

Efficient charge generation from triplet excitons in metal-organic heterojunctionsFriedrich Roth,^{1,2} Stefan Neppel,^{3,*} Andrey Shavorskiy,^{3,†} Tiberiu Arion,^{2,‡} Johannes Mahl,³ Hyun Ook Seo,^{2,§} Hendrik Bluhm,³ Zahid Hussain,⁴ Oliver Gessner,^{3,||} and Wolfgang Eberhardt^{2,4,5,¶}¹*Institute for Experimental Physics, TU Bergakademie Freiberg, D-09599 Freiberg, Germany*²*Center for Free-Electron Laser Science / DESY, D-22607 Hamburg, Germany*³*Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*⁴*Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*⁵*Institute of Optics and Atomic Physics, TU Berlin, D-10623 Berlin, Germany*

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The success of many emerging molecular electronics concepts hinges on an atomistic understanding of the underlying electronic dynamics. We employ picosecond time-resolved x-ray photoemission spectroscopy (tr-XPS) to elucidate the roles of singlet and triplet excitons for photoinduced charge generation at a copper-phthalocyanine–C₆₀ heterojunction. Contrary to common belief, fast intersystem crossing to triplet excitons after photoexcitation is not a loss channel but contributes to a significantly larger extent to the time-integrated interfacial charge generation than the initially excited singlet excitons. The tr-XPS data provide direct access to the diffusivity of the triplet excitons $D_{\text{CuPc}} = (1.8 \pm 1.2) \times 10^{-5} \text{ cm}^2/\text{s}$ (where CuPc is copper-phthalocyanine) and their diffusion length $L_{\text{diff}} = (8 \pm 3) \text{ nm}$.

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Metal-organic heterojunctions, such as metal-phthalocyanine (MePc) donor–C₆₀ acceptor systems [1–5], provide an important platform to advance understanding the electronic dynamics underlying many emerging molecular electronics concepts for photochemical and photovoltaic applications [6–16]. The prevailing picture for efficient charge generation is through singlet-exciton dissociation at the donor-acceptor interface within less than 1 ps after photoexcitation in order to avoid photon energy loss to nondissociating triplet excitons by fast intersystem crossing [17,18]. We employ picosecond time-resolved x-ray photo-emission spectroscopy (tr-XPS), a technique of choice for measuring electronic structure with elemental and chemical site specificity [19,20], to directly determine the triplet-exciton diffusivity and the ratio of singlet-and triplet-exciton dissociation efficiencies in a copper-phthalocyanine (CuPc)–C₆₀ planar heterojunction (PHJ). Contrary to common belief, ultrafast intersystem crossing from the initially excited singlet excitons to triplet excitons is not a loss channel but the long-lived triplet excitons contribute to a significantly larger extent to the time-integrated interfacial

charge than the short-lived singlet excitons. The findings are important for tailoring organic heterojunction devices and provide a link between femtosecond-range interfacial and picosecond-to-nanosecond-range bulk dynamics in organic semiconductors.

Optically induced charge-transfer (CT) dynamics in MePc–C₆₀ heterojunctions are commonly initiated by excitations from the highest occupied molecular orbitals (HOMO) to the lowest unoccupied molecular orbitals (LUMO) of the MePc chromophore. They are followed by exciton delocalization and/or diffusion throughout the donor domain, charge separation at the MePc–C₆₀ interface, and electron injection into C₆₀ LUMO polaron levels [1,3,4,8,10,15,16,18]. Based on extensive ultrafast optical transient absorption and two-photon photoemission studies, a picture has emerged that charge generation in these systems occurs only within the first ~1 ps after photoexcitation and is to a large extent limited by efficient intersystem crossing from the initially excited singlet states to the lower-lying triplet-state manifold followed by intramolecular recombination [2,17,18]. The short singlet-state lifetimes, in combination with an apparently strongly disfavored injection from triplet states and limited electronic coupling between bulk and interfacial donor molecules, have led to the suggestion that significant contributions to charge generation may be limited to only ~1–2 monolayers (MLs) of chromophores in the immediate vicinity of the interface [17,18]. Since typical bulk heterojunction domain sizes are on the order of tens of nanometers (i.e., 10s to ~100 MLs), this restriction seems to indicate a major, fundamental limitation to the amount of charge that may be generated from MePc–C₆₀-based heterojunction designs.

Here, we elucidate the roles of bulk and interfacial excitons for charge generation in MePc–C₆₀ heterojunctions by probing photoinduced electronic dynamics in planar bilayer

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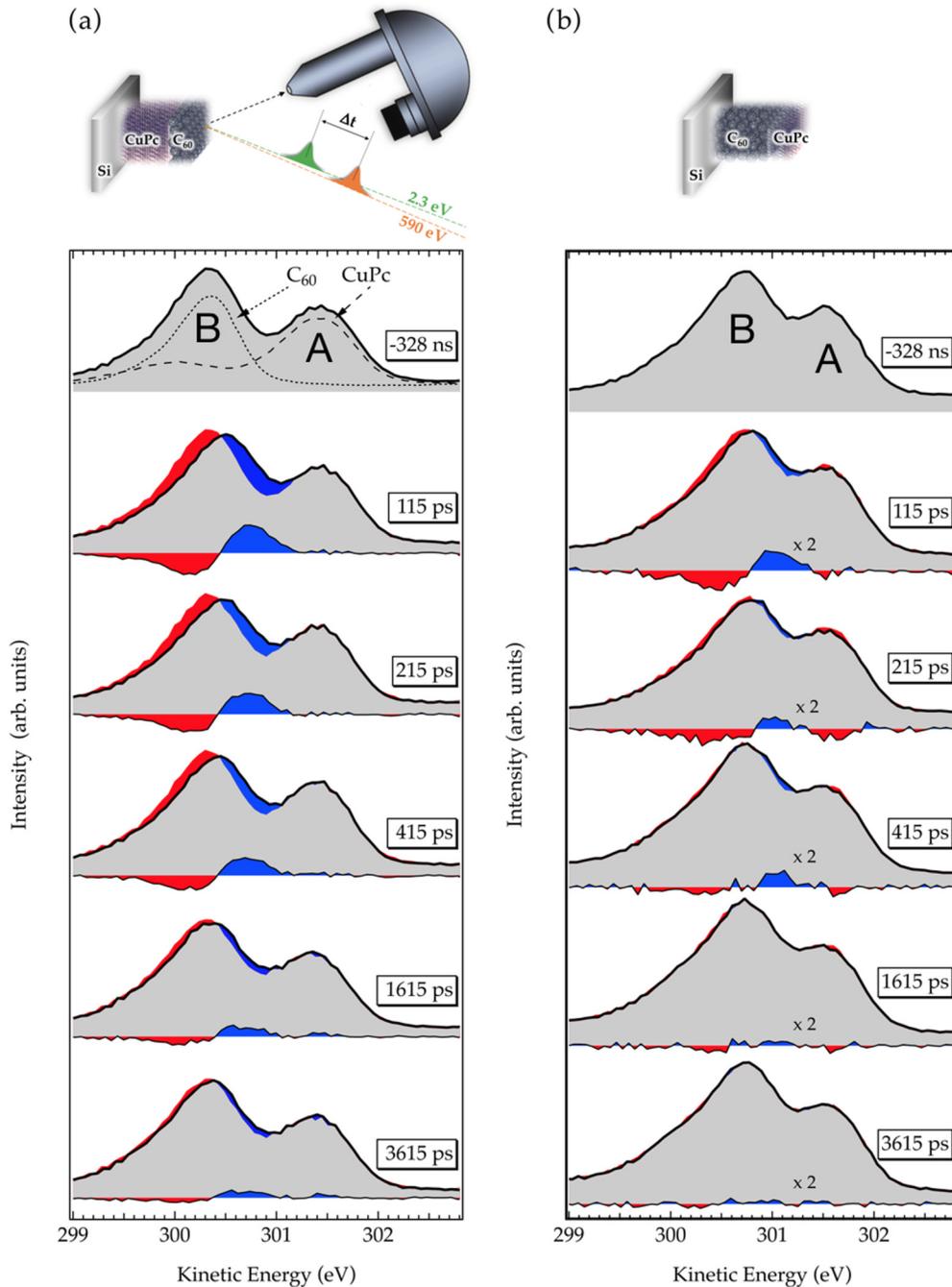


FIG. 1. Time-resolved XPS spectra for planar heterojunction configurations of (a) ~ 2 MLs of C_{60} deposited on top of a thin film of CuPc and (b) ~ 2 MLs of CuPc atop ~ 8 MLs of C_{60} . Pump-probe time delays are indicated in each panel. To highlight the photoinduced spectral changes, red and blue areas indicate missing and additional intensities, respectively, relative to the spectra recorded at a delay of -328 ns. Additionally, the difference spectra are shown and they are magnified by a factor of 2 in (b). The dotted and dashed spectra in the -328 -ns panel of (a) are from pristine films of C_{60} and CuPc, respectively. All films were supported by n -doped Si(100) substrates.

systems of CuPc and C_{60} molecules using picosecond tr-XPS [19–21] (Fig. 1). Two types of CuPc- C_{60} heterojunctions are studied under virtually identical experimental conditions. The first sample consists of ~ 2 MLs of C_{60} deposited on top of ~ 5 – 20 MLs of CuPc (“ $C_{60}/CuPc$ ”), the second sample of ~ 2 MLs of CuPc atop ~ 8 MLs of C_{60} (“CuPc/ C_{60} ”). In both cases, n -doped Si(100) substrates are used to support the films and the bottom layer is prepared with sufficient thickness to eliminate XPS signal contributions from the interface with the

Si substrate. The CuPc chromophores are excited using 10-ps-long pump laser pulses with a center wavelength of 532 nm (2.3-eV photon energy). Electronic dynamics are probed by monitoring the time-dependent carbon K -shell photoemission from the samples, using ~ 70 -ps-long x-ray pulses from the Advanced Light Source at a photon energy of 590 eV. See Secs. I and II of the Supplemental Material [22] for details of the sample preparation and the pump-probe experiment. Figures 1(a) and 1(b) show tr-XPS spectra of the $C_{60}/CuPc$ and

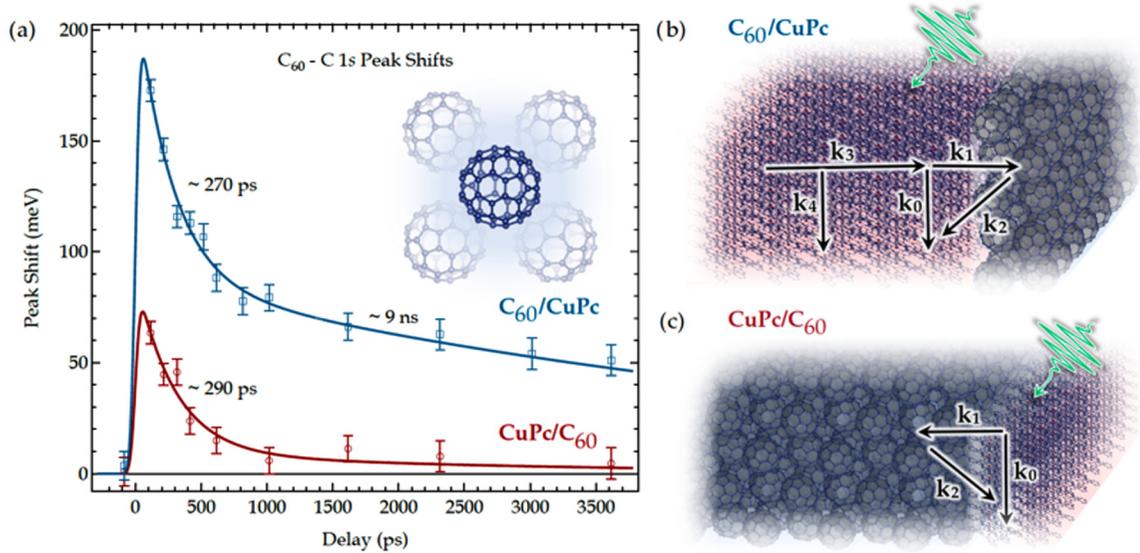


FIG. 2. (a) Temporal evolution of C_{60} -C $1s$ peak shift for $C_{60}/CuPc$ (blue squares) and $CuPc/C_{60}$ (red circles) heterojunctions. Symbols and error bars indicate measurements with $\pm 1\sigma$ uncertainties. Solid lines are the result of a fit to a coupled rate equation model taking into account the energy- and charge-transfer processes indicated in (b) and (c). Note that only $\tau_2 = 1/k_2 = (280 \pm 40)$ ps and $\tau_3 = 1/k_3 = (9 \pm 4)$ ns are derived from the fit while all other rates are known from literature. See text for details.

$CuPc/C_{60}$ samples, respectively, at a variety of time delays as indicated. The spectra shown in the uppermost two panels of Fig. 1(a) are based on data previously presented in Ref. [19].

The ground-state $C 1s$ core-level spectra recorded 328 ns before laser excitation agree qualitatively with previously recorded steady state $C 1s$ spectra of the same system [38]. Two peaks with well-separated maxima at 301.4 eV (A) and 300.3 eV (B) kinetic energy are readily distinguished for the $C_{60}/CuPc$ sample. Importantly, peak A is almost entirely associated with CuPc, while peak B is predominantly related to photoemission from C_{60} as indicated by the dashed and dotted spectra of the separate components in Fig. 1(a), which were recorded using pristine films of CuPc and C_{60} , respectively [19]. The ground-state $C 1s$ binding energies associated with C_{60} and CuPc in the $CuPc/C_{60}$ system are reduced by ≈ 0.4 and ≈ 0.1 eV, respectively, compared to the corresponding binding energies in the $C_{60}/CuPc$ system. This is largely attributed to a static dipole shift between the two layers as previously reported for heterostructures [39] and ordered films [40]. In addition, there could also be a screening contribution from the Si substrate when it is in contact with the C_{60} film.

For both heterojunction configurations, the laser-induced dynamics only affect peak B, which exhibits a significant shift to higher kinetic energies upon excitation, while the binding energy of peak A remains constant. The shift of peak B is a signature of electron transfer from the chromophore CuPc to the electron acceptor C_{60} and a reflection of the average concentration of charges within the C_{60} domain, as described in our previous work [19]. A crucial observation is that the amplitude and temporal evolution of the C_{60} -C $1s$ photoline shift differ significantly for the two heterojunction configurations as illustrated in Fig. 2.

Blue squares and red circles in Fig. 2(a) correspond to the time-dependent shifts of the C_{60} -C $1s$ photoline for $C_{60}/CuPc$ and $CuPc/C_{60}$ samples, respectively. For both PHJ arrangements, the C_{60} peak in the excited systems is shifted

to higher kinetic energies, i.e., lower binding energies. The extent, however, of the transient peak shifts and, in particular, their dynamic evolution differ significantly. For the $C_{60}/CuPc$ system, peak B shifts towards higher kinetic energies by ≈ 170 meV immediately after optical excitation while the $CuPc/C_{60}$ system exhibits a much smaller maximum peak shift of only ~ 65 meV. In both cases, the shift decreases rapidly within a few hundred picoseconds after excitation. On longer timescales, a long-lived dynamic component is very prominent in the $C_{60}/CuPc$ system but virtually absent in the $CuPc/C_{60}$ system.

We note that both CuPc and C_{60} absorb at 2.3 eV photon energy and, thus, the pump pulse induces electronic excitations in both domains. However, as discussed in more detail in Sec. IV of the Supplemental Material [22], the site-specific photoline shift is predominantly associated with core-hole screening effects by delocalized charges in the C_{60} acceptor domain after electron injection from the CuPc donor [19]. The peak shift is, therefore, a site-specific probe of the average amount of injected charge per C_{60} molecule. Neither a pure CuPc nor a pure C_{60} film deposited on the Si(100) substrate exhibits any photoinduced peak shifts beyond the independently quantified photovoltage response of the n -doped substrate [19]. This strongly suggests that CT dynamics at both the $CuPc/Si$ and the C_{60}/Si interface are of minor importance for the processes discussed herein. Instead, electronic dynamics within the organic donor/acceptor system must be responsible for the observed trends. In order to interpret the evolution of the average charge within the C_{60} acceptor phase for both heterojunction configurations within a consistent physical picture, we employ a set of first-order coupled rate equations based on the model illustrated in Fig. 2(b).

Within this model, the rates k_i are associated with the following processes: intramolecular relaxation back to the ground state within interfacial donors (k_0), charge injection from excited interfacial donors (k_1), interfacial acceptor-donor

electron-hole recombination (k_2), exciton migration from the donor bulk to interfacial layers (k_3), and relaxation to the ground state within the donor bulk (k_4). The comprehensive literature on relaxation dynamics in CuPc and CuPc- C_{60} systems together with self-consistency arguments provides all but two of the five rate constants in Fig. 2(b) (see Sec. III of the Supplemental Material [22] for details). The remaining two rates, k_2 and k_3 , are derived from a well-defined fit of both the C_{60}/CuPc and CuPc/C_{60} data sets as represented by the blue and red solid lines, respectively, in Fig. 2(a).

The procedure reveals the timescales for exciton bulk-to-interface migration $\tau_3 = 1/k_3 = (9 \pm 4)$ ns and for interfacial electron-hole recombination $\tau_2 = 1/k_2 = (280 \pm 40)$ ps. The differences between the dynamic trends observed in the two bilayer systems follow naturally from the described model. With only ~ 2 MLs of CuPc in the CuPc/C_{60} system, contributions of the slow bulk component to the transients are strongly suppressed while the interfacial electron-hole recombination rate is similar for both systems [Fig. 2(c)]. Note that no bias voltage has been applied in this study. Thus, injected charges are not expected to migrate far away from the interface due to their Coulomb interaction with holes in the donor. Nevertheless, the average amount of injected charge per C_{60} molecule is expected to be higher for the C_{60}/CuPc system as compared to the CuPc/C_{60} system at any given time due to the different ratios of donor and acceptor molecules within the photoactive regions of the samples. This may explain the different amplitudes of the C_{60} -C 1s peak shifts for the two different sample configurations.

Comparison of the intersystem crossing time of ≈ 500 fs in CuPc [5,17,18] with the 9-ns average excitation transfer time within the CuPc domain strongly suggests that the vast majority of donor states contributing to the long-term charge component must have relaxed to the triplet manifold. Based on ultrafast measurements on few-monolayer systems and energy considerations, injection from these states is generally considered extremely disfavored [17,18]. However, using a combination of several complementary spectroscopic techniques, Piersimoni *et al.* found that interfacial triplet excitons in a $\text{CuPc}-C_{60}$ PHJ may dissociate into separate charges with an efficiency comparable to that of singlet-exciton dissociation in a metal-free $\text{H}_2\text{Pc}-C_{60}$ PHJ [41]. The results presented here are consistent with these findings and suggest that for extended CuPc donor structures, injection from triplet excitons is actually the dominant charge-generation pathway while for few-monolayer structures it is much less prominent since it cannot compete with the significantly faster interfacial dynamics. Note that the exact mechanism for charge injection from triplet excitons is unknown and the rate may have any value $\gg (100 \text{ ps})^{-1}$ [17,41]. However, as discussed in Sec. III of the Supplemental Material [22], this does not affect the conclusions presented above and, for simplicity the same injection rate is applied for singlet and triplet excitons.

Due to the sensitivity of the tr-XPS experiment to both singlet- and triplet-exciton dissociation at the interface, the ratio of charge generation from both types of excitation can be directly determined. A component analysis of the fit in Fig. 2(a) suggests that bulk triplet states generate approximately ten times more charges in the acceptor than interfacial singlet states for the C_{60}/CuPc sample. In other words, on

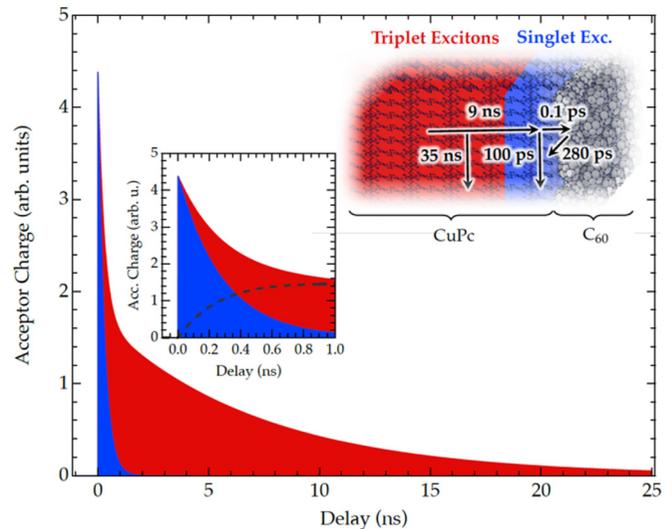


FIG. 3. Photoinduced charge generation in a planar $\text{CuPc}-C_{60}$ heterojunction. Blue- and red-shaded areas correspond to the time-dependent contributions to the acceptor charges from singlet- and triplet-exciton splitting, respectively. The triplet-exciton contribution is also plotted separately as a dashed line in the inset.

ultrafast timescales, injection from interfacial singlet states is the dominating charge-generation mechanism. On longer timescales, however, and in applicationlike, extended donor-acceptor systems, the integrated charge generated from bulk triplet states is significantly larger. These findings are illustrated in Fig. 3. It shows the calculated time-dependent contributions of singlet- and triplet-exciton dissociation to interfacial charge generation as blue- and red-shaded curves, respectively. Note that interfacial CT states may be transiently populated as well, but cannot be detected in the experiment due to their short ($\lesssim 1$ ps) lifetimes [17,18].

The maximum amount of charges that may be created via the triplet channel is given by the ratio of the bulk triplet-exciton transport rate and the bulk triplet-relaxation rate. This is the well-known “rule of thumb” for the design of bulk heterojunctions that requires the typical dimension of the donor phase to be on the order of the exciton diffusion length L_{diff} , i.e., the distance an exciton may migrate during its lifetime. Any larger donor domains lead to a lower light-to-charge conversion efficiency as absorbed photon energy is increasingly lost to exciton recombination.

In order to gain deeper physical insight into the charge-carrier dynamics, we analyze the tr-XPS results based on established models for energy transfer in organic semiconductors as well as previously determined exciton diffusion lengths. The timescale τ for exciton diffusion across a distance L is given by

$$\tau = \frac{L^2}{D}, \quad (1)$$

where D is the diffusion coefficient (diffusivity) that describes the mobility of excitons inside a material [8,17]. Exciton diffusion in organic semiconductor films proceeds via different mechanisms for singlet and triplet excitons. Singlet excitons migrate via Förster resonant energy transfer, triplet excitons via Dexter energy transfer [42–44]. The diffusion

coefficients D_D and D_F associated with Dexter- and Förster-type energy transport, respectively, usually differ significantly with $D_D \ll D_F$. Nevertheless, typical diffusion lengths of triplet excitons are often comparable to those of singlet excitons due to orders of magnitude longer triplet lifetimes [42,43,45]. With an average diffusion distance $L = (4 \pm 1)$ nm from the CuPc bulk to the C_{60} /CuPc interface and an average diffusion timescale of $\tau_3 = k_3^{-1} = (9 \pm 4)$ ns, Eq. (1) yields a diffusion coefficient for exciton migration in the CuPc domain of $D_{\text{CuPc}} = (1.8 \pm 1.2) \times 10^{-5}$ cm²/s. Note that this is a direct experimental determination of the exciton diffusivity within a CuPc donor domain.

The magnitude of D_{CuPc} is quite small for organic semiconductors, as expected for triplet-exciton diffusion [42]. While there are no CuPc diffusivity values available to directly compare the tr-XPS result with, several studies measured the exciton diffusion length of CuPc, yielding typical values for L_{diff} between 5 and 10 nm [41,46–49]. Combined with measured triplet-exciton lifetimes between ~ 9 and 35 ns [5,50], the range of possible CuPc diffusivities may be estimated by Eq. (1) to $D_{\text{CuPc}} \sim (0.7\text{--}11) \times 10^{-5}$ cm²/s. The diffusivity determined here is clearly within these boundaries but the direct access to the quantity in the tr-XPS experiment improves its accuracy significantly. Vice versa, the diffusion coefficient D_{CuPc} determined here and an exciton lifetime of 35 ns, as employed in the rate equation analysis, correspond to a diffusion length of $L_{\text{diff}} = (8 \pm 3)$ nm, in good agreement with most other measurements [41,46–48].

We note that alternative relaxation mechanisms have been examined but were found to be incompatible with the observed tr-XPS trends. Bartelt *et al.* observed nanosecond-range decay timescales in optically excited ZnPc/ C_{60} blends using transient terahertz spectroscopy [4]. The slowly decaying photoconductivity of the samples was interpreted as the signature of a diminishing electron concentration in the C_{60} phase due to nanosecond-scale recombination dynamics. In the case of the two heterojunction systems studied here, this interpretation is not applicable since it does not explain the vanishing long-term component in the CuPc/ C_{60} system. In fact, if the long-term component were associated with recombination dynamics, it would be expected to be more pronounced for the CuPc/ C_{60} system since the electrons would probably spend more time in the more-extended C_{60} acceptor phase compared to the C_{60} double layer of the C_{60} /CuPc system.

We have also considered the possibility that CT dynamics at the interface between the molecular films and the Si substrate may have an impact on the measurements. However, as noted above, neither a pure film of CuPc nor a pure film of C_{60} deposited on the substrate exhibits any peak shifts beyond the independently measured photovoltage response of the *n*-doped Si wafer [19]. This observation strongly suggests a minor role of CT between the Si substrate and the molecular adsorbates. We, nevertheless, evaluated the concept that the slow component in the C_{60} -C 1s peak shifts may be associated with discharging of the C_{60} electron acceptor instead of exciton transport in the CuPc electron donor. In this case,

the key idea to explain the lack of the long-term component in the CuPc/ C_{60} sample would be a more efficient charge extraction from the C_{60} domain across two interfaces (C_{60} -Si and C_{60} -CuPc) for the CuPc/ C_{60} sample compared to just one C_{60} -CuPc interface for the C_{60} /CuPc sample. However, this scenario would lead to two different monoexponential decay trends for the two sample configurations instead of the observed biexponential decays with varying relative contributions of slow and fast dynamics.

Note that the insight into the charge-carrier generation dynamics in this heterojunction system has been enabled by the ability to simultaneously determine both the length- and timescales of triplet-exciton migration. The length scale is defined by the sample preparation and characterization technique and the timescale is accessible through the simultaneous temporal sensitivity and site specificity of the x-ray probing technique. The experiment also gives direct access to the timescale for interfacial electron-hole recombination $1/k_2 = (280 \pm 40)$ ps at the CuPc- C_{60} interface, which is on the same order of magnitude as recombination timescales in other organic heterojunction systems employing fullerene-based acceptors [51,52]. The amount of information on interfacial energy- and charge-transfer dynamics gained in a single tr-XPS experiment is quite remarkable. Future studies will take advantage of this capability and translate it to even more extensive temporal and spatial scales. In particular, next-generation high repetition rate x-ray free electron laser (XFEL) light sources such as the European XFEL and the upgraded Linac Coherent Light Source (LCLS II) will provide excellent conditions to expand the reach of the method into the femtosecond domain such that virtually all relevant rates across multiple scales can be determined by a series of experiments at a single light source.

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