Femtosecond Fluorescence Up-Conversion Microscopy: Exciton Dynamics in α-Perylene Microcrystal

Tatsuya Fujino and Tahei Tahara*

Molecular Spectroscopy Laboratory, The Institute of Physical and Chemical Research (RIKEN), 2-1 Hirosawa, Wako 351-0198, Japan

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The femtosecond fluorescence up-conversion microscope has been developed. This new method was applied to the study of exciton dynamics in an organic microcrystal, perylene. Taking advantage of femtosecond time-resolution and nanometer space-resolution, the fluorescence from microcrystals was clearly time-resolved and the ultrafast relaxation dynamics of the free exciton and the Y state was clarified at room temperature. It was found that the exciton dynamics significantly depends on the position in the microcrystal, reflecting the spatial distribution of the defect.

Microcrystals of organic molecules attract much interest in the field of material science. The properties of organic microcrystals are significantly different from those of semiconductors or metals. For example, it is known that organic crystals show two types of size effects, the conventional quantum confinement effect and the finite size effect. The conventional quantum confinement effect is observed also in semiconductor particles with the size below 10 nm, whereas the finite size effect that appears in submicrometer crystals is unique for organic crystals. Many of the organic crystals, such as perylene,[1] polydiacetylene,[2] and pyrazolines,[3] show the finite size effect in absorption and emission spectra, which has attracted much attention in relation to development of new optoelectronic devices. To fully utilize unique characters of microcrystals for applications, it is indispensable to clarify and control their optical properties.

One of the most important factors that control the optical property of microcrystals is the behavior of the excitons created by photoexcitation. With optical excitation of organic crystals, the delocalized excited state (free exciton) is created in the crystal lattice that has the translational symmetry. Owing to strong exciton−phonon coupling, the generated exciton induces distortion of the lattice and then it is trapped (self-trapped excitons). Clarification of the exciton dynamics is very crucial for understanding the properties of microcrystals. However, ordinary spectroscopic techniques having low spatial resolution cannot provide information about the property of individual microcrystal, because they can only measure the averaged property of many microcrystals and hence miss the information of each crystal in inhomogeneous spectral broadening. Therefore, it is indispensable to utilize the time-space-resolved spectroscopy to investigate the exciton dynamics in microcrystals.

Transient absorption spectroscopy combined with a microscope has been applied to the study of organic crystals.[4] However, time-resolved fluorescence microscopy is highly desirable because the exciton fluorescence affords direct information of the energy of the exciton, which enables us to make straightforward interpretation. Time-resolved fluorescence microscopes realized to date were based on the time-correlated single photon counting (TAC)[5,6] or the streak camera,[7] so that the time resolution of the fluorescence microscope was not high enough to study the exciton dynamics in microcrystals.

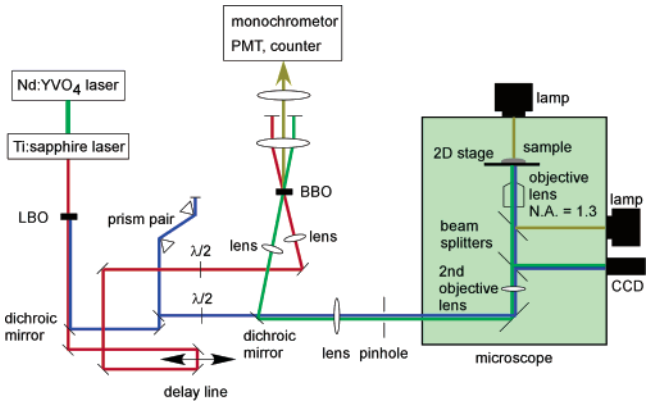

Figure 1. Schematic diagram of the femtosecond fluorescence up-conversion microscope.

In this paper, we present the first report of the femtosecond time-resolved fluorescence microscope, which was applied to investigate fluorescence dynamics of a perylene microcrystal. With use of high spatial resolution of the microscope, we could even examine position dependence of the exciton dynamics in the microcrystal.

The schematic diagram of the newly developed femtosecond time-resolved fluorescence microscope is shown in Figure 1. The second harmonics of the Ti:sapphire laser (800 nm, 9 nJ, 75 fs, 78 MHz; Coherent, MIRA-900F) is used as excitation light, and it is introduced into an inverted confocal microscope (TE-2000U, Nikon). The fluorescence from the sample is collected in the backscattering geometry, and it is guided to the outside of the microscope. Then, the fluorescence is focused into a nonlinear BBO crystal, where it is mixed with the time-delayed fundamental laser pulses to be up-converted. The up-converted signal was separated by filters and a monochromator (HR-320, Jovin-Yvon), and it was detected by a photomultiplier (H6180−01, Hamamatsu) with a photon counter (M8784, Hamamatsu). We achieved a time resolution as high as 600 fs with a 100× objective lens (N. A. 1.3, oil immersion). The horizontal spatial resolution (*XY*) was typically ∼800 nm,

* To whom correspondence should be addressed.

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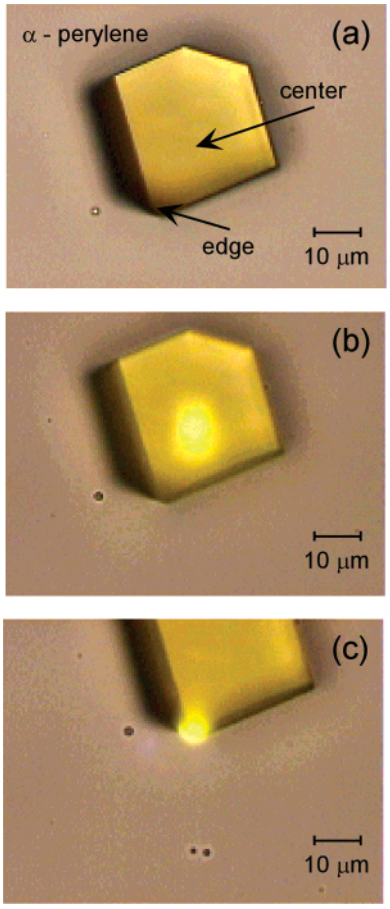

Figure 2. CCD camera image of the α-perylene microcrystal used for femtosecond fluorescence up-conversion microscopy (a). The excitation positions are indicated ("center" and "edge"). The CCD camera image during photoexcitation, center (b) and edge (c).

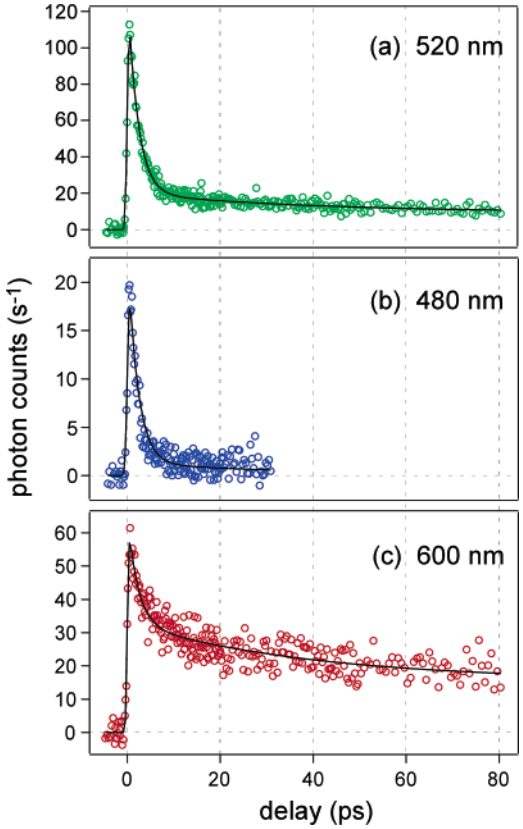

Figure 3. Femtosecond time-resolved fluorescence obtained with excitation at the crystal center. The fluorescence was monitored at 520 (a), 480 (b), and 600 (c) nm. The circles are the experimental data, and the black lines are the results of the fitting analysis. The lifetime of the free exciton and the Y state were determined to be 2.2 and 38.7 ps.

whereas the vertical resolution (Z) was evaluated to be ~5 μm. The vertical spatial resolution is achieved not only by the confocal configuration but also by the up-conversion process, because the up-conversion requires a very tight focus of the sample image on the mixing crystal.

In Figure 2a, we depicted the CCD camera image of an α-perylene microcrystal that was prepared according to the literature.[4] The crystal of perylene has two types of crystal structures: α- and β-perylene. In α-perylene, four molecules are in a unit cell with dimeric crystal structure, whereas two molecules with monomeric crystal structure form a unit cell in β-perylene. Because these two types of crystals show different fluorescence spectra,[8] we chose an α-perylene microcrystal under the microscope by checking the steady-state fluorescence spectrum. At room temperature, α-perylene exhibits very broad fluorescence in the visible region with the intensity maximum around ~600 nm. This broad fluorescence is considered to consist of three components that are attributed to the excitons having different magnitudes of the delocalization: The fluorescence in the blue region has been assigned to the emission of free excitons that are directly generated by photoexcitation. The free exciton is relaxed to the Y state (partially relaxed excimer), and the fluorescence around ~530 nm has been assigned to the Y state. Then, the Y state is relaxed to the E state (totally relaxed excimer, self-trapped exciton) that emits the broad intense fluorescence around ~600 nm. The emission from the E state dominates the steady-state fluorescence observed at room temperature.[8] We carried out time-resolved fluorescence measurements under the microscope, to clarify the exciton dynamics in the microcrystal at room temperature.

The time-resolved fluorescence (520 nm) observed from the center part of the α-perylene microcrystal is shown in Figure 3a (the CCD camera image during photoexcitation is depicted in Figure 2b). The observed decay was well fitted by a triple exponential function that was convoluted with the instrumental response. The first two time constants of the triple exponential were determined with high accuracy to be $\tau_1 = 2.2$ ps and $\tau_2 = 38.7$ ps, whereas the accurate determination of the third time constant was difficult owing to its very long lifetime. The observed florescence dynamics, as well as the relative amplitude of the three components, was not affected by the change of the pulse energy of the excitation (reduction of the pulse energy by half). This assured us that the concentration of the exciton is relatively small under the present experimental condition and that the exciton−exciton annihilation is negligible. The unambiguous assignments of the observed three decay components were made on the basis of the wavelength dependence of the time-resolved fluorescence signals. The fluorescence decay at 480 nm (Figure 3b), where the emission from the free exciton is dominant, contains a much larger contribution of the τ_1 component, compared with the fluorescence trace at 520 nm. The τ_2 component is very small and the third slow component is missing. On the other hand, a large contribution from the long lifetime component was observed in the fluorescence decay at 600 nm (Figure 3c). The observed wavelength dependence of the time-resolved fluorescence directly indicates that the τ_1 and τ_2 components are attributed to the fluorescence from the free exciton and the Y state, respectively, whereas the third slow

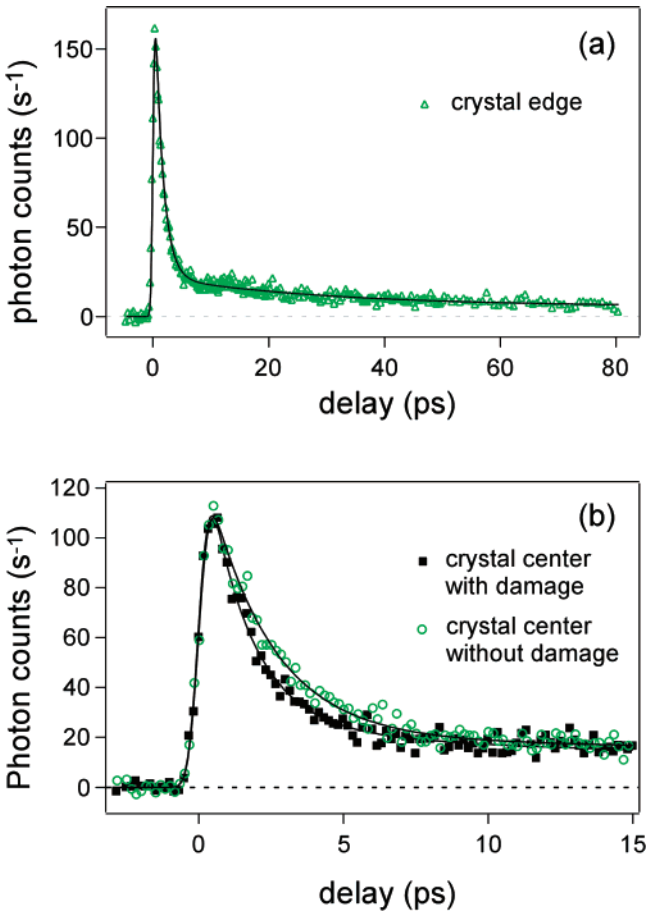

Figure 4. Femtosecond time-resolved fluorescence (520 nm) obtained at the crystal edge (a). The triangles are the experimental data, and the black line is the result of the fitting analysis. The lifetimes of the free exciton and the Y state were determined to be 1.4 and 29.8 ps at the crystal edge. The femtosecond time-resolved fluorescence (520 nm) obtained from a damaged point of the crystal (b). The dotted squares are the experimental data, and the black line is the result of the fitting analysis. The result obtained with the center excitation (without damage, green circles) is also shown for comparison.

component is assigned to the E state. Auweter et al. performed picosecond time-resolved fluorescence measurements of ordinary large perylene crystals at low temperature. They reported the lifetimes of the Y state and the E state to be 55 ps at 121 K and 85 ns at 49 K, whereas dynamics of the free exciton were not time-resolved because of their limited time-resolution.[9]

The high space-resolution achieved in the femtosecond fluorescence up-conversion microscope enabled us to examine the position dependence of the exciton dynamics in an α-perylene microcrystal. Figure 4a shows the time-resolved fluorescence signal (520 nm) measured with the excitation of the crystal edge. (The CCD camera image during photoexcitation is depicted in Figure 2c.) The observed decay was well fitted by a triple exponential function as in the case of the center excitation. However, the lifetimes of the free exciton and the Y state were significantly shortened: They become 1.4 (τ_1) and 29.8 ps (τ_2). Although we could not recognize a noticeable difference between the steady-state fluorescence spectra measured with center and edge excitation, it is clear that the local environment significantly affects the relaxation dynamics of the exciton. It is expected that the edge of the crystal is less ordered compared with the center and, hence, that the defect concentration is higher. Therefore, the observed change in the exciton relaxation is highly likely attributable to the difference in the defect concentration in the microcrystal. This argument was strongly supported by the following experiment. We made a small damage on the center part of the microcrystal by irradiation of a high laser power (~100 times higher than other ordinary measurements) and compared the time-resolved fluorescence signals before and after making the damage. As shown in Figure 4b, the lifetimes of the free excitons and the Y state become noticeably shorter after making the damage. Because the defect concentration at the damaged point is high, this result demonstrates that the presence of the defects affects the exciton dynamics and accelerates its relaxation process.

We have performed femtosecond time-resolved fluorescence measurements of an organic microcrystal, α-perylene, by using a newly developed microscope that achieves femtosecond time-resolution and nanometer space-resolution. We observed the ultrafast exciton dynamics, with spatially resolving the position in the microcrystal. It is obvious that the femtosecond fluorescence up-conversion microscope can be applied not only to the characterization of organic microcrystals but also to the study of the ultrafast dynamics of materials having microstructure, including devices and living cells. The femtosecond fluorescence up-conversion microscope can be a powerful tool to explore the properties of molecules in micrometer structures, which is a key for nanoscience and nanotechnology.

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