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Organic Electronics 5 (2004) 91–97

Organic Electronics

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Influence of molecular anisotropy on the optical properties of nanocrystalline films of π-conjugated systems

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Received 8 July 2003; received in revised form 9 January 2004; accepted 22 January 2004
Available online 19 February 2004

Abstract

Absorption and electroabsorption spectra of nanocrystalline films of sexithiophene (T6), quaterthiophene (T4) and 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) are presented and analysed by dielectric response theory and accounting for the coherent polarization induced by the incident light. Due to the anisotropic crystal structure absorption peaks do not occur at exciton transition energies but depend on the respective orientation of molecules and the wave vector of light. This directional dispersion causes the broad and rather featureless absorption spectra of nanocrystalline films. Electroabsorption spectra, however, resolve the fundamental exciton and its vibronic progression clearly. The analysis reveals that excited states interact via their dipole moments while exchange interaction and overlap of molecular states is negligible.

PACS: 71.36.+c; 78.20.Jq; 78.30.Jw; 78.66.Qn
Keywords: Optical anisotropy; Polaritons; Modulation spectroscopy; Nanocrystalline films; Oligothiophenes; PTCDA

1. Introduction: dielectric response theory

The primary response of matter to light is the coherent polarization $\vec{P} = N\vec{\mu}_i = (\varepsilon - 1)\varepsilon_0\vec{E}$ resulting from dipoles $\vec{\mu}$ induced in molecules via their molecular polarizability:

$$(\vec{\mu})_i = \sum_j \beta_{ij} E_j$$

$$\beta_{ij} = \sum_f \frac{(\vec{\mu}_{\rm fg})_j(\vec{\mu}_{\rm gf})_i}{E_{\rm f} - E_{\rm g} - \hbar\omega} + \frac{(\vec{\mu}_{\rm fg})_j^*(\vec{\mu}_{\rm fg})}{E_{\rm f} - E_{\rm g} + \hbar\omega} \qquad (1)$$

The tensor components β_{ij} involve the transition dipoles $\vec{\mu}_{\rm fg} = \langle f|e\vec{r}|g\rangle$ between the ground state $|g\rangle$ at energy $E_{\rm g}$ to all final states $|f\rangle$ at energies $E_{\rm f}$. Due to the energy denominator states near resonance contribute most and in case of a strong exciton, which is well separated from other transitions, it is sufficient to consider only that excited state. The induced molecular dipole depends on the orientation of the transition dipole with respect to the exciting electric field $\vec{E}$. It is important to realize that only in isotropic systems, like solutions, the field is transverse to the wave vector of light ($\vec{E} \perp \vec{k}$) and for normal incidence given by the polarization of light. However, in solids the large density N of induced dipoles creates a significant electric field, arising from the

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doi:10.1016/j.orgel.2004.01.001

macroscopic polarization $\vec{P}$, which in anisotropic solids may point in a different direction than the polarization of the incident light. This modification of the field $\vec{E}$ acting on the transition dipoles is the reason for the unusual optical properties of π-conjugated molecules in crystalline samples [1].

The optical response of such solids involves not only the quantum mechanical calculations of the molecular transitions dipoles in Eq. (1) but must comply with Maxwell's equations since it involves oscillating fields. In the simple case of an exciton in an otherwise isotropic medium the exciton transition dipole defines an optical axis in a crystal resulting in an orientation dependent response to light as shown in Fig. 1. Coulomb's law, $(\nabla\vec{D} = 0)$, requires the electric displacement $\vec{D} = \varepsilon_0\varepsilon\vec{E}$ to be transverse to the wave vector $\vec{k}$ of light while the driving field $\vec{E}$, rotates, depending on the ratio of the components of the dielectric tensor $\varepsilon_{//}(\omega)/\varepsilon_{\perp}(\omega)$ parallel and perpendicular to optical axis. Since the dielectric constant $\varepsilon_{//}(\omega)$ diverges at the exciton resonance frequency the field along the transition dipole vanishes, shifting the optical resonance to higher energy closer to ω_L where ε becomes positive again. The range of this shift is determined by the contribution χ of the exciton to the static dielectric constant $\varepsilon(0)$ where $\varepsilon(\infty)$ accounts for screening by high-energy transitions.

$$\left(\frac{\omega_L}{\omega_T}\right)^2 = \frac{\varepsilon(0)}{\varepsilon(\infty)} = 1 + \frac{\chi}{\varepsilon(\infty)} \tag{2}$$

This shift of the optical resonance due to the laws of electrodynamics depends in this uniaxial case only on the angle ϑ between optical axis and wave vector. The spectra can be derived from Maxwell's equations by modelling the dielectric tensor with Lorentz oscillators representing the exciton and its vibronic progression. Absorption spectra of films are calculated as sum of the transmittance of its domains and electroabsorption spectra are obtained from the change of their transmittance induced by an applied voltage, creating an additional quasistatic electric field $\vec{F}$ parallel to the polarization of the incident light [2].

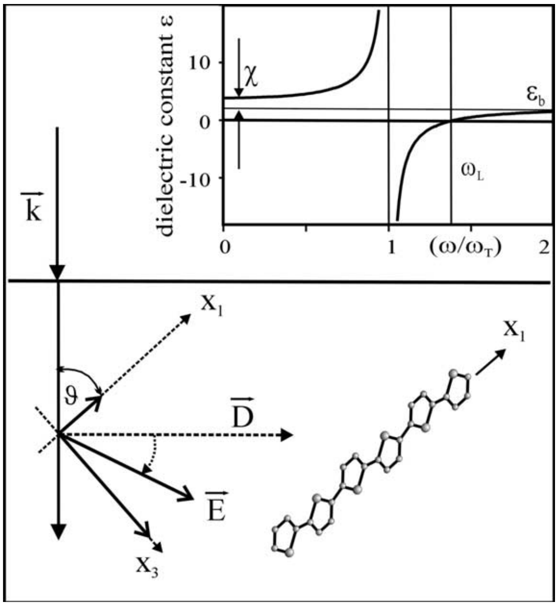

Fig. 1. Components of the electric displacement D and the electric field E of an electromagnetic wave parallel and perpendicular to the optical axis defined by the molecular transition dipole. The inset shows the dispersion of the dielectric constant due to a resonance at ω_T.

2. Experimental results

2.1. Spectra of sexithiophene

A single exciton, polarized along the molecular axis L, determines the absorption of T6 below 3.5 eV. Four molecules in the unit cell align almost perpendicular to the monoclinic axis b [3] which leads to two optically active Davydov components of very different strength [4]. Features of the very weak a_u exciton $(\vec{E}//b)$ are extremely narrow while those of the strong b_u exciton $(\vec{E} \perp b)$ which inherits the strength of all molecules in the unit cell are much broader due to their large dipolar interaction. Residual coupling to the forbidden polarization $\vec{E}//b$ avoids large polarization and enables the determination of the exciton transition energies from absorption spectra taken on the (1 0 0) face a 10 μm thin single crystal (Fig. 2). The absorption spectrum for strongly coupling light, $\vec{E}//c$, derived from the reflectivity, shows the absorption peak at 3.4 eV and the loss of vibronic fine structure. This large shift with respect to the

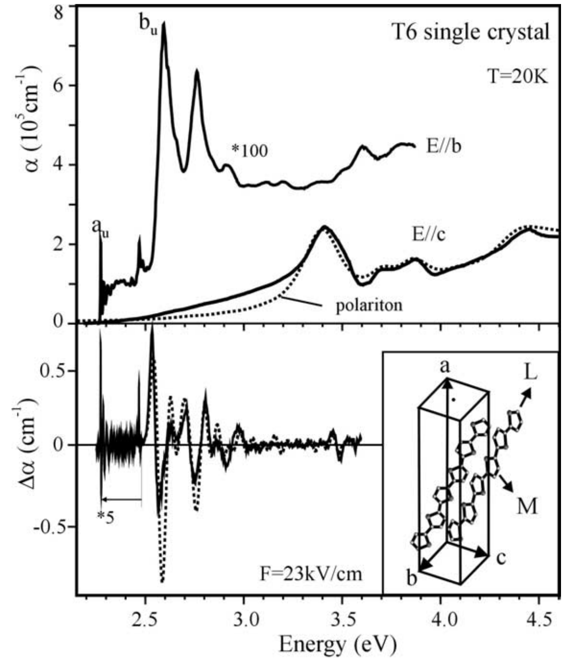

Fig. 2. Absorption α and electroabsorption spectra $\Delta\alpha$ of a sexithiophene single crystal for different polarization of light, E, and applied field F. The inset shows half of the unit cell.

transition energy 2.6 eV of the b_u exciton is due to the influence of the polarization of molecules strongly inclined with respect to the crystal face ($\vartheta(\vec{k},\vec{\mu}) = 25^\circ$) [5]. In electroabsorption spectra both Davydov components respond differently to an applied electric field $\vec{F}//c$. Features below 2.5 eV agree with the derivative of the absorption spectrum and arise from the Stark shift of the weak a_u exciton due to the molecular polarizability (915 Å^3) along the long axis. The Stark effect is far too small to explain the much larger signal at higher energy which has second derivative lineshape and arises from coupling the transition dipole $\vec{\mu}$ to the external electric field since the transition energy of the exciton to oscillates around its centre position with an amplitude $\Delta E = \vec{\mu}\cdot\vec{F}$. We expand the change of absorption to second order since the term linear in ΔE vanishes by integrating over the lifetime τ of the coherent polarization. The second moment corresponds to field-induced broadening and is proportional to the second derivative of the absorption spectrum [6].

$$\langle \Delta E^2 \rangle = \frac{1}{\tau}\int_0^\tau \mathrm{d}t(\vec{\mu}\cdot\vec{F})^2\cos^2\omega t = |\vec{\mu}_{\mathrm{eff}}\cdot\vec{F}|^2 \qquad (3)$$

Matching the signal requires a dipole moment $\mu_{\mathrm{eff}} = 4.3$ eÅ. This is close to the value 4.8 eÅ anticipated from dipole moment 2.4 eÅ of molecular exciton which is derived by applying the sum rule to a solution spectrum. The different spectra of the strong Davydov component b_u observed for weakly and strongly coupling light are due to the large polarization in the latter case, a unique feature of strong excitons. The large transition dipole of the b_u exciton is also responsible for the different lineshape of the electroabsorption spectrum, revealing that dipolar coupling prevails by far over exchange coupling which would affect both excitons equally since they derive from the same molecular state.

Since the response of the strong exciton to light and to an applied voltage depends on the orientation of its transition dipole this dependence must be included to analyse the spectra of nanocrystalline films which are treated as an ensemble of domains with some distribution of their optical axis around some preferential orientation ϑ_0. Details can be found in [7]. The spectra are not sensitive to the distribution of domain orientation since weakly absorbing domains (small ϑ) dominate the transmission and yield always a broad nearly featureless absorption spectrum of the strong exciton with a peak above 3 eV (Fig. 3). The calculation based on single crystal data does not reproduce the large and isotropic absorption constant of the film which exceeds the calculated absorption by almost an order of magnitude. The excess absorption of this 60 nm thin film is attributed to severe scattering since the lateral size of domains (100 nm), though sufficiently large for dipolar coupling of excitons, is too small to support coherent propagation of an electromagnetic wave of comparable wavelength. The wave vector has the same orientation in all domains but the energy propagation follows the Poynting vector $\vec{S} = \vec{E}\times\vec{H}$ which in neighbouring domains points into different directions, resulting in a short lifetime of the coherent polarization due to scattering. Electroabsorption spectra are less affected since they derive from the field-induced change of coherently transmitted

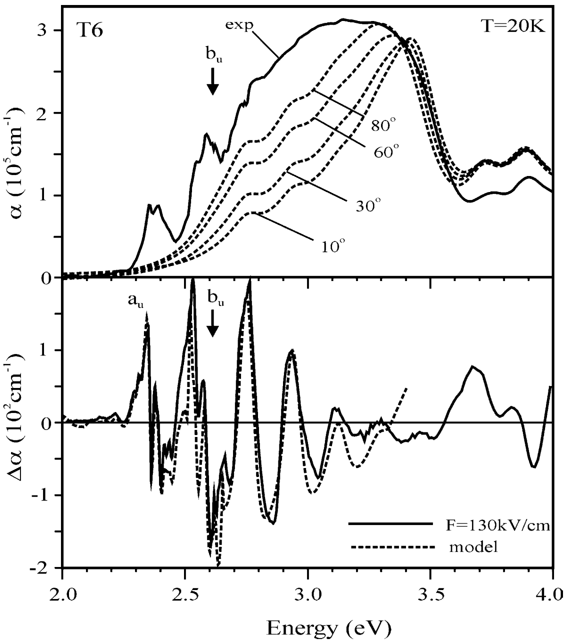

Fig. 3. Absorption α and electroabsorption spectra $\Delta\alpha$ of a 60 nm thick T6 film. Dashed lines show absorption spectra calculated for different preferential orientation of domains and a calculated $\Delta\alpha$ spectrum for a distribution around $\vartheta = 30^\circ$.

light. Each domain responds by the quadratic Stark shift of the weak and field broadening of the strong exciton. The calculated spectra are based on a preferential orientation $\vartheta_0 = 30^\circ$, similar to the situation in the single crystal. The position of the spectral features is insensitive to a variation of ϑ_0 which mainly alters the size of the various peaks. Matching calculated and experimental spectra yields a molecular polarizability of 415 Å^3 and a transition dipole moment near 5 eÅ. In view of the unknown distribution of dipole moments relevant for the Stark shift and the field broadening we consider that agreement as satisfactory since it is obtained without a free parameter.

2.2. Spectra of quaterthiophene films

T4 films grown on potassium phthalate acid (KAP) have the unit cell of α-T4 which contains four molecules [8]. The T4 molecules orient their axis along the c-axis of KAP resulting in strongly anisotropic spectra [9]. Depending on what crystal face lies parallel to the substrate two orientations are observed. In most domains the molecular axis is steeply inclined with respect to the substrate ($\vartheta = 29^\circ$) while in much fewer domains molecules have a smaller inclination angle ($\vartheta = 61^\circ$) [10]. The sample thus is better defined than the T6 film but a 25 nm thin film yields a similar featureless absorption spectrum (Fig. 4). The absorption peak with a long absorption tails at low energy is blue shifted compared to the spectrum of molecules in solution. From the solution spectrum we derive the oscillator strength $f = 3.65$ which is distributed to a vibronic progression to match the richly structured electroabsorption spectrum. The arrows indicate the position of the excitons, listed in Table 1 together with the linewidth γ and their contribution χ to the dielectric constant. Directional dispersion shifts the absorption peak from the exciton energy at 3.07–3.67 eV. Assuming for all domains the same orientation $\vartheta = 29^\circ$, which corresponds to a single crystal, produces the correct height but a too narrow absorption peak.

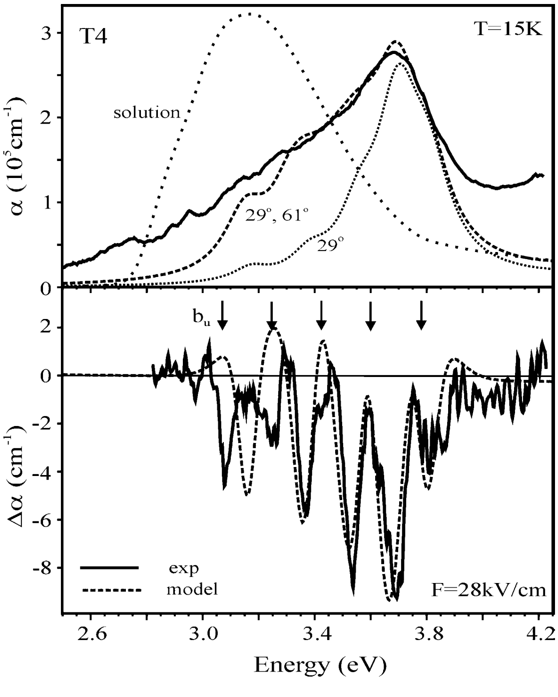

Fig. 4. Absorption and electroabsorption spectra of a 25 nm thick T4 film oriented on KAP. Dashed and dotted lines show calculated spectra. Arrows indicate exciton transition energies.

Table 1
Lorentz-parameter of the vibronic progression of the main exciton in T4 and the *b*-polarized exciton in PTCDA

	Transition	0–0	0–1	0–2	0–3	0–4	0–5
T4 $\varepsilon(\infty) = 2.6$	$\hbar\omega_T$ (eV)	3.070	3.247	3.424	3.600	3.780	
	χ	0.78	0.32	0.09	0.03	0.01	
	$\hbar\gamma$ (meV)	160	160	170	180	180	
PTCDA $\varepsilon(\infty) = 3.2$	$\hbar\omega_T$ (eV)	2.185	2.375	2.555	2.735	2.915	3.090
	χ	0.58	0.25	0.14	0.05	0.02	0.008
	$\hbar\gamma$ (meV)	110	125	150	160	170	170

Including 20% of domains with orientation $\vartheta = 61^\circ$ reproduces the observed absorption spectrum much better Fig. 5.

The electroabsorption spectrum is modelled by field broadening the strong transition dipole and by accounting for the effects of the coherent polarization. The calculation assumed again domains with narrow distributions around $\vartheta = 29^\circ$ and 61° as in the absorption spectrum and reproduces all the peaks of the $\Delta\alpha$ spectrum above 3.3 eV. It should be noted that all features occur close to exciton transition energies but their size is very different from the strength of nearby excitons (Table 1). The signal size corresponds to field broadening by 1.1 meV and yields a transition dipole $\mu = 3.9$ eÅ in excellent agreement with the value expected from four molecules in the unit cell with molecular dipole moments $\mu = 2.0$ eÅ, derived again from the solution spectrum. The calculation shows an additional peak near 3.2 eV, not present in the experimental spectrum, which instead shows two significant features at 3.08 and 3.255 eV and a dip near 3.43 eV matching a vibronic progression of 175 meV. The Stark shift of the weak Davydov component is no likely explanation of these features since no trace of this component is observed in the absorption spectrum. We tentatively assign these features to the response of flat lying molecules, possibly one or two layers closest to the substrate. The peak at 3.2 eV found in the calculated spectrum could compensate the positive peak expected from the leading structure at 3.08 eV.

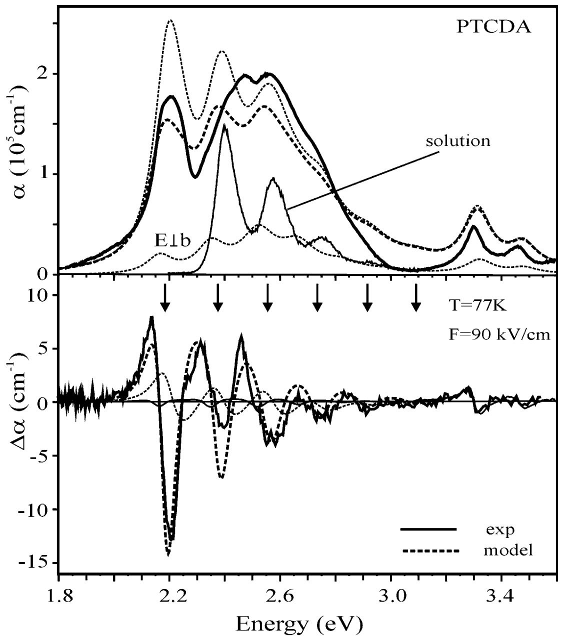

Fig. 5. Absorption α and electroabsorption spectra of a 50 nm thick PTCDA film. Dashed and dotted absorption spectra are calculated as sum of transmittance or of the absorption, of two excitons, respectively. The arrows indicate a vibronic progression for $E//b$.

2.3. PTCDA

The unit cell of PTCDA contains two molecules which are related to each other by a rotation around the monoclinic axis *b* [11]. The Davydov components are polarized parallel and perpendicular to *b* and of comparable strength. We distribute the molecular oscillator strength $f = 3.1$ evenly between both components and match again the transition energies to the electroabsorption spectrum. The parameters of the *b*-polarized exciton which dominates the spectra are listed in Table 1.

The isotropic absorption spectrum of the 50 nm thick film resembles that reported for single crystals and $\vec{E}//b$ [12]. The exciton $\vec{E}//[2\,0\,\bar{1}]$ shows no clear signal which makes modelling uncertain. We assumed the same progression as for the b-polarized exciton but shifted by 100 meV to lower energy. The growth direction is not known but growth along [0 0 1] is commonly found [11] and yields $\vartheta = 30^\circ$ for that exciton ($E \perp b$). Such orientation could explain its small contribution to the electroabsorption spectrum. The $\Delta\alpha$ spectrum resolves the vibronic progression of the double bond stretch mode and a good approximation is obtained if field broadening of the excitons is supplemented by a small contribution from the Stark effect. The Stark shift corresponds to a polarizability of 140 Å^3 while field broadening by 0.4 meV yields only half the value of the dipole moment expected from the molecular transition dipole ($\mu = 2$ eÅ). The signals is probably reduced by the large transmittance of the second Davydov component which may also be responsible for the deviation of modelled and experimental spectra near 2.4 eV in the range of the first vibronic satellite of the b-polarized exciton. We show two calculated absorption spectra. Spectrum A is the sum of the absorption of both exciton series while B is derived again by summing up the transmittance of domains. The latter is more appropriate for a transmission experiment and suppresses the strong absorption peaks.

3. Conclusion

The striking difference of the optical properties of nanocrystalline films and single crystals of π-conjugated molecules is a consequence of electrodynamics. The strong transitions dipoles of the fundamental excitons are coupled into a coherent macroscopic polarization which, due to the anisotropic crystal structure, alters the orientation of the electric field that drives the exciton dipoles. Absorption peaks correspond to maxima of Im(ε), the imaginary part of the dielectric constant, and deviate in their spectral position and strength from the exciton transition energies. The deviation of optical and exciton resonance depends on the respective orientation of exciton dipole and wave vector of light and increases as the molecules are tilted out of the plane of the substrate. We emphasize that these effects require strong excitons which are spectrally isolated, a situation encountered in many π-conjugated molecules. Absorption spectra of films consisting of small domains with different orientation loose despite their local order most of the spectral details found in single crystals but electroabsorption spectra resulting from field-induced broadening of the strong excitons still resolve their vibronic progression although the size of these features does not reflect the strength of vibronic excitons. All spectral peculiarities are consistent with the electrodynamics of a set of oriented strong transition dipoles. The dipole moments are those found in solution spectra of the molecules, indicating that molecular states are little affected by intermolecular interaction in a solid. Dipolar coupling dominates while exchange coupling, altering the molecular states and allowing for charge transfer transitions, is negligible.

Acknowledgements

We thank Dr. A. Sassella, Milano for providing the T4 samples and information on structural details, Dr. C. Taliani, Bologna for the T6 films and Dr. H. Port and M. Leonhard, Stuttgart for the PTCDA films.

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