = 1.45), which would lead to detection of perpendicular contributions as well. Moreover, unlike the Alexa molecules, the shape of the wet-chemically synthesized bu:Si-QDs is expected to be more spherical (Figure A.1) and hence it is unlikely that such QDs would show strong preferential alignment when drop-casted on the substrate. Potentially, the decay rate is therefore also partly influenced by perpendicular contributions and quenching at short substrate-mirror separation is not observed e.g. due to damage of the mirror. Since the amplitude of the oscillations

53
are strongest for the parallel LDOS, this will yield the most conservative estimate for the IQE and corresponding values of the radiative decay rate. Hence, we conclude that independent of the precise physics of the TDM orientation, the most conservative estimate of IQE are obtained by assuming parallel LDOS yielding an average IQE of $\sim 48\%$, with an associated mean radiative rate of $\sim 0.45 \text{ ns}^{-1}$. This radiative rate, determined here for the first time, is in good agreement with the theoretically predicted rates for C:Si-QDs [2, 7].

Another important finding is that the lower limit of the IQE of 48% obtained here is high in comparison with the QYs measured by us (Section 2.7) and encountered in literature for intrinsic PL of Si-QDs emitting below $\sim 620 \text{ nm}$, as shown in Figure 3.15. This thus demonstrates that bu:Si-QDs can emit very efficiently, provided that they are optically active. The fact that the QY is much lower (below $\sim 6\%$) indicates the existence of a large fraction of non-emissive ('dark') QDs that dilute the efficiency of the ensemble, by contributing to absorption but not to emission [9, 20, 127]. Hence there is a possibility to improve the QY to (at least) the level of the IQE measured here, if a way can be found to isolate the emissive subset of QDs from the ensemble or to resolve the mechanisms that make QDs dark. In the latter case, both when these QDs are permanently dark or temporary dark due to PL blinking, the low surface coverage by ligands and the resulting number of non-radiative surface defects are likely to play a crucial role [128, 129].

3.5 Conclusion

In conclusion, we report for the first time the experimentally determined IQE and radiative rates for Si-QDs emitting in the visible range by means of a Drexhage-type
3.6. Materials & methods

Experiment. In good agreement with our previous theoretical studies [2, 7], we find a mean radiative rate of \( \sim 0.45 \text{ ns}^{-1} \), comparable to the radiative rates of direct bandgap materials and fluorescent dyes. Moreover, the IQE of roughly 48% determined here for emission at \( \sim 550 \text{ nm} \) is, to the best of our knowledge, the highest reported value for intrinsic PL of Si-QDs in this spectral range. Our results demonstrate that the major limitation of the emission efficiency of Si-QDs is a low fraction of emissive QDs. This is either due to the presence of a large fraction of permanently dark QDs in the ensemble, or due to a low duty cycle of PL blinking, which will be studied in the next chapter. The high IQE shows the potential of organically capped Si-QDs for lighting and bio-imaging applications, where they possibly can replace toxic, expensive and or rare phosphors, such as CdSe- or In-based QDs.

3.6 Materials & methods

**Ensemble spectroscopy**

Dispersions were measured inside quartz cuvettes (Hellma Analytics). PL spectra are recorded using a spectrofluorometer (Horiba Scientific, Fluorolog) equipped with a spectrometer (Horiba Scientific, iHR320) and a CCD camera (Horiba Scientific, Synapse). PL spectra are corrected for the spectral sensitivity of the system. Time-resolved PL of the bu:Si-QDs was measured using a PMT (Hamamatsu R3809U-51) using a bin time of 0.1 ns, with excitation provided by a 445 nm wavelength diode laser (Lasos, BDL-SMN series), operated at 10 MHz with a \( \sim 40 \text{ ps} \) pulse width. The dried samples were prepared by drop-casting a dispersion containing the emitters on a substrate. For this we used quartz cover slips (Structure Probe Inc.), cleaned in an alkaline cleaning solution (base-Piranha or Hellmanex III) followed by a UV dry-cleaning procedure (oxygen descum or ozone treatment). PL spectra were acquired using an inverted microscope (Zeiss, Axio observer Z1) coupled to a spectrometer (Princeton Instruments, Acton SP2300) equipped with a CCD camera (Princeton instruments, Pylon400B).

**Time-resolved PL imaging**

The dried QD samples are studied using an inverted confocal microscope, where the QDs are excited by a linearly polarized pulsed laser that is focused to a diffraction-limited spot with a high NA immersion microscope objective. Emitted photons are collected with the same objective, filtered through a band-pass filter and detected using an APD. For the silicon-based samples we used a supercontinuum laser (Fianium) operating at 10 MHz (\( \sim 3 \mu \text{W} \)) filtered by an acousto-optical tunable filter (450-460 nm), a Nikon Eclipse Ti-U inverted microscope equipped with a 100x oil immersion objective lens (Nikon, Plan Apo Lambda, NA = 1.45) and an APD from ID-Quantique (ID100-20) connected to a Becker and Hickl DPC230 correlator card (0.16 ns per bin). The emission was filtered through a 550 ± 20 nm band-pass filter. For the CdSe QDs and Alexa dye we used an Olympus FV1000 microscope and a 60x water immersion objective lens (Olympus, UPLS Apo, NA = 1.2). PL was excited by a 480 nm laser diode (Picoquant, LDH-P-C-485).
CHAPTER 3. INTERNAL QUANTUM EFFICIENCY

operated at 5 MHz (∼10 µW) or 20 MHz (∼4 µW). The emission for the CdSe QDs and Alexa dye was filtered by a 593 ± 20 nm and 537 ± 13 nm band-pass filter, respectively, and detected using an APD (MPD, PDM) connected to a time-correlated single-photon counting module (Picoquant, Picoharp). Data was binned in time-bins of 0.512 and 0.16 ns.

Mirror preparation

The mirrors were prepared from spherical lenses (Edmund Optics, S-LAH79) with a diameter of 4 or 6 mm, which were cleaned in a base-Piranha solution and glued to coverslips. Using Electron Beam Physical Vapor Deposition (EBPVD) the spheres were then coated with 5 nm of germanium, 100 nm of silver and finally with 35 nm of SiO₂.

PL polarization anisotropy

For anisotropy measurements, PL is excited either in a right-angle geometry or reflection-geometry by the linearly polarized light from a 488 nm diode laser (Lasos, BDL-SMN series) filtered through a linear polarizer. Emitted photons are collected by a NA = 0.1 lens and filtered first by a 550 ± 20 nm bandpass filter and then by a linear polarization filter oriented parallel or perpendicular to the polarization of the excitation light. Finally, the emission is detected using an APD (ID Quantique, ID100-50). The arrival times of the detected photons with respect to the pump pulse are recorded with a timing card (Becker & Hickl, DPC-230). The measurements were corrected for the detection efficiency of both polarization directions, by exciting the sample with a polarization angle for which an equal intensity in both detected polarization directions is expected.

Data analysis

PL decay rates, $\gamma_{PL}(d)$, are extracted by fitting a mono-, bi- or stretched-exponential function to the falling edge of the PL decay, by optimization of the log-likelihood. For this we assume that the data follows a Poissonian probability distribution due to photon counting noise [130]. To extract the IQE, the decay rates against emitter-mirror separation are fitted by Equation 3.5. The uncertainty in the obtained IQE and radiative decay rate values was estimated from the uncertainties in the LDOS arising from the uncertainty in the refractive indices and dimensions of the system and from the width of the detected emission band (see Table 3.3). Time-resolved PL anisotropy is fitted using a least-squares method, where each data point is weighted following the scheme reported in References [131, 132].
3.7 Supplementary information

PL decay dynamics CdSe QDs

Figure 3.16: (a) PL spectrum of CdSe QDs in hexane under 488 nm wavelength cw excitation. (b) PL decay under 488 nm pulsed excitation, detecting 550 ± 20 nm. The green line shows a bi-exponential fit. (c) Maximum entropy method (MEM) \[112\] analysis of the PL decay of CdSe QDs in hexane (black), compared to simulated PL decays assuming a bi-exponential (green) and stretched-exponential decay (red). The solid lines show the lifetime amplitudes after 200 iterations, whereas the dashed lines indicate the MEM analysis after 5000 iterations. Independent of the number of iterations, there is good quantitative agreement between the data and the bi-exponential decay model.

PL decay dynamics Alexa 488 Fluor

Figure 3.17: (a) PL spectrum of Alexa Fluor in ethanol under 488 nm wavelength cw excitation. (b) PL decay under 488 nm pulsed excitation, detecting 550 ± 20 nm. The green line shows a mono-exponential fit. (c) MEM analysis of the PL decay of CdSe QDs in hexane (black), compared to simulated PL decays assuming a mono-exponential function (green). The solid lines show the lifetime amplitudes after 200 iterations, whereas the dashed lines indicate the MEM analysis after 5000 iterations. The lifetime of \( \sim 4.04 \) ns is in excellent agreement with literature values \[116\].
Quantum yield bu:Si-QDs

![Figure 3.18: QY of bu:Si-QDs in ethanol against excitation wavelengths. Courtesy of Dr. K. Dohnalova (University of Amsterdam, The Netherlands).](image)

PL decay dynamics bu:Si-QDs

![Figure 3.19: MEM analysis of the PL decay of bu:Si-QDs in ethanol (black), compared to simulated PL decays assuming a bi-exponential decay (green) and stretched-exponential decay (red). MEM is inconclusive after 200 iterations (solid lines), but shows better agreement with a stretched-exponential model after 5000 iterations (dashed lines).](image)

Emitter-mirror separation

For a spherical lens contacting the substrate, the substrate-mirror separation is given by 
\[ x = \sqrt{|\mathbf{r} - \mathbf{r}_0|^2 + R^2 - R}. \]
However, in case the mirror sits on top of the emitter-layer or when the evaporated mirror is damaged, the actual substrate-mirror separation, \( d \), might deviate from the calculated value: 
\[ d = x - \Delta d. \]
Fourier analysis (Figure 3.5 and 3.20) shows that the decay rates oscillate with a frequency corresponding to the LDOS oscillations. Hence, we exclude non-linear effects arising from the inhomogeneity of the pump intensity, and correct for the small phase shift between the LDOS and measured decay rates, by setting \( \Delta d \) so that the correlation between \( \gamma_{PL} \) and \( \rho(d) \) is maximum. The calculated shifts are shown in Table 3.1. The 130 nm shift for the bu:Si-QDs measurement potentially arises from damage of the used mirror’s coating, since it is very close to the thickness of the combined silver and SiO\(_2\) layer (135 nm, Table 3.2), used to create the mirror. Indeed, the diameter of the imprint that is observed after removal of
the mirror is larger than expected for a spherical object in a soft thin layer (<20 nm) (Figure 3.11b).

![Figure 3.20](image)

**Figure 3.20:** Amplitude of the fast Fourier transform of the PL decay rate oscillations of bu:Si-QDs in Figure 3.12 (gray), the LDOS modulations in front of the mirror (red, parallel LDOS) and of the oscillations in the pump intensity (blue). The mean PL decay rate is shown, obtained by assuming stretched-exponential decay dynamics, as well as both components obtained when assuming a bi-exponential function. The pump intensity is simulated by a sinusoidal signal with a period equal to half of the excitation wavelength.

**Table 3.1:** Substrate-mirror separation mismatch $\Delta d$ determined for all measurements.

<table>
<thead>
<tr>
<th>$\Delta d$</th>
<th>CdSe QDs</th>
<th>Alexa 488 Fluor</th>
<th>bu:Si-QDs</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 nm</td>
<td>-50 nm</td>
<td>-130 nm</td>
<td></td>
</tr>
</tbody>
</table>
Parameters used for LDOS calculations

Table 3.2: Parameters used for the calculations of the LDOS in Figure 3.1c

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emission wavelength</td>
<td>537 nm</td>
</tr>
<tr>
<td>Quartz refractive index</td>
<td>1.47</td>
</tr>
<tr>
<td>Emitter layer refractive index</td>
<td>1.0</td>
</tr>
<tr>
<td>SiO₂ refractive index</td>
<td>1.46</td>
</tr>
<tr>
<td>Silver refractive index</td>
<td>0.044+i3.6</td>
</tr>
<tr>
<td>Emitter layer thickness</td>
<td>20 nm</td>
</tr>
<tr>
<td>SiO₂ thickness</td>
<td>35 nm</td>
</tr>
<tr>
<td>Silver thickness</td>
<td>100 nm</td>
</tr>
<tr>
<td>Emitter position z</td>
<td>10 nm</td>
</tr>
</tbody>
</table>

Table 3.3: Parameters used for the calculations of the LDOS in Figure 3.12c

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emission wavelength</td>
<td>583 ± 10 nm</td>
<td>Estimated from transmission window of PL band-pass filter</td>
</tr>
<tr>
<td>Quartz refractive index</td>
<td>1.46</td>
<td>Rodney and Spindler [133]</td>
</tr>
<tr>
<td>Emitter layer refractive index</td>
<td>1.46 (1.0)</td>
<td>Estimated values</td>
</tr>
<tr>
<td>SiO₂ refractive index</td>
<td>1.46</td>
<td>Malitson [134]</td>
</tr>
<tr>
<td>Silver refractive index</td>
<td>(0.047+i3.9)) ± ± 0.1</td>
<td>McPeak et al. [135]</td>
</tr>
<tr>
<td>Emitter layer thickness</td>
<td>40 ± 10 nm</td>
<td>Estimated by AFM</td>
</tr>
<tr>
<td>SiO₂ thickness</td>
<td>35 nm</td>
<td>EBPVD</td>
</tr>
<tr>
<td>Silver thickness</td>
<td>100 nm</td>
<td>EBPVD</td>
</tr>
</tbody>
</table>
Chapter 4

Emission efficiency of individual nanoparticles

On the single-particle level, the emission efficiency is determined by PL blinking, i.e. the periodic switching between an emissive ON and a dark OFF state. Here we employ single-QD microscopy to study the PL blinking of bu:Si-QDs. By careful consideration of the effect of photo-degradation on the blinking dynamics, we determine the duty cycle - the fraction of time that each QD is in the ON state. We find that, in contrast to CdSe QDs, bu:Si-QDs are mostly OFF with a duty cycle below 4%. This shows that for efficient emission with organically passivated Si-QDs, blinking needs to be significantly suppressed, most likely to be achieved through a better surface passivation. Potentially, the short ON events with high PL intensity could make bu:Si-QDs interesting for super-resolution microscopy techniques.

4.1 Introduction

Almost all types of quantum emitters exhibit PL intermittency or PL ’blinking’, which is a random switching between an emissive (ON) state and a non-emissive (OFF) state. PL blinking emerges at the single-particle level and can significantly reduce the overall emission efficiency of emitters, when these are frequently trapped in an OFF state. For many applications, PL blinking is therefore detrimental, motivating the search for pathways to suppress it [17]. On the other hand blinking also provides opportunities. For example, blinking can be used to overcome the diffraction limit of optical imaging, as is done in super-resolution microscopy techniques such as photo-activated localization microscopy (PALM) [136], stochastic optical reconstruction microscopy (STORM) [137] and bleaching/blinking assisted localization microscopy (BALM) [138]. These techniques rely on the precise localization of separate emitters - within a denser ensemble - that are temporarily switched ON. In this way, a high resolution image can be reconstructed from a series of images, which sample a different subset of the emitters in the field of view. Also in this case, the blinking dynamics are crucial [139], i.e. the duration of the
ON events, and determine the spatial and temporal resolution of the imaging system.

There are two widely used models to explain the two types of PL blinking commonly observed in semiconductor QDs: A and B type blinking [19]. The charging model by Efros and Rosen [16] is used to explain A-type blinking by assuming that in the OFF state, the QD is charged as a result of trapping of one of the photo-excited carriers on the surface. Due to the remaining carrier in the core (electron or hole), a subsequent excitation of an electron-hole pair results in an increased recombination rate due to non-radiative Auger processes and hence in a low IQE. The ON state is restored when the trapped carrier returns to the core. The intensity fluctuations in A-type blinking are thus accompanied by changes in the PL decay rate. The model by Galland et al. [19] is used to explain B-type blinking, which manifests itself by intensity fluctuations without a change in the PL recombination rate. This model assumes the reversible introduction of a surface state, which serves as an efficient non-radiative recombination channel for hot carriers. Hence the number of carriers that end up in the bottom of the conduction band is reduced, but the PL recombination rate in the ON and OFF state is not affected. In both models, the surface assumes an important role and therefore full control over PL blinking lies in the surface design. Indeed a significant suppression of PL blinking in CdSe QDs was demonstrated as a result of growing an inorganic shell around the QD [128, 140], achieving duty cycles up to 100%.

The blinking dynamics of Si-QDs have been studied by multiple groups: both for Si-QDs with an SiO$_2$ passivation (O:Si-QDs) [141–144] and for organically passivated Si-QDs [145, 146]. O:Si-QDs can exhibit stable blinking over extended periods of time [143, 144], with duty cycles approaching 100% [144]. For C:Si-QDs, short ON periods with respect to the long-lived OFF states are typically found [145, 146], suggesting low duty cycles. The difference in the blinking behavior between both types of surface passivation suggests a critical role of the surface also for Si-QDs. Here we will study the blinking of individual bu:Si-QDs, to investigate if the duty cycle can be the cause for the discrepancy between the ensemble QY and IQE found in Chapters 2 and 3.

4.2 Single-QD microscopy

**PL imaging**

Insight into the emission inefficiency of individual QDs is obtained by employing single-dot microscopy. For this we use an inverted microscope coupled to an electron-multiplying CCD (EMCCD) camera in a wide-field scheme, as shown in Figure 4.1 (for more details, see the Materials & methods section). Using a long-pass filter, the scattered excitation light is filtered out, which enables the imaging of the PL of the sample. Compared to schemes employing a single-photon detector, the wide-field scheme has a limited time-resolution, but has the advantage that it enables to study multiple QDs simultaneously and thus the extraction of representative material properties in heterogeneous samples.
4.2. Single-QD microscopy

Figure 4.1: (a) Schematic of the wide-field single-dot microscopy setup. The PL of the spatially separated QDs is excited by a de-focused continuous wave laser in a wide-field scheme. We use either an oil immersion objective (NA = 1.4) or an air objective (NA = 0.75) to collect the emitted light, which is imaged using an EMCCD camera. (b) Example of a wide-field PL image of CdSe QDs under 488 nm excitation using an air objective.

The spatial resolution for optical imaging is given by Abbe's diffraction limit: $d = \frac{\lambda}{2 \times NA}$, i.e. the wavelength of the imaged light divided by the numerical aperture of the collection lens, with typically $d > 250$ nm. To resolve individual particles, we spatially separate the imaged QDs beyond this limit by drop-casting them from highly diluted dispersions onto a clean quartz substrate (Figure 4.1b). To excite and collect the PL of the sample, we either use an oil immersion objective with a high NA of 1.4 (Figure 4.1b), or an air objective lens with a NA of 0.75 in a dark-field illumination scheme, where we excite the sample from outside of the microscope (Figure 4.1c). The former setup has the advantage of improved spatial resolution and collection efficiency due to the high NA lens, whereas the latter has the advantage of a more homogeneous excitation spot and of a reduced background signal from the optical elements in the objective, the immersion oil and the substrate.

PL blinking

To quantify the PL switching, we record a sequence of images and extract the PL intensity of different diffraction limited bright spots in the field of view (FOV). For this we locate pixels that are characterized by a significant intensity with respect to the surrounding pixels. Examples of resulting time traces $I(t)$ are shown in Figure 4.2 for CdSe-based QDs (CdSe525 - see Chapter A.1). The PL signal is not continuous, but reversibly switches between bright ON periods and dark OFF periods. The occurrence of such two-level blinking is indicative of single quantum emitters and shows that the emitters are most-likely individually dispersed. Intensity traces of small ensembles of emitters within the same diffraction limited spot will show multiple bright intensity levels, resulting from different subsets of the small ensemble that reside in the ON state.

To distinguish the two intensity levels, we define an intensity threshold $I_{TH}$ (Figure 4.3). In frames in which the PL intensity exceeds this threshold the QD is considered to be ON, and is considered to be OFF otherwise. For $I_{TH}$ we use the definition of Kuno et al. [147] and set $I_{TH}$ to a multiple of the standard deviation of the background intensity.
From the number of ON and OFF occurrences the duty cycle is evaluated:

\[
\delta = \frac{T_{ON}}{T_{ON} + T_{OFF}} = \frac{T_{ON}}{T_{TOT}}. \tag{4.1}
\]

Here \(T_{ON}\) and \(T_{OFF}\) are the total time spent in the ON and OFF state respectively and \(T_{TOT}\) the total time.

**Figure 4.2:** Examples of PL intensity traces of CdSe QDs (red) under 488 nm cw excitation (\(\sim 70\, \text{W/cm}^2\)) compared to the background intensity (black). Traces are shifted for presentation purposes.

**Figure 4.3:** (a) PL intensity trace of CdSe QD (red) under 488 nm cw excitation (\(\sim 70\, \text{W/cm}^2\)) compared to the background intensity (black) and to the intensity threshold (blue horizontal line). (b) Histogram of the measured intensities in (a).

**Photo-degradation**

For the majority of fluorescence proteins, dyes and semiconductor QDs, the ensemble PL intensity is found to decrease over time, when exposed to laser irradiation. This has been observed for many materials and is typically the consequence of a decreasing number of emissive particles. The PL intensity of an ensemble of CdSe QDs is shown in Figure 4.4a. After the laser is switched on, the PL intensity decreases roughly exponentially, within an average time of \(\sim 920\, \text{s}\). The decreasing PL intensity is linearly proportional to the number of emitting QDs \(N_{ON}\) (Figure 4.4b), confirming that the loss of PL intensity is due to the discrete switching OFF of individual QDs and not due to the continuous
4.2. Single-QD microscopy

decrease in their PL intensity, which would happen e.g. through the gradual oxidation of the QD core [148].
The decreasing number of emissive particles is commonly interpreted in terms of irreversible photo-degradation of the individual emitters [149]. Most likely, it is related to photo-chemical reactions, e.g. through photo-oxidation effects [148], which introduce efficient non-radiative channels that quench the PL of the emitter (e.g. bottom two traces in Figure 4.2). In most cases this process is irreversible, or at least not detectable on the time-scales on which we measure, and leads to the permanent decrease of the emitting fraction and total PL intensity. Importantly, photo-degradation complicates the estimation of the efficiency associated with the reversible de-activation of the individual emitters, i.e. with blinking, as the permanent dark state resulting from photo-degradation is indistinguishable from a long temporary OFF state. Photo-degradation during the measurement leads to an overestimation of the total time spent in the OFF state $T_{OFF}$ and therefore to an underestimation of the duty cycle.

![Figure 4.4:](image)

Figure 4.4: (a) PL intensity integrated over 262 CdSe QDs against time under 488 nm cw excitation (∼70 W/cm²). The solid red line indicates an exponential fit yielding an average decay time of 920 s. (b) Integrated PL intensity versus the number of QDs in the ON state. The solid red line indicates a linear fit, showing that the decrease in PL intensity is the consequence of a decreasing number of emitting QDs.

To quantify the photo-stability, we determine the survival time $T_S$ [149], given by the time period before the last time at which the QD is observed to be ON (green shaded area in Figure 4.6a). The surviving fraction $F_S$, i.e. the fraction of dots that are either ON or temporary switched OFF, but still emitting at a later point in time, is shown for CdSe QDs in Figure 4.5. During the first 1500 s of the measurement $F_S$ decreases exponentially (red dashed line) with an average survival time of 1400 s, close to the decay time of total PL intensity in Figure 4.4. Towards to the end of the measurement this exponential behavior changes and $F_S$ decreases more rapidly. This is the consequence of an increasing amount QDs with OFF events that are not followed by ON events as these are cut-off by the experimental time window. In this time period the surviving fraction underestimates the stability of the material, although this effect can be avoided by measuring sufficiently long.

The duty cycle $\delta_i$ of each QD against the survival time $T_{i}^{s}$ is shown in Figure 4.6. During
the measurement of $\sim 2600$ s, $\delta$ assumes values between 0 and 60%, but the highest values are found only for QDs that survive towards the end of the measurement. For QDs that only appear shortly after the laser is switched on the duty cycle is close to zero, indicating that their duty cycle is underestimated as a consequence of photo-degradation. The average duty cycle $\bar{\delta}(t)$ of the surviving fraction (red line) indeed increases with time up to a value of $\sim 25\%$, the average duty cycle of the QDs that survive the entire measurement, and are not affected by photo-degradation. We assign this value to the average duty cycle associated with the PL blinking of this material.

![Figure 4.5](image)

**Figure 4.5:** (a) PL intensity trace of CdSe QD (red) under 488 nm cw excitation ($\sim 70$ W/cm$^2$) compared to the background intensity (black). The green area indicates the survival time, i.e. the time window $T_s$ in which the QD is observed. The horizontal dashed lines indicates the intensity of the ON state. (b) Histogram of the measured intensities in (a). (c) Surviving fraction obtained by analysis of 262 QDs during a measurement of $\sim 2600$ s. The red dashed lines indicates an exponential decay fitted to the first part of the data, yielding an average survival time of 1400 s.

![Figure 4.6](image)

**Figure 4.6:** (a) Duty cycle obtained for 262 individual CdSe QDs against the survival time, i.e. the time at which the dots last appear ON. The red line indicates the average duty cycle of the surviving fraction of QDs. (b) Distribution of the duty cycle.

### 4.3 Results: bu:Si-QDs

**PL blinking**

To study the duty cycle of C:Si-QDs, we investigate bu:Si-QDs, drop-casted from a dilute dispersion in ethanol on a quartz substrate. An example of a PL image used for blinking analysis is shown in Figure 4.7a, recorded using a NA=1.4 oil immersion objective. To
4.3. Results: bu:Si-QDs

account for the inhomogeneity in the excitation spot, we measure the excitation intensity distribution on a dense layer of QDs (Figure 4.7b). From the QD positions, excitation intensity distribution and measured laser power, we obtain the power density at each emitter’s position.

![Figure 4.7](image)

**Figure 4.7:** (a) Wide-field PL image of bu:Si-QDs under 488 nm (~0.8 mW) excitation. (b) The measured excitation intensity distribution.

Typical examples of intensity traces of bu:Si-QDs are shown in Figure 4.8. The intensity traces are characterized by short ON periods that typically last only a few seconds and long OFF periods that last up to 1000’s of seconds. In contrast to CdSe QDs, each trace consists only of a few ON events, the vast majority of which appears in the first part of the measurement, shortly after the laser is switched on (Figure 4.9, green triangles). Only a fraction of the QDs appear ON towards the end of the measurement.

![Figure 4.8](image)

**Figure 4.8:** (a) Representative examples of PL intensity traces of bu:Si-QDs (red) under 488 nm cw excitation (~28 W/cm²) compared to the background intensity (black). In total 120 traces were recorded. Traces are shifted for presentation purposes.

Interestingly, the fraction of bu:Si-QDs in the ON state $F_{ON}$ decays within ~250 s, whereas the surviving fraction $F_S$ decays much slower within ~1000 s (Figure 4.9, black circles). This shows that apart from photo-degradation, additional photo-induced changes occur in the sample, causing QDs to have a higher probability to be emissive in the first part of the measurement.
Duty cycle

To estimate the fraction of time spent by each QD in an emissive state, we extract the duration of the ON and OFF events from the intensity traces and compute the duty cycle using the procedure outlined in Section 4.2. For this, we quantify the survival time and duty cycle of 120 bu:Si-QDs during the total measurement time of $\sim 2600$ s (Figure 4.10a). The duty cycle appears between 0 and 30%, with the most frequently observed value around a few percent. Like for CdSe QDs, the duty cycle estimate for bu:Si-QDs that appear only in the first part of the measurement is close to zero. However, in contrast to CdSe QDs, bu:Si-QDs that survive towards the end of the measurement also have a low duty cycle, typically less than 4%. The average duty cycle $\bar{\delta}(t)$ (red line in Figure 4.10c) is roughly constant between 2 and 4% and is independent of the survival time.

To understand the decay in the fraction of the emissive QDs, $F_{ON}$, we separate the contribution of photo-degradation from other photo-induced changes. For this we evaluate the surviving ON fraction, i.e. the fraction of QDs that are still alive (and will appear at a later point in time) and are in the ON state at some point in time: $F_{ON}^{S}(t) = F_{ON}(t)/F_{S}(t)$. The surviving ON fraction is shown in Figure 4.10b (black symbols). At the start of the measurement $F_{ON}^{S}$ is around 30%, but decreases roughly exponentially within $\sim 300$ s to a value of around 4%. This value is close to the average duty cycle $\bar{\delta}$ (red curve).

The high surviving fraction of QDs in the ON state at the start of the measurement indicates that bu:Si-QDs are in a different equilibrium state before laser irradiation [139]. A potential reason for this could be that most QDs are initially uncharged and thus emissive [150]. Only upon laser irradiation does $F_{ON}^{S}$ reach an equilibrium dictated by the blinking dynamics. This occurs even though we keep the excitation intensity as low as possible, and shows that the initial decrease of the fraction of emissive QDs (Figure 4.9, green) is for a large part governed by the PL blinking rather than due to the irreversible photo-degradation (Figure 4.9, black).
4.3. Results: bu:Si-QDs

![Figure 4.10](image)

**Figure 4.10:** Estimated duty cycle against the survival time of bu:Si-QDs under 488 nm excitation (∼28 W/cm²). (b) Distribution of the obtained duty cycle values. (c) Average duty cycle (red, left axis) and surviving ON fraction (black, right axis) and against time. The surviving ON fraction is roughly 30% right after the laser is switched, but decays within ∼300 s, as indicated by the solid black line.

### Power-dependence of the duty cycle

Finally, we study the influence of the excitation power on the blinking dynamics of bu:Si-QDs, by recording intensity time traces for ∼120 QDs at lower excitation power densities of 18 and 11 W/cm². To quantify the change in blinking behavior, we compute the probability distribution of the recorded ON and OFF times. For this, we extract the duration of all ON and OFF periods in each trace \( \{ t_{ON}^i \} \) and \( \{ t_{OFF}^i \} \) and compute the associated probability densities \( P(t_{ON}) \) and \( P(t_{OFF}) \):

\[
P(t) = \frac{N(t)}{N_{tot} \Delta t}.
\]

Here, \( N(t) \) is the number of ON(OFF) events of length \( t \) and \( N_{tot} \) the total number of ON(OFF) event. The weighting-factor \( \Delta t \) represents the average time difference to correct for the low data density in the tail of the distribution, following the scheme proposed by Kuno et al. [147]. Furthermore, to obtain proper statistics, we compute the joint probability density by combining the time traces of 120 QDs.

\( P(t_{ON}) \) and \( P(t_{OFF}) \) are shown in Figure 4.11a and b. Both the ON and OFF times roughly follow a power-law \( P \propto t^{-m} \), as evident from the linear-dependence on a double-logarithmic scale (Figure 4.11). The power-law dependence holds over the full experimental time range for the OFF-times, whereas for the ON times it is truncated around ∼300 s. To estimate the power coefficients, we use a maximum likelihood estimation (MLE) method described by Hoogenboom et al. [151]. In this approach, an estimate for \( m \) is obtained by comparing the detected ON and OFF times with the probability distribution function of a power-law (for more details see References [151, 152]):

\[
p(t) = \frac{m - 1}{t_{min}^{1-m}} t^{-m}.
\]

Here, \( t_{min} \) is the lower bound of the range in which the power-law dependence holds.
For the ON and OFF times we obtain $m_{ON} \sim 2.0$ and $m_{OFF} \sim 1.4$. Importantly, the exponents are independent of the excitation power density (Figure 4.11c). We also determine the average duty cycle (Figure 4.11d), by averaging the duty cycles obtained for QDs that survived at least the first 1000 s in each measurement (Figure 4.11c). Also in this case, we observe no clear dependence on the excitation power density. From this we conclude that the character of the PL blinking is not significantly influenced in the excitation power regime studied here and that the associated single-QD emission efficiency is unaffected.

Figure 4.11: (a,b) Composite probability density of the ON (a) and OFF times (b) for three different excitation power densities. In each curve the histograms are obtained by combination of 120 intensity traces. Solid lines show fits using a pure power-law (OFF times). Curves are shifted vertically for presentation purposes. (c) Power law exponents as estimated using a MLE approach. (d) Estimated average duty cycle against excitation power. $\bar{\delta}$ was obtained by averaging the duty cycles obtained for QDs that survived at least the first 1000 s of the measurement.

4.4 Discussion & conclusion

In conclusion, using single-QD microscopy we study the PL blinking duty cycle of bu:Si-QDs. We demonstrate that bu:Si-QDs exhibit short emissive ON periods, but are most of the time OFF and are characterized by a duty cycle of $\sim 4\%$ for the timescales studied here ($\sim 2600$ s). This estimate might in fact be an upper limit of the duty cycle, since for longer measurements the probability of being trapped in a long OFF state increases as a result of the the power-law nature of the OFF times [153, 154]. Our finding thus suggest major implications for the emission efficiency of ensembles of bu:Si-QDs. However, for a direct comparison of ensemble and single-QD measurements, careful consideration of the excitation conditions in both cases is required, since typically much higher excitation powers are necessary to resolve the PL of individual emitters. Moreover, the dense packing of QDs in QD ensembles was shown to influence the blinking properties [145, 155]. In particular, both clusters of CdSe QDs and C:Si-QDs were observed to exhibit longer collective ON periods when compared to ensembles of isolated QDs [145, 155]. To ensure that we are in the same excitation regime with single-QD measurements, we limited the excitation fluxes below $30$ W/cm$^2$. In this regime, the PL intensity of
4.5 Materials & methods

bu:Si-QDs in the ON state increases linearly with the excitation power as shown in Figure 4.12. Assuming an absorption cross-section of $10^{-16}$ cm$^2$ [2], this yields an average number of absorbed photons per QD $N_{abs} \ll 0.001$ per emission cycle for the excitation powers used here. The linear-dependence of the PL intensity and the low value of $N_{abs}$ thus shows that we are well within the linear regime and that we can exclude any non-linear effects such as Auger recombination due to multiple excitations per QD. Moreover, despite the increase of the collective ON times that were observed in literature for clusters of QDs, the same studies showed that the total intensity and duty cycle were not affected by particle interactions [145, 155]. This suggests that the duty cycles that we obtain here for bu:Si-QDs can be directly compared to ensemble efficiency measurements. Hence our findings show that the low duty cycle constitutes a critical limitation of the emission efficiency of bu:Si-QDs.

To be considered for most applications, there is therefore an urgent need to suppress blinking in bu:Si-QDs. This is most likely to be achieved through improved surface passivisation strategies, since the QD surface assumes a critical role in the blinking of QDs [17, 128, 129]. Alternatively, the short ON times could make bu:Si-QDs interesting for super-resolution applications, where materials with a low duty cycle are preferred [139].

![Figure 4.12: Maximum ON intensity against the excitation power density for bu:Si-QDs. Each point is the determined by averaging over the traces of 15 QDs. The red solid line represents a linear dependence, with a slope of 1. On the top horizontal axis the estimated average number of excited electrons per QD is shown.](image)

4.5 Materials & methods

Single-dot microscopy

Single-dot PL was detected using an inverted microscope (Zeiss, Axio Observer Z1) coupled to a spectrometer (Princeton Instruments, Acton SP2300) and a CCD (Princeton instruments, Pylon 400B) in a wide-field scheme. Samples were prepared by drop-casting QDs from a dilute dispersion on a quartz cover slip (Structure Probe Inc.). The cover slips were cleaned by sonication in an alkaline cleaning solution (Hellma Analytics, Hellmanex III) for 60 minutes, followed by sonication in and rinsing with demineralized water (30
minutes), drying by nitrogen flow and an ozone dry-cleaning procedure (UVP, PR-100) for 
∼20 minutes. Cw excitation is provided by the 488 nm Ar+ laser line (Spectra-Physics, 
Stabillite 2017) attenuated by a Glan-Thompson polarizer. The emitted light is collected 
using a 100x objective (Zeiss, Epiplan-Neofluar NA 0.75) or 100x oil immersion objective 
(Zeiss, Plan-Apochromat NA 1.4) and is filtered by a 490 long-pass filter (Semrock, 488 
nm EdgeBasic) long pass filter to remove scattered excitation light. By selecting a mirror 
in the spectrometer, we then acquire a blinking movie by recording sequences of PL 
images of the sample. For the CdSe QDs we used an acquisition time of 0.5 s per frame, 
for the bu:Si-QDs we used 2 s. The read-out time of the CCD was set below 50% of the 
used acquisition time.

Data analysis

To extract the QD positions, we construct an image which contains the maximum 
intensity measured at each pixel throughout the entire stack of acquired images. QDs 
were located by searching for pixels characterized by a high intensity with respect to the 
neighboring pixels. We obtain the time traces $I_n(t)$ for each QD $n$ by integrating the 
intensity of 5 by 5 pixels centered at the QD position throughout the blinking movie. We 
do the same for a position close the QD that does not contain any bright spots to obtain 
the intensity time trace of the background $I_{bg}^{n}(t)$. The background intensity shows a 
slight decay during the measurement, which is most likely related to the emission from 
the optical elements in the microscope. We correct for this by fitting an exponential 
decay to the background intensity, which we subtract from the intensity time traces.
Part II

Emission of carbon based nanoparticles
Carbon dots

Carbon dots (CDs) are carbon-based fluorescent nanoparticles, a versatile material which comes in many different compositions and forms. CDs can exhibit excitation-dependent PL ‘tunable’ throughout the entire visible range, interesting for optoelectronic and imaging applications. The mechanism underlying this tunable emission is highly dependent on the exact structure of the material and hence remains debated, most prominently being ascribed to dot-to-dot variations that ultimately lead to excitation-dependent ensemble properties. Here we use single-dot spectroscopy to elucidate the origin of the excitation-dependent PL of CDs, produced by a facile one-step synthesis from chloroform and diethylamine. We show that the single dot spectra show several characteristic peaks differing in emission peak position, spectral width and shape, indicating the presence of distinct emission sites. These emission spectra slightly vary from dot to dot, but always retain their basic characteristics. By excitation-dependent single-CD measurement, we furthermore provide evidence that already individual CDs exhibit excitation-dependent emission spectra, indicating the presence of distinct emission sites within one and the same single CD. Based on our previous work, we relate these emission sites to the sp² sub-regions in the carbon core, coupled to specific functional groups on the surface. Since these CDs are produced via a facile single-step bottom-up synthesis, these results indicate that a straightforward synthesis route can lead to the integration of multiple emission sites within individual CDs.

5.1 Introduction

Fluorescent carbon dots (CDs) have, like Si-QDs, many advantageous properties such as bio-compatibility [44–47] and resource abundance. Moreover, CDs can be produced using relatively facile synthetic routes [43]. The emission mechanism is less well understood, however, owing to the large structural diversity and complexity of CDs [62]. Moreover, in literature the majority of studies employs ensemble spectroscopy techniques, which are unable to distinguish the individual microscopic contributions to the optical properties of the poly-disperse CD ensembles. Here we employ single-dot spectroscopy, to investigate
CHAPTER 5. CARBON DOTS

the PL of carbon dots emitting between 400 and 700 nm. Single-dot spectroscopy avoids ensemble averaging effects and enables the investigation of the individual single-dot spectra that underlie the ensemble spectrum.

5.2 Ensemble characterization

5.2.1 Size evaluation

CDs were prepared via a mild one-pot process by refluxing of chloroform and diethylamine\(^1\), as described in detail in \textit{Nie et al.} [50]. TEM and Raman spectroscopy data reveal that the resulting CDs are composed of a nano-crystalline core (graphitic sp\(^2\) carbon atoms with sp\(^3\) carbon defects) [50]. We evaluated the size of CDs using AFM, yielding an average height of 2.0 \(\pm\) 0.7 nm (Figure 5.1). When compared to the 2-4 nm range determined for this material previously [50] by TEM, this is a lower average value. The difference could be due to a lower sensitivity of TEM to smaller particles, or more likely, due to a slightly anisotropic, disk-like shape of the nanoparticles, leading to a different size in lateral dimension and height when measured with TEM and AFM (e.g. as observed for graphene QDs [156]).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{afm SCAN.png}
\caption{AFM topography scan of CDs on a mica substrate; the inset shows the height distribution histogram obtained from \(\sim\)1200 particles.}
\end{figure}

5.2.2 Ensemble spectroscopy

The PL of the ensemble of CDs is continuously tunable with excitation wavelength, extending through the whole visible range, as shown for a low concentration (\(\sim\)0.1 mg/mL) dispersion of CDs in ethanol in Figure 5.2a. The corresponding spectra for various excitation wavelengths are shown in Figure 5.2b, showing a narrow peak at 560 nm for

\(^1\)Samples courtesy of Dr. H. Nie and MSc. J. Bo (Jilin University, China)
530 nm wavelength excitation. The PL QY, determined following the procedure described in Chapter 2, is between 1 and 2.5% with the highest value of 2.5% for excitation at 530 nm, corresponding to a narrow spectral band with maximum at around 560 nm (Figure 5.2b). Absorption and PL excitation (PLE) spectra in Figure 5.2c and d provide further insights into the energy structure of the system. The emission wavelength changes with excitation wavelength, switching between a broad blue-green band emitting at 490 nm with excitation maximum at around 380 nm, and a narrow green band at 560 nm with excitation maximum at around 530 nm. In addition, in previous work [50] a red band, with emission at ~660 nm and the excitation maximum at around ~630 nm was observed, which is not included here as the internal correction function of our current system ends at 600 nm excitation.

The PLE spectral map (Figure 5.2c) shows narrow Stokes shifts of only 89 meV and 130 meV for the red [50] and green bands, respectively, as opposed to ~730 meV for the blue-green band. The dissimilar spectral characteristics of the blue, green and red bands suggest that those are related to different emission mechanisms. In previous work, Nie et al. [50] showed that these three emission bands are robust features of the synthesized CDs and related their origin to the core and oxygen (-C=O) and nitrogen (-C=N) related surface moieties respectively.

![Figure 5.2: Emission and absorption from a low concentration (~0.1 mg/mL) dispersion of CDs in ethanol: (a) Real-color photo of PL under pulsed ns laser excitation at specified wavelengths in nm. (b) PL intensity and absolute PL QY (inset) excited by a Xe lamp. The PL intensity is plotted normalized to the number of absorbed photons at respective excitation wavelengths. (c) PLE spectral map and (d) PLE spectra for specified detection wavelengths and absorption coefficient. Black dots in PLE maps indicate PL maxima for each excitation wavelength.](image-url)
5.3 Single CD spectroscopy

5.3.1 Single CD vs ensemble spectra

To obtain insight into the microscopic distribution of the blue, green and red emission within the CDs, we employ single-dot spectroscopy to circumvent ensemble averaging effects and enable investigation of the PL from individual CDs. To do so, we use an inverted microscope equipped with a spectrometer coupled to an EMCCD camera (Figure 5.3), where either a grating for spectrally resolved measurements is selected, or a mirror to record PL images enabling spatial localization of emissive CDs (for more details, see the Materials & methods section). We use highly diluted dispersions of CDs in ethanol, which we drop cast onto quartz substrates, to achieve spatially separated CDs at a particle density below 0.1 µm$^{-2}$. The low particle density ensures that on average, we should observe at most a single CD within a diffraction limited detection spot of radius $\sim$300 nm.

To verify that we measure with a large probability individual CDs, we record PL time-traces of individual bright spots in the FOV. The vast majority of observed bright spots displays intensity fluctuations between two distinct levels (Figure 5.4): a bright ON state and a dark OFF state. Such two-step blinking is characteristic for single quantum emitters (Chapter 4) [15] and was also previously observed for single CDs [55, 57, 64, 65]. To obtain further insight into the excitation-dependent PL of the ensemble, we selectively study the blue (490), green (560 nm) and red (660 nm) emission bands, by using excitation wavelengths close to their excitation maxima, i.e. 405, 488 and 638 nm respectively, in combinations with suitable detection filters. We select individual CDs using a slit to narrow down the FOV (Figure 5.3) and record $\sim$500 single-dot spectra. Several representative examples taken under 405, 488 and 638 nm wavelength excitations are shown in Figure 5.5 (top), while the superposition of all $\sim$500 spectra compared to the ensemble measurements are shown below.

As expected for single dots, most of the PL spectra are narrower than the PL spectrum of the ensemble. To link the single CD properties to the ensemble, we superimpose the single-dot spectra and compare the resulting spectrum to that of the ensemble. The
5.3. Single CD spectroscopy

Figure 5.4: Blinking of CDs under 488 nm (~50 W/cm²) excitation: (a) The number of CDs in emissive ON state as a function of time. The red line is a single exponential fit yielding an average time of ~4 minutes. (b,c) Examples of blinking time-traces of CDs; acquisition time per frame is 2 s.

Superimposed single-dot spectra show good agreement with the ensemble spectra, although there is significant variation in the single-dot spectra, indicating the polydispersity of the sample (bottom panels in Figure 5.5). For the green emission band for example, studied under 488 nm wavelength excitation (Figure 5.5b), the single CD spectra vary between 500 and 750 nm, clearly giving rise to the extended width of the ensemble spectrum, while the individual CD spectra are much narrower (~100-400 meV) as plotted in Figure 5.6. This is also observed for the red emission band, showing a FWHM of 50-200 meV (Figure 5.5c). For the blue emission band excited at 405 nm (Figure 5.5a), the single-CD spectra are significantly broader (300-700 meV), indicating a different emission origin (Figure 5.6).

Interestingly, ~17% of the green single-dot spectra display multiple peaks (such as the bottom spectra in Figure 5.5b) or a peak that is clearly asymmetric towards longer wavelengths. The blue and red single-dot emission spectra do not show clear replicas, again suggesting an origin different from the green emission band. These side peaks are typically ascribed to energy replicas due to optical energy losses to local vibrational states (bulk or surface phonons) [64, 157], trion formation [158] and/or vibrational coupling to the substrate defect centers (in case of quartz, ~170 meV has been reported [159]).

To quantify the replica’s data, the single CD spectra were fitted on the energy scale (corrected for the wavelength to energy conversion) by the sum of equally spaced normal distributions \( G(\mu, \sigma) : \sum_i A_i G(\mu - (i - 1)\Delta\mu, \sigma) \), with \( A \) the amplitude, \( \mu \) the main peak position, \( \Delta\mu \) the splitting energy, \( \sigma \) the standard deviation and \( i \leq 3 \). The average FWHM of the spectra with clear side-peaks structure is around 100 meV, which is very common for room temperature measured single dot spectra and is typically related to inhomogeneous broadening caused by local environment field fluctuations; this is an important factor especially for relatively long detection times as used here (~5 minutes).
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Figure 5.5: (a-c) Single CD spectra under 405 nm (a, ∼40 W/cm²), 488 nm (b, ∼50 W/cm²) and 638 nm (c, ∼125 W/cm²) wavelength excitation, single-dot spectra (top) and superposition of single-dot spectra compared to the ensemble spectrum of a low concentration (0.1 mg/mL) dispersion of CDs in ethanol (bottom). Solid lines are fits to the data. The superimposed spectra show good agreement with the ensemble spectrum; the deviation for green excitation in the red (>600 nm) might arise from the low emission intensity of red emitting particles being too weak to be efficiently detected by single-dot spectroscopy, or from the previously reported local environment dependence of the CD PL [56, 160].

Between ~500-600 nm, all structured single CD spectra reveal similar (average) phonon replica energy of around 160 meV (Figure 5.7a), independent of the emission peak energy, i.e. independent of the size of CD core and/or origin of PL. The replica energy is high in comparison to values reported previously for this type of material by Ghosh et al. (70-150 meV) [64] and could be related to a vibration from sp³ C defect in the graphene flakes in the CD core active in Raman spectroscopy at 1300 cm⁻¹ (160 meV) [50]. Other possible sources of losses with similar vibrational energy are surface vibrations of the C-O stretching mode (~150-160 meV [161]), contributing to the Fourier-transform IR (FTIR) absorption spectrum (Figure 5.7b). Possible relation of the replica energy to sometimes suggested trion formation [158], however, is unlikely, as the replica energy shows very weak (if any) spectral dependence (Figure 5.7). To evaluate the possible role of the quartz substrate [159], we have compared measurements from partially deposited
sample (part empty, part deposited with low CD concentration). On the clean area, we found under the same experimental conditions only very few non-blinking spots, with low brightness, in strong contrast with the side containing CDs, which shows multiple blinking bright luminescent spots. We thus expect that direct excitation of SiO$_2$ defects in the substrate does not significantly contribute to the detected emission. This does not mean, however, that the SiO$_2$ defects could not contribute to the energy losses from the CDs, i.e. into the phonon replicas. Still, both the average replica energy and PL peak energy is slightly lower than that reported for silica defects [159] (∼170 meV at 600 nm).

![Distribution of the full width at half maximum (FWHM) (top), and its relation to the emission peak wavelength of all recorded single-CD PL spectra (bottom). Colors indicate the different excitation wavelengths.](image)

To further investigate the microscopic origin of the energy replicas, we analyzed the spectral dependence of the Huang-Rhys factor, $S$, (Figure 5.7c), which gives the mean number of emitted phonons during radiative recombination. The Huang-Rhys factor can be obtained from the amplitudes $I$ of the energy replicas $n = 0, 1, 2, \ldots$: $I(n) \approx e^{-S} S^n / n!$ [162]. Analysis reveals weak exciton-phonon coupling with in average of 0.2-0.3 phonons emitted per emitted photon (Figure 5.7c), which is roughly constant over the whole spectral range. Lack of significant spectral dependence of both replica’s energy and Huang-Rhys factor in the green spectral region indicates that the vibrational structure (i.e. the energy losses) is independent of the origin of the emission site.

### 5.3.2 Excitation-dependent single-dot spectroscopy

In the following section, we also record the change in the PL of the spatially localized single CDs, by consecutive excitation at 638, 488 and 405 nm wavelength. Several selected spectra recorded at the three excitation wavelengths are shown in Figure 5.8. In some
cases, we observe the simultaneous presence of blue and green, and eventually blue and red emission bands. These emission bands differ in their spectral features with red and green spectra being narrower than the blue spectrum, similar to the spectra depicted in Figure 5.5.

We note that the majority of spots only show a single spectrum (such as the top spectrum in Figure 5.8), which could either be the result of photo-degradation during the measurement (Figure 5.4a) or due to only a single emissive site on the respective CD. To reduce the effect of photo-degradation, we record the spectrally unresolved PL intensity under the different excitation wavelengths, detecting the emission through band-pass filters to selectively study the three emission bands. Examples of such filtered images are depicted in Figure 5.9. Their comparison reveals that many blue and green emitting spots show spatial overlap (arrows). By comparing the location of spots in detail, we find roughly 45% overlap between the CDs excited at 405 and 488 nm, suggesting that they exhibit both blue and green emission. Overlap with red emitting CDs is observed as well: while only a small fraction of the dots emit in the red (∼5%), ∼24% of those CDs emitting in red display overlap with the ones emitting in green, and ∼30% with the ones emitting in blue. Furthermore, ∼15% of them appear under both blue and green
5.3. Single CD spectroscopy

excitation, indicating emission of all three colors.

![Figure 5.8](image1.png)

**Figure 5.8:** Excitation-dependent single CD PL spectra measured under subsequent excitation of 638 (≈125 W/cm²), 488 nm (≈50 W/cm²) and 405 nm (≈40 W/cm²) CW laser excitation. Smoothed PL spectra are shown in colored lines.

![Figure 5.9](image2.png)

**Figure 5.9:** False-color wide-field PL images of highly dilute drop-casted samples of CDs. The three panels show identical fields of view, taken at 405 (a) 488 (b) and 638 (c) nm wavelength excitation, detecting blue-green (480-520 nm), yellow (580-620 nm) and red (680-720 nm) emission, respectively. Arrows indicate examples of the same CDs luminescing under different excitation wavelengths. The exposure time per image was kept at 30 seconds to limit the effect of photo-degradation.

Such excitation-dependent PL of single CDs is surprising, as excitation-dependent PL spectra are commonly not observed for molecules or single quantum dots, indicating the presence of multiple independent emission sites within one and the same CD. This direct observation of excitation-dependent single-dot PL spectra thus substantiate suggestions of excitation-dependent PL from single CDs [51, 61, 163]. In contrast, Ghosh et al. [64] did not observe such shifts in the PL spectra when exciting individual CDs at different excitation wavelengths. However, the 467 and 488 nm wavelength excitation in their experiment might have been too close for efficient excitation of the separate emission centers. Also, the large degree of overlap observed in Figures 5.9 is clearly different from the observations made by Das et al. [65], where no overlap was found between green and
red emission. Our results are, however, in good quantitative agreement with a single CD study on the very same CDs, where the CDs were immobilized in a Poly(vinyl alcohol) film [163]. This shows that the excitation-dependent spectra do not arise from clusters which form upon drop-casting the CDs on a substrate, which is further supported by the spatial separation observed in the AFM topography (Figure 5.1).

5.4 Discussion

Regarding the emission mechanism behind the excitation-dependent single dot spectra, in previous work by Nie et al. [50] it was proposed that the blue, green and red emission sites in these CDs are related to the core and to oxygen and nitrogen containing surface functional groups respectively. Based on chemical characterization combined with ensemble spectroscopy, PL was shown to change dramatically after selective reduction of C=O and C=N bonds on the surface [50], in line with studies available in literature that show that the PL spectral position and width strongly depend on the type of surface functionalization [52, 54, 164]. The differences in the width, peak position and structure of the spectra that we observe here for single CDs, support the view of different origins of the emission bands. Hence, we arrive at the following mechanism underlying the excitation-dependent single CD emission (Figure 5.10): the green and red emission originates from C=O and C=N containing surface groups respectively [50, 163], while the blue emission originates from the core. Indeed, FTIR and X-ray photoelectron spectroscopy (XPS) measurements on our dots reveal the presence of O and N containing functional groups (such as –OH, C=O, and C=N) [50]. This is in line with the evidence for a common origin of the green emission in carboxyl/carbonyl (O-related) surface functional groups [52, 54, 64, 65, 165]. The core-related emission originates most likely from smaller sp² domains within the CD, as graphene QDs with a pure sp² structure and comparable size to our CDs (2.0 nm) are expected to emit in the red spectral region (>600 nm) and not in the blue-green [166], like in our case. This is reasonable as our synthesis does not yield graphene-like cores, but rather CDs with mixed sp² and sp³ phase as schematically shown in Figure 5.10.

![Figure 5.10: Schematic of the proposed CD structure giving rise to the three emission bands.](image)
5.5 Conclusion

Using excitation-dependent single-dot spectroscopy, we identified characteristic single-dot PL spectra with different emission peak positions, spectral widths and spectral shapes, indicating multiple active and independently excitable emission sites that can be present within a single carbon dot. Superposition revealed that these single-dot spectra are at the origin of the excitation-dependent PL of the ensemble. By quantifying the number of CDs that emit multiple colors, our findings suggest that while not all individual CDs exhibit excitation-tunable emission, it is possible to integrate and engineer different types of electron transitions in nanoscopic dimensions through facile chemical synthesis, making these CDs even more versatile than organic dyes or inorganic QDs. This makes this particular type of CDs interesting for optoelectronic applications as an excitation-tunable broad-band phosphor and for single-nanoparticle multi-color imaging.

5.6 Materials & methods

Synthesis
CDs were synthesized by refluxing of diethylamine (DEA) and chloroform (volume ratio of 1:10) at 62 °C for 60 h as described by Nie et al. [50]. The products were separated from the solution with a rotary vacuum evaporator and re-dissolved in ethanol. The CDs were purified by dialysis (weight cut-off: 3500) in water and then ethanol to remove any molecular byproducts. FTIR and XPS measurements reveal the presence of O and N containing functional groups (such as –OH, C=O, C=N) on the CDs [50]. Oxygen-containing functional groups are presumably introduced from water and oxygen, and nitrogen-containing functional groups are presumably introduced from DEA.

Atomic force microscopy
The size of the CDs has been evaluated from their height, measured from a drop-casted dilute solution of CDs on a freshly cleaved mica substrate using an AFM (JPK Instruments) in tapping mode. The driving frequency was set slightly lower than the cantilever’s resonance frequency in air in order to minimize the effect of substrate-tip interactions on the determined height [167]. For reference, an empty area was imaged, containing less than ~10 particles per 25 µm². From z-scan dimension data analysis of ~1200 particles we obtained an average CD size of 2.0 ± 0.7 nm (inset in Figure 5.1).

Ensemble spectroscopy
CDs dispersed in UV-grade ethanol were studied in a quartz cuvette (Hellma Analytics) excited either by pulsed laser excitation provided by a Nd:YAG laser (Solar LS) or by continuous wave (cw) excitation provided by a Xe lamp. PL was detected in a spectrofluorometer (Horiba, Fluorolog3-22) equipped with a double grating monochromator.
CHAPTER 5. CARBON DOTS

coupled to a photomultiplier tube (PMT; amamatsu, R36-10). PL spectra were measured at room temperature and are corrected for the spectral sensitivity of the setup.

Quantum yield

Absolute QY at 405 and 430 nm excited by a Xe lamp was determined inside an integrating sphere (for more details, see Chapter 2). Relative QY values were scaled to these values to obtain absolute QY estimates for longer excitation wavelengths.

Single-dot spectroscopy

Single-dot PL was detected using an inverted microscope (Zeiss, AxioObserver Z1) coupled to a spectrometer (Princeton Instruments, Acton SP2300) and a CCD (Princeton instruments, Pylon 400B) in a wide-field scheme. For this, a dilute dispersion of CDs in ethanol was drop-casted on a quartz cover slip (Structure Probe Inc.). The cover slips were cleaned by sonication in an alkaline cleaning solution (Hellma Analytics, Hellmanex III) for 60 minutes, followed by sonication in and rinsing with demineralized water (30 minutes), drying by nitrogen flow and an ozone dry-cleaning procedure (UVP, PR-100) for ~20 minutes. Cw excitation is provided by laser diodes with 405 nm (ThorLabs, ML320G2-11), 488 nm (Lasos, BLD-488-SMN) and 638 nm (Lasos, RLD-XT) wavelength or by the 488 nm Ar+ laser line (Spectra-Physics, Stabillite 2017). Emitted light is collected using a 100x objective (Zeiss, Epiplan-Neofluar NA 0.75) and is filtered by a long pass filter to remove scattered excitation light. All spectra are measured at room temperature and are corrected for spectral sensitivity of the setup.

Data analysis

For localization of the CD positions, bright domains with significant intensity compared to the background were identified as CDs. The position of the center of this domain was compared between different images of the same field of view. A tolerance of 1 pixel between center coordinates was allowed to count as overlapping CDs. The different band-pass filters used in our experiments result in a slight displacement of the recorded images, for which we correct by quantifying the shift from transmission images taken by white-light illumination on a reference sample.
PART III

Concluding remarks
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]:

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

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
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

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4 Samples courtesy of the group of Prof. Dr. H. Zuilhof (Wageningen University, The Netherlands)
5 Samples courtesy of Dr. N. Licciardello and Prof. Dr. L. De Cola (Karlsruhe Institute of Technology, Germany)
6 Samples courtesy of Dr. K. Kusova (Institute of Physics Czech Academy of Science, Czechia)
7 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), Amine-terminated Si-QDs (am:Si-QDs), methyl-passivated Si-QDs (me:Si-QDs) and dodecane-passivated Si-QDs (do:Si-QDs). 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.
Appendix

A.1 Samples

**Fluorescent dyes and proteins**

**Rhodamine 6G** (Chapter 2): High purity R6G was obtained from Sigma-Aldrich and dissolved in UV-grade ethanol (Merck KGaA, Uvasol). Different concentrations were prepared by dilution. The concentration was estimated by comparison of the measured absorption coefficients with the value specified by Birge [92].

**Alexa Fluor 488** (Chapter 3): Alexa 488 Fluor was purchased from Thermo Fisher Scientific and was dissolved in UV-grade ethanol.

**Green fluorescent protein** (Chapter 3): The enhanced-green fluorescent protein (eGFP) [172] in a buffer solution was obtained from Dr. Ir. M.A. Hink (University of Amsterdam, The Netherlands). For PL anisotropy measurements, the eGFPs were dispersed in de-ionized water (Milli-Q).

**Group II-VI semiconductor QDs**

**CdSe QDs**: CdSe/ZnSe/ZnS QDs - core/shell/shell - in hexane were purchased from the Center for Applied Nanotechnology (CAN, CANdots Series A CSS). The reported emission wavelengths were $\sim 525$ nm (CdSe-525, Chapter 4) and $\sim 575$ nm (CdSe-575, Chapter 2 and 3). The concentration of the QD dispersions was estimated from their dilution and the concentration reported by the manufacturer.
Silicon QDs

**bu:Si-QDs-A** (Chapter 3, 4 and 6): Butyl-passivated Si-QDs were prepared by Dr. C.P. Umesh, Dr. J.M.J. Paulusse and Prof. Dr. H. Zuilhof (Wageningen University, The Netherlands). Bromine-terminated Si-QDs were obtained by reacting magnesium silicide with bromine in refluxing n-octane and were subsequently passivated using n-butyl-lithium [34]. The bu:Si-QDs were dispersed in UV-grade ethanol. A TEM image is shown in Figure A.1 revealing an average size of 2.2 ± 0.5 nm. The energy-dispersive X-ray (EDX) spectrum is shown in Figure A.2c.

![Figure A.1: Transmission electron spectroscopy (TEM) image of bu:Si-QDs with a size-distribution of 2.2 ± 0.5 nm (inset).](image)

**me:Si-QDs-A** (Chapter 6): Methyl-passivated Si-QDs were prepared by Dr. K. Kusova (Institute of Physics Czech Academy of Science, Czechia) from oxide-passivated Si-QDs, obtained through electrochemical etching of p-type silicon wafers [11]. The oxide-passivated Si-QDs were re-passivated with organic ligands, including methyl groups, under continuous UV irradiation in a mixture of hydrocarbons [11]. The me:Si-QDs were dispersed in xylene. A scanning transmission electron microscopy (STEM) image and EDX spectrum is shown in Figure A.2a and c.

**bu/me:Si-QDs-B** (Chapter 2): A second batch of bu:Si-QDs was purchased from the Chemical Research Solution (CRS) using the same procedure as outlined above. In the same way, a batch of methyl-passivated Si-QDs (me:Si-QDs-B) was prepared, by using a different passivating ligand. The Si-QDs were dispersed in UV-grade ethanol.

**do:Si-QDs** (Chapter 2 and 6): Dodecane-passivated Si-QDs were prepared by MSc. S. Regli and Prof. Dr. J.G.C. Veinot (University of Alberta, Canada) following the procedures described in References [93, 94]. First, Si-QDs embedded in an oxide were produced by annealing a hydrogen silsesquioxane (HSQ) solution and were consequently liberated using an hydrofluoric acid etching procedure. The hydrogen-terminated Si-QDs were passivated with dodecane and the obtained do:Si-QDs were dispersed in toluene. The
A.2. Ray-tracing simulations

Ray-tracing simulations (RTS) were carried out on collaboration with MSc. I. Kondapaneni, Dr. A. Wilkie and Dr. J. Krivanek from the Computer Graphics Group of the Charles University (Prague, Czechia). For RTS the IS as described in Section 2.9 is modeled by a well subdivided icosahedron with approximately 8000 triangles. The light distribution inside the IS is described by the radiative transfer equation [174] that can be solved by means of Monte-Carlo simulations. Multiple paradigms how to do such simulations exist [175–177]; due to the combination of materials present in our setup, here we restrict our model to tracing light particles (‘photons’) from the input port, containing the excitation source, to the output port containing the sensor. By ‘photon’ we denote a simulation particle with associated weight which represents the differential concentration of the dispersion was estimated from the measured absorption coefficient and the absorption cross-section found in Reference [95]. A STEM image and EDX spectrum are shown in Figure A.2b and c

am:Si-QDs (Chapter 2 and 6): Allylamine-terminated Si-QDs were prepared by Dr. N. Licciardello and Prof. Dr. L. De Cola (Karlsruhe Institute of Technology, Germany) through reduction of tetramethyl orthosilicate (Si(OMe)4) in an inverse micelle approach [28, 173]. Tetraoctyl ammonium bromide (TOAB) was used as the surfactant. The obtained hydrogen-terminated Si-QDs were passivated using allyl-amine in the presence of a platinum catalyst. The procedure is a modification of those reported in References [28, 173]. Am:Si-QDs were dispersed in UV-grade ethanol.

me-un:Si-QDs (Chapter 2): Methyl undercanoate-passivated Si-QDs were obtained in collaboration with Dr. I. Sychugov (KTH-Royal Institute of Technology, Sweden) and co-workers. The samples were originally prepared by the group of Prof. Dr. J.G.C. Veinot (University of Alberta, Canada) by annealing of a HSQ solution, for more details see Reference [13].

Figure A.2: STEM images of (a) methyl- and (b) dodecane-passivated Si-QDs. (c) EDX spectra of bu:Si-QDs, me:Si-QDs and do:Si-QDs. All samples show the presence of copper and carbon atoms, as a result of the used substrate. The measurements were carried out on a Verios XHR scanning electron microscope (FEI).
flux carried by the particle [176]. For simplicity we model neither polarization, nor re-absorption events and we only keep notion of two types of photons characterized by two respective wavelengths: excitation and emission photons ($\lambda_{\text{exc}}$ and $\lambda_{\text{em}}$). Excitation photons colliding with the active part of the sample can be transformed into emission photons. Photons interacting with any surface or absorbing volume are attenuated and scattered according to an appropriate phenomenological model:

- The IS surface, baffle and the cuvette’s cap are modeled by a Lambertian model with reflectance at both wavelengths set to 0.97.
- Reflection on the quartz of the cuvette and aluminum sample and fiber holders is modeled according to Fresnel’s equations for unpolarized light.
- Scattering/absorption in the volume of the active sample is modeled according to the radiative transfer equation where we set the absorption coefficient in the range $0.02 \text{ cm}^{-1}$ to $2 \text{ cm}^{-1}$ to study single-pass absorption values between 2% and 87%, respectively.

A fraction of the initial photon flux that enters the sphere via the input port can, after a series of scattering events on various surfaces, end up in the active volume of the sample. There we sample the possibility of a photon being absorbed along its way across the volume (according to Lambert-Beer law) or leaving the volume unaffected. If absorption occurs, we sample the possibility that the photon is re-emitted with a probability given by the PL QY. Emission photons are emitted in a random direction uniformly distributed from the point of absorption. We do not consider re-absorption, which has been discussed in detail elsewhere [78], by setting $A_S(\lambda_{\text{em}}) = 0$. Photons of both kinds (i.e. excitation and emission) scatter around in the sphere, but also can be absorbed by the loss channels such as the input port (modeled as Lambertian surfaces with a 0 reflectance) or by the IS coating. Paths are terminated when they hit such a loss channel. Moreover to prevent photon paths of infinite lengths, we use the so called Russian roulette technique [175, 177] to stochastically terminate the simulation of photons with some probability after each interaction. In case the photon’s path is not terminated its energy weight is proportionally increased in order to compensate for terminated photons in such a way that the expected result of the simulation stays unaffected.

Since light can exit the sphere via the input and output ports, we insert in our model loss channels behind the excitation source and sensor so that photon paths hitting these are terminated. The loss channels are modeled as small rectangles with zero reflectance sitting on aluminum beds. The excitation source in the input port is represented by a small rectangular region in space without actual visible geometry associated. Each point of that region sends out photons into a cone with angle of 3.4 degrees. The sensor in the output port is modeled as a pinhole camera without any associated geometry either, with a field of view equal to 20 degrees, which approximates the optical cable’s numerical aperture of 0.22 used in our experiments.

Within the cone set by the NA, the sensor measures the flux impinging on it from different directions. This cone is divided into a disjunct set of cells (‘pixels’) each of
A.2. Ray-tracing simulations

which accumulates weights of excitation and emission photons coming from the associated directions. The resulting accumulated values in all cells are regarded as realizations of the same underlying random variable for which we estimate the mean and variance. They represent the incoming flux on the sensor, which is directly analogous to the measured photon counts in the real experiment. For estimating the QY we follow the methodology of the physical experiment described in Equation 2.2 using a test and a reference sample, where the latter does not absorb or emit. The cuvette in the setup is modeled according to a typical commercially available cuvette (Hellma Analytics). There are several material interfaces (air/quartz, quartz/air, quartz/liquid, air/liquid) which are accounted for in order to achieve appropriate accuracy of our model. The teflon cap is modeled as a Lambertian diffuser with a reflectance of 0.9. The holder is made of aluminum and serves also as a baffle preventing light going from cuvette directly towards output port. Reflectance of the aluminum at the excitation and emission wavelengths is computed from Fresnel’s equations.
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Summary

Fluorescent nanoparticles, such as molecules, proteins and semiconductor quantum dots (QDs) enable the control over light via the absorption and emission of photons. The strong dependence of the emission properties on the atomic composition, shape, structure and size of the particles makes these materials in general very interesting for a wide range of lighting applications. E.g for displays, light-emitting diodes but also for biological applications, such as bio-imaging, (bio-)sensing and super resolution microscopy. The most crucial property is the emission efficiency, i.e. the efficiency with which energy can be converted into emitted photons. In this thesis the emission efficiency of nanoparticles is studied in detail, starting with the efficiency of an ensemble of emitters, to the efficiency of individual particles. This is demonstrated on silicon quantum dots (Si-QDs). Si-QDs have in general many advantageous properties, such as bio-compatibility, resource abundance, surface functionalization options etc, but are not considered for applications due to their limited emission efficiency.

The ensemble emission efficiency is best quantified by the quantum yield (QY), given by the ratio of the number of emitted and absorbed photons. The correct evaluation of the QY is crucial for the development of emitters and therefore, in Chapter 2, the validity of the method that is commonly used to measure the QY is critically examined. Both experimentally and theoretically, it is demonstrated that the QY methodology suffers from an artifact, resulting in the underestimation of the QY when the absorption of the sample is low. By detailed theoretical simulations the artifact is identified and a remedy is proposed. The corrected methodology is then applied to determine the QY of different types of Si-QDs.

In Chapter 3 the internal quantum efficiency (IQE) is investigated, which gives the emission efficiency of the brightest emitters in an ensemble. The IQE therefore gives the upper limit of the material’s emission efficiency in case non-radiative recombination pathways cannot further be suppressed. The IQE is extracted from the photoluminescence (PL) recombination rate, through control of the local density of optical states (LDOS). For this, a Drexhage-type method that employs a spherical mirror is employed to study, for the first time, the radiative rate and IQE of a class of organically passivated Si-QDs (C:Si-QDs). This class of C:Si-QDs shows emission in the visible spectral range below 600 nm, which is inaccessible for most types of Si-QDs. It is shown that despite the low QY that is typically found for Si-QDs emitting in the visible spectral range, C:Si-QDs
have high direct bandgap-like radiative rates, which enable a high IQE of \( \sim 50\% \). This shows that in principle Si-QDs can be a competitive candidate for a phosphor in lighting applications and for medical imaging. Moreover, it is demonstrated that these C:Si-QDs have a static emission transition dipole moment, characteristic for a localized state involved in the radiative recombination.

To resolve the origin of the discrepancy between ensemble QY and IQE, in Chapter 4 the emission efficiency of individual QDs is studied. On this level, the emission efficiency is determined by PL blinking, which shows as the periodic switching between an emissive and a non-emissive state. Using single-QD microscopy the PL blinking of C:Si-QDs is studied. C:Si-QDs appear mostly OFF and are characterized by short bright ON periods with a duty cycle below 4%. These results demonstrate that blinking poses a critical limitation to the ensemble QY of C:Si-QDs. Most likely, blinking can be suppressed through improved surface passivisation strategies, since the QD surface assumes a major role in the blinking process. Alternatively the short, but high-intensity ON events could make C:Si-QDs interesting for super-resolution microscopy techniques.

In addition to Si-QDs, an alternative group-IV nanomaterial, carbon dots (CDs), is explored in Chapter 5. Using single-dot spectroscopy, the microscopic organization of different emission mechanisms within these complex materials is investigated. Under different excitation wavelengths the single CDs show different spectra with distinct peaks that vary in peak position, spectral width and shape, indicating the presence of distinct emission sites in the ensemble. Excitation-dependent single-CD measurements provide evidence that also individual CDs can exhibit multiple of such emission spectra, suggesting that the emission sites can be present already within the same single CD. These results indicate that a facile synthesis route can lead to the integration of multiple emission sites within this versatile material.

The insights obtained through the different emission efficiency measurements are combined for C:Si-QDs in Chapter 6. Blinking is identified as the major limitation of the emission efficiency. This means, however, that without any optimization of the blinking dynamics, C:Si-QDs could be promising for super-resolution microscopy, in which low duty cycles are required.
Samenvatting

Door het absorberen en uitzenden van licht kunnen nanodeeltjes, zoals moleculen, eiwitten en halfgeleider quantum dots (QDs) gebruikt worden om licht te manipuleren. Het uitgezonden licht hangt sterk af van de atomische samenstelling, vorm, structuur en grootte van de nanodeeltjes, interessant voor een breed scala aan toepassingen. Bijvoorbeeld voor het gebruik in beeldschermen en LEDs, maar ook voor biologische toepassingen zoals voor bio-imaging, als (bio-)sensoren en voor superresolutie microscopie. Voor al deze doeleinden is de emissie-efficiëntie, het rendement waarmee geabsorbeerde energie kan worden omgezet in licht, een cruciale eigenschap. In dit proefschrift wordt de emissie-efficiëntie in detail bestudeerd, beginnende met de emissie-efficiëntie van een verzameling van lichtgevende deeltjes, naar de emissie-efficiëntie van individuele deeltjes. Dit wordt hier onderzocht aan de hand van silicium quantum dots (Si-QDs). Si-QDs hebben over het algemeen veelbelovende eigenschappen - silicium is niet giftig, is veelvoorkomend op aarde en er zijn vele mogelijkheden om de oppervlakte van de Si-QDs te functionaliseren - maar worden niet overwogen voor toepassingen door hun lage emissie-efficiëntie.

De emissie-efficiëntie van een verzameling van deeltjes kan het best gekwantificeerd worden aan de hand van de quantum yield (QY), gedefinieerd als de verhouding tussen het aantal uitgezonden en geabsorbeerde fotonen. Het juist bepalen van de QY is cruciaal voor de ontwikkeling van nanodeeltjes en daarom wordt in hoofdstuk 2 de betrouwbaarheid van een methode die vaak gebruikt wordt voor het bepalen van de QY, getest. Zowel experimenteel als theoretisch wordt er aangetoond dat de methode gevoelig is voor een artefact, die als resultaat heeft dat de QY onderschat wordt als de absorptie van het bestudeerde materiaal laag is. Het artefact wordt met behulp van gedetailleerde theoretische simulaties geïdentificeerd en er wordt een oplossing voorgesteld. Vervolgens wordt deze aangepaste methode gebruikt om de QY van verschillende soorten Si-QDs te bepalen.

In hoofdstuk 3 wordt de internal quantum efficiency (IQE) bestudeerd, die de emissie-efficiëntie van de meest heldere deeltjes in de verzameling geeft. De IQE geeft daarmee de hoogst haalbare emissie-efficiëntie van het materiaal, in het geval niet-radiatieve vervalmechanismen niet verder onderdrukt kunnen worden. De IQE kan bepaald worden uit de vervalsnelheid van de fotoluminescentie, door controle over de local density of optical states (LDOS) uit te oefenen. Hiervoor wordt een Drexhage-methode toegepast, die gebruik maakt van een ronde spiegel, om voor het eerst de radiative vervalsnelheid
en de IQE van een type Si-QDs bedekt met organische moleculen (C:Si-QDs) te bepalen. Deze C:Si-QDs zenden licht uit in het zichtbare deel van het spectrum, met golflengtes onder de 600 nm, een gebied dat niet toegankelijk is voor de meeste soorten Si-QDs. Er wordt aangetoond dat ondanks de lage QY die meestal wordt gevonden voor Si-QDs die licht uitzenden in het zichtbare gebied, C:Si-QDs een hoge radiatieve vervalsnelheid hebben, die leidt tot een hoge IQE van ongeveer 50%. Dit toont aan dat Si-QDs in principe een goede kandidaat zijn als lichtgevend materiaal voor verlichtingstoepassingen en voor bio-imaging. Daarbij wordt er aangetoond dat C:Si-QDs een statisch emissie overgangsmoment hebben, wat duidt op een gelokaliseerde toestand die betrokken is bij het radiatieve verval.

Om de oorzaak van het verschil tussen de QY en IQE te herleiden wordt in hoofdstuk 4 de emissie-efficiëntie van individuele QDs onderzocht. Op deze schaal wordt de emissie-efficiëntie bepaald door fotoluminiscentie blinking (knipperen), wat zich uit als het periodiek schakelen tussen een toestand waarin het deeltje licht geeft en een toestand waarin het deeltje donker is. Met behulp van single-QD microscopy worden de blinking eigenschappen van C:Si-QDs onderzocht. De C:Si-QDs staan meestal uit en worden gekenmerkt door enkele korte heldere periodes met een aan-uit verhouding van minder dan 4%. Deze resultaten tonen aan dat het proces dat blinking veroorzaakt een belangrijke beperking is voor de QY van een verzameling van C:Si-QDs. Waarschijnlijk kan blinking onderdrukt worden door de oppervlakte van de QDs beter te passiveren, omdat de oppervlakte van de QD een belangrijke rol speelt in het blinking-proces. Daarentegen zouden de korte maar heldere lichtgevende periodes de C:Si-QDs geschikt kunnen maken voor superresolutie microscopietechnieken.

Naast Si-QDs wordt ook een alternatief groep-IV nanomateriaal onderzocht, koolstof deeltjes (CDs), in hoofdstuk 5. Met behulp van single-dot spectroscopie wordt de microscopische verdeling van de verschillende emissiemechanismen in deze complexe materialen bestudeerd. Onder verschillende excitatiegolflengtes vertonen de individuele CDs, emissiespectra met verschillende piekpositie, breedte en vorm, wat er op wijst dat er verschillende emissiemechanismen in het materiaal voorkomen. Excitatieafhankelijke metingen aan enkele CDs leveren bewijs dat individuele CDs deze verschillende emissie spectra al tonen, wat suggereert dat deze emissiemechanismen ook binnen één enkele CD aanwezig kunnen zijn. Deze resultaten doen vermoeden dat een eenvoudige synthese kan leiden tot het verengingen van meerdere afzonderlijke emissiemechanismen in dit veelzijdige materiaal.

De inzichten verkregen doormiddel van de verschillende emissie-efficiëntie metingen worden in hoofdstuk 6 voor de C:Si-QDs samengevoegd. Blinking wordt geïdentificeerd als de voornaamste beperking van de emissie-efficiëntie. Dit betekent echter dat zonder enige optimalisatie, C:Si-QDs een geschikte kandidaat zijn voor superresolutie microscopie, waar korte maar heldere lichtgevende periodes juist wenselijk zijn.
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