Evidence for Anisotropic Electronic Coupling of Charge Transfer States in Weakly Interacting Organic Semiconductor Mixtures

Valentina Belova,* Paul Beyer, Eduard Meister, Theresa Linderl, Marc-Uwe Halbich, Marina Gerhard, Stefan Schmidt, Thomas Zechel, Tino Meisel, Alexander V. Generalov, Ana Sofia Anselmo, Reinhard Scholz,* Oleg Konovalov, Alexander Gerlach, Martin Koch, Alexander Hinderhofer,* Andreas Opitz, Wolfgang Brüttting, and Frank Schreiber*

Institut für Angewandte Physik, Universität Tübingen, Tübingen 72076, Germany
‡Department of Physics, Humboldt-Universität zu Berlin, Berlin 10099, Germany
§Institute of Physics, Experimental Physics IV, University of Augsburg, Augsburg 86135, Germany
∥Faculty of Physics and Material Sciences Center, Philipps-Universität Marburg, Marburg 35037, Germany
¶Max IV Laboratory, Lund University, Lund SE-221 00, Sweden
#Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin 14109, Germany
††Dresden Integrated Center for Applied Physics and Photonic Materials (IAPP), Technische Universität Dresden, Dresden 01062, Germany
‡‡European Synchrotron Radiation Facility, Grenoble 38000, France

ABSTRACT: We present a comprehensive investigation of the charge-transfer (CT) effect in weakly interacting organic semiconductor mixtures. The donor–acceptor pair diindenoperylene (DIP) and N,N′-bis(2-ethylhexyl)-1,7-dicyanoperylene-3,4/9,10-bis(dicarboximide) (PDIR–CN2) has been chosen as a model system. A wide range of experimental methods was used in order to characterize the structural, optical, electronic, and device properties of the intermolecular interactions. By detailed analysis, we demonstrate that the partial CT in this weakly interacting mixture does not have a strong effect on the ground state and does not generate a hybrid orbital. We also find a strong CT transition in light absorption as well as in photo- and electroluminescence. By using different layer sequences and compositions, we are able to distinguish electronic coupling in-plane vs out-of-plane and, thus, characterize the anisotropy of the CT state. Finally, we discuss the impact of CT exciton generation on charge-carrier transport and on the efficiency of photovoltaic devices.

INTRODUCTION

One of the fundamental processes in devices based on organic semiconductors (OSC) is the charge transfer (CT) between electron donor (D) and electron acceptor (A) molecules at interfaces or in molecular mixed systems.1–4 The concept of CT as a mechanism of intermolecular interaction was described in the framework of Mulliken theory in the 1950s.5 In this theory, a donor and an acceptor form a CT complex, where the energy levels of the ground and excited states depend on the overlap of the D/A wave functions, and an electronic transition to the excited state is accompanied by partial or integer charge transfer.

In a simplified view, we can distinguish three nominal cases of CT systems depending on the degree of intermolecular interaction (Figure 1). To the first category (Figure 1a), we may assign systems where the intermolecular energy gap $\Delta E_{DA}$ between the highest-occupied molecular orbital (HOMO) of a donor and the lowest-unoccupied molecular orbital (LUMO) of an acceptor are almost identical to the individual energy gaps of the donor $\Delta E_D$ or the acceptor $\Delta E_A$. Thus, CT in the electronic ground state (GS-CT) is unlikely to be observed, and integer charges are mainly transferred because of exciton (D* and A*) formation and dissociation. As examples, the material combinations employed for planar heterojunction (PHJ) solar cells such as 6T/DCP, 6T/TPD, and DBP/ZCl can be considered. A second category (Figure 1b) describes weakly coupled molecules, where $\Delta E_{DA} < \Delta E_D$ or $\Delta E_A$. These weakly bound
Figure 1. Simplified schematic illustration of possible scenarios for energy levels at interfaces. (a) $\Delta E_{DA} \approx \Delta E_D$ or $\Delta E_A$. No ground-state interaction present, charges are transferred through molecular excitons formed preliminarily (D* or A*), yellow arrows depict electron transitions; (b) $\Delta E_{DA} < \Delta E_D$ or $\Delta E_A$. Weakly coupled molecules, partial GS-CT contributes to energy level shift, original levels are dotted, CT can occur either under direct excitation or via exciton dissociation; (c) $\Delta E_{DA} \ll \Delta E_D$ or $\Delta E_A$. Strong ground-state interaction, orbital hybridization resulting in energy splitting of a CT complex ($\Delta E_{CPX}$) is observed. Note that the full picture may be more complex and that for electronic transitions, the exciton-binding energy must be taken into account.\textsuperscript{10}

Figure 2. Chemical structure of DIP (part (a), C atoms—dark gray, H atoms—light gray) and PDIP-CN\textsubscript{2} (part (b), O — red, N — blue).\textsuperscript{16} The blue arrow indicates the orientation of the transition dipole moment $\mu$ (optical axis) of the lowest electronic transition; (c) Sketch of the structural geometries (red ellipsoids—donor, green ellipsoids—acceptor).

We chose three different architectures (Figure 2c). A planar heterojunction (PHJ) was chosen as the simplest model, and we chose a two-component mixed bulk-heterojunction film (BHJ) with different mixing ratios and a superlattice (SL) consisting of 20 alternating monolayers as an intermediate case. DIP and PDIP-CN\textsubscript{2} have a similar backbone size (Figure 2a,b) that enable good intermixing upon coevaporation and, as a consequence, more interface area.

In the present paper, we comprehensively study the CT mechanism in organic binary mixtures starting from morphological and structural investigations, via complementary forms of spectroscopy, to the implications in device applications. As a case study, we chose thin films of the small-molecule semiconductors diindenoperylene (DIP) and N,N'-bis(2-ethylhexyl)-1,7-dicyanoperylene-3,4,9,10-bis(dicarboxyimide) (PDIP-CN\textsubscript{2}, where R = C\textsubscript{8}H\textsubscript{17}, branched\textsuperscript{16}) (Figure 2a,b). Both materials belong to the group of perylene derivatives widely used as electron donors and acceptors in organic electronic devices.\textsuperscript{17–19} They are structurally well-defined and therefore can serve as a model system.

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Conductivity measurements were performed on blended films with different mixing ratios deposited on glass substrates using interdigitated ITO electrodes in the dark and under illumination with a halogen lamp using a Keithley 2612A source-meter unit.

Current density vs voltage (j-V) characteristics of solar cells were recorded with a Keithley 236 source-measure unit. The currents were measured in the dark and under one sun simulated AM1.5G, 100 mW/cm² illumination with a Xenlamp. Electroluminescence measurements were carried out by using a CCD camera (PyLoN:100BR eXcelon, Princeton Instruments) coupled with a spectrometer (SP2300i, Princeton Instruments). The measurements were performed under a dc voltage driven by a Keithley 2400 source meter. Incident-photon-to-current efficiency (IPCE) spectra were detected under monochromatic illumination (Omni - λ300 Monochromator/ Spectrograph, Zolix Instruments Co., Ltd.).

Details on near-edge X-ray absorption fine structure (NEXAFS) spectroscopy measurements (performed at MAX IV) are given in the Supporting Information.

**RESULTS AND DISCUSSION**

**Structural Characterization.** Prior to the examination of CT, the two compounds were characterized regarding the structural organization of the molecules during simultaneous or consecutive growth, as this is crucial for the formation of D/A interfaces. For this purpose, AFM and X-ray scattering measurements were applied.

AFM images of the thin films are shown in Figure 3 (for height profiles see SI). The morphology of the pristine DIP film reveals a typical "wedding-cake-like" structure with a step size 1.6–1.8 nm corresponding to one monolayer of upright-standing DIP molecules and a root-mean-square (σrms) surface roughness of 2.85 nm. For all mixed films, as well as pristine PDIR-CN₂ films, the grain sizes decrease significantly. This results in very smooth surfaces and σrms roughnesses below 1 nm, with no clear molecular steps to distinguish. Therefore, based on these AFM results, we have no evidence of phase separation.

The surface of the SL consists of similarly small grains with a roughness comparable to the molecular blends. The PHJ surface has a roughness similar to pristine DIP. The top layer of PDIR-CN₂ adopts a grain size of about 115 nm, which is comparable to the average DIP grain size underneath.

For more detailed structural information, we applied X-ray scattering techniques (i.e. reflectivity (XRR) and grazing-incidence X-ray diffraction (GIXD)). Specular scans are shown in Figure 4. The first Bragg peak of pristine DIP (red curve) is observed at \( q_d = 0.37 \, \text{Å}^{-1} \), which corresponds to the standing-up or \( \sigma \)-orientation of DIP with an out-of-plane lattice spacing of \( d_{(001)} = 16.9 \, \text{Å} \), and an \( \sim 83^\circ \) inclination angle of the molecular plane relative to the surface plane. One Bragg peak and a weak second-order reflection are observed in the XRR scan of the pristine PDIR-CN₂ for which the branched alkyl side chains inhibit long-range crystal formation. As known from the literature, PDIR-CN₂ forms a unit cell with an inclination angle of \( \sim 53^\circ \), which gives an out-of-plane lattice spacing of \( d_{(001)} = 16.5 \, \text{Å} \). The \( q_d \) value of the Bragg peak from the XRR scan (lowermost curve) corresponds to \( d_{(001)} = 17.1 \, \text{Å} \), which almost coincides with pristine DIP. In the case of the blended systems, the second-order Bragg reflection still persists in films with excess DIP (3:1) but disappears with increasing PDIR-CN₂ fraction. The exact peak maxima of the coevaporated films cannot be properly quantified through a strong interference effect. Nevertheless, an apparent gradual shift toward lower \( q_d \) points to changes in the lattice parameter.

**EXPERIMENTAL SECTION**

The samples were prepared by organic molecular-beam deposition (OMBD) in vacuum. Structural and optical investigations, two types of substrates were used: silicon wafers with a native oxide layer (thickness \( d_o \approx 2 \, \text{nm} \)) and glass. During film growth, the substrates were kept at 297 K, and base pressure in the chamber did not exceed \( 10^{-9} \, \text{mbar} \). Mixed films were produced by coevaporation of DIP (Prof. J. Pillaum, Universität Würzburg, Germany) and PDIR-CN₂ (ActivInk N1400 Polyera, U.S.A.) in different mixing ratios. The nominal thickness and deposition rate were monitored with a water-cooled quartz crystal microbalance (QCM) during film growth: 20 and 100 nm for each coevaporated and pristine film, 20 nm for each layer in a PHJ, and 1.7 nm for each monolayer of a SL (10 pairs of D/A layers) with a total rate of 0.5 nm/min.

For the preparation of the solar cells and the samples for UPS and conductivity measurements, we used glass substrates coated with prestructured 140 nm indium–tin oxide (ITO). A polymeric hole injection layer of HIL 1.3 (Clevios Heraeus) was spin-coated from an aqueous solution on the ITO, followed by annealing at 125 °C. DIP and PDIR-CN₂ were evaporated onto the substrate by OMBD under a vacuum of \( 10^{-7} \, \text{mbar} \) with rates of 3–6 nm/min and 0.2–6 nm/min, respectively, depending on the mixing ratio or sample structure. Aluminum (100 nm) was used as the cathode material, and it was deposited thermally through a shadow mask onto a previously applied 5 nm-thick exciton blocking layer of bathocuproine (BCP). For these measurements, we have modified the BHJ configuration by sandwiching the mixed layer between two thin neat layers of DIP and PDIR-CN₂, respectively. This configuration will be denoted planar-mixed heterojunction (PMHJ).

The surface morphology was measured by AFM using a JPK Nanowizard II instrument in tapping mode under ambient conditions. Image analysis was performed with Gwyddion. X-ray diffraction measurements were performed at the beamline ID10 of the European Synchrotron Radiation Facility (Grenoble, France) and at the beamline X005A of the Swiss Lightsource (Villigen, Switzerland) using a focused beam with a wavelength of \( \lambda = 0.9398 \, \text{Å} \) and \( \lambda = 0.8857 \, \text{Å} \), respectively. The raw data were processed and corrected for footprint and background contributions. XRR data fitting was done with GenX by evaluation of the Kiessig fringes with the Parratt formalism. IR spectra were obtained in transmission mode with a Vertex 70 (Bruker) FTIR spectrometer at the Brewester’s angle of Silicon (74°). The theoretical IR spectra were calculated with TURBOMOLE. UV–vis–NIR absorption spectra were obtained using a Varian Cary 5000 spectrophotometer (Agilent Technologies) at normal incidence. Photoluminescence spectra were acquired using a Horiba Jobin Yvon Labram HR 800 spectrometer with a CCD-1024 × 256-OPEN-359 detector. Excitation for PL was performed using a frequency-doubled Nd:YAG laser at a wavelength of 532 nm and a He:Ne laser at 633 nm; excitation was conducted at temperatures of 297 and 90 K. The anisotropic components of the extinction coefficient were determined by variable-angle spectroscopic ellipsometry (VASE) using a Woollam M-2000 ellipsometer with a rotating compensator.

The photoemission experiments were performed at the beamlines PM4 (end station LowDosePES) and UE52 (end station UE52-PGM Multicolor) at the synchrotron storage ring BESSY II at Helmholtz-Zentrum Berlin. The time-resolved PL studies were carried out with a Hamamatsu streak camera. The excitation wavelength was set to 460 nm, employing a lithium triborate crystal for second harmonic generation.
We used a three layer model (bulk Si-substrate−SiO₂ layer−organic film) to determine the film thickness $d$ and roughness $\sigma$ of the mixtures from the XRR (Table S1). Regarding planar heterostructures, PDIR−CN₂ molecules grown on top of a DIP layer adopt the same standing-up configuration (Figure 4, uppermost curve) and form a layer with increased roughness because of the rough DIP layer underneath. Roughness of the SL according to XRR is quite low, which may serve as evidence for the layer-by-layer growth mode or preferential filling of gaps.²⁸

The results of GIXD experiments on pristine and coevaporated films are shown in Figure 5. Very strong in-plane reflections of pristine DIP are less intense and broader in nonequimolar mixtures with an excess of pristine DIP molecules. In the equimolar mixture, DIP reflections almost vanish, which demonstrates a high miscibility between DIP and PDIR−CN₂ molecules, forming a system wherein the two kinds of molecules are mixed without noticeable phase separation.²⁹ PHJ and SL GIXD profiles present a simple superposition of pristine film patterns (Figure S2).

Since PDIR−CN₂ is less ordered than DIP, we used thicker films ($d = 100$ nm for the pristine PDIR−CN₂ and 1:1) in order to obtain a better diffraction pattern. All reflections in the PDIR−CN₂ spectrum at $q_{xy}$ values exceeding 0.76 Å⁻¹ can be assigned to the known crystal structure.¹⁸ However, the peak at
$q_{gs} = 0.63 \text{ Å}^{-1}$ does not originate from the known unit cell and stems from an unknown polymorph indicated as PDIR–CN$_2$*. Additional peaks are found in the equimolar mixed film at $q_{gs}$ equal to 0.92 Å$^{-1}$ and to 1.81 Å$^{-1}$. Because these two new reflections do not originate from the structures of the pure components, they are assigned to a new mixed phase polymorph. This observation indicates that the mixture is not completely random in the in-plane direction but has a preferred ordering, comparable to a cocrystal. The corresponding coherent island size evaluated from the full-width at half-maximum (fwhm) $l_f$ equals 3.5 nm, which is 5 times smaller than $l_l$ in pristine films (18.8 nm for DIP and 18.4 nm for PDIR–CN$_2$). In the blends with predominant PDIR–CN$_2$ content, the pure polymorph PDIR–CN$_2$* is more pronounced. It shows phase separation from the mixed phase whereas in the 3:1 film, weak phase separation between DIP and the mixed phase occurs.

Since PDIR–CN$_2$ molecules ($\sim$22.0 Å) are longer than DIP molecules ($\sim$18.4 Å), and because in a cocrystal the angle of the π-conjugated cores should be parallel in the unit cell, the increase of the out-of-plane lattice spacing $d_{001}$ in blends is explained by a change of the PDIR–CN$_2$ molecular-tilt angle. The orientational changes of both compounds can be quantified by NEXAFS spectroscopy, which probes the average backbone orientation (for details see SI). The inclination angle of PDIR–CN$_2$ changes from 53 ± 5° in the pure film to 58 ± 5° in the 1:1 blend. Correspondingly, the DIP inclination angle changes from 79 ± 5° to 76 ± 5°.

**Ground-State Properties.** Having shown that both compounds are well intermixed and that the intermolecular electronic interaction is not inhibited by phase separation, we apply spectroscopic methods for its characterization. Using infrared (IR)-absorption spectroscopy, it is possible to assign a shift of intramolecular vibration frequencies to the degree of charge transfer between donor and acceptor in the absence of electronic excitation (i.e. in the electronic ground state). In particular, the stretching mode of the nitrile group (−C≡N) present in PDIR–CN$_2$ molecules is highly sensitive to CT.

In Figure 6, we compare experimental IR spectra of pristine DIP and PDIR–CN$_2$ coevaporated equimolar DIP/PDIR–CN$_2$ films, calculated spectra of neutral PDIR–CN$_2$, and of its radical anion. In the presented spectral range, DIP does not reveal any IR-active vibration modes, which makes the CN-mode ideal for comparison. The CN-stretching mode appears at $\sim$2222 cm$^{-1}$ (all peak positions are vertically shifted for clarity. Peak positions are taken from a Gaussian fit). The inclination angle of PDIR–CN$_2$ changes from 53 ± 5° in the pure film to 58 ± 5° in the 1:1 blend. Correspondingly, the DIP inclination angle changes from 79 ± 5° to 76 ± 5°.

**Figure 6.** Infrared transmission of pristine DIP, PDIR–CN$_2$, equimolar mixture, heterostructures on silicon, and calculated spectra of neutral and ionized PDIR–CN$_2$ in gas phase. The spectra are vertically shifted for clarity. Peak positions are taken from a Gaussian fit.

shifted as in the blend, showing a smaller amount of interacting molecules.

Using ultraviolet photoelectron spectroscopy (UPS), we determined the HOMO-level onset and the work function of the molecular thin films, which are used to determine the ionization energies (IE). Part of the results is summarized in Figure 7. On weakly interacting, amorphous surfaces, such as SiO$_2$ or HIL 1.3-coated ITO, the DIP molecules grow almost upright standing, which results in IE = 5.40 eV. The IE for pristine PDIR–CN$_2$ is 7.10 eV on SiO$_2$ substrates. For details on the orientation-dependent IE of DIP and PDIR–CN$_2$, see SI.

In the following, we discuss the energetic interplay at planar and mixed DIP/PDIR–CN$_2$ (D/A) interfaces. Looking at the PHJ architecture on ITO/HIL 1.3 as shown in Figure 7a, we observe Fermi-level pinning of DIP on HIL1.3, as shown before. Upon subsequent deposition of PDIR–CN$_2$ on standing DIP molecules, we observe vacuum-level alignment between PDIR–CN$_2$ and DIP. The IE values for PDIR–CN$_2$ deposited on top of SiO$_2$ and on standing DIP molecules differ by $\sim$0.35 eV. Taking the HOMO-level offset of 1.35 eV and a transport gap for PDIR–CN$_2$ of 2.65 eV, the energy gap $\Delta E_{DA}$ is about 1.3 eV. The transport gap taken for PDIR–CN$_2$ is estimated from the HOMO onset of a pristine PDIR–CN$_2$ film together with the observed Fermi level pinning of the LUMO at about $\sim$0.40 eV (for details see SI). This obtained transport gap is nearly identical to the one of DIP with 2.60 eV, which is readily explained by the similarity of the π-conjugated cores and the optical gaps of both molecules. This also matches the measured transport gap of other perylene derivatives.

The blended film of DIP and PDIR–CN$_2$ was evaporated on top of DIP-precovered ITO/HIL 1.3 substrates (Figure 7b). We observed a slight shift of the vacuum level, which is also reported for several other systems. The HOMO onsets of the components were extracted from the deconvolution of the measured signal from the 100 Å-thick molecular blend (vertical
examples of individual molecules.41 42,43

energetically lowest peaks give the optical gap \( \Delta E_{\text{opt}} \) of 2.25 eV for pristine DIP and 2.17 eV for pristine PDIP–CN₂. Compared with the transport gaps given above, 2.60 and 2.65 eV respectively, an exciton-binding energy of 0.4–0.5 eV can be derived.

Considering the spectrum of an equimolar blend, one can observe several features which can only be explained by taking into account the excited-state interaction between the two different compounds (see also the calculated superposition of the two pristine components, black curve in Figure 8b). As can be seen from Figure 8a, even a low concentration of DIP causes a rapid decrease in the intensity of the lowest PDIP–CN₂ peak at 2.17 eV (1:9 and 1:3). The intensity decrease of this transition in PDIP–CN₂ probably originates in the disturbed structural long-range order. Similarly, the DIP spectrum is influenced by intermixing with PDIP–CN₂ (3:1) as can be observed by the decrease of the peak intensity at 2.8 eV.47

As mentioned in the introduction, the observation of CT states in optical-absorption spectra often requires more sensitive techniques48–53 because of the small cross section. However, the spectrum of the equimolar mixed film (1:1) clearly reveals a broad band at photon energies below the optical gaps of the pristine materials (1.4–2.1 eV, Figure 8c), which originates from direct excitation of CT states.54–56 This subgap band, which is related to charge-transfer interaction,55,56 was fitted using three Gaussian functions with peak positions at 1.58, 1.81, and 2.02 eV (fwhm = 0.25, 0.27, 0.20 eV). Together with a fourth Gaussian for the fundamental transition across the gap, the absorption spectrum in Figure 8c can be fitted over the whole measured range. Reasons for the observed splitting of the CT states may include variation in the unit cell or vibronic contributions. In contrast to the intermixed films, absorption spectra of PHJ and a superlattice (Figure 8b) are similar to a linear superposition of the spectra of the pristine materials, and a substantial contribution from CT states is absent.

Figure 8d shows photoluminescence spectra of single-component films and blended films with different mixing ratios recorded at low temperature (90 K) using an excitation energy of 2.33 eV. The DIP spectrum is in agreement with the literature.52,53 PDIP–CN₂ reveals very strong emission intensities with two maxima at 1.69 and 1.84 eV at low temperature.

The emission intensity sharply decreases upon mixing and completely disappears in the equimolar blend within the range that of the pristine component. Moreover, one can observe a new peak emerging around 1.4 eV that reveals a slight red shift and increase in intensity with increasing PDIP–CN₂ fraction. We suggest to assign this new emission band to radiative

Figure 7. Valence-region spectra (left) and work-function measurements (right) of PHJ (a) and PMHJ (b) on HIL 1.3/ITO substrates for layers of increasing thicknesses. The HOMO and WF onset values are indicated by the vertical dashed lines. The red graphs show the baseline spectra of DIP-covered substrates. All spectra are scaled and shifted vertically for clarity. Part (b) shows the deconvolution of the valence band with pristine valence signatures for a 100 Å-thick film in PMHJ geometry. The green and red vertical lines are used to align the single-fit components. Further measurements are given in SI.42,43

The HOMO-level offset differs for the PHJ (\( \Delta E_{\text{PHJ}} = 1.35 \) eV) and the PMHJ (\( \Delta E_{\text{PMHJ}} = 1.00 \) eV) device architectures. This is related to differences of the energy levels in the two structures. Morphological changes, such as disorder, molecular reorientation, and mixing affect the electrostatic field at the thin-film surface and the coupling between the molecules.41–45 Additionally, we find that a partial GS-CT shifts the HOMO levels as a whole but does not introduce a new feature in the UPS data. This finding contrasts with a HOMO-level offset between DIP and PDIP–CN₂ of 1.70 eV (which would give a smaller \( \Delta E_{\text{DA}} \) of only 0.95 eV). This HOMO-level offset is expected from vacuum level alignment using the IEs for the pristine films.

**Excited-State Properties.** Now we studied if CT plays a role upon excitation, having already confirmed the presence of CT in the electronic ground state. Absorption spectra, taken by UV–vis–NIR spectroscopy, are shown in Figure 8a–c. Crystalline thin films of DIP and PDIP–CN₂ are expected to reveal anisotropic optical properties due to the transition dipole moment of the lowest electronic transition being oriented along the long molecular axis.46 As the inclination angle of PDIP–CN₂ is smaller (\( \sim 53^\circ \)) compared to DIP (\( \sim 83^\circ \)), its absorption strength is, accordingly, higher in the in-plane direction (parallel to the substrate surface). The orientations of the transition dipole moments of individual molecules are depicted in Figure 2a,b. The positions of the energetically lowest peaks give the optical gap \( \Delta E_{\text{opt}} \) of 2.25 eV for pristine DIP and 2.17 eV for pristine PDIP–CN₂. Compared with the transport gaps given above, 2.60 and 2.65 eV respectively, an exciton-binding energy of 0.4–0.5 eV can be derived.

Considering the spectrum of an equimolar blend, one can observe several features which can only be explained by taking into account the excited-state interaction between the two different compounds (see also the calculated superposition of the two pristine components, black curve in Figure 8b). As can be seen from Figure 8a, even a low concentration of DIP causes a rapid decrease in the intensity of the lowest PDIP–CN₂ peak at 2.17 eV (1:9 and 1:3). The intensity decrease of this transition in PDIP–CN₂ probably originates in the disturbed structural long-range order. Similarly, the DIP spectrum is influenced by intermixing with PDIP–CN₂ (3:1) as can be observed by the decrease of the peak intensity at 2.8 eV.47

As mentioned in the introduction, the observation of CT states in optical-absorption spectra often requires more sensitive techniques48–53 because of the small cross section. However, the spectrum of the equimolar mixed film (1:1) clearly reveals a broad band at photon energies below the optical gaps of the pristine materials (1.4–2.1 eV, Figure 8c), which originates from direct excitation of CT states.54–56 This subgap band, which is related to charge-transfer interaction,55,56 was fitted using three Gaussian functions with peak positions at 1.58, 1.81, and 2.02 eV (fwhm = 0.25, 0.27, 0.20 eV). Together with a fourth Gaussian for the fundamental transition across the gap, the absorption spectrum in Figure 8c can be fitted over the whole measured range. Reasons for the observed splitting of the CT states may include variation in the unit cell or vibronic contributions. In contrast to the intermixed films, absorption spectra of PHJ and a superlattice (Figure 8b) are similar to a linear superposition of the spectra of the pristine materials, and a substantial contribution from CT states is absent.

Figure 8d shows photoluminescence spectra of single-component films and blended films with different mixing ratios recorded at low temperature (90 K) using an excitation energy of 2.33 eV. The DIP spectrum is in agreement with the literature.52,53 PDIP–CN₂ reveals very strong emission intensities with two maxima at 1.69 and 1.84 eV at low temperature.

The emission intensity sharply decreases upon mixing and completely disappears in the equimolar blend within the range that of the pristine component. Moreover, one can observe a new peak emerging around 1.4 eV that reveals a slight red shift and increase in intensity with increasing PDIP–CN₂ fraction. We suggest to assign this new emission band to radiative
recombination processes from the charge-transfer state between DIP and PDIR−CN₂ molecules.⁵⁷,⁶⁴−⁶⁶ In the equimolar blend, local exciton emission from the pristine compounds is almost quenched, which is consistent with a fully intermixed film. A similar effect was observed at low temperatures for other materials.⁶⁷ In addition, nonradiative recombination contributes much more strongly to the energy loss compared to the pristine materials, because the PL intensity observed in the 1:1 film is 1 order of magnitude weaker than in pristine DIP and three orders weaker than in pristine PDIR−CN₂. Using a red laser with an excitation energy of 1.96 eV, which is below the bandgap of the neat materials, the CT state can be excited directly, avoiding transfer from the higher-energy molecular excitons (Figure 8d).⁵⁷

Regarding the layered samples, the PHJ exhibits strong emission especially at low temperatures mainly by PDIR−CN₂ excitonic recombination. As expected, emission from the SL contains features of both components, and only weak emission features from the CT states can be observed at 1.4 eV.

The recombination process through the CT state is further confirmed by time-resolved photoluminescence (TRPL) studies. The TRPL data presented in Figure 9 indicate that the strong long-lived emission of the singlet population of pristine DIP and PDIR−CN₂ at 10 K is quenched because of charge transfer at donor/acceptor interfaces. Thus, it decays on a shorter time scale of picoseconds in the mixed films. In addition, we observe clearly defined CT emission with a rise time shorter than the instrument response time (~15 ps), indicating that most of the CT states are actually populated on this time scale. The recorded PL dynamics in blends is thus dominated by CT emission. The effective 1/ε decay times are shown in Table 1. The subnanosecond range has been typically observed for CT-emission decay.⁶⁶,⁶⁹ For the blends with excess PDIR−CN₂, the CT state dynamics are not substantially altered when the temperature is varied between 10 and 290 K.

They show clear monoexponential decays (see SI) with no evidence for side decay processes such as singlet exciton dissociation, which is expected to occur in the shorter time range.¹²,⁶⁷ In the case of the 1:1 blend, however, the PL decay becomes faster with increasing temperature, indicating the presence of a thermally activated quenching mechanism. Such quenching could be either resulting from the thermally
activated dissociation of CT states, or emerge from the presence of nonradiative recombination centers. However, thermally activated CT dissociation would require binding energies on the order of $k_B T$, which is much smaller than the value of 0.2 eV evaluated in the following (see Discussion), whereas the hypothesis of nonradiative recombination centers would imply a certain mobility of CT states with a temperature-dependent diffusivity coefficient.

From the comparison of intermixed and layered samples, where the CT signatures are only weakly present, one can assume an anisotropic character of the CT transitions polarized in the in-plane direction. In order to explore the anisotropy in detail, we performed variable-angle spectroscopic ellipsometry (VASE) on a film with the most pronounced CT effect, that is the 1:1 ratio (ellipsometry data for the other mixing ratios are given in SI). The in-plane and out-of-plane components of the extinction coefficient are presented in Figure 10. The CT band displayed in Figure 8b,c, there is a distinct difference in the spectral range above the gap (2–3 eV). In this spectral region, the PHJ device exhibits a 2- to 3-fold greater photocurrent as compared to the PMHJ device. The lower current of the latter cannot be fully explained by the lower absorptivity of the blend with respect to the bilayer structure (see Figure 8b), which results from a less-favorable molecular orientation for light absorption. Instead, the lower current indicates that the PMHJ suffers from a charge-transport problem because of the intimate intermixing of DIP and PDIR–CN$_2$ in the 1:1 blend. Because of the good miscibility of both components, there are no separate percolation paths for the extraction of the generated charge-carrier pairs, which are trapped and subsequently recombine in the mixed phase (see also the discussion on charge transport in the following section and ref 70). However, even in the PHJ device the IPCE stays below 10%, mainly because of insufficient light absorption resulting from the predominantly standing orientation of both molecular species.

In the logarithmic representation, Figure 11 shows EL spectra of a PMHJ device that was operated as a light-emitting diode (LED) under a forward bias of 3 V. The luminescence signal was normalized to the maximum at about 1.35 eV, which corresponds well to the CT-emission band observed in photoluminescence spectra of the blends (see Figure 8d). In addition, there is a much weaker band at about 1.8 eV, which could stem from luminescence of one of the pristine materials. For the PHJ device, there was no detectable EL emission in the spectral range above the gap (2.1–2.2 eV). The in- and out-of-plane components of the extinction coefficient are presented in Figure 10. The CT band

Table 1. Effective Decay Times Extracted from Monoexponential Fits of PL Transients Recorded at Low and Room Temperatures

<table>
<thead>
<tr>
<th>material</th>
<th>$\tau$ at 10 K</th>
<th>$\tau$ at 290 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIP</td>
<td>&gt;12.5 ns</td>
<td>257 ps</td>
</tr>
<tr>
<td>2:1</td>
<td>190 ps</td>
<td>182 ps</td>
</tr>
<tr>
<td>1:1</td>
<td>496 ps</td>
<td>342 ps</td>
</tr>
<tr>
<td>1:3</td>
<td>448 ps</td>
<td>418 ps</td>
</tr>
<tr>
<td>1:9</td>
<td>452 ps</td>
<td>433 ps</td>
</tr>
<tr>
<td>PDIR–CN$_2$</td>
<td>&gt;12.5 ns</td>
<td>151 ps</td>
</tr>
</tbody>
</table>

Figure 11. The orange curve represents the reduced EL spectrum of the 1:1 PMHJ sample measured at a 3 V bias voltage. The brown line shows the IPCE spectrum of the 1:1 PMHJ solar cell. The red dashed lines show the superposition of Gaussians corresponding to the CT-fit, which are light-blue and light-green for EL- and IPCE-fit, respectively. The gray dashed lines complete the light-green Gaussians to the IPCE-fit over the whole CT range (black dashed line). Note that the peak at 2.25 eV belongs to the pristine material. The inset displays linear-scaled IPCE measurements of PHJ and PMHJ cells. The sharp peak around 2.8 eV (IPCE of PMHJ cell) is a measurement artifact. All spectra were recorded at 297 K.

Figure 10. Anisotropic components of the extinction coefficient $k$ of the 1:1 film. The inset zooms into the range of 1.4–2.2 eV. The in-plane component corresponds to the absorption data in Figure 8.
CT states polarized in the out-of-plane direction seems to be extremely small.

As introduced by Tvingstedt et al.71 and refined by Vandewal et al.73 EL and IPCE spectra can be analyzed in the framework of Marcus theory to estimate the CT energy \( E_{\text{CT}} \) which can then be discussed in relation to the open-circuit voltage \( V_{\text{OC}} \) of the solar cells to quantify energy losses.86,74 As the EL data show an asymmetric peak, we modified the CT approach and fitted our data with the sum of two Gaussians (CT-fit, see Figure 11). Both the reduced absorption \( \sum_{i=1}^{2} \sigma_i(E)E \) and the reduced emission \( \sum_{i=1}^{2} I_i(E)E^{-1} \) were fitted with

\[
\begin{align*}
\sum_{i=1}^{2} \sigma_i(E)E &= \sum_{i=1}^{2} \left( \frac{f_{\sigma,i} I_i(E)}{4\pi\alpha_{\sigma,i} E_{\text{CT},i}^4} \exp \left( -\frac{(E_{\text{CT},i} \pm \lambda_{0,i} - E)^2}{4\lambda_{0,i} E_{\text{CT},i}^2} \right) \right) \\
\sum_{i=1}^{2} I_i(E)E^{-1} &= \sum_{i=1}^{2} \left( \frac{f_{\sigma,i} I_i(E)}{4\pi\alpha_{\sigma,i} E_{\text{CT},i}^4} \exp \left( -\frac{(E_{\text{CT},i} \pm \lambda_{0,i} - E)^2}{4\lambda_{0,i} E_{\text{CT},i}^2} \right) \right)
\end{align*}
\]

Here, \( \lambda_0 \) represents the reorganization energy related to the Stokes shift in the CT manifold. Variables \( f_{\sigma} \) and \( f_i \) are proportional to the square of the electronic-coupling matrix element. The plus and the minus sign are taken for reduced absorption and reduced emission, respectively. Consequently, we obtain two different CT energies: \( E_{\text{CT},1} = 1.35 \text{ eV} \) and \( E_{\text{CT},2} = 1.48 \text{ eV} \), with the latter value stemming from the peak with the stronger spectral weight. This energy splitting may stem from structural variations or a vibronic progression.

In order to confirm the superposition of different CT states included in the absorption band, we fitted the IPCE spectra (as in Figure 8c) with the sum of Gaussians as shown in Figure 11 on the right axis. Although the absorption CT band consists of at least four distinct states, obviously only two of them lead to radiative recombination. Similar behavior has been observed in the literature for systems with a spectrally broad manifold of CT states.75,76 However, whereas this can be seen as evidence for energetic relaxation in the CT density of states, there still remains the question of whether equilibrium is reached within the lifetime of carriers. Further investigations will have to clarify this issue.

**Device Behavior.** To elucidate the mechanisms of charge separation and transport, photoelectrical measurements were performed for solar cells built in the PHJ and PMHJ (1:1) device architectures. This allows for a direct comparison of the photocurrent and the open-circuit voltage between face-to-face (in-plane) and edge-on-edge (out-of-plane) stacking.

The solar cell architecture can be seen in Figure 12 alongside the \( j-V \) characteristics of PHJ and PMHJ solar cells in dark (dashed lines) and under one sun simulated AM1.5G illumination (solid lines). The solar-cell parameters extracted from \( j-V \) measurements are collected in Table 2. Note that the open-circuit voltage \( (V_{\text{OC}}) \) of both architectures is equal and amounts to \( 0.50 \text{ V} \), whereas the short-circuit current changes significantly from \( -0.65 \text{ mA/cm}^2 \) for the PHJ to \( -0.24 \text{ mA/cm}^2 \) for the PMHJ cell, which correlates very well with the IPCE results. The fill factor (FF) decreases from 57% (PHJ) to 40% (PMHJ). As a result, the efficiency is reduced from 0.18% for the PHJ to 0.05% for the PMHJ cell. This contrasts with phase-separating mixtures, where PMHJ cells provide higher efficiencies than their PHJ counterparts.37 Thus, some degree of phase separation, as opposed to perfect intermixing, is beneficial for charge separation in order to increase the device performance.

In general, the open-circuit voltage of an organic molecular D/A solar cell can be written as18,74

\[
V_{\text{OC}}(T) = \frac{E_{\text{CT}}}{q} - \Delta V_{\text{OC}}
\]

where \( q \) is the elementary charge, and \( E_{\text{CT}} \) sets the upper limit of \( V_{\text{OC}} \) which can be achieved only in the low-temperature limit. At a finite temperature, there is an energy loss \( q\Delta V_{\text{OC}} = q\Delta V_{\text{OC}}^\text{rad} + q\Delta V_{\text{OC}}^\text{nonrad} \), composed of thermodynamically inevitable radiative losses as well as nonradiative losses. For a wide range of organic D/A systems, the energy loss between \( E_{\text{CT}} \) and the \( V_{\text{OC}} \) at 300 K is in the range of 0.5–0.6 eV.7,72 In our case, from \( E_{\text{CT}}=1.48 \text{ eV} \) for the dominant optically detected CT state, we obtain an energy loss of \( q\Delta V_{\text{OC}} \) of about 1 eV, significantly larger than the typically observed range.

Furthermore, the photovoltaic gap \( \Delta E_{\text{DA}} \) from UPS is an additional measure for the \( V_{\text{OC}} \) limit in solar cells and was used before to estimate losses in \( V_{\text{OC}} \) in PHJ solar cells.77 For the planar heterojunction of DIP/PDIR–CN$_2$, the \( \Delta E_{\text{DA}} \) is 1.3 eV. Therefore, the losses for the open-circuit voltage regarding the energy-level offset amount to \( \sim 0.8 \text{ V} \), larger than for previously analyzed material combinations.77 As discussed in the previous section, the reason for the high energy losses and the low \( V_{\text{OC}} \) (and as a consequence for the low overall efficiencies) observed for both cell architectures could lie in the broad manifold of CT states with energy relaxation toward the lowest states from which only weak radiative recombination is observed.

In addition to \( j-V \) measurements on solar cells, we also determined the electrical conductivity in the dark \( \sigma_{\text{dark}} \) of pristine and blended films for varying molar doping ratios. The results are shown in Figure 13. Both pristine materials are

![Figure 12.](Image)

**Figure 12.** \( j-V \) diagram of PHJ and PMHJ DIP/PDIR–CN$_2$ based solar cells. Dashed lines represent measurements in the dark and the solid lines under illumination. The inset shows the stack architecture of the PHJ (left) and PMHJ (right) solar cells.

<table>
<thead>
<tr>
<th>config</th>
<th>( V_{\text{OC}} ) (V)</th>
<th>( j_{\text{sc}} ) (mA/cm$^2$)</th>
<th>FF(%)</th>
<th>( \eta(%) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHJ</td>
<td>0.50</td>
<td>-0.65</td>
<td>57</td>
<td>0.18</td>
</tr>
<tr>
<td>PMHJ</td>
<td>0.50</td>
<td>-0.24</td>
<td>40</td>
<td>0.05</td>
</tr>
</tbody>
</table>

*Corresponding \( j-V \) curves are shown in Figure 12.

Table 2. Solar Cell Parameters Extracted From \( j-V \) Characteristics of PHJ and PMHJ solar cells Recorded Under Illumination

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reported to form films with high mobility, DIP for holes and electrons, and PDIR−CN$_2$ only for electrons.$^{78,79}$ In the heterostructures, $\sigma_{\text{dark}}$ decreases by adding the other compound, which is readily explained by the altered crystal structure compared to both pristine materials and, as a consequence, lower ordering.$^{80}$ This minimum in $\sigma_{\text{dark}}$ is reached around equimolar mixing ratios. Additionally, we recorded the electrical conductivity under illumination to look at the photoconductivity of the blended system. The ratio of $\sigma_{\text{photo}}$ to $\sigma_{\text{dark}}$ is shown in Figure 13 (bottom panel). The strong decrease in the ratio of $\sigma_{\text{photo}}$ to $\sigma_{\text{dark}}$ supports the before-mentioned discussion on the photocurrent in solar cells. A similar conductivity decrease in molecular blends by dilution has been observed earlier.$^{72,81,82}$

As a result of the intimate mixture of the molecules in the blended films, high recombination losses and charge trapping are present. This results in low conductivities of blended films together with the absence of increased conductivities under illumination in these films. These effects are limiting the overall performance of the PMHJ solar cells, as discussed before.

Discussion. The presence of a CT interaction between donor and acceptor materials has recently attracted attention because of its importance for organic solar cells and organic light-emitting diodes$^{83}$ as well as the associated fundamental challenges. It was shown that the CT energy can serve as a limit for the open-circuit voltage in solar cells.$^{84}$ However, even if the resulting exciton has charge-transfer character, ground-state interactions are still present.$^{61,85}$

The two perylene derivatives DIP and PDIR−CN$_2$ are an excellent model system to study CT effects in organic semiconductors. Mixtures are well ordered in the out-of-plane direction, which means each molecule has a well-defined inclination angle to the substrate. In the in-plane direction, mixed films have a small coherent island size but nevertheless exhibit preferential D/A stacking, which enables the CT state formation in this direction. Intermolecular D/A interactions are directly related to the overlap of their frontier orbitals, which is maximal in π−π stacking or face-to-face geometry. Therefore, the presented CT is stronger in mixed films (BHJ and PMHJ), where the molecule reorientation facilitates orbital overlap, in contrast to planar interfaces (PHJ and SL) with almost exclusively edge-on-edge stacking.

We observed a partial charge transfer in the ground state of 0.17 electrons, as determined from IR spectroscopy and DFT calculations. This leads to a shift of the HOMO levels of both compounds toward each other. Judging from UPS data, we find that the HOMO-level offset in the mixture is only 1.00 eV in contrast to the 1.70 eV expected from the vacuum-level alignment. Although we found this relatively strong shift in the HOMO levels, there are no hints for new states or orbital hybridization in the ground state, because the mixed film valence region spectrum is just a superposition of the pristine film spectra taking into account the change of IE. The opposite is true for the excited state, where we observe new states via UV−vis−NIR absorption spectroscopy and PL/EL spectroscopy. The resulting energy diagram for mixed films is presented in Figure 14, where the energy gap $\Delta E_{DA}$ of 1.65 eV and the dominant CT state of 1.48 eV give a CT exciton-binding energy of about 0.2 eV. This is smaller than the exciton-binding energy of the pristine materials (0.4−0.5 eV). The lower exciton-binding energy of the CT state can be explained by the wider charge separation compared to the exciton associated with the first HOMO−LUMO transition in the pristine materials.$^{86,87}$

For many photovoltaic material combinations, highly sensitive methods are necessary to measure the weak CT transitions. However, for the case presented here, some of the strong CT absorptions are detectable with standard UV−vis−NIR absorption spectroscopy. Furthermore, the CT absorption is present not only close to the absorption edge of the pristine materials, but it has a rather broad energy range of about 0.6 eV. We also find a corresponding feature in photoluminescence and electroluminescence at 1.4 eV with a strong quenching of...
emission from the single components. The drastic change of molecular absorption and emission spectra provides strong evidence for the formation of a D/A complex with new electronic properties. Time-resolved PL reveals that the CT state lifetime of 400–500 ps is significantly shorter compared to the individual compounds at 10 K and nearly independent from temperature. Judging from this, the CT states open the dominant recombination channel.

Importantly, our findings demonstrate the anisotropic character of the electronic transition to the excited CT state. As sketched in Figure 14 (bottom), it is strong in the in-plane character of the electronic transition to the excited CT state. Thus, π−π stacking is a prerequisite for the efficient intermolecular coupling, which is the main characteristic for GS-CT (Figure 1). If an intimately mixed structure is established, further properties of the formed complex are primarily determined by the energy level difference ΔE_{D/A}, which in our case amounts to 1.65 eV. This is apparently too high for a substantial hybridization of the molecular orbitals. By considering the structural prerequisite of molecules to form π−π stacking and the magnitude of ΔE_{D/A}, one may make a prediction for the interaction type that a D/A combination will exhibit. We note further that the anisotropic character of CT is not in contradiction with our observation of equal V_OC for PHJ and PMHJ solar cell configurations, because the rough polycrystalline DIP layer shown in Figure 3 offers enough surface area for σ−π stacking with PDIR−CN_3 molecules even in a PHJ. Thus, the equality of the observed V_OC,s underlines the dominance of the energetically favorable face-to-face CT recombination pathway.

The formation of coupled but weakly ordered crystalline D/A complexes, where excited CT states serve as traps for excitons, and open pathways for radiative and non-radiative recombination, is accompanied by a decrease of charge-carrier conductivity and an increase of energy losses. Nevertheless, material combinations with strong CT absorption could lead to increased short-circuit current by using more photons from the infrared region. The overall efficiency could be increased by using well-ordered mixed-stack charge-transfer crystals because of an improved extraction efficiency and applying them as donor and/or acceptor in photovoltaic cells. Combining the higher degree of structural order, the broad CT absorption and reduced energy losses might lead to new device architectures.

**SUMMARY**

In summary, a comprehensive study of an organic D/A molecular system (DIP/PDIR−CN_3) prepared by OMBD involving structural, optical, electronic, and device characterization has been performed. We have identified the formation of a CT complex characterized by a weak ground-state interaction expressed in a partial CT of 0.17 electrons per molecule and a strong excited-state CT, which is highly anisotropic in nature. The strong intermolecular coupling together with the intimately mixed structure without phase separation contributes to the large energy losses in solar cells from these materials.

**REFERENCES**


