Time-resolved photoluminescence spectroscopy of charge transfer states in blends of pentacene and perfluoropentacene

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Charge transfer states in blends of organic semiconductors have significant importance for the functioning of organic optoelectronic devices, but are also interesting from the perspective of fundamental research as many of their properties as well as their influence on the photophysics of the material are not yet completely understood. We report on a time-resolved photoluminescence study of the photophysics of the charge transfer state in the prototypical donor–acceptor system pentacene mixed with its perfluorinated counterpart. We find indications for the existence of two distinct charge-transfer states, one of them formed in the bulk of the mixed phase, the other one formed at the interface to phase-separated pentacene domains. We discuss the implications of the difference in temperature dependence of the emission intensity and the lifetime observed for these charge transfer states.

1 Introduction

Charge transfer (CT) from a donor to an acceptor component in blends of organic semiconductors is of vital importance for the functioning of state-of-the-art optoelectronic devices [1–6]. Moreover, just recently, the role of CT states in mediating complex photophysical processes such as singlet fission has been demonstrated in pristine films [7]. Despite the technological relevance, a detailed picture of the processes that govern the complex photophysics of CT states in mixed systems is still missing. Understanding the energetics at donor/acceptor interfaces is not trivial and requires approaches far beyond a simplistic consideration of the electronic states assigned to the individual compounds. Interactions between the molecules in the ground state can alter the overall electronic structure of the mixture [8–10] and partial transfer of charges in the ground state may influence the stability of CT states [11, 12]. In the excited state, Coulomb interactions between the charges must be taken into account. On the other hand, CT dissociation can be facilitated by charge delocalization and a high polarizability of the local environment [3, 13, 14]. The mechanisms behind the recombination and dissociation kinetics at donor/acceptor interfaces are subject of ongoing research [3–6].

In order to shed light on the nature of CT states in donor–acceptor systems and their effects on the photophysics, time-integrated optical spectroscopy techniques are not sufficient, although they can be powerful tools to identify CT states [8]. However, to obtain a more detailed insight into the kinetic processes that govern the photophysics of a mixed system and potential effects of intermolecular interactions, time-resolved optical spectroscopic measurements are necessary. For such investigations, a system with complete intermixing of the donor and the acceptor compound would be ideally suited to maximize the effects of charge transfer on the photophysical properties. Blends of pentacene (C_{22}H_{14}, PEN) and its perfluorinated
counterpart perfluoropentacene (C\textsubscript{22}F\textsubscript{14}, PFP) are such a prototypical donor–acceptor system. When mixed in equimolar ratios, PFP and PEN form a mixed crystal with new unit cell parameters and alternating stacking of molecules of both compounds [15]. In non-equimolar blends, a co-existence of pure phases and the intermixed phase is observed [15]. The optical properties of PFP:PEN blends have been investigated in detail before, and a CT is observed in the absorption spectrum as well as in the photoluminescence spectrum [8, 9].

Taking advantage of the detailed knowledge obtained previously for this system, we study the effects of CT from PEN to PFP on the lifetime of excited states using time-resolved photoluminescence spectroscopy. In order to separate effects of the intermixed phase from those of the pure phases, we investigate neat films of PEN and PFP, as well as blends of both components with different mixing ratios: a blend with an excess of the donor PEN, an equimolar mixture and a blend with an excess of the acceptor PFP. In the following, we will refer to these mixed samples as [3:1], [1:1], and [1:3] blends, according to their respective (PEN:PFP) molar mixing ratio. For spectroscopic studies, we vary the temperature of all samples between room temperature and 10 K to gain insight into potential quenching processes, allowing us to draw conclusions about the CT stability.

2 Experimental Pentacene (C\textsubscript{22}H\textsubscript{14}, PEN) and perfluoropentacene (C\textsubscript{22}F\textsubscript{14}, PFP) were purchased from Sigma–Aldrich and Kanto Denka Kogyo Co., respectively, and used as received. Mixed films were prepared by coevaporation [9, 15] using molecular beam deposition in ultra-high vacuum at a substrate temperature of 297 K with a total growth rate of 0.2 nm min\textsuperscript{−1} on quartz glass substrates. A quartz crystal microbalance (QCM) calibrated with X-ray reflectivity was used to adjust the mixing ratio before growth and to monitor the growth rate during deposition as well as the final thickness. The error in the mixing ratio is 10% and is determined by the error of the QCM. Time resolved photoluminescence (TR-PL) measurements were performed at substrate temperatures ranging between 10 and 290 K using a frequency doubled Ti:Sa-laser with a repetition rate of 80 MHz and a pulse width of 100 fs.

3 Results The photophysics of the pure compounds has already been investigated in detail [8, 16–18]. The photoluminescence spectrum (PL-spectrum) of PEN is composed of emission from the S\textsubscript{1} state of PEN at 1.84 eV and a long-lived emission from trap states at 1.55 eV [18]. In the PL-spectrum of PFP there is only one pronounced peak observable at 1.65 eV, which is related to emission from the S\textsubscript{1} state of PFP [8]. At 10 K both, PEN as well as PFP show a fast decay of the singlet emission within 80 fs [17] for PEN and less than 300 fs [16] for PFP. In complete agreement with these results, the decay of the singlet emission could not be resolved in our experiments.

Mixing PFP and PEN by coevaporation significantly changes the photophysics as can be clearly seen in the time-integrated spectra and the time-resolved data in Fig. 1. Short-lived emission related to singlet states is apparent in all mixed samples in the energy range between 1.6 and 2 eV.

Figure 1 Time-resolved two-dimensional plots of the PL intensity and time-integrated spectra of the three mixed systems (a–f), neat PEN (g and h) and PFP (i and j). The PL intensity in the false-color plots is normalized and presented on a logarithmic scale. The PEN:PFP mixing ratio is indicated in the intensity plots. The tentative assignment of the peaks is also shown schematically, with I corresponding to emission from the interface CT state between the intermixed and the phase separated PEN-domains, II corresponding to emission from the bulk CT state in the intermixed phase, and III corresponding to the emission from singlet states of PEN and PFP. The low-energetic emission in pure PEN is highlighted in violet and either related to low-energetic excitonic states or impurities. The inset shows the chemical structure of PEN and PFP (gray: carbon, white: hydrogen, green: fluorine).
The longer-lived PL emission at lower energies is differing for the three samples, in particular when comparing the blend with an excess of PEN to the other blends. In contrast to the equimolar blend and the blend with an excess of PFP, in the blend with an excess of PEN, see Fig. 1(a) and (b), there is only one distinct emission peak at 1.38 eV. This peak has been observed in low-temperature PL-spectra of PFP:PEN blends before and has been assigned to emission from a CT state [8]. Interestingly, the intensity of this CT signature is most pronounced in blends with an excess of PEN (Fig. 1(a)). This cannot be explained by the different absorbances of the material at the excitation wavelength of 455 nm (2.73 eV), see Fig. S1 in the supporting information, and hence, is a surprising result, as one would expect the highest CT yield in the blend, where the amount of donor/acceptor interfaces is at its maximum. If this CT state was formed in the intermixed phase we would expect its highest intensity in the equimolar blend. The much higher intensity in the blend with excess of PEN indicates that the signature observed around 1.4 eV is related to a CT state forming at the interface between domains of pure PEN and the intermixed phase.

In the equimolar blend (Fig. 1(c) and (d)), we observe two distinct peaks with different dynamics at 1.4 and 1.56 eV. Based on the previous discussion, we tentatively assign the peak at 1.4 eV to a CT state at the interface between the mixed phase and pure PEN-phase. Since the peak at 1.56 eV is most pronounced in the equimolar blend, a possible explanation for this feature is emission from a CT state between PEN and PFP molecules in the intermixed phase. An explanation why we do not observe this CT state in the blend with an excess of PEN could be a fast energy transfer process to the interface CT state as the emission of the bulk CT state in the intermixed phase is at 1.56 eV, which overlaps with the absorption of the interface CT at 1.6 eV [9] making Förster resonance energy transfer possible. Moreover, the signature at 1.56 eV in the [3:1] blend could be masked by the much brighter emission at 1.4 eV. The feature at 1.56 eV is also present in the [1:3] mixture. In this blend with a higher PFP fraction, the low-energetic emission in the range of 1.4 eV is reduced to such an extent that it only appears as a low-energetic shoulder of the signature at 1.56 eV, which is in agreement with our assignment to a CT state at the interface to pure PEN.

Although the presence of the signature at 1.56 eV can be consistently explained with the occurrence of an intermixed phase in blends of PEN and PFP, it is important to note that there are remarkable similarities between the peak at 1.56 eV in the blends and the low-energetic long-lived emission in neat PEN, suggesting that the emission in the blends could also result from the remaining pure PEN domains. The low-energetic emission in PEN might arise from self-trapped excitons, CT states between PEN molecules or impurities [8]. For better comparison of the signatures in neat PEN and the blends, time- and temperature-dependent spectra of the low-energetic emission are presented in the supplemental material (Figs. S2 and S3 in the supporting information). The peak at 1.56 eV in the blends is superimposed by other signatures, but nevertheless, similar thermal quenching behavior at low temperatures is observed. We also studied the PL dynamics and compared the long-lived decay in neat PEN to the PL decay in the energy range between 1.5 and 1.65 eV in the blends (see Fig. 3). At 10 K the decay constants are comparable (0.65 and 0.95 ns for the blends and 0.85 ns for neat PEN), whereas with increasing temperature the PL decay becomes slightly faster in the blends. These findings indicate that there are only subtle differences in the temperature-dependent PL dynamics and intensities. However, an important difference arises from the peak energy, which is 1.51 eV for the signature in neat PEN and 1.56 eV in the [1:1] and the [1:3] blend. Given this energetic difference of 50 meV between the emission in the neat material and in the blends and the absence of a gradual shift of the emission energy with varying mixing ratio, it appears unlikely that the signature in the blends is related to the same low-energetic states as in the PEN bulk phase. Moreover, if the same feature was present in the blend, we would also expect a spectral broadening due to a plethora of possible configurations upon intermixing with PFP, but this is not observed. Finally, structural investigations of the PEN:PFP system suggest that most of the PEN in the equimolar mixture is actually in an intermixed phase with PFP, in which a PEN molecule has only PFP nearest neighbors, whereas contributions of the PEN bulk phase are negligible [15]. Due to the uncertainty in the mixing ratio of 10% we cannot exclude the existence of PEN molecules which have PEN as nearest neighbors and in fact, this would explain the observation of the emission at 1.4 eV, but most of the PEN molecules will have PFP nearest neighbors. Based on these considerations, our assignment of the blend emission at 1.56 eV to a CT state in the intermixed phase seems justified, although potential contributions from the trap-state emission of PEN cannot be completely excluded.

In contrast to our results for the blend with a higher fraction of the donor PEN, we find no indications for the formation of an emissive CT state at the interface of the intermixed and the pure PFP phase in blends with an excess of the acceptor molecule PFP. This might be due to the energetics at the interface, which could induce non-radiative decay to the ground state or destabilize the CT state, giving rise to dissociation. One of the suggested processes might explain why the optical signatures from the CT states are weaker in PFP-dominated blends, but a detailed investigation is beyond the scope of this work.

In order to study the dynamics of the different contributions to the PL-spectra discussed so far and to test for further indications for the presence of two distinctive CT states we will focus in the following on the PL transients obtained from three different energy ranges of the PL emission: (i) the PL in the low-energy range of the emission between 1.24 and 1.50 eV, which we attribute to a CT state at the interface between the pure PEN phase and the intermixed phase; (ii) the PL in the intermediate range...
between 1.50 and 1.65 eV, resulting from CT emission from
the 1:1 mixed phase in the low-temperature regime; and (iii)
the PL in the energy range from 1.65 to 2.07 eV from singlet
states.

The transients of the blends and the corresponding fits in
the first energy range (1.24–1.50 eV) are presented in Fig. 2.
In all cases, a biexponential fit function was found to
approximate the experimental data well. Thus, biexponen-
tial fits were used to quantify the PL decay, although we will
not attempt to associate a specific mechanism with these.
With increasing temperature, the decay of the CT emission
becomes faster, suggesting the presence of a thermally
activated non-radiative quenching channel. Higher mobility
of the CT excitons in combination with the presence of non-
radiative recombination centers leads to a preferential non-
radiative decay at higher temperatures, which is consistent
with the reduction in overall PL-intensity. However, the
existence of mobile CT states appears counterintuitive, as
their migration would be constrained to interfacial sites.
Furthermore, the overall weak absorbance and the poor
overlap of the CT absorption and emission spectra peaking
around 1.4 eV make CT exciton diffusion via Förster
mechanism unlikely. Nevertheless, the CT emission in
the blend with excess PEN reveals some characteristics,
which are typically related to mobile excitations, such as
multi-exponential decay kinetics and spectral relaxation of
the emission with increasing time after excitation [19–22].
Mobile CT states migrating along the donor–acceptor
interface in blends of m-MTDATA:3TPYMB have been
observed before [23]. In the observed time-window of about
600 ps, the PL spectra recorded for the [3:1] sample at 10 K
show a red shift of approximately 20 meV and moreover, the
high-energy tail decays faster than the low-energy tail
(Fig. S5 in the supporting information). Such behavior can
be consistently explained with the phenomenon of exciton
hopping within a disordered density of states. In the low-
temperature regime, excitons will preferentially relax
toward lower-energetic sites, leading to the observed overall
red-shift of the PL emission with increasing time after
excitation. We also observe a red shift of the CT signature in
the [3:1] sample with increasing temperature, which could
be due to kinetic frustration of the relaxation process in the
low-temperature regime, similar to observations made for
triplet states [22].

Although the low-energetic emission is less pronounced
in the other two blends, the decay dynamics around 1.4 eV is
comparable for all samples and can be fitted with a
Figure 4 PL dynamics in the energy range 1.65–2.07 eV. (a) PL transients of the PEN:PFP blends with different mixing ratios and (b) neat films for comparison. The decay times extracted from biexponential fits (black curves) of the blend emission are presented in panel (c). The time constant $T_1$ characterizes the short-lived decay and $T_2$ corresponds to the longer-lived component. Temperature-dependent PL intensities obtained from the integral over the biexponential model function are summarized in panel (d).

fast component of 50–100 ps and a slower component of 500–1000 ps, suggesting that the same species is present in all blends. For the [1:1] sample, however, we observe no spectral relaxation of the signature at 1.4 eV (Fig. S4 in the supporting information), which might indicate that the CT states formed in the [1:1] blend are less mobile. Different reasons could account for such behavior, *inter alia*, that the density of CT states is lower in the [1:1] blend, which is a likely scenario, since we assume that these CT states are formed at the interface to a pure PEN phase.

The PL emission in the intermediate energy range between 1.50 and 1.65 eV (Fig. 3) yields several contributions, which are probably related to different emissive species. The fits reveal a short-lived component of about 40 ps without pronounced temperature dependence for all studied blends (Fig. 3(a) and (c)) and a long-lived emission, which shows a more distinct temperature dependence. Below a temperature of 100 K, we observe a long-lived component in the [1:1] and the [1:3] blend, which we assign to the CT state in the mixed phase peaking around 1.56 eV, as discussed before. This contribution disappears above a temperature of 100 K. From the extracted decay times, it becomes apparent that the dynamics and the temperature dependence of this signature clearly deviate from the characteristics of the CT emission at lower energies, further supporting our assumption that two different emissive CT species are present in the blends studied. We speculate that the longer life time of the CT state assigned to the PEN:PFP intermixed phase compared to the low-energetic emission at the PEN interface could be due to weaker Coulombic coupling and weaker oscillator strength. When the charges are only weakly bound, the CT state can be dissociated by means of thermal energy, which would in turn explain, why the CT state of the mixed phase is already quenched at a temperature of 100 K. We assume that for higher temperatures, the decay characteristics in this energy range results from a superposition of the signatures in the low- and the high-energy range.

The interplay between the low-temperature emission in the 1.5–1.65 eV energy range and signatures from singlet states at higher photon energies leads to the peculiar temperature dependency of the PL intensity presented in Fig. 3. In case of the [1:1] and the [1:3] samples, the PL intensity first decreases with increasing temperature but rises again in the range of higher temperatures. This rise results from an increase in the decay times of the singlet states with increasing temperature (see Fig. 4). This observation is consistent with previous steady-state PL measurements [8], which have displayed an increasing PL intensity from excitons of PFP or PEN with increasing temperature in blends of PEN and PFP.

4 Discussion

Having a closer look at time-resolved spectroscopy of this prototypical charge-transfer system, the behavior of CT states in PEN:PFP blends especially of non-equimolar mixing ratio reveals important and surprising features. Our data are consistent with the existence of two distinct CT species, one formed at the interface between a domain of pure PEN and the 1:1 intermixed phase, while the other CT states forms in the bulk of the intermixed phase. From the energetic differences of their emission and the different thermal quenching behavior, we anticipate different degrees of stabilization for these two states [13, 24].

The origin of a CT energy varying with the mixing ratio has been discussed in theoretical studies [25, 26] and is assigned to several effects, including the Coulomb binding energy, screening at the donor–acceptor interface, delocalization of the CT state and the polarizability of the local molecular environment. Experimentally, a variation of the CT energy has been reported before in blends of N,N'-diphenyl-N,N'-bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine (NPD) with C$_{60}$ [13] and has in this case been related to two effects. First, a change in the background dielectric constant, which affects the relaxed binding energy of the CT state and second, a change in the size of C$_{60}$ crystallites [13]. The precise microscopic origin for the presumably varying degrees of CT stabilization in blends of PEN:PFP is not yet clear and would require more detailed investigations which are beyond the scope of the present work. However, following our assignment of the CT signature around 1.4 eV to the interface between the
intermixed PEN:PFP phase and pure PEN domains, the presence of differently sized PEN domains could lead to different degrees of polarizability in the local molecular environment. This could significantly influence the stability of the interfacial electron–hole pair and explain why the emission energy of the lower-energetic CT state varies with the blend composition. In contrast to that, the CT emission related to the mixed phase appears at similar emission energies in the [1:1] blend and the [1:3] blend. An explanation for this could be that the CT states formed in the intermixed phase are facing a more homogeneous local environment.

A second interesting effect is the temperature dependence of the CT emission. An increase in the intensity of the CT emission with decreasing temperature has been observed before in time-resolved studies [27–29]. In some of these studies, the CT dynamics did not depend on temperature, which lead to the conclusion that thermal quenching of the CT emission occurs via a small activation barrier through an excited CT precursor state [27, 29]. This is clearly in contrast to our data in which we observe a faster decay of the emission with increasing temperature, indicating an increase in the non-radiative decay of the energetically relaxed CT state. Such quenching could result from thermally activated dissociation of the relaxed CT states [28] and we also have hypothesized that this is the reason why the CT signature in the PEN:PFP mix phase can only be observed at temperatures below 100 K. However, in case of the other CT signature, which we have attributed to the interface to pure PEN domains, we argue that non-radiative decay after exciton migration is the more likely scenario to explain the observed thermal quenching. This statement is based on previous considerations of the molecular energy levels, from which a binding energy of 130 meV has been estimated for this species [8]. Such an energetic barrier would impede CT dissociation in the temperature range we studied. However, such considerations should be rather understood as a first-principle approximation of the actual exciton binding energy. For example, it has been demonstrated that the excitonic coupling can be altered by thermal motions [30] and that the role of entropy in driving charge separation should be considered as well [24]. Potential ambiguities arising in the interpretation of the TR-PL results could be removed by field-dependent measurements of the PL, as they provide a direct access to the activation barrier for CT dissociation. To the best of our knowledge, there is only one previous report on mobile CT states. Combining time-resolved PL studies with Monte Carlo simulations, Deotare et al. [23] have suggested an asynchronous hopping mechanism to explain the observed spectral relaxation. Certainly, the study of excitonic transport processes at donor/acceptor interfaces provides valuable insights into the interfacial density of states and we hypothesize that transport of CT excitons could also result in the population of sites from which dissociation is favored.

5 Conclusions In summary, we performed a time-resolved photoluminescence spectroscopy study of blends of pentacene and perfluropentacene. We found indications for two different types of CT excitons with lifetimes of up to 800–1000 ps at 10 K. The lower-energetic CT signature is most pronounced in the blend with excess PEN and we suggest that it is formed at the interface between the intermixed phase and phase separated PEN domains. The lifetime of this CT exciton increases as the temperature is reduced. Moreover, we observe a spectral red-shift of the PL emission in the blend with excess PEN with increasing time after excitation. This would indicate that a diffusion process is involved in its decay, which would not be unrealistic if it is formed at the interface between two phases.

The temperature dependence of the second CT species is much more pronounced so that its intensity decreases by a factor of up to 3 between a temperature of 10 and 100 K in the 1:1 blend. This signature dominates the PL spectrum of equimolar blends and blends with an excess of PFP molecules in particular at low temperatures. Since it exhibits its highest intensity in the equimolar blend, we suggest that its origin is a CT state in the 1:1 mixed phase. The CT emission of the intermixed phase exhibits a longer lifetime than the CT exciton formed at the interface to the PEN excess phase, possibly due to a weaker Coulombic coupling.

Supporting Information Additional supporting information may be found in the online version of this article at the publisher’s web-site.

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