



Research paper

# Understanding the emission pattern produced by focused laser beam excitation of perylene square single crystals



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## ABSTRACT

Square single crystals of perylene ( $\alpha$ -crystals) exhibit a peculiar emission pattern when excited by a focused laser beam. Fluorescence spots are observed at the point of excitation and at four edges, with the lines connecting the excitation point and edge emissions being perpendicular to the edges irrespective of the excitation position. Two different mechanisms explaining this emission pattern have been proposed so far. Our newly designed experiment and analysis revealed that the involved mechanism features a combination of the waveguide effect and total internal reflection by crystal edges.

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## 1. Introduction

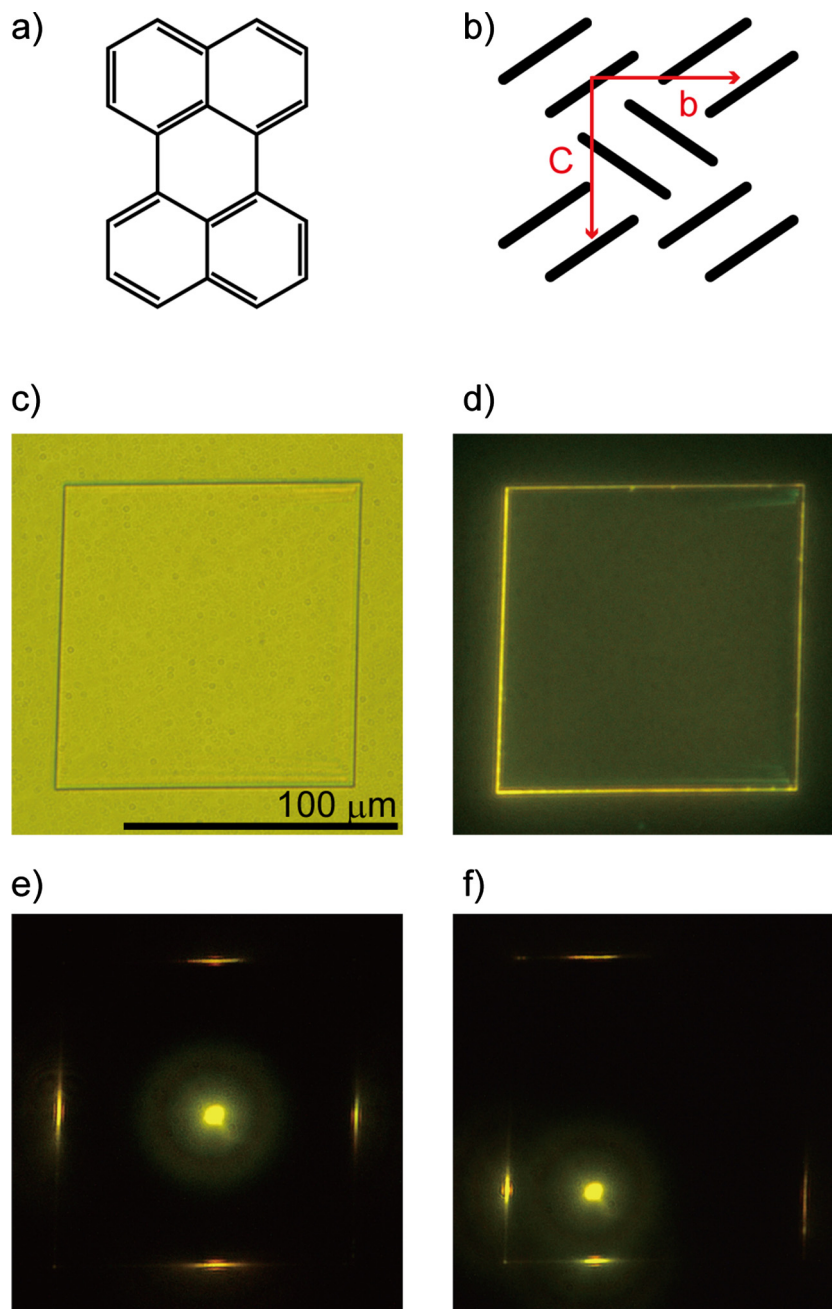
The electronic excited state of an organic crystal composed of aromatic molecules is generally a Frenkel exciton state, and the fluorescence/luminescence properties of such crystals are governed by the excitons and their dynamics. In addition to determining the crystal's fluorescence spectrum, excitons can also influence the spatial distribution of the fluorescence intensity throughout the crystal. Frenkel excitons propagate through the crystal, and thus, fluorescence can occur at positions outside of the area illuminated by the excitation light. The propagation length of a singlet exciton is typically on the nanometer scale [1], whereas that of long-lived excitons, such as H-aggregate excitons [2] and triplet excitons [3], can reach the micrometer scale.

A single crystal of perylene (Fig. 1a) is a typical example of a crystal whose excited state is the Frenkel exciton state. The use of perylene and its derivatives in various electronic and optoelectronic applications, including electroluminescence diodes and solar cells, has attracted substantial interest, and excitons play an important role in these devices [2,4]. Single perylene crystals can be grown using solution-phase or sublimation processes and exhibit two polymorphic forms—the so-called  $\alpha$ - and  $\beta$ -crystals—both of which possess monoclinic  $P2_1/c$  symmetry [5].  $\alpha$ -Crystals contain four molecules per unit cell and exhibit a dimeric structure (Fig. 1b), whereas  $\beta$ -crystals contain two molecules per unit cell and are monomeric. Because of the differences in their crystal structures, the exciton properties of these crystals differ. In both crystals, delocalized free excitons are generated by optical excitation at a wavelength of  $\sim 400$  nm and relax to self-trapped excitons (STEs) because of strong exciton-phonon interaction [6–12]. Thus,

fluorescence from the STE state is substantially red-shifted with respect to the excitation wavelength. Because the energy of the STEs differs between these two types of crystals,  $\alpha$ -crystals exhibit orange fluorescence peaking at  $\sim 600$  nm, and  $\beta$ -crystals display green fluorescence peaking at  $\sim 550$  nm [13]. In addition,  $\alpha$ - and  $\beta$ -crystals also have different morphologies:  $\alpha$ -Crystals exhibit a square plate form, whereas  $\beta$ -crystals possess a rhombic plate form [13]. Therefore, these two crystal types can be easily identified by their fluorescence color (orange or green) and shape (square or rhombic).

Liao et al. reported a peculiar emission pattern of square  $\alpha$ -crystals produced by excitation with a focused laser beam [14]. The emission pattern reproduced by us is displayed in Fig. 1c–f. Fig. 1c and d shows an optical micrograph and a fluorescence microscopy image of a square  $\alpha$ -crystal ( $102 \mu\text{m} \times 102 \mu\text{m}$ ), respectively, with a thickness of a few hundred nanometers. When the center of the crystal was excited with a focused beam at 405 nm (408 nm in Ref. [14]), bright orange emission spots (or lines) were observed at the four crystal edges and the excited position (Fig. 1e). Interestingly, the directions from edge emissions to the excited position are perpendicular to crystal edges. When the laser spot was moved away from the center, the edge emissions also moved, maintaining the perpendicularity of the above directions to the crystal edges (Fig. 1f). Liao et al. recorded edge emission spectra by varying the distance between the edge and the laser spot and observed that the edge emission intensity gradually decreased with increasing distance. Based on these observations, they concluded that the observed emission pattern was attributed to the waveguide mechanism. Namely, the fluorescence radiation from the STE states generated at the laser spot is confined within the crystal and guided in directions perpendicular to the edges.

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**Fig. 1.** (a) Chemical formula of perylene. (b) Structure of perylene  $\alpha$ -crystals, with black bars representing individual molecules. Optical micrograph (c) and fluorescence microscopy image (d) of an  $\alpha$ -crystal. Fluorescence microscopy images were obtained by exciting the central (e) and an off-center position (f).

They claimed that perylene crystals provide an opportunity to investigate such anisotropic waveguiding in organic crystals.

Recently, Tanaka et al. proposed a different interpretation of this emission pattern [15]. They recorded fluorescence microscopy images of  $\alpha$ - and  $\beta$ -crystals excited by the focused laser beam at 408 nm and observed an emission pattern similar to that in Fig. 1e and f. By investigating the intensity distribution of this pattern, the authors found the edge emission intensity to be as high as or higher than that of the excited position. Their theoretical analysis of the intensity distribution showed that the edge emission should be weaker than that at the excited position if the former is caused by the waveguide mechanism. Therefore, the waveguide mechanism was concluded to be inconsistent, and another one was proposed instead. In this mechanism, the excitation laser beam is

scattered at the irradiation spot, reaching the crystal edges. The free excitons produced at the edges by the scattered laser light are relaxed to STEs that cause fluorescence. The radiative transition from the STE to the ground state is forbidden in bulk crystal [14]. However, the symmetry at the crystal edges is lowered compared to that in bulk crystal, enhancing the radiative transition. Consequently, the fluorescence intensity at the edges can exceed that at the excited position. They also considered the exciton propagation mechanism, in which the free excitons generated by laser excitation propagate through the crystal to the edges, relax to STEs, and emit orange fluorescence at the edges. However, they concluded that the free excitons cannot reach the crystal edges within their lifetime.

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