Ultrafast Relaxation in Quasi-One-Dimensional Organic Molecular Crystals

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We present a comprehensive study of ultrafast relaxation properties of optical excitations in thin films of quasi-1D stacked organic materials PTCDA (3,4,9,10-perylenetetracarboxylic dianhydride) and MePTCDI (N, N'-dimethylperylene-3,4,9,10-dicarboximide) over five decades of time. Pump-probe experiments reveal excitonic intraband relaxation time constants of 65 fs for MePTCDI and 100 fs for PTCDA. The initial time-resolved luminescence anisotropy is consistent with the exciton model of Davydov-split states. The subsequent decay of the anisotropy can be explained with a thermally activated exciton hopping process. A full understanding of the pump-probe experiments calls for an explanation beyond the models presently available.

Organic semiconductors have recently attracted considerable interest due to promising device applications like organic solar cells [1] or light emitting diodes (OLED) [2]. Despite first commercial applications, the understanding of the electronic properties and relaxation processes in organic semiconductors is rather limited, in particular in comparison to their inorganic counterparts. Much interest has recently focused on materials forming quasi-1D molecular stacks, since such materials would allow thin films with rather high mobility due to the close coupling of the molecules in the stack. A number of recent studies have addressed as model materials perylene derivatives [3], investigating, e.g., the influence of the intermolecular interaction on the structural, optical, and electronic properties [4]. Exciton models [5–9] have been developed to describe linear absorption spectra and related properties of electronic excitations. However, in contrast to other vanguard material classes like *J*-aggregates in solution [10], polymers [11], or other organic molecular crystals such as oligothiophenes [12], where ultrafast relaxation processes have been extensively studied, information about stacked quasi-1D molecular crystals is scarce.

Here, we present the first study of the ultrafast relaxation processes of optical excitations in this material class, addressing the two most prominent representatives PTCDA (3,4,9,10-perylenetetracarboxylic dianhydride) and MePTCDI (N, N'-dimethylperylene-3,4,9,10-dicarboximide). Excitonic relaxation in the lowest excited state can be explained in the framework of band structure models [5–9], with the common observation of negative dispersion, which implies that luminescence occurs only as indirect emission from the border of the Brillouin zone (BZ). In our experiments, we have investigated the excitonic intraband relaxation in *k*-space on individual stacks of molecules and the diffusion of excitons through the sample, using ultrafast pump-probe techniques for photoinduced absorption and polarization-dependent time-resolved luminescence.

As samples, we used polycrystalline thin films of $\sim$25 nm thickness evaporated on sapphire substrates in high vacuum (10^{-6} mbar). The size of the crystallites was estimated by atomic force microscopy (AFM) to be on the order of 100 nm. In the time-resolved luminescence measurements, excitation was at 2.82 eV into the higher vibronic states of the $S_0 - S_1$ transition with the second harmonic of a mode-locked Ti:sapphire oscillator, creating excitation densities of $\sim 10^{17}$ cm^{-3}. Luminescence was recorded with a streak camera for both parallel and perpendicular components with respect to the linearly polarized excitation. The overall temporal resolution was 5 ps. Low temperature data were taken in helium vapor continuous flow in a bath cryostat. For the pump-probe measurements, a Ti:sapphire regenerative amplifier with a repetition rate of 1 kHz was used to pump a home-built noncollinear noncollinear parametric amplifier (OPA) [13] with subsequent prism compressor. The linearly polarized output pulses were centered around 2.16 eV for MePTCDI and 2.22 eV for PTCDA, to excite at the lowest vibronic state $|a\rangle$ of the $S_0 - S_1$ transition, with exciton densities of 3×10^{19} cm^{-3}. The probe pulses originated from a femtosecond continuum generated in a 2 mm sapphire plate. Their spectral amplitude and phase were controlled by an acousto-optical programmable dispersive filter [14]. A broadband zero order half wave plate tilted the polarization by 45° with respect to the pump beam, allowing us to simultaneously probe parallel and perpendicular polarizations, which were separated by a polarizing beam splitter after passing the sample. Time resolution was 30 fs, measured by cross correlation. The pump-probe data were taken at room temperature.

We first discuss the initial ultrafast excitonic intraband relaxation in the Brillouin zone (BZ) on individual stacks of molecules as shown in Figs. 1(b) and 1(d) for mutually parallel pump and probe polarizations. Negative $\Delta T/T$ indicates that the signals result predominantly from photoinduced absorption (PA). This is reasonable because the Gaussian probe spectra [shaded area in Figs. 1(a) and 1(c)] were centered around 1.94 eV with $\sim$100 meV FWHM, below the onset of linear absorption. For both systems, $|\Delta T/T|$ initially rises with time resolution, which is indi-
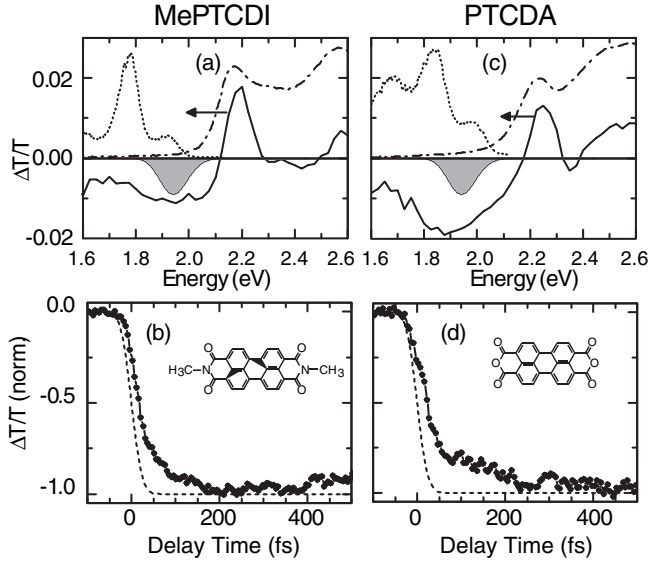
FIG. 1.   Top: linear absorption (dash-dotted line) and transient transmittance at 1 ps delay (thick solid line) of MePTCDI (a) and PTCDA (c) at room temperature. Dotted curves: transient luminescence (0–50 ps) at 10 K. Shaded area: probe beam spectrum. Bottom: fs-pump-probe differential transmittance for parallel polarization for MePTCDI (b) and PTCDA (d). Dashed lines: integrated cross-correlation curves.

cated by the integrated cross correlation in Fig. 1. However, a subsequent delayed rise is clearly visible in both cases. If we describe $|\Delta T/T|$ by a sum of two exponentials, the convolution $|\Delta T/T| \propto [1 - \sum_i A_i \exp(-t/\tau_i)] \otimes XC(t)$ with the Gaussian cross-correlation envelope function $XC(t)$ allows us to fit relaxation curves to the pump-probe signal. Best fit results yield decay time constants $\tau_{M,1} = 30$ fs and $\tau_{M,2} = 65$ fs for MePTCDI and $\tau_{P,1} = 30$ fs and $\tau_{P,2} = 100$ fs for PTCDA, with the A_i being 0.5 in both cases. Because of the observation of two time constants, we assume to have two probed states involved. The smaller time constant $\tau_{i,1}$ is on the order of the time resolution and most likely describes the initial excitation into the absorbing states $|a_i\rangle$. The larger time constant $\tau_{i,2}$ definitely describes a time-resolved relaxation process, which we attribute to the depopulation of the initially excited state towards the border of the BZ [15]. After a few hundred femtoseconds, $|\Delta T/T|$ starts to decrease as a result of much slower exciton recombination. The dominating channel at this excitation density is exciton-exciton annihilation, which results in decay times much faster than in the luminescence measurements (see below).

We now turn towards the interaction between inequivalent stacks of molecules, using time-resolved luminescence anisotropy as a tool for investigation of the population dynamics in the excited state. Since the unit cell of both MePTCDI and PTCDA contains two molecules [Figs. 2(a) and 2(b)], quasi-1D states on the two stacks can coherently couple [16]. The resulting Davydov splitting ΔE was

verified in MePTCDI by polarized absorption ($\Delta E = 11$ meV) [17], and in α-PTCDA by ellipsometry ($\Delta E = 37$ meV) [18] at the Gamma point. At the border of the BZ, Davydov splitting has not been directly observed, but calculations for PTCDA indicate a strongly reduced splitting of $\Delta E \approx 1$ meV [8]. Accordingly, transition dipole moments to Davydov-split band states can be regarded as coherent superpositions of molecular transition dipole moments. In absorption (crystal with N molecules), this yields $\mathbf{P}_{\pm} = \sqrt{N} s_a (\mathbf{P}_A \pm \mathbf{P}_B)/\sqrt{2}$ [8], where $\mathbf{P}_A$ and $\mathbf{P}_B$ are the major electronic transition dipole moments along the molecular axes of molecules A and B (Fig. 2), and s_a is a vibronic overlap factor. The ratio $\xi = |\mathbf{P}_-|/|\mathbf{P}_+|$ is determined by the mutual orientation of the molecules in the unit cell. Although the shape of absorption spectra is discussed by a superposition of Frenkel and charge-transfer states (CT) [5–7,9], the transition dipole moments $\mathbf{P}_{\pm}$ are dominated by the Frenkel contribution.

In emission, the phonon-assisted indirect emission to higher vibronic states $|\chi_{\pm}\rangle$ of the ground state allows four transitions with transition dipole moments $\mu_{++} = \mu_{--} = s_e(\mathbf{P}_A + \mathbf{P}_B)$ and $\mu_{+-} = \mu_{-+} = s_e(\mathbf{P}_A - \mathbf{P}_B)$ [8], where s_e is the vibronic overlap factor for emission. The population dynamics in the excited Davydov-split states can be extracted from the luminescence anisotropy [19]

$$r(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)}, \quad (1)$$

where $I_{\parallel}$ and $I_{\perp}$ are luminescence signals parallel and perpendicular to the linearly polarized excitation, respectively.
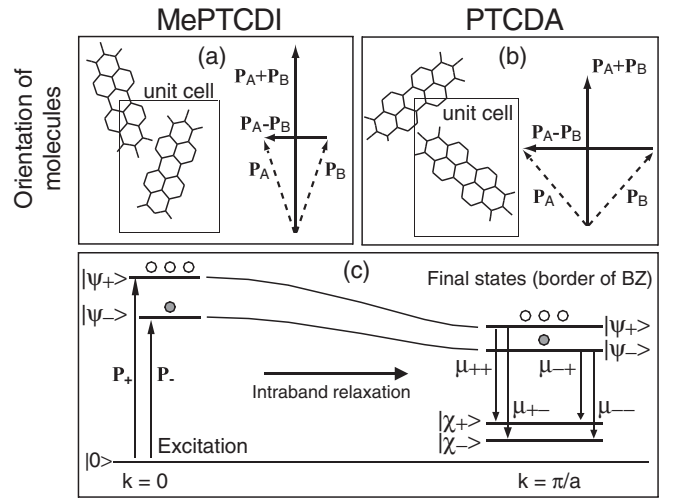

FIG. 2.   Top: mutual orientation of two molecules in the unit cells of MePTCDI (a) [3] and PTCDA (b) [24]. Stacking direction is roughly perpendicular to the drawing pane. Superposition of the major molecular transition dipole moments $\mathbf{P}_A$ and $\mathbf{P}_B$. Bottom: overview of excitation and population, intraband relaxation, and the transitions allowed in indirect emission. In the example (c) $\xi^2 = 1/3$.

The Davydov components $|\psi_\pm\rangle$ are initially populated according to their ratio ξ and their orientation with respect to polarized excitation light: $n_\pm(\theta) \propto (\mathbf{E}_{Pu}\mathbf{P}_\pm)^2$, where θ is the angle between the pump field $\mathbf{E}_{Pu}$ and $\mathbf{P}_+$. In Fig. 2(c), we illustrate $\xi^2 = 1/3$. The luminescence contributions are:

$$I_\parallel(\theta) \propto \sum_{i,j=+,-} n_i(\theta)(\mathbf{E}_{Pr\parallel}\mu_{ij,\parallel})^2 \qquad (2)$$

$$I_\perp(\theta) \propto \sum_{i,j=+,-} n_i(\theta)(\mathbf{E}_{Pr,\perp}\mu_{ij,\perp})^2 \qquad (3)$$

for parallel and perpendicular probe direction $\mathbf{E}_{Pr}$, respectively. We assume that the molecules and thus the plane spanned by the Davydov components lie parallel to the substrate [cf. [17]]. Then, all vectors $\mathbf{E}_{Pu}$, $\mathbf{E}_{Pr,\parallel}$, $\mathbf{E}_{Pr,\perp}$ are parallel to this plane. Averaging over θ gives the luminescence anisotropy

$$r = \frac{2 - 4\xi^2 + 2\xi^4}{5 + 14\xi^2 + 5\xi^4}. \qquad (4)$$

Even if the populations of the Davydov components would change by equilibration ($\tilde{n}_+ = \tilde{n}_- = (n_+ + n_-)/2$) or down-relaxation ($\tilde{n}_+ = 0, \tilde{n}_- = (n_+ + n_-)$), the anisotropy $\tilde{r}$ takes the same value as in Eq. (4).

Figure 3 shows the luminescence decay curves of MePTCDI and PTCDA for both polarizations at room and at low temperature, with the luminescence being spectrally integrated over the major emission peaks (MePTCDI ~ 1.78 eV, PTCDA ~ 1.83 eV). The resolution limited rise time of ≤ 5 ps is in accordance with the intraband relaxation time τ_2. For MePTCDI at room temperature [Fig. 3(a)], the initial anisotropy amounts to a value of $r \approx 0.2$. From the geometrical arrangement [7], one gets $\xi = 0.33$ and $r = 0.24$. An upper limit of $\xi = 0.5$ follows from the experimental polarization ratio [17] and gives $r = 0.13$. These estimates are in good agreement with the measured values.

In PTCDA, $\mathbf{P}_+$ and $\mathbf{P}_-$ are nearly equal in magnitude ($\xi \approx 0.9$), and one would expect a nearly vanishing anisotropy from Eq. (4). This behavior again agrees with the PTCDA measurement in Fig. 3(c), where r equals zero.

We now show that exciton diffusion to adjacent, differently oriented, crystallites is the most likely explanation for the further decrease of the anisotropy in Fig. 3(a). In a simple 1D diffusion model [20], the mean square displacement of an exciton created at $x = 0$ can be written as $\overline{x^2(t)} = \Lambda^2 t/\tau$, where τ is the exciton lifetime and Λ is the diffusion length, which is related to the macroscopic diffusion constant D via $\Lambda = \sqrt{D\tau}$. Recent measurements have shown that for PTCDA $\Lambda \approx 20$ nm at room temperature [21], and a similar value is expected for MePTCDI. Together with an approximate lifetime of ~ 150 ps for MePTCDI [22], we obtain $\sqrt{\overline{x^2(t)}} \approx 36$ nm after $t = 500$ ps. For circular crystallites of 100 nm diameter, approximately 50% of the excitons have left the parent
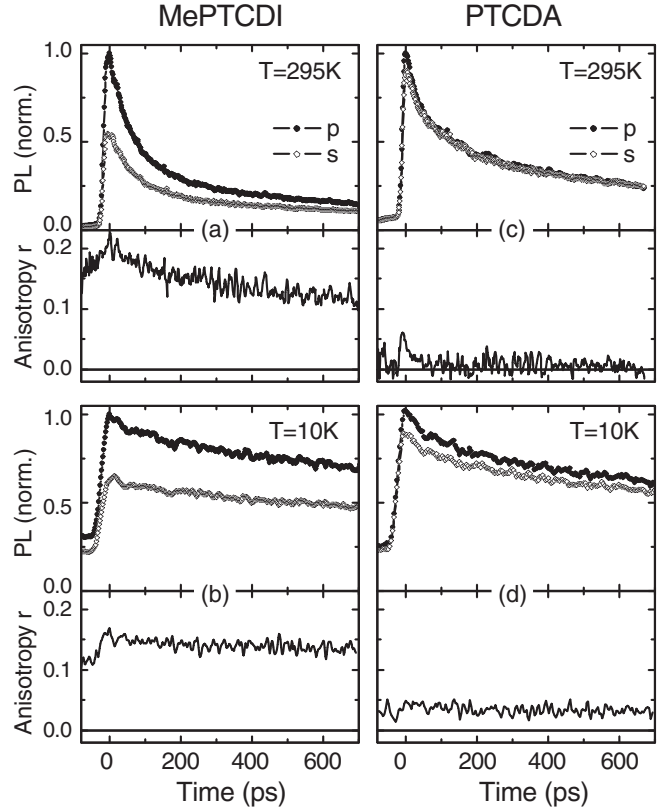

FIG. 3. Polarization-dependent time-resolved photoluminescence and the corresponding luminescence anisotropies computed as defined by Eq. (1) for MePTCDI and PTCDA. p (s) denotes parallel (perpendicular) polarization. (a) and (c) are at 295 K; (b) and (d) are at 10 K.

crystallite after 500 ps by diffusion and have transferred their energy to unit cells of adjacent crystallites with different orientation of the transition dipole moments, resulting in a loss of the polarization memory. For the initial value of $r \approx 0.2$ in Fig. 3(b), this simple model fits reasonably well with the measured value of $r \approx 0.12$.

The time-resolved luminescence at 10 K is shown in the third row of Fig. 3. A significant decay of r with time can neither be observed for MePTCDI nor for PTCDA. The absence of such a decay in Figs. 3(b) and 3(d) indicates that the diffusion process is strongly inhibited, making an energy transfer between crystallites impossible. Our findings agree with recent results [21] showing that the diffusion is described by a thermally activated hopping process. The activation energy of approximately 13 meV is much larger than the thermal energy at our measurement temperature of 10 K. We conclude that thermally activated exciton hopping is the major driving force for the diffusion at higher temperature.

For comparison, we have also determined the polarization anisotropies in the pump-probe experiments. The parallel and perpendicular differential transmittance data are shown in Figs. 4(a) and 4(c) for the two materials. Figures 4(b) and 4(d) illustrate the corresponding aniso-
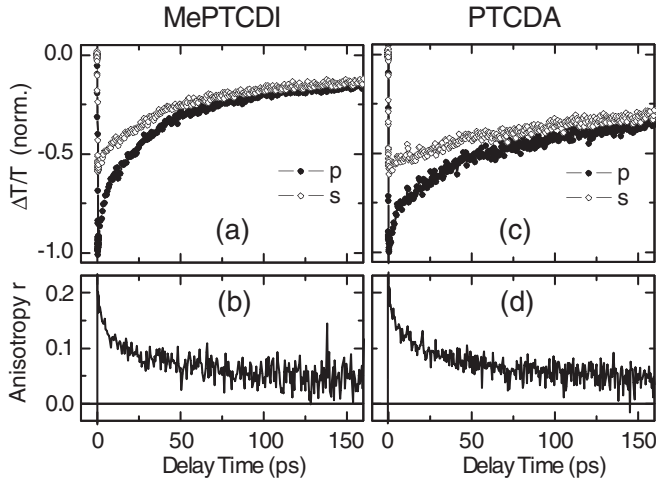
FIG. 4. Polarization-dependent ps-pump-probe measurements and the resulting anisotropies for MePTCDI [(a),(b)] and PTCDA [(c),(d)]. p and s denote parallel and perpendicular polarization of pump and probe beam, respectively.

tropies, which are astonishingly very similar for the two samples, contrary to the luminescence anisotropies. In particular, $r(0) \approx 0.2$ in PTCDA.

We thoroughly tried to exclude experimental errors: other samples of PTCDA and MePTCDI thin films reproducably show the same behavior, but in completely different systems other anisotropies have indeed been observed. Furthermore, the time dependence of the pump-probe anisotropy in Fig. 4 proves that the effect cannot be explained by a mere calibration error of the two channels.

The probe pulse excites into higher states $|\varphi_\pm\rangle$, which are Davydov split, corresponding to the $|\chi_\pm\rangle$ in luminescence. Again, the transition dipole moments μ'_{ij} [where $i, j = (+, -)$] for the $S_1 - S_x$ transition are to be considered analogously to Eqs. (2) and (3). Note that we do not make an *a priori* statement about their orientation. If $\mu' \parallel \mu$, we immediately get the same result as in Eq. (4), independent of whether the populations are equilibrated. Thus, $r = \tilde{r} \approx 0$ is expected for PTCDA, where $\xi \approx 0.9$. It is straightforward to consider transition dipoles $\mu' \perp \mu$. Again, one obtains $r = \tilde{r} = 0$ for $\xi = 1$. Hence, regardless of the mutual orientation of μ and μ', in PTCDA one expects $r \approx 0$ for any two states $|\psi_\pm\rangle$, $|\varphi_\pm\rangle$ that show Davydov splitting.

The experimental fact that $r(0) \approx 0.2$ in PTCDA implies that this contradiction may be resolved by additional states that do not form Davydov components. Treatment of the problem in an oriented gas model of noninteracting stacks would allow us to explain values of $r = 0.4$ (probed dipole $\parallel$ pumped dipole) or $r = -2/7$ (probed dipole $\perp$ pumped dipole) or in between (mixture of transitions). However, the oriented gas model clearly contradicts the observed luminescence anisotropy ($r \approx 0$ for PTCDA). Since even

the assumption of completely different states in luminescence and pump probe would not lead to a consistent interpretation of all experimental facts, a full understanding of the pump-probe anisotropy calls for novel models.

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