Formation of Solid-State Excitons in Ultrathin Crystalline Films of PTCDA: From Single Molecules to Molecular Stacks

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We directly follow the evolution of the absorption spectrum from a single molecule to a dimer and further to a one-dimensional molecular stack: We determine the optical absorption properties of ordered monolayer to multilayer films of PTCDA (3,4,9,10-perylenetetracarboxylic dianhydride) on muscovite mica(0001) surfaces by *in situ* differential reflectance spectroscopy. The data clearly show the transition from the single molecule to a dimer spectrum, followed by the exciton delocalization to a molecular crystal exciton. The accompanying spectral shifts compare favorably with recent model concepts.

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The excitonic optical properties of organic molecular systems are of great interest in physics, chemistry, and biology. For instance, the efficacy of natural photoactive systems like light harvesting complexes is mainly due to a fine-tuning of the degree of exciton (de-) localization [1]. The realization of highly efficient light-emitting diodes and solar cells based on organic molecular materials has renewed the interest in the properties of molecular organic thin films. Highly ordered films, which represent ultrathin organic molecular crystals, can provide a deeper insight into the physical processes occurring on the nanoscale [2]. Much effort has been put into the understanding of the absorption spectra of organic single crystals and vacuum deposited thin films [3–5]. However, a detailed understanding of *ultrathin* film spectra has not been achieved, mainly since (i) experimental data of well-defined small aggregates have not yet been obtained and (ii) very different theoretical concepts have been used to explain the crystal data.

In this Letter, we present the first experimental investigation of the transition from a single molecule via a dimer to a crystalline stack of an organic molecule, directly monitored by a variant of absorption spectroscopy. As a model system, we choose 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA), which represents an archetype for organic thin film growth since it usually forms smooth and highly ordered layers on a large variety of different substrates [2]. Also, the strong π-π interaction of the molecules along the stacking direction leads to largely anisotropic optical and electronic properties [2,6]. As a suitable experimental method, we apply differential reflectance spectroscopy (DRS), which compares the reflectance of an adsorbate-covered and a bare sample, $R(\omega)$ and $R_0(\omega)$ [7,8]. For films with a thickness much smaller than the wavelength of light, the Fresnel equations of the system can be linearized [7–9]. The DRS signal $\Delta R/R$ [Eq. (1)] consists of a mixture of the imaginary and real parts of the (complex) dielectric function of the substrate $\hat{\epsilon}_S$ and the adsorbate $\hat{\epsilon}_A$ [10]. In the case of the transparent substrate mica, the imaginary part of $\hat{\epsilon}_S$ is very small and almost constant over the visible wavelength range ($\mathrm{Im}\hat{\epsilon}_S \ll 1$, $\mathrm{Re}\hat{\epsilon}_S = \epsilon_S$). Hence, in the case of normal incidence (nearly realized here) the DRS spectrum represents mainly the imaginary part of the dielectric function $\hat{\epsilon}_A$ of the adsorbate film:

$$\frac{\Delta R}{R}(\omega) = \frac{R(\omega) - R_0(\omega)}{R_0(\omega)} \cong \frac{8\pi d_A}{\lambda}\frac{\mathrm{Im}(\hat{\epsilon}_A)}{1-\epsilon_S}, \qquad (1)$$

where d_A is the thickness the molecular adsorbate layer [11]. Although the absorption coefficient α of Beer's law is related to the imaginary part of the root of $\hat{\epsilon}$ [$\alpha \equiv \frac{4\pi\kappa}{\lambda} = -\frac{2\omega}{c}\mathrm{Im}(\sqrt{\hat{\epsilon}})$], a linearization of the corresponding Fresnel equation yields that the absorbance of *ultrathin* films ($d_A/\lambda \ll 1$) is proportional to $-\frac{d_A}{\lambda}\mathrm{Im}(\hat{\epsilon}_A)$ and therefore closely resembles the shape of the DRS spectra. In our experiments, the substrate is rather thin ($d_S \approx 50\ \mu$m), so that the backside reflection of the substrate also influences the DRS signal, causing an overall lowering of the signal depending on d_S in a first-order approximation.

The PTCDA films are deposited at room temperature in ultrahigh vacuum by organic molecular beam epitaxy (OMBE) on a thoroughly degassed sheet of mica, cleaved *ex situ*. The molecular flux was initially controlled by a quartz balance, while the final values were determined by comparing the integrated $\Delta R/R$ spectra of the thickest films with calculated values, using optical constants for PTCDA from [13].

Monomer-dimer transition.—The DRS spectra measured during deposition completely change their spectral shape with increasing film thickness, as can be seen in Fig. 1. The first spectra show a monomer absorptionlike shape: The three peaks (at 2.35, 2.55, and ~2.75 eV) belong to the lowest (i.e., $S_0 \rightarrow S_1$) transition, separated by a vibronic progression of $\Delta E \sim 0.17$ eV [3,5]. Beginning at a nominal thickness of 1.4 molecular layers (ML), a significant alteration occurs: the spectra differ from the previous ones by a noteworthy change in the ratio of the heights of Peak1 (2.34 eV) and Peak2

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(2.53 eV). Additionally, the second peak becomes considerably broader. For the consecutive measurements, the spectral character transforms further into the known thin film spectra. In the conversion range from 1.4 to 2.3 ML, Peak2 moves slightly downwards in energy (~ 20 meV), accompanied by a further broadening. Besides those spectral modifications, it is very intriguing to note the occurrence of two points of intersection in the set of DRS spectra in Fig. 1. These so-called isosbestic points appear in the thickness range from 1 to 1.9 ML and are a characteristic behavior of an equilibrium between two absorbing species [14]. This leads to valuable information regarding the growth mode: In a layer-by-layer growth regime, these two species represent the monomer and the stacked dimer, respectively.

To understand this, it is important to realize that the PTCDA crystal is highly anisotropic. For a qualitative discussion, it is useful to regard the crystal as being composed of two different types of physical dimers, *A* and *B* (Fig. 2). Within the (102) crystal plane the molecules lie flat and the arrangement corresponds to the herringbone structure typically found in ultrathin PTCDA films. The in-plane separation between the molecule's centers is quite large (~ 12–15 Å). Thus the interaction of the transition dipoles is very weak and even a closely packed monolayer behaves optically like an ensemble of monomers. Consequently, the monomer spectrum is observed up to 1 ML coverage. On the contrary, in the stacking direction (dimer *B*) a strong interaction of the overlapping π-electron systems is anticipated, because the molecular planes are separated only by 3.4 Å. This interaction is so much stronger than the in-plane interaction that PTCDA can be described as a quasi-one-dimensional crystal [15]. This readily explains the experimentally observed spectral changes once the stacked *B* dimer begins to build up in our films. The fact that the isosbestic points disappear above 2 ML coverage hints towards real layer-by-layer growth (note that the presence of exactly two absorbing species is only a necessary condition, not a sufficient one: it is also required that the spectra of the two species intersect in at least one point, a condition not being fulfilled for the dimer-trimer transition, and higher transitions). Finally, based on Eq. (1) one can directly derive an estimate for $\mathrm{Im}[\hat{\epsilon}_A(E)]$. This optical property of the material nicely reflects the spectral changes occurring during the buildup of the molecular chain. The quantity is independent of d_A, and interestingly all spectra with $d_A \geq 1$ ML show isosbestic behavior, as can be seen in Fig. 3. Also, a feature around 1.87 eV, occurring only in the submonolayer regime, becomes particularly apparent. A similar transition has been observed in *N*-methylpyrrolidone-PTCDA solutions [3] and has been assigned to a charge transfer complex between the polar solvent and the PTCDA. Because cleaved mica exhibits a polar surface, it is quite likely that this transition belongs to (partially) charged PTCDA monomers.

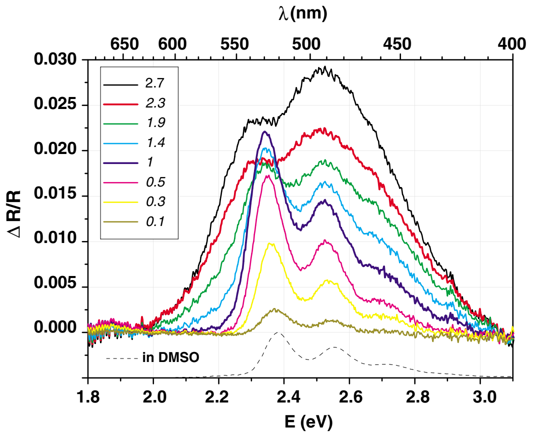

FIG. 1 (color online). Differential reflectance spectra of PTCDA on mica during the growth from 0.1 to 2.7 ML (± 10%) film thickness. Because of the acquisition time of ~40 s and a deposition rate of about 0.23 ML/ min, the layer thicknesses increase by 0.2 ML during the measurement. We give the mean coverage in italic style, i.e., *0.1* ML will read 0–0.2 ML. However, 2.7 ML corresponds to the total final thickness. Note the clear change in the characteristic spectral shape and the two intersection points at about 2.30 and 2.38 eV. For comparison, the absorption spectrum of PTCDA dissolved in dimethylsulfoxide is shown in the bottom (dashed line, shifted, arbitrary units).

In summary, the spectral changes occurring during the monomer-dimer transition can be understood as follows: up to a coverage of 1 ML, a monomeric behavior is observed since (i) the molecules couple electronically only weakly and (ii) the first layer tends more to completion than the molecules tend to stack on each other; i.e., the intensity of the spectra rises proportionally to the coverage. Otherwise the monomerlike shape of the spectra would vanish quite early in the deposition due to the strong π-π interaction of the stacked dimer *B*. Once the first monolayer is more or less completed, the stacked dimer, exhibiting a different spectral characteristic, starts to build up until the entire layer is converted into dimers. From the occurrence of isosbestic points, one can con-

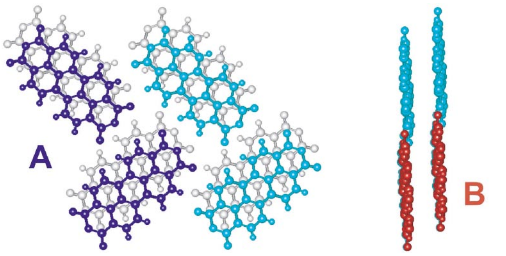

FIG. 2 (color online). The PTCDA herringbone structure: (left) top view onto the (102) plane of the PTCDA crystal, and side view (right). The two types of dimers, *A* (in-plane) and *B* (stacked), are indicated. The crystal data are (α modification) $a = 3.72$ Å, $b = 11.96$ Å, and $c = 17.34$ Å [2].

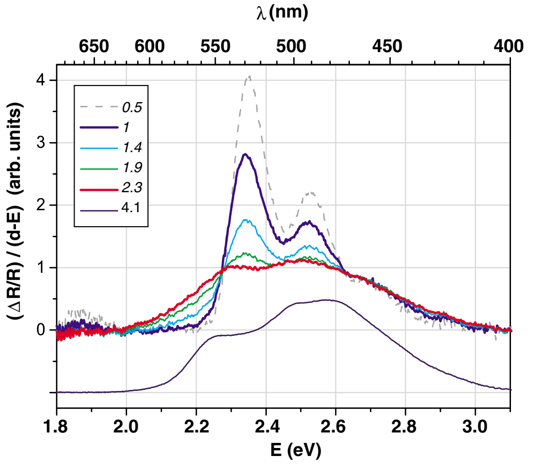

FIG. 3 (color online). The differential reflection spectra divided by the film thickness d and the energy E, a quantity which is proportional to $\mathrm{Im}[\hat{\epsilon}_A(E)]$, for several film thicknesses between 0.5–2.3 ML. Two isosbestic points at 2.27 and 2.62 eV occur, being compatible with the assumption of the growth of a linear chain. In the submonolayer regime, a weak feature at 1.87 eV is visible (see the text). In the bottom, the spectrum of a 4.1 ML PTCDA film is shown for comparison (different sample, shifted).

clude a coexistence region between monomers and dimerized molecules. Consequently, one can assume essential layer-by-layer growth, and the spectral changes are caused by the altering ratio of absorbing monomers to dimers. The observation of layer-by-layer growth for the first layers, i.e., complete wetting not only on stronger interacting substrates like metals or graphite, is also confirmed by photoluminescence studies of OMBE films of PTCDA on alkali halide crystal surfaces [16].

In a close view of Fig. 1, it becomes apparent that with increasing coverage up to 1 ML, a shift of the prominent peak to lower energies by ~30 meV (redshift) occurs, as quantified in Fig. 4. The shift of the molecular transition energy due to an influence of the surrounding medium, the solvatochromism, can be divided into (i) perturbations of the electronic system by interaction with the environment and (ii) changes in the local fields present due to the surrounding polarizable media [18]. Because the molecules themselves interact only very weakly *within* the first monolayer, this shift is an indication for an increasing dielectric screening (dielectric constant) in the layer. In the submonolayer-to-monolayer range, it is sufficient to consider the thickness of the layer to be defined by the z extension of the molecule (i.e., 3.4 Å), and the effective dielectric constant to be dependent on the coverage. Increasing the coverage, the local field imposed on a single molecule changes due to the increased polarizability of the layer, and the resonances are shifted to lower energies [12], similar as observed for amorphous PTCDA submonolayers [19]. Analogous to Ref. [19], the shift remains nearly uniform up to 1 ML, indicating the growth of small PTCDA islands; otherwise the shift would attenuate with increasing monolayer completion [20]. The effect of having two translational nonequivalent molecules in the unit cell (Fig. 2), leading to a Davydov splitting in the order of 10–35 meV [6,15], is by far too small to be resolved under our experimental conditions: Because of peak widths of the transitions in the $\Delta R/R$ spectra of ~130 meV (FWHM in monomer spectra), the Davydov splitting will contribute only to the overall broadening of our spectra, together with an inhomogeneous broadening being present as well (compare Ref. [19]).

Dimer-oligomer transition.—From ~1.9 ML on, the spectra grow proportionally to the thickness again, and Peak1 rapidly undergoes a rather strong shift downwards in energy and considerably broadens, already during the very limited conversion range between 1.9 and 2.3 ML. The total redshift of ~65 meV (from 2.325 to 2.26 eV) is accomplished at a coverage of 4 ML. The comparatively broad Peak2 around 2.50–2.55 eV splits into two bands (at 2.48 and 2.57 eV; see Fig. 3) which remain nearly constant with further increasing film thickness above 4 ML. Starting from a thickness of ~2.3 ML, the high energy shoulder of the spectra at 2.7 eV becomes less pronounced and completely smears out when a coverage of 4 ML is reached. In summary, the dimer-oligomer transition is basically completed at a coverage of about 4 ML. With a further increasing of the thickness, the DRS spectra change only slightly, and the spectral shape is then fully comparable to the spectra known for thicker PTCDA films (compare Refs. [2,15]).

Model descriptions of the absorption spectra of PTCDA films consider the exciton-phonon coupling to have a crucial influence on the spectral shape. In the framework of Holstein models, assuming a coupling of

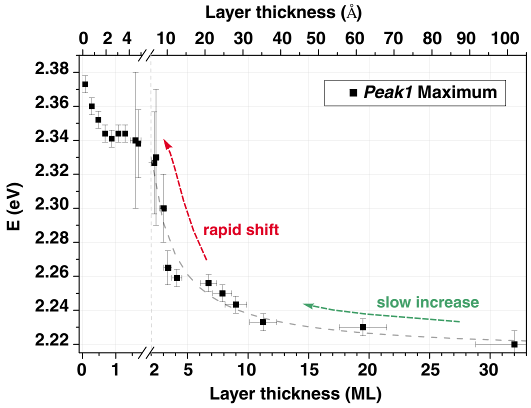

FIG. 4 (color online). The position of the low energy feature Peak1 in DRS during film growth of PTCDA of different samples. The error bars indicate the uncertainty of the Peak1 maximum and the layer thickness. Two different slopes of the shift are obvious, indicated by arrows. The dashed line shows the fit with the model of Agranovich *et al.* [17] ($E_0 = 2.215$ eV, $\Delta = 0.115$ eV; see the text).

Frenkel excitons (FE) and charge transfer excitons (CTE), a good description of the PTCDA bulk crystal spectra was recently achieved. Despite their influence on the transition energies, a relative oscillator strength of only 2%–3% is assigned to CTEs [4,5,15]. Hence, an application of a pure FE model like [4] to ultrathin films would also be promising. Still, there seems to be a contradiction: Large blueshifts should be observed in the transition from monomer to dimer (large excitonic splitting—H aggregate), in contrast to the observation in our experiments. However, this also can be explained by the two alternatives: First, it was found that FE-CTE mixing leads to dimer excitations with almost the same energy as found in the PTCDA monomer [15]. Second, also the pure FE model as applied to the PTCDA crystal [4] could be applicable to explain the spectra, by a reasonable consideration of the "solvent" or environment shift (shift of transition energies in the molecular crystal with respect to the free molecule–dielectric screening). This would compensate the shift caused by the excitonic splitting in the case of the dimer (nearest neighbor interactions).

In the following, we discuss the spectral shift of the low energy peak during the transition. Therefore, the shift of Peak1 in DRS is plotted against the film thickness (Fig. 4). Different slopes of the shift can be identified: For the largest film thicknesses (highest investigated coverage ~30 ML) down to 4 ML, only a small shift of about 40 meV of Peak1 occurs. It extends for further decreasing thicknesses, and Peak1 clearly shifts blue by ~65 meV compared to the dimer layer [21].

Confinement of delocalized extended CTEs with a radius of ~12 Å (Wannier-Mott–type) was proposed to explain the findings [2,22]; also a one-dimensional model of a finite molecular chain of π-stacked PTCDA was applied [24]. However, already the model of Agranovich *et al.* [17] explains our experiments quite well. It assumes a thickness-dependent ratio of bulk and surface molecules, which have different absorption due to on-site effects (e.g., reduced dielectric screening at the outermost surface layer). The strong broadening of Peak1 at 2–3 ML film thickness supports the interpretation of this feature as a superposition of two peaks (around 2.25 and 2.32 eV). To prove this assumption, we fitted the position of the maximum of the experimentally found (i.e., superimposed) absorption peak by $E_m \approx E_0 + 2\Delta/N$, with E_0 being the energy of the bulk absorption, Δ the shift in the absorption energy of the two outermost layers, and N the number of stacked layers. Excellent agreement can be seen in Fig. 4, resulting in a bulk transition energy of $E_0 \cong 2.215$ eV, which corresponds nicely to the position of the low energy peak (2.22 eV) in our thickest layers investigated (~ 30 ML) and in the case of 500 Å PTCDA films in [2]. This underlines the influence of local field effects due to different dielectric polarization as discussed above.

Finally, due to a combination of the precise methods DRS and OMBE, we can provide new data to quantify the size of the solid-state shift for PTCDA. Being a pure fitting parameter in recent models up to now [4,5], the overall shift of the low energy feature Peak1 for the entire monomer to oligomer transition on a mica substrate amounts to about ~160 meV.

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