Supplementary Materials for

Ultrafast Long-Range Charge Separation in Organic Semiconductor Photovoltaic Diodes

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S1. J-V and EQE of 90:10 p-DTS(FBTTh$_2$)$_2$:PC$_{71}$BM devices

Figure S1 – EQE and J-V curves of a 90:10 p-DTS(FBTTh$_2$)$_2$:PC$_{71}$BM device

The photocurrents generated in the 90:10 p-DTS(FBTTh$_2$)$_2$:PC$_{71}$BM devices, spun from chloroform, were found to be substantially lower (~250 fold) than those of similar devices spun from chlorobenzene with 0.25% DIO, as reported in reference (24). This suggests the formation of bound interfacial electron-hole pairs, unable to undergo long-range charge separation.
The p-DTS(FBTTh$_2$)$_2$ time-integrated TA spectrum is shown in figure S2. The spectral shape remains unchanged over time and the only excited state present is the singlet exciton. The 500-700nm region is due to the GSB and the 700-900nm region to the SE. These two features overlap substantially around 700nm. The strong peak around 1200-1300 nm and extending past 1600 nm is the PIA of the singlet exciton. No substantial thermal artefacts(35, 36) are observed in this neat film, indicating that the derivative-like feature observed in the blends does not arise from this effect.
S3. Dynamics of exciton dissociation in p-DTS(FBTTh$_2$)$_2$:PC$_{71}$BM blends

S3.1 On pico-to-nanosecond timescales

Using singular value decomposition (SVD, where USV$^T$ = SVD(X)), the long-time data (figure 2 in manuscript) can be separated into a linear combination of 2 spectra for each blend (90:10 and 60:40). The diagonal of the S matrix shows only two features with significant weight. As these are not physically-relevant features but a purely mathematical construct, they serve as a new basis that effectively reduces the parameter space of spectral reconstruction (~1000-fold, roughly the number of pixels spanning the 550-800nm range probed).

Using the singlet exciton spectrum of the neat p-DTS(FBTTh$_2$)$_2$ film, Figure S2, as a reference, it is possible to reconstruct the spectra of the two underlying species present in the blended film. For both blends, the singlet exciton component can be easily reproduced (Figure S3A, orange lines). The other component is shown in blue. For both blends the second spectrum has a similar shape with the exception of the 700 – 750nm region, where one (the 60:40 blend) contains EA and the other does not. Thus on the timescales probed (1ps – 2ns) most of the EA is generated within that first picosecond. The precise dynamics of the sub 1ps region are hard to assess due to the numerous fluctuations in the early-time signal and a time resolution is of order 300fs.

The kinetics associated with these spectra are shown in figure S3B. They show that the charge signal is entirely explained by the decay of the singlet population for both blends (black line). Moreover, it confirms that the excited-state absorption cross-section is the same in each blend (as expected). This implies that even excitons dissociated many picoseconds after excitation, i.e following vibrational...
relaxation, produce charges that undergo long range separation with the same efficiency as those formed within the first 100 fs.
S3.2 At low temperature

![Figure S4](image)

**Figure S4** – TA spectrum, measured at 300ps, and dynamics of the energy stored in the electric field.

Low-temperature TA measurements were performed on p-DTS(FBTTh$_2$)$_2$:PC$_{71}$BM blends with optimized morphologies (3:2, with DIO). A continuous-flow helium cryostat was used to cool the sample down to around 4K and TA was measured with ~300fs time resolution (the multiple windows of the cryostat limit pulse compression). A spectrum measured at 300ps is presented in figure S4 (left panel) and shows very similar features to those reported in Fig.2D (main text), albeit with sharper features. The panel on the right shows the kinetics of the electrostatic energy per electron-hole pair discussed in Figure 3E of the main text. We note that even at 4K the EA feature has substantial strength at the earliest time we can measure, 300fs. This suggests that the initial phase of charge separation, which gives rise to the large EA at the shortest times, is temperature independent. As in the room temperature measurements, Figure 3E, the initial rapid increase in energy is followed by a slower rise at longer times. This rise is substantially slower at 4K, occurring over 1ns, as opposed to 3ps at room temperature. However the same value of energy is eventually reached. This supports a model of rapid early time charge separation followed by temperature dependent charge hopping at later times.
S3.3 On sub-picosecond timescales (Global analysis)

Figure S5 – TA spectra of p-DTS(FBTTh$_2)_2$:PC$_{71}$BM excited using compressed pulses (30 fs).

To study the sub-ps dynamics of the 60:40 p-DTS(FBTTh$_2)_2$:PC$_{71}$BM blend, we first measure TA with compressed pulses (~30fs, spanning 525-625 nm). At the fluences used here (8μJ/cm$^2$), no non-linear population dynamics were observed within the presented time window (<3ps). The delayed appearance of the positive signal in the >700nm region is due to energy diffusion, while the early-time negative signal is consistent with the 82fs decay of the singlet exciton into charges. The short laser pulse induces a non-linear response in the sample at short times that leads to oscillations around 700nm, which quickly decay.

To perform a global fit of this data, a simple model involving two exponentials is used. The exciton and charge populations are described as follow:

$$S_1(t, \lambda) = A(\lambda) \left( pe^{-t/\tau_1} + (1 - p)e^{-t/\tau_2} \right)$$
$$C(t, \lambda) = B(\lambda) \left( p(1 - e^{-t/\tau_1}) + (1 - p)(1 - e^{-t/\tau_2}) \right)$$

where $p$ is the fraction of excitons that decay through the 1$^{st}$ mechanism ($0 < p < 1$) and $\tau_1$, $\tau_2$ the time constants of the two decay channels ($\tau_1$, $\tau_2 > 0$). The parameters $p$, $\tau_1$, and $\tau_2$ are fitted globally on the entire dataset while $A$ and $B$ are fitted at each wavelength. $A$ and $B$ are, respectively, the singlet-
exciton and charge TA spectra shown in figure 3A (manuscript). If the EA has different dynamics from those of the excited states modelled, than a 3\textsuperscript{rd} component will be observed when taking the difference between the fit and the data. This is indeed then case. An SVD analysis shows one dominant component whose spectrum is shown in figure 3B and matches that of CW EA. A linear combination of the 3 spectra obtained is then fitted at each time point to reconstruct the dynamics including the EA component. These kinetics are shown in figure 3B of the manuscript.
S4. Transient absorption of PCDTBT:PC$_{61}$BM blends

**Figure S6** – TA spectra of neat PCDTBT (A), and blended PCDTBT:PC$_{61}$BM in a 4:1 and 1:4 ratio (B and C respectively) excited using compressed pulses (30 fs).

The PCDTBT:PC$_{61}$BM samples were spincoated from a 20mg/ml dichlorobenzene solution on cover glass substrates. Three different blend ratio were used: 1:0, 4:1, and 1:4. The samples were excited using sub-30fs compressed broadband pulses and probed in the visible. For all samples, the EA kinetics do not differ from those of the charge population. The analysis method presented in S3.1 is therefore preferred over the one from in S3.3, as the latter is inapplicable. The results are presented in Figure 3C on the main text.

In films made from the 4:1 blend, fine intermixing is expected(23, 27), which inhibits charge extraction. By analogy to the analysis presented for p-DTS(FBTTh$_2$)$_2$:PC$_{71}$BM, we consider that the TA spectra in the low-fullerene blend is that of the interfacial bound electron-hole pairs. The spectrum of the difference with the optimized blend (1:4) is then in good agreement with the EA measured from devices (See main text, figure 3D).
S5. Device EA

**Figure S7** – EA induced in a (A) p-DTS(FBTTh2)$_2$:PC$_{71}$BM and (B) PCDTBT:PC$_{61}$BM device by changing the amplitude of the AC modulation bias.

The EA spectra (See main text) and AC dependence was measured for optimized devices of p-DTS(FBTTh2)$_2$:PC$_{71}$BM and PCDTBT:PC$_{61}$BM. In both systems, the peak EA amplitude was measured as a function of applied bias using a quasi-steady-state electro-absorption setup. The DC bias was set to -1V to avoid charge injection and the AC bias varied from 0V to 2.5V. The signal is not perfectly quadratic due to the small, yet non-negligible injection of charges. Fitting the data with a second-order polynomial, for an electric field $E$ in V/cm, yields values for the quadratic prefactor of $10 \times 10^{-15}$ for p-DTS(FBTTh2)$_2$ and $1.9 \times 10^{-15}$ for PCDTBT.
S6. Film Morphology \( p\text{-DTS(FBTTh}_2\text{)}_2\text{:PC}_{71}\text{BM films} \)

Two different compositions of \( p\text{-DTS(FBTTh}_2\text{)}_2\text{:PC}_{71}\text{BM} \) samples were studied. A 60:40 blend cast from chlorobenzene with the addition of 0.4% DIO, referred to as the 60:40 blend, and a 90:10 blend cast from chloroform.

The morphology of the 60:40 blend has recently been characterised by Love et al.\(^{(21)}\) using UV-Vis spectroscopy, transmission electron microscopy (TEM) and grazing incidence wide-angle x-ray scattering. It was found that upon casting from chlorobenzene absorption spectra of the blend film did not show the vibronic structure seen in pristine films. However, upon addition of DIO to the solution used to cast the films the vibronic structure reappears indicating better ordering of the \( p\text{-DTS(FBTTh}_2\text{)}_2 \). This was confirmed by TEM analysis, which indicated that the blend films were composed of more than one phase. One phase consisted of wire like grains of \( p\text{-DTS(FBTTh}_2\text{)}_2 \) 30-40nm in width which formed a continuous network. These grains are composed of well crystallised \( p\text{-DTS(FBTTh}_2\text{)}_2 \) with a repeat unit of 2.2nm across the width. This corresponds to the unit cell size for single crystals of \( p\text{-DTS(FBTTh}_2\text{)}_2 \), as determined by x-ray diffraction. This pure \( p\text{-DTS(FBTTh}_2\text{)}_2 \) phase appears to be surrounded by another phase in which the \( \text{PC}_{71}\text{BM} \) is likely to be mixed with the \( p\text{-DTS(FBTTh}_2\text{)}_2 \) along with aggregates of \( \text{PC}_{71}\text{BM} \), which are commonly observed at higher fullerene loading ratios\(^{(23)}\). The presence of a mixed and bulk phase support our experimental results where we observe two distinct rates of charge generation, 82fs and 22ps, which most likely arise from excitons generated at the interface which dissociate rapidly and excitons generated within the grains of pure \( p\text{-DTS(FBTTh}_2\text{)}_2 \), which must diffuse through the wire like grains to heterojunctions with \( \text{PC}_{71}\text{BM} \) before dissociation\(^{(37)}\).

In contrast to the 60:40 blend the 90:10 blend is spun from chloroform. This is likely to result in the formation of pure \( \text{DTS(FBTTh}_2\text{)}_2 \) phases, as seen in the pristine materials and also a mixed phase with the fullerene. However aggregation of fullerene is not expected to occur due to both the low boiling point solvent and the low fullerene loading ratio\(^{(23)}\).
S7. Differences between microscopic and macroscopic time-resolved E field measurements

Figure S8 – Macroscopic change in $|E|$ due to the drift of charges (left) and microscopic picture of randomly-oriented e-h pairs generated in a bulk heterojunction (right). In the right panel, $|E|$ averages to 0 but not $|E^2|$.

Within OPV diodes two regimes for charge separation are present. Below we highlight these differences and how they can be measured in experiments using pulsed excitation.

1. **Macroscopic regime**: Within this regime, charges generated via photoexcitation drift towards their respective electrodes (holes towards the anode and electrons towards the cathode) under the influence of the built in electric field in the device or an externally applied field. This drift of carriers causes a screening of the built in or an externally applied electric field. This change of the macroscopic electric field in the device can be measured experimentally using Electric Field-Induced Second Harmonic (EFISH)\(^{(30)}\) or time-resolved stark spectroscopy\(^{(15)}\). Assuming the system to be a parallel-plate capacitor, the mobility and e-h separations can be calculated and offer valuable insights on the dynamics of charges as they drift to the electrodes.

2. **Microscopic regime**: Within this regime, electron-hole pairs formed at heterojunctions within the active layer separate from each other. As the heterojunctions are randomly orientated (in the case of a bulk heterojunction) electrons and holes separate in random directions, i.e. there is no preferred direction of motion. Thus no macroscopic changes in the $E$ field will be observed (randomly oriented dipoles average to zero at long distance). Macroscopic techniques, such as those mentioned above, are therefore insensitive to these processes and a microscopic approach, such as the one used in this paper, must be applied, where the dipole field of individual electron-hole pairs is measured instead.

We note that the results obtained via measurements in both regimes are complementary, from the initial ultrafast separation component (measured here as $|E^2|$) to the long-range drift/diffusion through the device at later times (measured as $|E|$).
S8. Charge Delocalisation vs Exciton Delocalisation

It has recently been suggested that exciton delocalisation plays an important role in efficient OPV performance\(^{(33)}\). Our results point towards the importance of charge delocalisation rather than exciton delocalisation for rapid charge separation. Indeed, we show in figure S3 that even vibrationally relaxed (‘cold’) excitons (that must be localised) undergo charge transfer after diffusion (>20ps), separating with the same yield and to the same average distance as initial ‘hot’ excitons. This suggests that the initial exciton delocalization is not necessary for efficient charge separation.

It has also recently been suggested that electronic coherence between the initially photogenerated singlet exciton and charge transfer/separated states helps mediate efficient charge generation\(^{(38)}\). Again we stress that this is quite different from the model supported by the evidence presented in this paper, which is for coherent propagation of charge carriers (electrons) on ultrafast time scales (<300fs). Transient absorption measurements (such as those presented here) are unable to probe the presence of an electronic coherence between the singlet exciton and the charge transfer/separated state. Such processes could perhaps be probed by 2D electronic photon echo spectroscopy, but to the best of our knowledge no such evidence has yet been reported. We therefore refrain from making any claims on coherence between singlet excitons and charge transfer states. In contrast, the evidence for rapid separation of electron-hole pairs presented here strongly suggests coherent charge motion at early times, as we discuss in the main text.
S9. EA Calculation – The electrostatic picture

Experimental measurements provide the time-resolved EA amplitude per electron-hole pair. We can then convert this to an electrostatic energy using the calibrated volume-integral of $|E|^2$. In order to understand the meaning and implications of this quantity, it is helpful to look at the electrostatics of a separating charge pair. It is important to emphasize that, unlike other time-resolved EA measurements performed on devices, we are not looking at a macroscopic field between two electrodes but at multiple randomly oriented ‘dipolar’ fields localized in the vicinity of each photogenerated electron-hole pair. Although the total EA is still $\propto \int |E|^2 dV$, its origin is completely different.

In the macroscopic case, the average electron-hole distance can be calculated assuming a simple model where two sheets of charges of opposite sign move away from one another due to an applied bias. This model, however, is not valid for microscopic dipole-like fields when there is no preferential directionality to the separation process. This is the case in bulk heterojunctions where the interfaces are randomly oriented and the mean macroscopic field is 0 at all times.

We therefore use a classical electrostatic representation of the microscopic separation process where the work done to move an electron to a distance $r$ from the hole is proportional to $-1/r$ (with the energy at infinite distance normalized to zero). As the charges move away from one another, the total energy stored in the electric field will tend asymptotically towards that of two independent charges. Hence, the change in electrostatic energy induced by moving these charges further apart becomes small once the electron-hole pair are ‘free’ from their mutual attraction. The electro-absorption induced by a charge pair will therefore follow the same trend. This implies that microscopic-EA measurements are specifically sensitive to the separation from bound to free charges (up to around 5-6 nm separation); beyond such a distance the changes in electrostatic energy are less than $k_B T$ and we are unable to quantify further longer-range separation.

From the experiments on low fullerene content blends, we know that the initial nearest-neighbour charge-transfer state has no EA. Thus, the observed EA arises from an increase in the energy stored in the field, i.e. from the work done separating the electron-hole pair. This idealized model, derived for macroscopic length scales and equilibrium conditions, provides a simple way to understand qualitatively these results. The growth and saturation of the EA is the signature of electron-hole pairs overcoming their mutual Coulomb attraction and forming free charges. We provide a quantitative analysis of this phenomenon in the next section, in which theoretical modelling of the initial charge
separation as a process mediated by coherently delocalised states of the acceptor phase reproduces the typical saturated binding energies implied by the strength of the EA signal and allows us to link this to the ultrafast processes through which spatial coherence drives the charge separation.
S10. Theory and modelling

S10.1 Coherent model

We treat OPVs to be composed of small crystalline grains of donor and acceptor species, distributed randomly in space. Charge separation occurs when an excited electron on a donor molecule near an interface is transferred into the acceptor crystal. Our experiments show that charge separation occurs on two timescales. Ultrafast charge separation occurs when excitons are photo-excited near an interface. The longer time-scale reflects the diffusion of excitons within donor grains.

In this paper we seek to model the ultrafast component. We found in our experiments that long range charge separation was only efficient when PC$_{61}$BM was able to aggregate to form nanoscale crystals. We therefore neglect the crystalline structure of the donor aggregates, and treat a donor molecule as an isolated electron injection site into an acceptor crystal. In order to reduce the electron-hole pair to a single body problem, we assume that the hole remains fixed on this isolated donor site throughout our simulations.

The simplest possible model of a single electron moving in a crystal is the tight binding model of coupled nearest neighbour sites. Each acceptor molecule is reduced to a single energy level $E_i$, and nearest neighbours are coupled by a constant coupling strength $V$. We chose an FCC lattice with 4 unit cells along each edge, and we coupled a single donor injection site, Energy $E_d$, to a site near the centre of one face of the crystal. We initialised simulations with the electron localised on the donor site. We assumed that the Coulomb potential of the hole trapped on the donor site was spherically symmetric, which allowed us to calculate the Coulomb potential at each site of the acceptor crystal.

Molecules oscillate about their equilibrium lattice positions, and this leads to temporal variations in the nearest neighbour coupling strengths. Nuclear dynamics within individual molecules leads to variations in the on site energy $E_i$. However, in this model we consider that the dynamical dephasing induced by these processes is slower than the ultrafast initial charge dynamics (39), and we therefore treat these temporal variations as static on short timescales. For simplicity we introduced a static disorder term in the on site energies $E_i$, but held the coupling strength $V$ constant.

$$E_i = \frac{-\epsilon^2}{4\pi\varepsilon_0\varepsilon r_i} + \sigma_i.$$  

$\sigma_i$ is a Gaussian random number, standard deviation $\sigma$, and $r_i$ is the distance between the donor and the relevant acceptor site. The overall Hamiltonian is defined below,
\[ H = E_d |d><d| + V_d |d><a_1| + |a_1><d| + \sum_i E_i |a_i><a_i| + \sum_{i,j}^n n.V |a_i><a_j|. \]

\(a_1\) labels the donor site’s nearest neighbour within the acceptor crystal, and the final summation in \(j\) is performed over nearest neighbours of the acceptor lattice. Initially we choose \(V = 50\) meV, \(V_d = 60\) meV, \(\varepsilon = 3\) and \(\sigma = 0.1\) eV \((40)\). The FCC lattice constant is 1.5 nm \((41)\), and this was also the separation distance between the donor and its nearest neighbour.

In the absence of disorder, this lattice will exhibit a band of delocalised electronic states. The bandwidth of this lattice, \(B = 16\) V. Thus a coupling of 50 meV would imply a bandwidth of 0.8 eV. Disorder is not expected to localise the electronic states, unless the static disorder strength is greater than the bandwidth (the Anderson criterion). Thus for a wide range of possible disorder values a band of electronic states will emerge.

The amplitude of the acceptor eigenstates near the interface will be perturbed by the Coulomb well. However we anticipate that acceptor sites near the interface will remain well coupled to delocalised bulk band states; since the maximum depth of the Coulomb well on the crystal lattice, 0.32 eV \((W)\), is within the bandwidth. To illustrate this, a schematic diagram of the available acceptor eigenstates was included in the main text. It is the presence of delocalised band states at the interface which enables ultra-fast charge separation into the bulk.

For efficient charge separation the injection energy \(E_d\) must lie within the energy range of acceptor eigenstates delocalised across the entire crystal. For clarity we introduce a new parameter \(\Delta\), which measures the offset of \(E_d\) from the lower conduction edge CE defined in figure 4B of the main text, \(\Delta = E_d + 12V\).

In figure S9 we present simulations of the exciton population decay and the electron hole separation for a range of \(\Delta\) values. We emphasize that our simple model is primarily intended to clarify the charge separation mechanism, not to make exact predictions of the charge separation dynamics. As expected, we find that charge separation is efficient for injection energies within the conduction window, which lies roughly between \(\Delta = 0\) eV and \(\Delta = 0.6\) eV (the upper conduction edge lies slightly above B-W).
Our model is designed to capture the evolution of the electronic charge density immediately after the exciton dissociates. Within the fully coherent model, this evolution is taken to be quantum coherent. As mentioned above, a variety of dephasing processes will be present in the device; such as vibronic relaxation, coupling to lattice vibrations, impurity scattering and scattering due to the finite crystal size in real systems etc. These define a lifetime over which coherence is lost. Thus coherence will play an important role in charge separation if the timescale for coherent charge separation is shorter than the coherence lifetime. Our simulations find that this coherent charge separation timescale is approximately 50-100 fs, short enough to compete with the many typical dephasing mechanisms (39).

The exact nature of the PCBM aggregates within real devices is not known. Therefore in the main text we presented simulations for a range of different coupling strengths $V$ and disorder strengths $\sigma$ between 30-50 meV, and 0.1-0.2 eV respectively (32). $V_d$ was also fixed to $V$. For all of these simulations the energy $E_d$ was set to -0.36eV; this represents the “conduction edge” CE when $V = 30$ meV (see main text). These simulations are shown in figure S10. We see that coherent charge separation is effective for the full range of parameter values, and is resilient in highly disordered aggregates.

Figure S9- Charge dissociation and long range charge separation. A. Decay in the electronic charge density on the donor site for a range of injection energies. The black curve lies above the conduction channel, purple and blue lie within the conduction channel, red lies on the conduction edge and green lies below the conduction channel. The high energy electron does not dissociate, the low energy electron weakly dissociates and electrons within the conduction channel strongly dissociate. B. The mean electron-hole separation, calculated over
electronic density not lying on the donor site. Injection below the conduction channel couples to bound states, while injection within the conduction window couples to states delocalised across the acceptor crystal (maximum charge separation distance fixed by the crystal size). The purple curves above match the injection energy discussed in the main text. Each curve is averaged over 100 disorder realisations.

**Figure S10** –Coherent propagation for a range of crystal parameters. **A.** Exciton population decay for a range of couplings and disorder strengths. For all parameters considered, the exciton population strongly decays within the first 200 fs. **B.** Mean charge separation, calculated over separated charge density. Within 200 fs, the mean separation reaches 3-5 nm. All curves are averaged over 100 disorder realisations.

**S10.2 Example eigenstates**

In figure S11 we present a set of eigenstates calculated by exact diagonalisation of the model Hamiltonian. For clarity we neglect the static disorder, and we present simulations on a larger $18.75 \times 18.75 \times 18.75$ nm$^3$ crystal. We set $V_d$ to zero and consider the eigenstates of the acceptor crystal. All other parameters match the simulations of figure S9. We exhibit the eigenstate amplitude along a straight line through the acceptor crystal. We choose the cut which passes through the donor site and is perpendicular to the adjacent crystal face. Thus the donor site’s nearest neighbour (where the Coulomb well is deepest) lies at distance 0 nm, and we move linearly away from the donor site along the horizontal axis.

The eigenstate energies are given in terms of the parameter $\Delta$ introduced above. We observe bound states below the conduction edge, fully delocalised standing waves within the conduction window, and states whose amplitude decays on approaching the interface above the conduction edge.
Figure S11 - Example eigenstates of the tight binding lattice. A. $\Delta = -0.08$ eV, an interfacial bound state. B. $\Delta = 0.07$ eV, a fully delocalised standing wave just above the lower conduction edge. The decreasing wavelength at larger distances from the interface reflects the local slowing down of the propagating electron as it climbs out of the Coulomb well. This is prominent in this state as its total energy is only slightly greater than the potential well depth, and therefore has little kinetic energy at large distances. C. $\Delta = 0.47$ eV, a higher-energy and fully delocalised standing wave within the conduction window. D. $\Delta = 0.71$ eV, a high energy standing wave in the acceptor bulk, which decays as it approaches the Coulomb well at the interface. Without interfacial overlap, such a state cannot couple to the donor electron. In all figures the amplitude at zero distance is an effective measure of the coupling of the state to the initially localised electron on the donor.

S10.3 Temporally incoherent propagation through delocalised states
We start with the fully coherent Hamiltonian presented in section A.

\[
H = E_d |d><d| + V_d [|d><a_1| + |a_1><d|] + \\
\sum_i E_i |a_i><a_i| + \sum_{i,j}^{n,n} V |a_i><a_j|.
\]

The initial condition is unity occupation of the donor site. We have already presented results describing the fully coherent quantum dynamics of this model. To consider temporally incoherent dynamics, we must treat the donor-acceptor interaction perturbatively, ultimately deriving a set of Fermi golden rule transition rates from the donor site to the spatially coherent delocalised eigenstates of the acceptor lattice. Within this formulation we retain the coherently delocalised band structure of the acceptor lattice, but no coherences ever emerge between eigenstates. The donor site is treated as an isolated, localised eigenstate. Diagonalising the Hamiltonian of the acceptor lattice sites, we obtain a set of delocalised states \(|k> = \sum_i c_{ik}|i>\) with energies \(\omega_k\). The Hamiltonian

\[
H = E_d |d><d| + \sum_k \omega_k |k><k| + \sum_k V_d c_{1k} [|d><k| + |k><d|].
\]

From this Hamiltonian, we may write down the Fermi’s golden rule transition rates for population transfer from the donor site to a given k state(42)

\[
T_k = 2\pi V_d^2 \sum_j |c_{1k}|^2 \delta(\omega_k - E_d).
\]

The equation above comprised of three factors; the coupling strength \(V_d\), the probability weight of a given k state at the lattice site coupled to the donor \(|c_{1k}|^2\), and finally the density of states at the donor energy \(E_d\). The last component poses a problem, since our discrete lattice does not possess a continuous density of states.

To resolve this problem, and motivated by the fact that we are excluding coherences between k states, we assume that the k state energies are fluctuating due to environmental interactions. We assign each k state a continuous spectral width, according to a Lorentzian line shape. This generates a pure dephasing contribution. The FGR transition rates into each discrete k state may now be expressed as

\[
T_k = \sum_j \frac{2V_d^2 \gamma |c_{1k}|^2}{\omega_k - E_d)^2 + \gamma^2}.
\]
\( \gamma \) denotes the pure dephasing rate. Following a standard approximation, this may be expressed as

\[
\gamma = \lambda k_b T \tau.
\]

\( \lambda \) represents the reorganisation energy of the acceptor sites due to vibronic relaxation, \( k_b T \) represents the thermal energy at room temperature, and \( \tau \) denotes the characteristic relaxation time of molecular vibrations. For our system we take \( \lambda \) to be 0.1 eV and \( \tau \) to be 100 fs. Using the rate expression above, the simple coupled kinetics for the diagonal components of the density matrix may be expressed as

\[
\frac{\delta \rho_{dd}}{\delta t} = - \left( \sum_k T_k \right) \rho_{dd} + \sum_k T_k \rho_{kk},
\]

\[
\frac{\delta \rho_{kk}}{\delta t} = - T_k \rho_{kk} + T_k \rho_{dd}.
\]

Before presenting the results of simulating the dynamics above, we first emphasize some limitations of the Fermi golden rule approach in this context. First, the coupling between donor and acceptor was treated perturbatively, while the acceptor couplings were not. Yet in our model both these terms are similar in magnitude. The rapidity of experimentally observed ultrafast charge separation suggests that couplings across the heterojunction interface are not significantly weaker than couplings within aggregates in real devices. This implies that if short lived spatial coherence can survive between acceptor states, then short lived coherence should also survive between the donor site and acceptor states.

Furthermore, the derivation of FGR averages the transition amplitudes between eigenstates over infinite time; while the dynamics observed at early times in our experiments differs markedly from that observed in steady state experiments. The claim that transitions occur between system eigenstates, rather than between lattice sites, is a consequence of this averaging procedure. This claim implies that electronic probability density “hops” across several lattice sites in a single transition; an unphysical phenomenon explicitly forbidden in the original Hamiltonian. The severity of this flaw increases as the acceptor crystallite is increased in size, since the characteristic hopping length of the electron apparently increases. By contrast, if temporal coherences between eigenstates are preserved, then the electronic wavefunction smoothly propagates across the lattice in the real space basis. For these reasons the authors take the view that a combination of short lived spatial coherence and short lived temporal coherence provides a more intuitive and more physically realistic description of ultrafast charge generation in real devices.

We present results of simulations for the same range of couplings and disorder strengths presented in
the main text for the fully coherent case. As before, we plot the mean separation distance averaged only over separated charge density. This ensures our results can be directly compared with the experimental result.

Figure S12 shows that the mean charge separation distance at early times is roughly constant. Charge separation occurs via a single “hop” from the donor site to the mean displacement of a particular acceptor eigenstate. The rate of population decay on the donor site is approximately exponential. For all curves, the exciton has significantly decayed within 200 fs, and the electron hops to a mean separation distance of 3-5 nm. Note however than the size of the initial hop is primarily determined by the (constant) size of the acceptor lattice, which underlines the unphysical nature of FGR in this context.

Figure S12: A. Exciton population decay. B. Mean charge separation, averaged over separated charge density. For the same wide range of parameters as considered previously, FGR dynamics predicts efficient exciton decay into delocalised states whose mean location lies far from the interface. Note that the simulation curves do not lie in the same order as observed in the fully coherent case. This may be a result of insufficient disorder averaging, or it may be a consequence of introducing dephasing. Simulations are averaged over 100 disorder realisations.

S10.4 Fully incoherent, Marcus theory dynamics

Finally, we compute incoherent dynamics in a localised basis, following the equilibrium Marcus rate theory. The electron population at each lattice site $i$ is given by the master equation

$$\frac{\delta P_i}{\delta t} = -\sum_j T_{ij} P_i + \sum_j T_{ji} P_j.$$
Both summations are performed over nearest neighbours. The transfer rates are given by (31)

\[
T_{ij} = \frac{2\pi|V|^2}{\sqrt{4\pi\lambda k_B T}} \exp \left\{ -\frac{(\Delta E + \lambda)^2}{4\lambda k_B T} \right\}.
\]

\(T_{ij}\) gives the transfer rate from site \(i\) to site \(j\), where \(\Delta E = E_j - E_i\). We apply these dynamics to the model described in section A, where additionally \(\lambda = 0.1\) eV (as in the FGR dynamics). In order to ensure the exciton was able to dissociate efficiently, the injection energy \(E_d\) was increased to -0.31 eV (just above the energy of the adjacent site in the acceptor lattice).

We present a single simulation with \(V = V_d = 50\) meV and no disorder. As expected, the electron rapidly dissociates at the interface but becomes trapped on acceptor lattice sites near the interface. Long range charge separation does not occur.

![Figure S13: Marcus dynamics becomes trapped within the Coulomb well.](image)

**S10.5 Electrostatic binding energies of delocalised acceptor states**

In this section we present computations of the total work done against the electron-hole coulomb interaction while transiting from initially localised e-h pairs (separated by 1.5nm) to final states where the hole remains fixed and the electron is in a spatially coherent eigenstate of the acceptor lattice. This energy is calculated by subtraction of the field energies of these two configurations, accounting for the delocalised charge distribution of the electrons and the finite size of the aggregate, both of which generate important quantitative (though not qualitative) corrections to the heuristic point-charge picture presented in section S9.

In Fig. S14 we show the electrostatic energy stored in the field (EESF) of all eigenstates against their mean e-h separation distance for a series of FCC lattices of different sizes. We consider lattices of \(1^3\), \(2^3\), \(3^3\) and \(4^3\) unit cells with lattice constant of 1.25nm. The \(4^3\) case corresponds to the simulations
presented above. For simplicity we neglect static disorder, and use an average dielectric constant of 3.5. The coupling between acceptor molecules is 30 meV. The donor-acceptor coupling is set to zero, in order to consider the eigenstates of the acceptor lattice. All other parameters match the simulations presented previously.

For the lattice of $4^3$ unit cells used in the dynamical modelling of sections S10.2 & S10.3 we see that the vast majority of states are clustered around an EESF of 175 meV, in excellent agreement with the EESF extracted from the EA measurement of the polymer blend. Moreover, as described in sections S10.2 & S10.3, coupling the electron to this high density of states will lead to extremely rapid (<300fs) charge separation, making the assumption that coherent delocalised states are stable and available to mediate the process self-consistent. The high density of states in this region corresponds to the propagating states delocalised over the whole lattice (such as those shown in Fig. S11) which are not bound by the Coulomb well. The ultrafast appearance of the EA signal corresponding to this EESF indicates that the electron has propagated to an average separation of 4-5nm over this initial evolution through the delocalised states, which is again consistent with the dynamical calculations of sections S10.2 & S10.3. The slightly lower EESF inferred for the p-DTS(FBTTh$_2$)$_2$:PC$_{71}$BM sample implies an initial ultrafast separation dynamics to between 3-4nm, which may be related to a smaller average aggregate size in the sample as indicated in Fig. S14.

**Figure S14.** A. Mean electrostatic energy stored in the field (EESF) of the delocalised eigenstates for a series of FCC acceptor lattice (described in the text) as a function of their mean electron-hole separation distance for acceptor-acceptor coupling of 30meV and average dielectric constant of 3.5. The histograms (B,C) show the density of states for lattices of $3^3$ and $4^3$ unit cells (linear dimensions 3.75nm and 5.25nm, respectively), indicating that the majority of states have EESF consistent with the values obtained from the EA measurements. The large density of states of these “free” delocalised band states leads to the ultrafast separation dynamics discussed in S10 and observed in the experiment.
We further note from Fig. S14 that for very small lattices the EESF is very small. Indeed, for such aggregates, disorder is likely to lead to even stronger trapping and rapid formation of an interfacial bound state at small separation (which will further shrink upon environmental relaxation). We therefore predict almost no EA signal for samples with small acceptor phases, as was observed. Similarly, the EESF obtained for the final charge distribution predicted by Marcus theory is less than 10 meV (not shown). Finally, we reaffirm the point made in the main text, S10.1 & S10.2 that eigenstates of the acceptor lattices show that coherent coupling effectively softens the trapping due to the coulomb well; even the lowest energy bound states of the 5.25nm lattice (4³ units cells) show significant delocalisation away from the interface (~1.5nm). This leads to some revision of the classical criteria (Langevin, point-charge interactions) of when a charge pair can be considered “free”, as pointed by Scholes in Ref. (44). However, while this is important for the ultrafast separation dynamics that initially free the electron from the interfacial binding potential, we repeat that these states are not stable on timescales longer than a few hundred fs, and are thus unlikely to play a role in the long-time dynamics of charges in these systems.
Reference and Notes


