Supporting information for:

Ultrafast Charge-Transfer Exciton Dynamics
in C$_{60}$ Thin Films

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Figure S1: Using a fs laser amplifier and HHG in a bichromatic pump-probe setup, we perform trARPES studies of a C\textsubscript{60}/Ag(111) sample. a The high photon energy of our 22.2 eV probe pulse enables us to extract information about the occupied and unoccupied molecular orbitals of the sample in a single experiment. c In the unoccupied molecular orbital regime, we can extract the transient population dynamics of the electronic system, induced by our 3.2 eV pump pulse. d Simultaneously, we can observe transient changes in the occupied molecular orbital regime. The most prominent change is a transient change of the orbital width. e Extraction of the transient population dynamics characterized by the peak area of the orbitals shown in the inset. f Extracted transient broadening of the HOMO level fitted with a double exponential function. The two characteristic timescales of the decay represented by the decay parameters correspond to the lifetimes of the unoccupied molecular features.
Figure S2: Acquired, background-subtracted energy distribution curves (EDCs) for different time delays $\Delta t \in \{-60 \text{ fs}, 60 \text{ fs}, 120 \text{ fs}, 350 \text{ fs}\}$ together with fitting model based on Gaussian peaks. The EDCs have been obtained from the 2D raw data by integrating over a small angle range $\Delta \theta = 3^\circ$ and subtracting a time-independent exponential background, originating mostly from secondary photoelectrons. All distinct peaks in the spectrum have been fitted by the least amount of Gaussians. For the present study, only the HOMO and HOMO-1 are discussed further.
Details on the Data Acquisition and Analysis

We use femtosecond time and angle resolved photoemission spectroscopy (trARPES) with a femtosecond extreme ultraviolet (fs-XUV) probe pulse to map the molecular orbital structure with a photoelectron detector (Fig. S1b). The high 22.2 eV photon energy enables us to simultaneously observe the valence and the conduction orbital regimes. With a time-delayed 3.2 eV fs-light pulse, we create an excitonic state between the highest occupied molecular orbital (HOMO) and the second to lowest unoccupied molecular orbital (LUMO+1). Variation of the pump-probe time delay allows us to observe the excitation and relaxation dynamics in a slow-motion movie (Fig. S1a). Taking cuts through the Brillouin zone, we can extract time delay dependent energy spectra for the transiently occupied conduction (Fig. S1c) and occupied valence (Fig. S1d) molecular orbital regime. In the conduction orbital energy range, we observe the transient occupation of the lowest unoccupied molecular orbitals and the formation and decay of excitonic states. In the energy range of the highest occupied molecular orbitals, we simultaneously observe a sudden rise of the orbital’s width and a subsequent decay which we extract using a dedicated orbital fitting model based on density functional theory (DFT) calculations.\textsuperscript{S2} The lifetime of the transiently occupied molecular orbitals (Fig. S1e) corresponds to the decay of the transient broadening of the HOMOs (Fig. S1f). In our recent publication,\textsuperscript{S1} we proposed an explanation assuming that the LUMO+1 and LUMO derived excitonic states have a charge transfer character, which causes a dipole moment, as the electron and the hole are located on different molecular sites. These dipoles are acting as charge defects in the molecular film and will be screened by the surrounding molecules. We performed micro-electrostatic simulations showing that this screening results in the exact transient width change behavior that we observe in the experiment. Excitons with pure Frenkel character will not contribute to this effect, as they are charge neutral to the outside. This result gives an insight into the character of excitons and the link between optical excitation and transient transport level realignment which helps to understand the creation of free charge carriers in organic semiconducting devices. Our
findings are in agreement with independent transient and electron absorption measurements performed.\textsuperscript{S3}

**Details on the Spectral Analysis of Excited States**

To extract the transient population dynamics of the different excited states from the acquired raw data, we generated energy distribution curves (EDCs) for each pump-probe time delay by integrating over the electron emission angle degree of freedom recorded by our hemispherical analyzer. Thereafter, the obtained 1D spectra were averaged over the multiple delay scans recorded within the measurement. In a next step, a Gaussian background was subtracted for every time delay of the scan. The data obtained this way is plotted in Fig. S1c for distinct time steps. Furthermore, by application of a sliding average for the delay time and a smoothing in energy, the overview graph in figure 1a of the main text has been created from this data. Subsequently, we analyzed the spectral shape of the excited states of the un-smoothed, background-subtracted data by fitting each spectrum individually with three Gaussians. During the fitting procedure, the width and the peak positions were constrained to constant values. The peak positions and the peak width were optimized by iteratively repeating the fitting procedure with different, but time-independent width and position values. The only free fitting parameters are thus the peak heights of the three Gaussians. The time delay-dependent Gaussian peak area, being the observable describing the transient population of the respective excited states is shown in Fig. S1e and figures 3a,b and 5b of the main text.

**Details on the Analysis of the Population Decay of the Excited States**

From the transient peak areas obtained by the orbital fit of the excited states presented in the previous section, population decay constants of the excited states CT\textsubscript{2} and CT\textsubscript{1} have been extracted by fitting their time dependent intensity evolution by the exponential fitting
function $F_{CT_2}(t)$ and $F_{CT_1}(t)$:

$$F_{CT_2}(t) = G(t) \otimes \begin{cases} I_0 & t < t_0 \\ I_{CT_2}e^{-(t-t_0)/\tau_{CT_2}} & t \geq t_0 \end{cases}$$ (1)

$$F_{CT_1}(t) = G(t) \otimes \begin{cases} I_0 & t < t_0 \\ I_{CT_1}e^{-(t-t_0)/\tau_{CT_1}}(1 - e^{-(t-t_0)/\tau_{CT_1,R}}) & t \geq t_0 \end{cases}$$ (2)

$I_0$ is the background intensity, $\tau_{CT_2}$ the decay constant of the CT$_2$ level, $\tau_{CT_1,R}$ the rise time of the intensity of the CT$_1$ level, and $\tau_{CT_1}$ the decay constant of the CT$_1$ level. For the data analysis, the fit functions were convoluted with a normalized Gaussian function $G(t)$ with $T_{p-p} = 70 \text{ fs}$. The latter value corresponds to the pump-probe cross correlation on the sample surface and was determined experimentally. The best fitting results were obtained for $\tau_{CT_1,R} = \tau_{CT_2}$. The corresponding fitting functions are shown as solid lines in Fig. S1e and figures 3a,b and 5b of the main text. The transient S$_1$ population has not been fitted, but presented with a guide-to-the-eye function for better visibility of the temporal evolution.

**Details on the Spectral Analysis of Occupied States**

All spectra have been recorded using the snapshot mode of our detector ($E_{\text{pass}} = 100 \text{ eV}$) together with our femtosecond-XUV light source ($h\nu = 22.2 \text{ eV}$). Each data point is calculated from a 2D image with axis of kinetic electron energy $E_{\text{kin}}$ versus electron emission angle $\Theta$ for a fixed pump-probe delay (see Fig. S1a). Changing the pump-probe time delay $\Delta t$, we acquire our 3D-data stack $I(E_{\text{kin}}, \Theta, \Delta t)$. To obtain the shown 1D plots, we extract a cut along the energy and average the information in a small angle region of around 3$^\circ$ (see Fig. S2). The fitting routine is a two-step process, starting with the subtraction of a time-independent, exponential background, which has already been performed for the data.
shown in Fig. S1d and Fig. S2. The second step consists of analyzing the spectral line-shape of the valence band, using the least number of Gaussian peaks needed for a decent description of the spectrum. For the present study, only the HOMO and HOMO-1 were evaluated, modeled with one Gaussian per peak, with one free area, width and position each, as shown in Fig. S2. While the time evolution of the area and position stay constant in time within error bars, the spectral linewidth changes over time, as shown in Fig. S1f.

Details on the Analysis of the Transient Width Dynamics of the Occupied Valence Band States

After having obtained the valence orbital widths as described in section "Details on the spectral analysis of occupied states", the decay constants of the fast decay channel $\tau_{TB_2}$ and the slow decay channel $\tau_{TB_1}$ can be extracted from the width $\Delta E$ using the following relation:

$$\Delta E(t) = G(t) \otimes \begin{cases} 
\Delta E_0 & t < t_0 \\
\Delta E_0 + \Delta E_{TB_2} e^{- (t-t_0)/\tau_{TB_2}} + \Delta E_{TB_1} e^{- (t-t_0)/\tau_{TB_1}} (1 - e^{- (t-t_0)/\tau_{CT_2}}) & t \geq t_0.
\end{cases}$$

(3)

Here, $G(t)$ is a Gaussian function with a temporal width $T_{p-p} = 70$ fs, introduced to consider the temporal broadening introduced by the pump and probe pulse. The fit function describes a double-exponential decay process with refilling to model the two subsequent decay steps observed in the excited states. The fit functions obtained using this method are plotted in Fig. S1f and figures 2e,f, 3a, 4c and 5a,b of the main text together with the respective data.
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