

How surface interactions freeze polymer molecules at room temperature: a single molecule approach

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Abstract. The planar conformation assumed by polyfluorenes is used as a model system to investigate how solid surfaces interact with an individual polymer chain as well as to access the effects of substrates and interchain interactions on the polymer conformation. We demonstrate that confocal fluorescence microscopy is very sensitive to characterize photophysical processes associated to conformation assumed by a single conjugated unit of poly (9,9 dioctylfluorene) or PFO. Emissions from interacting molecules have been resolved for the first time between the energies of the planar (β phase) and the non-planar (amorphous) phase that were associated to perturbations of the primary chain conformation. But we have found the planar conformation is assumed by single PFO molecules due to strong interactions with the hydrophilic quartz surfaces. This PFO conformation persists frozen even at room temperature, although emission lines are significantly broadened due to interactions with vibrating substrate atoms.

1. Introduction

The properties of optoelectronic devices based on conjugated polymers show a straight relationship between molecular conformation and their performance. Understanding the nature of the optical processes related to intrinsic molecular arrangement and structure can lead to the development and synthesis of new materials and devices with improved characteristics [1]. Moreover, one of the major challenges in organic electronic is the control of molecular conformation and understand how chain conformation and processes are modified by surfaces and interfaces [2]. In this context, single molecule spectroscopy is a powerful technique in revealing the underlying origin of molecular conformation assumed by the chain at the interfaces and its influence on the photophysical phenomena of conjugated polymers [3,4].

2. Experimental Procedure

Poly (9,9 dioctylfluorene), PFO, was used as a model system deposited on quartz substrate. The polymer solutions were prepared by successive dilution of PFO using the precursor solution with a concentration $C_0 = 9.4 \mu\text{g/ml}$ in chloroform. The polymer samples were deposited on hydrophilic substrate surface by spin-coating technique in static mode. Laser Scanning Confocal Microscopy (LSCM) was used to study the relationship between the photophysical processes and polymeric conformation due interaction with quartz interface.



3. Results and Discussion

Figure 1 shows LSCM images of PFO spincasted on quartz surface from a highly diluted polymeric chloroform solution (9.4 $\mu\text{g/ml}$). With this procedure we expect to find one PFO molecule on $1.5 \mu\text{m}^2$. The Figure 1a was collected with 16 bits and over an area of $2135 \times 135 \mu\text{m}^2$ (668x668 pixels), which ensure a continuous intensity scale going in false color from dark red to white with a scanning process that just fills all area without either overlapping or leaving voids between pixels. The density of bright spots in the image is about $1.9 \mu\text{m}^2$, close to the expected value for measuring isolated PFO molecules. The digital zoom of Figures 1a ($2 \times 2 \mu\text{m}^2$ or 10×10 pixels) are depicted in terms of spectral (Figure 1b) and intensity images (Figure 1c). The high dispersion in spectral shapes and positions and the high emission efficiency, both evaluated for each bright spot, are consistent with typical single molecule emission characteristics.

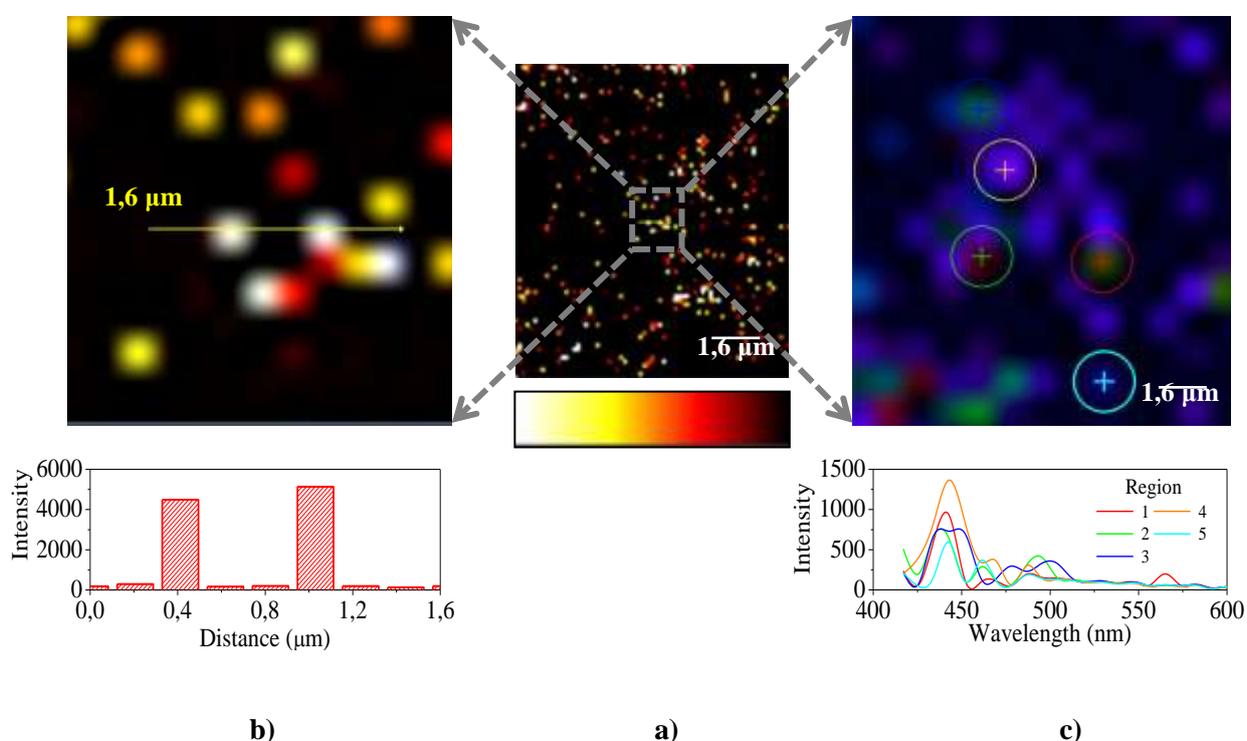


Figure 1: a) LSCM image of PFO spincasted on quartz surface from a highly diluted polymeric chloroform solution. b) Digital zoom ($2 \times 2 \mu\text{m}^2$ or 10×10 pixels) depicts details in terms of spectral and c) intensity images. Corresponding spectral data for different pixels (colored circles) and intensity profile over a $1.6 \mu\text{m}$ line are also shown.

The emission characteristics of PFO single molecules can be seen in greater detail in Figure 2. 10 PFO spectra recorded from isolated pixels on Figure 2a are compared in Figure 2b giving evidence the zero-phonon emissions in the range of the expected energies for the planar (β phase around 2.81 eV) and non-planar (disordered around 2.94 eV) conformations [5]. It is interesting to see the variety of spectral shapes and positions and that the planar conformation sets the lowest energy for the PFO emissions. The emission lines detected below 2.81 eV correspond to phonon replicas whose intensity demonstrate very low phonon coupling to PFO electronic states due to strong steric constraints between isolated molecules and the substrate. Zero-phonon lines positioned between the β and disordered phases can be associated to perturbations of the planar conformation associated to interchain interactions or partial loss of steric constraints with substrate.

Figure 2c compares PFO spectra of a 40 nm thick film (grey line) having only the non-planar phase, of a 1 nm thick film (orange line) and of a single molecule (green line) measured at 300 K with the spectrum of the same 1 nm thick film measured at 5 K. PFO spectrum having non-planar phase are broad and displaced to the high energies and present intense vibronic features at 300 K due to strong electron-phonon coupling. The 1 nm thick ultrathin film shows well resolved vibronic structures and the zero-phonon line positioned between the planar and non-planar phases. This intermediate emission feature can be associated to perturbed planar phase as a consequence of interchain interaction. However, the single PFO molecule present thinner 300 K emission line positioned at same position as the emissions of PFO ultrathin film measured at 5K. This find indicates that PFO single molecules preserve the planar phase even at 300 K due to strong interaction with hydrophilic quartz surface. In addition, the broadening of the single molecule zero-phonon line can be accounted to the perturbation introduced by the vibrational motion of the quartz atoms. The additional thermal energy at room temperature is not enough to break the PFO planar conformation. This means that PFO molecule is totally rigid (frozen) on the substrate surface at room temperature.

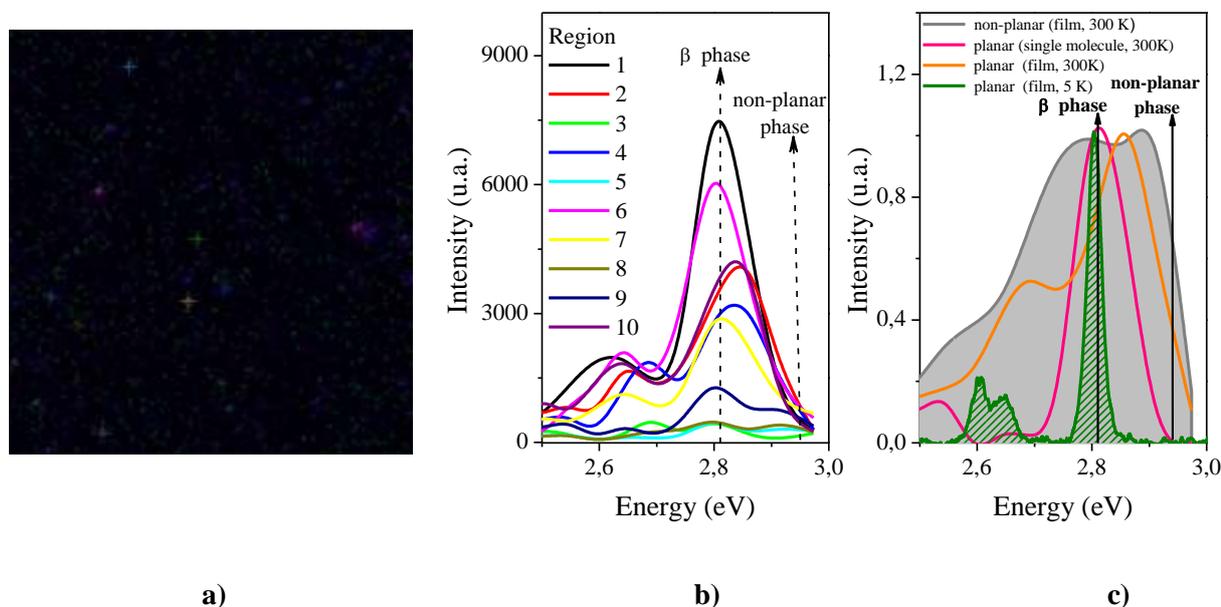


Figure 2: a) LSCM spectral image of isolated PFO molecules. b) 10 PFO spectra recorded from isolated pixels on this confocal image. c) PFO spectra of a 40 nm thick film (grey line) having only the non-planar phase, of a 1 nm thick film (orange line) and of a single molecule (green line) measured at 300 K with the spectrum of the same 1 nm thick film measured at 5 K.

4. Conclusions

In this study we used Laser Scanning Confocal Microscopy (LSCM) to investigate the influence of interaction between solid surfaces with a polymer chain and how this affects the polymeric conformation at interface. The microscopy results described here shown that LSCM technique is sufficient sensitivity to measure isolated molecule. Moreover, we find that the substrate imposes a form of freeze conformational in isolated PFO molecule at room temperature. Thermal perturbation due to quartz atoms is not enough to break the π conjugation (planar structure) at 300 K.

5. References

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Acknowledgments

This work was supported by CNPq, CAPES, FAPESP and INEO.