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Organic field-effect transistors based on J-aggregate thin films of a bisazomethine dye

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ABSTRACT

We report on the fabrication and the characterization of p-type organic field-effect transistors based on vapor-deposited J-aggregate bisazomethine dye thin films. The absorption spectra of this non-ionic organic semiconductor in the solid state show a strong influence of the film thickness on the J-aggregate formation. However, the electrical characteristics of the devices demonstrate that the hole transport properties do not vary significantly in films thicker than 100 nm. This is due to the fact that the J-aggregates are formed in this material at the surface of the crystalline grains and do not influence the semiconductor/gate dielectric interface and the charge transport properties of the devices. Hole field-effect mobilities as high as 2.4×10^{-4} cm^2 V^{-1} s^{-1} were obtained and could be slightly improved by a solvent vapor treatment due to changes in the film crystallinity. Overall, this study demonstrates that J-aggregate bisazomethine dye thin films are good candidates for the realization of organic electronic devices.

1. Introduction

Organic semiconductors have received considerable interest in the last decades because of their potential in a broad range of optoelectronic devices including organic light-emitting diodes (OLEDs) [1], organic photovoltaics (OPVs) [2] and organic field-effect transistors (OFETs) [3]. The performance of these devices has been greatly improved over the years through the development of new organic conjugated materials and the optimization of their fabrication methods. In particular, organic semiconductors forming J-aggregates [4–7] in the solid state have been the subject of intensive studies due to their intense absorption at specific wavelengths which make them attractive candidates for optoelectronic applications [8–15]. Because of their high absorption cross section, J-aggregates can strongly attenuate incident light in ultrathin films. However, these organic materials generally present in thin films charge carrier mobilities lower than 10^{-4} cm^2 V^{-1} s^{-1} [16]. Control of the aggregate formation, stability of the material and charge transport properties are currently the main critical issues which need to be improved for the practical use of these organic compounds in light-harvesting and optoelectronic devices [17].

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The molecule *N*,*N*′-bis[4-(*N*,*N*-diethylamino)benzylidene]diaminomaleonitrile (DE2) is a neutral dye which can form large-area homogeneous J-aggregate thin films by vapor deposition [18]. The chemical structure and the absorption spectra of DE2 are shown in Fig. 1. The J-aggregate absorption band observed in these films was found to be highly stable against heat and moisture. The good stability of this compound in comparison to more conventional J-aggregate dyes is essentially due to its non-ionic character [19]. The formation of J-aggregates in DE2 films leads to a strong enhancement of the third order non-linear optical properties [20]. In addition, this organic semiconductor was found to emit red fluorescence in both solution and thin films, which make this material an interesting candidate for OLEDs [21]. More recently, the demonstration of organic solar cells based on J-aggregate DE2 thin films provided evidence that this compound is a promising material for high performance organic photodetectors and photovoltaic devices [22]. Previous works have also shown that the orientation of the J-aggregates in DE2 films can be controlled by using an aligned poly(tetrafluoroethylene) (PTFE) surface [23,24]. A dichroic ratio as high as 25 was measured from the polarized absorption spectra of these highly oriented DE2 thin films. This important finding should be taken into account for the future use of DE2 molecules in optoelectronic and photonic applications.

In this manuscript, we report on the realization of top-contact bottom-gate OFETs based on vapor-deposited DE2 thin films with different thicknesses. The devices show a unipolar p-type behavior with hole field-effect mobilities as high as 2.4×10^{-4} cm^2 V^{-1} s^{-1}, which is one of the best values ever reported in J-aggregate organic thin films. The thickness dependence of the semiconducting properties of DE2 films can be explained by the formation of J-aggregates in the vicinity of the film surface. The possibility to tune independently the optical and charge transport properties of J-aggregate DE2 films is of great importance for the future realization of efficient light-sensing field-effect devices. Overall, this work provides new evidence that DE2 is a promising semiconducting J-aggregate material for organic optoelectronic applications.

2. Experimental

The DE2 molecule was synthesized following a method previously described in the literature [25]. OFETs were fabricated on top of precleaned n-type silicon wafers with a thermally grown 300 nm thick SiO_2 layer. DE2 thin films with a thickness ranging from 70 to 435 nm were deposited by vapor deposition at a pressure of about 3×10^{-4} Pa onto the substrates. Au top contact source/drain electrodes were then evaporated through a shadow mask. In all devices, the channel width and length were 4 mm and 45 μm, respectively. Chloroform vapor treatment of the DE2 films was performed before the preparation of the top contact electrodes and was achieved by placing the devices in a saturated solvent atmosphere. The characterization of the OFET properties was carried out using two picoammeter/voltage source units (Keithley, model 6487) interfaced to a computer. Absorption spectra of DE2 thin films deposited onto precleaned fused silica substrates were recorded using a Shimadzu UV-3100PC spectrophotometer. Film thickness was measured with a Sloan Dektak IIA profilometer. Surface morphology was examined by topographical atomic force microscopy (AFM) using a scanning probe microscope in the tapping mode (Dimension 3100 V, Digital Instruments).

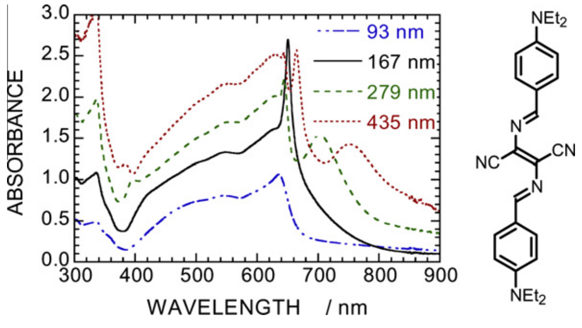

Fig. 1. Absorption spectra of DE2 thin films as a function of the film thickness. The chemical structure of DE2 is also shown.

3. Results and discussion

The absorption spectra of vapor-deposited DE2 thin films with different thicknesses are displayed in Fig. 1. Films thinner than 100 nm show a broad absorption band in the visible region. In thicker films, a sharp peak appears at about 650 nm. The shape and the location of this additional band slightly change with the film thickness. This was previously attributed to the thickness dependence of the J-aggregate formation in DE2 films [18]. Another peak with a maximum at about 550 nm can be seen in the spectra. The position of this peak does not change significantly in the J-aggregate films, suggesting that non-aggregated DE2 molecules are mixed in the films with the aggregates.

The AFM images in Fig. 2 show the surface morphology of four DE2 thin films with thicknesses ranging from 35 to 400 nm. The surface of the non-aggregate thinnest films presents a large density of small grains with a block shape. The J-aggregate thicker films display a different morphology. In that case, the crystalline grains show a prismatic shape and their boundaries are not well-defined. The influence of a 20 h chloroform vapor treatment on the absorption spectrum and the surface morphology of a 150 nm thick J-aggregate DE2 film is shown in Fig. 3. The solvent vapor treatment leads to a decrease of the J-aggregate absorption band and to a fine-grained crystalline structure. These results suggest that the vapor-deposited DE2 films present two phases: a J-aggregate phase and a non-aggregate crystalline phase. Whereas the non-aggregate crystalline phase is dominant in films thinner than 100 nm, the two phases are present in thicker films. In addition, the transition from the J-aggregate to the non-aggregate crystalline phase can be controlled by a simple vapor solvent treatment. A model based on the nucleation mechanism of crystallization has been previously proposed to describe the J-aggregate formation in DE2 films [26]. This model suggested that the J-aggregates are formed when the crystalline grains are sufficiently large to be in contact with

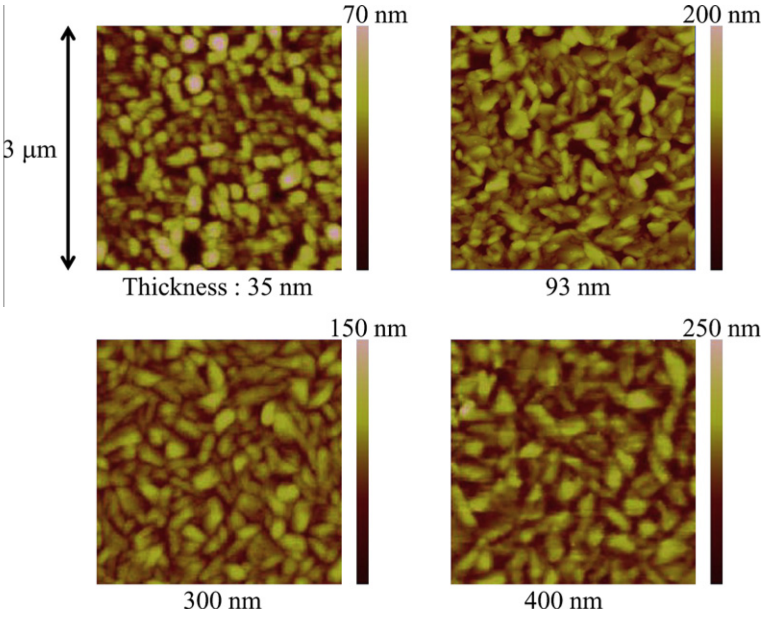

Fig. 2. AFM images of DE2 thin films showing the thickness dependence of their surface morphology and of the crystalline grain formation.

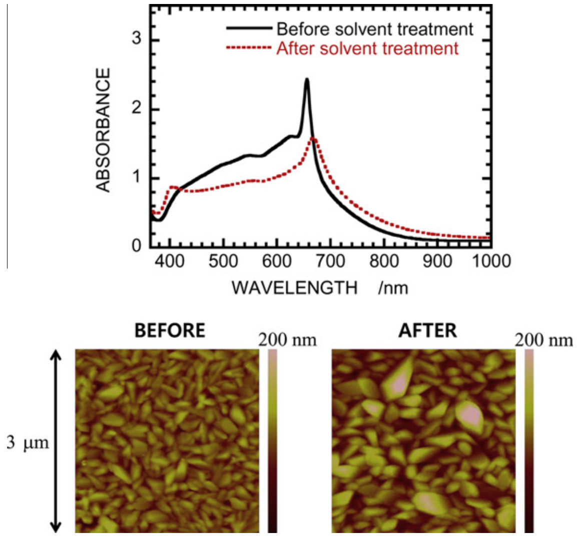

Fig. 3. Absorption spectra and AFM images of a 150 nm J-aggregate DE2 film before and after a 20 h chloroform vapor treatment.

each other. It was also reported that the aggregates remain presumably located at the surface of the films.

Fig. 4a displays a schematic representation of the DE2 OFET structure. The ionization potential of DE2 in thin films has been previously measured by UV photoelectron spectroscopy to be around 5.2 eV [22]. It was also shown that DE2 thin films present p-type semiconducting properties in Schottky-type organic solar cells [22]. Taking into account these previous results, we used gold for the source and drain top electrodes in order to minimize contact resistance effects and obtain good hole injection properties. The output characteristics of an OFET based on a 150 nm thick J-aggregate DE2 thin film are displayed in Fig. 4b. Saturation of the drain current (I_d) is clearly observed at high negative drain voltage (V_d), indicating that the device operates in the hole accumulation mode. The p-type behavior of DE2 OFETs can be seen as well in the transfer characteristic shown in Fig. 5. This result was obtained in a device based on a 279 nm thick DE2 film and at $V_d = -100$ V. The on/off current ratio I_{on}/I_{off} is slightly higher than 100 and the value of the threshold voltage V_{th} is around 1.8 V. The field-effect mobility μ was determined from the transfer characteristics in the saturation regime using the standard equation: $I_d = (W/2L) C_i\mu(V_g - V_{th})^2$, where W and L are the channel width and

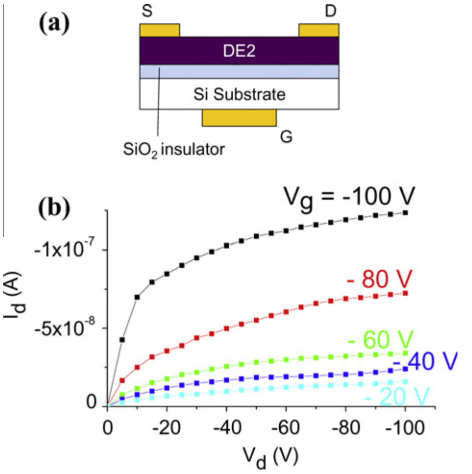

Fig. 4. (a) Schematic representation of the DE2 OFET structure. (b) Output characteristic of a 150 nm thick DE2 OFET measured at various positive gate voltage V_g.

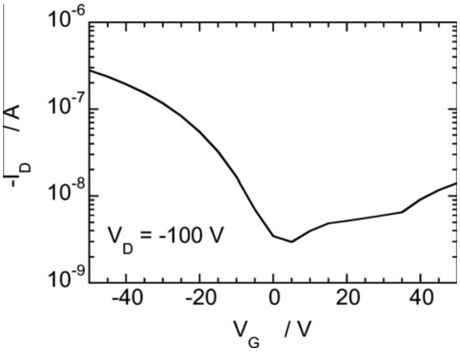

Fig. 5. Transfer characteristic of a 279 nm thick DE2 OFET measured at a drain voltage $V_d = -100$ V.

length of the device, respectively and C_i is the capacitance of the gate dielectric per unit area. Fig. 6 shows the thickness dependence of the hole field effect mobility measured in DE2 OFETs. In DE2 films thicker than 100 nm, the hole field-effect mobility does not depend significantly on the film thickness and presents a value of about 2.4×10^{-4} cm^2 V^{-1} s^{-1}. In thinner films, the field-effect mobility drops by about one order of magnitude to reach a value of about 2×10^{-5} cm^2 V^{-1} s^{-1}. These results can be explained by the influence of the thickness on the DE2 film morphology. We attribute the low charge carrier mobilities in thinner films to charge trapping at the grain boundaries or more likely to a poor molecular packing in the non-crystalline regions. In thicker films, the crystalline grains are in contact with each other. This better crystallinity leads to an increase of the hole field-effect mobilities. In contrast to their optical properties, the charge transport properties of these thicker films are found to not vary significantly with thickness. This can be explained by the fact that the formation of J-aggregates takes place only at the surface of the films and do not affect the dielectric/DE2 film interface [27–33].

The influence of the chloroform vapor treatment on the electrical properties of J-aggregate DE2 OFETs was also examined. Fig. 7a shows the output characteristics of a 150 nm thick J-aggregate DE2 device that has been solvent vapor-treated for 20 h. The curves present a clear saturation regime at high V_d. Transfer characteristics of the device measured before and after the vapor treatment at $V_d = -80$ V are compared in Fig. 7b. The results show that the vapor treatment leads to a slight decrease of the I_{on}/I_{off} current ratio, a variation from 38 to 27 V in the threshold voltage and a little improvement of the hole field-effect mobility. It has been shown that the solvent vapor treatment strongly affects the degree of aggregation at the DE2 film surface but do not modify substantially the crystalline structure of the grains [19]. From these considerations, we can reasonably assume that the organic layer at the dielectric/DE2 interface is not greatly modified by the treatment and we attribute the slight increase of the hole mobility to a little improvement in the film crystallinity.

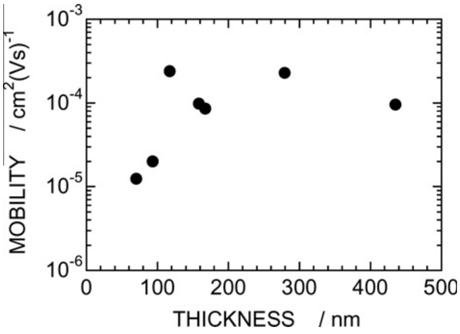

Fig. 6. Thickness dependence of the hole field-effect mobility in DE2 OFETs.

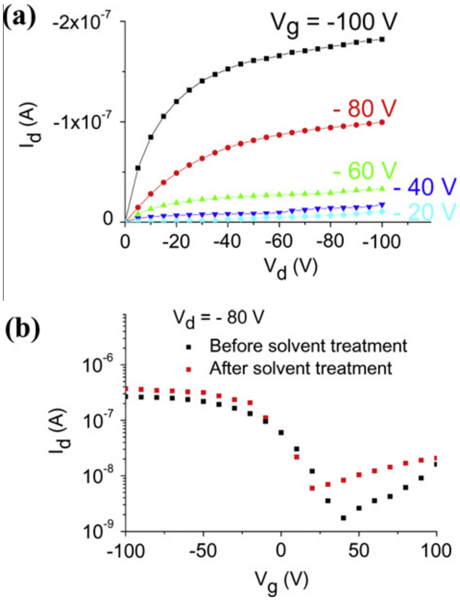

Fig. 7. (a) Output characteristics of an OFET based on a 150 nm thick DE2 film which has been exposed to a chloroform vapor treatment for 20 h. (b) Transfer characteristics of a DE2 OFET before and after a solvent vapor treatment, measured at $V_g = -80$ V.

Overall, this study demonstrates that J-aggregate DE2 thin films can be used for organic electronic applications. The possibility to control independently the optical and the charge transport properties of J-aggregate DE2 films is unique and might offer some interesting future opportunities in the realization of high performance organic photodetectors and other light-harvesting organic electronic devices.

4. Conclusion

In summary, we have demonstrated p-type bottom-gate top-contact OFETs based on vapor deposited J-aggregate DE2 thin films. The influence of the organic film thickness on the J-aggregate formation and the electrical properties of the devices have been examined in details. The absorption spectra of the films show that the optical properties of the J-band strongly depend on the film thickness. In contrast, the hole charge transport properties of the DE2 OFETs do not vary with film thickness when the DE2 layer is thicker than 100 nm. This behavior is due to the fact that the aggregates lie at the surface of the film and do not play any role on the properties of the dielectric/organic semiconductor interface. In addition, we have demonstrated that a solvent vapor treatment can be performed to control the degree of aggregation in DE2 films and to slightly improve the hole conduction properties. This study provides new important insight into the semiconducting properties of J-aggregate bisazomethine dye thin films. The high hole field-effect mobilities as well as the possibility to control the degree of J-aggregation and the charge transport properties independently in DE2 films demonstrate the high potential of this organic material for electronic and light-sensing applications.

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