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Probing the Radiative Transition of Single Molecules with a Tunable Microresonator

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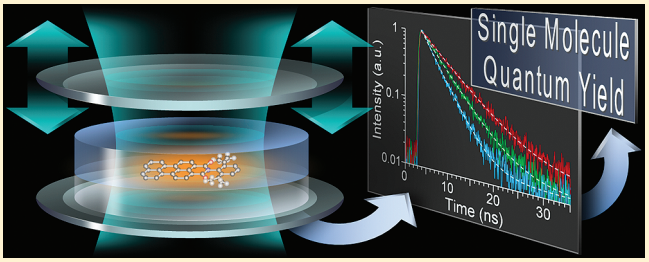
Supporting Information

ABSTRACT: Using a tunable optical microresonator with subwavelength spacing, we demonstrate controlled modulation of the radiative transition rate of a single molecule, which is measured by monitoring its fluorescence lifetime. Variation of the cavity length changes the local mode structure of the electromagnetic field, which modifies the radiative coupling of an emitting molecule to that field. By comparing the experimental data with a theoretical model, we extract both the pure radiative transition rate as well as the quantum yield of individual molecules. We observe a broad scattering of quantum yield values from molecule to molecule, which reflects the strong variation of the local interaction of the observed molecules with their host environment.



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One of the fascinating aspects of single molecule fluorescence spectroscopy is that it allows for studying discrete transitions between an electronically excited and the ground state in an individual quantum-mechanical system. This becomes even more fascinating by the option to change the physics of that transition by placing a molecule into a cavity. As E. M. Purcell already pointed out in his seminal contribution to the meeting of the American Physical Society in 1946,[1] the cavity will change the coupling of the intramolecular transition to the vacuum electromagnetic field, thus leading to an acceleration of the radiative transition in a molecule. This has been confirmed in bulk by measuring the fluorescence lifetime as function of the molecules' distance to a metallic mirror.[2] A thorough theoretical description of these measurements had been developed by Chance et al.[3] using a semiclassical approach based on Fermi's Golden Rule.[4] However, the radiative transition constitutes only one of the possible ways for returning from the excited to the ground state when considering molecules embedded in a condensed matter environment (e.g., solid or liquid). Because of collisions/interactions with surrounding molecules, so-called nonradiative transitions constitute a significant alternative way of de-excitation. The ratio of radiative to nonradiative transition rates is quantitatively described by the fluorescence quantum yield (QY) that is defined as the average chance to emit a photon (radiative transition) upon return from the excited to the ground state or

$$\phi = \frac{k_r}{k_r + k_{nr}} \qquad (1)$$

where k_r and k_{nr} are the radiative and nonradiative transition rates, respectively.

From a spectroscopic point of view, the QY of fluorescence is the parameter that is most challenging to assess. Whereas absorption and emission spectra as well as excited state lifetime (fluorescence lifetime) are straightforward to measure with modern measurement techniques, QY values are mostly determined in a comparative manner against a standard of known QY. Nonetheless, precise knowledge of QY is important for many practical applications such as the development of materials for organic and inorganic light emitting diodes,[5] single-photon sources,[6] solar cells,[7] laser technology,[8] or labeling in biological research.[9]

The first successful estimates of the QY of fluorescent solutions had been made by Vavilov in 1924[10] by comparing the fluorescence with scattering intensities. This approach was used, although much refined, over the following decades.[11] Only by 1978, Brannon and Magde developed a method for absolute measurements of QY via sensitive measurements of sample heating upon illumination.[12] However, extending this idea to the single-molecule level seems rather impossible due to the minute amount of heat generated by a single molecule upon nonradiative de-excitation.

Thus, when considering the QY of individual molecules, an appealing idea is to use the aforementioned sensitivity of the

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radiative transition to the local electromagnetic field mode density, which can be changed by placing the emitter close to a mirror or within a cavity. On the single-emitter level, this effect has been demonstrated by several authors, either by measuring the fluorescence lifetime of an emitter in two different environments[13,14] or by placing the emitter on or close to a sharp tip.[15,16] Sandoghdar has recently extended this approach to measuring the fluorescence lifetime of a single molecule as a function of its distance to a metallic mirror,[17] thus replicating Drexhage's original measurements on a single molecule level.

An even more efficient method to change the local mode density of the electromagnetic field is to place an emitter into an optical microcavity.[18,19] Furthermore, if the cavity is tunable, it becomes a powerful tool for changing the mode density and resulting radiative transition rate of an emitter in a continuous way. We have recently used such a tunable microcavity to watch, on one and the same molecule, the varying emission spectrum while changing the cavity width.[20]

Here, we present absolute measurements of the QY of individual molecules using the tunable microcavity. The distance between the cavity mirrors is reduced down to the range of one-half of the emission wavelength, therefore there is only one resonance frequency maximum, which is tuned when the cavity length is changed. Since the mode structure and the coupling between the molecule and the resonator are both frequency dependent, variation of the cavity length leads to a modification of the radiative transition in a molecule according to Fermi's golden rule.[4] The core idea is to record the fluorescence lifetime of the same single molecule as a function of cavity width, in that way changing the radiation rate via the optical mode density in the resonator while leaving at the same time the nonradiative rate of the molecule unaffected. This information is then compared with theoretical modeling for extracting both the pure radiative transition rate and the QY for a given molecule. We observe a broad distribution of QY values from molecule to molecule, which reflects the strong variation of the local interaction of the observed molecules with their host molecules. The method is of fundamental importance wherever one is interested in investigating interactions between fluorescent emitters and surrounding host molecules, which is most sensitively reported by the nonradiative transition rate. This is different to the modification of the QY of a molecule by a plasmonic nanostructure when the molecule must be so close to the metal that absorptive losses to the metal may even dominate the nonradiative relaxation.[21−23]

Figure 1 depicts a schematic of the experimental setup with the tunable microcavity. The cavity mirrors are made by placing thin silver layers (50 nm bottom and 100 nm top) on a glass substrate (see Supporting Information for further details). The bottom semitransparent silver mirror is covered with a 30 nm SiO_2 layer that acts as a spacer between sample molecules and the silver surface. A droplet of a highly diluted solution of fluorescent PI molecules (a perylene derivative; a molecular structure is shown in the inset of Figure 1) was spin coated onto the SiO_2 surface (rotation speed 1000 r/min), resulting in a sparse distribution of molecules across the surface. The molecules were covered with a 70 nm layer of poly(methyl methacrylate) (PMMA) for fixation by spin coating a 1% polymer solution dissolved in dichlormethane (see Supporting Information). Between the top of the polymer layer and the top cavity mirror was air. The cavity height was adjusted with a piezo actuator and the width value was determined by measuring the white light transmission spectrum (see 19 and Supporting Information).

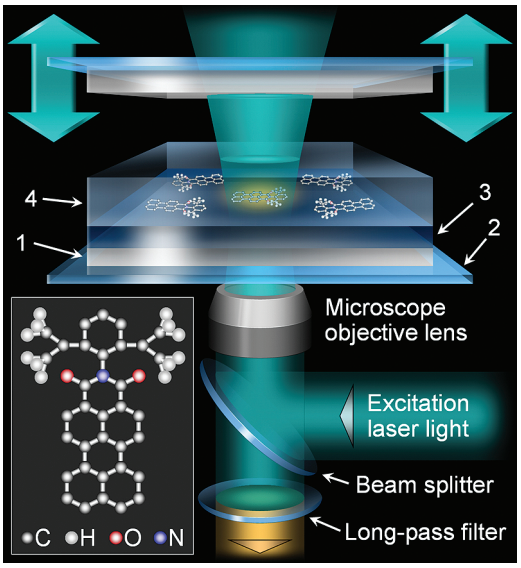

Figure 1. Scheme of the experimental setup. The tunable microcavity consists of the following: silver layers (1) sputtered on the glass surface (2); silica layer (3), acting as a spacer between the metallic surface and the molecules; a polymer layer (4), immobilizing molecules and protecting them from the interaction with atmospheric oxygen. The vertical position of the top mirror is adjusted with nanometer precision by piezo actuator. The inset shows a molecular structure of PI molecule.

An important issue when aiming at an accurate QY determination of single molecules is to have precise knowledge of their position and orientation within the cavity. Both information determine the electromagnetic field mode density that is sensed by a molecule. In our experiment, a molecule's position is given by the position of the SiO_2 surface. However, determining its orientation is more challenging. For that purpose, we scanned molecules with a focused laser beam having higher-order beam modes and thus exhibiting a well-defined three-dimensional polarization geometry of light within the focus. The higher-order beam modes were prepared from a Gaussian beam of an Ar^+-laser (λ_{exc} = 488 nm) by using a laser-mode conversion system (see refs 24−28 and Supporting Information). We have successfully applied this method in the past for probing single molecules orientations inside the cavity.[29,30] Our measurements show that all observed molecules have a dipole orientation parallel to the SiO_2 surface, which can be explained by the fact that the aromatic perylene ring system lays flat down on the surface upon spin coating and subsequent solvent evaporation.

The lifetime measurements within the microcavity were performed with a home-built confocal scanning microscope with a fluorescence lifetime imaging extension (see Supporting Information).

After selecting a single molecule, we acquired fluorescence decay curves for the same molecule at different cavity lengths. Before each lifetime measurement, the cavity width was adjusted by applying a defined voltage to the piezo-actuator and determined by measuring a cavity white-light transmission spectrum with a wide-field transmission microscope. The measured single-molecule fluorescence decays could be well fitted by single-exponential decay functions, yielding the excited state lifetimes of the observed molecules. In total, we collected data for 28 molecules. Figure 2 shows the result of the measured fluorescence lifetime values (red dots) as a function of cavity width (measured

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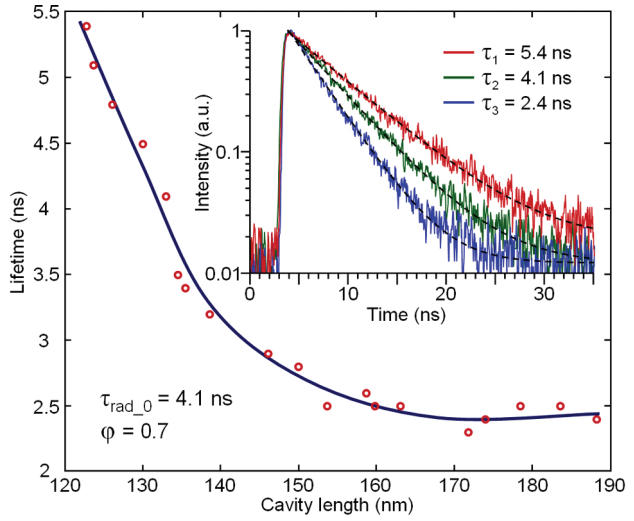

Figure 2. Cavity-controlled fluorescence lifetimes of a single horizontally oriented molecule (red dots) measured at different values of mirror spacing. The solid curve shows the best fit to the experimental data, giving values of $\varphi = 0.7$ and $\tau_{rad\_0} = 4.1$ ns for the single molecule fluorescence quantum yield and the inverse radiative transition rate, respectively. Inset shows fluorescence decays of the single molecule inside the microresonator acquired at the following three different cavity lengths: 123 (red curve), 133 (green curve), and 174 (blue curve) nm. All transients were fitted using monoexponential decay functions (dashed lines).

via maximum of transmission spectrum). The dependence exhibits a strong decrease of the lifetime value with decreasing cavity width, which is due to the gradual shift of SM emitter position toward the center of the cavity where stronger coupling to optical modes occurs.[20] The blue curve shows a theoretical fit as calculated using the theory of Chance et al.[3] and the full information about the cavity's structure and geometry, as well as the molecules' position, orientation, and emission spectrum (for modeling details, see Supporting Information). There are only two free parameters when fitting the theoretical curve against the measurement, the inverse radiative transition rate (τ_{rad_0}), and the QY. For the shown measurement, the best fit to the experimental data yields values of 0.7 for QY and 4.1 ns for τ_{rad_0}.

We employed a bootstrap algorithm for estimating the mean square deviation of the fitted lifetime for each molecule at each cavity width.[31] Mean square deviations of the single molecule lifetime values did typically not exceed 0.1 ns. We also used a bootstrap analysis for estimating the mean square deviation of the QY and the inverse radiative transition rate as obtained by fitting theoretical curves against the experimentally determined dependencies of fluorescence lifetime on cavity width. Assuming that, for each molecule, these mean square deviation values describe the widths of a corresponding two-dimensional Gaussian distribution in QY$-\tau_{rad}$ parameter space, we superimposed these Gaussian distributions of all molecules in one plot, resulting in a probability density plot of QY versus τ_{rad} values. This plot is shown in the Figure 3. The maximum of the probability density distribution corresponds to a value 0.72 for the QY and of 4.1 ns for τ_{rad}, which is in excellent agreement with values obtained from ensemble measurements (0.75 and 4.2 ns, respectively).[19] The solid line represents a linear least-squares fit through the distribution. An inclination of 0.18 ns^{-1} shows that the molecule-to-molecule variation in τ_{rad} is much smaller than that of QY. This is in excellent agreement with the expectation that local

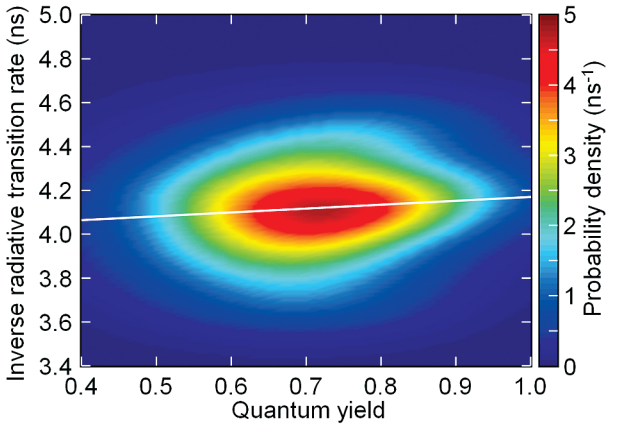

Figure 3. A probability density distribution quantum yield and inverse radiative transition rate obtained from 28 molecules. The distribution has its maximum at 0.72 and 4.1 ns, respectively. The solid white line represents a linear least-squares fit through the distribution.

variations in interaction between a fluorescent molecule and its surrounding (SiO_2, polymer) will mostly affect its nonradiative transition rate but not so much its radiative transition rate, which is mostly determined by the coupling of the transition to the electromagnetic field.

In summary, tuning of the radiative transition rate of individual molecules by placing them into a microcavity of changing width has been demonstrated. This allowed us to extract radiative as well as nonradiative transition rates and to determine QY of individual molecules, which are fundamental parameters of any quantum emitter. Average values thus obtained showed excellent agreement with the results from ensemble measurements. Moreover, we found a broad distribution of QY values, whereas radiative transition rates did not change significantly from molecule to molecule. This reflects the heterogeneous local nature of the host, which determines the nonradiative relaxation of an excited molecule via interaction with the local chemical environment. Our technique can be applied to any single quantum emitter of interest, such as dye molecules, semiconductor nanoparticles, carbon nanotubes, and so forth. Thus, the tunable cavity method makes it a versatile tool for single molecule spectroscopy and QY measurements of individual emitters.

■ ASSOCIATED CONTENT

Supporting Information. Details on preparation of cavity, controlling the cavity geometry, polymer solution and spin-coating, determining molecular orientation, lifetime measurement, and lifetime modeling. This material is available free of charge via the Internet at http://pubs.acs.org.

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