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Scanning force microscopy and optical spectroscopy of phase-segregated thin films of poly(9,9'-dioctylfluorene-*alt*-benzothiadiazole) and poly(ethylene oxide)

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We describe the formation of ordered phase-segregated domains at the hundred nm scale in thin films prepared from two molecular systems of interest as active materials in light-emitting electrochemical cells, *i.e.* the ion-transport polymer poly(ethylene oxide), PEO, and the well-known electron-transport macromolecule poly(9,9'-dioctylfluorene-*alt*-benzothiadiazole), F8BT. Scanning force microscopy investigations revealed signs indicative of self-organization processes taking place during film deposition, and characterized by the formation of PEO crystalline lamellae arranged either face-on or as intertwined fibres assembled in an edge-on fashion surrounding large and disordered F8BT grains. This self-segregated architecture, prepared by a single step co-deposition of the two components from a chloroform solution, provides unambiguous evidence for the poor miscibility of the two polymers. Fluorescence titration studies in solution and measurements of the photoluminescence quantum efficiency of thin solid state films showed little change of the optical properties upon addition of PEO to F8BT, thus confirming the modest interaction, at the molecular level, between the PEO and F8BT macromolecular strands. The results obtained are significant to the understanding of the parameters contributing to the interfacial and intermolecular interactions.

Introduction

Solution processability is one of the most compelling advantages of organic over inorganic semiconductors since it enables fabrication based on simple and low cost techniques such as spin-coating or ink-jet printing.¹ The solution processing of π -conjugated (macro)molecules has been proven to be a viable approach to fabricating different molecular electronic devices^{2,3} including light-emitting diodes (LEDs),^{4–6} field-effect transistors,^{7,8} solar cells,^{9,10} light-emitting electrochemical cells (LECs)¹¹ and light-emitting transistors.^{12,13} Many characteristics of the devices, including their performance, strongly depend on the interplay between the electronic and structural properties on scales that span from a few nanometres up to some tens of micrometres.^{14–18} Among other properties, both charge carrier mobility and exciton migration depend on the solid-state packing of the conjugated chains.^{19,20} In order to prepare thin films with a pre-programmed order at the supramolecular level it is crucial to take into account that

structures of films obtained from solutions are generally kinetically controlled since the evaporation rate of solvents is often faster than the time required to reach a thermodynamically stable structure.²¹ Most polymers undergo phase-segregation.^{22,23} This has been used, for example, to induce the formation of interpenetrated polymer networks and thus to generate large area heterojunctions.²⁴ Such structures are interesting since they afford high yields for exciton dissociation, eventually resulting in large photovoltaic efficiency, in cells with polymer pairs featuring an appropriate mismatch of the frontier energy levels (highest occupied molecular orbital, HOMO,²⁵ and lowest unoccupied molecular orbital, LUMO). Similarly, large area heterojunctions between polymers whose energy structures support exciplex formation and radiative emission, together with thermally assisted exciton regeneration.²⁶ In general, it is typically accepted that controlling the phase-segregation between different polymers when processed in thin films represents a key route towards the tunability of the optoelectronic properties of functional multicomponent architectures. We have chosen two molecular systems of significant interest as active materials in light-emitting devices. Poly(ethylene oxide), PEO (see Fig. 1 for chemical structure) is an ion-transport polymer which has been successfully employed for the fabrication of light-emitting electrochemical cells.¹¹ Poly(9,9'-dioctylfluorene-*alt*-benzothiadiazole), F8BT,^{27,28} (Fig. 1) is a polyfluorene (PFO) derivative with well-known electron-transport properties due to the presence of the benzothiadiazole group that significantly stabilizes the LUMO level, and therefore also increases electron affinity and

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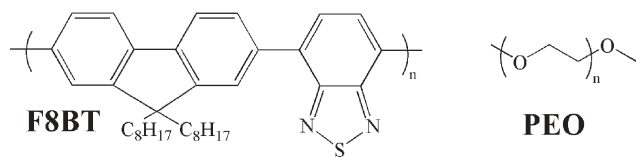


Fig. 1 Structural formulae of poly(9,9'-dioctylfluorene-*alt*-benzothiadiazole), F8BT, and poly(ethylene oxide), PEO.

electron injection from environmentally stable electrodes. Much work has been focused on blends of F8BT with the parent polymer PFO or hole-transport derivatives, such as poly[9,9'-dioctylfluorene-*alt*-N-(4-butylphenyl)-diphenylamine] (TFB) or poly[9,9'-dioctylfluorene-*alt*-bis-N,N'-(4-butylphenyl)-bis-N,N'-phenyl-1,4-phenylenediamine], PFB^{28–32} but blending of F8BT with PEO has received considerably less attention. Here we report a scanning force microscopy (SFM) study on the morphology and surface roughness of spun thin films of polymer blends consisting of PEO and F8BT. Fluorescence investigations were also used to gather additional useful information to shed light on the intermolecular interactions between the two components. SFM^{33,34} is a very powerful tool to gain insight into the structure and morphology of π -conjugated thin films with a resolution spanning from hundreds of micrometres down to the nanoscale.³⁵

Results and discussion

Fig. 2 shows a representative SFM height image of the morphology of a 100 nm thick PEO film supported on ITO processed by spinning a 20 mg ml^{−1} aqueous solution. On the submicrometre scale the film exhibits flat crystalline lamellae arranged face-on (A) on the substrate surface, and intertwined fibre-like architectures assembled edge-on (B). Such intertwined structures possess lateral dimensions of a few nanometres, suggesting that they correspond to a single lamellar crystal.^{36–38} These architectures are very similar to those observed in the nanostructured films of PEO supported on flame-treated glass cover slips, prepared by evaporation of the water at approximately 45 °C in an air environment.³⁶

The morphology of the film 60 : 40 F8BT : PEO spun from a chloroform solution on ITO is displayed in Fig. 3. The height image shown in Fig. 3a reveals flat areas and grains with diameters as large as 300–600 nm, made up of smaller grains.

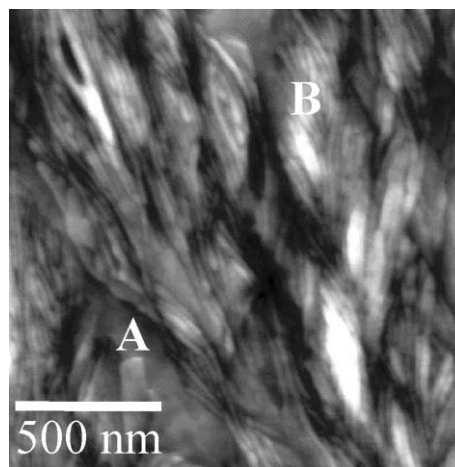


Fig. 2 SFM height images of a 100 nm thick film of PEO on ITO. At (A) lamellae are packed face-on; at (B) edge-on. Z-scale: 40 nm.

The phase images (b and c) are particularly well resolved and reveal additional details of the grain border as well as of the surrounding matrix typical of the crystallized PEO. The latter includes the flat crystalline lamellae arranged face-on (A) and intertwined fibers assembled edge-on (B). The presence of those areas and huge yet poorly ordered grains (C) provides unambiguous evidence for the occurrence of a strong phase-segregation between the two components. The comparison of the morphology of these two film types makes it possible to unambiguously ascribe the grains to the hydrophobic F8BT and the matrix, which conveys both face-on arranged lamellae and edge-on intertwined fibres, to the hydrophilic PEO. The polydispersity of F8BT and the finite rigidity of the long polymer chains, which can be quantified in terms of persistence length, hinder the formation of broad ordered architectures. It is worth stressing that the persistence length of a polymer, as F8BT, possessing a bent or coiled conformation can be expected to be below 10 nm. However, the strong π – π interactions drive the self-organization towards the observed disordered grain aggregates. Differently, the formation of lamellae and fibres from individual linear PEO chains is primarily governed by van der Waals interactions. The formation of phase-segregated structures on the sample surfaces, because of their existence on the several tens of nanometres scale, can be mostly ascribed to the scarce affinity between the

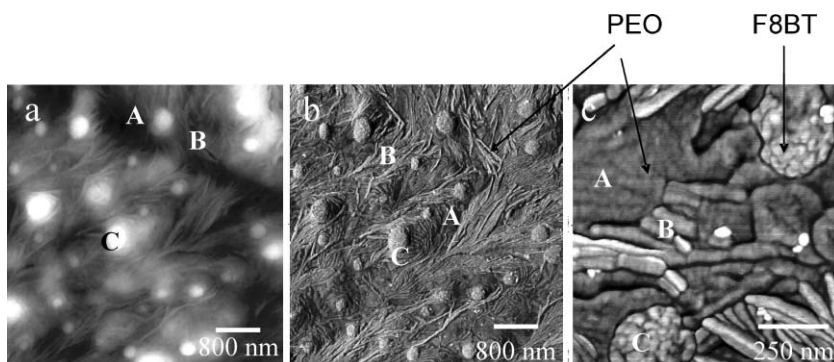


Fig. 3 SFM (a,b) height and (c) phase images of a 100 nm thick film of the polymer blend 60 : 40 of F8BT : PEO deposited on ITO, at different scan lengths. The disordered grains of F8BT are marked by C; the lamellae of PEO are arranged at (A) face-on, at (B) edge-on. (a) Z-scale: 20 nm.

two components, rather than to a de-wetting process.³⁹ These phase-segregated structures can be monitored by measuring the film roughness. The surface flatness of the film was characterized by its root-mean square roughness:

$$R_{\text{rms}} = \sqrt{\left[1/(N^2 - 1)\right] \sum_{mn=1}^{N \times N} (h_{mn} - \bar{h})^2}$$

where $N \times N$ is the number of pixels (512×512), h_{mn} is the height value of the pixel mn and \bar{h} is the mean height of the pixel calculated from the $N \times N$ values. The high R_{rms} of (31 ± 10) nm, as calculated from 2.5×2.5 μm images of F8BT–PEO blends, is in the range typical for strong phase-segregation between two polymers,⁴⁰ thus confirming the demixing of the F8BT and PEO in the blend films. Interestingly, the nature of PEO–F8BT blends is hence dramatically different from the nature of blends of PEO and polyelectrolytic conjugated polymers and polyrotaxanes, that instead display a strong binding.⁴¹ Considering the very high surface roughness of our films we decided not to prepare LECs based on them. However, to gain further understanding of the interaction between the two macromolecules we have measured the photoluminescence (PL) efficiency of thin films as a function of the blend ratio, and we also performed PL titration experiments on CHCl_3 solutions.

Results for the PL efficiency of the blend thin films are reported in Table 1. For the sake of comparison, some literature values are also displayed. For pure F8BT we find a value of $67 \pm 7\%$, essentially consistent with the values reported in literature, *e.g.* with Snaith and Friend that report a range from 55 to 65% depending on molecular weight⁴² (note that we used F8BT with a molecular weight of about 16 000) and Corcoran *et al.* who report 72% to 77% depending on solvent.⁴³ As expected, increasing the PEO concentration leads to little variation of the PL efficiency that changes in the range between $63 \pm 7\%$ and $76 \pm 8\%$ without a clear dependence on the PEO content of the films, although we do observe a somewhat higher value for the 75% PEO films. Such results are consistent with the absence of significant dilution of the emitting chromophores that is usually accompanied by a significant increase in the PL efficiency.⁴¹

F8BT²⁸ in solution exhibits an absorption profile characterized by a lowest-energy peak at 452 nm (ϵ *ca.* $3.52 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$, for an estimated $M_w = 15\,000 \text{ g mol}^{-1}$).⁴⁴ Upon excitation at this wavelength, an unresolved emission band is registered at room temperature, with $\lambda_{\text{em}}^{\text{max}} = 535 \text{ nm}$, and lifetime $\tau = 3 \text{ ns}$. These features correspond well to a singlet excited state, possibly of ligand-centred and charge transfer mixed character. For F8BT–PEO mixtures, given that PEO does not absorb at $\lambda > 330 \text{ nm}$, selective excitation of F8BT is possible. On this basis, titration experiments were conducted by monitoring the absorption and luminescence features of F8BT. Results of the experiments are illustrated in Fig. 4; in this case, $[\text{F8BT}] = 6.7 \times 10^{-7} \text{ M}$ and aliquots of PEO were sequentially added in the range $[\text{PEO}] = 6.7 \times 10^{-7}$ to $6.7 \times 10^{-5} \text{ M}$. As one can see from Fig. 4, no changes in the absorption and luminescence properties of F8BT were observed. The fact that the electronic properties, including the lifetime, of the F8BT chromophore remain essentially unperturbed by the presence of PEO is consistent with the absence of significant interactions and thus miscibility between the two macromolecules.

If one takes into account a 1 : 1 association process, $\text{A} + \text{B} \rightleftharpoons \text{AB}$, the association constant is

$$K_{\text{AB}} = \frac{[\text{AB}]}{[\text{A}][\text{B}]} \text{M}^{-1}$$

Within this simple association scheme, and upon an estimated value limit of less than 5% for the experimental uncertainty regarding the results of Fig. 41f and 41f¹, given $[\text{AB}] = 6.7 \times 10^{-7} \times 0.05 = 3.35 \times 10^{-8}$, $[\text{A}] = 6.7 \times 10^{-7} \times 0.95 = 6.37 \times 10^{-7}$, and $[\text{B}] = 6.7 \times 10^{-5} \times 0.95 = 6.37 \times 10^{-5}$, one could draw a $K_{\text{AB}} \leq 1 \times 10^3 \text{ M}^{-1}$ for the (hypothetical) F8BT : PEO association.

Ongoing work in our laboratories is addressed towards gaining a deeper understanding of the interactions between the different macromolecules investigated here by SFM extending the studies to approaches capable of mapping the films in three dimensions, *i.e.* angle-resolved X-ray photoelectron spectroscopy (AR-XPS) and time-of-flight secondary ion mass spectrometry (TOF-SIMS).

In general, phase separation in polymer blends, as we have previously observed on other macromolecule pairs,^{28,41} is a

Table 1 Summary of the values of photoluminescence quantum efficiency as a function of the F8BT : PEO blend ratio that we measured and the ones reported in literature for F8BT

	PL efficiency (%) of F8BT : PEO (weight ratio)					$M_w/\text{g mol}^{-1}$	Solvent
	100 : 0	75 : 25	60 : 40	50 : 50	25 : 75		
Our results	67 ± 7	63 ± 7	66 ± 7	60 ± 6	76 ± 8	16 000	Chloroform
Xia and Friend ³¹	77						Xylene
Kim and Bradley ⁴⁴	50.8					15 000	Xylene
Snaith <i>et al.</i> ^{42,50}	55					62 000	Xylene
	65					129 000	
	56					188 000	
	80						
	77						Chloroform
Morteani <i>et al.</i> ⁵¹ Corcoran <i>et al.</i> ⁴³	72						Xylene
	74						Isodruene
	58 \pm 5						Toluene
Xia <i>et al.</i> ⁵²	57.7						Chloroform
Arias <i>et al.</i> ⁵³	48.3						Xylene
Murata <i>et al.</i> ⁵⁴	74						

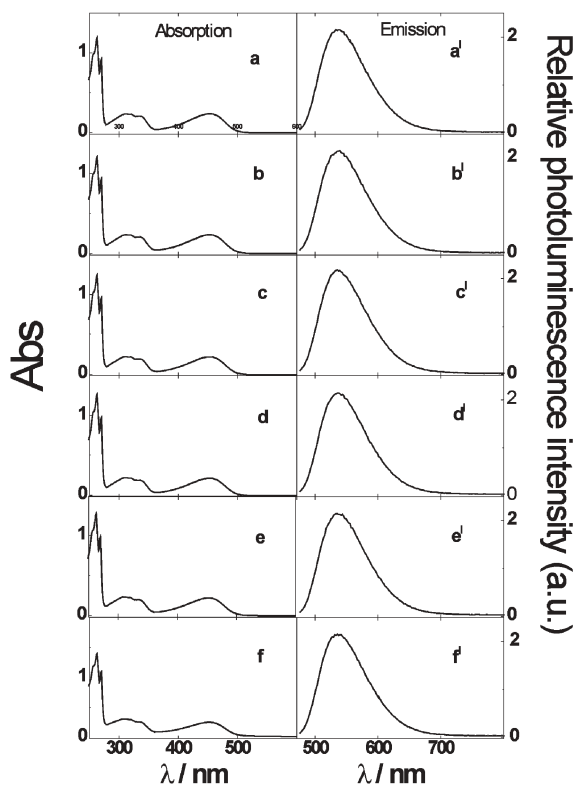


Fig. 4 Titration of a 6.7×10^{-7} M solution of F8BT with PEO in CHCl_3 . (a–f) Absorption spectra of a 6.7×10^{-7} M solution of F8BT in the presence of PEO at the concentration of (a) 6.7×10^{-7} , (b) 2.7×10^{-6} , (c) 5.4×10^{-6} , (d) 6.7×10^{-6} , (e) 1.4×10^{-5} , (f) 6.7×10^{-5} M. (a'–f') = PL spectra of F8BT at the same PEO concentrations. Excitation at 450 nm, temperature 25 °C.

thermodynamically driven process which is ruled by chemical compatibilities between the different polymer molecules. Chemical or structural differences between the components in the polymer blend are sufficient to produce excess free energy contributions that usually tend to hinder full miscibility of the components. In general, this can be well described by the Flory–Huggins interaction parameter.^{45,46}

Conclusions

We have described the self-organization of PEO and F8BT into highly ordered bi-component architectures which exhibit a phase-segregation on the hundreds of nanometres scale. While the hydrophobic F8BT self-organizes into disordered grains where the individual chains interact primarily through π – π forces, the van der Waals interactions between single hydrophilic PEO chains yield micrometre long lamellae and fibers. Scanning force microscopy investigations provided evidence for the de-mixing of the two components on ITO as determined by the poor affinity between the molecular systems and their different electronic properties. This poor association was confirmed by fluorescence spectroscopy studies in solution. Therefore, the careful choice of the molecular systems and their processing protocols are fundamental to controlling the self-organization in bi-component films.

Experimental

PEO with a mass average molar mass M_w of 100 000 g mol^{−1} (Aldrich) was dissolved in deionised water ($\rho = 18 \text{ M}\Omega \text{ cm}^{-1}$) at different concentrations. Films of the pure polymer were deposited by spin-coating (velocity = 1000 rpm, spinning time = 120 s) a 50 μl drop of the solution. The blends of F8BT and PEO were prepared by mixing solutions of both single components in an identical solvent, *i.e.* chloroform (99%, Aldrich), leading to a mass fraction of F8BT : PEO of 60 : 40. This ratio was chosen as typical for preparation of thin films for LECs.⁴¹ Films with a thickness of 100 nm of the pure PEO and of its blend with F8BT were deposited by spin-coating (velocity = 1000 rpm, spinning time = 120 s) a 50 μl drop of the solution. The spin-coating process, being very fast, does not yield thermodynamically stable architectures, and it is widely employed since for that reason it enables the preparation of films which are both homogeneous over many hundreds of micrometres and exhibit a limited surface roughness. The nominal film thickness was ~ 100 nm as routinely determined using a profilometer Alpha Step 200 (Tencor Instruments). Indium tin oxide (ITO) coated glass substrates (Merck Balzer) were employed as supports. ITO was chosen in view of its relevance to LED technology, determined by its transparency and by the relatively high work function that makes it suitable as a hole-injecting electrode. Prior to being used, ITO was treated for 5 min in an ultrasonic bath of CHCl_3 , for 5 min in ethanol and finally exposed to an oxygen plasma. Such a treatment impacts in a favourable way a variety of surface properties, including work function, roughness and hardness, sheet-resistance and surface energy.^{47,48}

Neat PEO films have been studied by tapping mode scanning force microscopy using a commercial instrument (Dimension 3100/Nanoscope IV, Digital Instruments, Santa Barbara, CA) running in an air environment at room temperature with scan rates of 1–1.5 line s^{−1}. On the other hand, PEO–F8BT blend films have been investigated in intermittent contact SFM employing Autoprobe CP research (ThermoMicroscope, Veeco, Santa Barbara, CA) operating in an air environment at room temperature with scan rates in the range between 1 and 0.25 line s^{−1}. In both cases SFM images with scan lengths ranging from 30 μm down to 500 nm have been recorded with a resolution of 512 \times 512 pixels using either tapping mode microfabricated silicon nanoprobe (length 125 μm and width 30 μm ; Digital Instruments) with a spring constant (k) in the range 17–64 N m^{−1} or Si ultralever with $k = 2.1 \text{ N m}^{-1}$. In both tapping and intermittent contact SFM measurements the height signal (output of the feedback signal) and the phase signal (phase lag of the oscillation relative to the driver) have been recorded simultaneously. While the first type of image provides a topographical map of the surface, the latter is extremely sensitive to structural heterogeneities on the sample surface, being therefore ideal to identify different components in a hybrid film.⁴⁹ No correction for tip size was performed on measured widths. The size of grains and crystals as well as roughness and height analysis were performed using the facilities of Scanning Probe Image Processor (SPIP) (version 2.000, Image Metrology ApS, Denmark) software.

Thin films of blends (20 mg ml⁻¹ in chloroform) of F8BT ($M_w = 16\,000\text{ g mol}^{-1}$) and PEO ($M_w = 100\,000\text{ g mol}^{-1}$) used for PL efficiency measurements were spun in air (1000 rpm, 120 s) on pre-cleaned spectroil substrates increasing the weight of PEO. A diode laser ($\lambda_{\text{em}} = 414\text{ nm}$ –0.15 mW) excited the samples placed inside an integrating sphere while a monochromator at the exit of the sphere selected the wavelength of the signal that was detected by a cooled photomultiplier. The samples were kept in a nitrogen atmosphere during the measurements in order to reduce photobleaching of the polymers.

The absorption spectra of solutions in CHCl₃ were obtained with a Perkin-Elmer Lambda 45 UV/vis spectrometer. The room temperature luminescence spectra for air-equilibrated solutions were measured using a Spex Fluorolog II spectrofluorimeter. The samples were dissolved in CHCl₃ and the excitation wavelength was 450 nm. Band maxima and relative luminescence intensities are determined with uncertainty of 2 nm and <5%, respectively. The luminescence lifetimes (τ) were obtained with IBH single photon counting equipment by using pulsed diode NanoLED sources with excitation at 465 nm. Analysis of the luminescence decay profiles against time was accomplished by using software provided by the manufacturers.

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