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Efficient Charge Generation from Triplet Excitons in Metal-Organic Heterojunctions

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I. Sample preparation

Heterojunction samples were prepared by in-situ sequential evaporation on a pre-cleaned and annealed n-doped Si(100) wafer. They consisted of approximately two monolayers (MLs) of C_{60} deposited on top of a ~ 6 nm (~ 5 -20 MLs) thick film of CuPc for the first sample (C_{60}/CuPc), and about 2 MLs of CuPc atop a ~ 6 nm (~ 8 MLs) thick film of C_{60} for the second sample (CuPc/C_{60}). The upper layer (C_{60} or CuPc, respectively) thickness was estimated by the relative intensities of the CuPc and C_{60} XPS signals, similar to earlier reports [1,2]. A careful sample characterization was performed prior to the pump-probe experiments to ensure that neither sample configuration was subject to any time-averaged charging effects.

II. Pump-probe experiment

The time-resolved XPS experiments were performed at Beamline 11.0.2 of the Advanced Light Source (ALS), using the High-Pressure Photoemission Spectroscopy (HPPEs) endstation [3-5]. The ALS was operated in two-bunch filling mode with a bunch-to-bunch spacing of 328.2 ns and a pulse width of ~ 70 ps [6,7]. The pump laser system provided 10 ps long pulses at a wavelength of 532 nm. The laser was operated at a repetition rate of 126.9 kHz and synchronized to the ALS X-ray pulse train [4,5].

The absolute pump-probe time delay and the temporal resolution were calibrated by performing a laser/X-ray cross-correlation measurement using the ultrafast transient surface photovoltage (SPV) response of a clean Si(100) substrate [4,6]. A fit of the SPV response to a Gauss error function defines the position of zero delay (t_0) within <10 ps and indicates an experimental time resolution of 69 ps (Full-width-at-half-maximum, FWHM), corresponding to

the bunch length of the ALS [7].

The laser spot size was $450\ \mu\text{m} \times 450\ \mu\text{m}$ with a synchrotron beam spot size of $70\ \mu\text{m} \times 70\ \mu\text{m}$, ensuring good spatial overlap and homogeneous excitation conditions. The pump laser fluence on target was $\sim 1\ \text{mJ}/\text{cm}^2$. The samples were continuously scanned during the experiment in order to mitigate the impact of sample damage effects. The scan rate was calibrated by performing damage tests on sacrificial areas of the samples prior to recording the pump-probe data.

III. Data analysis

The pump-probe time-delay dependent shifts of peak B are obtained by a fit procedure that employs the ground state spectrum in the range of peak B as a template and applies a rigid shift and an amplitude factor close to 1 as free fit parameters to approximate the spectra after photoexcitation. In addition to the relative peak shifts due to electronic dynamics within the CuPc-C₆₀ heterojunction, the surface photovoltage response of the Si substrate induces a rigid shift of the entire spectrum, which is independently characterized and taken into account during the analysis as described previously [1]. No laser-induced peak shift beyond the SPV response of the Si substrate is observed for either a pure film of CuPc or a pure film of C₆₀.

The data presented in Fig. 2a of the main manuscript are interpreted by means of a system of coupled 1st order rate equations taking into account various relaxation rates as illustrated in Fig. 2b. Singlet-triplet intersystem crossing timescales in CuPc are on the order of $\sim 500\ \text{fs}$ [8-10], which is essentially instantaneous within the temporal resolution of this experiment and can be neglected in the formulation of the rate equations. Charge separation by exciton splitting within the CuPc bulk is expected to be negligible [11-13]. As noted in the main

text and discussed in more detail in section IV, only processes are modeled where the 532 nm pump pulses lead to an initial population of singlet-excited CuPc chromophores and subsequent exciton relaxation, migration, and interfacial dissociation leads to charge injection into the C₆₀ acceptor domain. Based on these definitions and boundary conditions, the instantaneous amount of donor excitations in the bulk region, $B(t)$, and interfacial region, $D(t)$, and the amount of charges $A(t)$ in the acceptor are described by:

$$B(t) = B_0 \exp(-(k_3 + k_4)t) \quad (1)$$

$$D(t) = B_0 \frac{k_3}{(k_0 + k_1) - (k_3 + k_4)} [\exp(-(k_3 + k_4)t) - \exp(-(k_0 + k_1)t)] \\ + D_0 \exp(-(k_0 + k_1)t) \quad (2)$$

$$A(t) = B_0 \frac{k_1 k_3}{(k_0 + k_1 - k_3 - k_4)(k_2 - k_3 - k_4)} [\exp(-(k_3 + k_4)t) - \exp(-k_2 t)] \\ + \left[D_0 \frac{k_1}{(k_2 - k_0 - k_1)} - B_0 \frac{k_1 k_3}{(k_0 + k_1 - k_3 - k_4)(k_2 - k_0 - k_1)} \right] \\ \cdot [\exp(-(k_0 + k_1)t) - \exp(-k_2 t)] \quad (3)$$

Evidently, the description of the transient acceptor charge $A(t)$ according to Eq. (3) contains a significant number of adjustable parameters. A free fit of this description to the data shown in Fig. 2a does not yield any relevant physical information since a variety of parameter combinations provide comparable fit results. Instead, we resort to the available literature that

provides enough boundary conditions for parameters k_0 , k_1 , and k_4 , such that the remaining degrees of freedom k_2 and k_3 are sufficiently restricted to gain further insight into the energy- and charge-transfer dynamics of the two bi-layer systems.

Among the various rate constants illustrated in Fig. 2b, the interfacial charge-injection rate k_1 and the intramolecular relaxation rate k_0 have been subject to particularly intense studies using ultrafast spectroscopy techniques. Based on the works of Dutton, Robey, Zhu, Toney and others [9,14-16], we assign values of $k_0=(100 \text{ ps})^{-1}$ and $k_1=(100 \text{ fs})^{-1}$ for intramolecular relaxation within the first ~ 1 -2 MLs of interfacial donors and interfacial charge injection, respectively. McVie et al. [17] and Caplins et al. [8] found triplet state lifetimes of CuPc between ~ 9 ns and 35 ns, which define a reasonable range for the values of k_4 . Concerning the model's dynamic rates, this procedure leaves only the average bulk-to-surface excitation transport rate k_3 and the interfacial electron-hole recombination rate k_2 to be determined based on a fit of the data in Fig. 2a. Furthermore, the ratio of initially excited donor bulk and donor interfacial states is expected to differ by at least an order of magnitude for the two sample configurations considering the different numbers of bulk CuPc molecules within the pump laser path. This condition is used to define the starting values of B_0 and D_0 in the fit procedure, and to narrow down the value of k_4 to $(35 \text{ ns})^{-1}$. The apparatus function of the experiment is implemented in the fit procedure by convoluting the instantaneous charging function $A(t)$ (Eq. 3) with a 70 ps wide (FWHM) Gaussian function.

Note that the exact mechanism and the rate for charge transfer from interfacial triplet excitons is unknown [18]. However, in order to facilitate efficient triplet exciton dissociation as observed by Piersimoni et al. [18] and in our work, the charge transfer rate has to be large compared to the triplet relaxation rate, which essentially corresponds to the effective

intramolecular relaxation rate $k_0=(100 \text{ ps})^{-1}$ [9]. Within the presented rate equation model, the absolute value of the triplet exciton dissociation rate has no significant impact on the presented results as long as it is large compared to the relaxation rate. For simplicity, we have therefore applied the same charge injection rate for both singlet and triplet excitons, $k_1=(100 \text{ fs})^{-1}$.

IV. Excitations and line shifts

Thin films of both CuPc and C_{60} exhibit noticeable absorption at 2.3 eV [10,19,20], thus, the pump pulse induces electronic excitations in both domains. However, while excitations in the CuPc donor domain are the driver of the dynamics discussed herein, there is no indication that excitations in the C_{60} acceptor domain have any impact on the observed C1s line shifts and their physical interpretation on picosecond to nanosecond timescales. We re-emphasize that the critical line shifts (beyond the SPV response of the Si substrate) affect only the C1s peak associated with the C_{60} domain but not the CuPc domain. If C_{60} excitations would affect these peak shifts, the effects should be particularly prominent for pristine C_{60} films. However, as described in [1] and the main text, this is not the case. Indeed, the C_{60} -C1s peak shift is *only* observed in the CuPc- C_{60} heterojunction configuration but not for the pristine C_{60} film, which strongly indicates that excitations within the C_{60} domain have negligible impact on the dynamics discussed herein.

This conclusion is further supported by the results presented in the main text. The C_{60} -C1s line shifts are significantly larger and contain a long-lived component for the configuration with an only ~ 2 ML thick C_{60} domain on top of ~ 5 -20 ML thick CuPc film while they are significantly smaller and exhibit no long-lived component for the much more extended, ~ 8 ML thick C_{60} film covered by ~ 2 ML of CuPc. This behavior is consistent with the presented model

but not with a significant contribution from C_{60} excitations to the observed line shifts.

Additional evidence for these conclusions is provided by the results of a very recent experiment performed at the FLASH free electron laser. In this experiment, 100 fs long pump pulses with a central wavelength of 775 nm (1.6 eV photon energy) are used to excite planar $C_{60}/CuPc$ heterojunctions and pristine C_{60} and CuPc films prepared in the same fashion as in the ALS experiment. Note that only CuPc absorbs at this pump photon energy while C_{60} does not [10,19,20]. The photoinduced dynamics are probed by 200 fs long X-ray pulses with a photon energy of 496-498 eV. The trXPS fingerprints induced by excitation with 1.6 eV photons are very similar to those in the ALS measurement. In particular, no C1s line shifts are observed for pristine C_{60} and pristine CuPc films but a distinct shift of the C_{60} -C1s line emerges for the heterojunction configuration. This strongly suggests that the C_{60} -C1s line shift indeed predominantly reflects dynamics originating from excitations in the CuPc domain. A detailed analysis of the FLASH data is ongoing and will be the subject of a future publication.

We speculate that the root cause for the selectivity of the observed trXPS response regarding different excitations lies in the different natures of C_{60} electronic configurations and/or dynamics induced by charge transfer and by direct photoexcitation. The detected trXPS signal corresponds to a rigid shift of the entire C_{60} -C1s photoline, which is indicative for an underlying electronic configuration that is delocalized across the sample area probed by the X-ray pulse. A typical example for such a situation is the photo-induced bending or flattening of electronic bands in a semiconductor material toward an interface. These dynamics typically affect all probed atoms simultaneously and, therefore, lead to rigid photoline shifts [5,6,21,22]. In contrast, localized electronic excitations, such as excited molecular valence orbital configurations in films of dye-sensitized nanocrystals [23] or self-assembled monolayers of organic molecules [24] lead

to fractional line shifts, usually observable as peak shape variations, since only the photoelectron signals associated with the excited molecules exhibit a transient response.

Based on our previous, femtosecond time-resolved two-photon photoemission (2PPE) work on films of C_{60} , one expects that direct photoexcitation of the C_{60} domain into LUMO/LUMO+1 bands is followed by relaxation into localized excitons on ≤ 100 ps timescales [25,26]. Thus, if direct photoexcitation of C_{60} would lead to a prominent trXPS response in the ALS experiment, a fractional line shift would be expected that typically manifests itself in a change of the peak shape [23,24]. Instead, a rigid shift of the entire peak is observed, which is more consistent with the concept of a delocalized electronic configuration that may result from injecting electrons into the LUMO/LUMO+1 bands of the C_{60} domain via charge transfer from the CuPc donors. These “additional” electrons do not recombine within in the C_{60} domain to form localized electron-hole pairs but instead return to the CuPc domain to neutralize the donor holes, maintaining their delocalized nature throughout most of the injection/recombination cycle. Within this picture, the delocalized electron density leads to enhanced screening of C1s core holes in the C_{60} domain and a corresponding shift of the C_{60} -C1s photoline to higher kinetic energies, as observed in the experiment.

We note that we cannot exclude that localized C_{60} excitations may also lead to minor contributions to the trXPS response. However, at a pump laser fluence of ~ 1 mJ/cm², we expect that only a few percent of the C_{60} molecules are directly excited [27], which is probably too low for a reliable detection of corresponding spectral line shape changes in the current experiment. By contrast, the rigid shifts induced by a delocalized response are readily apparent.

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