

Intralayer vs. interlayer electronic coupling in perylene imide thin films



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ABSTRACT

Optical absorption spectroscopy was performed on thin films of the perylene imide dye PD18-CN2 during film growth by physical vapor deposition. The spectra showed an energy shift of 40 meV for the lowest energy transition with increasing film thickness from a sub-monolayer thickness regime to about 40 nm average film thickness with a clear step indicating the complete formation of the first monolayer. To analyze the observed characteristics a model was developed which is based on different contributions of transition dipole coupling in different crystalline directions. Clear dominance of intralayer coupling in the *a*–*b* crystal plane was found whereas interlayer coupling was found to be negligible. This was rationalized by the presence of alkyl chains as a spacer between the aromatic cores oriented along the *c*-direction. Atomic force microscopy of the films revealed layer-by-layer growth for the first monolayers and confirmed a texture with the *c*-axis perpendicular to the surface. The growth mode was correlated with the extent of intermolecular coupling in the different crystalline directions. We will discuss perspectives to optimize electron transport in PD18-CN2 thin films which have been proposed as molecular semiconductor in organic field effect transistors (OFET).

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1. Introduction

Organic dye molecules showing semiconducting behavior are of interest within the scientific community as they show a wide range of potential applications in electronics and electrical device engineering [1]. A physical understanding of the aggregation and electronic coupling of such molecules in thin films is crucial for a continued successful realization of photonic devices like organic light emitting diodes or organic photovoltaic cells. Optical investigations of organic semiconductors are very sensitive to study such intermolecular interactions because of large changes in the transition dipole coupling arising from changes in aggregation and film structure [1–3] as clearly confirmed also by theoretical treatments of Frenkel excitons and charge-transfer states [4]. Perylene dyes, in particular perylene

tetracarboxylic dianhydride (PTCDA) and dimethyl perylene tetracarboxylic diimide (MePTCDI) served as excellent model systems [5–8]. Optical absorption measurements performed in situ during film growth are of special interest to study the development of the intermolecular arrangement starting from early stages of film formation [9–11]. It has been shown that the lowest energy absorption of perylene dyes, which is attributed to molecular excitons, is shifted to the red when increasing the number of molecular layers [10,12]. The assumption of this shift to be caused by an averaging superposition of bands stemming from volume vs. interface absorption leads to a 1/*d* dependence with *d* representing the average film thickness or, simply, the amount of deposited material [9,13,14]. Similar shifts can also be explained by a cosine dependence of the transition energy on the extent of intermolecular coupling in different directions of growing crystalline domains [15].

As a characteristic example that allows to clearly distinguish among the two models for exciton coupling in

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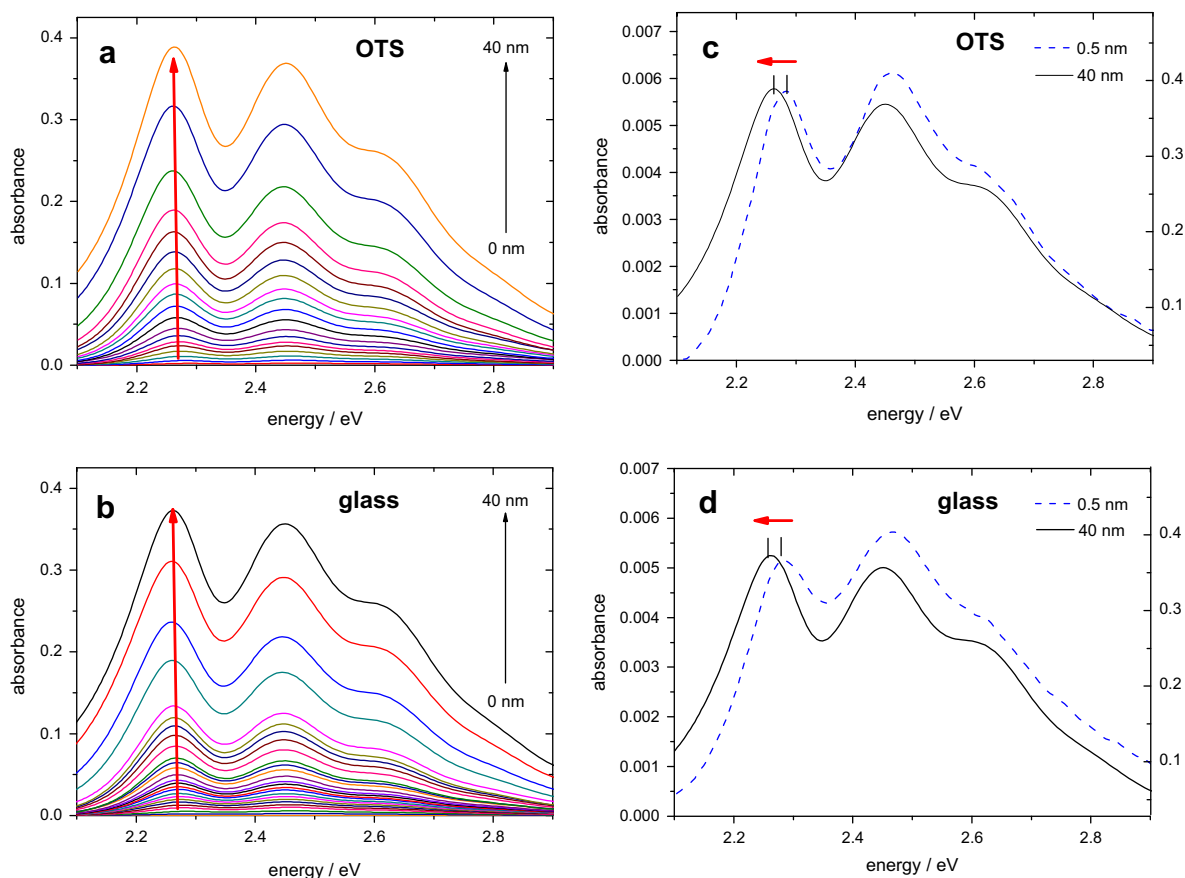


Fig. 1. Absorption spectra of PDI8-CN2 films (0 nm–40 nm average film thickness) on OTS-coated (a) or bare glass substrates (b). The red arrows indicate the position of the lowest energy transition at around 2.27 eV shifting slightly to lower energy for increasing film thickness. On the right hand side spectra of 0.5 nm (left axis) and 40 nm thick films (right axis) are directly compared on OTS-coated (c) or bare glass substrates (d). Black bars indicate the energetic shift of the lowest energy transition with increasing film thickness. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

organic semiconductor thin films and their influence on observed systematic shifts in absorption spectra with increasing film thickness we discuss in this work optical absorption spectra collected in situ during the growth of thin films of *N,N'*-bis(*n*-octyl)-(1,7&1,6)-dicyanoperylene-3,4,9,10-bis(dicarboximide) (PDI8-CN2), a perylene imide carrying alkyl substituents at the imide nitrogen and cyano substituents in the bay positions of the aromatic ring system [16]. Thin films of PDI8-CN2 have proven as suitable materials to establish air-stable *n*-type semiconducting channels in organic field-effect transistors (OFET) [16] in particular when their growth was optimized by proper control of interfacial interaction and growth conditions [17,18]. In the optical absorption of thin films of PDI8-CN2 only a small shift of about 0.11 eV of the lowest energy transition was observed relative to solution spectra indicating only weak intermolecular interaction compared with other perylene derivatives [17,18]. Investigations on the crystal structure of PDI8-CN2 in films grown from solution [19], for bulk powder samples [20] and also in evaporated thin films [20] showed a formation of a triclinic unit cell with the parameters $a = 0.9399$ nm, $b = 0.5028$ nm

and $c = 2.057$ nm for films grown from solution [19] which was recently refined to $a = 0.5028$ nm, $b = 0.8930$ nm, $c = 1.9944$ nm, $\alpha = 99.8^\circ$, $\beta = 90.6^\circ$, $\gamma = 100.7^\circ$ [20], almost identical to a structure with $a = 0.5019$ nm, $b = 0.8841$ nm, $c = 2.0195$ nm, $\alpha = 101.51^\circ$, $\beta = 92.33^\circ$, $\gamma = 100.15^\circ$ determined for bulk powders [20]. Detailed analysis of evaporated thin films of PDI8-CN2 with an average film thickness of 10 nm, 40 nm or 100 nm deposited on SiO₂ at RT, 80 °C or 120 °C showed small deviations which were, however, considered as small distortions of this bulk structure [20].

In this study we will investigate in detail the development of the optical absorption spectra of PDI8-CN2 during formation of the first monolayers on glass with different surface modification as a model surface for OFET substrates. We will show that the cosine- dependence of the transition energy holds for the formation of PDI8-CN2 thin films because the intermolecular coupling within the *a*–*b* plane dominates over the coupling in other crystal directions. We used atomic force microscopy (AFM) to show that the strong coupling within the *a*–*b* plane leads to a layered growth of PDI8-CN2 thin films with the *a*–*b* plane

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