Fluorescent impurity emitter in toluene and its photon emission properties

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Single fluorescent emitters like colloidal quantum dots or single molecules are usually prepared in solutions and spin-coated onto cover glasses for studying. Toluene has been a widely used solvent in such studies. Here, we report on a fluorescent impurity emitter contained in toluene and its optical properties. The emission spectra of the single emitters show multiple peaks with the main peak varying from 2.03 eV (610 nm) to 2.14 eV (580 nm) and a red-shifted side peak with an average separation of 167 meV from the main peak. The emitted photons show a strong anti-bunching with a fluorescence lifetime of a few nanoseconds. They show very fast blinking behavior which cannot be properly detected by time-trajectory of photoluminescence intensity. An analysis based on the second-order correlation functions reveals that a three-level model can explain our measurements well and that the blinking transition time ranges only a few tens of microseconds. This single emitter in toluene is clearly distinguished from the fluorescent centers in the cover glass by their respective emission spectra. The single emitters in the cover glass also exhibit fast blinking behavior. These background emitters should be carefully identified and distinguished while studying the single fluorescent emitters.

Results

We investigated the photon emission properties of the fluorescence centers on a cover slip where a few drops of toluene were dried. The sample was excited with a continuous wave (cw) 532 nm laser. Details of the sample preparation and the detections are given in the Methods section. Figure 1a shows photoluminescence spectra of three selected emitter centers. They commonly show two peaks – a main peak and a red shifted side peak. The
main peak position varies for each particle and ranges from 2.03 eV (610 nm) to 2.14 eV (580 nm) for 30 individual centers. The average separation between the main and the side peaks is 167 meV, as shown by the black dotted line in Fig. 1b. Red solid circles in Fig. 1b show the FWHMs (full width at half maximum) of the main peaks as a function of the main peak energy. Although data points are spread, there is a tendency of broader widths for peaks at lower energies (longer wavelengths). This suggests that the difference in the PL peak positions of individual emitters is probably caused by different local environment (effective refractive index) for each emitter. It was not possible to measure the continuous absorption spectrum of the emitter, but we measured the absorption cross-section at four wavelengths of 405, 448, 532, and 594 nm. Figure 1c shows the PL intensity curves as a function of the pump intensity obtained at 532 nm excitation. (e) Normalized second-order correlation function $g^{(2)}(\tau)$ at a short time scale ($|\tau| < 100$ ns). $g^{(2)}(0) = 0.10$ with background subtraction. (f) Spectral comparison between the impurities in toluene (blue curve) and in cover glass (black curve). The inset is the $g^{(2)}(\tau)$ of a defect center in cover glass.

Discussion

In order to find whether the above discussed emitters indeed come from toluene instead of being the silica-based impurities of the cover glass, we compared the two emitters through the following measurements. For the cleaned cover glass sample, the emitter centers survive only a few seconds. The emission peak is at a shorter wavelength (~564 nm) and broader in bandwidth compared to that of the emitter from toluene. The emission from the cover glass also showed photon anti-bunching as can be seen in the inset of Fig. 1f. These properties of the emitter in the.
cover glass are consistent with those cited in a recent report by Rabouw et al.

From the noticeable differences in their PL spectra shown in Fig. 1f, we conclude that the two are different kinds of emitters. We observed the PL spectrum shown by the blue curve in Fig. 1f only when we put toluene solution onto cover glass and dried it. Furthermore, our target emitters also appeared when we tried with toluene solutions from different manufacturers (Sigma Aldrich, Daejung). Hence, we concluded that the single emitter is an impurity in toluene and not in the cover glass. It is worth mentioning that the single emitters in this work are very similar to CdZnSe/ZnSe QDs reported by Wang et al.16. In their studies, they characterized two samples by spin coating a dilute solution of CdZnSe/ZnSe QDs in toluene or CdSe/ZnSe QDs in water onto a quartz coverslip. The main contrast between the two samples, except the compositions of QDs, was the solvent; toluene or water. Hence, we believe that they observed the single emitter from the impurities of toluene and not from the CdZnSe/ZnSe QDs or silica centers as mentioned by Rabouw et al.22.

As the next step, we characterized our target emitters further on their photoluminescence intermittence, often called blinking. This blinking can restrict the photon emission capability of single emitters severely and, hence, it has been an intense research topic for several decades since its first observation by Cook et al.23 in the middle of the 1980s. Figure 2a shows the PL intensity trajectory of the same emitter as the one in Fig. 1e. The excitation intensity was set at a value of *I* = 3.5 kW/cm². With a time bin size of 1 ms, which is a typical time bin size used in the blinking studies of QDs10,24, the emitter seemed to be non-blinking. However, when we decreased the time bin size down to 40 μs, as shown in Fig. 2b, the intensity trajectory started to show the corresponding "OFF" states. In our measurements, the detection photon counts as high as 6 × 10⁵ cps could be attained; hence, the time bin size could be reduced to few tens of microseconds. The histogram of the photon number per time-bin shown in Fig. 2c clearly shows the "ON" and "OFF" contributions. In the zoomed in trajectory shown in Fig. 2d, there are short "OFF" durations. The average photon number per time-bin of 40 μs as high as 6 × 10⁵ cps could be attained; hence, the time bin size could be reduced to few tens of microseconds. The histogram of the photon number per time-bin shown in Fig. 2c clearly shows the "ON" and "OFF" contributions. In the zoomed in trajectory shown in Fig. 2d, there are short "OFF" durations. The average photon number per time-bin of 40 μs is 27 and the Poisson statistics cannot explain the small photon numbers below 11 (outside 3 times of standard deviation) without assuming the "OFF" states, the blinking. Figure 2e and f show the probability distributions of the "ON" and "OFF" durations in semi-log plots25 (for details, please refer to the Methods section). Both show clear exponential decays with time constants of 1.26 ms (for ON) and of 20 μs (for OFF), respectively. These time constants indicate the average durations of the "ON" and "OFF" states. The average OFF time duration of 20 μs found in Fig. 2f is below the minimum time bin size of 40 μs applied in our analysis; thus, the result can be inaccurate due to unclear distinction between the ON-OFF states.

To further look into the blinking behavior of the single emitter, we applied the second-order correlation function method that was reported by Fleury et al.26, in which they measured g²(τ) curves in short- and long-time ranges for different excitation intensities. To explain the anti-bunching and bunching of a single terrylene molecule at short- and long-times, respectively, they proposed a 3-level energy band scheme. This scheme included a meta-stable triplet state (level 3) associated with the intersystem crossing rate (κ₂₃) and the reverse intersystem crossing rate (κ₃₂ + κ₃₁)26. We adopted the same 3-level energy model for analyzing our target emitter because the

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**Figure 2.** Blinking study by the PL intensity trajectory. (a) PL intensity trajectory of a single emitter with a time bin size of 1 ms. (b) The same data in (a) but with a smaller time bin size of 40 μs. (c) Histogram of the photon count events of the time trajectory in (b). (d) A zoomed in intensity trajectory of (b). Probability distributions of (e) "ON" and (f) "OFF" time durations presented in semi-log scale. Single exponential fittings (red lines) are applied.
ON/OFF probability distributions shown in Fig. 2e and f are well described by single exponentials. This implies that there is one dominant energy level involved in the blinking processes, instead of the multi-levels as in many quantum dots which usually follow the power law in their blinking behaviors. The schematic of adapted energy level structure is shown in Fig. 3a. We started our analysis by obtaining the transition rates $k_{12}$ and $k_{31}$, which were found from the short-time $g^{(2)}(\tau)$ measurements. As shown in Fig. 1e, the short-time $g^{(2)}(\tau)$ curves were fitted with double-side exponentials. The exponential decay constants for different excitation intensities were fitted to $T_{ON}^{-1} = k_{12} + k_{32}$, where $k_{12}$ is proportional to the pump intensity ($k_{12} = \sigma_{12} I$) while $k_{32}$ is a constant. Note that this fitting becomes valid when $T_{ON}^{-1}$ is much higher than the other decay rates of $k_{31}, k_{23}$, and $k_{32}$. The validity of this assumption will be discussed after deriving all the values of decay constants. We found that $k_{12} = (0.14 \pm 0.01) \times 10^8$ s$^{-1}$ cm$^{-2}$/kW Hz, $k_{32} = (3.0 \pm 0.1) \times 10^8$ Hz, and the corresponding lifetime to be $3.3$ ns (=1/$k_{12}$). The other three decay rates of $k_{31}, k_{13}$, and $k_{23}$ were smaller in their values compared to $k_{12} + k_{32}$, as confirmed later; they can be derived from the long-time $g^{(2)}(\tau > 100$ ns), or $g^{(2)}(\tau)$ over a long timescale was obtained from the time-tagged time-resolved (TTTR) data, as shown in Fig. 3c and was fitted with the function $g^{(2)}(\tau) = 1 - C \exp(-\beta \tau)$, where $C$ is a fitting constant and $\beta$ is the decay rate associated with the metastable state (level 3). Under the assumption that $k_{12} + k_{31} \gg k_{31}, k_{23}, k_{32}$, we find $\beta \approx k_{31} + k_{32} + (k_{32})_{max} k_{23}$, where $(k_{32})_{max} = k_{12}/(k_{12} + k_{23})$. For the details, please refer to the Methods section. Here, $k_{31}$ and $k_{23}$ are constants and $k_{32} = \sigma_{32} I$. Figure 3d displays $\beta$ as a function of the excitation intensity. The fitting curve yielded the transition rates $k_{31} = (4.4 \pm 0.1) \times 10^4$ Hz, $k_{32} = (0.59 \pm 0.02) \times 10^4$ Hz, and $k_{23} = (6.3 \pm 1.7) \times 10^4$ Hz. Acquired values of $k_{31}$ and $k_{32}$ were larger than those of $k_{33}, k_{31}$, and $k_{32}$ by more than 3 orders of magnitude in our detection range, thus justifying our assumption. Using these transition rates, as shown in Fig. 3c, we calculated the average values of the ON/OFF time durations as $T_{Average} = 130 \mu$s and $T_{OFF} = 15 \mu$s at $I = 3.5$ kW/cm$^2$. While $T_{Average} = 15 \mu$s is close to $20 \mu$s in Fig. 2f, but $T_{Average} = 130 \mu$s is much lower than the value obtained using PL intensity trajectory method, which was 1.26 ms. It is easy to understand that, in the PL intensity trajectory method, the average OFF state time duration is too short to be accurately detected resulting in a longer duration of the ON state. It is interesting, however, to note that the time bin size brings a larger error for the longer $T_{ON}$ than for the shorter $T_{OFF}$. Figure 3f shows the OFF-time ratio calculated utilizing the transition rates. At a specific pump intensity of 12 kW/cm$^2$, the OFF-time ratio reaches its maximum value of 17%, reducing the emitted photon flux by the same amount due to the blinking. For more details about analyses and calculations, please refer to the Methods section.
In their recent work, Rabouw et al. reported a non-blinking fluorescent defect centers (DCs) in a silica cover glass and gave an extensive discussion along with single emitters in previous studies. When we compared our single emitters with them, we detected several similarities. Both the reported data show multi-peaks, have similar peak positions, and the fluorescence lifetime is 3.3 ns in our case and 3.4 ns in their work. With the time bin size of 1 ms, we also recognized a non-blinking-like emission intensity trajectory; however, with an even smaller time bin size or by applying $g(2)(\tau)$ analysis we concluded that this emitter blinks with very short OFF durations (a few ~a few tens of $\mu$s). At this stage, we measured the fluorescent silica DC on cover glass. The DCs from cover glass gave much weaker fluorescence signal and bleached fast, not allowing us to measure enough photons for quantitative analysis. We could measure the PL spectrum (black curve in Fig. 4a) or short-time $g(2)(\tau)$ (inset of Fig. 1f) only at a few instances. In order to extend the surviving time of a single DC, we spin coated a para-Terphenyl (pT) crystal layer onto a clean cover glass. Though under this situation, it was not clear if the signal center originated from the cover glass or the pT layer, we could observe fluorescent signal with a similar peak position but broader emission band, as shown in Fig. 4a. If we accept this emitter as the DC on the cover glass, the broadened band possibly can be explained by the additional phonon broadening by the pT crystal layer. The short-time $g(2)(\tau)$ of this DC showed a good anti-bunching with $g(2)(0) = 0.11$ and the fluorescence lifetime of 3.3 ns. Figure 4c displays the PL intensity trajectory at an excitation intensity $I = 2.1$ kW/cm$^2$. Although the fluctuation between ON-OFF state is not clear enough, the long-time $g(2)(\tau)$ shown in Fig. 4d clearly demonstrates a bunching behavior suggesting that this DC also has a fast blinking behavior. However, when we applied the same 3-level model we found a larger error than for the impurity in toluene. More studies for improving the photon detection capability and for finding a more suitable energy band scheme are underway.

**Conclusion**

In this study, we have reported a bright single fluorescent emitter contained in toluene. Its emission spectrum showed a progression of peaks separated by ~167 meV, with the main peak position varying from 2.03 eV (610 nm) to 2.13 eV (580 nm). The fluorescence lifetime was found to be around 3.3 ns, and emitted photons were found to show a strong anti-bunching. Blinking studies by two methods, namely, the PL intensity trajectory and the $g(2)(\tau)$ analysis, revealed that this emitter blinked very fast with an average “OFF” time duration of only a few tens of $\mu$s. A 3-level energy band scheme was shown to plausibly explain our measurements. The blinking parameters were derived in order to discuss the details of its blinking behavior.
We compared the photon emission properties of the impurity in toluene with other reported single fluorescent centers including the DC on the silica cover glass. Our results confirm that this impurity in toluene is clearly distinguishable from silica DCs. Further, its blinking was too fast to be properly studied by the conventional PL intensity trajectory method. Toluene is a very common solvent for the solutions of colloidal QDs and single molecules; therefore, researchers should be very careful not to confuse background emitters like this impurity in toluene with their target emitters.

Methods
Sample preparation. Microscope cover glasses (Marienfeld, borosilicate glass, 18 × 18 mm²) were immersed in an Aqua Regia (HCl/HNO₃ 3:1 in volume ratio) for 30 mins for cleaning, followed by 5-min sonication in DI water, and finally dried with N₂.

Toluene solutions were purchased from two manufacturers; Sigma-Aldrich (ACS reagent, ≥99.5%) and Daejung (>99.5%). Few drops of toluene on the cover glasses were evaporated on a hot plate at 86 °C. Para-terphenyl (Sigma-Aldrich, >99.5%) was dissolved in toluene (Sigma-Aldrich) with a concentration of 1.2 mg/ml and then spin coated on cleaned cover glasses at 2000 rpm for 5 s.

Sample measurement. In order to excite a single emitter from the sample, we used a cw 532 nm laser focused by an oil objective lens (Nikon Plan Apo VC, 100×, NA = 1.40). Three other excitation sources of 405 nm, 448 nm, and 594 nm lasers were used only in measuring the absorption cross section. The stream of emitted photons was collected by the same objective lens, separated from the excitation light via a long-pass filter (Semrock, 532 nm), and guided to a CCD camera or Hanbury Brown-Twiss (HBT) set-up where photons were detected by the two single photon counting avalanche photo diodes (Perkin Elmer, SPCM-AQ4C). Spatial filtering was applied to select the signal only from single emitter position in order to reduce the background. The short-time mode of Pico-Harp (model300, PicoQuant, 4 ps time resolution) and the long-time $g^{(2)}(100 \text{ ns} < \tau < 50 \mu s)$ was reconstructed from the intensity time trace recorded by TTTR mode of Pico-Harp. Each TTTR dataset was measured for 10 s. All the measurements were performed at room temperature.

PL intensity trajectory analysis by threshold method. The PL intensity trajectory was analyzed by a threshold method. In brief, the threshold intensity was selected (red dashed in Fig. 2b and c) and the intensities above(below) the threshold were considered as “ON” (“OFF”). To calculate the probability distributions $P(\text{ON/OFF})$ we divided the number of occurrences of a given event by the average time duration between the neighboring pre- and post-events. $P(\text{ON/OFF}) = \frac{N_{\text{ON/OFF}}}{N_{\text{ON/OFF}}}$.

Transition rate equations, $g^{(2)}(\tau)$, and blinking analysis. The rate equations of the 3-level model adapted in this work can be written as:

$$\frac{d}{dt} \begin{pmatrix} N_1 \\ N_2 \\ N_3 \end{pmatrix} = \begin{pmatrix} -k_{12} & k_{21} & k_{31} \\ k_{12} & -k_{21} - k_{23} & k_{32} \\ 0 & k_{23} & -k_{31} - k_{32} \end{pmatrix} \begin{pmatrix} N_1 \\ N_2 \\ N_3 \end{pmatrix}$$

where $k_{12}$ and $k_{32}$ are proportional to the pump intensity while the other three rates are constants. $N_i (i=1, 2, 3)$ denotes the population density at $i$-level with a constraint of $\sum N_i = 1$. $g^{(2)}(\tau)$ is proportional to $N_1(\tau)$ with the condition $N_1(0) = 1$. By the normalization condition of $g^{(2)}(\tau \rightarrow \infty) = 1$, $\frac{N_1(\tau)}{N_1(\infty)} = g^{(2)}(\tau)$. By measuring and fitting short-time $g^{(2)}(\tau)$ for different pump intensities, we arrived at $\tau_{\text{ON}} = \frac{k_{12} + k_{31} - \sigma_{32}}{k_{12} + k_{21}}$, which depends linearly on excitation intensity $I$ with $k_{31}$ being the y-intercept. Here, $\tau_{\text{ON}}$ is the decay constant of exponential fitting shown in Fig. 1e. By solving Eq. (1), we found that the decay rate of the long-time $g^{(2)}(\tau > 100 \text{ ns})$ could be described as follows: $g^{(2)}(\tau) \rightarrow 1 \approx Ce^{-\beta\tau}$, where

$$\beta \approx k_{31} + k_{32} + N_2^\text{max}k_{23} = k_{31} + \sigma_{32}I + \frac{k_{12}}{k_{12} + k_{21}}k_{23},$$

or

$$\beta \approx (k_{31} + \sigma_{32}I) \times \left( 1 + \frac{\alpha}{1 + \frac{k_{12}}{\sigma_{32}}I} \right),$$

where $\alpha = \frac{C}{1 + A + AC}$. To derive Eq. (3) from Eq. (2), we use the condition that short- and long-time $g^{(2)}$ curves should be continuous to each other. Values of $A$ and $C$ were determined from short- and long-time $g^{(2)}$ curves, as shown in Figs 1e and 3c, respectively. By fitting $\beta$ values obtained for different pump intensities with Eq. (3) we derived $k_{12}$ and $\sigma_{32}$. The value of $k_{23}$ is finally derived from eq. (2) by inserting pre-determined values of $k_{12}$, $k_{31}$, $\sigma_{32}$, and $k_{23}$.

The average duration times of the ON (OFF) states were calculated as follows:
\[
\tau_{\text{ON Average}} = \frac{1}{N_k 23}
\]

and

\[
\tau_{\text{OFF Average}} = \frac{1}{k_{31} + \sigma_{32}}.
\]

The OFF-time ratio, shown in Fig. 3f, was obtained as \(N_k(\tau \to \infty)\). For this duration of time, the emitter stays in its OFF-state and does not emit photons. Note that this OFF-time ratio is valid only for the cw-mode excitation case and not for the pulsed excitation cases.

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Author Contributions
C.T. Trinh and J. Lee conducted the experiments. C.T. Trinh and K.-G. Lee analyzed and interpreted the data. K.-G. Lee supervised the research. C.T. Trinh and K.-G. Lee wrote the paper.

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