

# Photoluminescence Study of Sexithiophene Thin Films

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To determine the exciton diffusion length of sexithiophene (6T) thin films, quenching of the photoluminescence (PL) of vacuum-deposited 6T films on TiO<sub>2</sub> and on quartz has been investigated. For films with a thickness of more than 22 nm and at temperatures below 100 K, additional PL lines appear in luminescence spectra. This feature is related to the structural properties of 6T films. The PL intensity is thermally activated with an activation energy of 18 meV on TiO<sub>2</sub> and 6 meV on quartz. When 6T is applied on TiO<sub>2</sub>, exciton quenching occurs for films up to 120 nm. For 6T on quartz this value is reduced to 60 nm. By comparing the relative luminescence intensities of 6T on quartz and on TiO<sub>2</sub> substrates, an exciton diffusion length of  $60 \pm 5$  nm is derived.

## Introduction

Solar cells based on dye-synthesized films of nanocrystalline TiO<sub>2</sub> are low-cost alternatives to inorganic (Si-based) semiconductor devices. The photoelectrodes consist of anatase TiO<sub>2</sub> nanoparticles, which are sintered together to form a three-dimensional nanostructured network and are covered with a monolayer of a Ru-based dye. Solar energy conversion efficiencies of up to 11% have been achieved with these films, if used in conjunction with a liquid-redox electrolyte.<sup>1,2</sup> In the present study, the focus is on the sensitization of TiO<sub>2</sub> with sexithiophene (6T), in which 6T acts as a visible light absorber and as a hole conductor. When 6T is optically excited, it can inject electrons into the conduction band of TiO<sub>2</sub>. Upon irradiation, bound electron–hole pairs (excitons) are generated in the 6T oligomer and diffuse toward the active interface, where they split into free electrons and free holes.<sup>3</sup> The presence of an internal electric field at the interface of 6T/TiO<sub>2</sub> ensures fast separation of the electrons and holes. The holes travel through the 6T by a hopping process because there is always some disorder in 6T thin films. The morphology of 6T films has important consequences for the electronic and optoelectronic properties of these materials. In recent years, significant progress in the understanding of charge carrier dynamics in disordered organic materials has been accomplished.<sup>3–7</sup>

6T has been studied extensively, both as single crystals and as polycrystalline thin films.<sup>8,9</sup> Thin films are relevant for technological applications, but since their optical properties are strongly dependent on the morphology and on structural defects such as grain boundaries, advancement of oligomer-based devices is tedious.<sup>10</sup> Vacuum sublimation yields ordered films<sup>11,12</sup> with a morphology that is determined by the deposition rate,<sup>14,15</sup> the substrate temperature,<sup>13</sup> the film thickness,<sup>14</sup> and the angle of the substrate with respect to the impinging molecular beam. 6T films are polycrystalline, and on substrates such as quartz or indium tin oxide (ITO) the molecules align themselves at an angle of about 30° to the substrate surface, if kept at room temperature during deposition.<sup>11,12</sup>

Recently, much attention has been focused on conjugated oligothiophenes and their derivatives. These oligomers combine a good conductivity with suitable optical properties. 6T is a p-type organic semiconductor with a band gap of 2.3 eV. It is studied in thin film transistors (TFT) because its hole mobility of  $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  is high enough for “all-plastic” thin-film electronics.<sup>16,17</sup> Field-effect transistors (FETs)<sup>18,19</sup> photovoltaic (PV) solar cells,<sup>20,21</sup> and light-emitting diodes (LEDs)<sup>22a</sup> are examples of devices that have been demonstrated with sexithiophene as the active material. The photophysical processes taking place in 6T thin films are rather complex, and despite several spectroscopic investigations,<sup>23,24</sup> there are still several questions concerning the charge-transfer mechanism to be resolved.

Halls et al.<sup>25</sup> have studied PPV/C<sub>60</sub> heterojunctions and have shown that excitons are mobile with a diffusion length of a few nanometers, which results in efficient energy transfer to low-lying states. The photoluminescence or exciton recombination occurs from these low-lying states, and a low concentration of these states has a disproportionate effect on the photoluminescence and on the efficiency of free-carrier generation.<sup>26</sup>

The dissociation of excitons can take place either at the surface or in the bulk. There are several mechanisms that can give rise to exciton dissociation in the bulk. The influence of the electric field on the luminescence intensity has been used to elucidate the charge separation mechanism in organic photoconductors.<sup>27</sup> The presence of polarons can be investigated by measuring the luminescence intensity as a function of the pump intensity.<sup>4</sup>

Numerous studies have focused on the photovoltaic properties of 6T in combination with metals such as Al<sup>27</sup> or molecules such as fullerenes.<sup>28,29</sup> Heterojunctions of oligothiophenes (like 6T) with inorganic semiconductors, such as TiO<sub>2</sub><sup>30</sup> and half-metallic manganites,<sup>31</sup> have been investigated only recently using PL spectroscopy, which is a powerful tool to investigate the exciton diffusion length.<sup>3,4,30</sup>

Here, the exciton diffusion length is investigated for vacuum-sublimed thin films of 6T on quartz and on TiO<sub>2</sub> by comparing the luminescence intensity of 6T films as a function of the thickness. We measured the PL spectra at controlled tempera-

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tures in the range 10–300 K for 6T films with a thickness between 10 and 250 nm and then determined an exciton diffusion length of  $60 \pm 5$  nm for 6T on both quartz and TiO<sub>2</sub> substrates.

## Experimental Aspects

**Sample Preparation.** Thin films of anatase TiO<sub>2</sub>, with a thickness of 100 nm, are deposited on quartz and on SnO<sub>2</sub>:F-coated glass (transparent conducting oxide (TCO):  $20 \Omega \text{ cm}^{-2}$ , Libbey Owens Ford) by metal–organic chemical vapor deposition (CVD) at 300 °C, as described elsewhere.<sup>32</sup> Titanium tetraisopropoxide (TTIP, Aldrich, 98%) is used as precursor and nitrogen as carrier gas (flow 60 sccm). Saturated TTIP vapor at 50 °C is carried into a hot-wall CVD reactor and then reacts with oxygen. Before deposition of TiO<sub>2</sub>, the substrates are thoroughly cleaned in an ultrasonic bath with ethanol and acetone and are then dried with dry air. The TiO<sub>2</sub> films are annealed for 2 h at 450 °C in air and then stored in the dark.

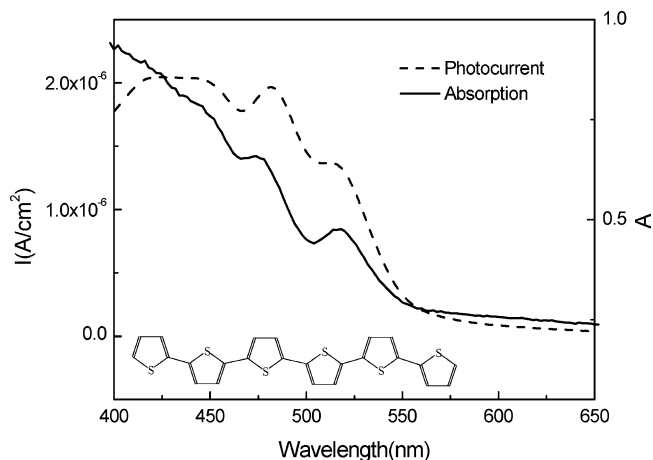
Thin films of 6T are deposited using a thermal evaporation set up. Sexithiophene powder is obtained from Syncom (Groningen, The Netherlands) and is purified by zone sublimation (courtesy of D. Fichou, Laboratoire des Matériaux Moléculaires, CEA Saclay, Thiais, France). The quartz and TiO<sub>2</sub>-coated quartz substrates are positioned 3 cm above the crucible containing 6T and are at normal incidence in a vapor phase deposition system (Balzers). The crucible temperature, 280 °C, is stable during deposition. The substrate temperature during evaporation can be changed. 6T molecules are thermally evaporated (vacuum  $1 \times 10^{-7}$  mbar) onto a quartz and TiO<sub>2</sub> layer. The rate of evaporation is kept at 40 pm/s and the substrate temperature at 300 K. A shutter stops the flow of material when the desired nominal thickness is reached. The film thicknesses have been varied between 10 and 250 nm.

The samples have been kept in the dark to avoid exposure to light, as this is known to cause degradation of semiconducting thiophenes.<sup>30,45,49</sup>

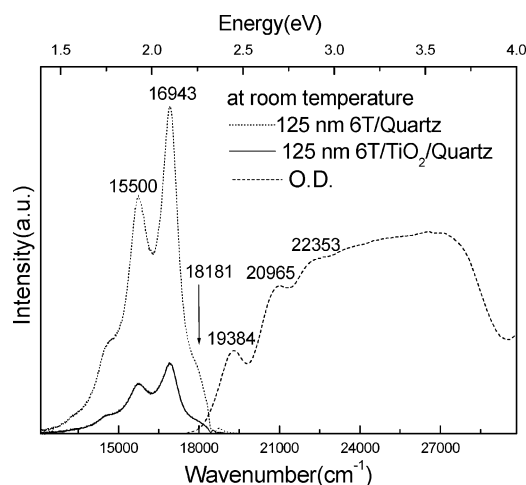
**Measurements.** AFM measurements are performed in air with a scanning probe microscope SOLVER P47H (NT-MDT) using a tapping-mode silicon probe tip NSG11 (NT-MDT) on a scale of 3000 nm  $\times$  3000 nm. The surface roughness has been calculated with Smena v8.45 software. The roughness of the TiO<sub>2</sub> films is found to be 9 nm. The roughness of the 6T film is found to be only about 2 nm. The film thickness of the 6T films is determined in two ways: with optical absorption measurements using a Perkin-Elmer Lambda 900 spectrometer and with profilometry using a Dektak (Veeco model 8, equipped with a low-force stylus) step profiler.

The samples are mounted in a helium closed-cycle cryostat (Displex Closed-Cycle System CSW-204SL), in which the temperature can be varied between 10 and 300 K. A continuous 5 W Nd:YVO<sub>4</sub> laser (Spectra Physics, Millennia), operating at 532 nm, is used to irradiate the films. Neutral-density filters are used to reduce the laser power to 0.02 mW. The luminescence is detected with a LN-cooled CCD camera (Princeton Instruments). The corrections for the filters and the sensitivity of CCD camera are applied.

The optoelectronic properties of 6T/TiO<sub>2</sub> cells are examined in air and argon. Current–voltage characteristics of cells are examined in argon atmosphere with a Keithley model 2400. Photocurrent action spectra are recorded using a 250 W tungsten–halogen lamp in combination with a monochromator (Acton Spectra Pro-275) and appropriate filters. Irradiation always takes place through the transparent TCO electrode.



**Figure 1.** Absorption (solid) and the photocurrent action spectra (dotted) of a TCO/TiO<sub>2</sub> (80 nm)/6T (100 nm)/Au cell.

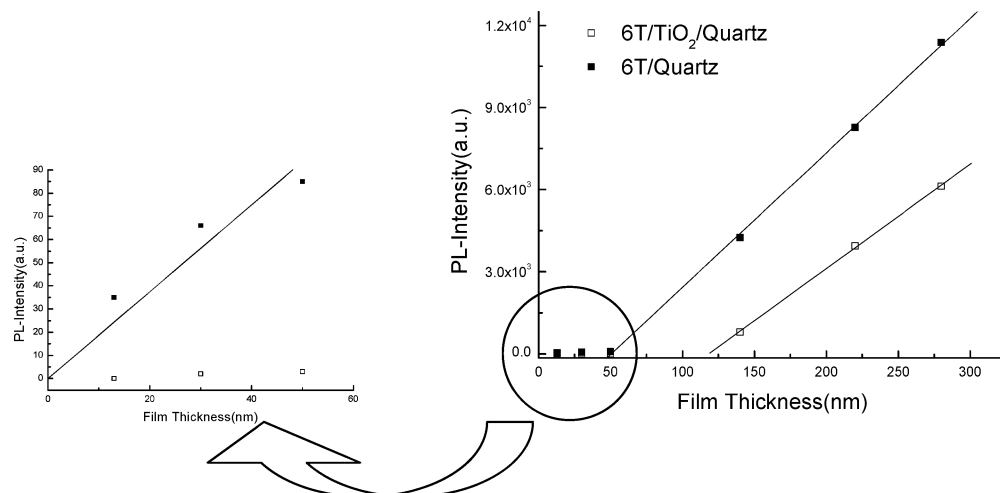


**Figure 2.** Optical density (dashed) and the PL spectra (at room temperature) of a 125-nm thick 6T film on quartz (dotted) and on TiO<sub>2</sub> (solid) substrates.

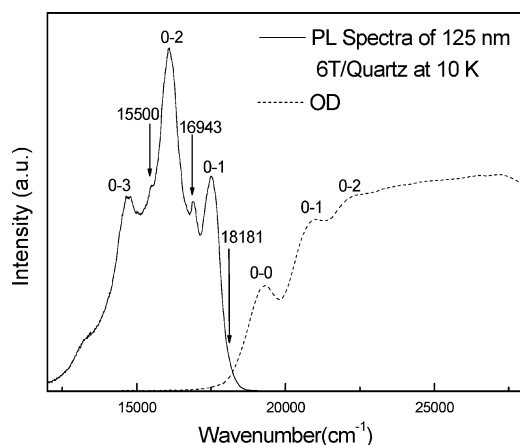
## Results

The current–voltage (*I*–*V*) characteristics of TCO/TiO<sub>2</sub>/6T/Au heterojunctions are measured for 6T films with a thickness of 100 nm in argon atmosphere. Figure 1 shows the absorption and the photocurrent action spectra of a typical cell. The action spectrum, obtained when the sample is illuminated through the TCO side, closely resembles the absorption spectrum. It proves that 6T acts as sensitizer for TiO<sub>2</sub>. Light absorption in 6T leads to generation of excitons, which are separated into electrons and holes at the 6T/TiO<sub>2</sub> interface. Electrons are injected into the conduction band of TiO<sub>2</sub>, and holes are transported to the gold electrode, which gives rise to a photocurrent. Although the shapes of the absorption and action spectra are alike, the peak positions are not exactly the same. The photocurrent reveals two peaks at  $\lambda = 470$  ( $0.66 \mu\text{A}/\text{cm}^2$ ) and 520 nm ( $0.48 \mu\text{A}/\text{cm}^2$ ) and decreases sharply for  $\lambda > 560$  nm.

**1. Optical Density and Photoluminescence Spectra of 6T at Room Temperature.** The optical density (OD) and the photoluminescence (PL) spectra of a 125-nm thick 6T film on quartz and on TiO<sub>2</sub> substrates at room temperature and in a vacuum are shown in Figure 2. At room temperature the emission spectra of 6T/TiO<sub>2</sub> and 6T/quartz consist of three bands located at: 2.25 (18 181  $\text{cm}^{-1}$ ), 2.10 (16 943  $\text{cm}^{-1}$ ), and 1.92 eV (15 500  $\text{cm}^{-1}$ ), which is in excellent agreement with the literature.<sup>10,33</sup>



**Figure 3.** Relative PL intensities of 6T on quartz and on TiO<sub>2</sub> substrates at 2.10 eV (16 943 cm<sup>-1</sup>) at 297 K. The left-hand plot is an enlargement of the right-hand plot, focusing on the first 50 nm.



**Figure 4.** PL spectra of a 125-nm thick 6T film on quartz at a temperature of 10 K (solid). The optical density spectrum (dotted) is added for convenience.

The relative luminescence intensities versus film thickness of 6T on quartz and on TiO<sub>2</sub> substrates at room temperature are presented in Figure 3. Since the luminescence spectra of 6T on quartz and on TiO<sub>2</sub> are similar, the intensity of the peak at 16943 cm<sup>-1</sup> (2.10 eV) is used as a measure for the total intensity of the photoluminescence. The PL intensity of 6T films deposited on TiO<sub>2</sub> consists of two regimes. For thick films (120–270 nm), the luminescence intensity increases linearly with the film thickness. At thicknesses below 120 ± 10 nm, the luminescence is almost completely quenched. Comparing the intercepts of different sample batches, an inaccuracy of 10 nm is found, which is probably related to the surface roughness. The PL intensity of 6T films on quartz also shows two regimes, but in this case, the demarcation occurs at 60 nm. In both regimes, linearity is observed between the PL intensity and the film thickness, but for films thinner than 60 nm, the proportionality factor is much smaller than for thicker films.

Previous investigations have shown that PL quenching is observed up to 20 nm for MEH/PPV/TiO<sub>2</sub><sup>3</sup> junctions and up to 5 nm for P3OT/TiO<sub>2</sub> junctions.<sup>4</sup> Here, PL quenching is found to occur over a much larger distance, which is probably related to the ordered structure of 6T films compared to polymeric films.

**2. Influence of the Temperature on the PL Spectra of 6T.** Photoluminescence spectra recorded at 10 K (Figure 4) exhibit a well-resolved fine structure with equidistant lines in emission and absorption, corresponding to vibronic progressions of 0.173

**TABLE 1: Energies<sup>a</sup> for Absorption and Emission Spectra of 125-nm 6T Film Measured at 10 K**

band position	absorption eV (cm <sup>-1</sup> )	PL (Contribution I) eV (cm <sup>-1</sup> )	PL (Contribution II) eV (cm <sup>-1</sup> )
0–0	2.40 (19384)	2.27 (18350)	2.25 (18181)
0–1	2.59 (20965)	2.17 (17560)	2.10 (16943)
0–2	2.77 (22353)	2.00 (16160)	1.92 (15500)

<sup>a</sup> Given in eV and in cm<sup>-1</sup>.

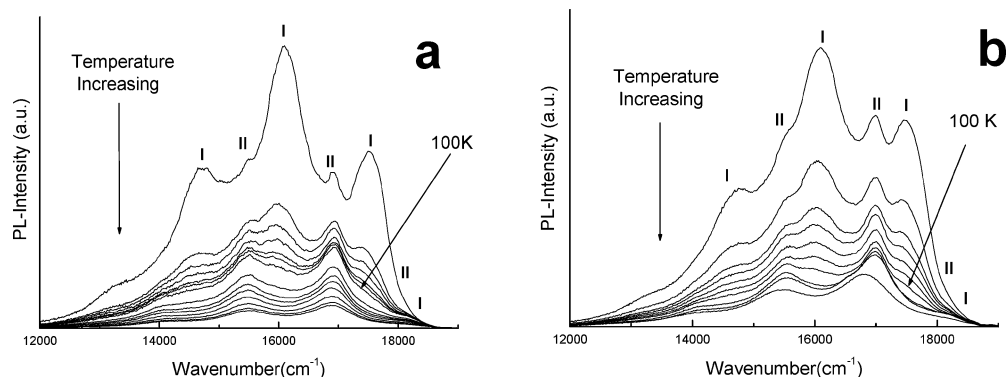
(1400 cm<sup>-1</sup>) and 0.196 eV (1581 cm<sup>-1</sup>), respectively. Spectroscopic data are collected in Table 1. The observation of different vibronic progressions in absorption and emission spectra indicates an excited state with a distorted, quinoid-like structure, as explained by the polaron–exciton model.<sup>34</sup> We observe a Stokes shift of 0.128 eV (1034 cm<sup>-1</sup>), while Gebauer<sup>33</sup> et al. have derived a Stokes shift of 0.20 eV (1645 cm<sup>-1</sup>) for a 200 nm 6T film at 5–10 K.

The PL spectra of 6T appear to be strongly temperature dependent, as is shown in Figure 5. At room temperature, the highest-energy emission peak, identified as the 0–0 excitonic transition, is located at 18 350 cm<sup>-1</sup>, in agreement with the value of 18 350 cm<sup>-1</sup> reported by Mark et al.<sup>22b,c</sup> When reducing the temperature below 100 K, additional PL lines are observed. Emission spectra of 6T at low temperature have two contributions. The four bands at 2.27 (18 350 cm<sup>-1</sup>), 2.17 (17 560 cm<sup>-1</sup>), 2.00 (16 160 cm<sup>-1</sup>), and 1.83 eV (14 766 cm<sup>-1</sup>) belong to Contribution I, which is only active at low temperature. The other lines belong to Contribution II, which is active at every temperature. The peaks in the PL spectrum of Contribution I are shifted with respect to those of Contribution II, but decreasing the temperature from 300 to 10 K does not affect the positions of the PL peaks, as concluded from peak fitting of the entire spectra.

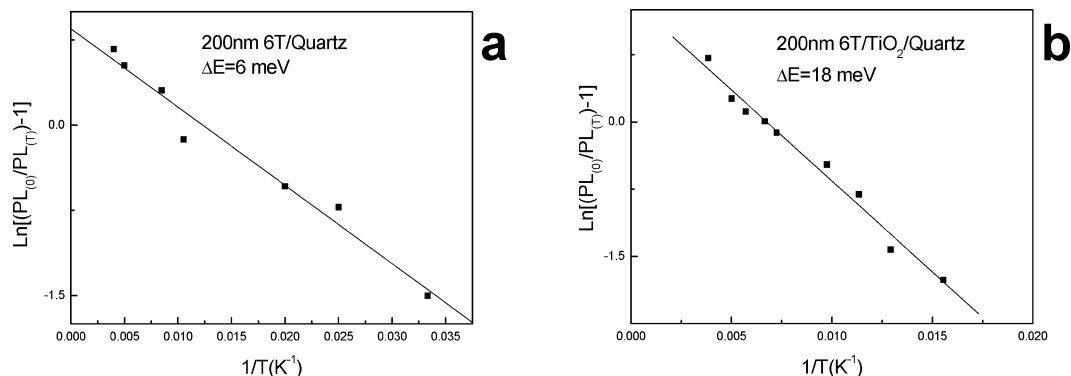
Figure 6 shows the temperature dependence of PL intensity of 200 nm 6T on TiO<sub>2</sub> and quartz substrates by applying Curie's law:

$$[PL_{(T)}/PL_{(0)}] = 1/(1 + C e^{-\Delta E/kT}) \quad (1)$$

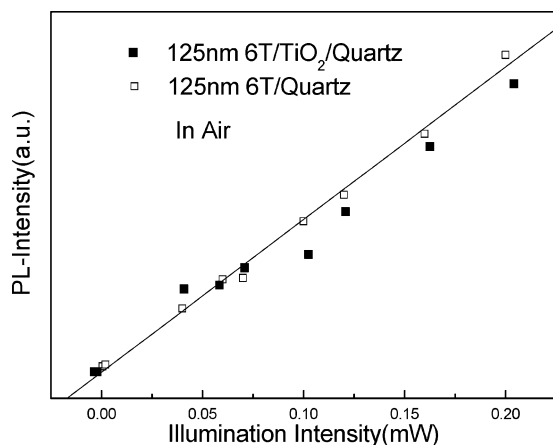
where PL<sub>(0)</sub> is the emission intensity at  $T = 0$  K,  $\Delta E$  the activation energy of the thermally activated process,  $k$  the Boltzmann constant, and  $C$  is a constant. PL<sub>(0)</sub> is taken at the lowest temperature point, i.e., 24 K for 6T/TiO<sub>2</sub> and 16.5 K for 6T/quartz. The influence of PL<sub>(0)</sub> on the derived activation energy  $\Delta E$  is rather small; a variation of ~10 K shows only a



**Figure 5.** PL spectra of 125-nm 6T on quartz (a) and on  $\text{TiO}_2$  (b) from room temperature to 10 K. The excitation wavelength is 532 nm.



**Figure 6.** Temperature dependence of the PL-intensity at 2.10 eV (Contribution II). The depopulation process of 200-nm 6T on quartz (a) and on  $\text{TiO}_2$  (b) follows the Curie law, eq 1.



**Figure 7.** PL intensity of 125-nm 6T films on  $\text{TiO}_2$  and on quartz vs pump intensity at 2.10 eV.

minor effect on  $\Delta E$ . The peak at 2.10 eV, which belongs to Contribution II, is used as a measure for the total intensity of the photoluminescence. A linear relationship is observed for  $\ln[(\text{PL}_0/\text{PL}_T) - 1]$  with temperature; as is shown in Figure 6, the depopulation process is thermally activated with an activation energy of 18 meV on  $\text{TiO}_2$  and 6 meV on quartz.

Figure 7 shows the relationship between the PL intensity of 120-nm 6T films on  $\text{TiO}_2$  and on quartz versus the irradiation intensity. In both cases, a linear relationship is found, which supports a monomolecular mechanism of PL emission.

**3. Influence of the Film Thickness on the PL Spectra of 6T.** While the temperature has a strong effect on the shape of the PL spectra, the film thickness does not.

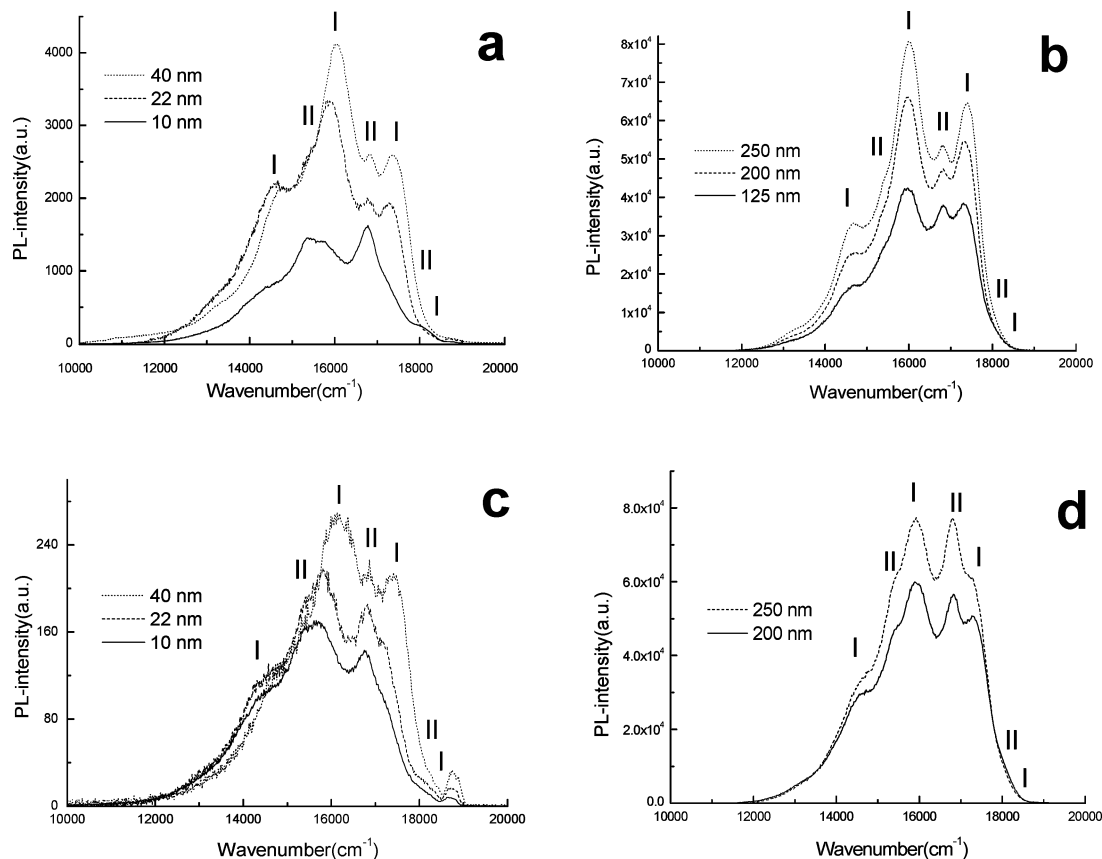
Figure 8 shows PL spectra of different thicknesses of 6T between 10 and 250 nm at 10 K. For thicknesses above 22 nm, both Contributions I and II are observed. Gebauer<sup>34</sup> et al. also

observed two PL contributions at low temperature and reported that Contribution II increases with respect to Contribution I if the film thickness increases from 40 to 200 nm. This is not what we find. In our experiments, films less than 22 nm thick only show Contribution II, but for thicker films, the ratio between Contributions I and II changes in favor of Contribution I, i.e., increasing the film thickness leads to a relative increase of Contribution I with respect to Contribution II.

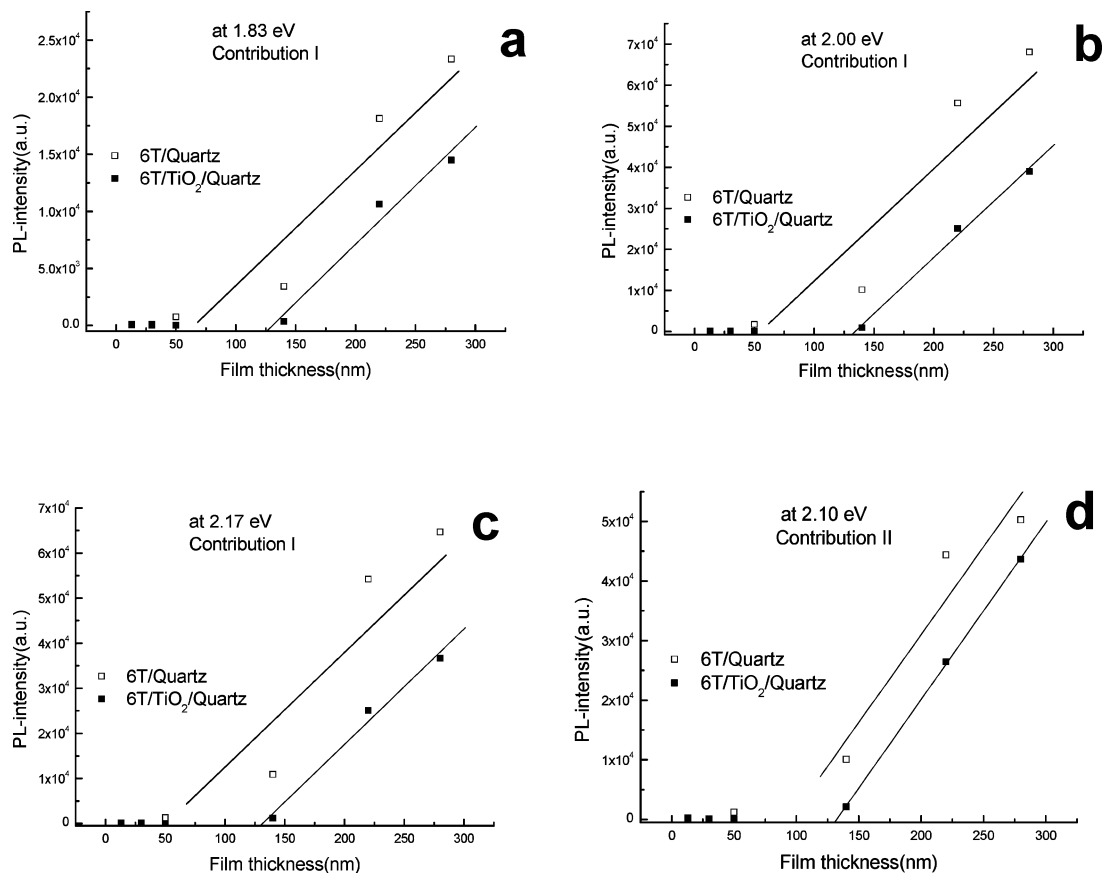
In Figure 9, the relative PL intensities of 6T on quartz and on  $\text{TiO}_2$  substrates at 10 K are presented as a function of film thickness. The intensity of the peaks at 1.83 (14 766  $\text{cm}^{-1}$ ), 2.00 (16 160  $\text{cm}^{-1}$ ), and 2.17 eV (17 560  $\text{cm}^{-1}$ ) are used to identify Contribution I, and the peak at 2.10 eV (16 943  $\text{cm}^{-1}$ ) to identify Contribution II. The luminescence on  $\text{TiO}_2$  shows two regimes. For 6T films thinner than  $120 \pm 10$  nm, the luminescence is almost completely quenched, while above this threshold, the luminescence increases linearly with the film thickness. For 6T films on quartz, the same is observed, except that now the demarcation occurs at 60 nm. These results are in agreement with the PL quenching at room temperature, as shown in Figure 3.

## Discussion

Since the photocurrent action spectrum matches the absorption spectrum of 6T, there can be no doubt that 6T can act as sensitizer for  $\text{TiO}_2$ . Accordingly, excitons are quenched at the 6T/ $\text{TiO}_2$  interface, leading to electrons in the conduction band of  $\text{TiO}_2$  and holes in the HOMO band of 6T. This process can be monitored conveniently with photoluminescence spectroscopy. At room temperature, the PL of 6T is largely dominated by excitonic emission, and the quantum yield is 0.5%.<sup>37</sup> However, at 30 K, the PL spectrum is dominated by Contribution I, which can be related to the presence of aggregated domains and has a quantum yield of 6%.<sup>35</sup> For 6T films thicker

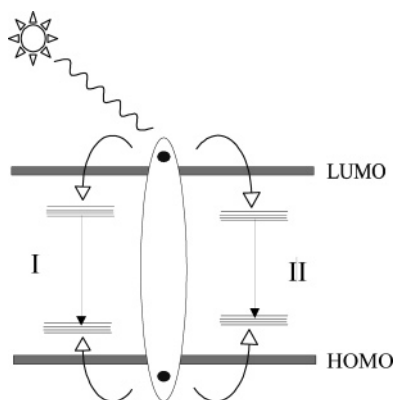


**Figure 8.** PL spectra for 6T films with different thicknesses (10, 22, 40, 125, 200, and 250 nm) on quartz (a and b) and on TiO<sub>2</sub> (c and d) at 10 K. Contributions I and II are shown on the spectra.



**Figure 9.** Relative luminescence intensities of 6T on quartz and on TiO<sub>2</sub> substrates at 10 K, at 1.83 (a), 2.00 (b), and 2.17 eV (c) related to Contribution I, and at 2.10 eV (d) related to Contribution II.





**Figure 10.** Schematic energy diagram for the optical transitions in 6T thin films. Contributions I and II can be regarded as radiative traps. Contribution I (low  $T$ ) is blue-shifted with respect to Contribution II.

than 22 nm, Contribution I appears in the PL spectra if the temperature is below 100 K. When the film thickness increases from 10 to 250 nm, Contribution I increase with respect to Contribution II, as shown in Figure 8. The presence of two contributions to the PL spectra of 6T indicates two different morphologies. From X-ray analysis, the crystal structure of 6T is known to be of the herringbone type with four<sup>36–38</sup> or two<sup>39</sup> molecules arranged in a monoclinic unit cell. As is known for many oligomers, 6T also shows polymorphic crystallization.<sup>36,40,41</sup>

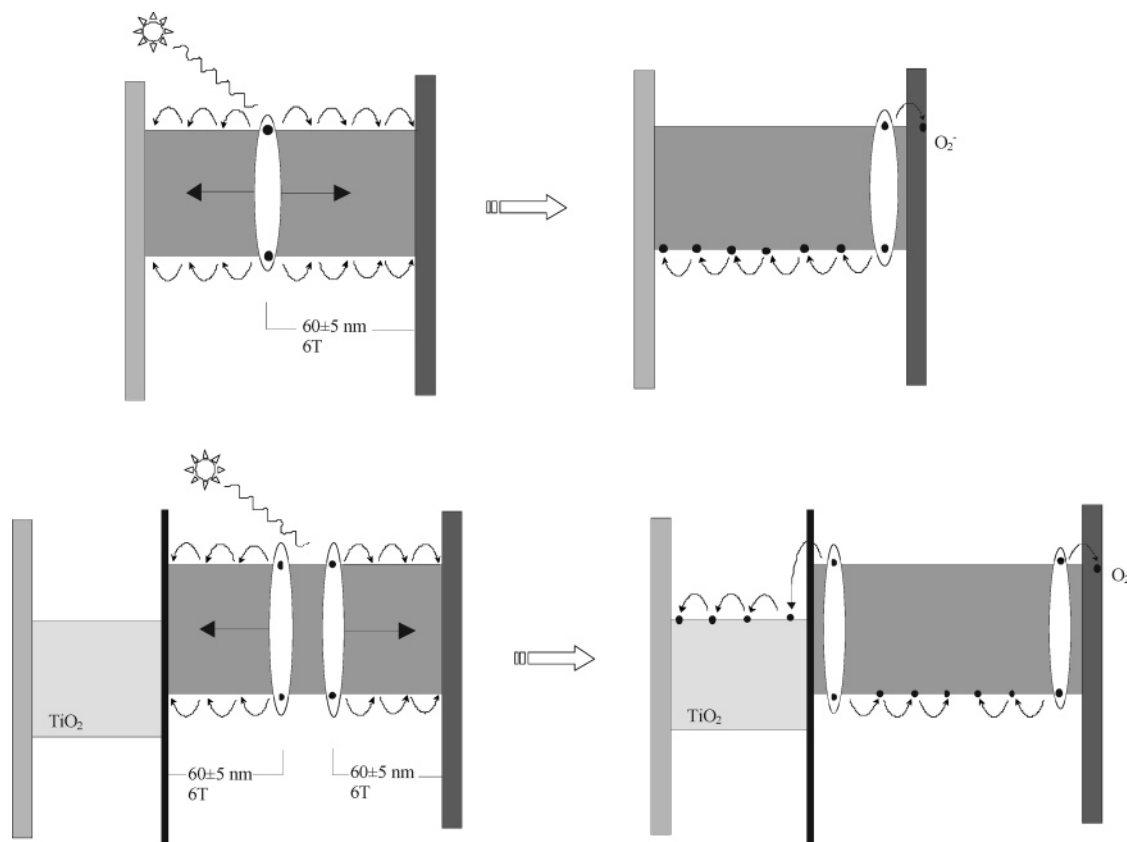
From the data, we are unable to determine how Contribution II (always PL active) and Contribution I (only PL active at  $T < 100$  K) are related to the details of the polymorphic crystallization. The energy difference between the 0–0 transition in absorption and PL spectra defines the so-called Stokes shift. For 6T, a large Stokes shift of 0.128 eV ( $1034\text{ cm}^{-1}$ ) is found.

Such a large Stokes shift indicates disorder in the vapor-deposited polycrystalline material, which causes energy relaxation into deep traps. To study the relationship between the PL spectra and the structural properties of 6T films, Gebauer et al.<sup>33</sup> varied the substrate temperature during the deposition. They report that the two PL contributions can be resolved only for films that are grown at temperatures of 300 K and higher.

As is shown in Figure 10, Contributions I and II can be regarded as radiative traps. Contribution I (low  $T$ ) is blue-shifted with respect to Contribution II. The PL Contribution II is due to emission from an inhomogeneously broadened density of deep electronic states. The absorption and emission spectra of single crystals are similar to those of evaporated thin films, although for single crystals, the PL peaks are sharper. Broadening of the PL lines in thin films can be caused by surface or interface states, which are created because of abrupt change of the potential landscape.

The intensity of the PL emission at 2.1 eV is a function of temperature and is well described by eq 1. The activation energies are 18 meV on  $\text{TiO}_2$  and 6 meV on quartz. These energies are in good agreement with the energy separation that occurs between the bottom of the free exciton band and trapped exciton states, i.e., a state in which the free exciton is bound near a defect or in a small crystallite. Cerminara et al. calculated an activation energy of  $10 \pm 5$  meV for the progression that is only detectable below 40 K.<sup>10</sup> A similar progression was detected in 6T single crystals by Horowitz et al.<sup>48</sup>

To explain the relationship between the PL intensity and the film thickness, we postulate that not only the excitons arriving at the 6T/ $\text{TiO}_2$  interface but also those arriving at the 6T/vacuum or 6T/air interfaces are quenched. The reason for exciton quenching at the outer surface is not exactly clear yet but can be related to the abrupt change of the dielectric medium. Another



**Figure 11.** Schematic presentation of the sequence of light absorption, exciton migration ( $60 \pm 5$  nm), and charge separation in 6T films in  $\text{TiO}_2$ /6T/vacuum and quartz/6T/vacuum.

possibility is that oxygen is present on the surface, even in a vacuum. In this case, excitons may dissociate at oxygen sites, creating  $O_2^-$  radicals and holes. It is well-known for PPV and polythiophene that this oxygen reduction reaction occurs and even leads to the formation of singlet oxygen in the case of PPV polymers.<sup>42–47</sup> Also for  $TiO_2$ /phthalocyanine heterojunctions, superoxide radicals are formed under the influence of light.<sup>5</sup> This kind of photodegradation reaction may also occur in 6T, but this topic is beyond the scope of the present paper.

Heterojunctions of  $TiO_2$  and 6T show quenching of the PL for films thinner than  $120 \pm 10$  nm. In conjunction with the idea that excitons are quenched on both sides, we conclude that the exciton diffusion length is  $60 \pm 5$  nm. Indeed, when 6T is applied onto quartz PL, quenching occurs for films thinner than  $60 \pm 5$  nm, in excellent agreement with our expectations. In Figure 11, exciton migration and quenching in  $TiO_2$ /6T/vacuum and quartz/6T/vacuum devices are illustrated.

Kalinowski et al.<sup>27</sup> studied the modulating electric field effect on the luminescence (EML) and photoconduction (PC) in solid films of 6T sandwiched between Al electrodes and conclude that the exciton diffusion length is 110 nm. They assume that triplet excitons are involved, as in the case of anthracene, but give no further evidence for this claim.<sup>26,27</sup>

Another remarkable outcome of our experiments is that the exciton diffusion length is temperature independent, i.e., the values found at 10 and 300 K are identical. This implies that multiple trapping, which is a thermally stimulated process, does not occur. We conclude that exciton transport over 60 nm is a single event and needs no thermal activation.<sup>27</sup>

## Conclusions

Quenching of excitons in 6T thin films on quartz and on  $TiO_2$  substrates has been investigated with photoluminescence spectroscopy. There are two contributions to the PL spectra. Contribution I is only active at temperatures below 100 K and with films thicker than 20 nm. Contribution II is always active. The intensity of the PL depends on the temperature following Curie's law, with activation energies of 18 meV on  $TiO_2$  and 6 meV on quartz.

For 6T films on quartz, exciton quenching occurs for films thinner than  $60 \pm 5$  nm. In contrast, 6T films on  $TiO_2$  show exciton quenching up to a film thickness of 120 nm. We conclude that the exciton diffusion length in 6T is  $60 \pm 5$  nm and that both the 6T/ $TiO_2$  interface and the 6T/vacuum (or air) interface are active. It is found that the exciton diffusion length does not depend on the temperature. The exciton diffusion length of 60 nm is an order of magnitude larger than that of thiophene polymers, which underlines the advantage of using 6T oligomers in PV devices.

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