Ultrafast Excited State Dynamics in Diindenoperylene Films
Marc Hänsel,† Valentina Belova,†,‡,§ Alexander Hinderhofer,† Frank Schreiber,‡ Katharina Broch,† and Petra Tegeder*,†,‡

ABSTRACT: Diindenoperylene (DIP) is an interesting organic molecular semiconductor as a component in organic solar cells. Here, we studied the ultrafast excited state dynamics of DIP after optical excitation in thin films on sapphire and SiO2 substrates, respectively, using femtosecond (fs) time-resolved second harmonic generation (TR-SHG). Sapphire, an inert and noninteracting substrate, is known to deliver no noteworthy contribution to the SHG-signal; thus, the pure response of DIP to the electronic excitation can be resolved in contrast to the measurements on SiO2. For DIP/sapphire, the initial optical excitation leads to the generation of delocalized excitons, which localize within approximately 100 fs in order to generate singlet molecular excitons (Frenkel excitons) or excitons localized on dimers. These excitons have a lifetime of 470 ± 100 fs. In a subsequent step, they form excimer states, which decay on a time scale of 680 ± 110 ps. For DIP/SiO2, the molecular excitons decay on a faster time scale of 210 ± 95 fs and populate either substrate-mediated trap states or excimer states. The present study provides important insights in the excited states dynamics of DIP on the so far unresolved ultrashort time scale, essential for understanding the photophysics of DIP.

INTRODUCTION
Understanding the dynamics of electronically excited states after optical excitation in organic semiconductors is crucial for the optimization of organic molecule-based optoelectronic devices, especially for organic photovoltaics (OPV).5,6 In organic solar cells, separation of optically excited electron–hole pairs and long-range charge transport play an important role for the efficiency.7 Thereby, competing relaxation pathways lead to a decrease of the efficiency. For instance, ultrafast energy transfer to lower-lying self-trapped states has been reported to occur on the same time-scale as charge transfer.3,4 In donor/acceptor (D/A) systems, exciton trapping competes with charge separation and charge transport and may therefore reduce the efficiency of organic solar cells.1

Diindenoperylene (DIP, see Figure 1a), is a well-studied organic semiconductor with many promising properties.5–8 It forms highly ordered films on many different substrates,9–12 and exhibits a high exciton diffusion length.13,14 It has been successfully used in bilayer OPVs5,6,16,17 and is a promising material for transistor applications.18,19 Recently, time-resolved photoluminescence and transient absorption experiments have been performed to gain insight into the fundamental decay dynamics of excited states in DIP in solution and solid films on the picosecond (ps) to nanosecond time scale.5 In DIP films, no indication for neither long-lived singlet exciton states nor singlet fission has been found, contrary to crystals with similar packing motifs such as crystaline anthracene,20,21 perylene,22,23 tetracene,24 and pentacene.25–27 However, the dynamics on the ultrafast femtosecond time scale is so far unresolved.

In this contribution, we study the dynamics of photoexcited electronic states in crystalline DIP films with time-resolved second harmonic generation (TR-SHG) on the femtosecond time scale. TR-SHG has been proven to be a powerful method to measure the dynamics of electronically excited states in organic semiconductors.28–31 SHG is a second-order nonlinear optical process, i.e., the SHG signal is generated by the second-order nonlinear susceptibility of the sample, which is sensitive to electronic excitations.32–34 For symmetry reasons, there is no bulk contribution to the SHG signal from centrosymmetric materials.35 Thus, SHG is intrinsically surface sensitive for centrosymmetric media. We investigated the ultrafast dynamics directly after optical excitation in DIP films adsorbed on sapphire and SiO2 (Si with a thin native oxide layer), electronically noninteracting and weakly interacting substrates, respectively. For DIP/sapphire, we found a rapid localization of the initially delocalized excitons on a time scale of around 100 fs, depending on the excitation energy. The relaxation results in the formation of molecular (Frenkel) excitons or excitons localized on dimers, which decay within 470 ± 100 fs generating excimer-like states. For the DIP/SiO2, the molecular excitons decay on a faster time scale of 210 ± 95 fs, leading to the population of trap states which originate from the SiO2 substrate or excimer states.

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EXPERIMENTAL SECTION

Thin films of DIP were prepared by organic molecular beam deposition in an ultrahigh vacuum (UHV) chamber on substrates of sapphire (CrysTec, single crystal, (0001) surface, both sides polished) and silicon covered with a native oxide layer of approximately 2 nm (Si-Mat, doped with boron, resistance: 17–23 Ω cm, cut along (100) crystal plane), respectively. The substrates were cleaned in an ultrasonic bath using acetone and isopropanol and heated to 650 K in the UHV chamber. During DIP deposition, the background pressure was 1 × 10⁻⁷ mbar, and the substrates were kept at a temperature of 297 K. The deposition rates of 0.5 and 0.3 nm/min during growth on SiO₂ and sapphire, respectively, were controlled by a water-cooled quartz microbalance with at least 4 measurements on different sample positions with 10 repetitions at each spot to improve the signal-to-noise ratio. All experiments were performed under inert gas (N₂) at room temperature using acetone and isopropanol and heated to 650 K in the bath using acetone and isopropanol and heated to 650 K in the UHV chamber.

The TR-SHG experiments were carried out using a Ti:sapphire laser system. A femtosecond regenerative amplifier (RegA, 300 kHz, λ = 800 nm) was seeded by a mode-locked Ti:sapphire oscillator. Both systems were pumped by a frequency doubled Nd:YAG cw-laser. The RegA output was split into two beam paths. One beam was used to pump a tunable optical parametric amplifier. The output was frequency doubled by phase-matched bulk second harmonic generation, creating visible light of wavelengths between 650 and 550 nm with bandwidths of approximately 25 nm. This light was used as the pump pulse to optically excite the sample. The other beam (800 nm) was used as probe pulse. A temporal delay was introduced between the two beams with a piezo-driven automatic stage. Both beams were focused onto the sample with an incident angle of 45° with respect to the surface normal. The SHG signal (400 nm) was focused into a monochromator and detected by a photomultiplier. The analog signal was converted by a counting unit and acquired using a PCI counting device. The polarization of the pump beam was fixed to p-polarization, and the polarization of the probe beam was controlled by a half-wave plate. Except for the polarization-resolved measurements, p-polarization was used. Using p-polarization leads to a perpendicular and a parallel component of the light with respect to the sample plane, whereas s-polarized light only has a parallel component. The overlap (spatial and temporal) of pump and probe beam was optimized by maximizing the sum frequency signal from the sample surface. The cross-correlation determined by sum frequency generation (SFG) was 78 fs, corresponding to a laser pulse of 55 fs. The probe intensity was 360 μJ/cm² in all experiments, and the pump intensity was 135 μJ/cm² except for the power series. Every TR-SHG trace shown here is the average of at least 4 measurements on different sample positions with 10 repetitions at each spot to improve the signal-to-noise ratio. All experiments were performed under inert gas (N₂) at room temperature. The DIP films are polycrystalline; thus, we have grain boundaries. Accordingly, the measured SHG signal arises also from interfaces within the crystal.

To model the DIP on sapphire SHG data, a three-step first-order kinetic model (states A–C) has been used, which has been convoluted with a Gaussian function to describe the intensity distribution of the excitation laser pulse:

\[
f(t) = A e^{-k_{A0} t} + \frac{B}{k_{BC} - k_{AB}} (e^{-k_{A0} t} - e^{-k_{C0} t}) \\
+ C \left(1 - \frac{1}{k_{BC} - k_{AB}} e^{-k_{A0} t} + \frac{k_{AB}}{k_{BC} - k_{AB}} e^{k_{C0} t}\right)
\]

(1)

A–C are the TR-SHG signal changes due to the three involved species, and \(k_{AB}\) and \(k_{AC}\) are the transfer constants between the states. All later shown transfer times are the inverse of the transfer constants. A decay of state C was not included into the model, due to the completely different time scale of the decay compared to the time range of the measurements. During the fits, all amplitudes have been kept independent, and the amplitude of the initial excitation (state A) has been held at zero. The width of the Gaussian function has been calculated from SFG cross-correlation measurements. In order to describe the DIP/SiO₂ TR-SHG data, the fit model from DIP/sapphire was modified by an additional directly populated excited state (feature D), which decays independently of the three-step dynamics of A–C.

RESULTS AND DISCUSSION

Our study focuses on investigations of the dynamics of electronically excited states in DIP on the ultrafast femtosecond time scale using TR-SHG. We used two different substrates, sapphire and SiO₂, for the following reasons: Sapphire generates an SHG signal close to zero. No excitation occurs by the pump pulse, and it does not interact electronically with the DIP molecules. Therefore, the SHG signal and the pump-pulse-induced changes in the signal from DIP on sapphire can directly be correlated to processes in the DIP layer. In contrast, for DIP on SiO₂ we expect contributions to the SHG signal originating from the substrate, because of the symmetry breaking in and at the native silicon oxide layer. Furthermore, interactions of charge carriers in the DIP layer and the silicon oxide layer can occur. Importantly, the molecular adsorption geometry and the ordering on both substrates is very similar; thus, influence of the molecular orientation on the observed excited states dynamics can be excluded (see below).

DIP on Sapphire. Figure 1 displays TR-SHG results from DIP on sapphire. A strong signal intensity increase of nearly 25% is observed due to the pump-pulse-induced electronic excitation. The signal consists of two components, a fast one and a slower one (features B and C). In addition, the rise of the pump pulse is steeper than that of the signal rise, and the signal still increases after the pump pulse has passed (see Figure 1b). The latter observation clearly indicates that the initial optical excitation does not lead to a signal change. Moreover, the decay of the initially excited species (labeled as A) leads to the generation of a second excited state (feature B). However, the decay of state B induces the population of state C, thus we propose a three-step process. In order to describe the data, we used a three-step first-order kinetic model (states A–C), which has been convoluted with a Gaussian function to model the intensity distribution of the excitation laser pulse. The width of the Gaussian function has been calculated from SFG cross-correlation measurements on the samples. All amplitudes have been kept independent, and the amplitude of the initial excitation (state A) has been held at zero during the fitting procedure. The final decay to the ground state after the three-step process has not been taken into account in the model because it occurs on a much longer time scale of several
hundred ps (see below). As can be seen in Figure 1a, our model describes the measured data convincingly. From the fit, we get times of $70 \pm 20$ fs for the transfer from A to B and $470 \pm 100$ fs for that from B to C. To elucidate the dynamics for longer time scales, we measured up to 40 ps as shown in Figure 1c. The data have been modeled by an initial excitation and a single exponential decay. Note that the ultrafast processes could not be resolved in this measurement. From the single exponential fit, we obtain a decay constant of $680 \pm 110$ ps. Picosecond time-resolved measurements on DIP films have identified a biexponential decay with the time constants of $166$ ps and $1.1$ ns.\(^8\) The value found here could be interpreted as a composition of these two time constants.

To gain deeper insights into the excitation behavior of DIP films and the underlying decay processes, which we could nicely describe by the three-step kinetic model, we performed pump pulse intensity-, energy-, and polarization-resolved measurements. The result of the pump pulse intensity-resolved measurements are shown in Figure 2a. For low pump pulse intensities of up to approximately 50 $\mu J/cm^2$, an increase of both amplitudes is observed, while for higher intensities, saturation takes place. The amplitude of feature B saturates at a higher level compared to the amplitude of feature C. The variation in the amplitudes after saturation arises from small inhomogeneities of the sample, which is caused by laser-spot-dependent intensity changes. The previously determined dynamics are not influenced by these variations. However, in the saturation regime, the difference in the nonlinear optical (NLO) contrast between the amplitude of feature B and C does not change. We take this as further evidence for a coupling between states B and C. The initial rise of the amplitudes can be explained by an increased number of excited species. The reason for the saturation after 50 $\mu J/cm^2$ is most likely due to exciton–exciton annihilation. An explanation for the level of B being higher compared to C may be an incomplete transfer of state B to C.

As a next step, we performed pump pulse energy-dependent measurements as shown in Figure 2b. We used three different pump energies, 2.03, 2.14, and 2.23 eV, covering the first rise of the UV/Vis absorption spectrum of DIP and the highest one (2.23 eV) being resonant with the first excitation.\(^6\) All three measurements have been done with pump intensities of 135 $\mu J/cm^2$ for which the maximal signal change has been observed in the saturated regime as discussed before (see Figure 2a). The measurements show an increase in signal intensity for short
time scales, while for longer times no intensity changes are seen. Thus, the transfer time from feature B to C seems to be independent of the initial excitation energy. In contrast, the transfer time scale from feature A to B changes significantly. The values are 140 ± 60 fs at 2.03 eV, 71 ± 19 fs at 2.14 eV, and 20 ± 30 fs at 2.23 eV, i.e., for the resonant excitation at 2.23 eV we find the fastest relaxation time which becomes slower for off-resonant excitation energies. For similar aromatic molecules, namely 3,4,9,10-perylenetetracarboxylyl dianhydride (PTCDA) and N,N′-dimethylylene-3,4,9,10-dicarboximide (MePTCDI), similar decay times of 100 fs for PTCDA and 65 fs for MePTCDI have been observed. They have been attributed to excitonic intraband relaxation.38

Changing the polarization of the probe beam from p to s has a pronounced impact on the SHG signal as can be seen in Figure 2c. While the dynamics of excited states can be resolved with the p-polarized probe beam (see above), the measurements with the s-polarized probe beam cause no detectable signal changes. As described in the Experimental Section, the s-polarized beam only probes an excitation parallel to the surface. Hence, the main component of the excited states leading to both features B and C in the SHG signal is oriented perpendicular to the surface; accordingly, it is only detectable with p-polarized light. Detailed X-ray diffraction measurements have revealed that DIP molecules adopt an adsorption geometry in which the long axis of the molecules is aligned nearly perpendicular with respect to the surface.39 Therefore, we can conclude that for both involved excited states the transition dipole moments are oriented parallel to the long molecular axis.

Combining all above-discussed results we propose the following two different pathways for the variable involved excited states and their dynamics (see Scheme 1): (a) The state labeled as A is most likely attributed to a delocalized (hot) exciton, which localizes via intraband relaxation forming a molecular (Frenkel) exciton (state labeled as B). These delocalized excitons exhibit no preferential orientation; thus, we detect no contribution to the SHG-signal. For resonant excitation at 2.23 eV, the relaxation time is much faster compared to the times for off-resonant excitations. The transition dipole moment of the Frenkel exciton in DIP is oriented mostly parallel to the long molecular axis.39 This clearly explains the disappearance of the SHG signal from the Frenkel exciton for s-polarized light. Time-resolved measurements of DIP films studying the excited state dynamics in the time regime above 1 ps proposed that after 1 ps the main excitation leads to the generation of an excimer-state (CT-like).39,41 Following this proposal, we assign the state labeled as C to an excimer. Thus, the molecular exciton decays on a time scale of 471 ± 100 fs via a charge transfer from an excited DIP to a neighboring molecule forming an excimer. The transition dipole moment of this excimer state is oriented mainly perpendicular to the surface plane of sapphire. Thus, our polarization-dependent measurements support this assignment since it is not detectable with s-polarized light. It decays to the ground state on a time scale of 680 ± 110 ps. As discussed above, this value could be the superposition of the time constants of 166 ps and 1.1 ns observed with time-resolved photoluminescence.39 (b) On the basis of recent calculations performed by Engels and Engel,40 a different assignment to the involved state has to be considered. In their calculations on gas phase DIP dimers, the energetically lowest state is a Frenkel-like excimer without a charge-transfer character (CT-state).40,42 Additional calculations on similar compounds, namely, PTCDA and PTCDI,39 showed that surrounding molecules stabilize the Frenkel state more than the CT-state. In contrast, earlier calculations by Gisslen et al.39 (see above) resulted in the CT-state as the state with the lowest energy. Thus, depending on the used computational approach, the energetic of the involved states are different. However, taking into account the results by Engels and Engel,40 which additionally showed that the first step after optical excitation is a relaxation to a CT state of the dimer occurring on a ultrafast time scale, we still assign state A to a delocalized exciton. Contrary to the pathway suggested above, state A relaxes into the CT-state of a DIP dimer (B) and finally relaxes via a conical intersection into a Frenkel-like excited dimer state (C). The time scales according to the calculations are 200 fs for the first step and 400−500 fs for the second step. In our SHG experiment, the first step is significantly faster (19−140 fs), but the second transfer time of 470 ± 100 fs fits perfectly to the predicted relaxation time.

In summary, the difference between the two interpretations (pathways (a) and (b)) lies in the character of the lowest excited state (Frenkel vs CT) in DIP crystals, which depends on the involved model used for the calculations. In both cases, an excited dimer formation is the key process leading to a relaxation of the initially excited state into a lower lying state, which has excimer character. However, on the basis of our TR-SHG experiments, we cannot distinguish between both pathways, but both are supported by our TR-SHG measurements.

**DIP on SiO₂.** On the basis of our understanding of the excited states dynamics in DIP on sapphire, we investigated the influence of the silicon substrate with a native oxide layer (SiO₂) on the dynamics at the interface and within the DIP films.

Compared to the TR-SHG measurements on DIP/sapphire (see Figure 1a), the results on DIP/SiO₂ (see Figure 3a) show large differences. First, the relative signal change is much smaller, i.e., only around 5% compared to 25% for DIP/sapphire, which leads to a highly reduced signal-to-noise ratio. This can be attributed to a higher background signal from the SiO₂ substrate compared to sapphire, as mentioned before. Furthermore, an additional very short-lived component (labeled as D) arises, which is directly populated by the pump pulse. It obviously decays faster than the next state (feature B) is populated, leading to a clear dip in the TR-SHG
With this extended model, the TR-SHG data of DIP/SiO$_2$ can be very well described (see Figure 3a). The model gives a decay constant of $20 \pm 95$ fs for A to B and $210 \pm 95$ fs for B to C.

To gain further information on the involved electronic processes leading to SHG signal changes we also performed polarization-dependent measurements. The results are depicted in Figure 4 together with the corresponding measurements on DIP/sapphire. For DIP on SiO$_2$, the amplitude of the feature C is reduced compared to this feature on sapphire for p-polarized light. In the case of s-polarized light, for which DIP/sapphire no pump-pulse-induced SHG signal changes have been found (see above), we observe here a clear signal for feature C. Thus, the behavior of feature C in particular changes drastically for DIP on SiO$_2$. Assuming a similar molecular orientation and ordering in DIP films on sapphire and SiO$_2$, the corresponding electronically excited state is obviously not oriented parallel to the long molecular axis as found for DIP/sapphire. In contrast, the state associated with feature B is aligned parallel to this axis as observed in DIP/sapphire.

Comparing the results on the excited state dynamics in DIP after optical excitation, we find a clear influence of the underlying SiO$_2$ substrate. Apart from a new short-lived feature (D) with a lifetime of $22 \pm 14$ fs, the properties of feature C in particular are different on SiO$_2$. Generally, the following processes influencing the excited states dynamics may be considered: (1) In SiO$_2$, electrons could be excited by multiphoton processes due to the high pump pulse intensities, which then undergo self-trapping. \cite{48} (2) SiO$_2$ has a high density of trap states at the surface, which are energetically favorable for excited electron in DIP. \cite{12} (3) An optically induced electron transfer from the native oxide to the DIP molecules could be relevant. (4) Momentum relaxation due to scattering processes can take place on ultrashort time scales (32 fs). \cite{49} Most likely, the latter can be associated with feature D, which has no influence on the excited states dynamics in the DIP film (see above), i.e., it is a substrate-related feature.

To account for the difference in the SHG signal changes on SiO$_2$, we consider the following processes a posteriori: (1) Electrons or holes could be excited by multiphoton processes on SiO$_2$. (2) The initial optical excitation leads to the formation of delocalized excitons (feature A) followed by self-trapping. \cite{45, 46} (3) SiO$_2$ has a high density of trap states at the surface, which are energetically favorable for excited electrons. (4) Field-induced electron transfer from the native oxide to the DIP molecules could be relevant.
suggested assignment for the excited states and their dynamics are summarized in Scheme 2.

Scheme 2. Proposed Processes in DIP on SiO2 after Optical Excitation at 580 nm

<table>
<thead>
<tr>
<th>Relaxation 160±50 fs</th>
<th>Energy transfer 210±51 fs</th>
<th>Molecular excitation or Exciton (localized in donor) 20±15 fs</th>
<th>Trap state (Extractor) 420±51 fs</th>
</tr>
</thead>
<tbody>
<tr>
<td>A Delocalized excitation</td>
<td>B Delocalized excitation</td>
<td>C Substrate-related</td>
<td>D GS</td>
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</table>

### CONCLUSION

We have investigated the ultrafast excited state dynamics of diindenoperylene (DIP) in solid films using femtosecond time-resolved second harmonic generation (TR-SHG). Two different substrates have been employed, sapphire as an inert and electronically noninteracting substrate and silicon with a thin native oxide layer (SiO2) where weak adsorbate/substrate interactions and optical excitations of the substrate occur. In addition, sapphire yields no contribution to the SHG signal; thus, changes in the signal after optical excitation can be directly related to processes in DIP molecules. However, it has been assumed that on both substrates DIP molecules adopt a very similar adsorption geometry. In DIP/sapphire, optical excitation (λ<sub>exc</sub> = 556, 580, and 610 nm) leads to the generation of delocalized excitons. Depending on the excitation energy, these excitons localize via intraband transitions on a time scale of around 100 fs for off-resonant excitation and within 19 ± 30 fs for the resonant process. The relaxation results in the formation of a molecular excitons or excitons localized on dimers. These molecular excitons decay on a time scale of 470 ± 100 fs forming excimer states (charge-transfer-like or Frenkel-like). A decay of the excimers proceeds within 680 ± 110 ps. For the DIP/SiO2 system, we have identified a clear influence of the underlying substrate on the dynamics and the involved processes. While the formation of molecular excitons is also observed and occurs on similar time scales (160 ± 80 fs) as for DIP/sapphire, the decay is much faster, i.e., it occurs within 210 ± 95 fs, populating substrate-mediated trap states or excimer states. Our study has elucidated the so far unresolved processes and lifetimes of electronically excited states in DIP films below 2 ps, viz., on the femtosecond time scale.

### AUTHOR INFORMATION

**Corresponding Author**
E-mail: tegeder@uni-heidelberg.de. Phone: +49 (0) 6221 548475. Fax: +49 (0) 6221 456199.

**ORCID**
Valentina Belova: 0000-0002-8142-2090
Petra Tegeder: 0000-0002-5071-9385

**Notes**
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