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Novel Polarized Photoluminescent Films Derived from Sequential Self-organization, Induced-Orientation, and Order-Transfer Processes

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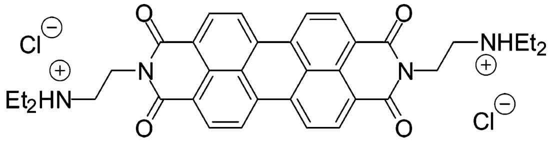
The fabrication of materials and devices through molecular self-assembly and self-organization processes is becoming one of the premier frontiers in chemistry.[1−18] In this communication, we present the fabrication and properties of a novel photoluminescent polarizer that exploits the self-organization and induced orientation of the readily available fluorescent mesogen, *N*,*N*′-bis(*N*,*N*-diethylaminoethyl)perylene-3,4:9,10-bis(dicarboximide) dihydrochloride **1**.



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Photoluminescent polarizers are an essential component of a recently developed polarization sensing technique for visual detection of analytes.[19,20] In addition, photoluminescent polarizers may be used in place of the combination of sheet polarizer and color filters employed in color liquid-crystal displays.[21−23] Because of the wide applications of visual displays, the development of processes that allow cheaper and simpler manufacturing of materials and more flexible designs of components for displays has been an active area of research.[24] Novel approaches to the fabrication of photoluminescent polarizers that employ readily available fluorophores and allow direct deposition of polarizing materials on device substrates may facilitate the development of display technologies and other optical devices.

Perylenebis(dicarboximide) derivatives are known to be excellent fluorophores with quantum yields as high as 0.99 in solution.[25−28] Their photophysical and semiconducting properties, along with high thermal and photochemical stabilities,[29,30] render them particularly useful as laser dyes, fluorescent probes, and photoconducting and photovoltaic materials in optoelectronic devices.[13,31] We reported previously[32,33] that **1** self-organizes in aqueous solution to form a lyotropic, chromonic liquid-crystalline phase. When a mechanical force is applied to coat the liquid-crystalline solution of **1** onto a glass slide, the shearing force simultaneously induces the orientation of the liquid-crystalline domains into bulk order. This order is then transferred to the solid state by evaporation of solvent under ambient conditions. Previous studies indicated that the long molecular axis and the absorption transition moment of **1** are aligned perpendicular to the shearing direction of the films.[33] In addition, polarized infrared spectroscopy studies suggested edge-on orientation of the molecules on the glass substrate, and small-angle X-ray diffraction studies suggested a distorted hexagonal packing of **1** in the films.[33] These films exhibit highly anisotropic absorption of light with dichroic ratios (the ratio of absorbances in the directions perpendicular and parallel to the shearing axis) that routinely exceed 25. We expected these films to exhibit polarized fluorescence emission and therefore sought to examine the fluores-

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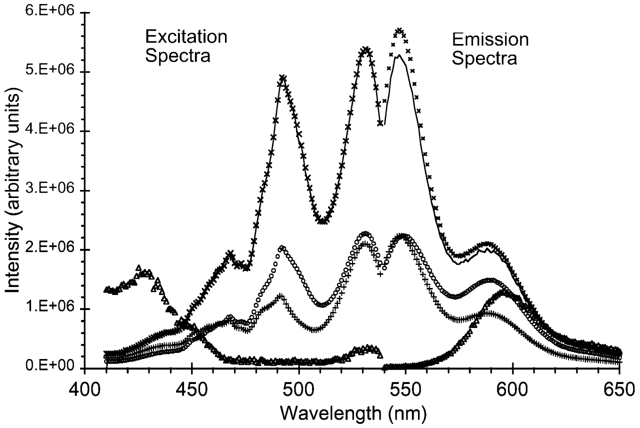

Figure 1. Excitation spectra (400−540 nm, acquired at an emission wavelength of 547 nm) and emission spectra (540−650 nm, acquired at an excitation wavelength of 530 nm) of **1** in aqueous solutions. (—) 3.5×10^{-8} M (the signal intensity was magnified by 100× to allow comparison with spectra at other concentrations); (×) 3.5×10^{-7} M (intensity magnified by 10×); (○) 3.5×10^{-6} M; (+) 3.5×10^{-5} M; (△) 3.5×10^{-4} M (intensity magnified by 100×).

cence properties of **1** in solution and in the oriented solid films.

Fluorescence emission was observed from aqueous solutions of **1** at concentrations as low as 10^{-9} M. The emission intensity increased linearly with increasing concentrations up to at least 3.5×10^{-7} M (Figure 1). With rhodamin 6G as the reference standard,[34,35] the quantum yield of **1** in a 1×10^{-7} M solution was determined to be 0.12. The excitation maximum at 530 nm and weaker peaks at 493 and 468 nm may be assigned to the S_0-S_1 electronic transition and its vibronic progressions.[12,25,26,36,37] The emission peaks were at 547 and 590 nm. Deviation from linearity occurred at higher concentrations and the emission intensity gradually decreased with increasing concentrations. Furthermore, changes in spectral shape were observed. At concentrations around 3.5×10^{-4} M, the excitation and emission maxima shifted to 430 and 597 nm, respectively. Presumably, the formation of H-aggregates[33] at concentrations above 10^{-7} M results in the changes of fluorescence spectral properties in addition to the decrease in emission intensity caused by self-absorption and increased nonradiative decay.

The excitation and emission spectra of the sheared solid films (Figure 2) differ significantly from those of the dilute solutions, presumably due to intermolecular interactions in the solid state. The $\lambda_{\max}$ of the broad excitation band was at about 490 nm and the emission band covered the range from about 600 to 800 nm with a maximum at 690 nm. The large Stokes shift may offer advantages for applications of these films in optical devices or in analytical applications. For instance, it may allow excitation light to be filtered easily from emitted light, greatly simplifying optics design. The solid films of **1** may also be useful as optical materials

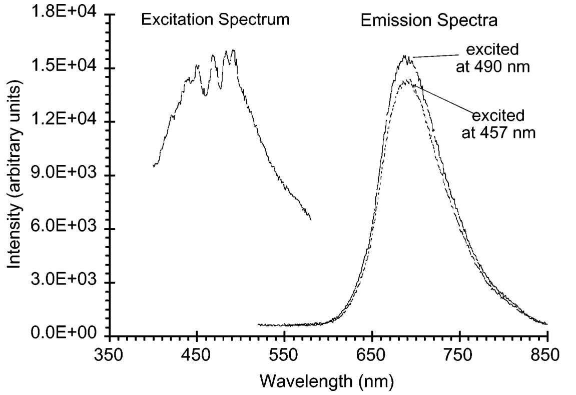

Figure 2. Excitation spectrum (400−580 nm) of a sheared film of **1** was acquired at an emission wavelength of 690 nm. The emission spectra (530−850 nm) were acquired at excitation wavelengths of 490 nm (—) and 457 nm (- - -).

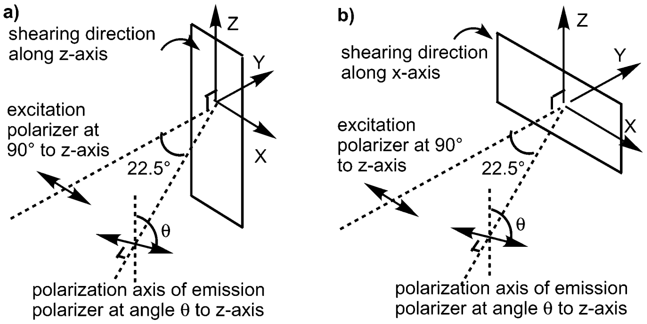

Figure 3. Schematic diagram showing the relative orientations of the sample and the polarization axes of the excitation and emission polarizers. The sample was mounted with the shearing direction along (a) the *z*-axis and (b) the *x*-axis.

that emit near the red limits of the visible spectrum. The quantum yield of **1** in the solid films was very low, estimated to be about 10^{-8}, presumably due to self-absorption and self-quenching in the solid phase. Nevertheless, fluorescence emission from the films can be observed because of the high density of **1** ($\sim 1 \times 10^{-7}$ mol/cm^2) in the films in addition to the large extinction coefficient of **1**.[33]

Polarized fluorescence emission from the oriented films of **1** was examined with the polarization axes of the excitation and emission polarizers set in the same direction (horizontal, $\theta = 90°$). Initially, the films were mounted in an orientation (shearing direction along the *z*-axis as shown in Figure 3a) such that the highest absorption of the polarized incident light occurred. When excited at 457 nm, intense fluorescence emission was observed. The films were then rotated 90° (as shown in Figure 3b)[38] such that the absorption transition dipoles of the majority of the molecules were oriented perpendicular to the polarization axis of the incident light. Consequently, the emission intensity decreased dramatically. Representative spectra of the polarized emission of the films studied are shown in Figure 4. At 690 nm, the ratio of the emission intensity I_{z90} (when irradiated perpendicular to the shearing direction) to I_{x90} (when irradiated parallel to the shearing direction) for this film was calculated to be 30 ± 2. The dichroic

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[38] By rotating the solid sample instead of the emission polarizer, the effect of the polarization bias of the emission monochromator was minimized.

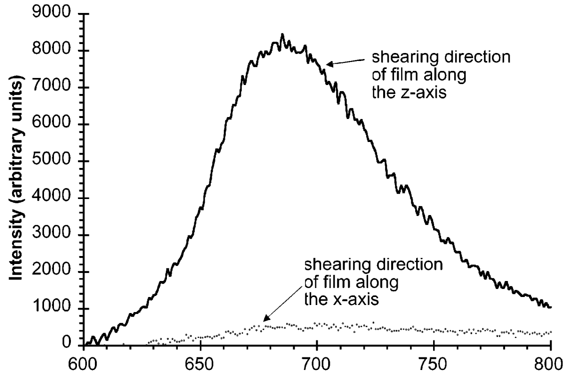

Figure 4. Fluorescence emission spectra of a film of **1** with shearing direction along the *z*-axis (—) or *x*-axis (···). Both the excitation and emission polarizers were in the horizontal positions ($\theta = 90°$).

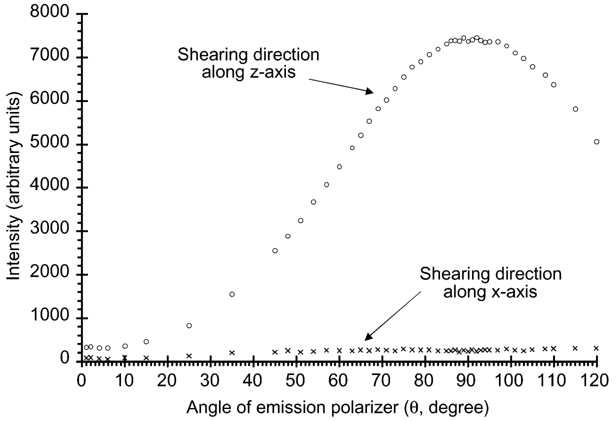

Figure 5. Emission intensity at 690 nm of an oriented film of **1** as a function of θ. The polarization axis of the 457-nm excitation light was along the *x*-axis (see Figure 3a). The shearing direction of the film was along the (○) *z*-axis and (×) *x*-axis. The data shown were corrected for background due to scattered light and dark counts but uncorrected for the polarization bias of the fluorometer.

ratio (A_z/A_x) of the same film at 457 nm was determined to be 36 ± 1.

To further examine the anisotropic fluorescence properties of oriented films of **1**, we studied the angular dependence of emission intensity upon excitation with incident light linearly polarized along the *x*-axis (horizontal). Figure 5 shows the results for the same film that was used to obtain the spectra shown in Figure 4. Again, the film was mounted in an orientation (as shown in Figure 3a) such that the highest absorption of the polarized incident light occurred. The emission intensities at 690 nm were collected at different angles ($\theta = 0°-120°$) of the emission polarizer and plotted as a function of θ. The highest emission intensity of the film was observed when θ was ~90° (the angle at which the polarization axes of the emission and excitation polarizers were parallel). After correction for background and the polarization bias (caused by differences in the transmission of horizontal vs vertical polarized light) of the fluorometer, the emission intensity at 90° (I_{z90}) was found to be about 4.2 times higher than the intensity at 0° (I_{z0}). This result is expected for compounds that have their emission dipoles aligned with their absorption transition dipoles.[37] The value of the fluorescence anisotropy[39] (calculated as $(I_{z90} - I_{z0})/(I_{z90} + 2I_{z0})$) was 0.52 ± 0.03, indicating that significant fluorescence depolarization occurred. The values of I_{z90}/I_{z0} and anisotropy obtained for the other films studied were as high as 5.0 and 0.57, respectively. We also attempted to determine the fluorescence anisotropy of the film when its shearing direction was along the *x*-axis (as shown in Figure 3b). However, the emission intensity was too low to allow reliable determination of the anisotropy.

The fluorescence depolarization observed was presumably caused by three factors. First, as for most compounds, the radiating dipole may not be collinear with the absorption transition dipole (a small angle may exist between these vectors).[39] Second, differential reabsorption of the emitted light may occur. Third, although these solid films of **1** were highly oriented, the presence of molecules aligned at different angles to the *z*-axis was expected. Energy transfer among these closely packed molecules in different directions of the film would lead to fluorescence depolarization. Nevertheless, because of the high dichroic absorption (A_z/A_x) of these films, the overall fluorescence emission of the oriented films of **1** remained highly anisotropic (as indicated by the ratio of I_{z90}/I_{x90} that was as high as 30). Detailed studies to investigate the causes of depolarization are underway.

In summary, this work demonstrates the feasibility of fabricating highly anisotropic fluorescent films by the induced orientation of fluorescent liquid-crystalline compounds, although the practical uses of the films of **1** may be limited by the low quantum yield in the solid phase. The application of this straightforward procedure to other fluorescent mesogens with higher quantum yields is being explored.

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Supporting Information Available: Experimental conditions (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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