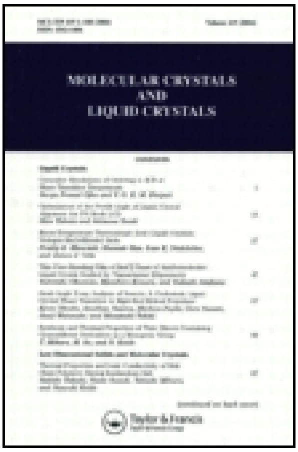

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Optical and Charge Transport Properties of an Ambipolar Quinoidal Oligothiophene Derivative

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Optical and Charge Transport Properties of an Ambipolar Quinoidal Oligothiophene Derivative

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We report on the charge transport and absorption properties of a low bandgap quinoidal oligothiophene derivative [QQT(CN)4]. Organic field-effect transistors based on as-prepared QQT(CN)4 thin films show an ambipolar p-type dominant behavior and can be converted to n-type by thermal annealing at 100° C for 30 minutes. Absorption spectra and atomic force microscopy measurements carried out in both neat films and polymer blends provide new important insights into the role of the degree of aggregation and the intermolecular interactions on the semiconducting and photophysical properties of this organic electronic material.

Keywords Quinoidal oligothiophene; ambipolar organic transistor; majority carrier type conversion; degree of aggregation; optical properties

1. Introduction

Solution-processable organic semiconducting materials have been recently the subject of intensive studies because of their potential for optoelectronic devices such as solar cells, light-emitting diodes and organic field-effect transistors (OFETs). In particular, ambipolar organic semiconductors have received considerable attention for their application in light-emitting field-effect devices and complementary logic circuits [1–3]. Despite outstanding progress in the development of these materials and their integration into OFETs and integrated circuits, their field-effect mobilities and their stability still need to be dramatically improved for practical electronic applications.

Among the different classes of organic semiconductors developed for the realization of high performance OFETs, dicyanomethylene-terminated quinoidal oligothiophene derivatives are now considered as good candidates for n-type and ambipolar devices [4]. Recently, we demonstrated air-stable solution-processed ambipolar OFETs based on the low bandgap quaterthiophene derivative [QQT(CN)4] with hole and electron field-effect mobilities as high as 0.1 and 0.015 cm^2/Vs respectively [5,6]. In addition, these devices can be converted

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from p-type dominant ambipolar to n-type by laser irradiation or by thermal annealing at 180°C for about 10 seconds [7–9]. This majority carrier type conversion was also found to be reversible using a chloroform vapor treatment [10]. The unique charge transport properties of this organic material in the solid-state were attributed to strong variations in the molecular packing. The possibility to control selectively and spatially the dominant carrier type by direct laser writing or thermal lithography techniques provides an effective and innovative approach for the fabrication of complementary metal oxide semiconductor (CMOS) integrated circuits and lateral p-n diodes in organic thin films based on a single solution-processable organic semiconductor [5–11].

In this work, we demonstrate that the majority carrier type conversion can be achieved in QQT(CN)4 OFETs by thermal annealing at 100°C, which is a lower temperature than that used in previous works [5,7]. In addition, absorption spectra and atomic force microscopy (AFM) measurements will show the influence of thermal annealing on the degree of aggregation and the intermolecular interactions in QQT(CN)4 thin films. Overall, this study provides new important insights into the role of the film morphology on the charge transport and photophysical properties of quinoidal oligothiophene derivatives.

2. Experimental Methods

The molecule QQT(CN)4 was synthesized following a modified method adapted from the literature [7]. Its chemical structure is shown in Fig. 1. Bottom-gate top-contact OFETs were fabricated on silicon wafers with thermally grown 300 nm thick SiO_2 layer. After the cleaning of the substrates in ultrasonic baths and UV-ozone treatment, a monolayer of octadecyltrichlorosilane (OTS) was deposited by self-assembly onto the SiO_2 layer. The 90 nm thick QQT(CN)4 films were then prepared by spin-coating and top-contact gold source/drain electrodes were evaporated through a shadow mask. The channel length and width were 45 μm and 4 mm respectively. Note that the thermal annealing at 100°C for 30 minutes was performed in air before the deposition of the top electrodes. OFET characteristics were recorded under ambient atmosphere using two picoammeter/voltage source units (Keithley 6487) interfaced and controlled by a computer.

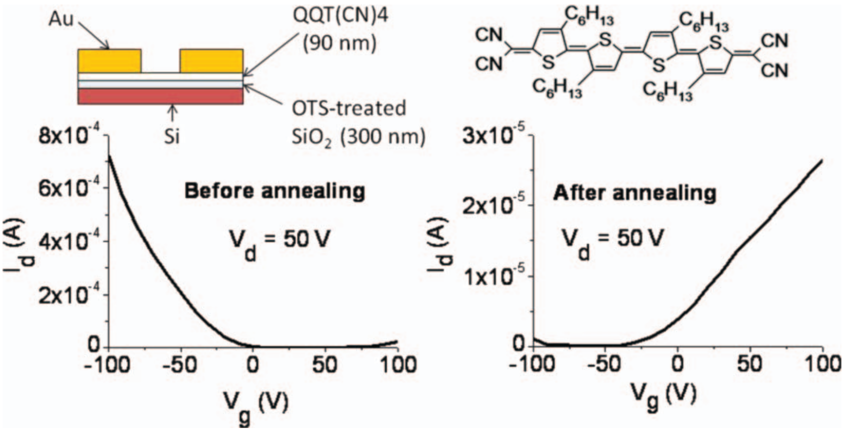

Figure 1. Transfer characteristics of QQT(CN)4 OFETs measured at a drain voltage of 50 V before and after a thermal annealing at 100°C for 30 minutes. The schematic representation of the device and the chemical structure of QQT(CN)4 are also shown in the inset.

QQT(CN)4 neat films were also prepared by spin-coating onto fused silica wafers. In addition, QQT(CN)4 was also blended into a poly-N-methyl methacrylimide (PMMI) host at various concentrations providing a way of controlling its degree of aggregation in the solid state. Note that PMMI films are known to present a good optical quality and this polymer presents a glass transition temperature of about 150°C, which is higher than that of polymethylmethacrylate (PMMA). Thermal annealing was achieved by placing the films on a hot plate at 180°C for 10 s. The absorption spectra of these samples were recorded by an absorption spectrophotometer. AFM experiments were carried out using a scanning probe microscope in the contact mode.

3. Results and Discussion

A schematic representation of the QQT(CN)4 OFETs fabricated in this work as well as the transfer characteristics measured in as-prepared and annealed devices for a drain voltage (V_d) of 50 V are displayed in Fig. 1. In the case of the as-prepared QQT(CN)4 OFET, contributions from both hole and electron conductions to the electrical response of the device can be observed at negative and positive gate voltage (V_g), respectively. However, it can be clearly seen that the hole current is more than one order of magnitude higher. This indicates that the device is ambipolar with a predominant hole-transport character. In the annealed device, the electron current has not been affected significantly by the treatment but the hole current at negative V_g has vanished. The result confirms that a conversion of the majority carrier type can be obtained in QQT(CN)4 OFETs by a simple thermal treatment [5,7]. These unique charge transport properties were attributed to strong changes in film morphology and molecular packing upon annealing. It is worth noting that the unipolarization from ambipolar p-type dominant to n-type behavior in QQT(CN)4 OFETs was achieved in previous works by heating the samples at 180°C for about 10 seconds [5,7]. This study demonstrates that similar conversion is obtained after annealing at 100°C but the annealing time must be increased to at least 30 minutes. This is due to the fact that the dynamics of the morphological effects responsible of these changes in the charge transport properties are highly temperature dependent. The possibility to obtain a majority carrier type conversion in QQT(CN)4 OFETs at much lower temperatures than 180°C is of strong interest for making complementary organic integrated circuits on flexible substrates and for reducing detrimental effects associated with any potential thermal degradation of the organic layers.

Figure 2 shows the absorption spectrum of QQT(CN)4 in chloroform solution as well as the influence of a thermal annealing on the optical properties of the thin films. The

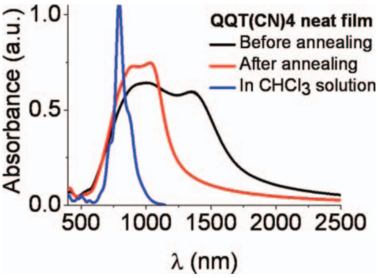

Figure 2. Absorption spectra of QQT(CN)4 in $CHCl_3$ solution and in neat films before and after a thermal annealing at 180°C for 15 seconds.

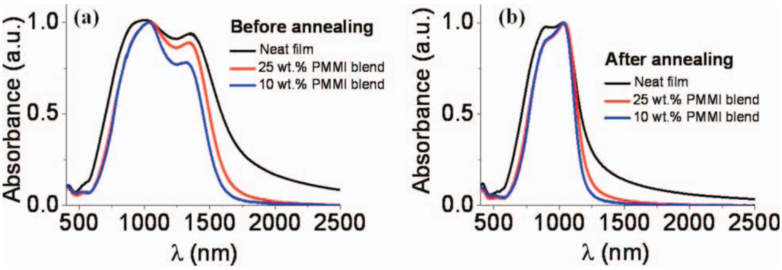

Figure 3. Normalized absorption spectra of QQT(CN)4 neat film and QQT(CN)4 : PMMI blends at different concentrations measured before and after thermal annealing.

spectrum in solution presents absorption features in the near infrared region with a peak maximum located at 795 nm. The spectra measured in both as-prepared and annealed thin films are much broader and this was previously assigned to the presence of aggregates in the solid-state [7,10]. The spectrum measured in annealed film is notably sharper than in the as-prepared film, which is due to the significant variations in molecular packing and degree of aggregation induced by the thermal treatment.

To gain further important insights into the optical properties of QQT(CN)4 in the solid-state, the quinoidal oligothiophene molecule was blended at different concentrations in a PMMI polymer host. Figure 3 shows the absorption spectra of the neat film as well as the 25 wt.% and 10 wt.% blends before and after thermal annealing. A clear narrowing of the absorption spectra measured in as-prepared samples is observed when decreasing the concentration of QQT(CN)4. This result indicates that blending is an effective approach to control the degree of aggregation of QQT(CN)4 in the solid-state. Nevertheless, the absorption spectrum obtained in the 10 wt.% blend is still very broad which implies that the optical properties of this composite sample are still completely dominated by the contribution from the aggregates. Similar behavior is observed with the annealed samples and it is important to mention that the influence of annealing on the absorption properties remains nearly the same even in the 10 wt.% blend. Because the limited solubility of QQT(CN)4 in chloroform, it has not been possible to deposit films with thickness higher than 150 nm up to now. The results suggest the possibility to prepare much thicker films based on a PMMI:QQT(CN)4 blend with similar optical properties as those observed in

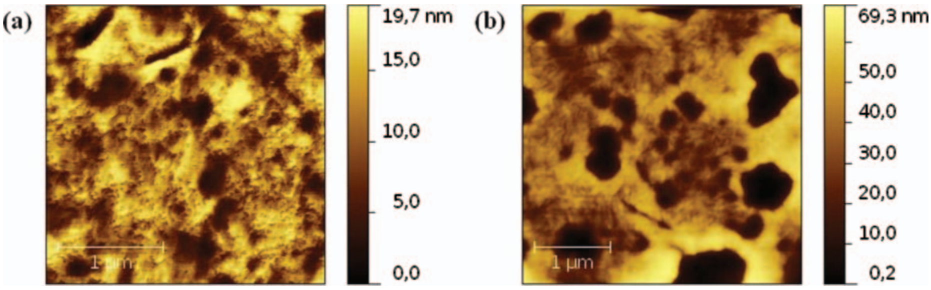

Figure 4. AFM images of a film made from QQT(CN)4 : PMMI blend (25:75 wt.%) before (a) and after annealing (b).

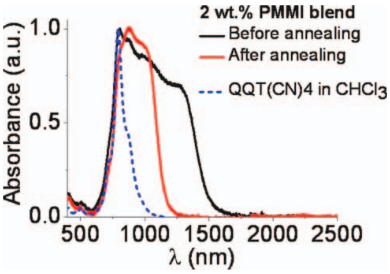

Figure 5. Normalized absorption spectra of QQT(CN)4 : PMMI blend (2:98 wt.%) before and after annealing. The spectrum of QQT(CN)4 measured in $CHCl_3$ is also shown for comparison.

the neat films. This finding may have strong implications in the future use of quinoidal oligothiophenes for photonic applications.

Figure 4 shows the AFM topography images of the 25 wt.% blend before and after thermal annealing. Whereas QQT(CN)4 thin films are known to be polycrystalline [5,10], the surface of the blend does not present any crystalline grains observable at the scale used for this experiment. However, in some parts of the films, some holes can be seen, presumably caused by some residual solvent droplets during the sample preparation. This result confirms the fact that blending is a good method for controlling the aggregation of QQT(CN)4 in films. Thermal annealing is often used to optimize the morphology of organic thin films and control their semiconducting properties [12,13]. In particular, this can cause strong phase separation between different compounds mixed in a blend [14]. The absence of such phase separation in QQT(CN)4 : PMMI blends is another important advantage of these composite materials for optical devices.

The absorption spectra of the 2 wt.% blend before and after thermal annealing are displayed in Fig. 5. The normalized spectrum of QQT(CN)4 chloroform solution is also shown. Compared to the absorption properties of the neat film and the blends at higher concentrations of QQT(CN)4, the spectrum of the as-prepared 2 wt.% blend presents additional features. In particular, a new peak appears at 795 nm which corresponds to the wavelength where the spectrum in solution shows its maximum. This can be explained by the fact that, at such a low concentration in the PMMI matrix, some QQT(CN)4 molecules are not aggregated and the contribution from these isolated chromophores leads to significant changes in the absorption spectrum of the blend. This important result fully supports our interpretation that the broad absorption spectrum of QQT(CN)4 film is due indeed to the formation of aggregates in the solid-state.

4. Conclusion

In conclusion, the influence of a thermal treatment on both charge transport and absorption properties of QQT(CN)4 films was examined. The results demonstrate the possibility to achieve a conversion of the majority carrier type in QQT(CN)4 OFETs by annealing at 100°C. The data also show that the absorption properties of QQT(CN)4 in thin films can be modified either by thermal annealing or by blending the chromophores in a polymer host. This study provides important information on the role played by the degree of aggregation on the optical properties of QQT(CN)4 and should be taken into account for the future development of optoelectronic applications based on this organic conjugated material.

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