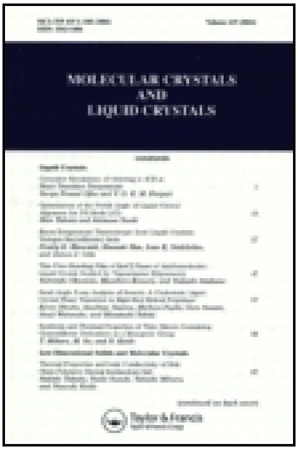

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Amplified Spontaneous Emissions from π-Conjugated Dye Doped Polymer Film with Possible Dye Ordering

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Smooth polymer films doped with π-conjugated organic dyes, formed around a multimode silica fiber under the influence of capillary force, exhibited very narrow photoluminescence peaks upon laser excitation as compared with the fluorescence in solution. The peak position showed no dependence on the excitation wavelength, indicating that it could not be explained by a whispering gallery mode that should be observed in a medium with broad optical gain. The peaks can be explained by amplified spontaneous emissions (ASE) because the intensity depended linearly on the excitation intensity with a threshold. When the dye-doped film was formed on the portion of a fiber with the clad etched out and was excited by the linearly polarized laser propagating inside the fiber core, we observed ASE peaks not of the dyes but of the optical fiber itself, suggesting the possibility that the dyes were oriented with their transition moment pointing parallel to the film surface, therefore incapable to be photoexcited. These fiber ASE peaks shifted to longer wavelength when we varied the excitation wavelength to shorter wavelength, which clearly ruled out the possibility of silicate Raman scattering as the origin.

Keywords: dye assembly; dye doped; photoluminescence; pi conjugated dye; polymer film

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INTRODUCTION

Under the influence of both the capillary force and the electrostatic attraction, self-organized arrays of sub-micrometer particles of organic dye were formed on a glass substrate and they did not show near-field photoluminescence (PL) under near-field excitation [1]. Polarized evanescent field excitation showed the PL with the intensity depending on the polarization direction of the excitation, suggesting that dye molecules were unidirectionally oriented within every particle [2]. The observation further suggested that this orientation was correlated between adjacent particles, proving that the dye particles were formed in a self-organized manner. Particles formed from dye-polymer mixture, however, were not reported to have such dye ordering [3]. To elucidate the underlying mechanism leading to the dye ordering, we have prepared dye specimen embedded in a transparent polymer film, where the dyes should be under the influence of capillary force during the film formation, however this capillary force would be substantially modified by the existence of the polymer. Such transparent polymers are generally regarded as good host materials to hold the dye molecules, presumably in well-dispersed manner and in a random orientation, providing a homogeneous medium of the established index-of-refraction and with broad gain spectrum [4]. Homogeneity of the resulting film suggests the influence of capillary force that may induce some sort of self-organization of dye molecules. In this paper we compare amplified spontaneous emissions (ASE) of thus formed dye-doped films under different excitation schemes. Especially to excite them by optical fields polarized vertically to the film, we have fabricated a cylindrical film around a silicate optical fiber and optically pumped it by a linearly polarized laser propagating inside the fiber core to compare with the side excitation.

MATERIALS AND METHODS

Pyrromethene 597 (2.5 mg, Exciton Inc., Fig. 1(a)) was dissolved in 8 ml chloroform solution of 40 mg polymethylmethacrylate (PMMA, $M_w = 1.36 \times 10^4$, Fig. 1(b)) polymer. Other π-conjugated dyes, rhodamine 6G (Rh6G) and pyridine 4, were also dissolved in chloroform solution of PMMA at similar concentration. A multimode silica fiber was dipped in this specimen solution and a cylindrical dye-doped polymer film was formed around the fiber surface with 125 μm diameter [5] (Fig. 1(c) inset). Since the specimen prepared in air atmosphere degraded under laser excitation, the specimen was prepared in a glove box filled with argon. Dried nitrogen gas was bubbled through the

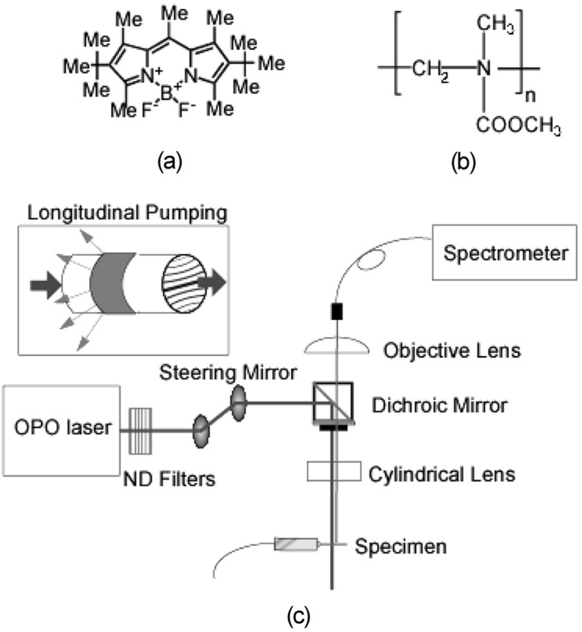

FIGURE 1 (a) and (b) Molecular structure of pyrromethene 597 dye and transparent host polymer PMMA, respectively. (c) Optical setup for the PL detection with "transverse" pumping. Inset: Dye-doped polymer film formed around the multimode fiber surface and the "longitudinal" pumping scheme with optical fields vertical to the film.

solvent chloroform in advance to remove oxygen and water from the solvent. For optical reflection measurement at a fixed incident angle to evaluate the absorption, a dye-doped polymer film was formed on a flat glass plate with a similar procedure.

The film was "transversely [6]" pumped by an optical parametric oscillator laser (OPOTEK Opolette 355 II, variable wavelength, 5 ns pulse width, 2 mJ/pulse at 20 Hz repetition rate) focused by an $f = 8$ mm cylindrical lens to an estimated beam waist of about 8 μm by 2 mm (Fig. 1(c)). PL from the specimen was collected by the same cylindrical lens, passed through a dichroic filter block, and coupled into a bundle optical fiber whose constituent nineteen fibers were realigned at the spectrometer entrance perpendicular to the dispersing direction of the spectrometer, enabling an efficient collection of photons without sacrificing the wavelength resolution. The PL spectrum was recorded by a back-illuminated CCD camera cooled down to −70°C by Peltier elements with on-chip multiplication capability

(Princeton Instruments, PhotonMAX:97EMB). For comparison the specimen was also "longitudinally [6]" pumped (Fig. 1(c) inset), i.e., pumped by the polarized laser propagating inside the fiber core, and the resulting PL was recorded using the similar arrangement of dichroic filter block and spectrometer. In this scheme, the excitation optical fields are almost vertical to the fiber surface and becomes zero where the fields point parallel to the surface.

RESULTS AND DISCUSSION

Figure 2 shows the PL spectra of a pyrromethene-doped film with varying power of the excitation laser at 525 nm. Three sharp peaks emerged at 590.3, 611.5, and 617.0 nm above the broad luminescence when the excitation power was increased. The peak at 525 nm is the excitation light remaining even in the presence of a dichroic filter that rejects the light below 585 nm. The peak height at 590.3 and 611.5 nm increased proportionally with the amount of excitation power over the 0.15 mJ threshold as shown in the Figure 2 inset, suggesting that these peaks represent ASE. The peak at 590 nm was in good

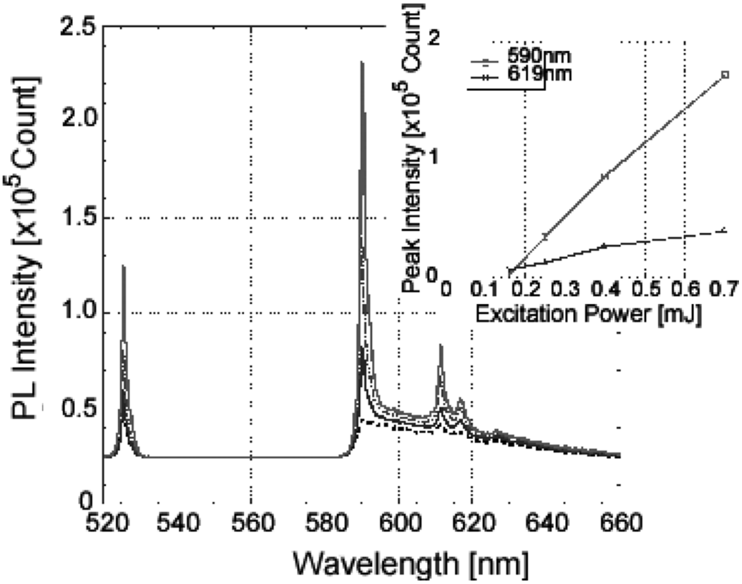

FIGURE 2 PL spectra of a pyrromethene-doped film with varying powers of the "transverse" excitation at 525 nm. Inset: Dependence of major two peak intensities on the excitation power.

agreement with the reported lasing wavelength 582–597 nm of the dye in ethanol or *p*-dioxane solution [7,8]. The relative intensity of the three peaks depended strongly on individual samples and also varied with subtle difference in excitation alignment. Figure 3 shows the PL spectra of another specimen that showed a PL peak only at 611.5 nm (indicated by an arrow), two other peaks at 590.3 and 617.0 nm missing independent of the excitation power, even around the threshold level of excitation.

If this single peak were selected as a result of mode competition, we could expect all the three peaks would appear near the threshold. The fact that we did not observe any mode competition depending on the excitation power indicates that the PL peak should be ascribed to an ASE whose peak position was determined by the electronic state of the dye, not by the ring-cavity modes of the cylindrical film [4].

When the excitation wavelength was changed, this PL peak position stayed unchanged as shown in Figure 3, which indicates that the optical gain of the film was achieved at fixed wavelength, instead of having a broad gain spectrum, further suggesting that the electronic property of the dye determined the ASE peak position.

By varying the focus under microscope observation, film thickness was estimated to around several micrometers. This thickness may

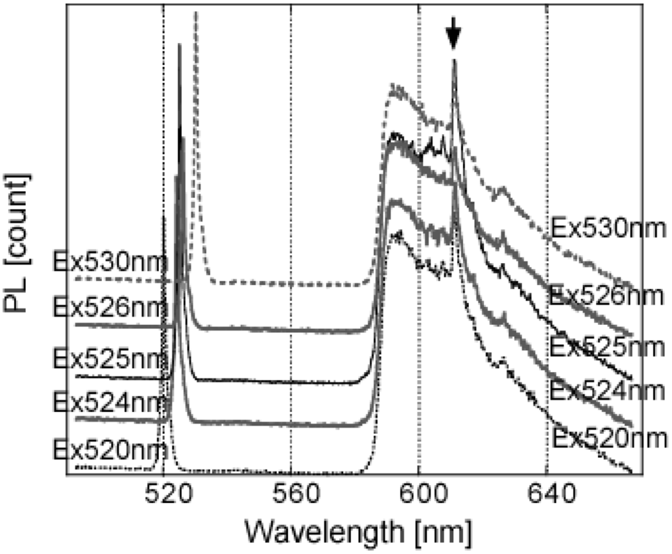

FIGURE 3 Dependence of PL spectrum on the excitation wavelength with "transverse" pumping.

be the reason why not observing whispering gallery modes in the PL spectra and why the threshold excitation level was much higher than those reported [4–7] on similar π-conjugated organic dye specimens. Another possibility was a partial and inhomogeneous illumination of the specimen: the focused excitation beam waist of 8 μm was much smaller than the specimen diameter 125 μm. We used a lens with high numerical aperture to collect the specimen PL photons at high efficiency, which could have lead to unpreferable heat strain to the specimen by the excitation laser. However these possibilities can not explain the fact that our dye-doped film did not have broad gain spectrum, but had gains at specific wavelengths with irregular interval. This gain specificity suggests that it reflects an excitonic band of regular assembly of dyes.

To inspect possible dye assembly, the dye-doped film was then "longitudinally" pumped, i.e., pumped from the inside of the fiber by a polarized laser propagating in the fiber core (as shown in Fig. 1(c) inset). A sharp peak was observed, but at different positions from those of "transverse" pumping, as shown in Figure 4. The peak was

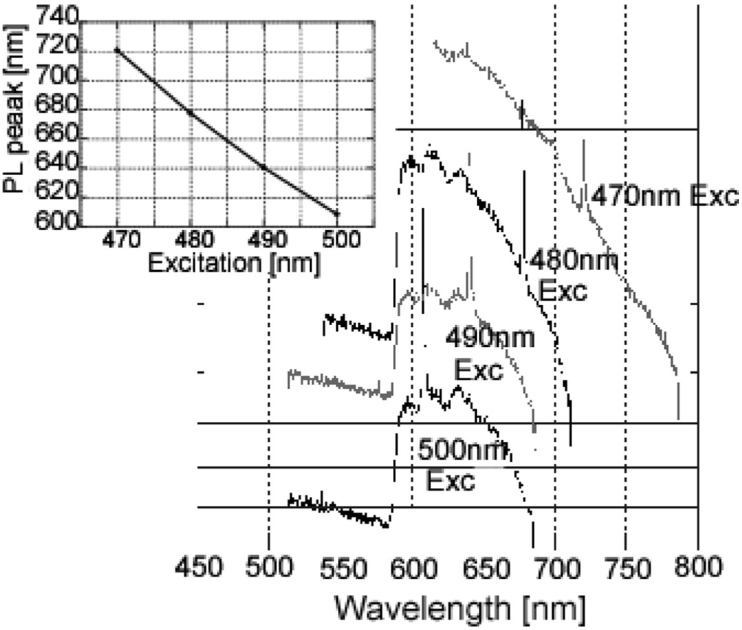

FIGURE 4 Dependence of PL spectrum on the excitation wavelength with "longitudinal" pumping. Inset: Dependence of PL peak position on the excitation wavelength.

also observed and the position was identical even when we used an optical fiber without any specimen film. Therefore the sharp PL peak in Figure 4 should be interpreted as arising from the optical fiber itself. Since we observed the peak only when we coupled a strong laser light into the core region of the fiber, this luminescence should also be an ASE and metal ions doped in the core may be responsible for the sharp PL peak in this case. As shown in Figure 4 inset, the peak position shifts 110 nm to longer wavelength when we moved the excitation wavelength by 30 nm to shorter wavelength. The PL peak position showed linear dependence on the excitation power, but the shift direction was reversed, indicating that this peak could not be assigned as Raman scattering of the silicate fiber. Although we have no explanation of the mechanism of this peculiar PL peak behavior at present, the dependence on the excitation wavelength and the high threshold suggest that nonlinear optical processes may be involved in this ASE.

Then we have etched a portion of fiber to remove the clad region (8 μm thickness) and formed a dye-doped film around the exposed core (final diameter was 60 μm). When excited similarly by a linearly polarized laser coupled in the core, observed ASE was still not of the dye, but of the fiber core, suggesting the possibility that the dyes were not excited because of the orientation of their transition moment pointing parallel to the film surface, therefore perpendicular to the electric field of the excitation. Major optical mode HE_{11} propagating in the core, that a linearly polarized laser efficiently coupled to, has almost unidirectional electric field (orthogonal fields have relative intensity of about -30dB) parallel to the end facet of the cleaved fiber, and almost perpendicular to the fiber surface. The field intensity becomes zero where the electric field is parallel to the surface. Dye ordering with the transition moment pointing parallel to the film surface was also observed in the self-organized particles of Rh6G without polymers [2], and would explain the gain specificity of our dye-doped film.

We further tried to prepare thin-films doped with Rh6G and pyridine 4, shown in Figure 5(a) and (b), respectively. Though we did not observe ASE's in both specimens, Rh6G-doped films show metallic reflections under slant illumination of room light (Fig. 5(c)). It showed a uniform reflection spectrum, which should be proportional to the absorption spectrum, over a wide visible wavelength, even without an annealing to put the film into a thermodynamic equilibrium, as shown in Figure 5(d). These observations imply that some dye aggregates were grown inside the Rh6G-doped film due to the capillary force exerted while the doped film formation, similar to the one observed in the self-organized dye particles without polymers [2],

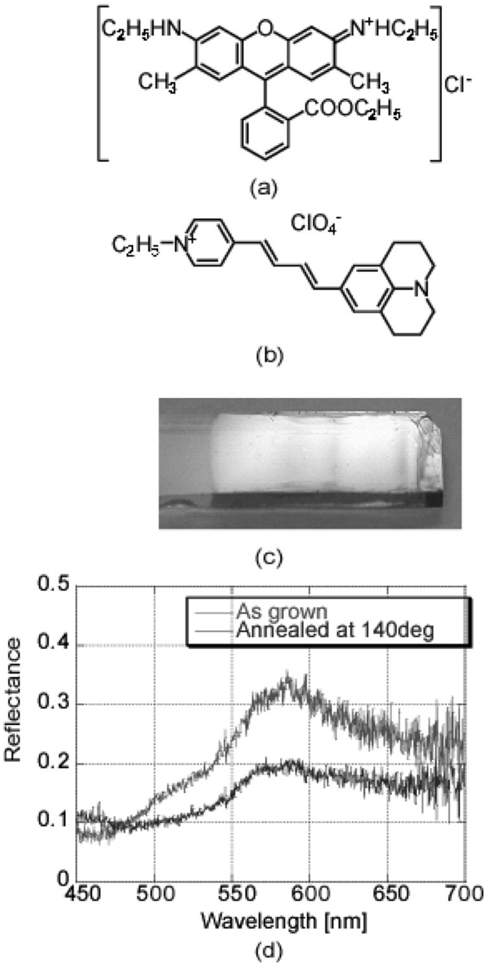

FIGURE 5 (a) and (b) Molecular structure of Rh6G and pyridine 4 dye, respectively. (c) Appearance of a Rh6G-doped polymer film slantly illuminated with room light. (d) Photoreflectance spectra of the Rh6G-doped polymer film at normal incidence before and after 1 hour annealing at 140°C.

further supporting the possibility of ordered dye assembly also in the case of pyrromethene due to the capillary force.

CONCLUSION

Polymer thin film doped with a π-conjugated organic dye showed sharp peaks over a broad PL spectrum upon photoexcitation over a threshold intensity. These PL peaks were ascribed to ASE based on the observation that the peak wavelengths were unchanged while varying the excitation wavelength. The dye ASE peaks disappeared, and the ASE from the optical fiber itself was observed, when a dye-doped film formed around the bare core of a fiber was excited by a polarized laser propagating inside the fiber core. It suggests the possibility that the dyes were oriented with their transition moment pointing parallel to the film surface. In contrast to many reports that observed series of whispering gallery modes, where the ASE peak position was determined by the cavity geometry, the ASE of our film may be determined by the excitonic structure of the possible dye assembly, which enabled a single mode ASE.

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