Enhanced photoluminescence at poly(3-octyl-thiophene)/TiO₂ interfaces

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The photoluminescence (PL) of poly(3-octyl-thiophene) (P3OT) thin films applied on TiO₂ substrates is compared to the PL of P3OT films applied on quartz. Quenching of excitons occurs at the P3OT/TiO₂ interface and not at the P3OT/quartz interface. Yet, in the former case the PL intensity is stronger than in the latter. In particular, P3OT films less than 5 nm thick lumines much more when applied on TiO₂, which is in striking contrast to what one expects. For films thicker than 10 nm, the increase of the PL as function of the film thickness is the same for TiO₂ and for quartz, which indicates that the PL enhancement originates at the interface. The dissociation of excitons at the P3OT/TiO₂ interface yields positive polarons in P3OT, which is not the case at the P3OT/quartz interface. We postulate that interaction between positive polarons and excitons explain the observed enhancement of the PL at the P3OT/TiO₂ interface. © 2004 American Institute of Physics. [DOI: 10.1063/1.1699447]

The study of photoluminescence (PL) spectra of conjugated polymers, applied on metal-oxide substrates, is a powerful tool to investigate energy and charge-transfer mechanisms at active and nonactive interfaces. These interfaces are important in polymer solar cells and in polymer lightemitting diodes (poly-LEDs). In the field of polymer solar cells, charge transfer from the polymer to an electron acceptor, such as a fullerene, CdSe, or TiO2, is generally accompanied by quenching of the photoluminescence.¹⁻³ For poly-LEDs the ratio between the electroluminescence and photoluminescence quantum yields is limited to 25% by spin-degeneracy statistics.⁴ However, recent studies by Beljonne et al.,⁵ Ye et al.,⁶ and references therein, reveal that the singlet/triplet formation ratio can be broken by interchain mechanisms. In that case the 25% rule no longer applies. The observations presented in this letter are in line with these theoretical considerations. While charge carrier generation and transport in polythiophene films have been investigated thoroughly,⁷⁻¹⁴ the interaction between positive polarons and excitons has not been taken into account. In the present letter we report on the enhancement of the poly(3-octyl-thiophene) (P3OT) photoluminescence when applied onto TiO_2 versus when applied onto quartz. In the first case, positive, polarons are generated in P3OT and in the latter case not. Our experimental results strongly suggest that positive polarons can interact with nonemissive excitons to give them more radiative character. Future experiments and theoretical studies are required to elucidate exciton-polaron interactions in more detail.

An 80 nm flat film of anatase TiO_2 was deposited on quartz and on SnO_2 :F-coated glass by chemical vapor deposition, using Titanium-Tetra-Iso-Propoxide as precursor (Everest Coatings, The Netherlands). Prior to application of the polymer film, the TiO₂ film was dried in air for 1 h at 250 °C. For some experiments the TiO₂ surface was chemically modified, by soaking the TiO₂ films overnight in a 1

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mM NaOH solution or a 60% HNO₃ solution. The polymer P3OT was used as received from Aldrich. Films were deposited on quartz and on TiO₂-coated quartz by spin casting at 1500 rpm from a chloroform solution. The film thickness was varied from 3 to 150 nm (O.D. of 0.016-0.8) by applying concentrations from 0.3 to 20 mg/ml. The film thickness was determined with a step profiler (Dektak 3st) and was confirmed with optical absorption measurements, using a Perkin-Elmer Lambda 900 photo-spectrometer. The luminescence was measured with a home-built setup. A continuous 5 W Nd:YVO₄ laser (Spectra Physics, Milennia) operating at 532 nm was used to irradiate the films. Neutral density filters (Schott) were used to vary the intensity and the luminescence was detected with a LN-cooled CCD camera (Princeton Instruments, model 1100 PB).

The excited state of the P3OT chain relaxes mostly nonradiatively to the ground state; the fluorescence quantum yield of P3OT films is only 2%.¹⁵ Figure 1 shows the normalized absorption spectrum (dotted line) of a thin P3OT film on quartz and the photoluminescence spectra of a 7 nm



FIG. 1. Photoluminescence spectra of a 7-nm-thick P3OT film on quartz (solid line) and on TiO_2 (dashed line), and the absorption spectrum (dotted line).

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FIG. 2. Luminescence intensity at 1.7 eV vs film thickness on quartz (closed symbol) and on TiO₂ (open symbol).

P3OT film on quartz and on TiO₂ (solid and dashed lines, respectively). The absorption spectrum shows a maximum at 2.4 eV and has a shoulder at 2.05 eV. The luminescence maximum at 1.7 eV has a shoulder at 1.85 eV, in good agreement with the literature.^{16,17} The absorption and photoluminescence spectra of P3OT on quartz and on TiO₂ are similar, which allows us to use the intensity of the 1.7 eV maximum as a measure for the total intensity of the photoluminescence. For irradiated P3OT films deposited on TiO_2 , the generated excitons that reach the active P3OT/TiO2 interface are quenched and a reduction of the photoluminescence is expected.^{9,18–21} However, Fig. 1 shows that the luminescence intensity is not reduced at all but is much stronger for films on TiO₂ than for film on quartz. Considering the fact that excitons are quenched at the TiO₂ interface, this observation contradicts common intuition.

For P3OT films on quartz, the intensity of the photoluminescence increases linearly with film thickness, as shown by the closed symbols in Fig. 2. For P3OT films on TiO_2 , linearity is only observed for films thicker than 10 nm. Films less than 10 nm thick show a very strange PL behavior, as is presented in (Fig. 2 open symbols). For films thinner than 10 nm, the PL intensity of P3OT on TiO₂ has a much steeper gradient than for P3OT on quartz, which leads to a remarkable PL offset. Clearly, a remarkable process occurs in the vicinity of the P3OT/TiO₂ interface, which gives rise to a significant enhancement of the photoluminescence.

The irradiated P3OT/TiO₂ interface differs from the irradiated P3OT/quartz interface in four ways: (i) a different interface roughness, (ii) a different interface chemistry, (iii) the presence of conduction band electrons in the TiO₂ film, and (iv) the presence of positive polarons in the P3OT film. These issues are considered in the following. The roughness of the TiO₂ substrates has been determined with atomic force microscopy and is 6.5 nm with a lateral spacing of 25 nm. It is likely that P3OT films less than 10 nm thick have a different morphology than films of 150 nm. Indeed the optical absorption spectra of P3OT films thinner than 10 nm is different from those of thicker films. This could give rise to a different PL quantum yield. But, since the absorption spectra of 10 nm films on TiO₂ and quartz are identical, morphological effects cannot explain the differences between the PL efficiencies. We conclude that at the metal-oxide interface Downloaded 16 Aug 2010 to 131.180.130.114. Redistribution subject to AIP license or copyright; see http://apl.aip.org/about/rights_and_permissions



FIG. 3. Luminescence intensity at 1.7 eV vs pump intensity for P3OT on quartz (closed symbols) and P3OT on TiO_2 (open markers symbols). The curves represent different P3OT film thicknesses and have been individually rescaled to emphasize their different shapes.

P3OT films have a different morphology, but since this is the case for both substrates it cannot be responsible for the observed PL enhancement on TiO₂.

The surface of TiO₂ and quartz are usually terminated with absorbed water and OH⁻ groups. To monitor the influence of the interface chemistry on the PL intensity, the TiO₂ surface has been modified, by changing the acidity of the surface, prior to spin casting polymer films. This has been achieved by soaking the TiO₂ films in HNO₃ and KOH solutions, respectively. While the luminescence intensity indeed shows a small change after surface modification, the intensity of the PL remains a lot stronger for P3OT films on TiO₂ than for P3OT films on quartz. Hence, the surface chemistry of TiO₂ films is not responsible for enhancement of the photoluminescence.

The P3OT/TiO₂ interface is an active interface at which the excitons are dissociated. Consequently, electrons will be present in the conduction band of TiO₂ near the interface, which will influence the interfacial electric field strength. In order to study the effect of this field, the PL intensity is monitored as a function of the applied electric field. When a field of 1×10^7 V m⁻¹ is applied, the luminescence intensity variation is less than 5%. We conclude that the concentration of conduction band electrons in TiO₂ does not influence the PL intensity to a large extend.

Finally, the presence of positive polarons in P3OT on the PL intensity is considered. It is known that in general polarons stimulate the decay of excitons. But maybe for P3OT applied on TiO₂ this general rule is not obeyed. In P3OT only 2% of the excitons are originally in an emissive state and it can be possible that polarons have a special type of interaction with these excitons. For instance, it seems possible that exciton decay is accompanied by population exchange between nonemissive and emissive excitons. This type of interaction would lead to the observed increase of the steady-state luminescence.

If such type of interaction between positive polarons and excitons is present, a nonlinear variation of the luminescence intensity with laser pump power is expected, in contrast to the linear relation between laser power and PL quantum yield for monomolecular decay. Figure 3 shows that indeed the luminescence of a P3OT film on quartz and the pump intensity relate linearly, whereas the luminescence of the P3OT film on TiO_2 varies with a power law. This confirms that the photoluminescence of a P3OT film on TiO_2 is not monomolecular but involves at least two coexisting particles. We postulate that polarons stimulate exciton emission in the polymer film by transferring nonradiative excitons to radiative ones. The following types of processes may occur.

Since in P3OT most excitons are in the triplet state it is possible that interaction between positive polarons and triplet excitons yield singlet excitons, which are more emissive. A possible route is that when a positive polaron meets a triplet exciton, dissociation of the exciton into a free electron and a free hole (a negative and a positive polaron) occurs. These free charge carriers will quickly associate to form an exciton, which can be either triplet or singlet. In this way, triplet excitons will have the chance to become singlet excitons, which leads to enhancement of the photoluminescence quantum yield. The energy associated with this transfer amounts to the energy difference between singlet and triplet excitons, being about 0.5-1 eV. A first-order approximation of the polaron-exciton interaction energy, when their separation is 1 nm, is about 4 eV, which is sufficient to convert triplet excitons into singlets.

Alternatively, polarons may reduce the rate of intersystem crossing. Previous investigations have shown that in highly ordered polythiophene films intersystem crossing is strongly inhibited.^{22,23} It is possible that also in this case it is polarons that suppress intersystem crossing, because in ordered films spontaneous dissociation of excitons into polarons is more likely than in disordered films.

It is also possible that interaction between positive polarons and triplet excitons will lead to a new spin state of the combined system, which may also provide transition probability to the emissive process.

Finally, one can think of a mechanism in which positive polarons are able to transfer interchain excitons into intrachain excitons, which are more emissive.

At the moment, time-resolved photoluminescence experiments are being performed, and the first results support the first mechanism. Furthermore, a kinetic model is under development, in which transfer of population from nonemissive to emissive excitons is included. Numerical simulations of the PL behavior of P3OT on TiO₂ are in qualitative agreement with the observations. In future communications we shall provide a detailed account of these studies.

If the idea is correct that photoluminescence enhancement is due to interaction between positive polarons and excitons, the effect only occurs at the interface between P3OT and TiO₂, because only there the polaron concentration is very high. Since there are no electrical contacts, the electrons in the TiO₂ and the polarons in the P3OT accumulate at the interface, where they form an electrical double layer. Only those nonradiative excitons that are able to reach this double layer will have the change to be converted into radiative excitons. Figure 2 shows that luminescence enhancement only occurs within 5 nm from the interface, which implies that the exciton diffusion length in P3OT films is about 5 nm, in excellent agreement with the literature.²⁴ In conclusion, we have shown that the PL of a polythiophene film is enhanced if applied on TiO_2 . This enhancement occurs when positive polarons interact with excitons. Although the exact nature of this interaction is still unknown, we postulate that a fraction of the nonemissive triplet excitons is converted into emissive singlet excitons. These results are of interest for polymer solar cells and polymer light emitting diodes. At the moment, it is debated whether the upper limit of electroluminescence can be higher than 25%. Our findings show that indeed this is the case. Interaction between positive polarons and excitons can change the relative concentrations of singlet and triplet excitons and thus lead to a higher luminescent quantum yield.

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