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Cross-shaped photoluminescence of excimers in perylene crystals

Daichi Tanaka[1] · **Yudai Numata**[1] · **Kazuya Nakagawa**[1] · **Takayoshi Kobayashi**[2,3] ·
Eiji Tokunaga[1]

Abstract Cross-shaped excimer (self-trapped exciton) luminescence from α- and β-perylene single crystals of 50–100 μm was found when they were excited at the center of the crystals with a continuous-wave (cw) laser resonant with the exciton absorption. The cross shape is formed by the two lines which intersect at the excited position and are perpendicular to the sides of the crystals of parallelogram shape. Luminescence is emitted from the excited spot and 4 side edges in the cross shape. The most striking feature is that the luminescence intensity at the edges was as high as or higher than at the excited spot. The possibility of the exciton propagation or the waveguide effect is rejected both experimentally and theoretically. This phenomenon can be reasonably explained only when the radiative transition probability of excimers is significantly enhanced at the crystals side edges than at the center due to the lower symmetry.

1 Introduction

The Frenkel exciton in a molecular crystal is a coherently propagating wave of the excited state delocalized over a significant volume much larger than the unit cell in the

✉ Eiji Tokunaga
eiji@rs.kagu.tus.ac.jp

1 Department of Physics, Faculty of Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan

2 Advanced Ultrafast Laser Research Center, The University of Electro-Communications, 1-5-1, Chofugaoka, Chofu, Tokyo 182-8585, Japan

3 CREST, Japan Science and Technology Agency, 4-1-8, Honcho, Kawaguchi, Saitama 332-0012, Japan

crystal. Since it carries a large interaction strength with light, i.e., a large oscillator strength, the exciton is important for understanding of optical processes in both organic and inorganic crystals. Recently, it is understood that the exciton plays a crucial role in efficient energy transfer in photosynthesis [1], organic electro-luminescence devices [2], and organic solar cells [3]. In these applications, excitons play a role of photoexcited energy conveyers. The propagation mechanisms and schemes of excitons, therefore, are one of the most fundamental issues among many research interests about excitons. Increase in the propagation length of excitons as well as increase in the coherence length of excitons [4] attracts a particular interest in research and development of these devices. The exciton diffusion length or the migration length is reported to be typically several tens of nanometers [3] for singlet excitons. For excitons with a longer lifetime such as H-aggregates excitons [5] and triplet excitons [6, 7], the propagation length is reported to amount to 250 nm to 5 μm. The exciton coherence preserved over tens of micrometers is also reported for conjugated polymer chains [4].

The optical waveguide is ubiquitous in the modern optical technology, utilized for efficient transport of electromagnetic waves. The waveguide effect has been attracting much attention also in solar energy industry. Luminescent solar concentrators [8–10] are typical examples, which concentrate diffuse solar light energy into the small-area solar cells by converting it to red-shifted luminescent energy and utilizing the waveguide effect.

In this paper, we have observed excimer luminescence spatially distant by more than 50 μm from the excitation spot in perylene crystals. We refer to this luminescence as a cross-shaped luminescence, because a cross (+) or X-pattern is shaped with spatially separated luminescent spots

when the excitation spot is positioned at its center in rectangular crystals or in rhombus crystals, respectively. We have found that the cross-shaped photoluminescence has remarkable spatial intensity distribution. That is, excimer emission from the crystal edges is more intense than from the excited spot. This is a striking result which might indicate a long distance propagation of excitons over 50 μm or unusually efficient transport of luminescent light via the waveguide effect. We have investigated this crossed luminescence to elucidate its origin.

As shown in Fig. 1, perylene is one of the most typical polycyclic conjugated hydrocarbons, and molecular crystals of perylene derivatives have been widely applied to various optical devices, such as EL displays and solar cells [3, 5]. There are two different types of structure in perylene crystals, i.e., a dimeric crystal called "α-crystal" and a monomeric crystal called "β-crystal" [11, 12]. In perylene crystals of both types, it is well known that delocalized free excitons generated by photoexcitation are rapidly relaxed into self-trapped excitons (STE) due to strong exciton–phonon interaction [13–20]. Since the STE in perylene is self-stabilized by structural deformation in crystal to form a paired excited dimer with face-to-face stacking configuration, this is a so-called H-dimer, which is structurally similar to an excimer formed by association of excited and ground-state perylene molecules in solutions [21, 22]. In this paper, therefore, we refer to STE's as excimers. They emit spectrally red-shifted, broadened excimer luminescence, which is forbidden transition since they are H-dimers [16]. Photoexcited dynamics of perylene crystals have been studied to elucidate detailed relaxation processes of excitons [17–20]. Surprisingly, however, there is little detailed study on the exciton propagation in perylene crystals [20]. This is probably because rapid relaxation into excimers (within a few ps) [17–19] prevents excitons from being propagated even over tens of nanometers. In this respect, it leads to curiosity why the cross-shaped luminescence occurs. It is interesting to note that observation of spatial pattern of excimer luminescence in perylene α- and β-crystals has been previously attempted [17, 20], but there have been no reports of observation.

In this paper, we examine the unique characteristics of the cross-shaped luminescence. Then, we present three possible models to explain them and assess the validity of each model from both experimental and theoretical point of view.

2 Experimental methods

Perylene (>99.0 %) was purchased from Tokyo Chemical Industry Co., Ltd. and purified by a sublimation refining method. We prepared an 8 mM perylene–acetone solution

and dropped a solution droplet onto a cover glass plate (20 mm × 20 mm). Then, perylene crystals in size of 50–100 μm were recrystallized from the solution at room temperature.

The experimental setup is shown in Fig. 2a–c. A spatial luminescence pattern in a crystal was observed with an inverted microscope (Nikon ECLIPSE TE300, or Olympus IX71) by photoexcitation with a 408 nm cw laser diode for resonant excitation of excitons. The intensity of the laser light at the sample position was estimated to be 9.7×10^2 W/cm^2, which was attenuated from its original intensity with a variable ND filter. Spatially resolved spectra were measured as follows: The magnified luminescent image was focused directly on the entrance slit of an imaging spectrometer with a cooled CCD; then, the slit was displaced horizontally to measure the spectra on the whole spatial positions of the crystal as shown in Fig. 2a. For comparison, the waveguide effect of a color glass filter Y50 (HOYA) was observed by two ways with the setup in Fig. 2b, c. The laser diode at 408 nm was used to excite the glass filter. Firstly (Fig. 2b), right behind the sample, we put the aperture with a hole of 5 mm diameter to selectively detect luminescence spectra at the excited position (A) and the edge (B) from the front side of the filter. Secondly (Fig. 2c), luminescence from the excited position (I) was observed from the front, while that from the edges (II, III) was from the side. The luminescence light was transferred to the fiber bundle connected to an imaging spectrometer with a cooled CCD.

3 Results

3.1 Size and shape dependence of cross-shaped emission

First, correlation was investigated between the shape and size of the perylene single crystals and the cross-shaped emission on resonant excitation at 408 nm. This wavelength is well above the absorption edge of the crystals within the exciton band. Figure 3 shows the typical microscopic images of the perylene crystal in different shapes and sizes under the photoexcitation. Cross shape, i.e., +(α-perylene) or X (β-perylene) like shape of photoluminescence image was observed. That is, the cross shape is formed by the two lines intersecting at the excited spot and perpendicular to the four sides of the crystals of parallelogram shape. Luminescence is found to emit mainly from the 5 spots within the cross, i.e., the center of the cross (excitation spot) and the 4 intersections between the cross and the four crystal side edges. As depicted in the figure, in almost all the cases, the cross-shaped emission was observed, irrespective of the

Fig. 1 The structure of perylene. **a** Molecule, **b** dimer, **c** β-crystal, **d** α-crystal

(a) Molecule

(b) Dimer

(c) β-crystal (Unit Cell)

(d) α-crystal (Unit Cell)
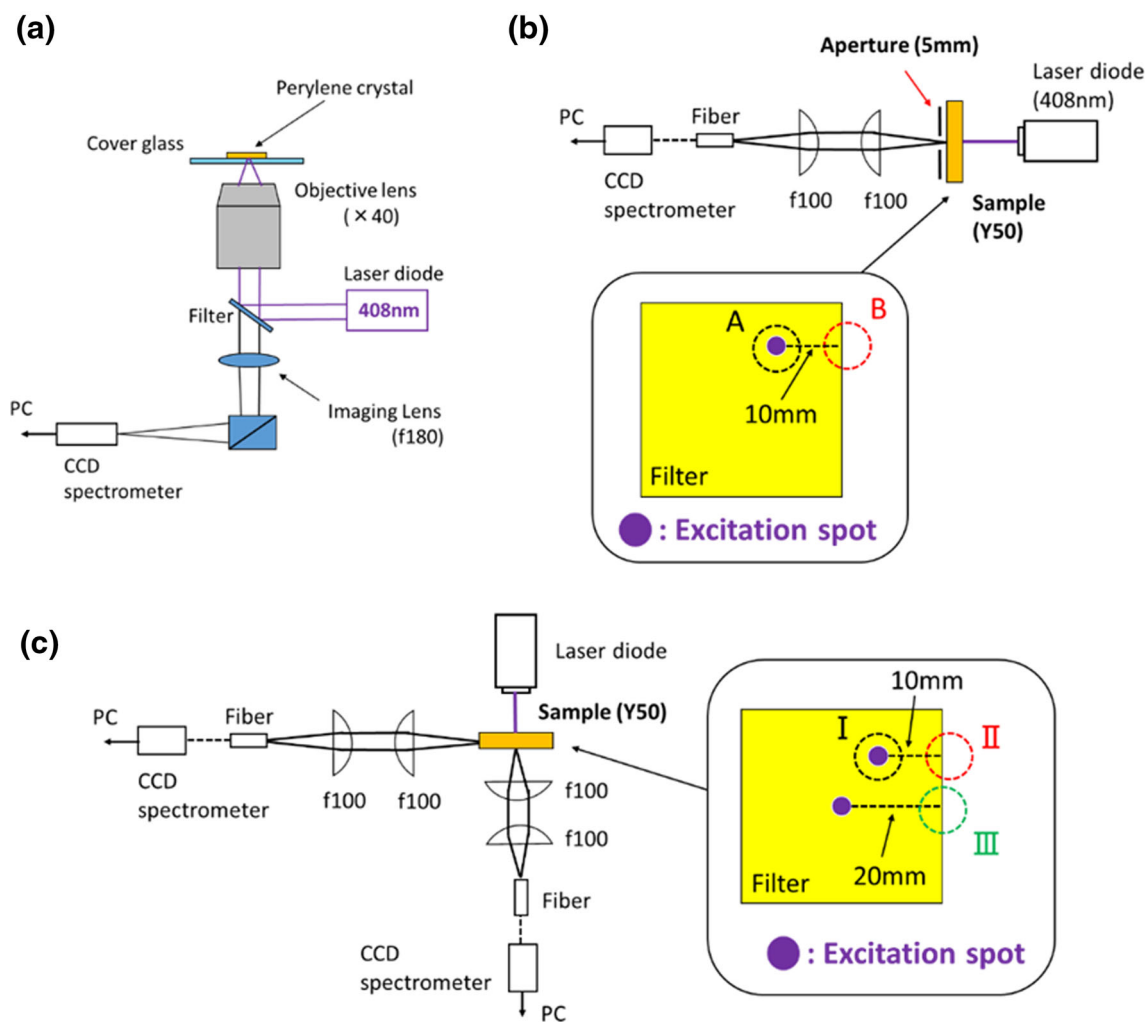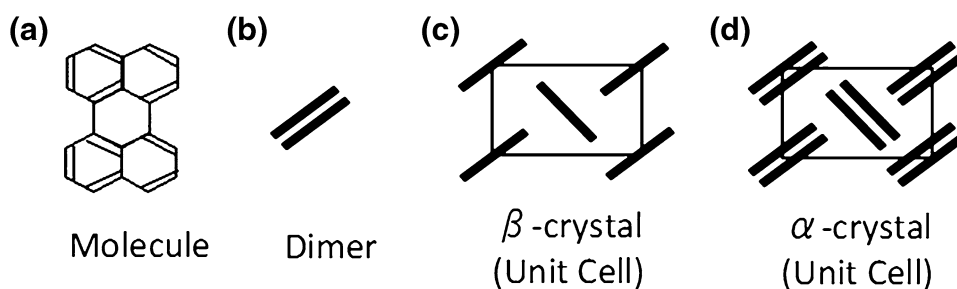
Fig. 2 **a** Optical system for spatially resolved emission spectroscopy of single perylene crystals. **b**, **c** Experimental setup for emission spectroscopy of a color glass filter (Y50). The *insets* in **b**, **c** show the shapes or sizes of the crystals. The largest cross pattern reaches nearly 200 μm in the longest length of the cross.

detecting positions of luminescence as depicted by *dashed circles* (*A*, *B*, *I*, *II*, *III*) on the sample

3.2 Spatially resolved luminescence spectroscopy

Next, we carried out the spatially resolved spectroscopy to measure the emission spectra over the perylene single crystals on the resonant excitation. The experimental setup is shown in Fig. 2a, and all the results are shown in Fig. 4. Figure 4a is the microscopic image of the sample crystal, and Fig. 4b shows the spatially resolved emission spectra along the line on the part of the cross-shaped emission, which is denoted by the red arrow in Fig. 4a. The color maps in Fig. 4c show the spatial distribution of the
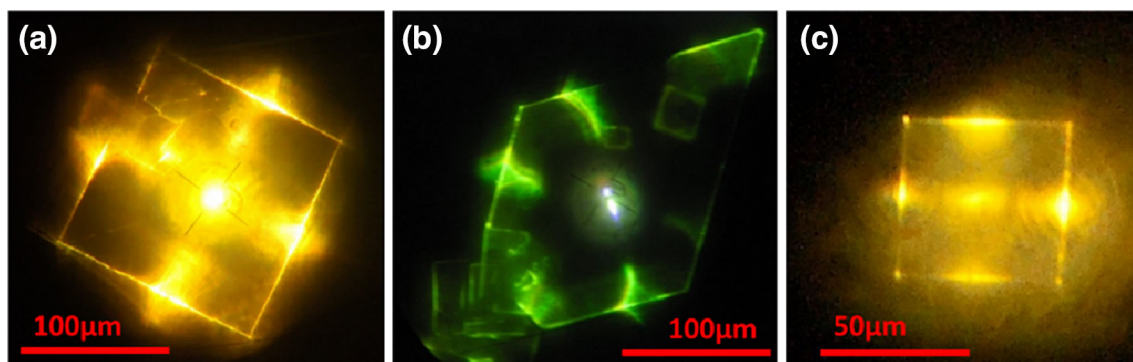
Fig. 3 Microscope images of cross-shaped emission for perylene crystals in different sizes and shapes: α-perylene (**a**, **c**), β-perylene (**b**)

Fig. 4 a Microscope luminescence image of a single α-perylene crystal. **b** Space-resolved emission spectra. **c** 2D maps of the emission intensity at 532, 600, 650, 700 nm
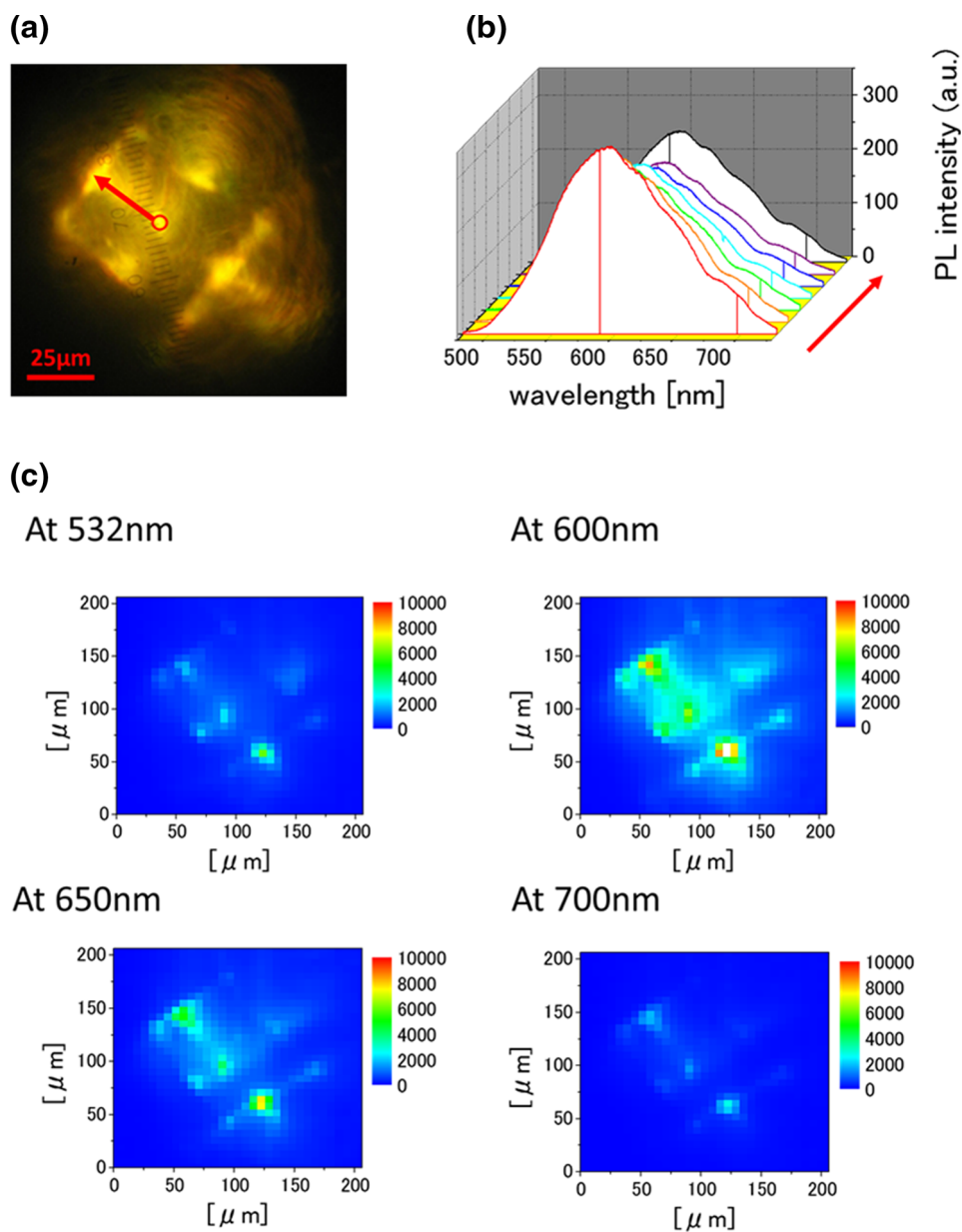
emission intensity at the different luminescence wavelength (532, 600, 650, 700 nm). It deserves highest attention that the emission intensity from the crystal edges is as high as or higher than from the center.

The spatially resolved luminescence spectra show that the cross-shaped emission is identical to the perylene STE luminescence (excimer luminescence). When the excitation laser spot is moved on the crystal surface, the position of the cross-shaped emission also moves in such a way that the two lines which form the cross shape always intersect at the excitation spot. From these results, it is evident that the cross-shaped emission is perylene excimer luminescence, and that the positions of the excited spot and the cross-shaped emission are correlated.

3.3 Waveguide effect in a color glass filter

The result (3.2.) suggests that the waveguide effect may play a crucial role in the present phenomena. Color glass filters are known to exhibit the intense emission at the edges due to the waveguide effect, and with this, we may explain the mechanism how the cross-shaped emission could be formed. Therefore, we measured the luminescence spectra of a glass filter Y50 (HOYA) at two different positions at the excitation spot (A) and the edge of the filter (B) as shown in Fig. 2b. If the emission intensity is higher at the edge than at the excitation spot, then it might imply that the waveguide effect plays an important role to form the cross-patterned emission. Figure 5a, b show the image of the glass filter (Y50) of $50 \times 50 \times 2 \text{ mm}^3$ in size. The transmittance and absorption spectra are shown in Fig. 5c. This filter is transparent to light with a wavelength longer than 500 nm and absorbs one shorter than 500 nm to emit luminescence. Figure 6a shows the luminescence spectra of Y50 measured at two different positions (A and B). As it is seen, the emission intensity is much larger at the excitation spot (A) than at the edge (B). To check the validity of this result, we rotated the sample in such a way that the

edge of the filter faces in the direction of the fiber as shown in Fig. 2c. With this modification, we expect that more luminescence light is collected from the edge, and this is more precise way to compare the emission intensities at the two positions (I) and (II) in Fig. 2c. The result is shown in Fig. 6b. In this case, the luminescence intensity at the edge is larger compared to the previous measurement (Fig. 6a), but it is still clear that the emission is more intense at the excitation spot than at edges.

4 Discussion

The cross-shaped emission of the single perylene crystals seems to be related to the exciton transfer or the waveguide effect. It is remarkable that luminescence occurs at the positions distant by more than 50 μm away from the photoexcitation spot. As possible mechanisms, the following 3 models are conceivable for the dynamics of the cross-shaped luminescence.

[Model 1] After the photoexcitation, free excitons are generated, and they are propagated inside the perylene crystal to the edges. Thereby they are relaxed to the self-trapped excitons to emit excimer luminescence to form cross-shaped emission. (exciton transfer).

[Model 2] After generation of free excitons by photoexcitation, they are immediately relaxed to the excimers to emit excimer luminescence. Then, this emission is propagated inside the crystal aided by total internal reflection to be emitted at the crystal side surfaces. A part of the emission or scattered emission at the crystal edges is directed toward the collection lens, which forms the cross emission. (waveguide effect).

[Model 3] The excitation laser light is scattered at the center to reach the crystal edges. The free excitons are excited there by the scattered light, and they are relaxed to the self-trapped excitons to emit excimer luminescence, which is forbidden transition. At the crystal edges, the
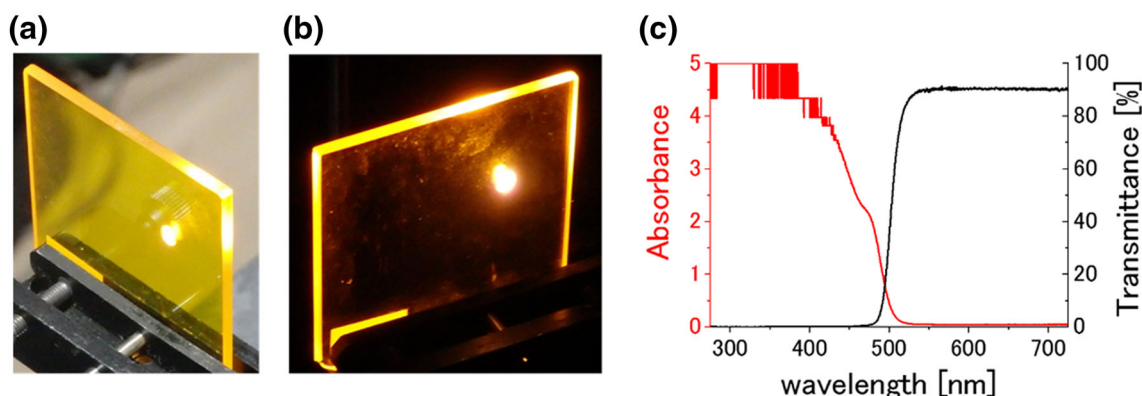
Fig. 5 **a** A color glass filter Y50. **b** The luminescence image of the color filter. **c** The transmittance and absorption spectrum of Y50
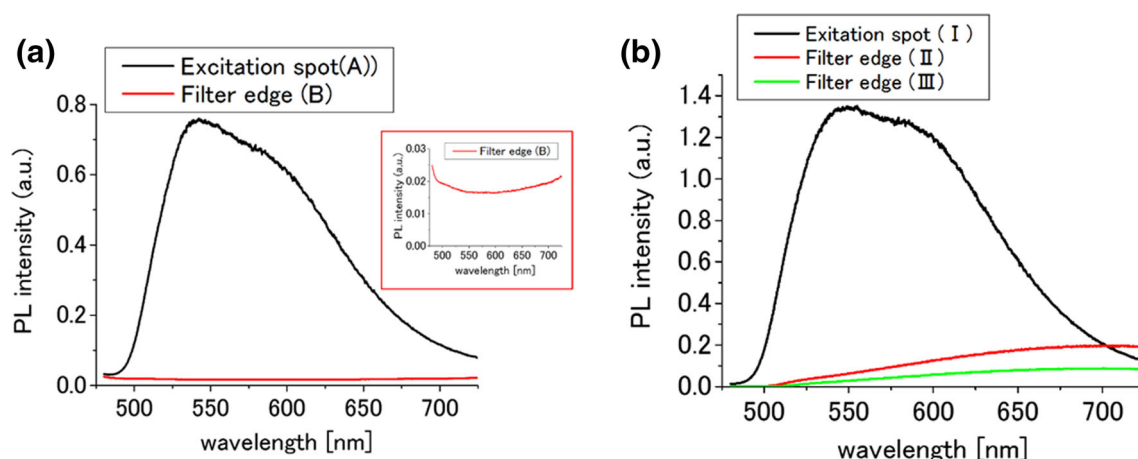
Fig. 6 Luminescence spectra of the color filter (Y50) measured with the experimental setup in (**a**) Fig. 2b and (**b**) Fig. 2c, respectively. Each of the emission spectrum was measured at different positions of the sample filter: the excited spot (*A*, *I*) and the edge of the filter (*B*, *II*, *III*). *Inset* in **a** Magnified spectrum of the edge emission

lower symmetry enhances the radiative transition probability, which forms the cross-shaped excimer luminescence. (enhanced excimer radiative transition at edge).

In the following, we assessed the validity of the three models above from both experimental and theoretical aspects.

[Model 1] We need to estimate the following two parameters to assess the validity of the Model 1: the propagation velocity of the free excitons and the lifetime needed for free excitons to be relaxed to excimers. The relaxation lifetime of free excitons is measured to be within a few picoseconds [17–19], and the propagation velocity is estimated to be much less than the light speed since excitons are populated around the bottom of the exciton band at $K = 0$. Purely theoretically, the velocity of free excitons should be determined by the group velocity in the exciton dispersion (E–k) curve. However, there is little literature which studies the velocity of the Frenkel exciton in terms of the dispersion curves, but the exciton propagation is usually analyzed in terms of diffusion (energy transfer mediated by the transition dipole–transition dipole interaction or the Forster mechanism). This is due to the following reason: After photoexcitation of higher excited states, they promptly relax into the lowest excited states, i.e., free exciton states which have some momentum and spatial distribution. The dynamics of the distribution obeys the Boltzmann equation, but it is difficult either to solve the equation or to determine the precise distribution. Hence, a phenomenological diffusion equation is employed instead. Among crystals of perylene or perylene derivatives, the longest exciton diffusion length reported is 250 nm, corresponding to the lifetime of excitons of about 15 ns [5]. Considering a much shorter lifetime (within a few ps) of excitons in perylene crystals due to self-trapping, therefore,

it is impossible for free excitons to travel over 50 μm distance from the center excitation spot to reach the crystal edges. In fact, the exciton diffusion length is estimated to be as small as 2 nm in β-perylene crystals [20]. Thus, the Model 1 is rejected.

To be strict, a self-trapped exciton is not completely immobilized but can move together with its deformation cloud [23]. A much longer lifetime of excimers as long as 100 ns [14, 15] than free excitons leaves the possibility of excimer transport, but it is difficult to consider this effect quantitatively because of the lack of the study of excimer transport. At least, it is certain that excimer transport is less effective than the waveguide effect of excimer luminescence proposed in Model 2.

[Model 2] If the Model 2 is correct, the emission intensity should decrease as it travels away from the excitation spot. Actually, the experiment on the waveguide effect with the filter clearly demonstrates that the spectrally integrated emission intensity from the edge (B) is much smaller (about 20 times) than that from the excited spot (A) when they are both observed from the front. Even if the edge emission is observed from the side, the difference is nearly 5 times for 10 mm distance (position II) and 10 times for 20 mm distance (position III) from the excitation spot (I). For the cross-shaped luminescence, by contrast, the emission intensity at the crystal side edges is as large as or larger than at the center, as typically shown in Fig. 4c. This cannot be explained by the waveguide effect from the following discussion, so that the Model 2 is rejected.

For α-crystal, the molar density is 5.23 mol/L and the molar absorption coefficient at 408 nm is 1.53×10^4 L/(mol cm) [12], so that the penetration depth of the excitation light is $1/\alpha = 130$ nm, where α is the absorption coefficient. For the filter of 2 mm thickness, the absorbance

at 408 nm is more than 4, so that $1/\alpha = 174\ \mu m$ if the absorbance is assumed to be 5. The refractive index of α-perylene is estimated to be 1.5 at largest, from calculation of dielectric constants according to Ref. [24, 25] as $\varepsilon_{aa} = 1.44 + 0.006\ i$, $\varepsilon_{bb} = 1.83 + 0.003\ i$, $\varepsilon_{cc} = 2.32 + 0.12\ i$, $\varepsilon_{ac} = 0.23 + 0.025\ i$ at 2.4 eV(516.5 nm). This is nearly the same as that of the glass filter. Considering that the thickness of the perylene crystals is about 2 to 3 μm (estimated from the interference spectra of the perylene crystals with the refractive index assumed to be 1.5), the area is about 100 μm × 100 μm, and the excitation spot size is about 2 μm, the relative geometrical sizes of the slab waveguide and the excitation volume in perylene crystals are similar to those for the experiment with the filter. The waveguide effect of excimer luminescence, therefore, should yield the similar intensity ratio of the edge emission vs. the center emission.

Furthermore, the emission intensity from the excitation spot and from the edge is analytically estimated as follows. Suppose the luminescent slab waveguide has a refractive index of $n = 2$ at the luminescence wavelength and high absorbance at the excitation wavelength. For simplicity, we assume a thin circular plate of radius R and thickness D for the waveguide as shown in Fig. 7a and that it is excited at the center for the whole luminescent light emitted from the plate to be collected. We can equivalently assume that the excited volume consists of a point light source which emits a spherical wave with the total photon flux of unity. Because of the high absorbance (short penetration depth) and in order to simplify the analysis, the excitation volume can be assumed to be a circular thin plate of radius $r(<R)$ and thickness d ($<D$) which is luminescent with uniform

intensity, consisting of the uniformly distributed point light sources of the number density N. Spherically radiated light from the point source which is embedded in the $n = 2$ plate is allowed to exit from the plate only within a limited solid angle of radiation due to total internal reflection. For $n = 2$, the light internally incident on the front surface within the incidence angle of 30° is emitted to the outside, while that at an angle larger than 30° is totally reflected to be propagated in the lateral direction. When it reaches the side surface, the light incident within the incidence angle of 30° is emitted from the side surface, as shown in Fig. 7b. In other words, the light incident on the front surface at an angle larger than 60° is emitted from the side surface. To be summarized, the light emitted from the front surface is within the cone of the apex angle of 60° and emitted from the side surface is within the rotationally symmetrical body as shown in Fig. 7c. Since the total photon flux from the point light source is assumed to be unity, 0.067 is emitted from the front surface and 0.5 is emitted from the side surface. The total photon flux from the excitation volume is $\pi r^2 dN$, of which $0.067\pi r^2 dN$ is emitted from the front and $0.5\pi r^2 dN$ is emitted from the side. Therefore, the photon flux density (proportional to the luminescence intensity) from the front surface is $I_f = 0.067dN$ while that from the side surface is $I_s = 0.5\pi r^2 dN/(2\pi RD) = 0.25 r^2 dN/(RD) = (3.73 r^2/RD)I_f$. Note that $R = r$ is the case of luminescent solar concentrators, where $I_s = (3.73R/D)I_f$ with $R \gg D$, realizing a significant solar energy concentration. We substitute the experimental parameters $r = 1$ mm, $R = 10$ mm, $D = 2$ mm into the equation to obtain $I_s = 0.187\ I_f$. If we adopt $n = 1.5$, which is closer to the experimental condition, the ratios of the geometrically

Fig. 7 a Schematic of the waveguide and the excitation volume used for calculations of the total photon flux from the excitation volume. b Incident angle dependence of the area where light is emitted from the waveguide (shown in *red* and *blue lines*) and confined inside the waveguide (*black line*). c, d The ratio of the solid angle with respect to the whole solid angle (depicted as a spherical surface) where light is emitted from the waveguide, with the refractive index of $n = 2$ (c) and $n = 1.5$ (d) (color figure online)
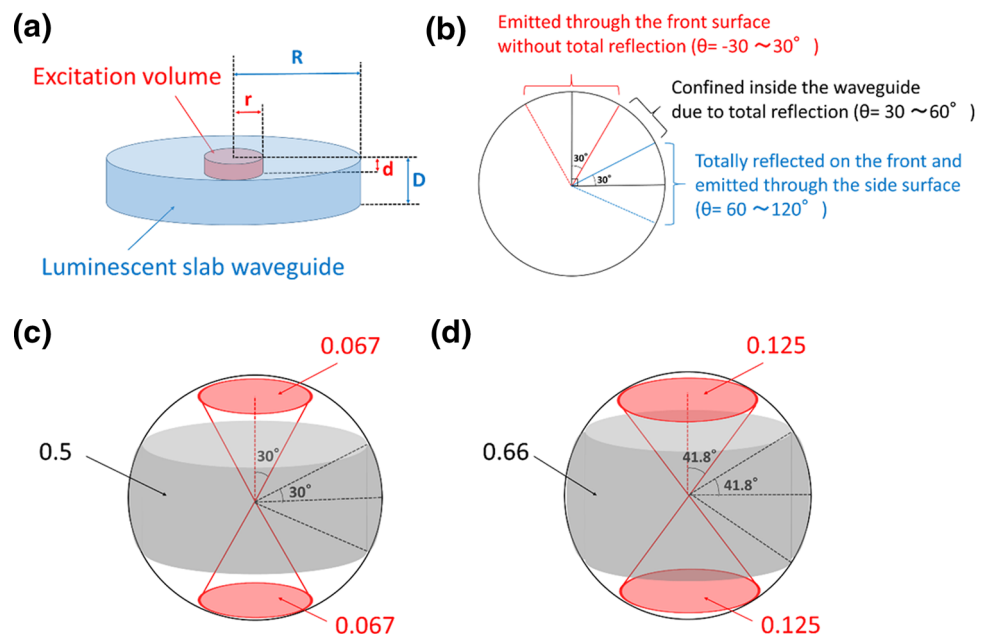
detectable photon flux are changed to as depicted in Fig. 7d to obtain $I_s = 0.132\ I_f$. These estimates explain very well the results in Fig. 6b, although the analysis presumes the case when the whole light emitted over 2π solid angle of observation is collected. If the experimental collection angle determined by the NA of the collection lens is considered, the collected light intensity from both positions is decreased, but the intensity ratio should be almost the same because the collection angle is decreased in the same manner. The result in Fig. 6a could be explained in the present analysis, too, considering the experimental light collection angle carefully.

We also carried out both 2D and 3D FDTD (finite-difference time-domain) calculation to estimate the electric field energy density of luminescence in a perylene crystal, by placing an oscillating linear and point dipoles at the center for 2D and 3D calculations, respectively. The perylene crystal was assumed to be a dielectric having an isotropic dielectric constant of 2. As a result, we found that no significant cavity enhancement effect occurs in the field intensity pattern due to multiple reflection for both 2D and 3D, but the field intensity decays smoothly as the distance from the dipole is increased.

[Model 3] The Model 3 is the one which we think is the most reasonable model to explain the cross-shaped emission. In all the experimental results, the emission intensity at the crystal edges is as high as or higher than at the excitation spot. This is consistent with the Model 3, which claims that lower symmetry at the crystal edges enhances the radiative transition probability of excimers.

Comparison of the perylene excimer photoluminescence dynamics between the crystal center and crystal edge was previously performed by Tahara et al. [17, 18]. They observed significant reduction in the photoluminescence decay time at the edge than at the center, implying possible enhancement in the radiative decay rate of excimers, although they did not argue which of the radiative or non-radiative decay rate is increased. The remarkable experimental fact that luminescence intensity at the edge distant from the excitation spot is higher than that at the excitation spot itself provides strong evidence that the radiative decay rate, i.e., the oscillator strength is significantly enhanced at the crystal edge. The physical mechanism of the enhancement is discussed before summarizing the paper.

Throughout the paper, we have mentioned that the excimer emission occurs at the crystal edge. Considering that the crystal is a 3-dimensional body in reality, we must specify where the enhanced emission occurs on the side surface of the crystal, compared with inside the crystal, namely at the surface, at the edge, or at the vertex? Presently, these differences are not experimentally discriminated directly, but careful consideration may help us to answer. Let us remember that excimers (STE's) are

H-dimers of face-to-face stacking. In the lowest excited state where radiative transition occurs, the transition dipoles of the constituent molecules are aligned anti-parallel to make an optical quadrupole moment. This is why the excimer emission is the forbidden transition, because it is well known that the quadrupole transition probability is about 10^{-6} times lower than the dipole transition probability. If an excimer is on the crystal surface, the transition dipole of one of the constituent molecules which is closer to the surface should be significantly perturbed for a net dipole moment to be induced in the excimer. From this consideration, the enhancement should take place at the crystal surface, and it should be even larger at the edge or at the vertex because of the much lower symmetry.

If significant enhancement occurs at the surface, one cannot neglect the effect of the scattered excitation light which reaches the front surface immediately above the excited spot without attenuation. This may cause the excimer emission larger in intensity at the center than at the edge, where the scattered light reaches attenuated. Even without scattering, the front surface excitation by the incident light itself has a substantial effect. From this consideration, the significant enhancement should occur at the edges and the vertexes, whereas the enhancement at the surface should be only moderate.

5 Conclusion

Cross-shaped excimer (self-trapped exciton) luminescence from perylene single crystals of 50–100 μm was found when they were resonantly excited at the center of the crystals. The luminescence intensity at the crystal 4 side edges was as high as or higher than at the center (excited spot). The phenomena are shown to be irrelevant to the exciton propagation, or the waveguide effect due to multiple internal reflection of scattered light or excimer luminescence, but relevant to the enhanced radiative transition probability of excimers at the crystal edges. They are reasonably explained by the following excitation and emission mechanism.

For the excitation light resonant with excitons, the light is absorbed to yield weak excimer luminescence at the center because it is forbidden transition. At the same time, a part of the excitation light is scattered at the center to reach the crystal edges. The free excitons are excited there by the scattered light, and they are immediately relaxed into self-trapped excitons and subsequently emit excimer luminescence. At the crystal edges (intersection between the two surfaces), the radiative transition probability is significantly enhanced by the lower symmetry to yield more intense excimer luminescence than at the center, despite the fact that it is excited by faint scattered light.

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