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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE January 11, 1999	3. REPORT TYPE AND DATES COVERED Technical Report # 45		
4. TITLE AND SUBTITLE J-Aggregation and Excimer Emission of Anisotropic Solutions and Solid Films of a Liquid Crystalline Conjugated Polymer		5. FUNDING NUMBERS N00014-94-1-0540 Kenneth J. Wynne R & T Code 3132111		
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Rochester Department of Chemical Engineering 206 Gavett hall, Box 270166 Rochester, NY 14627-0166		8. PERFORMING ORGANIZATION REPORT NUMBER # 45		
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 North Quincy Street Arlington, VA 22217-5000		10. SPONSORING / MONITORING AGENCY REPORT NUMBER		
11. SUPPLEMENTARY NOTES Submitted for publication in MACROMOLECULES.				
a. DISTRIBUTION / AVAILABILITY STATEMENT Reproduction in whole or in part is permitted for any purpose of the United States Government. This document has been approved for public release and sale; its distribution is unlimited.		12. DISTRIBUTION CODE		
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14. SUBJECT TERMS J-aggregation; excimer emission; exciton coupling effects; liquid crystalline polymers; smectic C phases; self-ordered solid films; luminescent polymers.		15. NUMBER OF PAGES 17		
		16. PRICE CODE		
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Unlimited	

OFFICE OF NAVAL RESEARCH

GRANT NO: N00014-94-1-0540

R&T Code 3132111

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Technical Report NO. 45

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By

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Submitted for Publication

In

MACROMOLECULES

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January 11, 1999

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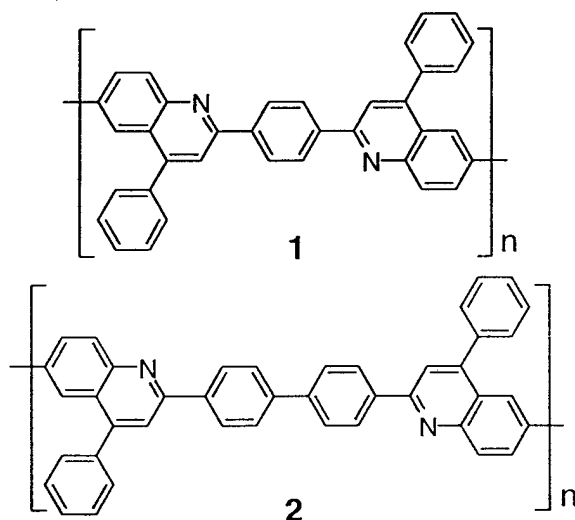
Abstract

Novel features in the absorption and emission processes in liquid crystalline solutions and solvent-cast, self-ordered solid films of a luminescent conjugated polymer are reported. Dominant excimer emission with a minor blue edge aggregate emission were observed in isotropic solid films spin coated from isotropic solutions of polyquinoline 2. New, strongly red shifted, absorption and excitation bands observed in concentrated solutions exhibiting Smectic C like mesophase evidenced J-aggregation but the emission was characteristic of excimers. J-aggregated chromophores with excimer luminescence and emission dichroism were also observed in solvent-cast ordered solid films. These results demonstrate that excimer emission can arise from J-aggregates or ground state complexes of conjugated polymers. The results also exemplify how the interplay of self-organization and solution processing method can significantly influence the photophysics of conjugated polymers.

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π -conjugated polymers are often considered to be quasi-one-dimensional (1D) semiconductors or natural quantum wires because of the dominant roles of *intramolecular* structure (conjugation length, conformation, geometric relaxation, etc) on their electronic structure and electronic, optical, and nonlinear optical properties.^{1, 2} However, there is growing evidence that self-organized supramolecular assemblies of conjugated polymers with local or global 2D or 3D order can exist in solid films²⁻¹⁰ and even in relatively dilute solutions,^{8b, 10} resulting in significant modification of photophysics, charge transport, and other properties.²⁻¹⁰ Recently, we reported observation of *J-aggregates* of the conjugated polyquinoline **1** and its side-chain derivative in dilute solutions (20 mM or less) and solid films spin coated from the isotropic solutions.¹⁰ Here, we report novel features in the absorption and emission properties of liquid crystalline solutions and solvent cast, self-ordered, solid films of a luminescent conjugated polyquinoline **2**. Excimer emission and polarized photoluminescence are observed from the J-aggregated chromophores in liquid crystalline solutions and solid films. The results demonstrate how the interplay of self-organization and method of solution processing can significantly influence the morphology of solid films and the photophysics of conjugated polymers.



Many dye molecules are well known to aggregate in solution, at surfaces, and in self-organized media into ordered supramolecular assemblies having strong intermolecular exciton coupling effects that lead to bathochromic shift (J-aggregates) or hypsochromic shift (H-aggregates) in spectral properties compared to the isolated molecules.¹¹⁻¹³ In the case of J-aggregates of dyes, the exciton coupling effects can extend over hundreds of molecules and result in novel cooperative optical properties such as resonant emission, enhanced radiative emission rate (superradiance), and enhanced nonlinear optical properties.¹³ Our laboratory is currently investigating chromophore aggregation in self-organized assemblies of conjugated homopolymers¹⁰ as well as rod-coil block copolymers containing conjugated polymer blocks.¹⁴ Results of the former studies, reported here, suggest that J-aggregates of conjugated polymers are very promising model systems for fundamental studies of exciton coupling effects, finite size effects, and cooperative properties as well as for applications in light emitting devices.

Solutions and solid films of the conjugated rodlike poly(2,2'-(p,p'-biphenylene)-6,6'-bis(4-phenylquinoline)) (PBPQ, **2**) were investigated by polarized optical microscopy (POM), UV-visible spectroscopy, and photoluminescence excitation (PLE) and emission (PL) spectroscopies at room temperature (23°C). The synthesis^{15a} and linear optical,^{15b} nonlinear optical,^{15c,d} electrochemical^{15e} and electroluminescent^{15f} properties of PBPQ have been described. The PBPQ sample had an intrinsic viscosity of 8.5dl/g in 0.1 mol % di-*m*-cresyl phosphate/*m*-cresol which implies a very high molecular weight.^{15a} The PLE and PL spectra were taken on a Spex Fluorolog – 2 spectrofluorimeter by using the front face configuration as described previously.^{2, 14}

Dilute formic acid solutions of PBPQ (10 mM, 0.5 wt % or less) between a microscope slide and cover glass were observed under crossed polarizers of an optical microscope and found to be completely isotropic. However, investigation of these dilute solutions of PBPQ by PLE and PL spectroscopies showed clear evidence of J-aggregates similar to previously reported results for polyquinoline **1**.¹⁰ For example, the characteristic, sharp, red shifted J-band at 490 nm for the 10 mM solution, resolved by PLE, was accompanied by a resonant emission band (see Supplementary Material). Progressive solvent

evaporation from these dilute solutions at ambient room temperature (23°C) produced concentrated solutions exhibiting liquid crystalline (LC) mesophases as revealed by POM observations.

Figure 1a shows a typical texture of an LC solution of PBPQ (ca. 30 wt %). The observed LC texture is similar to the characteristic sanded texture of the smectic C (S_C) phase.¹⁶ Although concentrated solutions (>10 wt %) of PBPQ and other rodlike polyquinolines have been reported to exhibit LC mesophases, however, their textures have not previously been assigned.^{15a, 17} Therefore, detailed future studies including X-ray diffraction will be essential to confirm this S_C assignment. What is significant for the photophysical properties of interest here is that tilt of the rodlike PBPQ chains, with respect to the layer normal, implied by an S_C phase is confirmed by evidence of J-aggregation discussed below.

Solvent cast solid films obtained by slow solvent evaporation¹⁸ from initially isotropic (0.5 wt %) or liquid crystalline (ca. 30 wt %) solutions were found to preserve the smectic C morphology of the LC phase. Figures 1b and 1c show the typical textures of solvent cast solid films as revealed by POM photomicrographs. They are both similar to characteristic textures of the smectic C phase. For comparison, solid films spin coated from the initially isotropic solution (0.5 wt %) were observed by POM and found to be completely isotropic (non-birefringent) under crossed polarizers. Because the same initial isotropic solutions produced dramatically different solid state film morphologies by solvent casting and by spin coating, these results demonstrate that self-organization and solution processing method and time scale critically influence the macroscopic morphology of solid films of rodlike conjugated polymers.

Effects of solid state morphology and solution anisotropy on the photophysical properties of PBPQ were probed by absorption, excitation, and emission spectra. Figure 2a shows the optical absorption, excitation, and emission spectra of an isotropic, spin coated, thin film of PBPQ. The absorption spectrum with λ_{max} at 402 nm (3.08 eV) is very similar to the polymer's dilute solution spectrum (not shown). The PLE spectrum (570-nm emission) of this isotropic film tracks the absorption

spectrum fairly well except that an additional broad shoulder in the 450-510 nm region is observed. This new absorption feature is evidence that the J-aggregates observed in solution in the same spectral region are preserved in the spin coated, isotropic, solid films. The PL spectrum (Fig. 2a) has a broad emission band centered at 571 nm and a broad shoulder at 440-500 nm. This blue shoulder in the emission is resonant with the new absorption feature in the PLE spectrum and is also in the same position as the J-aggregate emission band observed in solution. It can, therefore, be assigned to J-aggregate emission. The dominant, broad, 571-nm emission band is assigned to excimer emission since its alternative interpretation as "J-aggregate emission" is ruled out by the preceding discussion and the observed Stokes shift of 0.91 eV is characteristic of an excimer state.^{3a, 19} The measured PL decay dynamics of the 570-nm emission band showed that three lifetimes were needed to describe the data: 3.13 ns (66%), 0.69 ns (24%), and 0.11 ns (10%). The rather long lifetime of the dominant emitting species is also consistent with excimers.^{3a, 19} However, we point out that the excimers observed here are not the conventional excited state dimers with dissociative ground state proposed by Birks^{19a} but excited complexes whose ground states can be stable aggregates, similar to well known pyrene excimers formed from preassociated aggregates.^{19b}

The UV-vis and PLE spectra of the LC solution and solvent cast solid films, whose morphologies were shown in Figure 1, are given in Figure 2b. Because all three absorption spectra were identical, only one spectrum is shown (curve 1). It has a peak at ~400 nm (3.10 eV) and, more importantly, a broad shoulder in the 440-510 nm region which was absent in the spin coated isotropic films. This new absorption feature in the UV-vis spectra is a clear evidence of J-aggregation which is confirmed by the PLE spectra. In the case of the LC solution, the broad PLE spectrum (curve 2) extends from 550nm to below 300 nm and has peaks at 465 and 424 nm. The PLE spectra of the solvent cast solid films (curves 3 and 4) are very similar to that of the LC solution; there is a slight variation in the position and intensity of the lowest energy excitation peak in the 472-478 nm region which reflects variation in the geometry, e.g. the tilt angle, of the J-aggregates and extent of exciton coupling effects.¹¹⁻¹³ The profound difference

in the PLE spectra of these solvent cast solid films with S_C morphology (or LC solutions) and spin coated isotropic films reflects the macroscopic order of the J-aggregates of the former versus local order in the latter.

The PL emission spectra (400-nm excitation) of the LC solution and solvent cast, ordered, solid films are also shown in Figure 2b. Identical emission spectra were obtained by varying the excitation wavelength, including direct excitation of the J-aggregate band at 450-500 nm. All three emission spectra are very similar with a broad structureless band centered at 607-610 nm (~ 2.04 eV). Compared to the spin coated isotropic films, these emission spectra are red shifted by about 39 nm (~ 0.13 eV), have a larger Stokes shift (1.06 eV) and lack the 440 to 500 nm broad shoulder we previously assigned to aggregate emission. Thus only excimer emission is observed from the LC solution and ordered solid films having J-aggregates with macroscopic order. Since the absorbing chromophores in these self-organized ordered media are the J-aggregates and any isolated chains, the mechanism of excimer emission likely involves efficient energy transfer or internal conversion from the absorbing states to the emissive excimer state.^{19b} Extensive π -stacking with an intermolecular distance of 3.6 Å has been found in the X-ray single crystal structure of an oligoquinoline model of PBPQ.²⁰ Intermolecular distances in the range of 3-5 Å are ideal for efficient excimer formation.^{3a, 19} These results demonstrate that the existence of ground state aggregates does not preclude excimer emission in conjugated polymers. Therefore, we point out that previous reports of "aggregate emission", based on the fact of ground state association and existence of aggregate states, must be re-examined.^{4, 5}

Polarized photoluminescence was observed from the unoriented, as-cast, ordered solid films having the S_C morphology (Figure 1) as shown in Figure 3. The dichroic ratio between the parallel and perpendicular polarizations of the PL emission was 2.35. Much higher photoluminescence polarization ratios have been observed in carefully oriented LC polymers envisioned for polarized light generation applications.²¹ The orientational order parameter S ²² estimated from the dichroic PL spectra of Figure 3

was 0.31 and since¹⁶ $S = [3 \cos^2\theta - 1]/2$ we also estimated the tilt angle between the layer normal and the macromolecular chain axis, θ , to be 43° . However, in J-aggregates the relevant tilt angle α is that between the molecular axis and the layer plane, that is $\alpha = 90 - \theta = 47^\circ$ which meets the requirement ($\alpha < 54^\circ$) for J-aggregation.¹¹⁻¹³ This interesting connection between chromophore aggregation, their photophysical properties, and the morphology of LC conjugated polymers suggests that photophysical techniques, if fully developed, could be very useful for the characterization of the morphology of self-organized conjugated polymers.

In summary, novel features in the absorption and emission processes in liquid crystalline solutions, spin coated solid films, and solvent cast, self-ordered solid films of a luminescent conjugated polymer are reported. Dominant excimer emission with a minor aggregate emission were observed in isotropic solid films spin coated from isotropic solutions of PBPQ. New, strongly red shifted, absorption and excitation bands observed in concentrated solutions exhibiting Smectic C like mesophase evidenced J-aggregation but the emission was characteristic of excimers. J-aggregated chromophores with excimer luminescence and emission dichroism were also observed in solvent cast ordered solid films. These results demonstrate that excimer emission can arise from J-aggregates or ground state complexes of conjugated polymers and that the interplay of self-organization and solution processing can significantly influence the photophysics of conjugated polymers.

Acknowledgement. This research was supported by the Office of Naval Research and in part by the National Science Foundation (CTS-9311741, CHE-9120001).

Supporting Information Available: Figures showing dilute solution absorption, PLE and PL spectra, thin film PL decay dynamics of **2**, schematic structure of smectic C and J-aggregate geometry, and figure captions (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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- (18) Solvent cast films were prepared by placing solutions onto glass or silica substrates and drying in ambient air at room temperature (23°C) overnight (ca. 12 hours). Both cast and spin coated solid films were further dried in a vacuum oven at 60°C for 12-16 hours before POM observations and spectroscopic characterization.
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FIGURE CAPTIONS

Figure 1. Polarizing optical micrographs of textures of (a) concentrated solution (~30 wt %) of PBPQ, (b) solvent cast solid film of PBPQ and (c) a different area of the solid film in (b). Original magnification 100X.

Figure 2. (a) Absorption (1), PL excitation (570-nm emission) (2), and PL emission (400-nm excitation) (3) spectra of a solid film of PBPQ spin coated from an isotropic solution. (b) Absorption (1), PL excitation (600-nm emission) (2), and PL emission (400-nm excitation) (5) spectra of a LC solution of PBPQ. Absorption (1), PL excitation (600-nm emission) (3, 4), and PL emission (400-nm excitation) (6,7) spectra of a solvent cast film of PBPQ. The different excitation and emission spectra of solid films come from the different textures in Figure 1.

Figure 3. Polarized photoluminescence of solvent cast PBPQ film on a glass substrate. The spectra are for 400-nm excitation and parallel ($\parallel$) and perpendicular ($\perp$) polarizations.

Figure 1

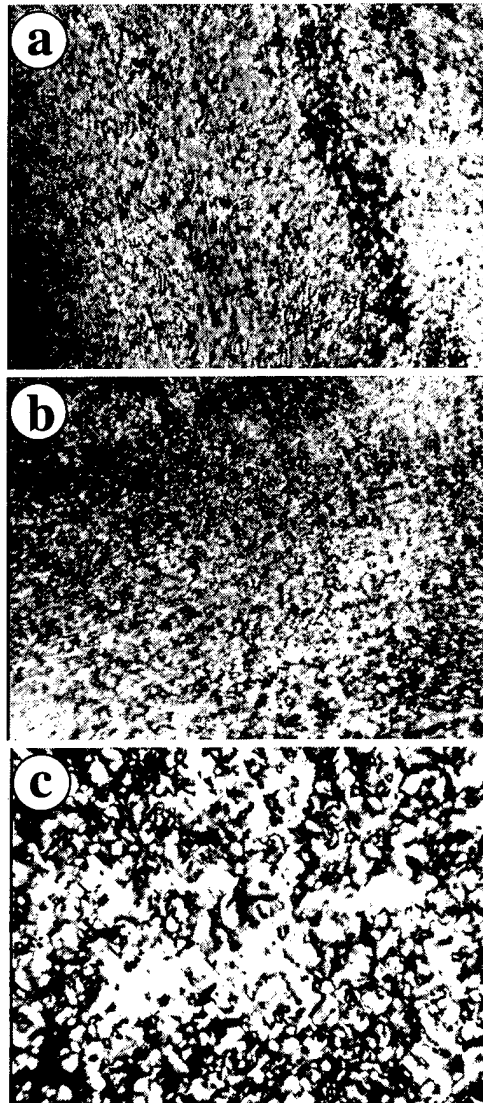


Figure 2

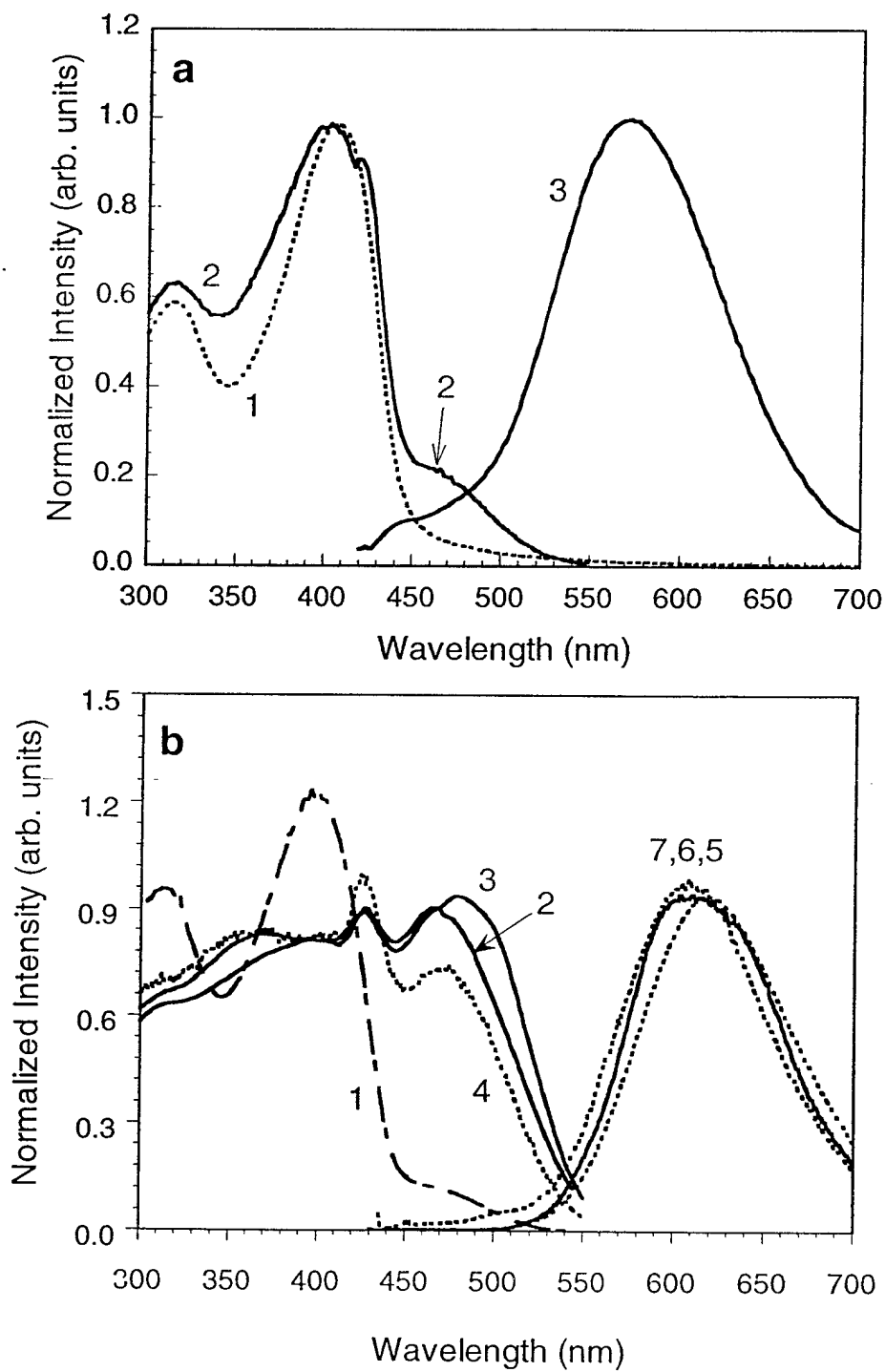
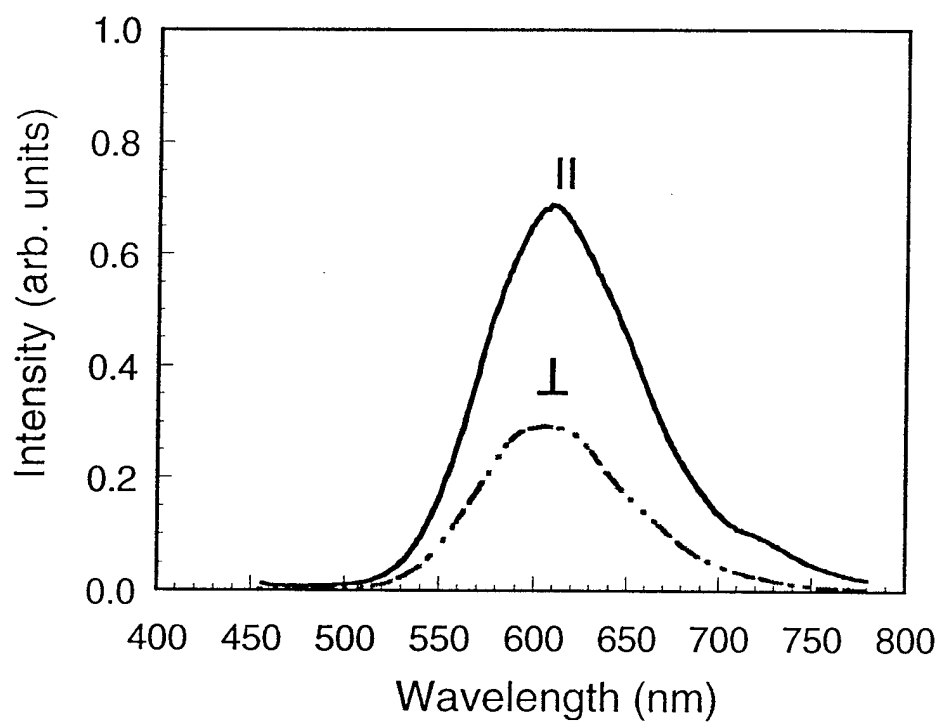


Figure 3



J-Aggregation and Excimer Emission of Anisotropic Solutions and Solid Films of a Liquid Crystalline Conjugated Polymer

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SUPPLEMENTARY MATERIAL

Our previous¹⁰ dilute solution (about 1 μ M to 20 mM, based on polymer repeat unit) studies of polyquinoline **1** showed clear evidence of the characteristic features of J-aggregates,¹¹⁻¹³ when probed by absorption and photoluminescence excitation (PLE) and emission (PL) spectroscopies. Similar dilute solution studies have been done on polyquinoline **2** (PBPQ) and the results are given here (Fig. S1) to avoid duplication in the present paper which focuses on concentrated (liquid crystalline) solutions and solvent cast ordered solid films. The PL decay dynamics data from which lifetime information was extracted are presented in Figure S2. An idealized layer structure of the smectic C phase and related J-aggregate geometry are shown in Figure S3. Note that because of polydispersity in the actual conjugated polymer PBPQ it would not have uniform molecular sizes as shown; however, the conceptual picture and especially the tilt angles are not affected by this.

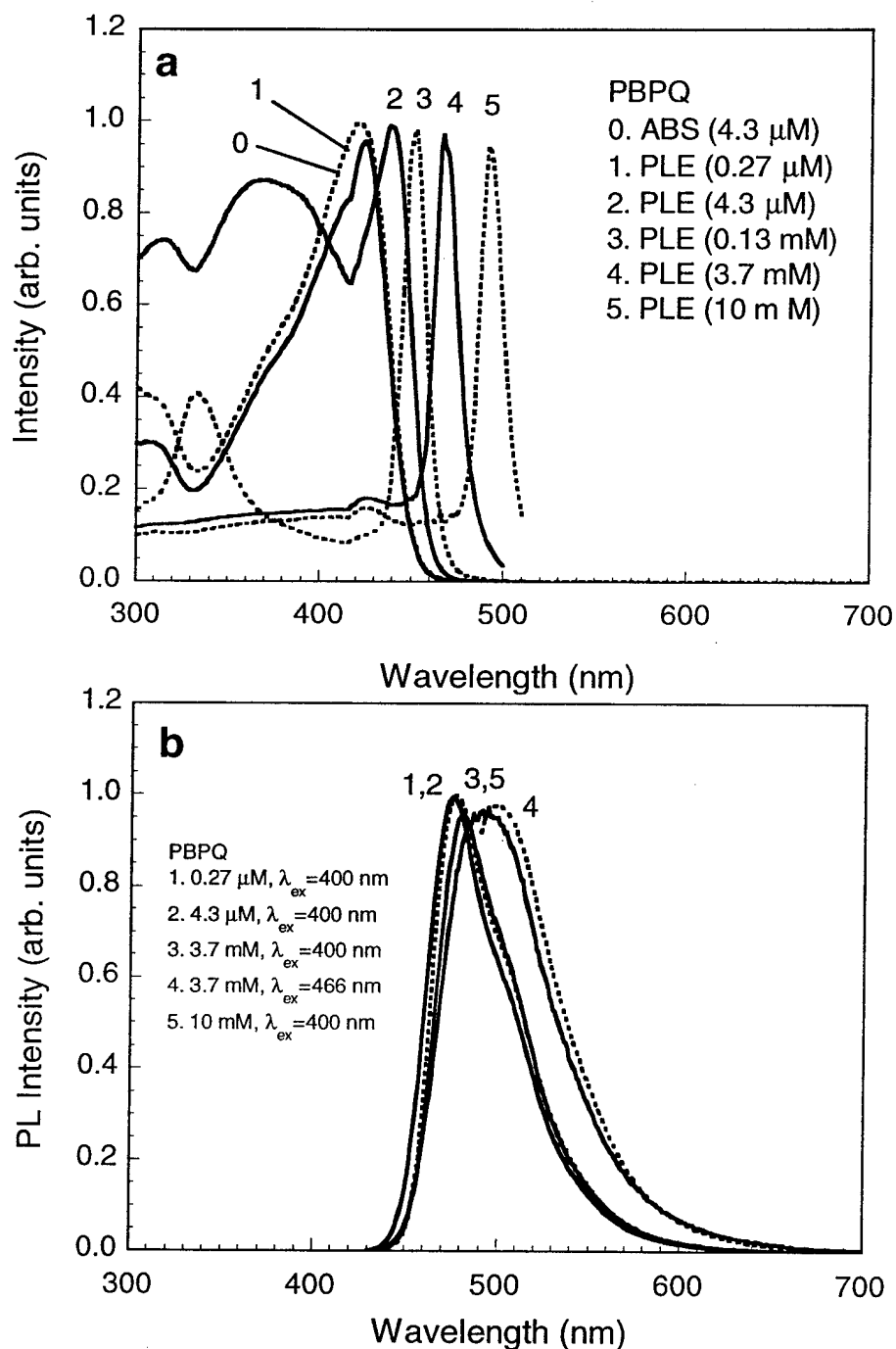


Figure S1. (a) Absorption (0) and PLE (1-5) spectra of PBPQ solutions in formic acid. The corresponding emission wavelength for the PLE spectra was 530 nm. (b) PL spectra of PBPQ solutions.

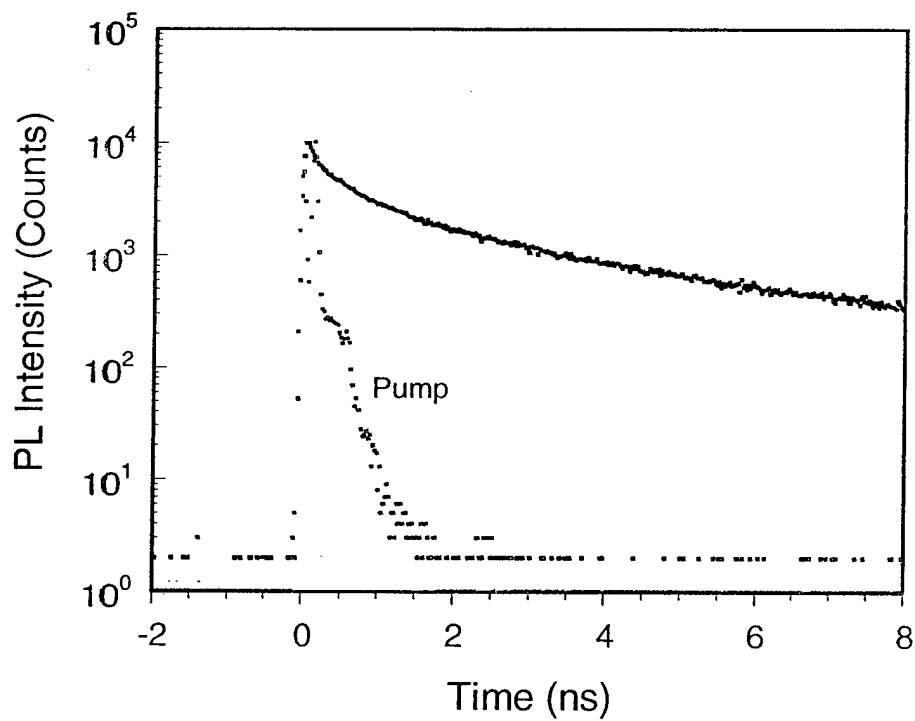


Figure S2. Photoluminescence (PL) decay dynamics of a PBPQ thin film. The excitation wavelength was 350 nm and the monitoring wavelength was 570 nm. The data were obtained by using a single photon counting technique and equipment previously described in: Osaheni, J. A.; Jenekhe, S. A. *J. Am. Chem. Soc.* **1995**, *117*, 7389.

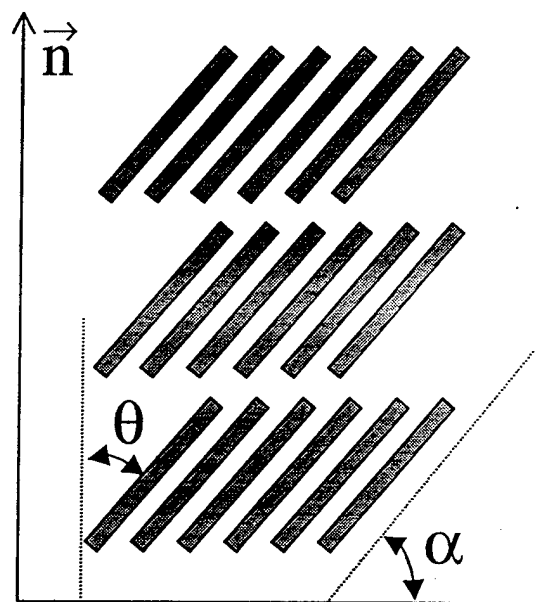


Figure S3. Schematic (idealized) supramolecular structure of smectic C phase with tilt angle θ . This structure is identical to a J aggregate with tilt angle $\alpha < 54^\circ$.