

Control of β -phase formation in polyfluorene thin films via Franck–Condon analysis

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Abstract

In the blue light-emitting polymer poly(9,9-dioctylfluorene) (PFO) two distinct morphological phases have been identified, that is the glassy phase and a planar β -phase. We show that the proportion of the formation of the two phases can be controlled by simply spinning thin films from different solvents such as chloroform and cyclopentanone. We use a Franck–Condon analysis with vibrational modes obtained from Raman spectra to analyze the emission spectra at low temperature. Films spun from cyclopentanone are dominated by from the β -phase emission while films spun from chloroform have a high fraction of glassy phase emission. Comparison between absorption and emission spectra shows evidence for spectral diffusion from the glassy to the β -phase. We discuss the Huang–Rhys parameters for both phases.

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1. Introduction

The photophysical properties of poly(9,9-dioctylfluorene) (PFO) are strongly influenced by the morphology of the film such as the glassy and β -phases [1–3]. The latter is thought to be planar because its emission is very similar to that of the planar rigid LPPP polymer [2]. The fractions of α - and β -phases determine the number of triplet excitons and polarons formed and thus the photoluminescence and electroluminescence efficiency, thus having control over the formation of these phases fractions is crucial for the performance of light-emitting diodes [1].

Approaches to alter the morphology of PFO thin films include thermal and vapour treatment [2], though a dependence on solvents has also been reported [4]. We control the formation of the two phases by spinning thin films using two solvents with different polarities and boiling points, that is cyclopentanone and chloroform. In absorption, the β -phase can be identified by a narrow sharp peak just below the main absorption band [1]. In emission, we use a Franck–Condon analysis to determine the fraction of emission from the β -phase.

2. Experimental

All measurements were made using thin films with typical thickness of 30–50 nm spun onto quartz substrates from the chloroform and cyclopentanone solutions of the polymer using a conventional photoresist spin-coater. The optical absorption was measured with a Hewlett-Packard ultraviolet-visible (UV-Vis) spectrometer. Measurements of photoluminescence (PL) were made with the sample in a continuous-flow helium cryostat. For PL measurements, excitation was provided by the UV lines (355 and 365 nm) of a continuous wave (cw) argon ion laser. Typical intensities used were a few mW/mm^2 . The emission spectra were recorded using a spectrograph with an optical fibre input coupled to a cooled charge coupled device (CCD) array (Oriel Instaspect IV). Raman spectra were taken with a Renishaw Raman microscope connected to a spectrometer with a CCD camera.

3. Absorption and photoluminescence

Fig. 1 shows the absorption spectra from the thin films spun from cyclopentanone and chloroform solutions. For the film spun from cyclopentanone solution, we observe a low-energy absorption peak around 2.84 eV that is characteristic for β -phase formation, while there is no absorption

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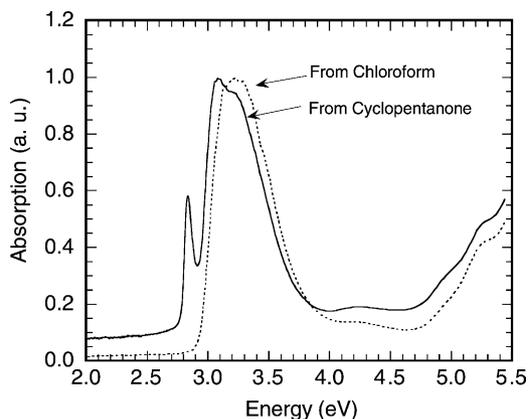


Fig. 1. The room temperature absorption spectra of thin films of F8 spun from a chloroform solution (dotted line) and spun from a cyclopentanone solution (solid line).

feature associated with the β -phase for the films spun from chloroform. Using the intensity of the peak at 2.84 eV and the β -phase absorption spectrum from literature [1], we infer that the β -phase absorption accounts for about one-quarter of the total absorption of the cyclopentanone-spun film. Cyclopentanone has a high boiling point and high polarity, which makes it a poor solvent for PFO and so induces β -phase formation.

The photoluminescence spectra of the two films are shown in Fig. 2. The onset of emission and the vibronic structure is very different for the films spun from the two solvents, both at 300 and 5 K. Upon cooling, the spectra shift to the red and inhomogeneous broadening reduces, so the vibronic structure becomes more resolved. The low-temperature spectrum of the cyclopentanone-spun film very closely resembles that of a fully planar MeLPPP and can thus be attributed to β -phase emission [1]. The red-shift between the spectra at 5 and 300 K is sometimes attributed an increase in conjugation

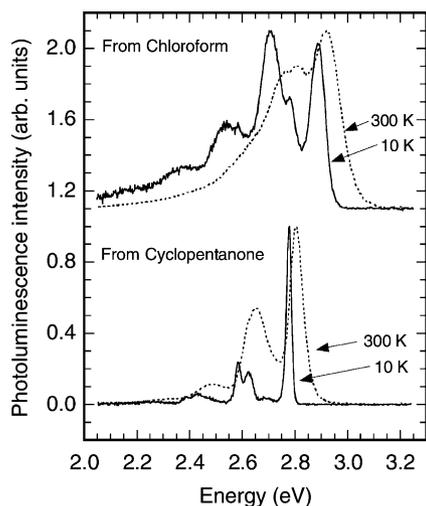


Fig. 2. The photoluminescence spectra of thin films of F8 spun from a chloroform solution (upper half) and spun from a cyclopentanone solution (lower half) taken at 300 K (dotted line) and at 10 K (solid line).

length due to a planarization of the polymer backbone. The fact that it can be observed for the film spun from cyclopentanone suggests that the bathochromic shift may rather arise from the freezing out of exciton migration between sites of lower to higher energy. There is a small vibronic shoulder at 2.77 eV in the spectrum of the chloroform-spun film at 5 K. This shoulder coincides with the peak of the emission in the cyclopentanone-spun films. In order to identify whether there is any β -phase emission in the film spun from chloroform, we have analyzed the Franck–Condon terms of the 5 K emission spectra.

4. Franck–Condon analysis

The vibronic structure of the photoluminescence in conjugated polymers is determined by the Franck–Condon factors. The emission spectrum $P(\hbar\omega)$ in photons/energy interval can be modelled as:

$$P(\hbar\omega) = n^3 (\hbar\omega)^3 \sum_{n_i=0} I_{0-n_i} \Gamma \delta[\hbar\omega - (\hbar\omega_0 - n_i \hbar\omega_i)] \quad (1)$$

where $\hbar\omega_0$ is the energy of the 0–0 peak, $\hbar\omega_i$ the vibrational energies of the modes i , $n_i = 0-4$ denotes the number of vibrational overtones, Γ is the Gaussian lineshape operator (and was kept at constant full-width-half-maximum for all modes i and overtones n_i), n is the refractive index which we measured by ellipsometry [5] and I_{0-n_i} is the intensity of the 0– n_i vibronic transition of the mode i . I_{0-n_i} is related to the Huang–Rhys parameter S_i by:

$$I_{0-n_i} = \frac{e^{-S_i} S_i^{n_i}}{n_i!} \quad (2)$$

Thus, the ratio of the 0–0 peak to the 0–1 peak just gives the Huang–Rhys parameter of a mode. The total Huang–Rhys parameter is the sum of all the individual modes. It is a measure for the difference between the ground and excited state geometries. The energies of the vibrational modes were determined by Raman measurements, which we found to be in good agreement with those published by Ariu et al. [6]. We considered seven modes i and $n_i = 4$ overtones for each mode. In detail we considered a mode (7) at 1605 cm^{-1} which has been assigned to a symmetric ring stretching mode, three modes (6–4) which we placed at about 1137 , 1282 and 1411 cm^{-1} to account for a number of peaks in the $1400-1100 \text{ cm}^{-1}$ range (mostly C–C stretching modes between phenylene rings and C–H in-plane bending modes), and three modes (3–1) at about 604 , 806 and 838 cm^{-1} which take low Huang–Rhys parameters in all fits.

Fig. 3 shows the emission and the Franck–Condon-fit for the film spun from cyclopentanone solution. To fit the emission, we varied the intensities of the 0–1 transitions for the seven modes and the Gaussian linewidth, and compared the resulting emission spectrum according to Eq. (1) with the experimental spectrum. An excellent agreement can be obtained assuming a single emission with the 0–0 origin at

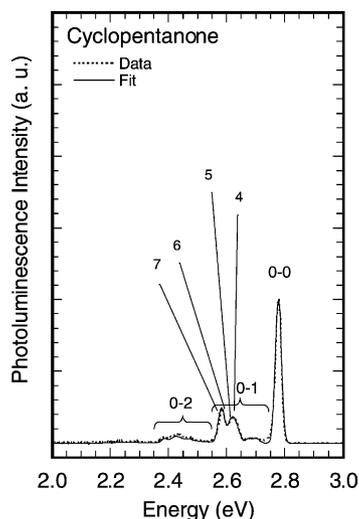


Fig. 3. The photoluminescence spectrum at 5 K of PFO spun from cyclopentanone solution (dotted line) and the Franck–Condon fit to it (solid line). The positions of the 0–0, 0–1 and 0–2 vibrational transitions are also indicated along with the 0–1 peaks of modes 4–7.

2.78 eV. This suggests that all of the emission occurs from β -phase sites, even though these sites only contribute to about a quarter of the room temperature absorption. The complete lack of any glassy phase emission indicates efficient spectral diffusion from the higher energy glassy phase to the lower energy β -phase, unless more β -phase is formed upon cooling. The β -phase has a low overall Huang–Rhys parameter of 0.7 consistent with a long conjugation length, and a narrow linewidth of 25 meV. The Huang–Rhys parameters are distributed over the modes as $S_7 = 0.24$, $S_{6+5+4} = 0.28$, $S_{1+2+3} = 0.06$. The high intensity of the modes 6–4 in the 1400–1100 cm^{-1} range compared to the ring stretching mode 7 is consistent with the relative intensity distribution in the Raman spectra [7].

In contrast, it is not possible to model the emission of the film spun from chloroform by a single Franck–Condon progression, but only as a superposition of two progressions. To obtain a good fit it was further necessary to subtract a broad Gaussian peak centred around 2.3 eV, which we attribute to some aggregation or defect sites [1]. Fig. 4 shows the experimental data along with the fit and its two components. In one component we assume a β -phase, so we take the 0–0 peak to be at 2.78 eV and use the same Huang–Rhys parameters as above. A slightly wider Gaussian linewidth of 34 meV is required for a good fit. In the second component we place the 0–0 position at 2.89 eV, that is the peak position of the glassy phase, and we need to use a much wider linewidth of 64 meV. The total Huang–Rhys parameter for the α -phase is 1.4, which is twice as much as for the β -phase and suggests a much shorter conjugation length. Such a wide linewidth can be caused by low-energy torsional modes [8] that are as well as increased configurational disorder. The individual S_i for the α -phase are $S_7 = 0.46$, $S_{6+5+4} = 0.73$, $S_{1+2+3} = 0.18$. Thus the absolute and rel-

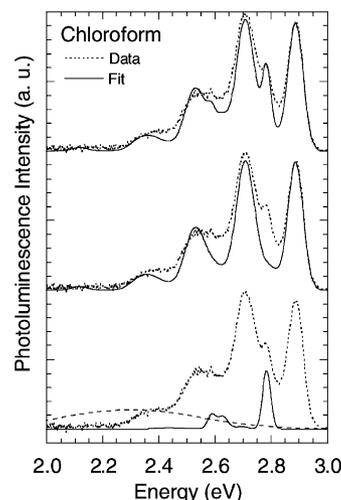


Fig. 4. The photoluminescence spectrum at 5 K of PFO spun from chloroform solution (dotted lines, top, middle and bottom position) along with a Franck–Condon progression for the β -phase (solid line, bottom position), for the glassy phase (solid line, middle position) and for the sum of two phases (solid line, top position). A broad Gaussian background was subtracted from the data, and is also shown (dashed line, bottom position).

ative contribution of the high-energy ring stretching mode 7 is lower in the α -phase than in the planar β -phase. The sum of the Franck–Condon progressions from the two phase models the experimental data well. The β -phase contributes to about one-tenth of the total emission, even though there is no sign of the β -phase in the absorption spectrum. The absorption was taken at room temperature, and further work will clarify whether some β -phase forms upon cooling.

Acknowledgements

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