

Sub-Picosecond Charge-Transfer at Near-Zero Driving Force in Polymer:Non-Fullerene Acceptor Blends and Bilayers

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Abstract

Organic solar cells containing conjugated polymers and non-fullerene acceptors (NFAs) have recently taken the community by storm, thanks to high power conversion efficiencies of 16-17%. Such devices show increased photovoltage owing to the low energetic driving force for interfacial charge-transfer. However, it is believed that the low driving force also slows down charge generation, leading to a tradeoff between voltage and current. In contrast, we unambiguously demonstrate here that charge-transfer timescales remain short on the order of a few hundred femtoseconds even at near-zero driving force. This is consistent with the rates predicted by Marcus theory in the normal regime, at moderate electronic coupling and at low re-organization energy, as determined by DFT calculations for the highest-efficiency investigated system. We disentangle intrinsic charge-transfer rates from morphology-dependent exciton diffusion by comparing different blend and bilayer sample configurations for a series of polymer:NFA systems. Moreover, we establish the influence of the interfacial energetics on the electron transfer (ET) and hole transfer (HT) rates separately, since the polymer donor and NFA both contribute significantly to light harvesting and photocurrent generation via those two processes. Our findings reveal that the energy offset at the donor:acceptor interface can be minimized without jeopardizing the charge-transfer rate and efficiency. We thus show that concerns about current-voltage tradeoffs in low driving force non-fullerene solar cells are not an issue in the design of high efficiency devices.

Introduction

Organic heterojunctions between electron donors (D) and acceptors (A) are of vital importance for diverse applications ranging from photocatalysis, to batteries and solar energy conversion.^{1, 2, 3} Appropriately selected D:A combinations have enabled high performance in organic electronic devices such as organic photovoltaics (OPVs) or organic light emitting diodes (OLEDs).^{3, 4} Future

optimization of the fundamental optoelectronic processes occurring at the heterojunctions of OPV systems crucially relies on measuring and understanding the dynamics of photogenerated interfacial species. Typically, excitons dissociate at the D:A heterojunction by charge-transfer processes and subsequently separate into free charges, which are extracted as photocurrent. Common electron transfer theories predict that the driving force, namely the free energy difference between the charge-transfer (CT) state and the photoexcited (S_1) state, is a key factor determining the rate of the charge-transfer.^{5, 6, 7, 8, 9} In OPV systems, a dependence of the charge-transfer rate and yield on the driving force has indeed been observed for fullerene-containing model systems.¹⁰ ¹¹ This is consistent with the previously reported empirical lower limit of a 0.3 eV driving force required for efficient charge-transfer in typical polymer:fullerene blends.^{12, 13} Understanding the impact of driving force on the charge-transfer dynamics is particularly important in organic solar cells, since the CT state energy also determines the open circuit voltage (V_{OC}), so that a small driving force is desirable, but might lead to a tradeoff in current generation if the recombination of excitons competes with their slow dissociation.^{13, 14, 15, 16, 17}

In this respect, the recent success of non-fullerene acceptors (NFAs), that have taken the OPV community by storm with record device efficiencies over 16%,^{3, 9, 18, 19, 20, 21, 22, 23} has been attributed to efficient current generation in polymer:NFA blends even at very low or absent driving force, reducing V_{OC} losses.^{3, 19, 24} Moreover, NFAs show high absorption in the visible and near-infrared (NIR) range, which can be complemented with the donor absorption to cover a broad spectrum for light harvesting. For a further optimization of the power conversion efficiency, it is now essential to understand how the charge generation dynamics are impacted by acceptor light harvesting and the low driving force for charge-transfer, which both distinguish the NFA systems from fullerene blends. Several reports on polymer:NFA systems claim a reduced charge-transfer

rate on the picosecond time scale, attributed to the low driving force.^{15, 16, 25, 26} There are however two major shortcomings in these studies. First, the investigations have not clearly established whether the observed charge-transfer rates reflect only interfacial processes or whether they are limited by exciton diffusion in the complex morphology of the investigated blends.^{15, 16, 25, 27, 28, 29} Second, awareness must be raised that charges in NFA systems are generated by distinct ET or HT channels, with different driving forces and possibly different rates.

In this work, we have carried out a carefully designed transient absorption (TA) study on polymer:NFA systems. We disentangle intrinsic charge-transfer rates from morphological aspects (determined using X-ray diffraction techniques) by comparing the HT rate of the optimized blend with the corresponding planar heterojunction (bilayer) system and a dilute blend containing a low NFA concentration. We show that in the absence of exciton diffusion, HT occurs on the sub-picosecond time scale in spite of a negligible ≈ 0.05 eV driving force, which we establish using sensitive external quantum efficiency (sEQE) and electroluminescence (EL) measurements. We find that in blends of the same NFA component mixed with different polymers, the intrinsic HT time (inverse rate) decreases from 400 to 80 fs when the driving force increases from 0.05 eV to 0.4 eV. The behavior at low driving force is consistent with the trend expected in the Marcus normal region for charge-transfer with moderate electronic coupling, whereby the high rates can be explained by a small reorganization energy. Using DFT calculations, we find indeed moderate electronic coupling (21 meV) and low reorganization energy (161 meV) for HT in our highest-efficiency system. Moreover, we demonstrate that HT is generally slower (< 1 ps) than ET (< 0.1 ps) at comparable driving force, likely related to a higher transfer integral (electronic coupling) for ET. The ultrafast ET rates can no longer be described within the non-adiabatic Marcus limit, as already established for polymer:fullerene blends.^{30, 31, 32, 33} Overall, the sub-picosecond times for

both charge-transfer pathways over a large range of driving forces demonstrate that the energy offset at the heterojunction can be minimized without jeopardizing the charge-transfer rate and efficiency. This positive message eliminates the concern about current-voltage tradeoffs in the future design of highly efficient non-fullerene solar cells with low driving force.

Results

We select the J61:m-ITIC system (Fig. 1a) for our investigation (see chemical structures of all materials in Fig. S1, and full name of these chemicals in the experimental details). This system is chosen since i) the optimized 1:1 blend shows high OPV efficiency of around 12%,³⁴ ii) m-ITIC is representative of the ITIC-based core structure and general acceptor-donor-acceptor backbone motif of highly efficient (>16%) NFAs^{34, 35, 36} iii) the distinct absorption of the J61 donor and the m-ITIC acceptor allows for selective excitation of either (Fig. S2), and iv) the system has a low driving force for HT leading to high V_{OC} of 0.9 V and a typical voltage loss ($E_{CT}-V_{OC}$) of 0.65 eV.³⁴ ³⁷ By combining different donor polymers with m-ITIC, we are able to generalize our conclusions to a broad range of donor:NFA systems. Even if other NFA-based devices with lower voltage loss have been reported (current record PCE >16% with V_{OC} = 0.86 eV and voltage loss = 0.53 eV),³⁶ which might show different recombination dynamics, the range of donor:acceptor blends we use here should reflect most state-of-the-art NFA systems when addressing the question of how the low driving force affects the hole transfer mechanism.

Hole transfer dynamics in J61:mITIC

In the optimized 1:1 (mass ratio) blend under 700 nm excitation of the acceptor, only the signatures of photo-excited m-ITIC (slightly red shifted compared to the neat film) are present in the TA

spectra at early time delays and gradually convert to the signatures of charges, as the m-ITIC excitons dissociate by HT (Fig. 1b, Fig. S3-S4). To determine the HT rate, we have decomposed the TA spectra at each time delay into a linear combination of the m-ITIC exciton spectrum and the charge spectrum, using a linear least square fitting procedure (only two components are needed, see details in the SI).³⁸ The temporal evolution of the two components (Fig. 1c) shows a correlated decay of the excitons and rise of the charges with global time constants of 0.8 ps, 12 ps and 82 ps (Tables 1 and S1), indicating that the m-ITIC excitons decay primarily by efficient dissociation. In principle, the average HT time of 35 ps agrees with relatively slow HT reported in literature for polymer:NFA systems with low driving force.^{15, 16, 29} However, the weak 0.8 ps (14%) component points to a sub-picosecond intrinsic HT time scale if excitons are generated near a D:A interface or in an intermixed D:A region,³⁹ while the multiphasic slower charge generation could be limited by exciton diffusion.

To verify this hypothesis, we move away from the morphological complexity of the optimized BHJ, to different sample configurations with more structural control, namely a bilayer fabricated by a lamination process,^{40, 41, 42, 43, 44, 45, 46} and a 5:1 BHJ where the m-ITIC acceptor is present in dilute concentration (TA spectra in Fig. S4). In the former, the lamination method has been shown by X-ray reflection and X-ray photoelectron spectroscopy (XPS) to yield a flat and well-defined interface with minimal molecular interdiffusion ($< 0.01\%$ mass),^{46, 47} maintaining the absorption properties of each neat layer (Fig. S2) and allowing a precise determination of the interfacial exciton density. In the latter, we aim to disperse the acceptor in the polymer matrix in order to minimize the exciton diffusion before it reaches the heterojunction. Grazing-incidence wide-angle X-ray scattering (GIWAXS) and resonant soft X-ray scattering (R-SoXS) agree with the existence of m-ITIC-rich domains (leading to exciton diffusion) alongside ordered pure J61 and possibly

polymer:NFA mixed regions in the 1:1 blend, while the acceptor is largely intermixed within the polymer matrix (which maintains similar J61 aggregation) in the 5:1 blend (see details in the SI, Fig. S5). We use a simultaneous analysis of the reduced EL and sEQE spectra with bi-Gaussian functions to find both the S_1 and CT state energies of the samples (Fig. 1d, Tables 1 and S2). We thus determine that the driving force for HT is relatively low (0.12 eV) and similar in the 1:1 and 5:1 BHJ blends (see bilayer results in Fig. S6).

From the TA dynamics (Fig. 1c, Table 1), we find that in the bilayer, the average HT time is slightly slower (38 ps) than in the 1:1 blend due to enhanced exciton diffusion through the 9 nm m-ITIC layer (Fig. 1e), and that not all excitons reach the D:A interface for dissociation (55% charge yield compared to the optimized BHJ). On the other hand, in the 5:1 dilute blend, the charge generation is much faster (2.6 ps on average), evidencing the successful dispersion of m-ITIC in J61 and reduced exciton diffusion (Fig. 1e). Most importantly, we observe the sub-picosecond rise of charges in all three sample, as shown by the fastest time constant of 0.4 (70%), 0.8 (14%) and 0.9 ps (17%) for the 5:1 blend, 1:1 blend and bilayer, respectively (Table 1). The dilute 5:1 BHJ, in particular, shows that 70% of the charges are formed by HT with an intrinsic time constant (not limited by exciton diffusion) of only 0.4 ps in spite of a low driving force of 0.12 eV. The remaining 30% of the charge rise (in 7.8 ps) could be due to residual aggregation and exciton diffusion in the 5:1 blend, or due to less favorable D:A geometries in the blend. Indeed, DFT calculations show that the electronic coupling and hence the transfer rate dramatically drop when the molecules are slightly further apart than in the equilibrium conformation (see discussion below). The slightly slower onset of HT in the other samples (1:1 blend and bilayer, 0.8 and 0.9 ps) can be explained by a less precise determination of the fastest time constant due to its low weight (14% and 17%), by a different molecular conformation between the donor and acceptor (we expect better

coupling when m-ITIC is surrounded by J61 in the dispersed system),⁴⁸ or by the influence of different molecular aggregation on the charge-transfer rate.^{10, 49} Nevertheless, the intrinsic time scale for HT remains surprisingly fast (<1 ps) no matter what phase morphology is present, in sharp contrast to previous observations (HT in ≈ 10 ps) where the influence of exciton diffusion was not accounted for.^{15, 16, 26, 29}

Electron transfer dynamics in J61:mITIC

HT from photoexcited m-ITIC (at 700 nm) is only one of the channels for current generation in polymer:NFA heterojunctions, so that we also examine polymer excitation at 480 nm. We compare in Fig. 2a (top) the TA dynamics for the optimized J61:m-ITIC (1:1) BHJ with both excitation wavelengths. Only in the case of 480 nm excitation, charges appear at the shortest measurable time that is defined by the 60 fs time resolution of our experiment. Detailed analysis of the TA spectrum at 0.1 ps reveals that about 36% J61 excitons, 28% m-ITIC excitons and 36% charges are present (Table S3), while only m-ITIC excitons are observed at the early time delay with selective acceptor excitation at 700 nm (Fig. S7a). We use kinetic modelling of the TA dynamics to elucidate the underlying photophysics (Fig. 2a (bottom), details in the S.I.). Multiphasic and diffusion-mediated processes are approximated by average time constants, causing small discrepancies with the experimental data. For 480 nm excitation, three phenomena are observed (Fig. 2b and 2c): i) About 28% of absorbed photons lead to direct excitation of m-ITIC (in agreement with the absorption spectrum, Fig. S7b), which then undergoes intrinsic and diffusion-mediated HT similar as is modelled with 700 nm excitation. ii) About half of all J61 excitons are generated close to a m-ITIC interface and undergo ET within the time resolution of the experiment. This leads to ultrafast appearance of charges in < 60 fs, which is not observed for HT with m-ITIC excitation. iii) The

other J61 excitons, generated further away from an interface in the ordered J61 domains, undergo diffusion-mediated ET in competition with excitation energy transfer (EET), whereby EET takes over due to a shallower distance dependence compared to ET. The absorption spectrum of m-ITIC overlaps indeed with the emission spectrum of J61 (Fig. S2), and we calculate a Förster radius of 5.2 nm (see SI), in agreement with other NFA systems.^{50, 51} EET populates m-ITIC excitons near an interface, which then undergo HT with the intrinsic 0.8 ps time constant. As the population of m-ITIC excitons is gradually replenished by EET from J61, the faster m-ITIC exciton decay obtained at 700 nm is not observed at 480 nm. We conclude that intrinsic ET is ultrafast (< 60 fs) and that delayed charge generation with 480 nm excitation occurs predominantly via HT following direct m-ITIC excitation or EET to m-ITIC. Overall, our results demonstrate an unbalance of the ET and HT rates in the same J61:m-ITIC (1:1) blend, with HT being over an order of magnitude slower (intrinsic time constant of 0.8 ps *vs* < 60 fs for ET).

Given the clean interface and well-defined excitation profiles obtained by transfer-matrix modelling (TMM, see SI) in the J61:m-ITIC bilayer, this sample is used to confirm the above findings and to evaluate the distance over which J61 and m-ITIC excitons can undergo intrinsic charge transfer without need for diffusion. With 480 nm excitation, we predict from the excitation profile that 77% of all absorbed photons are absorbed by J61 and 23% by m-ITIC (Fig. 2d). This corresponds well to the sum of J61 excitons and charges (59% +16% = 75%) and to the m-ITIC exciton population (25%) in the early 0.1 ps TA spectrum (Fig. S7a, Table S3), respectively. We therefore confirm that the ultrafast charge generation in J61:m-ITIC with 480 nm excitation is due to prompt ET from photoexcited J61 and that some m-ITIC is directly excited. In the bilayer, we find a percentage of excitons undergoing quenching by intrinsic HT (13% in 0.9 ps with 700 nm excitation, Table S1) and by intrinsic ET (16% in <60 fs with 480 nm excitation, Table S3)

corresponding to excitons generated within 1.2 nm and 1.9 nm from the interface for the acceptor and donor, respectively (as calculated from the excitation profiles in Fig. 2d). This shows that J61 excitons generated slightly further away from an interface can undergo ET without needing to diffuse, likely due to a higher exciton delocalization in the conjugated polymer compared to the small molecule.⁵² The same is observed in the J61:m-ITIC (1:1) blend, where we find 34% charge rise due to intrinsic ET (480 nm), but only 14% due to intrinsic HT (700 nm, Table 1). Together with different J61 and m-ITIC domain sizes, leading to different bulk-to-interface ratios, the exciton delocalization can explain the higher weight of intrinsic ET in the BHJ sample.

Driving force dependence in different polymer:m-ITIC blends

Having unambiguously established a sub-picosecond intrinsic HT rate in the J61:m-ITIC sample with only 0.12 eV driving force, we now further address the question of how this driving force affects the HT rate in different polymer:NFA blends with varied energetics. To this effect, we continue the strategy to dilute the m-ITIC acceptor in different polymer matrices (5:1 blends). These polymers exhibit similar absorption spectra as J61 (allowing for selective m-ITIC excitation, Fig. S2), but different CT energy levels and thus HT driving forces when combined with m-ITIC (Fig. 3a). This is clearly depicted in the sEQE spectra by the gradual shift of the CT band in the sub-bandgap region with respect to the acceptor S_1 state (see complete sEQE/EL analysis in Fig. S8 and Table S2). When we trace the decay of m-ITIC excitons and the concomitant rise of the charges obtained from the analysis of the TA data, we find that all 5:1 blends undergo significant HT already within 1 ps (Fig. 3b). The fastest time constant (intrinsic HT without exciton diffusion) always has a significant weight (>60%) due to effective m-ITIC dispersion (Table 1). Importantly, this time constant remains on the sub-picosecond time scale (0.4 ps) even when the driving force

approaches zero (0.05 eV). HT then gets faster with increasing driving force and becomes ultrafast (0.08 ps) above 0.4 eV. To access also the intrinsic ET rates at different energetics, TA measurements with 480 nm excitation on 1:1 polymer:m-ITIC blends were carried out and reveal an ultrafast (<60 fs) ET component for all donors (Fig. S9, Table 1).

We summarize our findings about the driving force dependence of HT and ET in polymer:m-ITIC systems in Fig. 4a, where we plot the intrinsic charge transfer rate (inverse of the first time constant obtained from the analysis of the TA dynamics) against its corresponding driving force. Note that using the average charge rise time instead does not reveal clear trends (Fig. S10), due to the random contributions of exciton diffusion, non-optimal D:A conformations and EET (at 480 nm). Within the time resolution of our experiment, the intrinsic ET rates remain ultrafast (<60 fs) in the 0.3 to 0.8 eV driving force range, similar to what has been reported in typical polymer:fullerene blends.¹⁰ On the other hand, there is a clear dependence of the intrinsic HT rate on the energetics, with charge-transfer times varying on the sub-picosecond scale (from 0.5 to 0.08 ps) for driving forces from 0.05 to 0.4 eV. Such fast rates are crucial to be competitive with the natural m-ITIC exciton lifetime during HT. Although the exciton lifetime of m-ITIC (and ITIC derivatives in general) is highly multiphasic and dependent on the environment and molecular packing (see dynamics in neat m-ITIC film, m-ITIC solution and m-ITIC:polystyrene blends in Fig. S11),^{16, 53} we find that the fastest component decays with a 3 ps time constant for m-ITIC molecules in the neat film. In the 1:1 blend, the X-ray data indicates the presence of m-ITIC-rich domains, where we expect a comparable packing and short exciton lifetime. Therefore, for HT to be efficient, the observed few-hundred femtosecond charge-transfer times at low driving force are essential to prevent any exciton loss mechanisms.

Discussion

To evaluate whether the observed charge-transfer rates are consistent with a Marcus type description, we have carried out DFT calculations of the transfer integral (electronic coupling) for the ET and HT processes in complexes of J61 and m-ITIC, which is the highest-efficiency OPV system of our study (see SI for details). We find an almost co-facial structural fit of the acceptor molecule on top of the donor polymer that maximizes the overlap of the molecular cores despite sterically demanding side chains (Fig 4b). The transfer integral is higher (32 meV) for ET (LUMO-LUMO) than for HT (21 meV, HOMO-HOMO), which might be at the origin of the generally higher ET rates compared to HT rates in the investigated polymer:m-ITIC systems, even at similar driving force. The electronic coupling dramatically decreases when the D:A distance increases beyond the distance of 4.5 Å (Fig. 4c), highlighting that slower charge-transfer rates can occur even without exciton diffusion for non-optimal geometries in the blend. Furthermore we simulated the individual molecular relaxation energies and we find a very low re-organization energy of 161 meV for the J61:m-ITIC charge-transfer complex (105 meV and 56 meV for m-ITIC anion and J61 cation, respectively). With the calculated values, we predict an intrinsic HT time of 0.13 ps using the semiclassical Marcus-Levich-Jortner (MLJ) model for a driving force of 0.12 eV (see details in the SI).^{5, 33, 54} This is close to the experimental sub-picosecond value of 0.4 ps, which is thus consistent with a MLJ description in the Marcus normal region, at moderate electronic coupling (21 meV) and at low re-organization energy (161 meV). Indeed, the Marcus formalism predicts a maximal charge-transfer rate when the driving force and re-organization energy are similar, so that a low re-organization energy shifts the low driving force region towards higher rates. An ET time of 0.08 ps is predicted for a driving force of 0.45 eV (Marcus inverted region)

and a relatively high transfer integral of 32 meV, which in principle also agrees with the ultrafast experimental value (< 0.06 ps).

Although the measured trend of increasing HT rates with driving force agrees qualitatively with the MLJ model in the normal region (Fig. 4a), one should keep in mind that the re-organization energy and transfer integrals of the other donor:m-ITIC systems can be different (MLJ curves for different electronic couplings are included in Fig. 4a to illustrate the effect on the charge-transfer rates). We also note that the inverted region (decrease in rate upon increase in driving force) is experimentally not observed for the HT and ET rates, which can be mainly assigned to the broadness of the MLJ rate spectrum.⁵⁵ The absence of the Marcus inverted region for polymer:fullerene blends has also been attributed to the fact that sub-100 fs rates are too fast to be described within the Marcus formalism for non-adiabatic ET, warranting a description in the adiabatic limit.^{30, 31, 32, 33} It is therefore likely that MLJ is not the best model to describe the ultrafast ET rates in our NFA systems, even if the predicted value matches the measured rate for m-ITIC:J61. Finally, strong coupling and low driving forces (CT state close to S_1 state) can lead to hybridized locally excited (LE) and CT states.^{8, 56} However, given the moderate electronic coupling (21 meV) compared to a driving force of 120 meV, hybridization should not contribute more than 3% to the HT mechanism in J61:m-ITIC (although we cannot exclude more hybridization in the near-zero driving force PCDTBT:m-ITIC complex). Negligible hybridization is consistent with the distinct CT and S_1 features in the sEQE/EL spectra (for J61, pBTTT and P3HT blends), the absence of hybridized state signatures in the TA,⁵⁷ and the clean conversion of the S_1 excitons (with similar spectral signatures as in neat m-ITIC) to charges (which do not change spectral shape in time). In conclusion, we have investigated here both the electron and hole transfer dynamics in heterojunctions of the non-fullerene acceptor m-ITIC with four polymeric donors having different

driving forces and sample configurations. In contrast to previous work, we have decoupled the effects of morphology-dependent exciton diffusion from the intrinsic charge-transfer rates, by comparing both optimal and dilute bulk heterojunctions with bilayer samples. We demonstrate an unbalance of the electron and hole transfer processes in the high-efficiency J61:m-ITIC system (hole transfer is slower), due to different transfer integrals and driving forces for the two pathways. In contrast, both the electron and hole transfer rates are ultrafast in typical polymer:fullerene systems.³¹ By investigating a series of polymer:m-ITIC blends, we evidence a clear dependence of the hole transfer rate on the energetics, while electron transfer is always ultrafast (<60 fs). This sparks future interest in the efficiency of charge generation in NFA blends across the solar spectrum, to investigate any differences in regions of donor or acceptor excitation. Nevertheless, our main conclusion is that in spite of this unbalance, the hole transfer is much faster than in earlier reports and remains on the sub-picosecond time scale in all investigated samples, even for a near-zero driving force. The sub-picosecond component is particularly prominent in dispersed systems, where exciton diffusion is minimized. Sub-picosecond hole transfer rates at low driving force are consistent with the predictions in the Marcus normal region for charge-transfer with moderate electronic coupling, whereby the high rates can be explained by a small reorganization energy. Hybridization of the excited and charge transfer state is negligible for our highest-efficiency J61:m-ITIC system, which is possibly advantageous in terms of reducing charge recombination.⁵⁶ Overall, we show that the driving force for interfacial charge transfer does not present a limiting factor for efficient charge-transfer at near zero energy loss, as long as the morphology and donor-acceptor geometry are optimized. This presents new opportunities to manipulate energy levels of materials to enhance photovoltage without any tradeoff in photocurrent, opening new paths towards high performance organic photovoltaics.

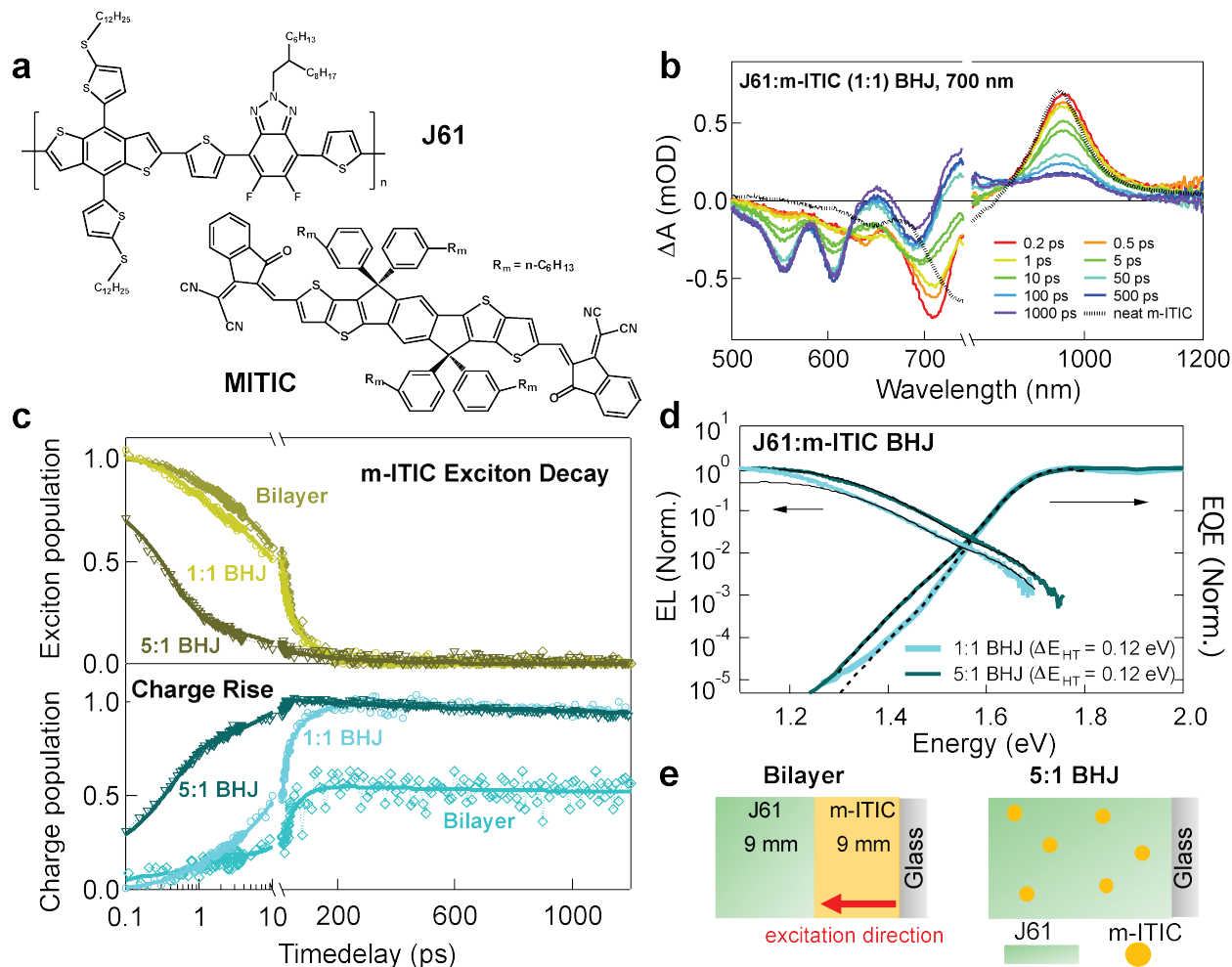


Fig. 1 | HT in J61:m-ITIC heterojunctions with different sample configurations. **a.** Chemical structure of m-ITIC and J61. **b.** TA spectra at selected time delays (see legend) recorded for the J61:m-ITIC (1:1) BHJ following excitation at 700 nm. **c.** m-ITIC exciton decay (top) and charge rise (bottom) dynamics for J61:m-ITIC samples under different morphological scenarios, upon selective m-ITIC excitation at 700 to 730 nm, obtained from the analysis of the TA data. The y-axis is expressed as a fraction of the total absorbed photon density. Symbols are the experimental data and solid lines are exponential fits obtained globally for the exciton decay and charge rise. **d.** sEQE and EL spectra for the J61:m-ITIC BHJ blends with 1:1 and 5:1 mass ratio. The solid and dashed black lines are fits to the EL and sEQE spectra with bi-Gaussian functions, respectively, yielding the S_1 and CT energies as global parameters. **e.** Schematic illustration of the morphology in the J61:m-ITIC bilayer and dilute (5:1 BHJ) samples.

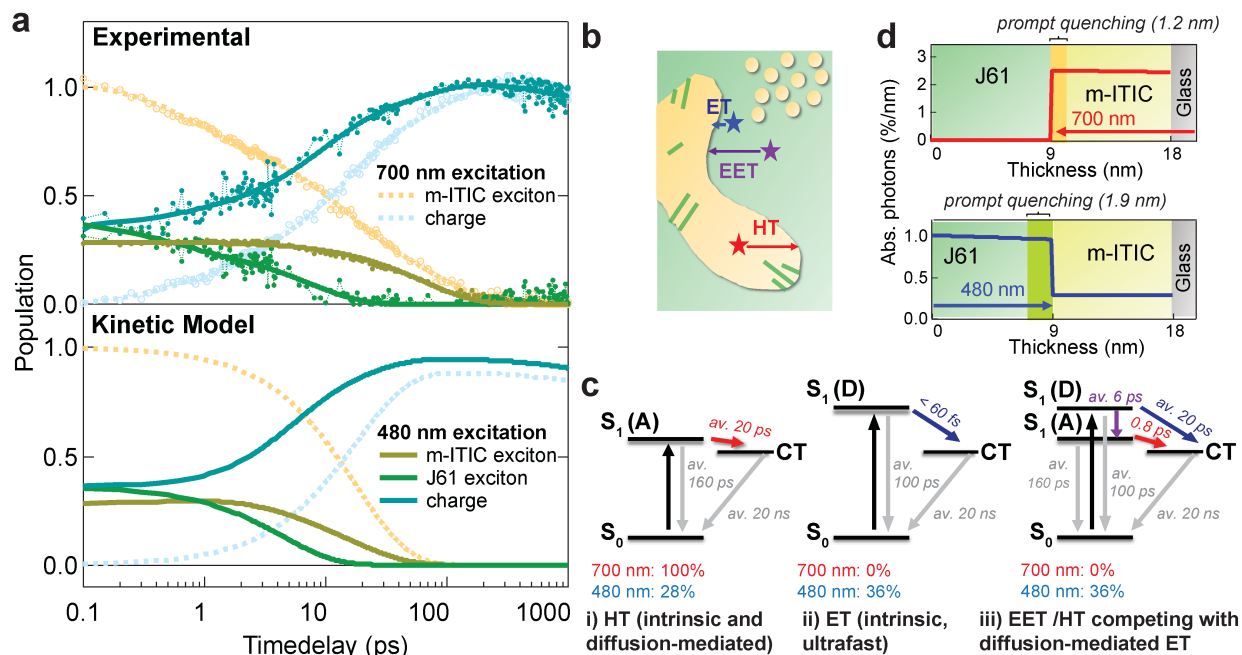


Fig. 2 | Comparison of the ET and HT processes in J61:m-ITIC. **a.** m-ITIC and J61 exciton decay and charge rise dynamics in the J61:m-ITIC (1:1 BHJ) sample under 700 nm and 480 nm excitation obtained from the analysis of the experimental TA data (top), and corresponding dynamic simulated by kinetic modeling (bottom). **b.** Schematic representation of the processes used in the kinetic model within the phase morphology of the blend, which comprises m-ITIC-rich domains, neat ordered polymer domains and intermixed donor-acceptor regions. **c.** Jablonski diagram and time constants for the processes described by the kinetic model: i. 100 % and 28 % of photons are directly absorbed by m-ITIC at 700 nm and 480 nm, respectively, which then undergoes intrinsic and diffusion-mediated HT; ii. At 480 nm, J61 excitons generated within 1.9 nm of a m-ITIC interface undergo ultrafast ET; iii. J61 excitons generated further from an interface undergo diffusion-mediated ET in competition with EET followed by interfacial intrinsic HT, which is predominant due to a shallower distance dependence of EET. Note that all multiphasic processes are approximated with average time constants, leading to some differences with the experimental data. **d.** Excitation profiles (percentage of total incident photons absorbed per nanometer, calculated by TMM) for the bilayer sample at both excitation wavelengths.

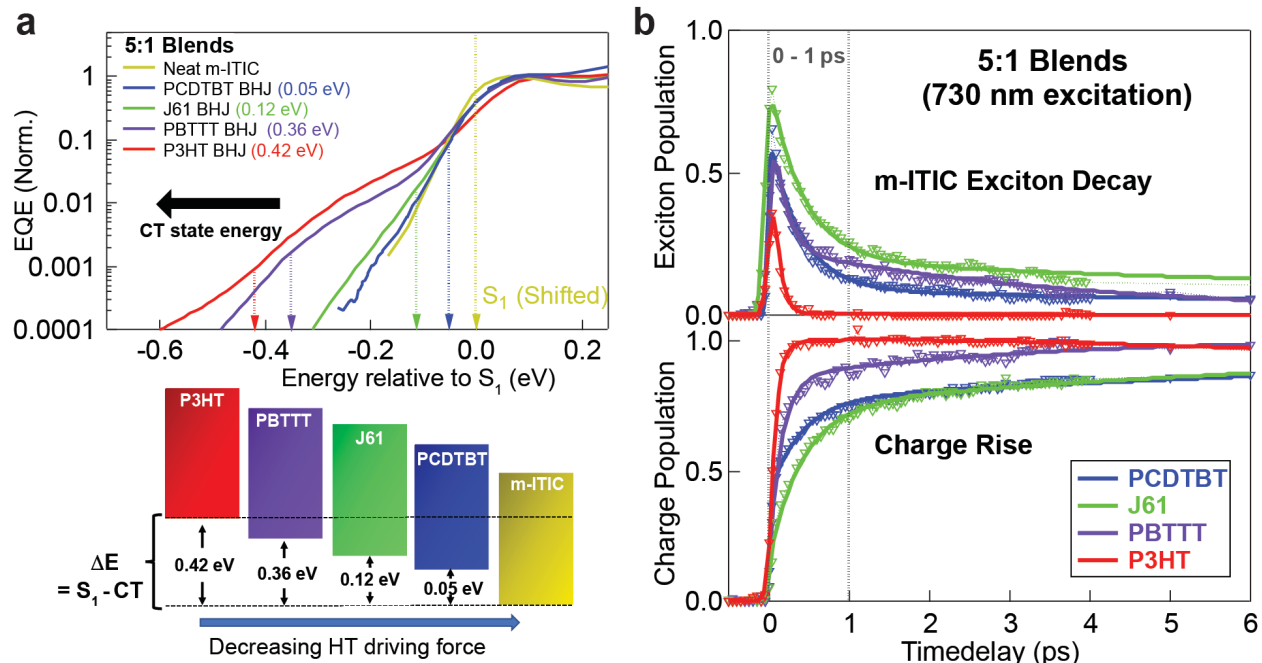


Fig. 3 | Driving force dependent sub-picosecond HT in polymer:m-ITIC blends. **a.** sEQE spectra for the polymer:m-ITIC 5:1 blends and neat m-ITIC. The curves are shifted to always have the m-ITIC S_1 energy (from a bi-Gaussian fit of the sEQE and EL data) at 0 eV for better comparison. At the bottom, a schematic illustration of the driving forces for HT in polymer:m-ITIC 5:1 BHJ samples is shown. **b.** m-ITIC exciton decay (top) and charge rise (bottom) dynamics for polymer:m-ITIC 5:1 BHJ samples, upon selective m-ITIC excitation at 730 nm, obtained from the analysis of the TA data. The y-axis is expressed as a fraction of the total absorbed photon density. Symbols are the experimental data and solid lines are exponential fits obtained globally for the exciton decay and charge rise.

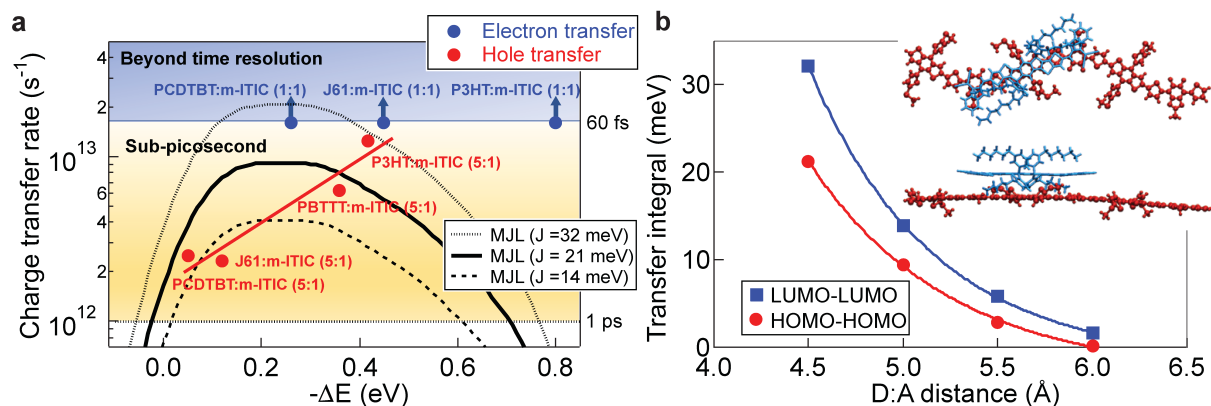


Fig. 4 | Relationship between the driving force and the HT and ET rates. a. The charge-transfer rate (inverse of the first time constant obtained from the analysis of the TA dynamics) for ET and HT in different polymer:m-ITIC BHJ blends is plotted against the driving force (obtained from the sEQE and EL spectra). The red solid line is a guide for the eye to show the trend in HT rate, while the black curves represents the charge transfer rate predicted from semiclassical Marcus-Levich-Jortner theory (with transfer integral $J_{DA} = 14$ -32 meV, Huang–Rhys parameter $S = 1$ and outer reorganization energy $\lambda_o = 0.15$ eV). **b.** LUMO-LUMO transfer integral for ET and HOMO-HOMO transfer integral for HT as a function of the donor:acceptor distance. The geometry as obtained by DFT calculations (at 4.5 Angstrom) is depicted in the inset.

Table 1 | Charge-transfer rates for different driving forces. Excited-state (S_1) energy of the acceptor (700-730 nm excitation) or donor (480 nm excitation), CT state energy (E_{CT}) and driving force for exciton splitting (ΔE). The charge rise time constants (in ps) and their weight (%), as well as their average, obtained from the analysis of the TA data, are also shown. The first time constant (bold) corresponds to the intrinsic charge-transfer rate.

Sample	λ_{ex} (nm)	S_1 (eV)	E_{CT} (eV)	$-\Delta E$ (eV)	Rise times of charges (ps)
J61:m-ITIC (1:1)	700	1.67	1.55	0.12	0.78 (-14%) 12 (-50%) 82 (-36%)
J61:m-ITIC bilayer	700	1.65	n.a	n.a.	0.92 (-17%) 46 (-83%)
PCDTBT:m-ITIC (5:1)	730	1.68	1.63	0.05	0.40 (-57%) 13 (-43%)
J61:m-ITIC (5:1)	730	1.68	1.56	0.12	0.43 (-70%) 7.8 (-30%)
PBTtT:m-ITIC (5:1)	730	1.70	1.34	0.36	0.16 (-78%) 4.0 ps (-22%)
P3HT:m-ITIC (5:1)	730	1.69	1.27	0.42	0.08 (-92%) 2.6 ps (-8%)
PCDTBT:m-ITIC (1:1)	480	1.88	1.62	0.26	<0.06 (-40%) 0.3 (-35%) 17 (-25%)
J61:m-ITIC (1:1)	480	2.00	1.55	0.45	<0.06 (-34%) 0.5 ps (-5%) 8.4 ps (-39%) 57 (-22%)
P3HT:m-ITIC (1:1)	480	2.00	1.20	0.80	<0.06 (-13%) 0.5 ps (-18%) 8.7 ps (-69%)

Acknowledgements

Y. Z. and M. C. contributed equally to this paper. Y. Z., M. C., J. R. and N. B. thank the Swiss National Science foundation (grants PP00P2_150536 and 200020_184819), as well as the University of Bern, for financial support. J. B. and K. V. thank the German Federal Ministry for Education and Research (BMBF) for financial support through the InnoProfile project “Organische p-i-n Bauelemente 2.2”. J. K. thanks the German Academic Exchange Service (DAAD) for financial support (Grant No. 57214224). F. G. acknowledges financial support from Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP, project number: 2018/15670-5). F. O. would like to thank the Deutsche Forschungsgemeinschaft for financial support (project OR-349/1). Grants for computing time from the Zentrum für Informationsdienste und Hochleistungsrechnen Dresden (ZIH) are gratefully acknowledged. B. Xiao and E. Zhou thank the support from the Key Research Program of Frontier Sciences, Chinese Academy of Sciences (Grant No. QYZDB-SSW-SLH033), the National Natural Science Foundation of China (NSFC, Nos. 51673048, 51473040). Portions of this research were carried out at the 11-BM Complex Materials Scattering beamlines of the National Synchrotron Light Source II, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Brookhaven National Laboratory under Contract No. DE-SC0012704, and at beamlines 6.3.2 and 11.0.1.2 of the Advanced Light Source, which is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under contract no. DE-AC02-05CH11231. R. Li (NSLS-II) and C. Wang (ALS) are acknowledged for assisting with the experimental setup and providing instrument maintenance. Daniel Sunday (NIST) is gratefully acknowledged for assistance with NEXAFS measurements. All thank Prof. K. Sivula at École Polytechnique Fédérale de Lausanne (EPFL) for helping to measure sample thickness.

Author contributions

Y.Z. and M.C. contributed equally to this paper. Y.Z. prepared the samples; M.C., G.J.M. and Y.Z. measured TA; Y.Z., M.C. and N.B. analyzed the TA data; J.R. and P.K. calculated the excitation profiles; B.X. and E.Z. synthesized J61 and m-ITIC. Y.Z., K.Y., P.K., R.S., J.K., J.B., S.C.B.M. and K.V. did sEQE measurement and analysis. G.J.M., E.B., and D.N. performed EL measurement

and analysis. S. M., L. R., D. D. did X-ray measurement. F. G. and F. O. performed theoretical modelling and DFT simulations. N.B. supervised the whole project. Every author contributed to manuscript preparation.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information is available for this paper at ...

Data availability statement

Data in Figures 1-4 will be made publicly available (BORIS repository, University of Bern).

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