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Adsorption Structures Affecting the Electronic Properties and Photoinduced Charge Transfer at Perylene-Based Molecular Interfaces

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Perylene-based organic semiconductors are widely used in organic electronic devices. Here, we studied the ultrafast excited state dynamics after optical excitation at interfaces between the electron donor (D) diindenoperylene (DIP) and the electron acceptor (A) dicyano-perylene-bis(dicarboximide) (PDIR-CN₂) using femtosecond time-resolved second harmonic generation (SHG) in combination with large scale quantum chemical calculations. Thereby, we varied in bilayer structures of DIP and PDIR-CN₂ the interfacial molecular geometry. For an interfacial configuration which contains a edge-on geometry but also additional face-on domains an optically induced charge

Introduction

In devices based on organic semiconducting molecules such as organic solar cells, an efficient separation of photoexcited excitons into free charge carriers involves a charge transfer (CT) between electron donor (D) and acceptor (A) molecules at interfaces. This crucial step strongly affects the device

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S ≥ 2023 The Authors. Chemistry - An Asian Journal published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made. transfer (CT) is observed, which leads to a pronounced increase of the SHG signal intensity due to electric field induced second harmonic generation. The interfacial CT state decays within 7.5 ± 0.7 ps, while the creation of hot CT states leads to a faster decay (5.3 ± 0.2 ps). For the bilayer structures with mainly edgeon geometries interfacial CT formation is suppressed since π - π overlap perpendicular to the interface is missing. Our combined experimental and theoretical study provides important insights into D/A charge transfer properties, which is needed for the understanding of the interfacial photophysics of these molecules.

performance.^[1,2] The charge generation depends on the ultrafast built up of charge transfer excitons (an electron from the donor is transferred to the acceptor or a hole is transferred from the acceptor to the donor, if the acceptor is photoexcited).^[3] This process is largely influenced by the film structure and the molecular orientation at the interface,^[4] the arrangement of energy levels,^[5] and the excitation energy.^[2,6,7] The formation of CT excitons is the central elementary reaction in photovoltaics, as a precursor for free charge carrier generation but also as a potential loss channel due to geminate recombination.^[8]

In the present study, we investigate the ultrafast excited state dynamics after optical excitation at interfaces between the electron donor diindenoperylene (DIP) and the electron n,n'-bis-(2-ethylhexyl)-1,7-dicyanoperylene-3,4:9,10acceptor bis(dicarboximide) (PDIR-CN₂) a perylene diimide (see Figure 1a, b) using femtosecond (fs) time-resolved second harmonic generation (TR-SHG) and quantum chemical calculations. Both DIP and PDIR-CN₂ are perylene derivatives, which have widely been used in organic electronic devices.^[9-12] Both materials form structurally well-defined thin molecular films.^[4,13–16] The utilization of fs TR-SHG, which has been proven to be a powerful method to investigate the dynamics of electronically excited states, is of particular interest in the case of studies of interfacial processes.^[6,7,17,18] SHG is a second-order nonlinear optical process, viz. the SHG signal is formed by the second-order nonlinear susceptibility of the sample, which is sensitive to changes in the electronic structure.^[19-21] For symmetry reasons SHG is forbidden in centrosymmetric media, thus no bulk contributions are expected and making SHG intrinsically surface or interface sensitive.^[22-25] Accordingly, studying CT processes at D/A-interfaces with SHG is very sensible, since the separation of positive and negative charges





Figure 1. (a) Molecular structures of DIP and PDIR-CN₂. Sketched bilayer film structures (b) DIP_{RT} on PDIR-CN₂, (c) PDIR-CN₂ on DIP_{RT} , and (d) PDIR-CN₂ on DIP_{LT} .

lead to the formation of a high static electric field at the interface, which significantly increases the SHG signal. This effect is known as electric field induced second harmonic (EFISH) generation.^[7,18,26,27]

TR-SHG in combination with large scale quantum chemical calculations has recently been applied to study the excited states dynamics in DIP and PDIR-CN₂ thin films, respectively.^[28] It has been found that in DIP the initial optical excitation induces the formation of delocalized excitons. These excitons localize on dimers on a ultrafast time-scale of < 50 fs to 150 fs depending on the excitation energy. In contrast, in PDIR-CN₂ optical excitation leads directly to the formation of localized excitons. In both DIP and PDIR-CN₂ localized excitons decay within hundreds of fs into Frenkel-like trap sites. The relaxation to the ground state occurs in DIP on a time scale of 600 \pm 110 ps, in PDIR-CN₂ this relaxation time is one order of magnitude faster (62 \pm 1.8 ps). The differences in the exciton formation and decay dynamics in DIP and PDIR-CN₂ are attributed to differences in the aggregation structures as well as to the respective structural and energetic disorders within the materials.^[28,29]

Here, we varied the interfacial molecular geometry in planar heterojunctions (bilayer structures) of DIP and PDIR-CN₂ (see Figure 1b–d).^[4,13] We studied (i) DIP films deposited on PDIR-CN₂ at room temperature (DIP_{RT}), which leads to an edge-on geometry at the interface between both compounds (see Figure 1b). (ii) PDIR-CN₂ on DIP_{RT} (Figure 1c) and (iii) PDIR-CN₂

on DIP_{LT} (LT: low temperature, see Figure 1d). The latter results into a configuration in which the DIP_{LT} films consist of an edgeon geometry but also additional face-on domains exist.^[4,13,30] We found a strong enhancement of the TR-SHG signal for the PDIR-CN₂ on DIP_{LT} system which is attributed to the EFISH effect induced by the formation of CT states at the interface. In contrast, for the other two configurations no interfacial CT formation is observed. Utilizing time-dependent density functional theory (TD-DFT) in combination with optimal tuned range separated functionals^[31] the experimental findings can be explained using model aggregates in a polarizable environment.

Experimental Section

Sample preparation

The DIP/PDIR-CN₂ bilayers were prepared by organic molecular beam deposition in an ultrahigh vacuum chamber on sapphire substrates (CrysTec, single crystal, (0001) surface, both sides polished). Two different preparation procedures were used with respect to the substrate temperature during deposition of the molecules: The substrate temperature was kept (i) at room temperature (labeled as RT) or (ii) at 220 ± 10 K (labeled as LT: low temperature) at a base pressure of 1×10^{-9} mbar. The deposition rate of 0.3 nm/min during growth was controlled by a quartz crystal microbalance calibrated by X-ray reflectivity (XRR). The nominal thickness of each layer was 20 nm. The film structures were studied by XRR measurements.^[4,14-16]

SHG experiments

As described in Ref. [29] for the TR-SHG measurements a regenerative amplified Ti: sapphire laser system which generates laser pulse of 50 fs and a with a spectral width of 25 nm was used. The wavelength of the pump beam was varied between 650 nm and 550 nm. The probe beam was set to 800 nm leading to a SHG signal of 400 nm. The measurements were taken in reflection under an angle of 45° with respect to the surface normal. Thus, a p-polarized beam results in a perpendicular and a parallel component of the light with respect to the surface plane, while s-polarized light exhibits only a parallel component.^[20,21,32] A probe beam intensity of $360 \,\mu\text{J/cm}^2$ and a pump intensity of $135 \,\mu\text{J/cm}^2$ were used. To obtain a good signal to noise ratio at least 10 measurements were summed up on one spot and at least 4 different spots on the sample were used for each signal trace. The sapphire substrate was used since sapphire generates a SHG signal close to zero. All experiments were performed under inert gas atmosphere (N₂) and at room temperature. To describe the TR-SHG data we utilized to different models for DIP and PDIR-CN₂. In the case of DIP a threestep first-order kinetic model with the amplitude A set to zero and overlaid with an oscillating part (see Ref. [29] and SI) was used. For PDIR-CN₂ a two-step (A to B) combined with a single exponential decay and the oscillating term first-order kinetic model was used (see Ref. [28] and SI). The signal decaying on the picosecond timescale in DIP and PDIR-CN₂ was modeled by a single exponential decay function.

Computational details

Solid-state approaches in principle encompass the entire system and provide very accurate information, e.g., on absorption

spectra.^[33] However, problems arise if relaxation effects should be considered since the employed unit cell has to be increased considerably. Therefore, we used cluster approaches to describe the disordered structures shown in Figure 1c, d. Due to defects, these structures contain different arrangement of DIP and PDIR-CN₂, while in the ordered arrangement in Figure 1b the orientation are all the same. Cluster approaches only include parts of the system but were found to capture relaxation effects of disordered excitonic systems very well.^[34-37] They employed model aggregates. These consisted mostly of two DIP and two PDIR-CN₂ monomers, to include both the interactions in the respective layers and the interactions at the interface (see Figure 2).

To generate a valid guess of the arrangement of molecules at an ideal interface, layers of the single-material crystal structure were moved with respect to each other and the most stable configuration was determined using force-field calculations. Details are presented in the Supporting Information (SI). The limiting case of high-disorder regions was also investigated by a fully optimized heterodimer, which consists of one DIP and one PDIR-CN₂ molecule. An even description of Frenkel- and CT-excitations poses a challenge for TD-DFT calculations but can be achieved by rangeseparated (RS) hybrid functionals. To achieve similar accuracies an IP-tuned version of ω B97X-D3^[38] in combination with the def2-SVP^[39] basis set were employed if not noted otherwise. Gradientcorrected or hybrid functionals give reliable excitation energies for localized states (Frenkel states) but often underestimate the excitation energies of CT states by more than 1 eV.[40] Rangeseparated functionals provide more accurate predictions for CT states^[41,42] but tend to overestimate their excitation energies. Optimal tuned functionals which are range-separated functionals for which the corresponding range-separation parameter ω is tuned, correct this error to a large extent. In such functionals ω is varied to minimize the differences between the computed ionization energy and the HOMO orbital energy and between the computed electron affinity and the LUMO orbital energy.^[31,43] This procedure has the advantage that ω is not fitted with respect to some experimental parameter but enforces Koopmans' theorem for the neutral and the anionic system as accurately as possible. Please note that Koopmans' theorem should hold for the exact Kohn-Sham-theory.^[44] Hence, a better description of CT states may occur since computed ionization energies are strongly improved, as shown by the inventor of this approach.[45] The advantages of optimal tuned functionals for cluster approximations of thin films were recently proven for the absorption spectra of pentacene thin films. Using the optimal tuned wB97XD approach (wTB97XD) the spectra including Frenkel as well as CT states could be reproduced by an accuracy of about 0.1 eV.[37] To achieve this accuracy it is necessary to tune the respective cluster while it is not sufficient to use parameters optimal tuned for monomers as shown by Herbert and co-worker.^[46] In this work both were used. The optimal values used in this work are listed in Table 1.

Calculations were done in Orca 4.2^[47,48] and QChem 5.3.^[49] To account for screening effects of the environment, the conductorlike polarizable continuum model (C-PCM)^[50,51] with a static and optical dielectric constant ($\varepsilon = \varepsilon_{inf} = 3$) suitable for an organic semiconductor system^[52,53] was applied. Continuum models neglect molecular solvent effects resulting from the orientation of the monomers in the crystal but experience shows that they are



Figure 2. Tetramers chosen to model the interface with DIP in standing-up (σ) and lying (λ) configuration. σ -geometries are found in bilayer systems consisting of DIP_{R7}/PDIR-CN₂ and DIP_{L7}/PDIR-CN₂. λ only in PDIR-CN₂/DIP_{L7}. DIP monomers are highlighted in red, PDIR-CN₂ in blue. Grey molecules are included to display the surroundings in crystal layers.

Table 1. Optimal values for the range-separation factor $\boldsymbol{\omega}$ for different systems.		
$\sigma_{\rm c}~({\rm model})^{\scriptscriptstyle [a]}$	0.12	
σ_{c} (full)	0.12	
λ_b (model) ^[a]	0.11	
λ_b (full)	0.10	
DIP monomer	0.14	
PDIR-CN ₂ ^[b] monomer (model) ^[a]	0.14	
PDIR-CN2 ^[b] monomer (full)	0.13	

[a] If not noted otherwise, we used a model system for PDIR-CN₂ throughout this work for all energy calculations, were the alkyl chain was cut and replaced by a methyl group. This does not influence the excitation behaviour as it was verified in a former work.^[28] [b] As described in the SI. PDIR-CN₂ had to be kept flat during the optimization to mimic the crystal environment.

sufficiently accurate to describe the main effects.^[28,34,36] To characterize the excited states we computed in general 30 electronically excited states.

Results and Discussion

To investigate the influence of the interfacial adsorption structure on CT processes between DIP and PDIR-CN₂, we prepared three different configurations (see Figure 1b–d): (i) We generated a PDIR-CN₂ film at room temperature, thus the molecules adopt a standing up configuration, and on top DIP has been deposited (DIP_{R7}/PDIR-CN₂). This leads to an edge-on geometry at the interface. (ii) A DIP_{R7} film has been prepared composed of standing up molecules. On top of these films PDIR-CN₂ has been deposited adopting also a perpendicular configuration (PDIR-CN₂/DIP_{R7}). (iii) On top of a DIP_{L7} film, which contains laying down DIP domains, we evaporated PDIR-CN₂. The morphologies of these bilayer films have been studied using X-ray diffraction measurements.^[4,13]

In the case DIP_{RT}/PDIR-CN₂ the TR-SHG data can be described by the dynamics of the single components (see SI, Figure S3). Thus, for this system no interfacial interactions, i.e., no charge transfer can be observed. For PDIR-CN₂/DIP_{LT} the TR-SHG results are displayed in Figure 3. At 610 nm (2.03 eV) optical excitation and on the ultrafast timescale, the bilayer data can completely described by a superposition of the traces from the single PDIR-CN₂ and DIP₁₇ layers (see Figure 3a). The observation is also found in the PDIR-CN₂/DIP_{RT} bilayer (see SI, Figure S2). Increasing the pump pulse energy from 2.03 eV (610 nm) to 2.25 eV (550 nm) leads to a pronounced signal rise of more than 60% as can be seen in Figure 3b). In addition, pump energy dependent lifetimes are observed in the TR-SHG signals. The lifetimes decrease with increasing pump energy from 7.5 \pm 0.7 ps for 2.14 eV to 5.3 \pm 0.2 ps for 2.25 eV. For the long-lived component no pump energy dependence is found. It exhibit a lifetime of 700 \pm 200 ps, which is similar to the lifetime of the Frenkel-like trap state in bare DIP_{17} films (600 ± 110 ps^[28]). Note that for the PDIR-CN₂/DIP_{RT} bilayer no pump energy dependency on the dynamics has been observed (see SI,



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Figure 3. TR-SHG results of the bilayer of PDIR-CN₂ on top of DIP_{LT} measured with a p-polarized pump and probe beam. (a) Comparison of the bilayer trace with the traces of the single layers for different timescales. (b) Dependence of the bilayer trace on the excitation energy.

Figure S2). We attribute the differences in the SHG-signal intensity for PDIR-CN₂/DIP_{LT} to the formation of interfacial CT-states and accordingly to EFISH, which will be underlined by our calculations.

The influence of the model system in comparison to those tetramers with PDIR-CN₂ with its full alkyl-chain have been investigated. Furthermore, geometric relaxation effects as described by Deutsch et al.^[54] have been included. The results for the σ_c and λ_b are displayed in Figures 4 and 5, respectively.

Figure 4 comprises the relevant results found for the σ_c cluster which was used to model the ordered interface structures depicted in Figure 1b and partly also in Figure 1c. In this orientation DIP and PDIR-CN₂ are aligned on top of each other. The left column depicts vertical energies for the model systems including the alkyl chains. The lowest excited states represent Frenkel excitations localized on the PDIR-CN₂ monomers (dark blue). Frenkel states localized on the DIP monomers are slightly higher in energy (green 0.1–0.2 eV). The lowest states with CT characters are about 0.5 eV higher in energy (orange). The σ_c (model) column which reflects the data obtained without alkyl chains strongly resembles the σ_c (alkyl)



Figure 4. Excited states calculated (ω B97X-D3/def2-SVP/ ω = 0.12/C-PCM) for σ_c . The first column (σ_c (alkyl)) presents calculations on the tetramer with full alkyl-chains. The following ones are based on our usual model system (σ_c (model)). Columns 3–5 show the best approximations to the relaxation to a CT- (σ_c (CT)), local DIP- (σ_c (DIP, LE)) and local PDIR-CN₂-(σ_c (PDIR-CN₂, LE)) state. These states are approximated by relaxation of the monomers to S₁-, anion- or cation-geometry while the positions in the crystal are kept frozen. More details can be found in the SI. The colours indicate the character of the excited states.

data showing that the alkyl groups can be neglected. CT states should be stabilized with respect to Frenkel states if the tetramer adopts the corresponding geometries (see SI section 7). The corresponding values are given in column $\sigma_c(CT)$. Indeed, a stabilization is seen but the lowest states still possess Frenkel characters. That relaxation effects have an influence is also seen in columns $\sigma_c(\text{DIP, LE})$ and $\sigma_c(\text{PDIR-, LE})$ in which DIP or PDIR-CN₂ adopts geometries optimized for the S₁ state of the respective monomers (see SI section 7). If the DIP monomers are relaxed to their S₁ geometry while the PDIR-CN₂ remains in their ground state geometries the lowest state is localized on the DIP part (green) otherwise it is localized the PDIR-CN₂ monomers. In both cases the CT states are shifted to higher energies. This shows that, even in the geometry which best approximates the relaxed CT one (third column Figure 4), the CT state is still 0.2 eV above the lowest Frenkel excitation. This is in line with the TR-SHG results on PDIR-CN₂/DIP_{RT} which show no EFISH effect and thus no indication for the population of CT states at the interface.

Figure 5 gives the results obtained for λ_b cluster which models the situation of PDIR-CN₂ on DIP_{LT} sketched in Figure 1d



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Figure 5. Excited states calculated (ω B97X-D3/def2-SVP/ ω = 0.11 (ω = 0.10 for full alkylchains)/C-PCM) for λ_b . The first column (λ_b (alkyl)) presents calculations on the tetramer with full alkyl-chains. The following ones are based on our usual model system (λ_b (model)). Columns 3–5 show the best approximations to the relaxation to a CT- (λ_b (CT)), local DIP- (λ_b (DIP, LE)) and local PDIR-CN₂-(λ_b (PDIR-CN₂, LE)) state. These states are approximated by relaxation of the monomers to S₁-, anion- or cation-geometry while the positions in the crystal are kept frozen. More details can be found in the SI. The colours indicate the character of the excited states.

right hand side. In this arrangement DIP lies horizontal while the PDIR-CN₂ stands in the upright position thus, both are twisted by 90° with respect to each other. Again, the differences between λ_b (alkyl) and λ_b (model) are small underlining the minor influence of the alkyl chains. In contrast to the σ_c orientation in which the lowest excited states possess Frenkel character regardless of the geometries of the excited states (Figure 4) the lowest states for the λ_b clusters always show CT character.

The differences between the energetic positions of CT states in σ and λ orientations result from the different distances between the charge centers of the positively and negatively charged monomers forming the CT dimers, respectively. Upon excitation to a CT state, an electron is partially transferred from the donor to the acceptor. If we assume that this happens completely, we have a zwitterion whose stability is essentially determined by the strength of the Coulomb interaction between the two charges. If one also neglects the delocalization of the charges across the monomers, but concentrates them on the respective charge centers, the Coulomb law applies and the energy of the system increases with 1/r, where r is the distance between the charge centers. For real systems, in addition to the

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delocalization of the charges across the monomers, it must also be taken into account that the charge transfer never takes place completely. Nevertheless, for CT states, one finds that their stabilities increase with approximately 1/r, where r is again the distance between charge centers of the monomers, which can also be well approximated by their centers of mass.^[55,56] In contrast, the energetic position of the Frenkel states depends only slightly on the distance between the monomers. Although the Davidov splitting, Frenkel states decrease approximately with $1/r_{r}^{3}$ the energetic limit of the Frenkel state for infinite distances is the excitation energy of the monomer, which in general does not differ much (< 0.5 eV) from the excitation energy of the bulk. As a consequence, the excitation energies of CT states decrease strongly for shorter distances which is not the case for Frenkel states. For the σ orientations, the distance is guite large due to the edge-on geometry. In the λ_b configuration, the PDIR-CN₂ and DIP are rotated by 90° with respect to each other, while in the σ_c orientation they are aligned (Figure 1) on top of each other. Due to the different orientation, the distance between the centers of mass of PDIR- CN_2 and DIP for the λ_b arrangement is 12 Å. For the σ_c orientation with 16 Å, the distance is significantly larger. Since CT states stabilizes with respect to Frenkel states if the distance decreases, they lie below the Frenkel states for the λ_b but above them for the σ_c arrangement.

Hence, interfacial CT states can be populated and the SHG signal is strongly enhanced for PDIR-CN₂/DIP₁₇ bilayers. The strong excitation energy dependence of the EFISH signal (see Figure 3b) can be explained by closer inspection of the energetic positions of the energy levels. The position of the lowest CT state in the full λ -tetramer is calculated to be located at 2.05 eV. However, these CT excitations are dark (oscillator strengths < 0.05) and hence cannot be directly populated. This explains the absence of an increased SHG-signal at 610 nm (2.03 eV). However, with an excitation energy of 580 nm (2.14 eV) the population of a bright CT state at the interface is possible, which therefore leads to an intensity increase in the SHG-signal due to EFISH. Optical excitation at even higher energies, i.e., 550 nm (2.25 eV) may lead to a rise in the CT yield^[6,7] which is accompanied by a further increase of the SHGsignal intensity (Figure 3b). On the other hand, the creation of hot CT states explains the faster decay of these states (5.3 \pm 0.2 ps) compared to the CT states formed at 2.14 eV (7.5 \pm 0.7 ps).

Conclusions

We have investigated the excited state dynamics at interfaces between the electron donor (D) diindenoperylene (DIP) and electron acceptor (A) dicyano- perylene-bis(dicarboximide) (PDIR-CN₂) bilayer systems after optical excitation utilizing femtosecond time-resolved second harmonic generation (SHG). Large scale quantum chemical calculations for various model systems have been performed to interpret the experimental results on the basis of the energetic ordering of the excited states. Different interfacial D/A adsorption geometries have been prepared to study the effect on the interfacial electronic properties. This included two adsorption structures which mainly consist of edge-on geometries (standing-up) and one which possess also face-on domains (lying down) leading to smaller distances between the center of mass or charge of the monomers. For the latter low-lying interfacial CT states have been identified by employing TD-DFT with the optimal tuned range-separated functional wTB97XD including model aggregates in a polarizable environment. At this D/A-interface an enhanced SHG signal has been detected due to CT formation and accordingly to the so-called electric field induced second harmonic (EFISH) generation effect. The CT state decayed within $7.5\pm0.7\ ps$ and the corresponding hot CT state on a shorter timescale of 5.3 ± 0.2 ps. For the two bilayer structures with edge-on geometries no energetically low-lying CT states have been identified in the calculations and also in the SHG experiments they have not been observed. This has been attributed to larger distances between the center of mass or center of charges for edge-on geometries. Our study underlines the importance of the interfacial D/A adsorption structure on the electronic properties and photoinduced charge transfer characteristics.

Supporting Information

Description of the kinetic models used for the SHG-data, additional SHG measurements on DIP_{LT} and $\text{DIP}_{RT}/\text{PDIR-CN}_2$ as well as PDIR-CN₂/DIP_{RT} bilayers. Additional computational details.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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