Spatially and temporally resolved emission from aggregates in conjugated polymers

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We present results of cw, time-resolved, and spatially resolved spectroscopic studies of emission and absorption in a model conjugated polymer, poly(p-pyridyl vinylene) (PPyV). The redshifted film spectra suggest the formation of aggregated regions. The $\sim 4\times$ reduction in emission efficiency in films vs solution is attributed to a longer radiative lifetime for aggregate excitons, as is evidenced by time-resolved fluorescence measurements. We present direct optical imaging of aggregates in a conjugated polymer via near-field scanning optical microscopy. The aggregate emission and absorption are found to be localized to partially aligned regions of the film ~ 200 nm in size. [S0163-1829(96)51530-4]

Conjugated polymer light-emitting diodes (LED's) have seen remarkable progress since the first report of their fabrication in 1990,[1] with performance specifications approaching industry standards.[2] Nevertheless, important obstacles are still to be overcome; among these, their typically modest photoluminescence (PL) and electroluminescence efficiencies. Improvement of these devices necessitates a detailed understanding of the underlying photophysics of conjugated polymers. It is now generally accepted that emission in these systems arises from intrachain *excitons*: Coulombically bound, germinate electron-hole pairs. However, the role of interchain interactions in the luminescence processes of conjugated polymers, though often stressed,[3–7] is controversial. Several authors have suggested the role of the *excimer*,[8] an intermolecular entity that is only stable in the excited state. For poly(p-phenylene vinylene) (PPV), it has been suggested that the majority of species created after photoexcitation are nonemissive interchain excimers, or ''polaron pairs,''[3,4] which compete with emissive singlet excitons, drastically reducing the PL quantum yield. More traditional emissive excimers have been reported in rigid-rod planar polymers such as poly(p-phenylene-2,6-benzobisoxazole).[5,9]

Another manifestation of interchain interactions is the formation of *aggregate states*,[10] where both the ground- and excited-state wave functions are delocalized over several polymer chains. Such entities have been proposed to occur in ''ladder'' poly(p-phenylene)s (L-PPP's) (Refs. 6, 11, and 12) based on photoluminescence and photocurrent measurements. As with excimers, the formation of aggregates is suggested to be detrimental to the luminescence efficiency of the polymer.[13,14]

Like the L-PPP's, pyridine-based polymers such as poly (p-pyridyl vinylene) (PPyV, Fig. 1) have shown promise for LED applications.[15,16] We recently have suggested that aggregate states are responsible for the emission in films of
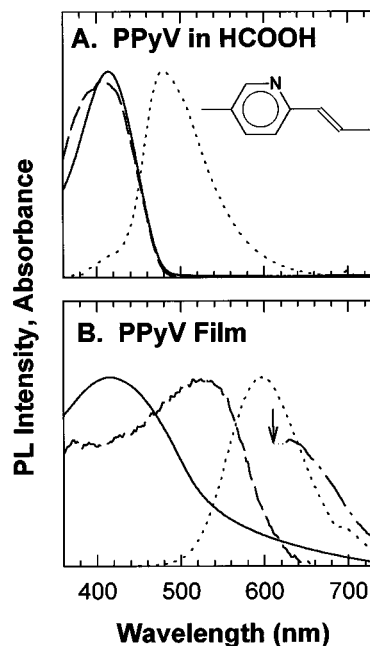

FIG. 1. PL emission (dotted), PL excitation (dashed), and absorption (solid) spectra for (a) 10^{-5} M PPyV in HCOOH; (b) PPyV film on quartz. Dot-dashed curve in (b) is PL excited at 610 nm (arrow).

these systems as well.[17,18] In this paper, we examine the emissive properties of PPyV using cw, time-resolved, and spatially resolved photoluminescence and absorption spectroscopy. We present a study of aggregate formation in a conjugated polymer via near-field scanning optical microscopy (NSOM).[19,20] This technique allows direct optical imaging of features which are below the resolution of confocal microscopy, and has been successfully applied to the study of aggregates in molecular systems.[21–23] We demonstrate that the emission from PPyV films arises from oriented, localized regions of the sample, and that the excitons readily migrate to these areas, where emission occurs with low quantum yield.

The PPyV synthesis has been reported elsewhere.[24] The polymer was dissolved in formic acid (HCOOH) and drop- or spin-coated onto quartz substrates for study. Absorption and PL spectra were recorded using a Perkin-Elmer Lambda-19 UV/VIS/NIR spectrometer and SPEX Fluorolog fluorometer, respectively. Time-resolved PL measurements were performed with $\sim$50 ps resolution via time-correlated single-photon counting using $\sim$5 ps, 1 nJ pulses centered at 440 nm from a Coherent 700-series synchronously pumped dye laser. The near-field images were recorded with $\sim$100 nm spatial resolution using a modified Topometrix Aurora NSOM employing a tapered aluminum-coated fiber optic probe.[22,23] All measurements were performed at room temperature.

The aggregate nature of the emission from PPyV films is suggested by cw absorption and PL studies. Figure 1(a) shows the absorption (solid), PL (dotted) and PL excitation (dashed) spectra for a 10^{-5} M solution of PPyV in HCOOH. The solution PL efficiency is $\sim$25% with respect to a Rhodamine 6G standard. The PL excitation spectrum closely follows the absorption spectrum in accord with Vavilov's Law.[8] The corresponding film PL spectrum, shown in Fig. 1(b), is notably redshifted by about 100 nm versus solution and is featureless. The external PL efficiency of the film sample is only $\sim$1%, corresponding to an peak internal PL efficiency of only $\sim$6%. Structureless, redshifted emission with low quantum yield has been cited as evidence for excimer formation in polymer systems;[5,25] however, excimer formation in our samples can be ruled out by considering the absorption and excitation spectra, also shown in Fig. 1(b). Both spectra argue for directly accessible low-energy sites in the film samples. The absorption spectrum merely shows evidence for extra low-energy oscillator strength in the film sample; however, the PL excitation spectrum of the film is dramatically different that of the solution, peaking in a region where the solution absorption is essentially zero. More importantly, substantial PL can be excited from the film by 610 nm radiation, as is indicated by the dot-dashed curve in Fig. 1(b). The vanishing Stokes shift ($<$250 cm^{-1}) between the peak of the PL and the exciting line (arrow) is again inconsistent with the formation of excimers, as excimers cannot be directly excited.[8] We suggest the redshifted emission is therefore due to the formation of aggregate regions in the film, where the ground-state and excited-state wave functions are delocalized over two or more chains. The $\sim$0.5 eV redshift for the PL is on the order of that expected from calculations for crystalline PPV (Ref. 26) and PPP.[27]
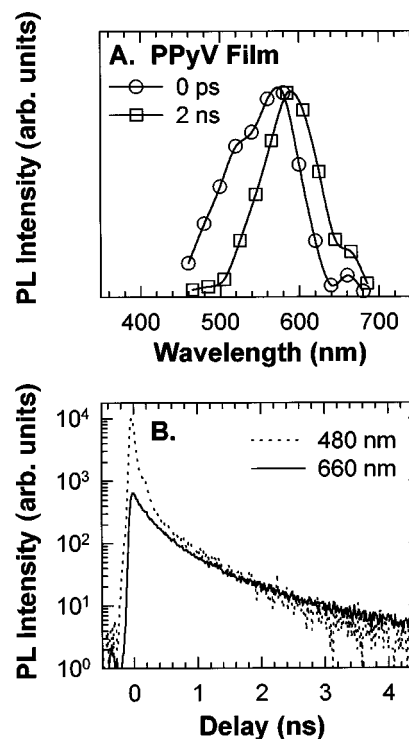

FIG. 2. (a) PL spectrum within 50 ps of (circles) and 2 ns after (squares) 440 nm pulsed excitation. (b) Decay of PL at 480 nm (dotted) and 660 nm (solid).

The origin of the reduced quantum efficiency of the aggregate becomes clear when the time dynamics of the PL are considered. Figure 2(a) displays the PL spectrum within 50 ps (circles) of and 2 ns (squares) after pulsed excitation at 440 nm. Comparison with the cw spectra of Fig. 1 indicates that the ''0 ps'' film spectrum contains contributions from both intrachain (solutionlike, $\sim$480 nm) and aggregate ($>$600 nm) emission. In contrast, by 2 ns, the solution-like emission has disappeared, leaving only the aggregate emission.

Figure 2(b) presents the time decay of the solutionlike emission (480 nm) and aggregate emission (660 nm) in the film sample. While the solution PL decay (not shown) is nearly single exponential with a lifetime $\sim$400 ps, the 480 nm film emission consists of a very fast component ($\sim$30 ps) and a long-lived component ($\sim$1 ns). The 1 ns component dominates the 660 nm decay, suggesting its association with the aggregate emission. The extremely fast decay of the solutionlike emission suggests a rapid diffusion of excitons to aggregate sites that is likely facilitated by efficient Förster transfer due to the strong overlap of intrachain emission and aggregate absorption.[10] The rise time of the aggregate emission was not observable, possibly due to the limited time resolution of the measurement ($\sim$50 ps), the overlap between the intrachain and aggregate emission spectra, and the direct excitation of a substantial number of aggregate excitons [$\sim$50% from Fig. 2(a)].

Comparison of the fast component of the film PL with the solution PL lifetime suggests that $<$10% of the film emission comes from intrachain excitons. The long lifetime of the aggregate emission suggests that the associated transition is less allowed than the corresponding intrachain transition,[10]
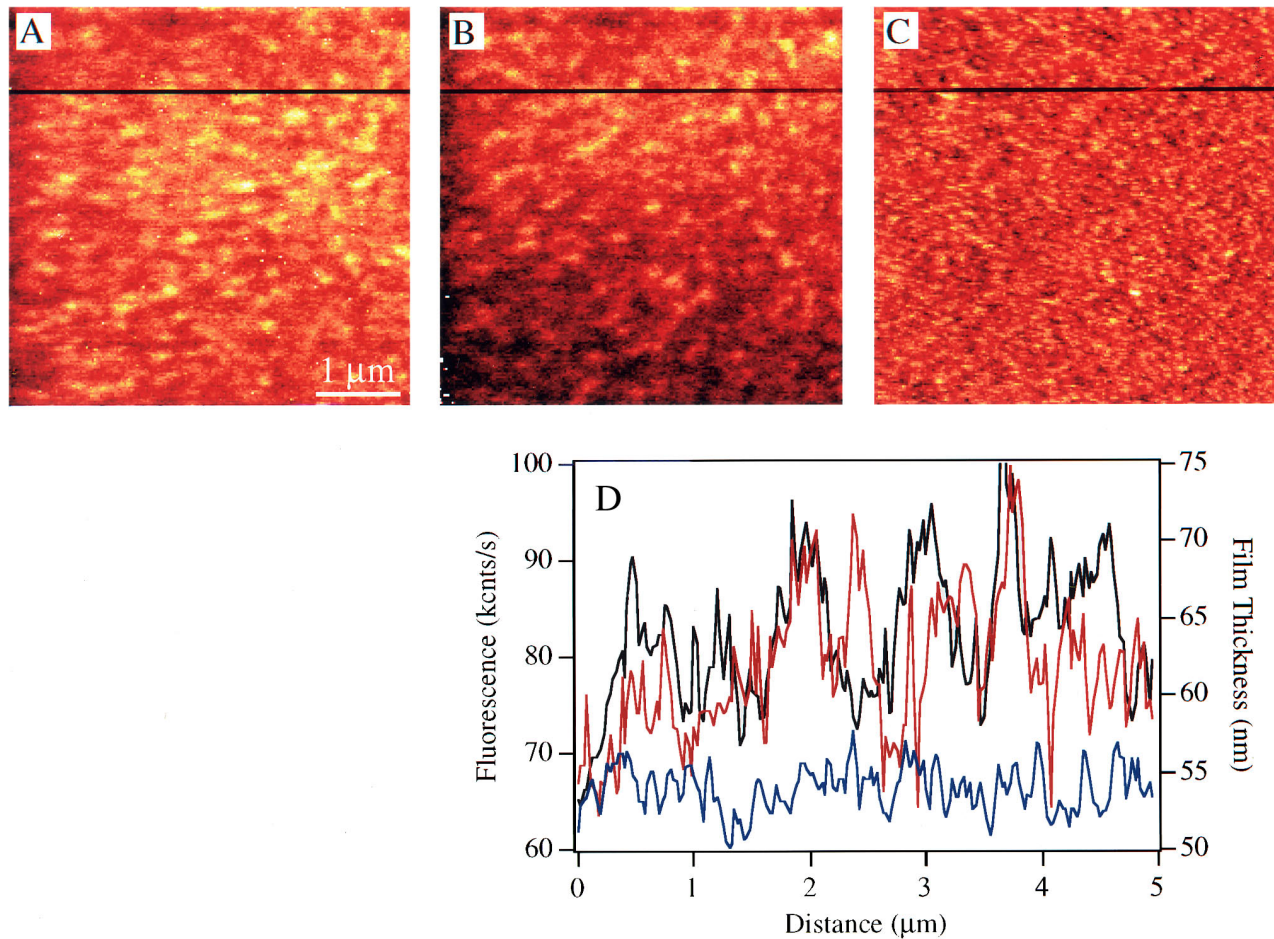
FIG. 3. Polarized NSOM excitation images of PPyV film PL with (A) vertical polarization; (B) horizontal polarization. The laser is polarized at 45° with respect to vertical. Brightest and darkest colors correspond to 120 and 50 kcounts/sec, respectively. (C) Topography of sample. Full scale is 20 nm. (D) Line scans of vertical (black) and horizontal (red) intensity and topography (blue) along the dark stripes indicated in (A)–(C).

thereby leading to the reduced PL efficiency of the film samples.

Direct evidence for aggregated domains in the films comes from NSOM PL excitation measurements. Here, the sample was excited through the fiber optic probe using 488 nm radiation from a cw argon-ion laser polarized at 45° with respect to "vertical." The emission from the entire sample was subsequently recorded using a 488 nm notch filter and two avalanche photodiodes to detect the two orthogonal po-

larizations simultaneously. Figures 3(a) and 3(b) present polarized NSOM excitation images for a 5×5 μm region of a PPyV film sample. Figure 3(c) shows the corresponding topography. Both polarization images show clear features that have a characteristic size of approximately 200 nm. Additionally, both PL images differ strongly from the topography of the sample, indicating that the variation in emission intensity is not due to differences in absorption due to sample thickness. Moreover, the images for the two different polar-
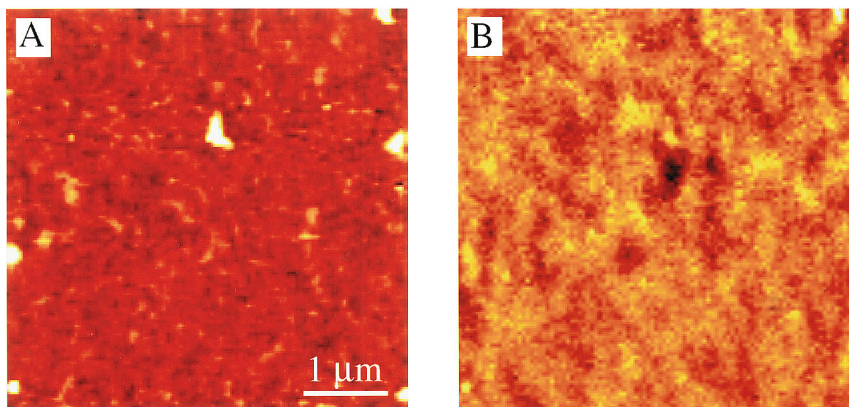

FIG. 4. (A) Topography of PPyV sample (20 nm full scale). (B) NSOM transmission anisotropy image of PPyV film. Light areas correspond to ~2.5% polarization anisotropy.

izations are clearly different from each other, suggesting that the vertically and horizontally polarized emission comes from oriented regions of the sample. The localized nature of the excitation and the subsequent polarized emission argues strongly for the formation of aggregate sites in the film.

A more quantitative comparison is shown in Fig. 3(d), which displays line scans of the film thickness and PL intensity along the dark lines shown in the images of Figs. 3(a)–3(c). The film thickness is measured to be ~ 50 nm (Ref. 28) and shows little variation with distance along the sample (< 2 nm rms). In contrast, the vertically and horizontally polarized emission displays intensity variations as large as 25% across the sample. These results reinforce the point that the emission in PPyV films originates from localized, aligned regions of the sample. It should be noted that the variations in PL intensity and polarization are not merely the result of a statistically small number of chromophores, as is evidenced by smooth decay kinetics in photobleaching experiments.[29]

More evidence for aggregation is found in the NSOM transmission measurements of the films. For these experiments, the polarization of the 514 nm light from the near field probe was modulated through 180° at 2 kHz and the total transmitted light was collected with a photomultiplier tube. The polarization anisotropy in transmission causes a 2 kHz variation in transmitted intensity that can be measured with a lock-in amplifier.[30] Figure 4 shows the topography and anisotropic transmission, respectively, for the PPyV film. For the transmission image, the signal from the lock-in was ratioed to the total transmission through the sample. Again, the NSOM image is not correlated with the topography of the sample. The anisotropic transmission image shows clear contrast features that are very similar in size to those seen in the fluorescence images, again suggesting aligned domains in the film. The full scale of modulation on the image represents a change in transmission of 2.5%, corresponding to a change in optical density of ~ 0.011. The average optical density of the film is only ~ 0.045; therefore, the polarization anisotropy in optical density across the sample is again $\sim 25\%$, similar to the fluorescence. It is also noted that similar transmission images of poly vinyl (1-methyl) pyridinium bromide, a non-aggregate-forming polymer, show no features of any kind.[29]

The observed domain size (200 nm) is much larger than the crystalline coherence length of the polymer (< 2 nm from x-ray diffraction[31]). We therefore conclude that the 200 nm domains are not the actual aggregate sites, but partially aligned regions of the sample where the aggregates are most likely to form. The aligned regions of the sample are reminiscent of the card-pack arrangement of H aggregates in small molecular systems, where the lowest optical transition is completely forbidden.[10] Apparently the lowest transition of the PPyV aggregate is not completely forbidden, suggesting oblique alignment for the transition dipoles on neighboring polymer chains.

Aggregate formation is apparently detrimental to the efficiency of polymer LED's, as is evidenced by the reduction in PL efficiency of our film samples. Several studies[3,4,14,17,31,32] have suggested means to circumvent aggregate formation: namely, the introduction of disorder into the sample, e.g., through attaching bulky sidegroups to the polymer.

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