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Microscopic investigation of the poly(9,9-dioctylfluorene) photoluminescence dependence on the deposition conditions by confocal laser microscopy

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We studied the microscopic dependence of poly(9,9-dioctylfluorene) photoluminescence (PL) on the deposition conditions. We show that in films spin coated from chloroform phase separation of β and glassy phases is present, with micrometric β phase clusters covering about 6% of the sample surface. The exposure to toluene vapors leads to the disappearance of the β phase clusters, but increases the β phase content in the films due to swelling induced polyfluorene chain planarization. The deposition from toluene solution leads to nonuniform PL intensity, dominated by the β phase emission, attributed to an interplay between aggregation during the solvent evaporation and solvent swelling induced chain planarization. © *2006 American Institute of Physics.*
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Large attention has been devoted in the last decades to organic conjugated compounds, both polymers and short molecules, mainly due to their possible applications to low cost photonic, optoelectronic, and electronic devices.

Among the several polymers showing electroluminescence (EL),[1] optical gain,[2] lasing,[3] and field effect mobility,[4] fluorene based polymers have been recently employed to realize high luminance light emitting diodes,[5,6] photovoltaic devices,[7] and thin film transistor.[8] Strong tunable optical gain has been also demonstrated in this class of materials,[9,10] which has been recently exploited to realize optically pumped distributed feedback lasers (DFB) with one-dimensional and two-dimensional nanopatterning.[11]

Moreover some polyfluorenes, in particular, poly(9,9-dioctylfluorene) (PF8), are very interesting due to their mesomorphic behaviors[12] and the strong morphology dependence of their emission properties.[13] In PF8 thin films it has been demonstrated that different phases coexist, in particular, a disordered glassy phase, and a crystalline β phase characterized by molecules with higher planarity.[14] The relative quantity of each phase depends on the sample deposition conditions[15,16] and it can be modified by postdeposition processing.[17–19] A systematic investigations on the β phase content in samples deposited from different solvents allowed to conclude that the β phase formation is favored not only by a poor molecule solubility,[15] but also by a high solvent boiling point.[16] This peculiarity of PF8 allows detailed studies of the relationship between the optical properties and the geometrical structure of the molecules without the necessity of modifying the molecules chemical structure. Moreover, starting from the assumption that the deposition conditions affect the film morphology, the comparison of films deposited in different conditions was used to study the morphology dependence of the optical gain,[20] of the triplet and polarons formation rates,[18,21] of the photoluminescence (PL) quantum yield,[19] and of the vibronic coupling.[16]

However, despite these results, a direct microscopic investigation of the relationship between deposition conditions, β phase content, morphology, and photoluminescence is still missing. In this letter we investigated the local emission properties of PF8 thin films spin coated from chloroform (sample A) and toluene (sample C), characterized by a different boiling point, and exposed to toluene vapors after spin coating from chloroform (sample B). In all the investigated samples the glassy and β phase are present, with a relative β phase content in the range from 4.3% to 6.7%.

We show that in the films deposited from chloroform the glassy and β phase are partially separated, with β phase clusters with a characteristic size of few tens of micrometers and with a surface coverage of about 6%, and a very low β phase content in the regions outside the clusters. A postdeposition exposure to toluene vapors leads to an increased morphology uniformity and to a decrease of the total β phase content in the sample, due to the interplay between the disappearance of the β phase clusters and the increase of the β phase content in the uniform morphology regions, due to the swelling induced by the solvent vapors. Finally, the films deposited from a solvent with higher boiling point, such as toluene, show the highest content of β phase and a local PL spectra dominated by the β phase. Moreover a worse morphology uniformity is observed, with bright regions with a typical dimension of tens of micrometers and dark micrometric regions, suggesting that molecular aggregation on a microscopic scale takes place during the spin coating.

The PF8 (see Fig. 1) was purchased from HW Sands (OHA 2311) and used as received. The films were prepared

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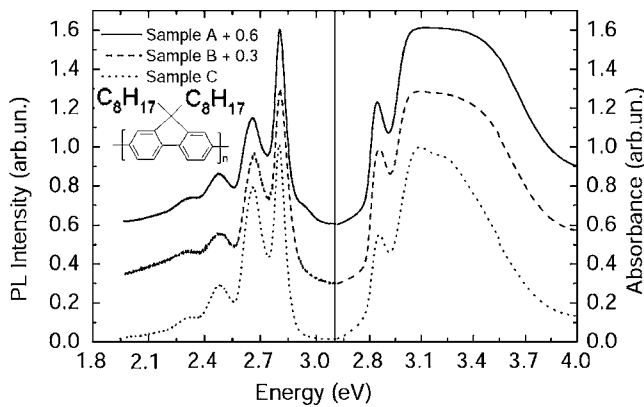
FIG. 1. PL (left) and absorption spectra (right) of the three samples. In order to allow an easier comparison of the line shape spectra, all the spectra are normalized to their peak value and vertically offset for clarity. The chemical structure of the PF8 is also reported.

by spin coating on quartz substrates from chloroform solutions (sample A), with a boiling temperature of 61 °C, from toluene solution (sample C), with a boiling temperature of 110 °C, and by postdeposition exposure for 12 h to toluene vapors of sample A (sample B). Standard PL measurements were performed by exciting a circular region of the sample with a radius of about 50 μm with a He–Cd ($\lambda = 325$ nm) laser. The film thickness was about 400 nm for all the samples. The emitted PL was then spectrally dispersed by a monochromator and detected by a Si-CCD (charge-coupled device). The absorption spectra were measured by a double beam spectrophotometer. The PL measurements with spatial resolution of about 1 μm were performed with an Olympus FV1000 confocal microscope by exciting the samples with a solid state laser ($\lambda = 405$ nm) and detecting the collected PL with a photomultiplier. All the PL measurements were performed with an excitation density of about 40 W cm^{-2} at room temperature in air.

The absorption spectra of the three samples (see Fig. 1) clearly show a low energy peak at about 2.84 eV, typical of the $S_0 \rightarrow S_1 \beta$ phase absorption, and a broadband at about 3.25 eV, due to the glassy phase $S_0 \rightarrow S_1$ transition. The relative β phase content, estimated from the absorption band

areas assuming the same oscillator strength for the glassy and the β phase absorption,[22] is 5.9% in sample A, 4.3% in sample B, and 6.7% in sample C. The PL spectra of sample A shows a high energy shoulder at about 2.93 eV, due to glassy phase emission,[22] and a main resonance at about 2.81 eV due to the 0-0 line of the β phase emission,[22] followed by evident vibronic replicas at lower energy. After toluene vapor exposure (sample B), despite the decrease of the total β phase content, the PL spectra are dominated by the β phase emission as no glassy phase emission is observed. Finally, the PL spectra of sample C, deposited from toluene, show only the β phase emission, and no glassy phase emission.

In order to investigate the microscopic origin of the difference in the PL spectra of the three samples and to analyze the effects of the deposition conditions on the films morphology, we performed spatially resolved PL measurements. The PL maps in the range of 2.605–2.857 eV are reported in Fig. 2 for a 82×82 μm^2 region of the three samples, representative of the typical film morphology.

Sample A is characterized [see Fig. 2(a)] by wide regions with uniform morphology and emission intensity and by clusters with a typical size of few tens of micrometers and a surface coverage of about 6%. We observe that the PL spectra collected from circular regions with 1.2 μm radius inside the cluster (spectra a1, a2, and a3 in Fig. 2) only show the β phase emission, while both glassy phase and β phase emissions are observed in the uniform region (spectra a4, a5, and a6). The absence of glassy phase emission in the clusters is also evidenced in Fig. 3 in which the PL maps at the peak energy of the glassy and β phase emissions are compared. Moreover the PL spectra from the uniform regions of sample A (see Fig. 2) show a PL intensity of the glassy phase relative to the β phase of about 60%, strongly increased with respect to the one of the standard PL spectra (about 9%). This result is consistent with the collection, in a standard PL experiment, of PL from regions in which only the β phase is emitting and from regions in which both phases are emitting. We observe that the presence of strong glassy phase emission in the PL spectra in the uniform regions, despite the efficient Förster energy transfer taking place from the glassy to the β
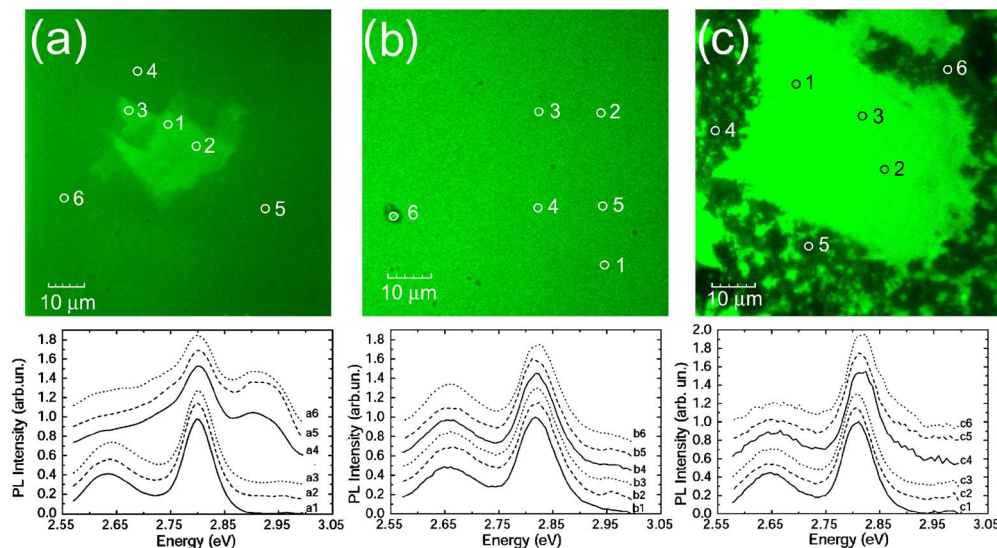

FIG. 2. (Color online) Top: PL maps of a characteristic 82×82 μm^2 region of (a) sample A, (b) sample B, and (c) sample C. Bottom: PL spectra from the 1.2 μm radius regions evidenced in the corresponding PL maps. All the spectra are normalized to their peak value and vertically offset for clarity.
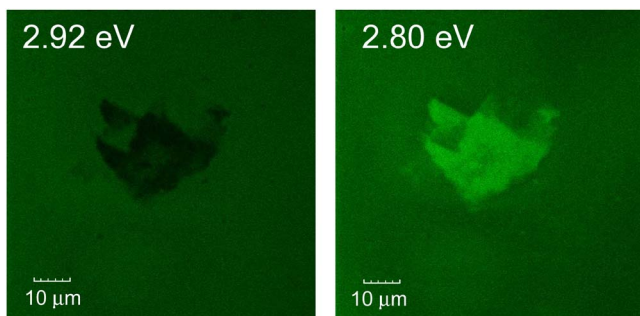
FIG. 3. (Color online) PL map of a 82×82 μm^2 region of sample A at the glassy phase PL peak energy (2.92 eV) (left) and at the β phase PL peak energy (2.80 eV) (right). It is evident that no glassy phase emission is observed in the cluster, which is instead characterized by a strong β phase emission.

phase,[16] clearly indicates a very low β phase content, thus allowing the presence of the donor emission in the spectra. Moreover we observe that the surface coverage of the clusters (about 6%) is almost identical to the relative β phase content in the film estimated from the absorption spectrum (5.9%). These results suggest that the clusters are completely made by molecules in the β phase, and then that the glassy and the β phase are almost separated.

The sample exposure to toluene vapors (sample B) leads to a decrease of the total β phase content, due to the almost complete disappearance of the β phase clusters [Fig. 2(b)] that are reduced to few residual clusters with a typical size decreased down to about 1 μm. However, no glassy phase emission is now observed in the uniform regions (spectra b1–b5 in Fig. 2), indicating an increase of their β phase content. This is likely due to the swelling caused by the solvent vapors that induces local mechanical stresses, forcing the polyfluorene molecules to a more planar geometry.[16] The fraction of molecules that changed conformation due to the solvent swelling can be estimated in about 4% by observing that the film shows a very uniform morphology and PL intensity (and then it is reasonable to assume an uniform surface density of β phase molecules), and that the relative content of the β phase estimated from the absorption spectrum is about 4.3%.

Finally, we investigated the spatial distribution of the PL in samples spin coated from toluene (sample C).

The PL map of sample C [see Fig. 2(c)] shows a worse uniformity with the presence of bright uniform regions in about the 50% of the sample surface, together with closely interconnected dark micrometric islands. Anyway no local variations of the PL spectra are observed (see Fig. 2) that both in the brighter and in the darker regions are typical of β phase emission, suggesting also in this sample that a β phase relative content high enough to allow the absence of the donor glassy phase luminescence is present. These results are consistent with the picture of aggregation on the micrometer scale during the spin coating, due to the lower solvent evaporation rate, and of a residual solvent vapors induced β phase formation.[16]

In conclusion we investigated the microscopic PL spectra in PF8 thin films with different content of β phase, modi-fied by acting on the solvent boiling point and by a postdeposition solvent vapor exposure. In the samples deposited from solvents with a low boiling temperature, phase separation between the glassy and the β phase is observed, evidenced by the presence of wide uniform regions with a very low β phase content, but also of micrometric β phase clusters, with a surface coverage of about 6%. The postdeposition exposure to toluene vapors leads to the disappearance of the β phase clusters but also to a swelling induced β phase formation in about 4% of molecules initially in the glassy phase. Finally, the deposition from solvents with higher boiling point such as toluene leads to a nonuniform morphology suggesting the presence of aggregation on the micrometer scale during the solvent evaporation in the spin coating. Moreover the presence of residual solvent when the aggregation takes place leads to swelling effects similar to the ones of the vapor exposed sample that gives rise to a high total content of the β phase, which dominates the local PL spectra down to the micrometer scale.

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