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Transient absorption microscopic study of triplet excitons in organic crystals

Ryuzi Katoh *, Yoshiaki Tamaki [1], Akihiro Furube

National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

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Abstract

We have constructed a transient absorption microscope to study triplet excitons in organic crystals. Using the microscope, transient absorption of small crystals can be measured and the spatial distribution of triplet excitons can be obtained. Additionally, it was found that the contrast of the image becomes much better than that of a conventional bright-field microscope. These characteristic features of the transient absorption microscope will be discussed. We also report on the absorption spectra in benzophenone, anthracene and α- and β-perylene crystals. Absorption spectra due to triplet excitons in the crystals were similar to the corresponding solution spectra, although there were some minor differences.

Keywords: Transient absorption; Microscope; Triplet exciton; Organic crystal

1. Introduction

Recently, various photo-functional devices based on organic materials, such as organic light-emitting diodes and organic solar cells, have been extensively studied. Excitons play an important role in the function of these devices, and many studies aimed at clarifying the properties of excitons in organic materials have been undertaken. In organic materials, there are two important excitons: singlet excitons and triplet excitons. Singlet excitons emit fluorescence and can therefore be studied by means of fluorescence spectroscopy. In contrast, the emission yield of triplet excitons is negligible, and therefore detecting triplet excitons by luminescence spectroscopy is difficult. However, transient absorption spectroscopy is very useful for the observation of these non-luminescent species.

Although transient absorption spectroscopy is a common technique in the field of solution photochemistry, triplet excitons in organic single crystals have been studied in detail only for benzophenone crystals [1–3]. The lack of studies is due in part to the difficulty of preparing large transparent specimens. For benzophenone crystals, large ingots (typically 1 cm × 1 cm × 10 cm) can be prepared by the Czochralski method [1]. Transient absorption due to triplet excitons in these crystals can be detected easily, and the generation process [2], the annihilation process [1], and the reaction with dopant molecules [1] have been studied. An alternative technique for obtaining transient absorption spectra due to triplet excitons is transient diffuse reflectance spectroscopy [4]. Masuhara and co-workers have extensively studied triplet exciton absorption in powder samples by using this technique [5–7]. Although the technique can be applied to various materials, reproducing absorption spectra from diffuse reflectance spectra are difficult. Thus, quantitative studies are often difficult.

To collect absorption spectra due to triplet excitons for various organic crystals, transient absorption study of small sized crystals must be carried out. Thus, we have improved the transient absorption microscope developed previously [8] for this purpose. The technique can also be used to investigate the spatial distribution and temporal evolution of excitons. Herein we report on the absorption spectra and show images due to triplet excitons in several typical organic crystals to demonstrate the utility of the microscope.

2. Experimental

Benzophenone (Tokyo Kasei Co.) powder was used as received, and the sample was prepared by melting the powder between two glass plates placed on a hot plate. Single

* Corresponding author. Tel.: +81 29 861 4840; fax: +81 29 861 5301.
E-mail address: r-katoh@aist.go.jp (R. Katoh).
[1] NEDO fellow.

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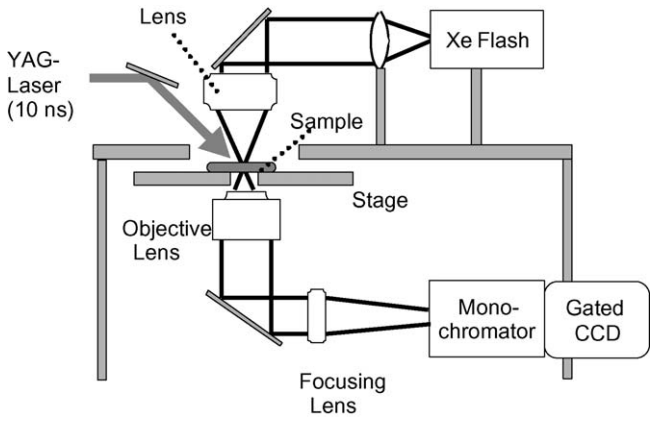

Fig. 1. Schematic diagram of the transient absorption microscope.

crystals of anthracene were grown by the sublimation method after being purified by extensive zone refining of purchased material (Merck, scintillation grade). The resulting single crystals were typically 10 mm × 5 mm × 0.05 mm. Single crystals of α-perylenewere grown from the melt by the Bridgman method after being purified by extensive zone refining of purchased material (Sigma). Single crystals, typically 8 mm × 5 mm × 1 mm, cleaved from ingots, were used as samples. Single crystals of β-perylene were grown from a toluene solution after being purified by recrystallization of purchased material (Tokyo Kasei Co.). The size of the crystals was typically 1.5 mm × 1 mm × 0.2 mm. The formation of β-perylene crystals was confirmed by fluorescence spectroscopy [9].

Fig. 1 is a diagram of the transient absorption microscope that we developed. A Xe flash lamp (Hamamatsu, L4642, 2 μs pulse duration) was used as a probe light source and to irradiate the sample. The transmitted probe light was collected with an objective lens. The microscope image was reproduced at the entrance slit of the imaging monochromator (Acton, SpectraPro-308) by a focusing lens. When the entrance slit of the monochromator was replaced with a square aperture (1.5 cm × 1.5 cm) and the grating was replaced with a mirror, the microscope image was transferred to the CCD camera (Roper Scientific, ICCD-MAX). By using the electronic gate of the CCD camera, time-resolved images were recorded. To measure transient absorption images, a laser pulse from an optical parametric oscillator (Spectra Physics, MOPO-SL) excited by a Nd^{3+}:YAG laser (Spectra Physics, Pro-230-10, 8 ns duration) was used as the exciting light. Intensity of the excitation light was kept below 5 mJ cm^{-2} to reduce the damage of sample specimens. To select the observation wavelength, optical filters were placed in front of the focusing lens. The spatial resolution of the microscope was about 2 μm and the time resolution was 8 ns which was determined by laser pulse duration. The sensitivity of the measurements was dependent upon experimental conditions, especially intensity of the probe light. If the gated time of the CCD camera was 1 μs, small absorbances ($<10^{-3}$) can be observed.

We measured four combinations of images in order to construct the image of the transient species: probe light intensity without excitation (I_0), probe light intensity with excitation (I), fluorescence intensity (pump only, I_F) and background (lacking both pump and probe lights, I_B). The image of the transient absorption (A) was calculated from the equation $A = \log((I_0 - I_B)/(I - I_F))$, and the image of the fluorescence (F) was calculated from the equation $F = I_F - I_B$. The image from the conventional microscope (bright-field image, B) was calculated from the equation $B = I - I_B$.

3. Results and discussion

3.1. Benzophenone crystals

Fig. 2 shows images of a benzophenone crystal recorded by the transient absorption microscope in various detection modes. Many pits on the sample can be seen in the bright-field image (Fig. 2, image B). Upon homogenous photo-excitation of the sample by a 355 nm light pulse, luminescence and transient absorption images can be obtained. Fig. 2 (image F) shows a luminescence image of the benzophenone crystal, whose origin is phosphorescence, observed around 450 nm. Upon irradiation with 355 nm light, excited species were generated homogeneously in the bulk of the crystal because of the small absorption coefficient of the ground state. In image F, pits and the edges of the crystal are bright because luminescence generated in the bulk of the crystal propagates through the crystal, acting as wave guide, and is released at the pits and the edges [10]. That is, the luminescence image does not directly reflect the spatial distribution of excited species.

Fig. 2 (image A) shows a transient absorption image of the benzophenone crystal recorded with 0–1 μs time gate at 550 nm through an interference filter. According to the previous study on transient absorption of a benzophenone crystal [2], upon photoexcitation singlet excitons are produced and immediately they covert into triplet excitons, thus, with the present time-resolution (8 ns), observed absorption can be assigned to triplet–triplet (T–T) absorption. In the transient absorption image (A), in contrast to the fluorescence image (F), the entire crystal was homogeneously bright, which suggests that excitons were generated homogeneously in the bulk of the crystal. This phenomenon occurs because the transient absorption signal is proportional to the density of excited species. Thus, the spatial distribution of triplet excitons can be evaluated quantitatively by means of the transient absorption technique. This is an advantage of the transient absorption microscope to study triplet excitons in organic crystals.

It was found that the contrast of image A in Fig. 2 is much better than that of image B. Although this may be a characteristic feature of the transient absorption microscope, the origin of the enhancement of the contrast is unclear. Tentatively, we suggest two explanations for the enhancement of the contrast. One explanation involves offset subtraction. The contrast of an image is known to be enhanced by subtraction of an offset from an original image. For transient absorption images, a small change in transmitted intensity is used as the signal, and therefore the offset subtraction is made effectively. The second explanation involves the refractive index change due to transient species. Differences in refractive index give bright-field images; i.e., when excited species are produced in a material, the refractive index of the

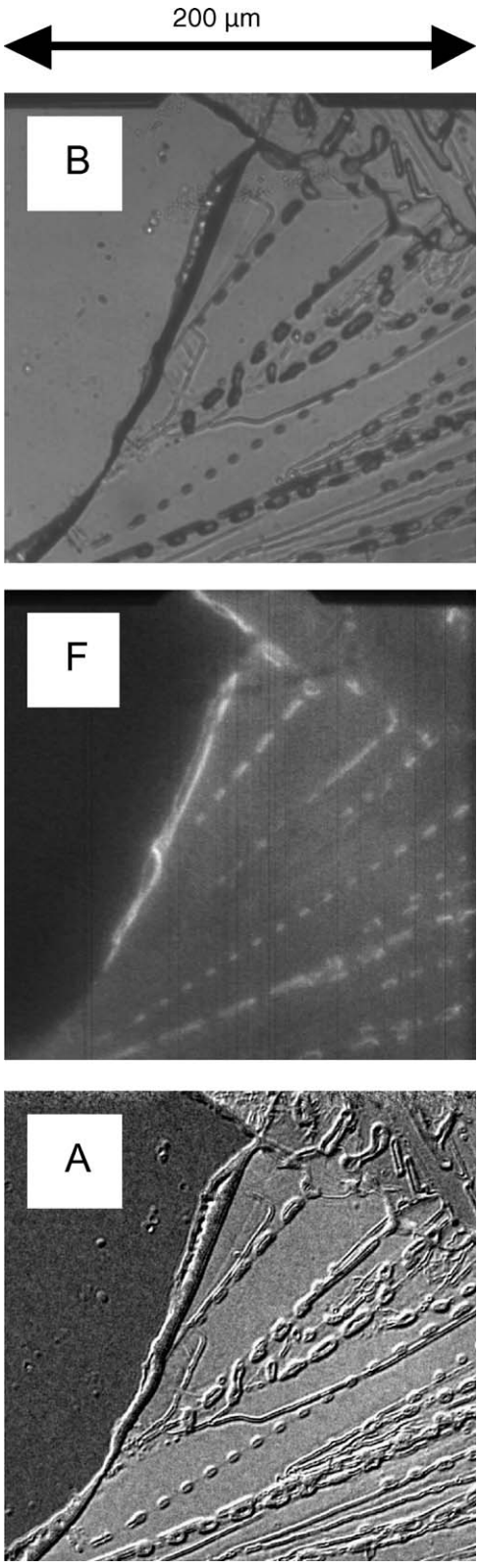

Fig. 2. Microscopic images of a benzophenone crystals in various detection modes: bright-field mode (B), fluorescence mode (F) and transient absorption mode (A).

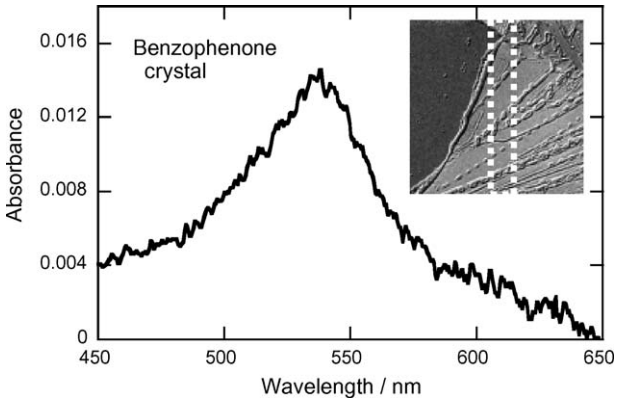

Fig. 3. Transient absorption spectrum of a benzophenone crystal measured with the transient absorption microscope. The inset depicts the area that was measured.

materials slightly increases. As a result, the bright-field image with excitation differs from that without excitation. This phenomenon would also result in contrast enhancement.

Fig. 3 shows the transient absorption spectrum of a benzophenone crystal recorded with the transient absorption microscope. To measure the absorption spectrum, we placed a slit at the entrance of the monochromator, which allowed the transient absorption spectrum of the centered area to be measured (Fig. 3, inset). Owing to the similarity of the spectrum in Fig. 3 with previously reported spectra of large size crystals [1–3], the observed spectrum can be assigned to the optical absorption due to triplet excitons in the benzophenone crystals. This result clearly shows that reliable transient absorption measurements can be made in a small area under the microscope, which we constructed. Thus, we can collect absorption spectra due to triplet excitons for various organic crystals using small sample specimens.

3.2. Anthracene crystals

In the bright-field image of the anthracene single crystal (Fig. 4, image B), many spot-like patterns are seen. These spots are pits on the surface, but they are not imperfections in the bulk of the crystal. Image A is the transient absorption signal observed around 440 nm at 20–500 ns after 410 nm light excitation. Under this excitation condition, excited species were generated homogeneously in the bulk of the crystal because of the small absorption coefficient of the ground state. Singlet excitons are generated primarily and decay within 20 ns. Thus, only the absorption due to triplet excitons can be expected to be observed. Charge carriers are possible intermediates for transient absorption measurements in general. For anthracene crystals, charge carriers are generated through photoionization of singlet excitons in this wavelength range [11]. Accordingly, efficiency is quite small because of geminate recombination, which is common behaviour for aromatic hydrocarbon crystals. Thus, the contribution of charge carriers in the transient absorption measurements is negligible.

At 440 nm, a strong absorption due to the triplet exciton is expected (see Fig. 5). The sample was irradiated with line-focused exciting light, and, therefore, a line-focused transient

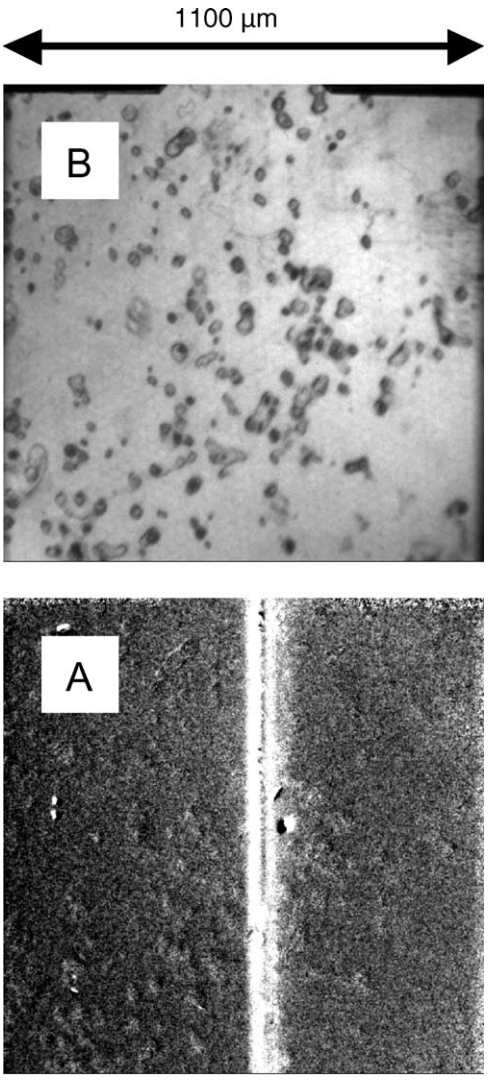

Fig. 4. Microscopic images of an anthracene crystal in various detection modes: bright-field mode (B) and transient absorption mode (A). For the transient absorption measurement, a line-focused laser beam was used for excitation.

absorption signal can be seen. Under the present experimental conditions, a line-shaped signal with a width of 50 μm can be detected. With the focused beam, site-selective excitation and detection can be accomplished.

Triplet excitons in anthracene crystals have been extensively studied by means of delayed fluorescence spectroscopy. The energy levels of triplet excitons [12] and the annihilation rate constant [13] have been estimated. Triplet excitons can move in the crystal, and the diffusion coefficient (D) is estimated to be 10^{-4} cm^2 s^{-1} [14]. Although we measured the temporal change in the transient absorption image up to 100 μs, no change in the image was detected. This result is reasonable because the expected diffusion length (L) within the time period (t_d) can be estimated from $(Dt_d)^{1/2}$, which gives a value of 1 μm for $D = 10^{-4}$ cm^2 s^{-1} and $t_d = 100$ μs.

The upper trace in Fig. 5 shows the transient absorption spectrum of an anthracene single crystal measured under the conditions used to obtain image A in Fig. 4. A strong absorption peak at 440 nm and a broad absorption peak at 620 nm can be

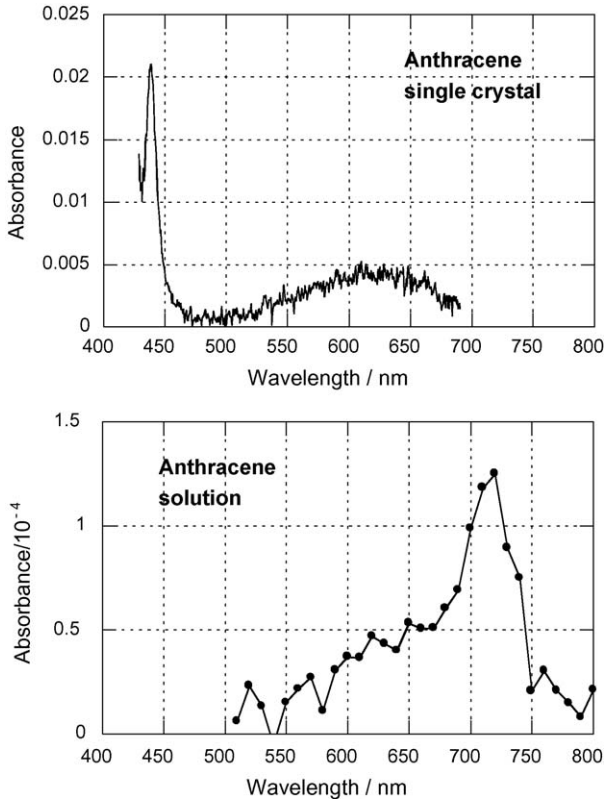

Fig. 5. Transient absorption spectrum of an anthracene crystal. The upper trace shows the spectrum in the crystal measured with the transient absorption microscope. The lower trace shows the spectrum in ethanol solution.

seen. In solution, strong absorption due to the triplet excited state has been reported at 440 nm [15], which is similar to the value measured for the crystal. Recently, we have developed a highly sensitive transient absorption spectrometer [16] that allows us to measure very small absorbance changes (<10^{-5}). Using this spectrometer, we successfully measured the weak T–T absorption spectrum of an ethanol solution of anthracene with a high signal-to-noise ratio (Fig. 5, lower trace). The absorption peak at 720 nm is slightly red-shifted (0.28 eV) relative to the peak for the crystal. In this wavelength range, weak T_2–T_1 absorption has been reported with a lower signal-to-noise ratio [17,18]. Thus, we tentatively assigned the peak in the crystal at 620 nm to the optical transition from the triplet exciton to the second excited triplet (T_2) state.

3.3. α- and β-perylene crystals

Fig. 6 shows images of a large (8 mm × 5 mm × 1 mm) α-perylene single crystal recorded with the transient absorption microscope in various detection modes. The black spots and lines in image B are small crystals adsorbed on the bulk crystal and step lines, respectively. To obtain the fluorescence image (image F), we used a 532 nm laser pulse excitation, and fluorescence was observed over the entire visible wavelength range (400–700 nm) except for 532 nm, which was eliminated with an interference filter. Under 532 nm excitation, excitons can be generated homogeneously in the bulk of the crystal because of

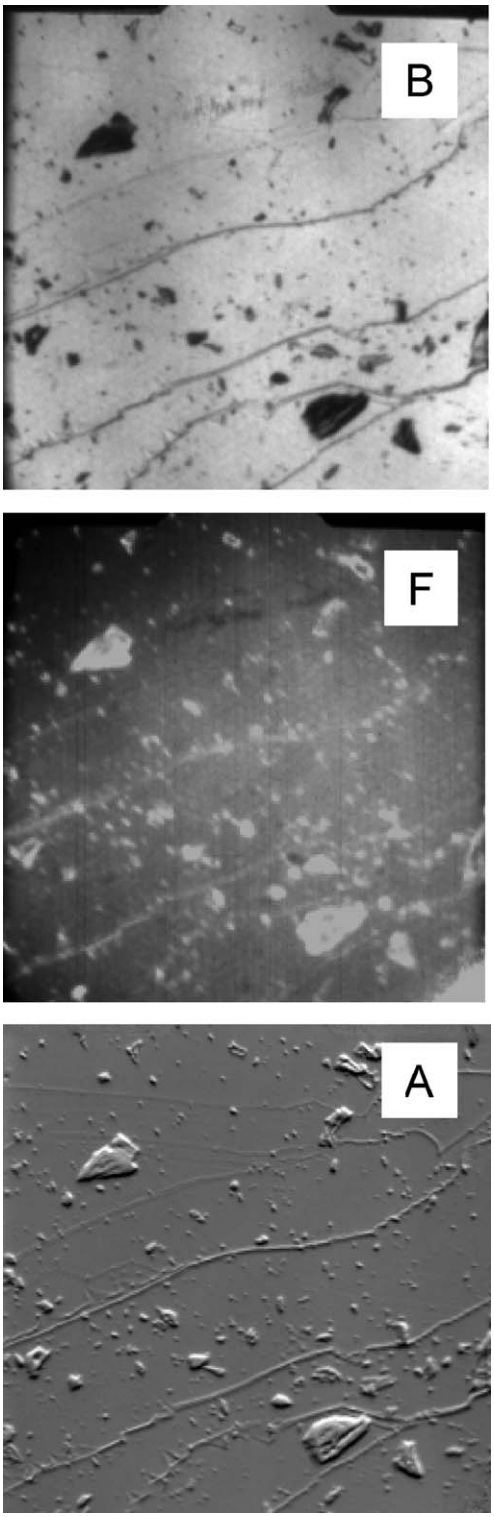

Fig. 6. Microscopic image of an α-perylene crystal in various detection modes: bright-field mode (B), fluorescence mode (F) and transient absorption mode (A).

the small absorbance for the ground state at the wavelength. In image F, the small crystals on the surface of the larger crystal are bright, and fluorescence at the step lines is pronounced. The contrast of image F is lower than that of image B because of the high-level background signal from the bulk of the crystal.

We also obtained a transient absorption image at 0–50 ns after 532 nm light excitation (image A), and a homogeneous image can be obtained with a 0.01 absorbance change over the entire area observed. Under these conditions, transient absorption due to both singlet and triplet excitons contributed to the image, because the fluorescence lifetime of α-perylene crystals is 80 ns. In image A, small crystals on the surface give a signal similar to the background due to the bulk, and the step lines can be seen with high contrast, which arises for the reason mentioned previously. These three images give complementary information

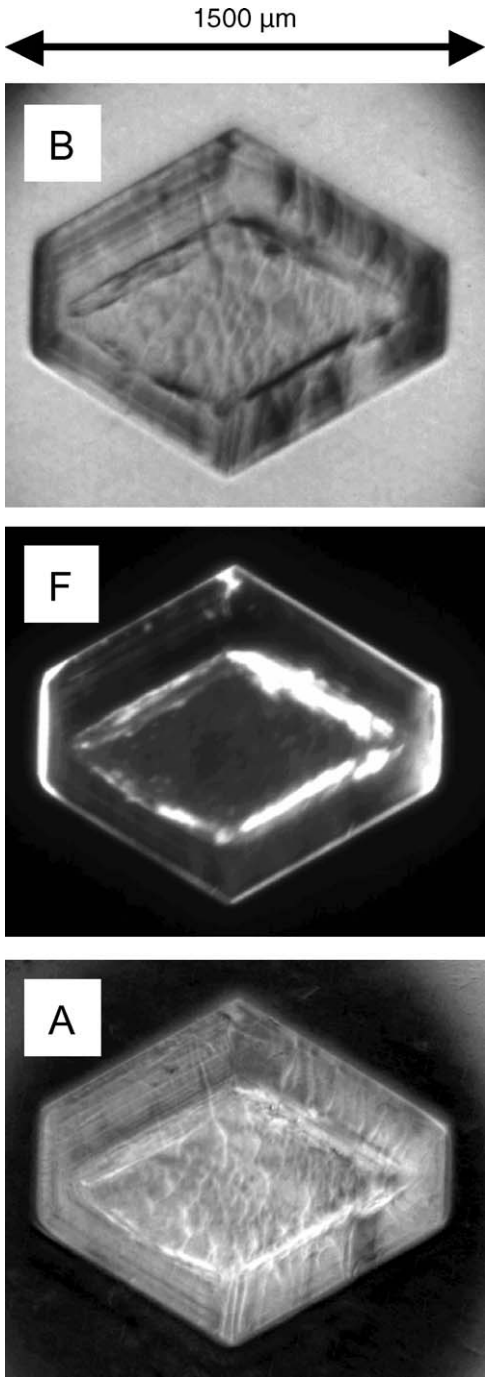

Fig. 7. Microscopic image of a β-perylene crystal in various detection modes: bright-field mode (B), fluorescence mode (F) and transient absorption mode (A).

about the surface structure of the crystal and the distribution of excited states.

Fig. 7 shows images of a β-perylene single crystal recorded with the transient absorption microscope in various detection modes. A well-shaped crystal can be seen in the bright-field image (Fig. 7, image B), which indicates that the sample is a single crystal. In the luminescence image of the sample observed around 550 nm after a 500 nm laser pulse excitation (Fig. 7, image F), the edge of the crystal is bright, as was the case for the benzophenone crystals, which suggests that the luminescence image does not directly reflect the spatial distribution of excited states.

Image A in Fig. 7 shows the transient absorption image recorded at 100–200 ns after excitation by a 500 nm light pulse. The fluorescence lifetime of the β-perylene crystal was 2 ns, and therefore triplet excitons contributed to the image. In image A, the entire sample is homogeneously bright, whereas only the edges are bright in image F. This difference clearly shows that triplet excitons were generated homogeneously in the bulk of the crystal.

Fig. 8 shows the transient absorption spectra of α- and β-perylene crystals recorded at 200 and 50 ns after pulsed excitation, respectively. The fluorescence lifetimes of the α- and β-perylene crystals were 80 and 2 ns, respectively, and therefore the spectra observed can be assigned to the optical transition from triplet excitons, which have a long lifetime. For both spectra, absorption at the shorter wavelength range (<550 nm) and a broad band around 750 nm can be seen. An absorption peak at 480 nm due to the triplet excited state in solution has been reported [14], but no absorption signal around 750 nm has been reported. We also tried to measure the transient absorption signal due to the triplet excited state in perylene solution by using a highly sensitive transient absorption spectrometer [16]. However, no absorption signal was detected. Hence, the longer absorption peak can be considered to be a characteristic absorption band for crystals. At present, the origin of the absorption is not clear. One possible origin is the transition from a triplet exciton to an ion-pair state, which forms only in the crystalline phase. Such an absorption has been detected for an excimer in solution [19,20] and in a crystal [21].

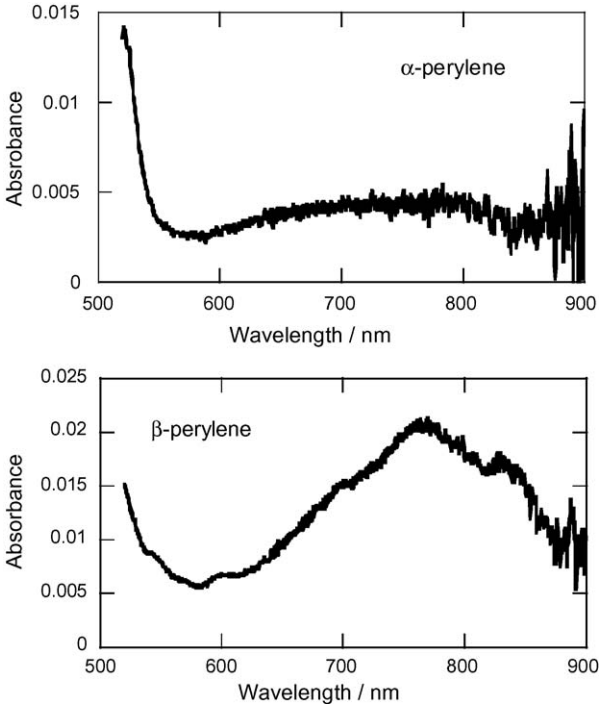

Fig. 8. Transient absorption spectrum of α- and β-perylene crystals measured with the transient absorption microscope.

4. Conclusion

We have studied triplet excitons in organic crystals using the transient absorption microscope, which we constructed. We succeeded in measuring transient absorption spectra from small areas of the crystals. This is advantage in the study of triplet excitons in organic crystals, because only a small sample specimen is available in many organic crystals. Another advantage of the transient absorption microscope is visualization of the spatial distribution of triplet excitons in contrast with a fluorescence microscope. Additionally, it was found that the contrast of the image becomes much better than that of a conventional bright-field microscope. These characteristic features show that the transient absorption microscope is useful tool for studying excited states in organic crystals.

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