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Effect of a ferroelectric polymer on the photophysical properties of a polyfluorene: Exciton quenching by local electric fields

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ABSTRACT

The photophysical properties of conjugated polymers are sensitive to the environment; hence they can be used as probe for local interactions. Here we report on the effect of a ferroelectric polymer in the photoluminescence of a conjugated polymer and show that the local electric field, created by the ferroelectric polymer, induces a photoluminescence quenching, translated into a reduction of the fluorescence intensity and lifetime. Blends and bi-layer systems were studied, with the blends showing a more pronounced effect.

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1. Introduction

The research on conjugated polymers, encompassing synthesis, properties and applications, has been very prolific, being also a remarkable example where the synergy between complementary competences has been fuelling a continuous development. The use of different tools and techniques allows for a better understanding of the various phenomena, contributing to the development of new materials and device architectures.

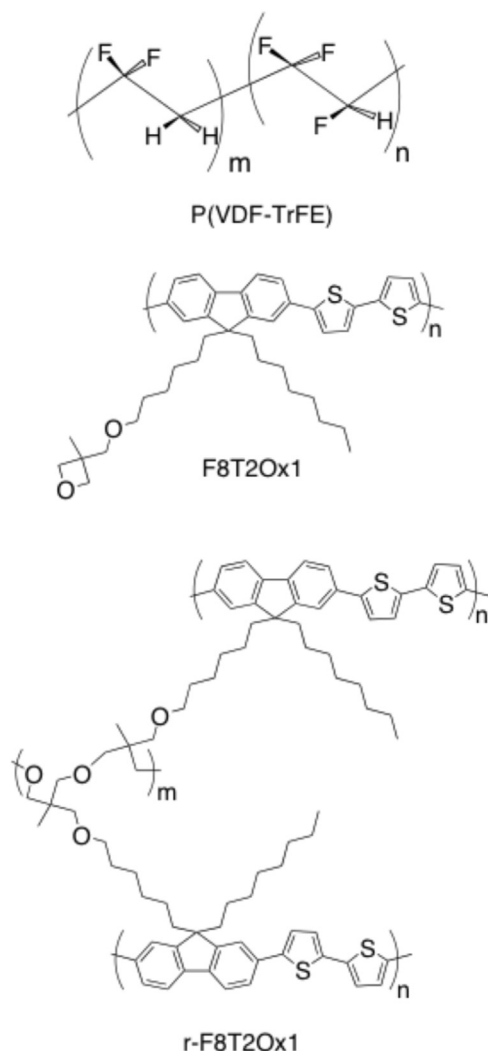
In the particular area of the resistive non-volatile memories, a key component in electronics circuitry, a significant breakthrough was reported by Asadi et al. [1], relying on the use of diodes based on blends of a conjugated polymer and a ferroelectric polymer, poly(vinylidene fluoride-co-trifluoroethylene), (P(VDF-TrFE)). The ferroelectric properties of P(VDF-TrFE) derive from the dipoles resulting from the presence of the high electronegative fluorine atoms [2]. It was shown that the polarization of the ferroelectric can modulate the charge injection barrier(s) in such diodes, which allows for an ON/OFF switch of the current flowing through the diode. This effect has been reported for various conjugated polymers (CP). Yet, the exact mechanism remains under debate. After a first proposal [1], relying on a particular phase separation geometry at the interface

with the contacts, this has been modified to a stray-field based mechanism [3], which assumes a sharp interface between the conjugated polymer and the ferroelectric domains (formed instantaneously during the spin coating film formation). Therefore, the unravelling of the phase separation in such blends is of key importance and has been the subject of several studies. In summary, the obtained results indicate the formation of columnar domains of the conjugated polymer that bridge the two contacts, embedded in a matrix of the ferroelectric polymer [4]. The existence of ferroelectric material within the columns of the conjugated polymer was also proposed [4].

We have previously reported on memory devices based on a blend of P(VDF-TrFE) and F8T2Ox1, a cross-linkable conjugated polymer [5]. It is usual on these devices that the films prepared by spin-coating undergo a thermal treatment during two hours at 135 °C (below the melting point of P(VDF-TrFE)) in order to evaporate the remaining solvent and to improve the ferroelectric characteristics by improving the crystalline phase. In this case, aside the P(VDF-TrFE) crystallisation, a cross-linking of F8T2Ox1 occurs, which allows the selective removal of the ferroelectric polymer, confirming the formation of columns of the conjugated polymer. In addition, we found evidence for a rather diffuse interface between the two systems, whose implications on the proposed working mechanism still need to be assessed. The morphology derived from these studies can indeed be described as a bi-layer system with a nanostructured diffuse interface (see model in Fig. S1 of Supplementary information).

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Scheme 1. Molecular structures of the ferroelectric polymer, P(VDF-TrFE), and of the conjugated polymer, in the soluble (F8T2Ox1) and in the cross-linked (r-F8T2Ox1) forms.

In this work we study the influence of P(VDF-TrFE) on the F8T2Ox1's photophysical properties (structures shown in Scheme 1) aiming, in particular, to gain further insight into the characteristics of the CP/ferroelectric polymer interface. We determined the fluorescence lifetime of F8T2Ox1 neat films, in both soluble and cross-linked (r-F8T2Ox1) forms, and compare it with that in blends with P(VDF-TrFE), before and after thermal annealing. For comparison, planar bi-layer structures were also prepared and characterized. We found that the cross-linking of F8T2Ox1 and the improved crystallinity of the P(VDF-TrFE) reduce PL lifetime. This quenching effect is mainly attributed to the effect of the local electric field created by the P(VDF-TrFE) dipoles, though excited state charge transfer to gap states of the ferroelectric polymer is not ruled out.

We note that Nalwa et al. [6] have proposed that the presence of P(VDF-TrFE), dispersed in the active layer of photovoltaic cells made of a blend of poly(3-hexylthiophene), P3HT, and PCBM, increased the local electric field, which, in turn, improved the exciton dissociation and the overall power conversion efficiency. Other studies have also explored the ordering of this polymer to improve the efficiency of organic photovoltaic cells [7,8], which highlights the relevance of learning about its effect on the photophysical properties of conjugated polymers.

Time-dependent PL intensity studies by Nalwa et al. [6] revealed that the addition of P(VDF-TrFE) up to a certain amount

(10% by weight) was leading to a decreased PL lifetime, which was considered as evidence for the effect of the local electric field created by P(VDF-TrFE) on the charge generation upon exciton dissociation. This explanation is supported by earlier studies showing that a reduction of PL lifetime occurs due to external electric fields, an effect rationalised in terms of electric field-assisted exciton dissociation, has been studied in the past [9,10].

Surprisingly though, Nalwa et al. [6] found that the PL lifetime was shorter for planar bi-layer structures, with the ferroelectric polymer separating P3HT layer from the top one made of PCBM (P3HT/P(VDF-TrFE)/PCBM structure) than for blends. This is unexpected, not only for the additional effect of PCBM in reducing PL lifetime as for the fact the P(VDF-TrFE) effect is much smaller in case of a bi-layer structure (with the P(VDF-TrFE) deposited on top of the P3HT film and beneath a PCBM film on top).

Our study, though motivated by a different application, provides additional insight into the existence of an electric field at the interface between P(VDF-TrFE) and F8T2Ox1 that, besides promoting a quenching of the conjugated polymer photoluminescence, is likely involved in the operation principle of the non-volatile resistive memories based on blends of P(VDF-TrFE) and conjugated polymers. Additionally, from these studies, we conclude that P(VDF-TrFE) domains are likely to exist within the F8T2Ox1 columns, complementing our previous conclusions [5] and in support of previous reports for other systems [4].

2. Experimental

P(VDF-TrFE) 70/30%mol was purchased from Piezotech (France) and used as received. F8T2Ox1 was synthesized as described in Ref. [5]. According to GPC results, its molecular weight is $M_n=5711$, $M_w=8874$, referenced to polystyrene standards. PEDOT:PSS was obtained from Heraeus (Clevios P, VP.AI 4083) and used as received.

P(VDF-TrFE):F8T2Ox1 blend films were prepared by spin coating from a 10:1 mixture, by weight, in cyclohexanone, with a total solid concentration of 4.9 wt%, on a PEDOT:PSS-coated glass. The PEDOT:PSS film was 60 nm thick and had been dried on a hot plate at 120 °C during 30 min in air. Some of the P(VDF-TrFE):F8T2Ox1 films were annealed at 135 °C during 2 hours under vacuum (at a base pressure of 10^{-4} mbar) to improve P(VDF-TrFE) crystallinity (a key process in the fabrication of the ferroelectric resistive memories) and to, simultaneously, cross-link F8T2Ox1. The thickness of the P(VDF-TrFE):F8T2Ox1 blend films is around 360 nm.

Neat films of F8T2Ox1 and P(VDF-TrFE) were prepared on quartz. The P(VDF-TrFE) films, with a thickness of 200 nm, were prepared from a cyclohexanone solution (5 wt%). F8T2Ox1 neat films (≈ 50 nm) were prepared from a solution of F8T2Ox1 in chlorobenzene (1.8 wt%). The annealing of the P(VDF-TrFE) films and the thermal cross-linking of the F8T2Ox1 films were performed using the same conditions as for the blend films. Using these same solutions, F8T2Ox1/P(VDF-TrFE) bi-layer films were prepared on quartz. A first film of F8T2Ox1 layer was cross-linked (135 °C, 2 h, 10^{-4} mbar), followed by the deposition of the P(VDF-TrFE) layer. Some of these bi-layer films were additionally annealed (135 °C, 2 h, 10^{-4} mbar) to increase P(VDF-TrFE) crystallinity.

UV-vis absorption spectra were recorded with a CECIL CE7200 spectrophotometer. Steady-state photoluminescence spectra were obtained with a SPEX Fluorolog 2121 spectrophotometer, at the right angle geometry, S/R mode and corrected for instrumental wavelength dependence. Photoluminescence decays were measured using the picosecond time-correlated single-photon counting (TCSPC) technique and the resulting fluorescence decays deconvoluted as described in Ref. [11,12]. The pulsed excitation source was a Ti:Sapphire Tsunami laser. Measurements were carried out by

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