

On the nature of the fluorenone-based emission in oxidized poly(dialkyl-fluorene)s

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2008 J. Phys.: Condens. Matter 20 045220

(<http://iopscience.iop.org/0953-8984/20/4/045220>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 29/05/2010 at 08:04

Please note that [terms and conditions apply](#).

On the nature of the fluorenone-based emission in oxidized poly(dialkyl-fluorene)s

T A M Ferenczi, M Sims¹ and D D C Bradley

Experimental Solid State Physics Group, The Blackett Laboratory, Imperial College London, SW7 2BZ, UK

E-mail: toby.ferenczi@imperial.ac.uk, Marc.Sims@usa.dupont.com and d.bradley@imperial.ac.uk

Received 14 September 2007, in final form 1 December 2007

Published 8 January 2008

Online at stacks.iop.org/JPhysCM/20/045220

Abstract

This study examines the underlying nature of the green emission band observed as a result of oxidation in dialkyl-fluorene polymers. Specifically, we set out to further determine whether an inter- (excimeric) or intra-molecular fluorenone-based excited state is involved. The emission properties of poly(9,9-dihexylfluorene) dispersed at low concentration in a solid polystyrene matrix are carefully explored. *In situ*, time-resolved photoluminescence measurements are made during photo-oxidation of the blend and during subsequent exposure to an atmosphere saturated with the vapour of a good solvent. The polystyrene matrix suppresses the appearance of the green emission band during oxidation but the subsequent solvent vapour exposure then activates it. The same effect (activation of the green emission) can be achieved by thermally annealing the matrix above its glass transition temperature. Moreover, the activation of the green emission can be reversed by dissolving the film and re-casting. This behaviour is attributed to controlling the phase structure of the polyfluorene/polystyrene blend and is considered strong evidence for an origin of the green band emission in the formation of excimer-like states between co-facially arranged fluorenone moieties. The photoluminescence behaviour of 9-fluorenone and fluorene molecular mixtures in solution is also studied. This model system allows analysis of the green emission band independent of relative intra- and inter-molecular energy transfer effects since this system is affected only by inter-molecular energy transfer. These results provide further evidence for an excimeric origin of the green emission.

1. Introduction

The inherent advantages of dialkyl-fluorene polymers [1] are to some extent negated by a lack of blue emission stability under oxidative degradation. Alongside an overall decrease in quantum efficiency, there is the appearance of a broad emission band in the green spectral region, which is highly detrimental to the colour performance of devices used in display and lighting applications [2]. Determining the origin of this emission (or 'g-band') is important both for improving device performance and for a better understanding of conjugated polymer physics. A direct causal link between the g-band

and the presence of 9-fluorenone defects has already been established [3–7]. Ambiguity remains, however, as to whether or not the emission arises from an excitation of isolated 9-fluorenone moieties within an otherwise dialkyl-fluorene backbone, or whether it results from an excimer state formed between two co-facially arranged 9-fluorenone moieties. The study reported here seeks to distinguish between these two scenarios.

Many studies of the intra- versus inter-molecular fluorenone-based nature of the g-band emission have already been published. These (by no means an exhaustive list of the work carried out in this field) include studies of statistical copolymers of dialkyl-fluorene and 9-fluorenone [4, 8–12], studies of conjugated oligomers containing dialkyl-fluorene and 9-fluorenone moieties [13–16], and studies of various

¹ Present address: DuPont Displays, 6780 Cortona Drive, Santa Barbara, CA 93117, USA.

other copolymer [17, 18] and blend [5, 19–21] systems. It is important to note, however, that despite the intense activity there is not yet a consensus on the origin of the g-band emission. Detailed discussion of results reported prior to 2004 can be found in several of these works (e.g. [4, 5]).

Sims *et al* [5] demonstrated that the formation of the g-band is entirely suppressed for poly(9,9-dioctylfluorene) (PFO) chains dispersed at low concentrations within a polystyrene (PS) matrix under photo-oxidation in air. This enhanced colour stability was attributed to the preclusion of excimer interactions between fluorenone moieties on adjacent polyfluorene chains and/or chain segments due to isolation within the rigid PS matrix. This conclusion is supported by an analogous result published by Chochos *et al* [17] for rod-coil di-block copolymers of terfluorene and polystyrene. These copolymers display strikingly similar characteristics to the matrix-isolated polyfluorene samples under UV exposure. Quenching of the blue emission is observed without the emergence of g-band emission.

Becker *et al* [12] have conversely argued forcefully in favour of a mono-molecular mechanism for the g-band, both by presenting new data and by making two specific criticisms of Sims *et al* [5]. The first criticism is that there are many potential products of photo-oxidation other than 9-fluorenone, as indeed has been demonstrated by Liu *et al* [7]. We note, however, that Sims *et al* discussed this very issue at length and were careful to base their conclusions only on data from the early stages of oxidation, during which the changing photoluminescence spectra showed a clear isobestic point consistent with a correlated exchange of transition probability between two discrete species and during which infrared spectra showed the formation of C=O. The same care has been taken in the present study—only the early stages of oxidation have been considered. The second criticism concerns the observed non-linear dependence of g-band emission on the concentration of 9-fluorenone molecules blended with PFO [5]. Sims *et al* proposed that at low 9-fluorenone concentration ($\leq 4\%$) excimer formation is disrupted by long chain PFO molecules in a manner similar to that of the matrix-isolated PFO in polystyrene. Becker *et al* argued that this result could, however, be explained by exciton energy transfer to acceptors dispersed in a polymer matrix being much *less* efficient than energy transfer to acceptors bound covalently within the polymer backbone, and therefore a mono-molecular origin of the g-band is not excluded. We reiterate two points in response. First, as the fluorenone content was raised to 4%, we recorded a steady reduction in PLQE without detecting any change in the emission spectral lineshape (i.e. no green emission). Therefore, even at the lowest concentrations ($\leq 4\%$), we have direct evidence for energy transfer from polyfluorene to fluorenone (leading to quenching). Second, there exists significant oscillator strength for the $\pi-\pi^*$ transition of fluorenone at the excitation wavelength (351 nm) used in the experiment, but no green emission was detected at concentrations $\leq 4\%$. So, even direct excitation of the fluorenone in these samples does not lead to g-band emission.

The statement made by Becker *et al* concerning the efficiency of energy migration contradicts that made in another

recent report that, like Becker *et al*, favours a mono-molecular fluorenone explanation for the g-band emission [19]. Cadby *et al* studied a blend of degraded PFO and polystyrene in the ratio 1:1 (i.e. a much higher PFO concentration than studied by Sims *et al* [5]). Phase separation into PFO-rich and PS-rich phases results at these concentrations. Using scanning near field optical microscopy (SNOM), Cadby *et al* found that the g-band emission is strongly suppressed in the PS-rich phases. This is consistent with the matrix isolation experiments of Sims *et al* [5] in that we expect the average distance between poly(dialkyl-fluorene) chains to increase in the PS-rich phase relative to the PFO-rich phase. Cadby *et al*, however, explained this result by stating that intra-chain exciton migration is a much slower and less efficient process than inter-chain migration; therefore, they concluded, the isolated poly(dialkyl-fluorene) chains in the PS-rich phase exhibit less g-band emission due to an inhibited energy migration to the fluorenone defects. Cadby *et al* supported this conclusion with fluorescence emission lifetime data that suggest a fractionally longer decay time for the blue emission although the lifetimes reported are significantly shorter than previously measured values [22]. This creates a situation wherein two wholly contradictory arguments have been advanced in order to try and explain different aspects of results reported by Sims *et al* [5] within a mono-molecular fluorenone picture. No such difficulty arises for the excimer description favoured by Sims *et al*.

The work that we report here seeks to further clarify the appropriateness of the excimer scenario via an extended study of the properties of matrix-isolated polyfluorenes. The photoluminescence of polyfluorene chains dispersed at low concentrations in an inert, rigid polystyrene matrix is studied *in situ*. After controlled oxidation, the system is manipulated to encourage phase separation of the two components and thus induce the proximity required for excimer formation. The observed emergence of the g-band under these circumstances provides strong evidence for its excimeric origin. The extinction of the g-band by dissolving and re-casting the polymer blend film proves the physical (rather than chemical) nature of the manipulation effect, again supportive of an excimer explanation. Finally, we examine a system of fluorene and 9-fluorenone molecules mixed in solution. The concentration dependence (total and fractional) proves revealing, and given the monomeric nature of the energy transfer pair there is no ambiguity over ‘intra-’ versus ‘inter-’ molecular energy transfer. These results also support an excimer description of the g-band emission.

2. Experimental details

Poly(9,9-dihexylfluorene) (F6) (figure 1(a)) was provided by The Dow Chemical Company with MW = 69 700. Polystyrene with a similar molecular weight (MW = 92 000, purchased from Sigma Aldrich) was therefore used. F6 (0.06 wt%) was mixed with polystyrene to form a 10 mg ml⁻¹ solution in chloroform. Blend films were prepared by ‘drop-casting’ onto quartz (Spectrosil-B) substrates and allowing the solvent to evaporate under ambient conditions. Measurements

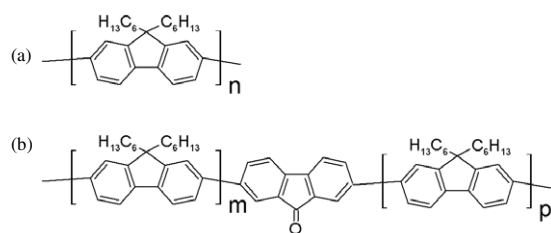


Figure 1. (a) Chemical structure of poly(9,9-dihexylfluorene) (F6). (b) Chemical structure of F6 with a single 9-fluorenone defect moiety ($n = m + p + 1$).

of the film photoluminescence (PL) were made using a cooled Instaspec charge coupled device (CCD) detector mounted on a spectrograph fed by a lensed fibre bundle collection optic. Films were excited using monochromated light output from a Bentham xenon lamp. Care was taken in these measurements to ensure that the substrate and optical components remained in a fixed position in order to record absolute changes in the PL intensity. Initial UV photo-oxidation in air was carried out using a Hamamatsu LC-5 mercury–xenon lamp. The light output incident on the film was held at a broadband intensity of approximately 50 mW cm^{-2} and was long-pass filtered to exclude wavelengths shorter than 380 nm.

Photoluminescence quantum efficiency measurements of solid films were made using an integrating sphere that was fibre-coupled to a spectrograph/cooled CCD detection system. An excitation wavelength of 355 nm (monochromated xenon lamp) was used for these measurements. Use of a CCD camera enabled us to minimize the integration time for signal collection negating unwanted additional photo-oxidation during measurement.

Solution PL spectroscopy was carried out using a SPEX Fluoromax-3 spectrofluorimeter. Mixed solutions of fluorene and 9-fluorenone molecules were prepared from stock solutions and placed in a quartz cuvette. PL was recorded using an excitation wavelength of 360 nm. The cuvette was placed in a fixed position within the spectrofluorimeter so that absolute changes in intensity could reliably be recorded. Absorbance measurements of solutions were made using a JASCO absorption spectrometer using quartz cuvettes.

3. Results and discussion

The photoluminescence spectra of a drop-cast film of poly(9,9-dihexylfluorene) (F6) dispersed in polystyrene at a concentration of 0.06 wt% is shown in figure 2. The effect of exposure to UV radiation in air over time is also shown.

During UV exposure, we observe a significant fall in the intensity of blue emission and a corresponding fall in the photoluminescence quantum efficiency (table 1). It is evident, however, that there is no significant growth of emission in the green spectral region (figure 2 inset) and that, therefore, the emission colour is essentially stable under these conditions.

This result (which reproduces that reported for PFO by Sims *et al* [5]) can be explained by the fluorenone–excimer model, that requires appreciable co-facial interaction between

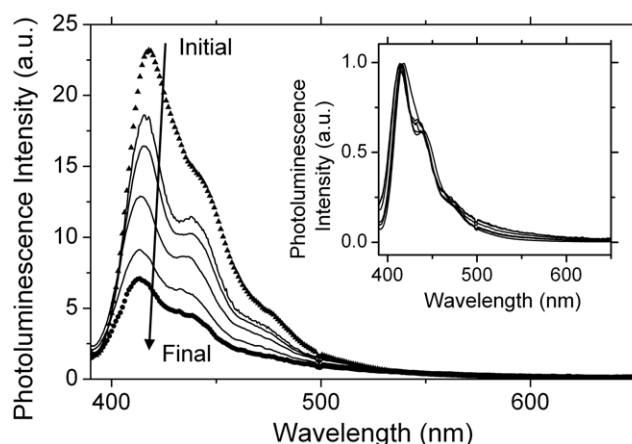


Figure 2. Effect of 4 h UV exposure (50 mW cm^{-2}) on the photoluminescence spectrum of F6 dispersed in a matrix of polystyrene at a concentration of 0.06 wt%. The inset shows the spectra normalized to peak intensity.

Table 1. Photoluminescence quantum yields for a range of F6 samples (see text for details).

Sample	PLQE (%)
F6 (100%)	26 ± 3
F6–PS blend (0.06% F6)	28 ± 3
F6–PS blend, photo-oxidized (28 min, 50 mW cm^{-2} UV)	2 ± 0.5
F6–PS blend, photo-oxidized and exposed to vapour	0.5 ± 0.5

9-fluorenone moieties for g-band emission. Polyfluorene chains uniformly dispersed within a polystyrene matrix at the concentration we have used here will have an average separation that is substantially greater than the maximum allowed for excimer formation ($\approx 3 \text{ \AA}$). We also expect that inter-segment interactions within the same chain will be substantially hindered by the rigid matrix.

There are several reasons why we expect the F6 chains to indeed be isolated within the polystyrene host. First, the fraction of F6 chains in the blend is very low. Second, we expect PS and F6 to be relatively miscible, as previously shown [23] to be the case for PS and PFO and consistent with the observation that chloroform is a good solvent for both PS and F6. The good matrix properties of polystyrene have also been shown by others [19]. Third, the emission in figure 2 (initial 0–0 peak at $\approx 418 \text{ nm}$) is blue-shifted in comparison with pristine, spin-coated films of PFO (0–0 peak at $\approx 425 \text{ nm}$ [5]). This observation is consistent with a matrix (solvent) dilution effect.

As already noted, the result of figure 2 is very similar to that reported by Sims *et al* [5], where poly(9,9-dioctylfluorene) (PFO) was dispersed in polystyrene at the same concentration. Here, we have chosen to use F6 instead of PFO so that any complications relating to the secondary conformational phase specific to PFO (the so-called β -phase) cannot play a role. β -phase samples can show significant variations in emission lineshape due to a superposition of spectral contributions from the glassy PFO matrix and from extended β -phase PFO chains

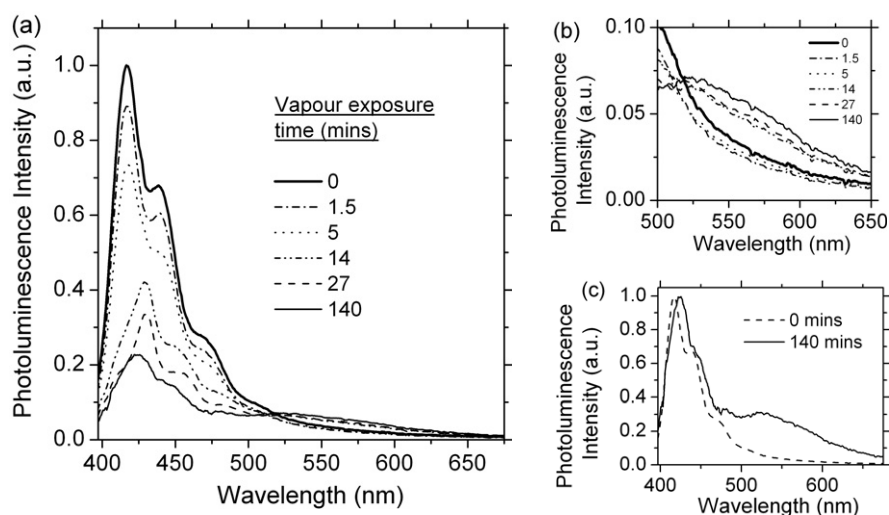


Figure 3. Effect of solvent vapour exposure on an oxidized (28 min, 50 mW cm^{-2} UV), 0.06 wt% F6 dispersed in PS drop-cast film. (a) *In situ* measurement of the evolution of PL emission during chloroform vapour exposure. Spectra have been normalized relative to the peak intensity of the blue emission before exposure to vapour. (b) Enlarged detail of *in situ* spectra depicting changes in the green spectral region. (c) Initial and final spectra normalized to the peak 0-0 F6 exciton emission intensity in the blue.

dispersed therein. The problem is then that the physical structure manipulations (solvent vapour exposure and thermal annealing) that we use below to activate g-band emission are expected to alter the proportion of β -phase chains—an undesirable ambiguity. Since F6 does not have any recorded tendency to form β -phase chains, this ambiguity is neatly avoided by the use of F6 in preference to PFO.

It has been suggested that inter-chain exciton migration is faster and generally more efficient than intra-chain migration [11, 19, 24] (although as noted above the opposite has also been proposed). Were this to be the case, increasing the separation of polyfluorene chains through matrix isolation might reduce the probability of excitons reaching a fluorenone site during their lifetime. If so, this could provide an alternative explanation for the observed suppression of ‘g-band’ emission. However, a recent study of the pressure dependence of poly(9,9-dioctylfluorene-co-benzothiadiazole) (F8BT) photoluminescence has shown that a large proportion of the pressure-enhanced spectral dispersion (dynamic red-shift) found in fully dense films also occurs in PS matrix-isolated samples [25]. Furthermore, were an inhibition of energy migration to fluorenone moieties responsible for the absence of g-band emission, one would not expect to see any quenching of the blue emission from fluorene singlet states. Our conclusion is that the suppression of g-band emission is not predominantly an effect of reduced energy migration to the fluorenone moieties, although, as we discuss later, energy migration effects do need to be carefully considered.

Having achieved suppression of the g-band emission, the effect of lifting the rigidity of the enveloping matrix can be studied. This is achieved by exposing the F6-PS blend system to an atmosphere saturated with chloroform vapour: a good solvent for both polymers. It is expected that the resulting swelling of the film will give the polymer chains greater motional freedom, reducing the terminal time for reptation. Because the solvent vapour exposure is carried

out at room temperature and without any UV light exposure, further chemical degradation of the F6 component is not expected. Figures 3(a) and (b) show the corresponding photoluminescence spectra. The initial spectrum ($t = 0 \text{ min}$) is for a sample of F6 dispersed in PS at a concentration of 0.06 wt% that has first been photo-oxidized for 28 min (50 mW cm^{-2} UV). Subsequent spectra show the effect of exposure to chloroform vapour over a period of 140 min. All measurements are made *in situ* in order to record absolute changes in spectral intensity. Figure 3(c) shows the spectra at 0 and 140 min normalized to their peak (0-0 vibronic transition) intensities. This figure clearly shows the increase in g-band emission relative to singlet emission that occurs (without further oxidation) as a result of exposure to solvent vapour. The corresponding time-resolved changes in the intensity of the singlet and g-band emission components are depicted in figure 4.

During the first ≈ 5 min of vapour exposure the intensity of the singlet peak at $\approx 420 \text{ nm}$ falls (figure 4(a)) with exposure to chloroform vapour, whilst the lineshape of the emission remains essentially unchanged. We observe also that the intensity of recorded emission intensity falls across all wavelengths, including at the g-band peak wavelength of 535 nm (figures 3(b) and 4(b)). PLQE measurements indicate a drop from $2 \pm 0.5\%$ to $0.5 \pm 0.5\%$ after vapour exposure (table 1). We consider that the fall in recorded emission intensity during this period is in significant part due to an optical effect associated with the collection of the luminescence signal. In particular we observe that vapour exposure reduces the tendency of the drop-cast films to scatter light, resulting in a reduction in PL collected in the forward direction. Related observations have provided an optical means to determine the crystallization temperature in thin film samples of PFO [26], with an approximately 1.5–2-fold increase in detected signal resulting from enhanced scattering upon crystallization. Increased exciton migration may also

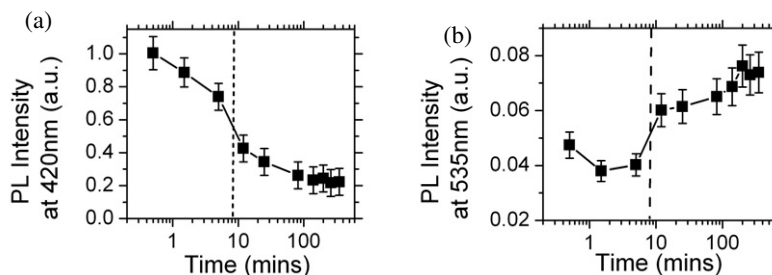


Figure 4. Evolution of emission intensity in 0.06 wt% F6 dispersed in PS blends at (a) 420 nm and at (b) 535 nm during exposure to chloroform vapour. Dashed lines demarcate the cross-over time in the spectral evolution (see text for details).

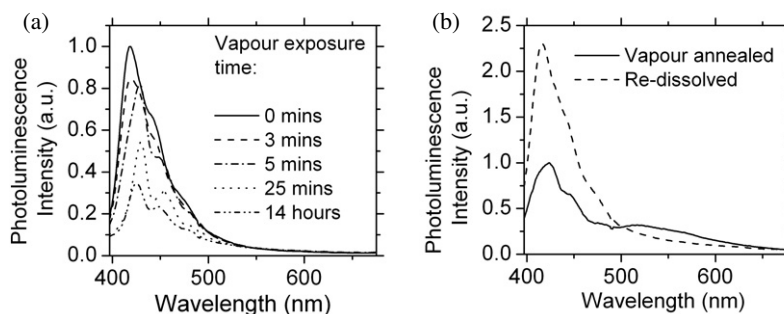


Figure 5. (a) Spectral evolution for an un-oxidized 0.06 wt% F6 dispersed in PS film subjected to chloroform vapour exposure. (b) Photoluminescence spectra of photo-oxidized (28 min, 50 mW cm^{-2}), drop-cast 0.06 wt% F6 dispersed in PS film after exposure to solvent vapour, then after re-dissolving and re-casting as a film.

play a role (see below) but, tellingly, there is no consequent appearance of g-band emission.

There is subsequently a qualitative change in spectral evolution with establishment of an isobestic point at $\lambda \approx 520 \text{ nm}$ and the emergence of the characteristic g-band component (figure 3(c)). This can also clearly be seen in the PL(t) data of figures 4(a) and (b), where the dashed vertical lines indicate the cross-over point. From this time onwards there is a seemingly correlated growth in g-band emission and reduction in F6 emission. Our working premise is that the latter behaviour is a direct result of changes in the physical structure (phase morphology) of our blend film samples. While it is entirely reasonable to expect that swelling a blend film in the vapour of a good solvent will induce such changes, we should also consider whether anything else might be occurring. One concern would be whether there was any unintended growth in the population of 9-fluorenone defects during this sequence of measurements. As already noted, precautions were taken to prevent, as far as possible, any further photo-oxidation. An additional argument that this concern is not material is that a different approach to physical structure manipulation, namely thermal annealing (see below), produces remarkably similar results in terms of spectral evolution, when we would expect quite different behaviour in respect of any unintended oxidation (see Sims *et al* [5]). Finally, we note that the activation of the g-band can be reversed (see below), something that would not be possible if its growth were indeed the result of further photo-oxidation.

Armed with this knowledge, we now further examine the spectral evolution during solvent vapour exposure. There are

two aspects to consider, namely (a) the continued reduction in F6 exciton emission in the blue and (b) the growth of the g-band emission at longer wavelengths. In relation to the first of these we have undertaken a control experiment in which a drop-cast film of 0.06 wt% F6 dispersed in PS was subjected to chloroform vapour exposure without first being photo-oxidized. The spectral evolution results for this sample are shown in figure 5(a). The key observation is that the F6 exciton emission intensity decreases with exposure time in a similar way to the initial behaviour of the oxidized sample (figure 3(a)) but without the appearance of any g-band emission. Thus whilst a preparatory photo-oxidation is necessary for the subsequent observation of a growing g-band emission it is not necessary in order to observe the drop in F6 exciton emission during solvent vapour exposure. What then causes this drop? We consider that it is analogous to the drop in luminescence efficiency seen for many conjugated polymers [27, 28] on going from solution to solid film samples and therefore that it signifies a rearrangement of the F6 polymer chains within the PS matrix. This rearrangement leads to a more ordered F6 chain structure and stronger inter-chain interactions (consistent with the red-shift and increase in vibronic structure visible in figures 3(a) and 5(a)) and a consequent reduction in emission efficiency. It is possible that one or more of (i) changes in scattering [26], (ii) a greater delocalization of excited state wavefunctions, and (iii) exciton migration to quenching sites is/are relevant here but we do not seek to discriminate amongst these effects since this does not directly impact on the central theme of our study; it is also not straightforward to disentangle the different contributions.

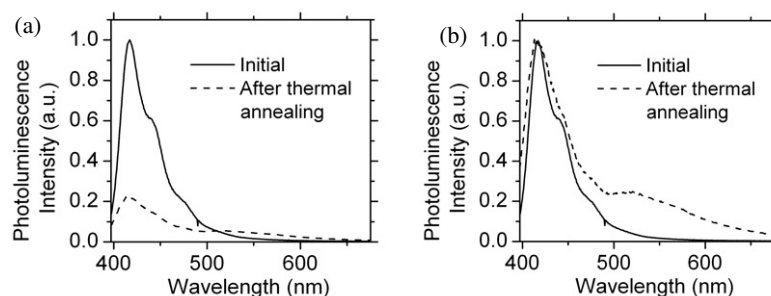


Figure 6. (a) Photoluminescence spectra of a photo-oxidized (28 min, 50 mW cm^{-2}), drop-cast 0.06 wt% F6 dispersed in PS film, before and after thermal annealing at 200°C for 90 min. (b) Data from (a) normalized to the peak 0-0 F6 exciton emission intensity in the blue.

Reiterating, the control experiment allows us to show that a continued drop in F6 singlet emission during solvent vapour exposure can occur independently of whether the sample has been initially photo-oxidized.

Returning to the data in figure 3 we can then understand the observed changes in the blue F6 exciton emission part of the spectrum as being a straightforward result of phase separation driven by the solvent vapour swelling. Again, the precise mechanisms contributing to the drop in PL intensity remain to be fully determined: it is likely for instance that an increased exciton migration to 9-fluorenone quenching sites plays a specific role here. The second effect in figure 3, namely the growth of g-band emission (which does not occur for the un-oxidized sample), is then understood to be the consequence of a facilitation of excimer formation resulting from the phase-separation-driven increase in the proximity between 9-fluorenone defect moieties. As phase separation and, potentially, chain folding occurs, the average separation between 9-fluorenone moieties will decrease (a process that is possibly further augmented by attractive forces between dipolar C=O groups). This increases the likelihood that 9-fluorenone moieties will be in sufficient proximity to form excimers.

A second control experiment involves re-dissolving an oxidized sample that had been subjected to vapour exposure (i.e. that shows g-band emission) and re-casting it on a new substrate. The process of re-dissolving involves removing (with a scalpel) the film from the substrate into a vial, adding chloroform and mechanically agitating to ensure that the material fully dissolves. After re-casting the fluorescence spectrum is again recorded (see figure 5(b), 're-dissolved'). The emission spectrum is very similar to that found prior to solvent exposure: dissolution and re-casting removes the g-band emission and returns a stronger short wavelength luminescence. This reversibility confirms the physical structural nature of the g-band generation and thus supports our excimer description.

The behaviour seen under solvent vapour exposure can be further demonstrated to be a general consequence of phase separation. This is done using thermal annealing above the glass transition temperature of PS to produce an equivalent structural relaxation. As for solvent vapour exposure we can take appropriate precautions to ensure that further oxidation is avoided. In this case, heating under nitrogen is sufficient to

avoid thermal oxidation [29]. Figure 6 shows the change in photoluminescence of a photo-oxidized blend of 0.06 wt% F6 in PS upon being heated to 200°C in a nitrogen atmosphere (glove box with oxygen content $\approx 0.6 \text{ ppm}$). In common with the vapour treated sample, there is a significant reduction in the absolute intensity of the singlet emission and a rise in emission intensity in the g-band region. The glass transition temperature of polystyrene is 95°C , so that phase separation of the two components in a similar fashion to vapour treatment is expected. Furthermore, 200°C is above the crystal to nematic liquid crystal phase transition temperature of PFO (170°C [26]), such that ordering of the polyfluorene chains can be expected. The observed increase in g-band emission can then again be attributed to the activation of excimer emission when 9-fluorenone defect moieties reach the required proximity for excimer formation. This activation of g-band emission is independent of the method (solvent exposure or annealing in an inert gas) used to lift the rigidity of the polystyrene matrix.

To investigate further the issue of inter- versus intra-chain energy migration, a study was made of systems comprising mixtures of fluorene and 9-fluorenone molecules in chloroform solution. For such systems only inter-molecular energy transfer can occur. In dilute solution [5, 11, 30–32] the photoluminescence of 9-fluorenone is characterized by a monomer emission band peaked at roughly 350 nm and a second, broad emission band that spans 420–700 nm. The latter closely mirrors the polyfluorene g-band emission spectrum and will therefore be referred to as the 9-fluorenone g-band below. It has a strong concentration and solvent dependence and has previously been assigned as an excimer state [5, 30–32].

Figure 7(a) shows the photoluminescence spectra for a series of 10 mg ml^{-1} samples containing varying weight fractions of fluorene and 9-fluorenone. It is evident that the intensity of g-band emission is strongly dependent on the relative proportions of fluorene and 9-fluorenone molecules in the mixture. Importantly, a significant g-band emission contribution is observed even for a 9-fluorenone weight fraction of 1%. It is interesting to compare this result with the thin film blends of PFO and 9-fluorenone studied by Sims *et al* [5]. There, g-band emission was not observed for 9-fluorenone concentrations below 4 wt%. A minimum concentration for the appearance of the g-band was thus observed, unlike the

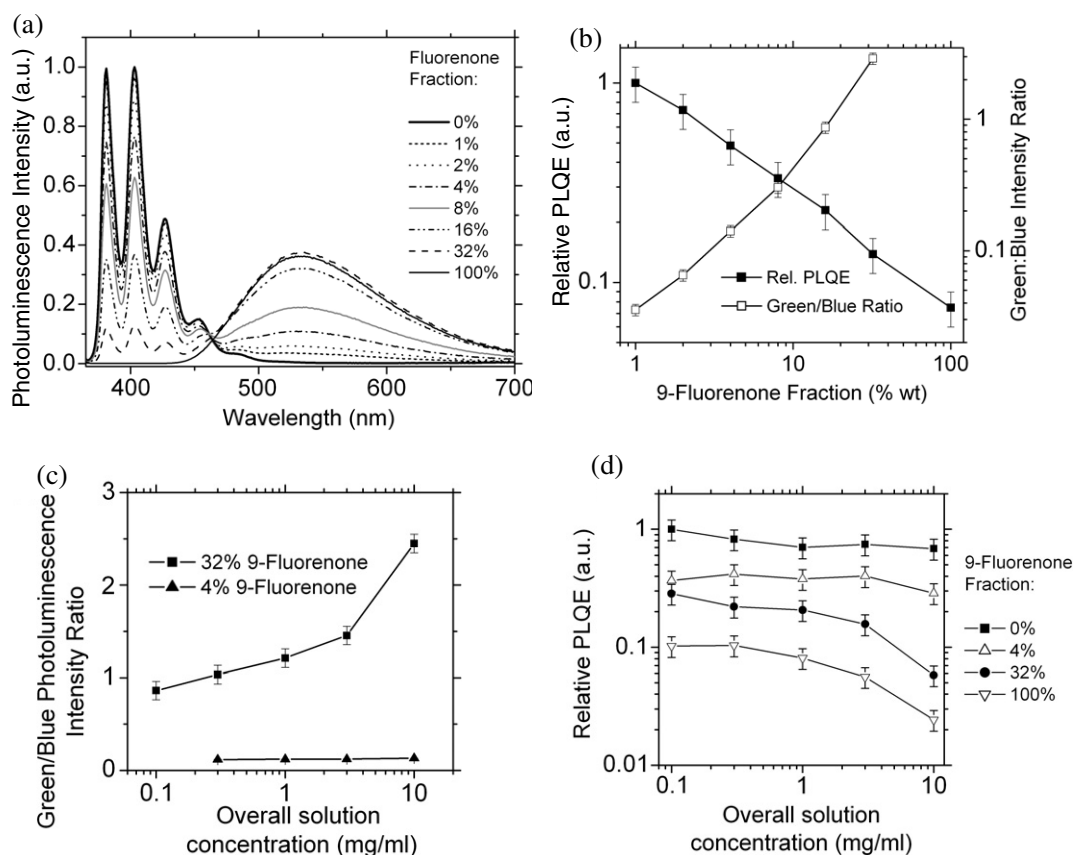


Figure 7. (a) Photoluminescence spectra of mixtures of fluorene and 9-fluorenone dissolved in chloroform. The overall solution concentration was kept at 10 mg ml^{-1} . All spectra are recorded under identical conditions (excitation wavelength, $\lambda = 360 \text{ nm}$) allowing comparison of intensities. Spectra have been normalized relative to the peak intensity of the 100% fluorene solution. (b) Relative PLQE and green/blue emission intensity ratio for a 10 mg ml^{-1} solution as a function of 9-fluorenone fraction. Relative PLQE is found by integrating the PL over the emission spectrum and dividing by the absorption fraction. (c) Ratio of green/blue emission intensity for two 9-fluorenone fractions as a function of overall solution concentration. (d) Relative PLQE as a function of overall solution concentration for a range of fluorenone fractions.

situation found here (figures 7(a) and (b)). The origins of this discrepancy provide further insight into the nature of the g-band.

The differences between the study presented here and that of Sims *et al* are the use of ‘monomeric’ fluorene as opposed to poly(dialkyl-fluorene) and that the samples are in solution rather than in solid phase. In solid phase film samples of 9-fluorenone dispersed in a poly(dialkyl-fluorene) matrix the molecules are densely packed, and therefore we can expect inter-molecular exciton migration to defects to be maximized. If the g-band emission originates from a 9-fluorenone-sited intra-molecular excited state then the overall intensity of g-band emission should increase even for small fluorenone concentrations due to the effective inter-molecular energy migration. The fact that this is not observed in PFO/9-fluorenone blends in solid phase can be explained by the fluorenone-based excimer model. The polymeric nature of PFO can disrupt the formation of excimers by preventing the close interaction of 9-fluorenone molecules. In the solutions presented in figure 7, excimer formation is not inhibited because both components are monomeric and do not therefore strongly inhibit each other’s motion.

Furthermore, molecules in solution have much greater kinetic freedom, which leads to frequent collisions between 9-fluorenone molecules, thus permitting the required proximity for excimer formation. Corresponding collisions between fluorene and fluorenone molecules enable the initial energy transfer that precedes excimer formation and that quenches the vibronically structured fluorene emission in the blue (figure 7(a)). Figure 7(b) shows the change in PLQE of a 10 mg ml^{-1} solution as the fraction of fluorenone increases. The corresponding change in the intensity ratio of g-band emission to blue, fluorene singlet emission is also displayed. Adding 9-fluorenone causes quenching of the fluorene emission and growth of the g-band.

Figure 7(c) shows the ratio between the peak intensities at the g-band emission peak (535 nm) and the blue, singlet peak (403 nm) for 32 and 4 wt% 9-fluorenone content. It is clear that as the overall solution concentration increases the ratio of g-band to singlet emission intensity increases, especially for the 32 wt% 9-fluorenone solution. The concentration dependence of the g-band emission in this system is consistent with the excimer hypothesis for the origin of the g-band. As the overall concentration increases (at fixed 9-fluorenone fraction) Γ_D (the excimer formation rate) is increased. More information

can be gained from knowledge of the solution PLQEs. Figure 7(d) shows how the PLQE varies with the overall solution concentration for four 9-fluorenone fractions. Both pure fluorene (i.e. 0 wt% fluorenone) and 4 wt% 9-fluorenone solutions show little sensitivity towards overall concentration within the range we have studied. This is consistent with the relatively small increase in g-band ratio ($\times 1.1$) over the same range for the 4 wt% 9-fluorenone solution (figure 7(c)). The indication is that the increase in Γ_D is insufficiently large to cause a significant change to the PLQE. Moreover, given the relative flatness of the PLQE concentration dependence, one can speculate that the fraction of fluorene and 9-fluorenone molecules that are excited either directly or indirectly in the experiment remains approximately constant throughout the concentration range studied. Moreover, from the seeming absence of concentration quenching in the 4% solution, one can also deduce that the diffusion-controlled mean free time, $\bar{\tau}$, between 9-fluorenone and 9-fluorenone collisions ($\propto 1/\Gamma_D$) is longer than the intrinsic excited state lifetime (τ) of 9-fluorenone over the same concentration range.

As the 9-fluorenone fraction is increased one begins to see a cross-over from $\bar{\tau} > \tau$ to $\bar{\tau} < \tau$, resulting in a sharp rise in Γ_D and a corresponding fall in PLQE. For the 32% case, the effect is manifested in the corresponding PL spectra, where the g-band ratio increases by a more significant factor of $\times 3.1$ over the same concentration range (0.1–10 mg ml⁻¹).

Figure 7(d) shows the effect that increasing the 9-fluorenone fraction (at a constant overall concentration) has on the solution PLQE. In a manner similar to increasing the 9-fluorenone fraction in PFO/9-fluorenone blend films [5], the PLQE follows a monotonic decrease up to the highest blend concentration studied. This can be explained by the combined effect of adding an increasing proportion of a less emissive compound and the influence of an increasing Γ_D for fluorenone. These types of plots are somewhat less insightful than the fixed fraction experiments, but nevertheless an important point can be made with regard to the 100% fluorenone solution. Unlike the previous study [5], in which the PLQE of a (100%) fluorenone solid state sample was shown to be three times higher than 1:1 PFO/fluorenone blend films, the 100% 9-fluorenone solution PLQE is lower than any of the mixed solutions studied here. This is consistent with our previous observations in PL lifetime measurements [5] in which τ_{PL} for the fluorenone excimer was found to be largely independent of concentration but significantly shorter than in the solid state. We consider this to be the result of a reduction in the non-radiative decay rate in the solid state due to lattice imposed constraints. In solution, the fluid medium facilitates a higher probability for non-radiative dissociation. In a separate study, we have observed similar phenomena to occur in well defined 9-fluorenone-substituted oligofluorenes, the results of which will be presented elsewhere.

4. Conclusions

In summary, we have reported a detailed study targeted at distinguishing between the two possible causes of the g-band emission in degraded poly(dialkyl-fluorenes) that have been

proposed in the literature. These are the decay of an excited state localized on a single 9-fluorenone based moiety, or the decay of an excimer delocalized over two, co-facially arranged 9-fluorenone groups. A series of experiments examining the emission characteristics of poly(9,9-dihexylfluorene), fluorene and 9-fluorenone based systems has been presented. It has been shown conclusively that the average separation between 9-fluorenone groups plays an important role in the emission intensity of the g-band. By isolating polyfluorene chains at low concentration in an inert rigid PS matrix, it is possible to entirely preclude the g-band emission. By lifting the rigidity of the matrix, localized phase separation of the two components occurs. This leads to an increase in the g-band emission, indicating the necessity of inter-molecular interaction. The importance of inter- and intra-molecular energy transfer efficiencies has also been studied using systems of fluorene and 9-fluorenone monomers co-dissolved in chloroform where all energy transfer is necessarily inter-molecular. While inter-molecular excitation transfer to 9-fluorenone defect moieties does, most likely, play a role in the activation of g-band emission, this issue alone is insufficient to explain the results presented in this report and elsewhere. The results presented constitute further evidence for a 9-fluorenone excimer state as the root cause of the g-band emission. Oxidation leads to quenching of the poly(9,9-dialkyl-fluorene) exciton emission, demonstrating that energy migration does occur. Vapour and thermal annealing drive phase separation, leading to a further 'concentration quenching' of the exciton emission and the emergence of g-band emission. These results together with the observed reversibility of g-band activation (dissolving and re-casting film samples of 0.06 wt% F6/PS with g-band emission turns the emission off) provide strong support for the excimer model proposed by Sims *et al* [5].

Acknowledgments

The authors are grateful to The Dow Chemical Company for providing the poly(9,9-dihexylfluorene) polymer used in this study. We also thank the UK Engineering and Physical Sciences Research Council (DTA studentship for TAMF) and the Commission of the European Community (STRP FP6-2006-IST 026365 POLYCOM) for financial support. Early stages of this work were supported by the UK EPSRC funded Carbon Based Electronics Consortium.

References

- [1] Friend R, Gymer R, Holmes A, Burroughes J, Marks R, Taliani C, Bradley D D C, Dos Santos D A, Bredas J, Logdlund M and Salaneck W 1999 *Nature* **397** 121
- [2] Bradley D D C, Grell M, Long X, Mellor H, Grice A W, Inbasekaran M and Woo E P 1997 *Proc. SPIE Int. Soc. Opt. Eng.* **3145** 254
- [3] List E, Guentner R, de Freitas P S and Scherf U 2003 *Adv. Mater.* **14** 374
- [4] Gong X, Iyer P, Moses D, Bazan G, Heeger A and Xiao S 2003 *Adv. Funct. Mater.* **13** 325
- [5] Sims M, Bradley D D C, Ariu M, Koeberg M, Asimakis A, Grell M and Lidzey D G 2004 *Adv. Funct. Mater.* **14** 765
- [6] Zhao W, Cao T and White J M 2004 *Adv. Funct. Mater.* **14** 783

- [7] Liu L, Qiu S, Wang B, Zhang W, Lu P, Xie Z, Hanif M, Ma Y and Shen J 2005 *J. Phys. Chem. B* **109** 23366
- [8] Kulkarni A, Kong X and Jenekhe S 2004 *J. Phys. Chem. B* **108** 8689
- [9] Romaner L, Pogantsch A, de Freitas P S, Scherf U, Gaal M, Zojer E and List E 2003 *Adv. Funct. Mater.* **13** 597
- [10] Hintschich S, Rothe C, Sinha S, Monkman A, de Freitas P S and Scherf U 2003 *J. Chem. Phys.* **119** 12017
- [11] Dias F B, Maiti M, Hintschich S I and Monkman A P 2005 *J. Chem. Phys.* **122** 054904
- [12] Becker K, Lupton J M, Feldmann J, Nehls B S, Galbrecht F, Gao D Q and Scherf U 2006 *Adv. Funct. Mater.* **16** 364
- [13] Lupton J, Craig M and Meijer E 2002 *Adv. Funct. Mater.* **80** 4489
- [14] Chi C, Im C, Enkelmann V, Ziegler A, Lieser G and Wegner G 2005 *Chem.—Eur. J.* **11** 6833
- [15] Jaramillo-Isaza F and Turner M 2006 *J. Mater. Chem.* **16** 83
- [16] Zhou Z, Zhang Y, Xie Y, Cao Y and Pei J 2006 *Macromolecules* **39** 3830
- [17] Chochos C L, Kallitsis J K and Gregoriou V G 2005 *J. Phys. Chem. B* **109** 8755
- [18] Lu H, Liu C, Jen T H, Liao J, Tseng H, Huang C, Hung M and Chen S 2005 *Macromolecules* **38** 10619
- [19] Cadby A, Dean R, Fox A, Jones R and Lidzey D 2005 *Nano Lett.* **11** 2232
- [20] Aharon C E, Albo A, Kalina M and Frey G 2006 *Adv. Funct. Mater.* **16** 980
- [21] Kulkarni A P and Jenekhe S A 2003 *Macromolecules* **36** 5285
- [22] Ariu M, Lidzey D, Sims M, Cadby A, Lane P and Bradley D D C 2002 *J. Phys.: Condens. Matter* **14** 9975
- [23] Grell M, Bradley D D C, Ungar G, Hill J and Whitehead K S 1999 *Macromolecules* **32** 5810
- [24] Nguyen T, Wu J, Doan V, Schwartz B J and Tolbert S H 2000 *Science* **288** 652
- [25] Schmidtke J P 2006 *Doctoral Dissertation* University of Cambridge, UK
- [26] Sims M, Zheng K, Campoy-Quiles M, Xia R, Stavrinou P N, Bradley D D C and Etchegoin P 2005 *J. Phys.: Condens. Matter* **17** 6307
- [27] Wang P, Collison C J and Rothberg L J 2001 *J. Photochem. Photobiol. A* **144** 63
- [28] Schwartz B J 2003 *Annu. Rev. Phys. Chem.* **54** 141
- [29] Bliznyuk V, Carter S, Scott J, Klaner G, Miller R and Miller D 1999 *Macromolecules* **32** 36
- [30] Rani S A, Sobhanadri J and Rao T A P 1996 *J. Photochem. Photobiol. A* **94** 1
- [31] Murphy R, Moorlag C, Green W and Bohne C 1997 *J. Photochem. Photobiol. A* **110** 123
- [32] Heldt J R, Heldt J, Jozefowicz M and Kaminski J 2001 *J. Fluor.* **11** 65