On-chain defect emission in electroluminescent polyfluorenes

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We present time-resolved photoluminescence measurements on a range of poly- and oligofluorenes with different molecular weights in both dilute solution and thin films. The commonly observed parasitic broad green emission band, which has previously been attributed to an excimer, is identified in all solution and film samples and assigned to an on-chain emissive defect. By comparison of the luminescence decay in the solid state at different temperatures it is shown that, at room temperature, intramolecular relaxation is faster in these polyphenylenes than intermolecular exciton diffusion. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1486482]

Conjugated polymers are a fascinating class of materials, which are becoming increasingly important for technological applications. One of the most significant conclusions of the enormous research effort over the past decades, which has helped to establish a scientific framework of understanding of these materials, is that many of the material properties are molecular or supramolecular in origin, and hence, depend sensitively on the exact chemistry of the material studied as well as the immediate environment.[1] It is, therefore, generally hard to build up a universal description of the isolated and bulk electronic properties of organic semiconductors. An important issue, which has received considerable attention over the past years, is the influence of intermolecular interactions on the bulk electronic properties of conjugated polymers. The clear observation of excimer formation in certain classes of conjugated polymers[2] has since been extrapolated to a wide range of other materials, without rigorously assessing all the physical criteria. An example of this is the class of polyfluorenes, which generally exhibit narrow emission bands accompanied by a broad redshifted emission contribution.[3–9] A range of efforts, such as block copolymerization,[10] endcapping,[11] and dendronization[12] have been undertaken to modify the bulk emission properties of polyfluorenes and have generally resulted in a correlation being made between the chemical structure and the bulk properties. This has led to a support of the picture that intermolecular interactions dominate the bulk material properties of polyfluorenes.[13–14] However, List *et al.* recently demonstrated that many of the emissive characteristics of polyfluorenes may be reproduced by incorporating keto defects into the polymer backbone,[15] which are readily identified by infrared spectroscopy.[16] We present here time-resolved photoluminescence (PL) measurements on a series of oligo- and polyfluorenes in dilute solutions and films. We observe identical emission characteristics in all systems, albeit with varying relative intensities of the different contributions. We find that intermolecular interactions do not give rise to any substantial new emission features, but instead modify the exciton diffusion significantly, leading to very different steady-state emission properties.

The polymers and oligomers investigated are derived from [9,9-di(S)-3,7-dimethyloctyl]fluorene. Monomer units were prepared by the dialkylation of 2-bromofluorene and 2,7-dibromofluorene with (S)-3,7-dimethyloctylbromide in the presence of an aqueous base and a phase transfer catalyst. Polymerization was carried out by the Ni(0) mediated coupling of the dibromo monomer to yield a polymer with M_W of 230 000 ($P_D = 2.9$), according to gel permeation chromatography (GPC) analysis against polystyrene standards. A low molecular weight polymer ($M_W = 10\,000$; $P_D = 1.5$, GPC), the hexamer and related shorter oligomers were prepared by the same coupling method with monobromo monomer units present as end-capping moiety, and were subsequently fractionated.

PL measurements were made using a Hamamatsu C4742 streak camera and a frequency-doubled mode-locked titanium–sapphire laser operating at 390 nm and a typical cw intensity of 1 mW. Figure 1 shows different delayed emission spectra of dilute toluene solutions (20 μg/ml) of oligo- and poly[2,7-(9,9-di{(S)-3,7-dimethyloctyl}fluorene)] (PFO, structure in Fig. 1), and of a pristine and annealed (120 °C, 1 h) film detected in different integration windows. All spectra exhibit a broad emission feature at approximately 530 nm, which has previously been attributed to emission from excimers.[4,7,13] The occurrence of the same emission feature, albeit extremely weak, in dilute solutions of the oligofluorene hexamer as in annealed films evidently excludes the possibility that this emission band is related to intermolecular interactions. Instead, it has previously been noted that the broad green emission band is identical in position and shape to that of molecular fluorenone.[15,16] This implies that fluorene chains may contain a certain average number of oxidizable sites, which may either be converted during synthesis[15] or occur through photo-oxidation after synthesis,[4,15] and could take the form of either a monoalkylated or unsubstituted fluorene. A comparison of the lifetime dependence on chain length is in full agreement with this

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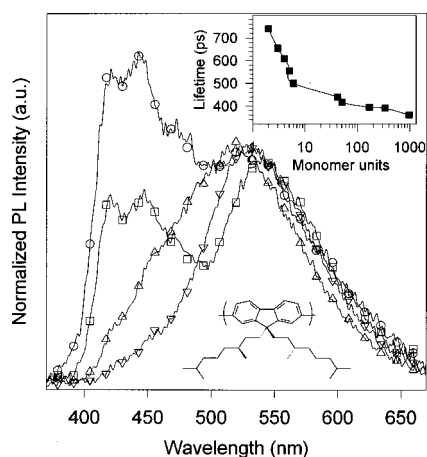
FIG. 1. Plot of delayed PL intensity of solutions and films of PFO: solution of long-chain polymer ($M_w = 230\,000$) detected in a 1.4 ns time window, 2 ns after excitation ($\square$); hexamer solution detected 3 ns after excitation in a 500 ps time window ($\bigcirc$); pristine PFO film, detected at a delay of 1.5 ns in a 200 ps window ($\triangle$); annealed PFO film, detected at a delay of 1.5 ns in a 200 ps window ($\bigtriangledown$). Inset shows the change of oligomer and polymer emission lifetime in solution with number of monomer units. The solid line is a guide to the eye. Also, inset is the structure of the polymer.
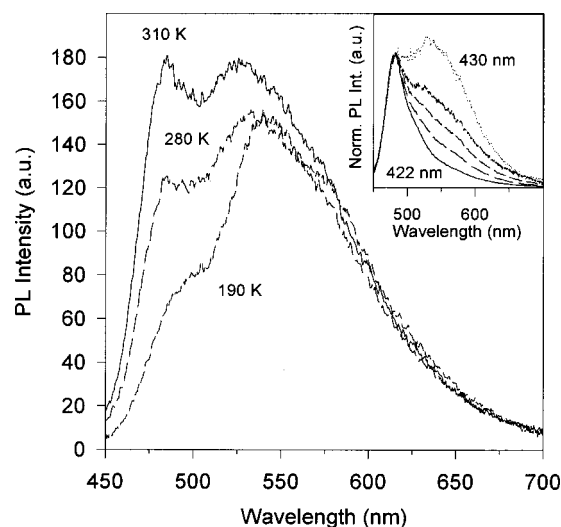

FIG. 2. Thermal activation of PFO solution PL detected in a 1.5 ns window 200 ps after excitation at 430 nm. The inset shows the relative change of defect to backbone emission as the excitation wavelength is changed (422, 424, 426, 428, and 430 nm from bottom to top).

assumption, as shown in the inset in Fig. 1. As the oligomer length increases, the energy gap decreases resulting in a reduction in lifetime following the Strickler–Berg relationship.[1] However, the broad green fluorenone emission is detected in dilute solutions of pentamer and hexamer, and is most probably present in all oligomers, although outside of the temporal detection window of the streak system used. Excitations may, therefore, be transferred to fluorenone sites on the backbone of the chain, resulting in an apparent reduction of emissive lifetime.[17] This reduction depends continuously on chain length, as seen in Fig. 1. It is most significant to note that there is no intrinsic difference between the emission in dilute solution and annealed films, other than accelerated diffusion to defect sites in the latter case due to enhanced intermolecular order after heating above the glass transition temperature.

In order to demonstrate unambiguously that the broad green emission band is due to emissive chain defects rather than excited state dimers we performed frequency up-conversion and site-selective fluorescence measurements on dilute solutions of the $M_w = 230\,000$ sample. It was recently demonstrated that the emission from PFO is thermally activated when excited to the red of the 0–0 emission band due to a phonon-mediated excitation process.[18] This effect can also be used in spectroscopy to identify the relationship between different emissive components. The PL spectra in Fig. 2 were detected through a 455 nm long-pass filter under excitation at 430 nm. As the temperature is reduced, the PFO emission decreases, but there is no change in the green band emission. This demonstrates that it is also possible to excite the green band directly, excluding the possibility of excimers formed in solutions of PFO. The inset in Fig. 2 shows the relative change of defect to PFO emission at room temperature as the excitation wavelength is changed. There is a large relative increase of the green band with respect to the PFO emission as the excitation wavelength is increased, demonstrating that the two emission components are of differing origin. From the wavelength dependence it is conceivable

that lower-energy sites of the polymer backbone, such as intrachain aggregates, preferentially form excimers, even in dilute solutions. However, the thermal activation of the spectrum clearly excludes this scenario.

Next, we investigate the concentration dependence of delayed PL spectra of the $M_w = 230\,000$ sample, shown in Fig. 3. The spectra were all detected in the same delayed time window of 1.5 ns at 1.5 ns delay. As the concentration is increased, the blue emission edge shifts to the red due to increased reabsorption. However, there is also a significant increase in emission intensity in the region of 450–500 nm, with a decrease in defect band emission. Time-resolved measurements on films also show strong emission in this wavelength region, but only for a short time (not shown). We attribute the enhanced emission at 480 nm to the formation of interchain aggregates, which have previously also been identified in film absorption spectra.[9] The keto defect band is lower lying in energy and has an absorption, as indicated by
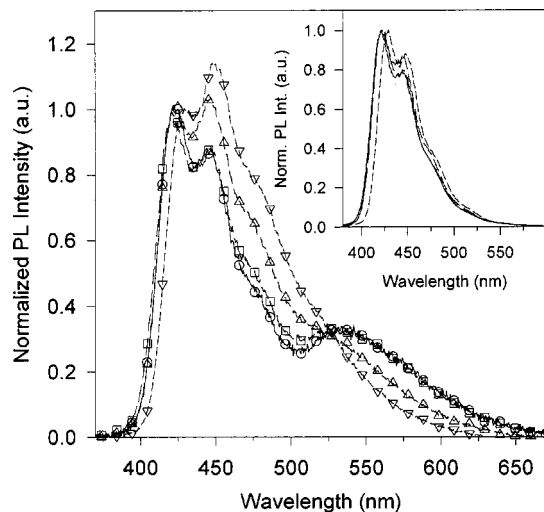

FIG. 3. Dependence of delayed PL (1.5 ns delay, 1.5 ns window) on solution concentration: 8.5 μg/ml ($\bigcirc$), 17 μg/ml ($\square$), 85 μg/ml ($\triangle$), and 170 μg/ml ($\bigtriangledown$). Inset shows the prompt PL spectra recorded in the first 100 ps after excitation.
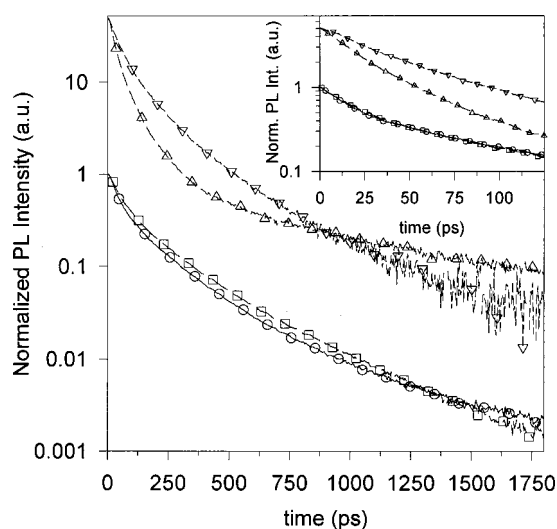
FIG. 4. PL decay of short ($M_w = 10\,000$) and long ($M_w = 230\,000$) pristine polymer films at 290 K (detection window 425–429 nm) and 4 K (detection window 426–430 nm): short polymer, 290 K ($\triangledown$); long polymer, 290 K ($\triangle$); short polymer, 4 K ($\square$); and long polymer, 4 K ($\bigcirc$). Traces are offset for clarity. Inset shows the initial fast decay measured in a 140 ps time frame.

Fig. 2, which overlaps the aggregate emission. In the solid state spectral diffusion in three dimensions from interchain aggregates to defect sites may, therefore, take place. This process is much less likely to occur in solutions where one-dimensional diffusion prevails, resulting in exciton trapping on the aggregate. The aggregate, hence, plays a comparatively small role in the solid-state emission properties. The prompt emission spectra are shown in the inset of Fig. 3. They are found to be virtually identical, except for the red-shift at high concentrations and a small increase in the 0–1 emission band resulting from increased reabsorption.

The decrease in emission lifetime in dilute solutions with increasing chain length demonstrates that defect site emission becomes more probable with increasing length. In the solid state, however, exciton diffusion is a three-dimensional process, and it is by no means clear whether the chain length will affect the cw emission properties. It was recently demonstrated for isolated chains of poly(phenylene–vinylene) (PPV) that intermolecular exciton diffusion is significantly faster than the intramolecular relaxation.[19] This would imply that the chain length in the present case should have very little effect on the decay of the solid-state luminescence. Figure 4 compares the luminescence decay of films of a long polymer ($M_w = 230\,000$) and a short polymer ($M_w = 10\,000$) at 4 and 290 K. The inset shows the same measurement made at a higher temporal resolution. At 4 K the decay is identical for the two samples. However, at 290 K the initial decay of the long polymer film is significantly faster, whereas the decay of the short polymer film is similar to that at 4 K. This indicates that intrachain exciton migration does contribute substantially to the activation of defect sites in the solid state. However, whereas the interchain relaxation process is primarily due to resonant dipole–dipole coupling, it appears that the intrachain mechanism in the present case involves also a thermally activated component, which is significantly faster than Förster-type relaxation at room temperature. It should be noted that the PFO backbone is much more rigid than the PPV backbone, which may explain why the on-chain relaxation is accelerated in the present case. We propose a charge transfer process as the origin of the on-chain relaxation mechanism, but it is clear that further work is required to identify the exact nature of this rapid relaxation as Förster theory alone cannot account for the spectral dynamics at elevated temperatures. We also note that the present observations are in line with previous attempts to minimize the parasitic green band emission–block copolymerization,[10] end capping of short polymer segments,[11] fractionization[7] and dendronization[12] all lead to a reduction in interchain or intrachain migration.

We have conclusively identified the origin of the broad green emission band in PFO as on-chain chemical defects, which are present in all compounds studied. As spectral diffusion is a three-dimensional process in the solid state, diffusion to defect sites[17] is dramatically enhanced leading to a strong modification of steady-state emission spectra. The occurrence of rapid on-chain diffusion at room temperature indicates a route for improving the performance of a wide range of materials. As long-chain polymers often have superior properties, the formation of block copolymers appears to be a sensible route for obtaining both satisfactory processing and emission characteristics.

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