Fluorescence Lifetime of Emitters with Broad Homogeneous Linewidths Modified in Opal Photonic Crystals

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We have investigated the dynamics of spontaneous emission from dye molecules embedded in opal photonic crystals. Fluorescence lifetimes of Rhodamine 6G (R6G) dye were measured as a function of both optical frequency and crystal lattice parameter of the polystyrene opals. Due to the broad homogeneous line width of the dye, the observed fluorescence lifetime varies only slightly with the frequency within the dye emission spectrum. The lifetime however does change as a function of the crystal lattice parameter. Our observations agree with theoretical calculations of the local density of optical states (LDOS) in the three-dimensional photonic crystals. The experiments and theory taken together reveal that the emission lifetime is modified over frequency ranges that are broader than the homogeneous emission line width of R6G dye.

I. Introduction

Photonic crystals are artificial periodic structures consisting of different dielectric materials where the index of refraction varies on length scales comparable to the wavelength of light. Because of this periodicity, light with specific frequencies is forbidden to propagate by wave interference along certain directions, similarly to Bragg diffraction of X-rays in atomic crystals. Such forbidden frequency ranges are called stopgaps. The larger the contrast between the refractive indices of the two materials, the more strongly the propagation of light is influenced and consequently the broader the stopgaps become. In the extreme case of the strong interaction between light and a photonic crystal, no optical modes at all exist within the photonic crystal. It was predicted in early theoretical works that, in this situation, known as a photonic band gap, propagation of light is forbidden in all directions, and spontaneous emission is completely inhibited for frequencies inside such a band gap.[1–3]

Control over spontaneous emission of light is crucial for many applications including miniature lasers, light-emitting diodes,[4] and solar cells.[5] Radiative properties of excited emitters are not solely determined by their internal nature but also by their environment.[6,7] According to Fermi's golden rule, the radiative decay rate (inverse lifetime) is proportional to the projected local radiative density of optical states (LDOS), to which the emitters couple.[8,9] This LDOS counts the number of electromagnetic states at the locations of the emitters for given frequency and orientation of the transition dipoles.

Since 1987, when the potential of photonic crystals in inhibition of spontaneous emission was pointed out,[2] there have been many efforts to observe modified emission rates in photonic crystals. Early emission experiments were performed on colloidal photonic crystals: these crystals consist of face centered cubic (fcc) lattices of monodisperse spheres of silica or polystyrene in a suspension and can be relatively easily fabricated by self-assembly. In a pioneering paper by Martorell and Lawandy,[10] the emission decay of a dye in an ordered aqueous suspension of polystyrene spheres was found to be inhibited by a factor of 1.75 compared with a disordered reference sample. In a subsequent experiment on dye molecules dissolved in similar colloidal suspensions,[11] a similar inhibition of the decay rate was observed. There, the observed large modification was identified to be related to variations of the chemical environment of the dye molecules. The conclusion from both papers is that identification of photonic changes of emission rates requires comparison to reference systems with the same chemistry as the photonic systems.

Later, in the measurements of the fluorescence of dyes in a polymer infiltrated in silica opals, multiexponential decays containing both accelerated and inhibited rates were observed[12] and referenced to the dye fluorescence in a polymer film. The resulting accelerated and inhibited rates differed by a factor of 2 and were attributed to a redistribution of the density of states across the emission spectrum. This explanation was disputed in refs 13–15: the opals had a low photonic strength and could only weakly modify spontaneous emission. Moreover, the observations were done at the red side of the first-order stopgap, where modifications of the LDOS are minimal. The large factor-of-two difference is most likely caused by the fluorescence from the backbone material: the excitation in ref 12 was performed in the UV range,[16] and the detected emission was not spectrally resolved. The conclusion from these works is that identification whether photonic crystals control the emission rates requires the use of reference systems with the same nanostructure as the photonic systems; a very useful reference is a photonic crystal with a small lattice parameter where the stopgaps are blue-shifted with respect to the emission.[17]

In the meantime, with the appearance of highly efficient quantum dots and periodic structures with high dielectric contrasts, the scientific interest was diverted away from dyes and opals. In experiments on quantum dots and quantum wells embedded in strongly photonic crystals, considerable modifica-

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tions of spontaneous-emission rates have been recently achieved.[18−22] Despite the high brightness of the quantum dots, however, difficulties in targeting proteins in living cells are the main limitation of using these sources as fluorescent labels. In contrast, there are a great variety of highly efficient water-compatible organic dyes that are widely used as bio-labels.[23,24] In optics of bio-organic systems, new research avenues can be opened by controlling the fluorescence dynamics.[25,26] There is, therefore, a need to investigate how photonic crystals modify radiative properties of organic dyes. A crucial question is whether the photonic crystals can modify the dynamics of spontaneous emission of the dye molecules, emitters with a broad homogeneous line width.

In this paper, we present the results of a time-resolved emission experiment on R6G dye in opal photonic crystals made from polystyrene. The fluorescence lifetimes hardly vary within the emission spectrum of R6G. However, when the crystal lattice parameter was changed, we observed both enhancement and inhibition of spontaneous emission. We undertake for the first time a quantitative comparison of the observed decay dynamics of dye molecules to the calculated LDOS in three-dimensional photonic crystals.

II. Experiment

The measurements were performed on opals from polystyrene colloids with different cubic-lattice parameters ranging from 178 ± 3 nm to 922 ± 25 nm, a total of 7 samples. The polystyrene opals are fcc crystals composed of close-packed polystyrene spheres (with 74 vol %) prepared from a colloidal suspension by self-assembly. Details of the preparation and characterization of the opals can be found in ref 27. All of the crystals have typical dimensions of $2 \times 2 \times 0.2$ mm^3 and contain high-quality domains with diameters larger than 50 μm. These domains have flat faces parallel to the (111) crystal plane. The polystyrene opals were doped with Rhodamine 6G (R6G), a well-known dye that has a high quantum efficiency of about 95% .[28,29] The infiltration with R6G was performed by soaking the opals in a dilute solution (10^{-6} mol/L) of the dye in ethanol for 30 min. Afterward, to remove the dye from the opal surface, the samples were rinsed in ethanol and dried. The dye molecules are distributed at random positions and with random orientations on the surfaces of the polystyrene spheres constituting the opals. Because of the very low doping concentration of R6G, correlation effects among the dye molecules, such as reabsorption, energy transfer, or even possible angular correlations, can be neglected.[30]

The excitation of the dye was performed at as low as possible frequencies to avoid fluorescence from the backbone of the photonic crystals. We found that the polystyrene backbone fluoresces when wavelengths shorter than 450 nm are used for excitation. Therefore, we used a pulsed LED (Picoquant, PLS 500), which emits at $\lambda = 502$ nm in a bandwidth of 32 nm and has a pulse width of 600 ps. The time between consecutive pulses was set to 50 ns. The excitation beam was focused to a diameter of about 1 mm on the sample surface. The scattered excitation light was filtered out with a low-pass filter. We used the same setup to detect R6G emission from the photonic crystals that is described in refs 30 and 31. The time-resolved fluorescence intensity was measured at different frequencies within narrow bands of $\Delta\omega \approx 85$ cm^{-1} using the time-correlated single-photon counting technique.[32,33] Because of the high quantum efficiency of R6G, the decay of the excited state is dominated by the radiative process, and the measured decay rate (inverse lifetime) γ_{tot} is nearly equal to the radiative decay rate γ_{rad}.
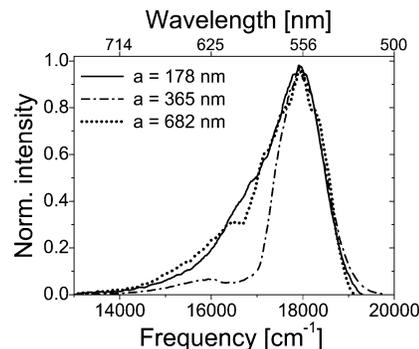
Figure 1. Normalized emission spectra of R6G in polystyrene opals with three different lattice parameters: $a = 178$ nm (solid curve), $a = 365$ nm (dash-dotted curve) and $a = 682$ nm (dotted curve). In the opal with $a = 178$ nm, the frequencies of R6G emission lie far below the first-order stopband. Emission from the opal with $a = 365$ nm reveals the first-order stopband, whose angle-dependence is presented in ref 30. The spectrum from the opal with $a = 682$ nm shows effects of the second-order stopbands that are presented in detail in ref 31.
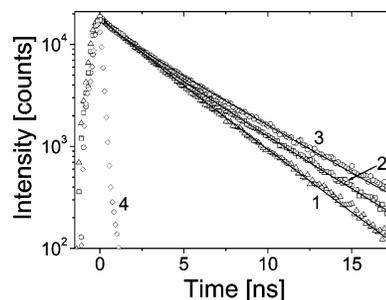
Figure 2. Fluorescence decay curves recorded at $\omega = 17985$ cm^{-1} ($\lambda = 556$ nm) from R6G dye in polystyrene opals with lattice parameters $a = 178$ nm (1), 365 nm (2) and 682 nm (3), together with the instrument response convolved with the excitation pulse (4). Curves 1 and 2 are overlapped at 0 ns with curve 3. Solid lines are fits with the stretched-exponential model.

III. Experimental Results

Propagation of emitted light in the polystyrene opals is affected by stopbands, as was experimentally demonstrated in the angle-resolved studies of emission spectra presented in refs 30, 31, 34, and 35. If the stopbands of a photonic crystal block a considerable part of the 4π solid angle, the LDOS in the crystal also changes. This can in turn affect the dynamics of spontaneous emission of embedded light sources. Therefore, in Figure 1, we plot emission spectra of R6G dye in polystyrene opals with different lattice parameters. The spectra from the opals with lattice parameters $a = 365$ and 682 nm are modified by the first- and second-order photonic stopbands, respectively. In contrast, in the opal with $a = 178$ nm, the emission frequencies of R6G are in the low-frequency limit, and therefore, no stopbands are observed. These results confirm that the dye molecules are indeed inside the photonic crystals.

In the time-resolved experiments, we study influence of the opal photonic crystals on the fluorescence decay of R6G by varying the crystal lattice spacing and detecting the fluorescence at different emission frequencies. Figure 2 shows examples of the time-resolved traces of R6G emission in polystyrene opals with three different lattice parameters. The decay curves were recorded at the maximum of the R6G spectrum at $\lambda = 556$ nm. The difference in the slopes of these decay curves indicates a modified radiative lifetime. Spontaneous emission in opals with lattice parameters $a = 365$ and 682 nm, which reveal stopbands within R6G emission spectrum, is inhibited compared with the

opal with $a = 178$ nm, which is in the low-frequency limit for $\lambda = 556$ nm.

It is known that the decay of R6G emission in homogeneous media is explicitly monoexponential. Indeed, the decay curves shown in Figure 2 are nearly single-exponential. The slight deviation from monoexponential decay is because the dye molecules at different positions and with different orientations on the polystyrene spheres couple to different LDOS and, hence, reveal different lifetimes. Effects of reabsorption and fluorescence quenching, which can also lead to non-exponential decays, are ruled out due to the very low doping concentration of the dye. Thus, to infer the fluorescence lifetimes (inverse decay rates), it is necessary to model the measured decay curves. It is reasonable to assume that the decrease of the number $n(t)$ of excited dye molecules in the opals is characterized by a very narrow distribution of lifetimes. This excited-state behavior can be modeled by the Kohlrausch stretched exponential, a widely used model with only two adjustable parameters (see, for example, ref 36), that is defined as

$$n(t) = n_0 \exp(-t/\tau)^\beta \tag{1}$$

Here, β is the stretch parameter that varies between 0 and 1, and τ is the time when $n(t)$ decreases by $1/e$. The stretch parameter β is qualitatively related to a lifetime distribution: β near 1 corresponds to a very narrow distribution, and small β corresponds to a broad distribution. The corresponding time-dependent fluorescence $I(t)$ is proportional to the time-derivative of $n(t)$[37] and is therefore equal to:

$$I(t) = I_0(\beta/t)(t/\tau)^\beta \exp(-t/\tau)^\beta \tag{2}$$

As was discussed in ref 37, this equation is properly normalized if $\gamma_{tot} = \gamma_{rad}$, where $\gamma_{tot} = \tau^{-1}$. In the case of R6G dye, an emitter with a nearly 100% quantum yield, the Kohlrausch stretched exponential is thus a useful model of the experiment. The main advantage of this model is that the average lifetime τ_{av} can be readily calculated:

$$\tau_{av} = (\tau/\beta)\Gamma(1/\beta) \tag{3}$$

where Γ is the Gamma function. We have modeled all measured fluorescence decay traces with the stretched exponential (eq 2): the results of modeling are shown by the solid curves in Figure 2. The stretch parameter β is close to 1, varying between 0.92 and 0.99. From the obtained parameters τ and β, we have calculated the average fluorescence lifetime using eq 3. For the modeling of the decay curves, we can also employ a more universal model, a continuous distribution of decay rates. That model has recently been used to explain non-exponential fluorescence decay curves of quantum dots[37,38] and dyes.[35] However, in our case with nearly single-exponential decay from R6G, the results obtained using the distribution model are very close to those from the stretched exponential.

A. Fluorescence Lifetime in Opals vs Frequency. In Figure 3, we present the frequency dependence of the average lifetime τ_{av} for R6G emission in several opals with different lattice parameters. The data from all samples reveal a slight (<8%) decrease of τ_{av} with increasing emission frequency, which is in agreement with previous results.[34,39,40] These small lifetime changes compared to expected ω^3 behavior in free space can be explained if the spectral width of R6G is dominated by homogeneous line broadening. Indeed, spectra of dye molecules including R6G are homogeneously broadened because of a splitting of electronic energy levels due to interaction with
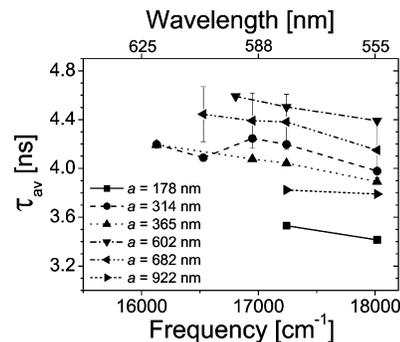
Figure 3. Average fluorescence lifetime τ_{av} vs detection frequency obtained using the stretched exponential (eq 2) for R6G emission in polystyrene opals with lattice parameters $a = 178$, 314, 365, 602, 682, and 922 nm. The error bars shown for $a = 682$ nm are typical for all samples and estimated from the difference between data on samples with similar a. The lines connecting the data points are guides to the eye.

molecular vibrational and rotational modes: the excited level consists of a ladder of sublevels $|a_i\rangle$ and the ground level, of a similar ladder of sublevels $|b_i\rangle$.[33,41] After excitation, a molecule quickly relaxes to the lowest excited electronic level $|a_1\rangle$ on a picosecond time scale. From this level, fluorescent transitions occur to different sublevels $|b_i\rangle$ of the ground electronic level. If, in a photonic crystal, a certain transition $|a_1\rangle \rightarrow |b_1\rangle$ is inhibited because of a low LDOS at the frequency of this transition, the excited-state will decay via another $|b_2\rangle$ sublevel at a different frequency within the homogeneous line width of the dye. Therefore, modifications of the fluorescence lifetime in dyes as a function of frequency can only be observed if the homogeneous line width is narrower than (or at least comparable to) features in the frequency dependence of the LDOS.

B. Decay Rates vs Crystal Lattice Parameter. As seen in Figure 3, the fluorescence lifetime is different in opals with different lattice parameters. This indicates that the LDOS in the opals is modified in frequency ranges comparable to or larger than the homogeneous line width of R6G. Figure 4a shows the measured decay rates (squares) of R6G versus reduced frequency $\omega a/2\pi c$, that is, at fixed emission frequency $\omega = 17985$ cm^{-1} and varying crystal lattice parameter a. The decay rates are normalized to $\gamma_{hom} = 0.264$ ns^{-1}, which is the decay rate in a homogeneous medium with refractive index $n = 1.45$.[42] This value of the decay rate was obtained knowing the quantum efficiency (95%) and decay rate (0.25 ns^{-1}) of R6G in ethanol ($n = 1.36$)[29] and using the following relation between the decay rates and the refractive index: $\gamma_{tot} = n\gamma_{rad} + \gamma_{nrad}$. The measurements reveal a 30% lifetime change, consisting of a 11% enhancement (compared to the homogeneous medium) at $\omega a/2\pi c = 0.32$ and a 14% inhibition at $\omega a/2\pi c = 1.08$.

In order to test if the observed modifications of spontaneous-emission rates ($\gamma_{av} = 1/\tau_{av}$)[43] agree with theory, we have calculated the LDOS for different positions on the internal surfaces of the opals, where dye molecules can be located. We used a recognized technique to calculate optical properties of periodic structures, known as the H-field plane−wave expansion method.[44,45] The calculations were performed using 725 reciprocal-lattice vectors. The polystyrene opals were modeled as fcc close-packed spheres with the dielectric function $\epsilon = 2.53$. The integration over wavevectors **k** was performed by representing the full Brillouin zone by an equidistant **k**-point grid consisting of 291 416 points.[45] In Figure 4b, we plot the relative LDOS at two illustrative positions in the opal, projected on two dipole orientations: parallel and perpendicular to the sphere surface. The LDOS is normalized to the LDOS in a homogeneous

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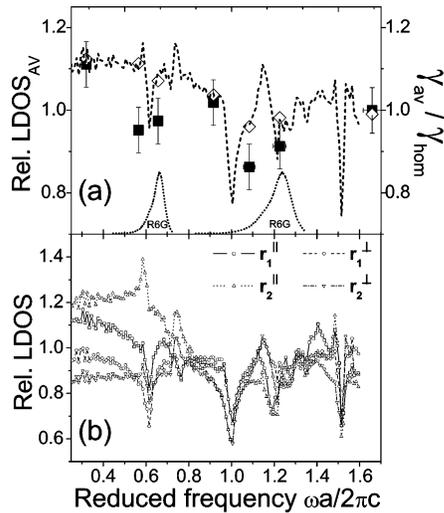
Figure 4. (a) Decay rates of R6G (squares) measured at $\omega = 17985$ cm^{-1} and normalized to the rate in a homogeneous medium $\gamma_{hom} = 0.264$ ns^{-1}. Dashed curve represents LDOS averaged over orientation and over five spatial positions in the reduced surface unit cell (1/12th of the total sphere surface) on the internal surfaces: at $\mathbf{r}_1 = \left(\frac{1}{2\sqrt{2}}\right)(1,0,0)$, $\mathbf{r}_2 = \left(\frac{1}{2\sqrt{6}}\right)(1,1,1)$, $\mathbf{r}_3 = \left(\frac{1}{4\sqrt{3}}\right)(1,1,2)$, $\mathbf{r}_4 = (0.33,0.13,0)$, and $\mathbf{r}_5 = (0.23,0.23,0.14)$. Normalized rates (diamonds) calculated from the averaged LDOS using eq 4. Dotted curves indicate R6G emission spectrum plotted vs reduced frequency for opals with a = 365 and 682 nm. (b) Relative LDOS at two positions on internal opal surfaces, r_1 and r_2, projected on dipole orientations parallel (∥) or normal (⊥) to internal polystyrene−air interfaces.

medium with refractive index $n = 1.45$, which is the effective refractive index of the polystyrene opals. Figure 4b clearly demonstrates that the LDOS varies with the reduced frequency, location as well as orientation of emitting dipoles, in agreement with earlier work.[38] In our experiments, we detected fluorescence from dye molecules that have likely randomly oriented transition dipoles and that are spatially distributed over the internal surface of the opals. Consequently, the measurements are compared to the LDOS that is averaged over 60 symmetry-inequivalent positions on the spheres and over random dipole orientations. While our measurements have insufficient resolution to track the narrow features in the calculated LDOS [Figure 4a (dashed curve)], the general trend of the experiments agrees with the theory, that is, enhanced decay rate at $\omega a/2\pi c = 0.32$, inhibited near 1.0, and unmodified near 1.6.

Because of the broad homogeneous line width of R6G, the decay rate of the dye is determined by the LDOS at all frequencies of its emission spectrum (dotted curves in Figure 4a). In the experiments on quantum dots in inverse opals,[38] the measured decay rates could be directly compared to the calculated LDOS because the homogeneous line width of those emitters ($\Delta\omega/\omega \approx 0.025$) is narrow with respect to the LDOS features in the inverse opals. In case of R6G, the emission spectrum is homogeneously broadened by $\Delta\omega/\omega \approx 0.09$. The decay rate of emitters with a homogeneous spectrum $S(\omega)$ coupled to the LDOS $N(\omega,a)$ is therefore calculated as:

$$\gamma(a) = A \int_0^\infty \omega S(\omega)N(\omega,a)d\omega \qquad (4)$$

where A is a parameter that includes the transition dipole moment of R6G, and a is the lattice parameter of the photonic crystal. By inserting the spectrum of R6G and the averaged LDOS (dashed curve, in units of $[4/a^2c]$) in eq 4, we derived the decay rates for opals with specific lattice parameters, which

were then normalized to the calculated rate in a homogeneous medium with $n = 1.45$. The resulting predicted values of the decay rate are depicted by the diamonds in Figure 4a. Similar to the experiments, the theoretical data (squares) show an enhancement at $\omega a/2\pi c = 0.32$, inhibition from 1.0 to 1.2, and no modified rate near 0.9 and 1.6. The deviations from the measured decay rates are possibly related to the fact that the calculated LDOS is averaged over insufficient positions, or that in some of the crystals, the distributions of dye molecules over the sphere surfaces reveal local variations that are difficult to model. At any rate, the 30% decay-rate variations are clearly apparent: they are not smoothed by the homogeneous emission spectrum. Such variations can only appear if the widths of the troughs and peaks in the LDOS in the opals are broader or comparable to the width of the dye emission spectrum.

IV. Conclusions

We have studied time-resolved spontaneous emission from Rhodamine 6G dye in opal photonic crystals made from polystyrene nanospheres. The observed fluorescence lifetimes hardly vary with changing optical frequencies within the dye emission spectrum. This effect is explained by a broad homogeneous line width of the dye, which means that dye molecules probe the LDOS in the photonic crystals that is averaged over all frequencies of the homogeneous spectrum. By changing the crystal lattice parameter, we do observe modifications of the fluorescence lifetimes, which testifies that the LDOS features in the opals are broader than the homogeneous line width of the dye. Therefore, photonic crystals can control emission dynamics of broadband sources such as organic dyes, even when their emission spectra are much broader than directional stopbands (cf. Figure 1). This result shows that knowledge on a directional stopband (typically obtained from reflectivity of transmission measurements) has limited predictive power about the possible emission-dynamics control of a photonic crystal. Furthermore, the results pave the way for biophotonic control of fluorescence from broadband sources such as natural light sources and fluorescent proteins.

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