

Charge Recombination in CuPc/PTCDA Thin Films

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The recombination kinetics of photogenerated charge carriers in perylene-3, 4, 9, 10-tetracarboxylic dianhydride (PTCDA) and copper phthalocyanine (CuPc) thin films grown by organic molecular beam deposition have been studied using transient absorption spectroscopy. Optical excitation is observed to generate long-lived polaron states, which exhibit power law recombination dynamics on time scales from microseconds to milliseconds. Studies as a function of excitation density and temperature, and comparison between heterostructures and PTCDA single layers, all indicate that this power law behavior results from trapping of PTCDA[−] polarons in localized states, with an estimated trap state density of $\sim 6 \times 10^{17}$ polarons cm^{−3}. This recombination behavior is found to be remarkably similar to that previously observed for polymer/fullerene blends, suggesting that it may be generic to a range of semiconducting materials.

1. Introduction

Molecular thin films are showing increasing promise in optoelectronic and electronic devices such as organic light-emitting diodes (OLEDs), photovoltaics (PV), and transistors.¹ Perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) has been one of the most intensively studied materials, with research focusing on basic film properties,² steady-state and transient optical spectroscopy,^{3,4} and electronic characteristics.⁵ Copper phthalocyanine (CuPc) has also been studied in detail since it forms the basis of some of the most successful molecular PV devices reported to date, when it is used as a hole-transporting layer in conjunction with perylene derivatives⁶ or fullerene.^{7,8} CuPc/PTCDA double-layer structures have also been used successfully for PV applications and form a donor/acceptor heterojunction with exciton separation at the heterointerface.⁹

The charge and exciton dynamics in molecular thin films are crucial for an in-depth understanding of device operation.¹⁰ Positive traps within PTCDA films have been identified by electrical^{11,12} and PV device measurements,⁹ but their dynamic and spectral properties have received little attention. Charge transport and trapping have been identified in metallophthalocyanines,¹³ and exciton dissociation mechanisms have been proposed.¹⁴ However, large discrepancies between exciton diffusion lengths in phthalocyanines, obtained either by simulations¹⁵ or photocurrent experiments,^{16,17} prove that more conclusive and direct measurements are still required.

In this work, we examine the formation of charge-separated polarons in PTCDA single layers, their spectral characteristics, and their decay dynamics using transient absorption spectroscopy (TAS). The introduction of a CuPc layer and the formation of a CuPc/PTCDA heterostructure lead to an increase in the quantum yield of charge separation. Our studies focus on a

comparison of the recombination dynamics in the single-layer and double-layer structures as well as their dependence upon carrier densities and temperature. Building upon our experience of studying recombination dynamics in analogous polymer/C₆₀ films,^{19,20} we employ low-excitation intensities ($1\text{--}40\text{ }\mu\text{J cm}^{-2}$) and highly sensitive detection electronics to monitor recombination dynamics for polaron densities comparable to those generated by solar irradiation.

2. Experimental Section

The films were grown by organic molecular beam deposition (OMBD) in an ultrahigh vacuum chamber with a base pressure of $\sim 2 \times 10^{-9}$ mbar. Glass substrates ($1\text{ cm}^2 \times 2\text{ mm}$) were obtained from BDH superpremium, cleaned in a methanol sonic bath, and dried under a stream of dry nitrogen prior to transfer to the growth chamber. CuPc (Aldrich, 98%), was twice purified by train sublimation, while PTCDA (Fluka, 98%) was used as received, since it was found that the film characteristics (morphology, crystallinity, electronic absorption, and emission) were unchanged by further purification. The molecular materials were thoroughly outgassed in the vacuum chamber for at least 15 h prior to deposition and were evaporated from two separate Knudsen cells at 360 and 380 °C for CuPc and PTCDA, respectively, corresponding to a growth rate of $5\text{ }\text{\AA s}^{-1}$. The film thickness was monitored in-situ using a quartz crystal microbalance positioned near the substrate. Ex-situ thickness calibration was performed by atomic force microscopy (AFM) and also by scanning electron microscopy (SEM) measurements on cleaved silicon samples. Typical thicknesses for CuPc were between 5 and 20 nm, and the PTCDA layers were 50 nm thick. The double-layer structures were deposited in the sequence quartz/CuPc/PTCDA, and unless otherwise stated, the respective thicknesses of CuPc and PTCDA are 20 and 50 nm. All layers were grown at room temperature, leading to the α -polymorphic forms for both CuPc and PTCDA, as verified by X-ray diffraction studies on single-layer films.^{2,18} Transient absorption measurements used excitation pulses obtained from a nitrogen-

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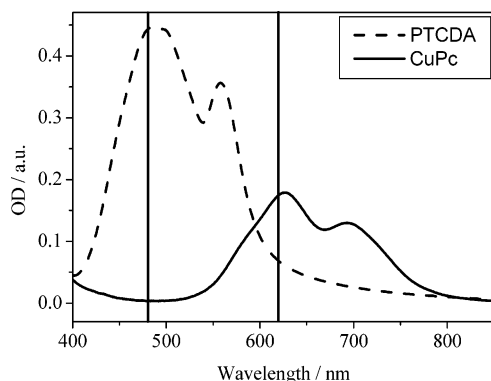


Figure 1. Electronic absorption spectra of a 50-nm-thick PTCDA single layer (dashed line) and a 20-nm-thick CuPc film (black line).

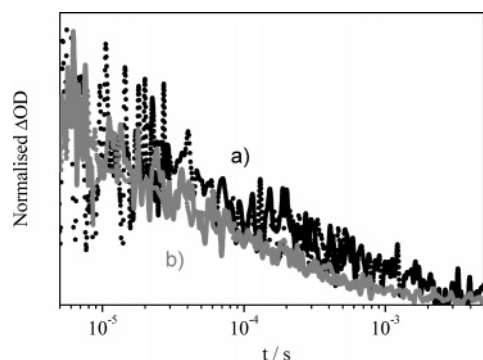


Figure 2. Transient decays of (a) a PTCDA single layer and (b) a CuPc/PTCDA double layer excited by a pulse at 620 nm and probed at 800 nm.

laser-pumped dye laser (repetition rate 4 Hz, pulse duration < 1 ns, intensity $\sim 1\text{--}50 \mu\text{J cm}^{-2}$ unless otherwise stated) and a tungsten lamp as a probe. These excitation conditions correspond to densities of absorbed photons of 6×10^{17} to $3 \times 10^{19} \text{ cm}^{-3}$. To minimize incident radiation on the sample and scatter contributions, the probe wavelength was selected by two monochromators before and after the sample. Transient decays result from an average of 300 laser shots.

3. Results and Discussion

Figure 1 shows the electronic ground-state absorption spectra of single-layer films of 20-nm CuPc and 50-nm PTCDA. Their spectral signatures are distinct, and 480 and 620 nm were chosen as the excitation wavelengths selective to PTCDA and CuPc, respectively.

Figure 2a shows the room-temperature transient absorption decay of a 50-nm PTCDA single-layer film. The absorption kinetics extend to time scales longer than milliseconds, independent of excitation wavelength, indicating long-lived photogenerated species. The intensity of the transient signal was found to decrease slightly with increasing film thickness, suggesting that the photogenerated species are created preferentially at the interfaces. Since the film is not strongly absorbing, the amount of light reaching both the PTCDA/atmosphere and PTCDA/quartz interfaces is approximately equal; it is therefore not possible to determine whether one interface leads preferentially to the formation of photogenerated species.

The decay dynamics of the transient absorption exhibit highly nonexponential (“dispersive”) behavior, extending over 3 orders of magnitude in time scale. Such dispersive dynamics suggest the transient signal should not be assigned to long-lived molecular triplet excitons. Confirmation of this point was achieved by undertaking experiments in the presence and

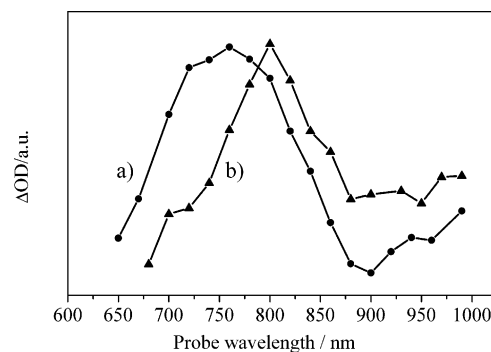


Figure 3. Transient absorption spectrum of (a) a PTCDA single layer and (b) a CuPc/PTCDA heterostructure. The spectra were averaged at a time delay of $400 \pm 100 \mu\text{s}$ after excitation at 620 nm.

absence of oxygen. The transient absorption decay dynamics of the PTCDA film under an inert argon atmosphere were found to be identical to the ones measured in ambient conditions, confirming that the photogenerated species are not due to triplet states, which would be quenched by oxygen. Rather, the transient absorption signal is assigned to long-lived PTCDA polaron states generated by dissociation of photogenerated excitons, most probably at interfacial trap sites. The oxygen insensitivity of the transient signal suggests that such trap sites are not oxygen species but rather inherent defects within the film. The observed transient signal in the PTCDA film is therefore assigned to the dissociation of PTCDA excitons at interfaces and defects, yielding charge-separated $\text{PTCDA}^+/\text{PTCDA}^-$ polarons, with the decay of the transient signal assigned to charge recombination of these photogenerated polarons.

The transient absorption spectrum of these PTCDA polarons is shown in Figure 3a, averaged at a time delay of $400 \pm 100 \mu\text{s}$ after excitation; it is broad, centered around 760 nm, and the shape is independent of excitation wavelength.

We turn now to considerations of the CuPc/PTCDA heterostructures. Transient decays contrasting the heterostructure with the PTCDA single layer are shown in Figure 2b, and the transient spectra are shown in Figure 3b. Control experiments conducted on CuPc single layers did not resolve any significant transient signals, indicating that photoexcitation of the CuPc alone did not result in significant yield of long-lived polaron states. Data are shown for the heterostructure excited at 620 nm, where the absorption of the CuPc is maximal, although the decay kinetics were found to be independent of excitation wavelength. The transient absorption spectrum of the heterostructure, as shown in Figure 3b, is shifted to longer wavelengths, consistent with the superposition of CuPc ground-state bleaching (600–750 nm) due to CuPc polaron (cation) formation upon the polaron photoinduced absorption signal. The transient signal of the heterostructures was again found to be oxygen-insensitive and cannot therefore be assigned to photogenerated triplet states. Rather, it is assigned to the generation of long-lived polaron states. On the basis of the differences in the activation energies and ionization potentials of the two layers and the difference in the transient spectra, these polarons were assigned specifically to CuPc^+ and PTCDA^- polarons. As shown in Figure 2b, the polaron decay kinetics in the heterostructure are similar to those observed for the PTCDA single layer, suggesting that in both cases the recombination dynamics of the photogenerated polarons are controlled by the diffusion of the same species, namely, PTCDA^- polarons. We discuss the nature of this diffusion process in more detail below.

For both the single-layer and heterostructure films, the decay

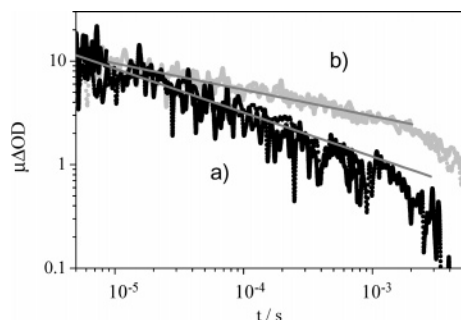


Figure 4. Transient decays of a CuPc/PTCDA double layer in a cryostat at (a) room temperature (298 K) and (b) 77 K, excited by a pulse at 620 nm and probed at 800 nm. Fits to the power law are also shown, with exponents given in the text.

dynamics are highly nonexponential. This is most clearly illustrated by the linear appearance of the decay dynamics on a log–log plot, as shown for the heterostructure in Figure 4a, which follows a power law decay of the form $\Delta OD \propto t^{-0.42}$. A similar power law has recently been observed for poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene vinylene] (MDMO–PPV)/1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C₆₁ (PCBM) blend films and assigned to the recombination of photogenerated polarons.^{19–21} The dispersive power law nature of the recombination dynamics was attributed to polaron trapping in an exponential tail of localized states extending into the band gap of the MDMO–PPV polymer. In this case, the similarity of the decay dynamics observed for the single-layer and heterostructure films suggests that in both cases the recombination dynamics are controlled by the diffusion dynamics of trapped PTCDA[−] polarons. Further confirmation of this polaron trapping/detrapping model (often referred to as the “continuous time random walk” or CTRW model²¹) was obtained from the temperature dependence of the decay dynamics, as shown for the heterostructure in Figure 4. When the sample is held at 77 K, Figure 4b, the decay is longer compared to room temperature (a) and extends to time scales longer than milliseconds, consistent with the recombination dynamics being controlled by thermally activated detrapping processes. The decay dynamics continue to follow a power law, with the exponent of the power law decay, α , decreasing from 0.42 at room temperature to ~ 0.25 at 77 K, consistent with our previous studies of MDMO–PPV/PCBM blends and in agreement with the CTRW model. The influence of background illumination on the recombination dynamics provides further insight into the population of the traps. Continuous white-light background illumination (25 mW cm^{−2}, approximately $\frac{1}{4}$ that of full solar irradiance) accelerates the recombination of CuPc⁺/PTCDA[−] polarons, with the exponent of the power law decay for the heterostructure increasing to 0.65, compared to 0.42 for measurements in the dark (data not shown). This dependence on background illumination is again remarkably similar to MDMO–PPV/PCBM blends,²⁰ and a similar interpretation can be applied. The dependence upon background illumination confirms, as we have discussed previously, that the polaron densities created by the pulsed excitation are comparable to those generated under solar irradiation. As previously, the acceleration of the recombination dynamics under background light is assigned to continuous occupation of the deepest traps available within the PTCDA. Therefore, the polarons created by the laser excitation pulse can only occupy shallower trap states, resulting in an acceleration of the recombination dynamics.

To address the yield of the polaron states and the density of polaron trap states, the transient absorption signal was measured

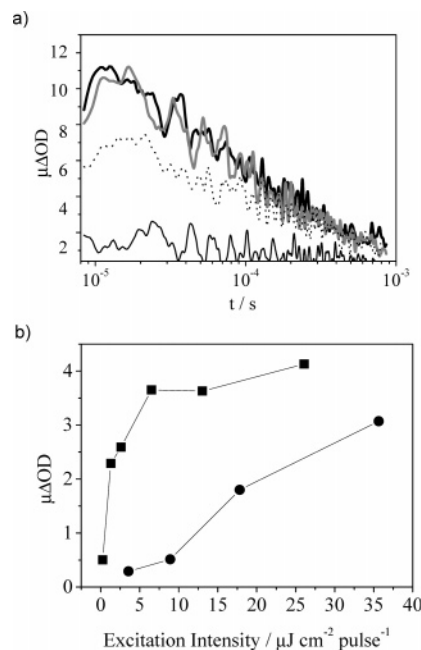


Figure 5. (a) Transient decays for a CuPc/PTCDA double-layer structure for different excitation intensities: 0.25 (black line), 1.25 (dotted line), 12.5 (thick black line), and 25 $\mu\text{J cm}^{-2} \text{ pulse}^{-1}$ (thick gray line). The samples were excited at 620 nm, and ΔOD detected at 800 nm. (b) Corresponding relative amplitude of the transient absorption signal for a PTCDA single layer (circles) and a CuPc(10 nm)/PTCDA double-layer structure (squares) as a function of laser excitation intensity. The conditions are as in (a), with signal amplitude averaged at $60 \pm 30 \mu\text{s}$ after excitation.

as a function of excitation intensity. Typical decays for a CuPc/PTCDA heterostructure are shown in Figure 5a. It is apparent that the transient signal increases in magnitude with increasing excitation intensities at low excitation densities, but becomes independent of excitation intensity at high excitation intensities. Signal amplitudes averaged at a time delay of $60 \pm 30 \mu\text{s}$ are shown in Figure 5b for both a PTCDA single layer and CuPc/PTCDA heterostructures. It is apparent that the heterostructure signal amplitude saturates at $\sim 5 \mu\text{J cm}^{-2} \text{ pulse}^{-1}$. Such saturation behavior was also observed in our previous studies of MDMO–PPV/PCBM blends and was attributed to filling of all available trap states in the material. Excitation intensities above this saturation threshold resulted in the generation of free carriers which recombine on nanosecond time scales. As such, this threshold intensity, corresponding to an effective “mobility edge” for the material, can be employed to estimate material trap density. By taking into account the density of incident photons absorbed and the probed volume of PTCDA (see details of the calculation in ref 22), and assuming a unity quantum yield for charge separation in the heterostructure, the density of PTCDA[−] traps can be derived as $\sim 6 \times 10^{17}$ polarons cm^{−3}, similar to the value of $\sim 10^{17}$ obtained in MDMO–PPV polymer blends.¹⁹ Our assumption of a high yield of long-lived polarons for this heterostructure at excitation densities below this threshold value is reasonably consistent with the magnitude of the observed transient signal,²³ and therefore with a significant proportion of the polaron recombination dynamics of this heterostructure being the micro- to millisecond dynamics reported here. It is also apparent from Figure 5b that the PTCDA single layer exhibits relatively low signal amplitudes for all excitation intensities compared to the heterostructure and no saturation behavior over the excitation intensity range employed, consistent with the expected relatively low quantum yield of charge separation in this single-layer structure. Due to this low

yield of charge separation in the single-layer structure, the excitation intensities employed are insufficient to result in full occupancy of the PTCDA[−] trap states, and therefore no saturation behavior is observed.

The similarity in behavior between vacuum-deposited CuPc/PTCDA bilayer heterostructures studied here and solution-deposited polymer/C₆₀ film blends may at first sight appear remarkable. However, we note that we have previously shown that the recombination dynamics of MDMO-PPV/PCBM films are independent of blend morphology, consistent with the recombination dynamics being controlled by the dynamics of thermal excitation from trap states within the polymer rather than by interfacial electron-transfer dynamics.¹⁹ The behavior we observe here appears to result directly from the presence of a significant tail of polaron trap states extending into the band gap of the materials. The observation of this behavior for two very distinct material systems suggests that it may be generic to a wide range of organic semiconductors. Further consideration of this issue and discussion of the materials properties resulting in this behavior will be given elsewhere.

4. Conclusions

We have identified long-lived polarons (lifetimes > milliseconds) photogenerated at defects and at the interfaces of PTCDA films. An additional CuPc layer leads to an increased yield of charge separation, resulting in the formation of CuPc⁺ and PTCDA[−] polarons. The saturation of transient absorption as a function of incident power in CuPc/PTCDA heterostructures allows us to derive the density of trapped PTCDA[−] trap states as $\sim 6 \times 10^{-17}$ polarons cm^{−3}. The deep traps observed in the molecular films are likely to limit the efficiency of charge transport but might prove beneficial for an increased exciton dissociation in the bulk of the film. Another remarkable result is the striking similarity of the photophysical trends in the molecular single- and double-layer thin films described in this paper with those observed for polymer/molecule blend structures. This implies that universal models can be applied to organic photovoltaic devices.

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- (22) At saturation, the $5 \mu\text{J cm}^{-2} \text{ pulse}^{-1}$ incident intensity at 620 nm corresponds to 13×10^{12} photons cm^{−2} pulse^{−1} arriving on the heterostructure. The optical density of the heterostructure at 620 nm is ~ 0.14 , as can be derived from the addition of the single-layer ground-state absorption spectra for the individual components in Figure 1. This corresponds to the absorption of 28% of the incident photons. Since the probed volume of PTCDA is 5×10^{-6} cm³, the density of PTCDA traps is $\sim 6 \times 10^{17}$ polarons cm^{−3}.
- (23) Determination of the quantum yield of the long-lived polarons addressed in this study is difficult to quantify in the absence of an independent measurement of the molar absorption coefficient of PTCDA anions. However, the magnitude of our absorption transients at 800 nm for the CuPc/PTCDA heterostructure is consistent with a significant proportion of the photogenerated polarons decaying on the micro- and millisecond time scales addressed here. Further studies extending these studies to nanosecond time scales are currently in progress. For the PTCDA single-layer structures, the smaller magnitude of the absorption transients is indicative of an approximately 10-fold lower yield of long-lived polarons.