Microscopic investigation of the emission efficiency of nanostructures
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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 ∼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:

$$IQE = \frac{\gamma_r}{\gamma_r + \gamma_{nr}}.$$  \hspace{1cm} (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:

$$\gamma_r = \frac{2\pi}{\hbar^2} \sum_f \left| \langle f | \hat{H} | i \rangle \right|^2 \delta(E_i - E_f).$$  \hspace{1cm} (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
concerns can be separated, yielding [24, 96]:

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

(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:

\[ \gamma_{PL} = \gamma_{nr} + \gamma_{r}^{\text{vac}} \frac{\rho}{\rho^{\text{vac}}}, \]  

(3.4)

where \( \gamma_{r}^{\text{vac}} \) and \( \rho^{\text{vac}} \) 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
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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](image)

**Figure 3.1:** Schematic of the experimental setup used for IQE measurements.

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:

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

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
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(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]:

\[
\rho_\perp = n_1^3 \frac{3}{2} \text{Im} \left[ \int_0^\infty \frac{(1 - r_{12}^p e^{-2\beta_{12}})(1 - r_{13}^p e^{-2\beta_{13}})}{1 - r_{12}^p r_{13}^p e^{-2(\beta_{12} + \beta_{13})}} \left(1 - r_{12}^s e^{-2\beta_{12}}\right) \left(1 + r_{13}^s e^{-2\beta_{13}}\right)}{1 - r_{12}^s r_{13}^s e^{-2(\beta_{12} + \beta_{13})}} \right] \frac{u^3}{l_1} du \]

\[
\rho_\parallel = n_1^3 \frac{3}{4} \text{Im} \left[ \int_0^\infty \left\{ (1 - u^2) \frac{1 + r_{12}^p e^{-2\beta_{12}}}{1 - r_{12}^p r_{13}^p e^{-2(\beta_{12} + \beta_{13})}} \left(1 + r_{13}^p e^{-2\beta_{13}}\right)}{1 - r_{12}^s r_{13}^s e^{-2(\beta_{12} + \beta_{13})}} \right\} \frac{u}{l_1} du \right].
\]

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 $R$:

$$d = \sqrt{|r - r_0|^2 + R^2} - R.$$  \hspace{1cm} (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
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) \cite{112} to determine the number of distinct lifetime components in the signal\(^1\). The MEM enables one to estimate the contribution of different lifetime components to a PL decay, without a priori assumptions on their distribution.

![Image of CdSe QDs and Alexa 488 Fluor](image.png)

**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 \( d = 300\text{nm} \) 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.

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 \( d \sim 100 \text{ nm} \) 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-

\(^1\)MEM 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]):

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

(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
Figure 3.6: (a) Schematic of an arbitrarily oriented dipole $p$ at a glass-air interface, excited by linearly polarized light that is focused by an objective lens. (b) Simulated absorbed intensity ($A(\theta, \phi)$) of the dipole as a function of its angle in the XY-plane ($\phi$, bottom axis) and in the XZ-plane ($\theta$, top axis). The simulations assume an excitation wavelength of 485 nm and are shown for an objective lens with NA=1.2 (solid lines) and NA=0 (dashed line). The NA leads to loss of the linear polarization of the excitation into the Z-direction.

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 an 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 ($\gamma_{r,NA}(\theta, \phi, z)$), i.e. modes for which $u < NA/n_2$:

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

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, $0 < d \leq 200$ 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 \(d < 100\ \text{nm}\) 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 \(d > 100\ \text{nm}\), 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.
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:** 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).

![Figure 3.9](image)

**Figure 3.9:** (a) 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) 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.).

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\(^2\)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: (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
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Figure 3.11: (a) Detected number of emitted photons obtained by a confocal scan of bu:Si-QDs with a spherical mirror placed on top of the sample. The gray areas represent parts that show increased brightness, most likely due to damage of the mirror, and have been excluded in data analysis. (b) Same field of view as in (a), but with the mirror removed. The dashed lines indicate pixels that lie within concentric rings of equal substrate-mirror separation. After removal of the mirror a bright area is observed around the contact point.

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.).

Figure 3.12: The measured PL decay rate as a function of the substrate-mirror separation for bu:Si-QDs under 455 nm wavelength excitation. The decay rates were obtained by fitting the decay dynamics to (a) a bi-exponential and (b) stretched-exponential function. Green lines represent fits assuming the mean isotropic LDOS, whereas red lines represent fits assuming the mean parallel LDOS. The shaded areas show the uncertainty in the fits resulting from uncertainties in the refractive indices and dimensions of the system and from the range of the detected emission wavelengths (see Table 3.3).

For both models, the decays rates are best fitted to Equation 3.5 for a static parallel
3.4. Efficiency limit of Si-QDs in the visible spectral range

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]:

\[
\psi = \frac{I_\parallel - GI_\perp}{I_\parallel + 2GI_\perp}.
\] (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 \(\mathbf{p}\) aligned with the pump field \(\mathbf{E}\) (Equation 3.12), is maintained [123]:

\[
\psi = \psi_0 e^{-t/\kappa_{pol}}.
\] (3.15)

Here, \(\psi_0\) is the initial anisotropy, given by the angle \(\beta\) between the excitation and emission TDMs \(\psi_0 = \frac{3}{2} \frac{3\cos^2 \beta - 1}{2} \) [123], and \(\kappa_{pol}\) is the depolarization time.
CHAPTER 3. INTERNAL QUANTUM EFFICIENCY

Figure 3.13: Schematic of the setup used for PL anisotropy measurements: The sample of randomly oriented emitters is excited with linearly polarized light and the PL intensity is measured parallel and perpendicular to the excitation polarization direction.

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, $\kappa_{pol} < 0.16 \text{ ns}$, 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 $\sim 60 \text{ s}$. 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]:

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

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 $\kappa_d \sim 1.9 \text{ ns}$, corresponding to a hydrodynamic radius of $1.13 \pm 0.02 \text{ nm}$, which is in good agreement with the diameter of $2.2 \pm 0.5 \text{ nm}$ 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.](image)

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].

**Figure 3.15:** Overview of the IQE (open symbols) and QY (filled symbols) of bu:Si-QDs (red) obtained in this work compared to values found in literature for different types of Si-QDs (gray). The yellow shaded area indicates the spectral region for which high QY and IQE values have been reported in literature. 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 IQE obtained for bu:Si-QDs assumes a parallel dipole orientation and stretched-exponential decay dynamics. The shaded area above indicates the value of the IQE obtained for an isotropic dipole orientation.

**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 $\pm$ 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).
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, $\gamma_{\text{PL}}(d)$, 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 ~ 4.04 ns is in excellent agreement with literature values [116].
Quantum yield bu:Si-QDs

![Figure 3.18](image)

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

PL decay dynamics bu:Si-QDs

![Figure 3.19](image)

**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).

Emitter-mirror separation

For a spherical lens contacting the substrate, the substrate-mirror separation is given by 

\[ x = \sqrt{|r - r_0|^2 + R^2 - R}. \]

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
3.7. Supplementary information

the mirror is larger than expected for a spherical object in a soft thin layer (<20 nm) (Figure 3.11b).

![Graph showing decay rate and LDOS modulations](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.

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

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

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<tr>
<td>Emitter layer refractive index</td>
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<tr>
<td>SiO$_2$ refractive index</td>
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<tr>
<td>Silver refractive index</td>
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<tr>
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<tr>
<td>SiO$_2$ thickness</td>
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<tr>
<td>Silver thickness</td>
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<td>Emitter position z</td>
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</table>

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

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<tr>
<td></td>
<td>537 ± 13 nm</td>
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<tr>
<td></td>
<td>550 ± 20 nm</td>
<td></td>
</tr>
<tr>
<td>Quartz refractive index</td>
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<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>SiO$_2$ refractive index</td>
<td>1.46</td>
<td>Malitson [134]</td>
</tr>
<tr>
<td>Silver refractive index</td>
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<td>McPeak et al. [135]</td>
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