Sub-picosecond charge-transfer at near-zero driving force in polymer:non-fullerene acceptor blends and bilayers

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Organic photovoltaics based on non-fullerene acceptors (NFAs) show record efficiency of 16 to 17% and increased photovoltage owing to the low driving force for interfacial charge-transfer. However, the low driving force potentially slows down charge generation, leading to a tradeoff between voltage and current. Here, we disentangle the intrinsic charge-transfer rates from morphology-dependent exciton diffusion for a series of polymer:NFA systems. Moreover, we establish the influence of the interfacial energetics on the electron and hole transfer rates separately. We demonstrate that charge-transfer timescales remain at a few hundred femtoseconds even at near-zero driving force, which is consistent with the rates predicted by Marcus theory in the normal region, at moderate electronic coupling and at low re-organization energy. Thus, in the design of highly efficient devices, the energy offset at the donor:acceptor interface can be minimized without jeopardizing the charge-transfer rate and without concerns about a current-voltage tradeoff.
Organic heterojunctions between electron donors (D) and acceptors (A) are of vital importance for diverse applications ranging from photocatalysis, to batteries and solar energy conversion1-3. Appropriately selected D:A combinations have enabled high performance in organic electronic devices such as organic photovoltaics (OPVs) or organic light-emitting diodes (OLEDs)4,5. 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 (CT) 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 CT state and the photoexcited (S2) state, is a key factor determining the rate of the CT5-9. In OPV systems, a dependence of the CT rate and yield on the driving force has indeed been observed for fullerene-containing model systems10,11. This is consistent with the previously reported empirical lower limit of a 0.3 eV driving force required for efficient CT in typical polymer:fullerene blends12,13. Understanding the impact of driving force on the CT dynamics is particularly important in organic solar cells, since the CT state energy also determines the open circuit voltage (VOC), 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 dissociation13-17.

In this respect, the recent success of non-fullerene acceptors (NFAs), that have taken the OPV community by storm with record efficiency over 16%, has been attributed to efficient current generation in polymer:NFA blends even at very low or absent driving force, reducing VOC 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 CT, which both distinguish the NFA systems from fullerene blends. Several reports on polymer:NFA systems claim a reduced CT rate on the picosecond time scale, attributed to the low driving force15,16,25,26. There are however two major shortcomings in these studies. First, the investigations have not clearly established whether the observed CT rates reflect only interfacial processes or whether they are limited by exciton diffusion in the complex morphology of the investigated blends15,16,25,27-29. 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 CT 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 to 0.4 eV. The behavior at low driving force is consistent with the trend expected in the Marcus normal region for CT 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.30-33. Overall, the sub-picosecond times for both CT pathways over a large range of driving forces demonstrate that the energy offset at the heterojunction can be minimized without jeopardizing the CT 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.

Hole transfer dynamics in the J61:m-ITIC blend. In the optimized 1:1 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, Supplementary Figs. 3 and 4). 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 Supplementary Note 1). 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, 12, and 82 ps (Table 1 and Supplementary Table 1), 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, 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 process10-46, and a 5:1 BHJ where the m-ITIC acceptor is present in dilute concentration (TA spectra in Supplementary Fig. 4). In the former, the lamination method has been shown by X-ray reflection and X-ray photoelectron...
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 700–730 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 S1 and CT energies as global parameters. e Schematic illustration of the morphology in the J61:m-ITIC bilayer and dilute (5:1 BHJ) samples.

Table 1 Charge-transfer rates for different driving forces.

| Sample                  | $\lambda_{\text{ex}}$ (nm) | $E_{\text{S1}}$ (eV) | $E_{\text{CT}}$ (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%)       |
| J61:m-ITIC (1:1)        | 480                       | 2.00                 | 1.55                 | 0.45             | <0.06 (34%) 0.5 ps (5%)     |
| P3HT:m-ITIC (1:1)       | 480                       | 2.00                 | 1.20                 | 0.80             | <0.06 (13%) 0.5 ps (18%)    |

Excited-state energy $E_{\text{S1}}$ of the acceptor (700 or 730 nm excitation) or donor (480 nm excitation), CT state energy ($E_{\text{CT}}$) and driving force for exciton splitting ($-\Delta E$). The charge rise time constants (in ps) and their weight (%), obtained from the analysis of the TA data, are also shown. The first time constant (bold) corresponds to the intrinsic charge-transfer time.
spectroscopy (XPS) to yield a flat and well-defined interface with minimal molecular interdiffusion (lower than 0.01% mass)\textsuperscript{16,46,47}, maintaining the absorption properties of each neat layer (Supplementary Fig. 2) 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 aggregation as pure J61) in the 5:1 blend (see Supplementary Note 2 and Supplementary Fig. 5). We use a simultaneous analysis of the reduced EL and sEQE spectra with bi-Gaussian functions (Supplementary Note 3) to simultaneously analyze of the reduced EL and sEQE spectra (which maintains similar aggregation as pure J61) in the 5:1 blend (see bilayer results in Supplementary Fig. 6).

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)\textsuperscript{11,49}, or by the influence of different molecular aggregation on the CT rate\textsuperscript{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 =about 10 ps, where the influence of exciton diffusion was not accounted for\textsuperscript{15,16,26,29}.

Electron transfer dynamics in the J61:m-ITIC blend. 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 (Supplementary Table 3), while only m-ITIC excitons are observed at the early time delay with selective acceptor excitation at 700 nm (Supplementary Fig. 7a). We use kinetic modeling of the TA dynamics to elucidate the underlying photophysics (Fig. 2a (bottom), Supplementary Note 4). 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, c): (i) about 28% of absorbed photons lead to direct excitation of m-ITIC (in agreement with the absorption spectrum, Supplementary Fig. 7b), which then undergoes intrinsic and diffusion-mediated HT similar as is modeled 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 shorter than 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 shorter distance dependence compared to ET. The absorption spectrum of m-ITIC overlaps indeed with the emission spectrum of J61 (Supplementary Fig. 2), and we calculate a Förster radius of 5.2 nm (see Supplementary Note 5), in agreement with other NFA systems\textsuperscript{30,51}. 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 (shorter than 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 modeling (TMM, Supplementary Note 6) 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 CT 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, respectively (Supplementary Fig. 7a, Supplementary Table 3). 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, Supplementary Table 1) and by intrinsic ET (16% in <60 fs with 480 nm excitation, Supplementary Table 3) corresponding to excitons generated within 1.2 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\textsuperscript{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, Supplementary Fig. 2), 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<sub>1</sub> state (see complete SEQE/EL analysis in Supplementary Fig. 8 and Supplementary Table 2). 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 (larger than 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 (shorter than 60 fs) ET component for all donors (Supplementary Fig. 9, 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 CT 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 (Supplementary Fig. 10), due to the random contributions of exciton diffusion, non-optimal D:A conformations and ET (at 480 nm). Within the time resolution of our experiment, the intrinsic ET rates remain ultrafast (shorter than 60 fs) in the 0.3–0.8 eV driving force range, similar to what has been reported in typical polymer:fullerene blends. On the other hand, there is a clear dependence of the intrinsic HT rate on the energetics, with CT 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:polymer blends in Supplementary Fig. 11), 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 CT times at low driving force are essential to prevent any exciton loss mechanisms.

Discussion

To evaluate whether the observed CT 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. 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, Supplementary Note 7). 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 CT 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 CT complex (108 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 (Supplementary Note 8)\(^5,33,54\). 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 CT 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 (shorter than 0.06 ps).

Although the measured trend of increasing HT rate with driving force agrees qualitatively with the MLJ model in the normal region (Fig. 4a), one should keep in mind that the reorganization 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 CT 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\(^5,35\). 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-adiaabatic ET, warranting a description in the adiabatic limit\(^30–33\). 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 a low driving force (CT state close to \(S_1\) state) can lead to hybridized
locally excited (LE) and CT states. However, given the moderate electronic coupling (21 meV) compared to a driving force of 7.5 mg mL$^{-1}$, 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 system). Negligible hybridization is consistent with the distinct CT and S$_f$ features in the sE QE/EL spectra (for J61, PBT TT and P3HT blends), the absence of hybridized state signatures in the TAs, and the clean conversion of the S$_f$ 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 CT 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-loss 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, sparking future interest in the efficiency of charge generation in NFA blends in regions of donor and acceptor excitation. Our main conclusion is that in spite of this unbalance, the intrinsic 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. Sub-picosecond hole transfer rates at low driving force are consistent with the predictions in the Marcus normal region for CT with moderate electronic coupling, whereby the high rates can be explained by a small reorganization energy.  

Hybridization of the excited and CT state is negligible for our highest-efficiency J61:m-ITIC system, which is possibly advantageous in terms of reducing charge recombination. Overall, we show that the driving force for interfacial CT does not present a limiting factor for efficient CT at near zero energy loss, as long as the morphology and donor–acceptor geometry are optimized.

**Methods**

**Sample preparation.** Poly[9-(1-octylnonyl)-9H-carbazole-2,7-diyli-2,5-thiophenediyli-2,1,3-benzothiadiazole-4,7-diyli-2,5-thienophenylidinyl] (PCDTBT) was purchased from Sigma-Aldrich, while 3,9-bis(2-methylene((3-(1,1-dicyanomethylene)-6/7-nediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl) (PCDTBT) was purified (HPLC) and further purified by preparative thin-layer chromatography (TLC) on silica gel 60 F254 plates (Merck) using a CH$_2$Cl$_2$ : MeOH (99:1) mixture as eluent. P3HT and P3HT:PCBM were purchased from Sigma-Aldrich, while 3,9-bis(2-methylene((3-(1,1-dicyanomethylene)-6/7-methyl)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2,3-b]indole (J61) were synthesized following the method previously reported. The CT efficiencies of the J61:PCBM system (hole transfer) are calculated by dividing the photogenerated current density ($J_{\text{hole}}$) by the polymer concentration. In addition, we have also determined the J61:PCBM system (electron transfer) by dividing the photogenerated current density ($J_{\text{electron}}$) by the polymer concentration.

**EL measurements.** The EL measurements were performed using an Andor SR-303i-B spectrometer equipped with a silicon (Si) and indium–gallium–arsenide (InGaAs) photodiode.

**TA spectroscopy.** TA experiments were carried out using a home-built femtosecond pulsed pump-probe laser setup. The excitation pump pulses at 480, 700, or 730 nm were generated with a commercial optical parametric amplifier (OPerA Solo, Coherent) from the fundamental 800 nm laser output from a Ti:sapphire laser system with regenerative amplification, providing 35 fs pulses at a repetition rate of 1 kHz (Astrella, Coherent). These pump wavelengths were chosen to selectively excite the donor polymers or the acceptor. 730 nm excitation was used in the 5:1 blends to exclude direct donor exciton excitation due to its high loading. The pump energy at the sample position was adjusted to be in a linear regime where the dynamic range of electron switching, whereby the electronic coupling (21 meV) compared to a driving force of 7.5 mg mL$^{-1}$, 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 system). To prevent device heating when the EL signal was measured in the near-IR, the voltage used was the same throughout the entire spectrum for the silicon (and germanium detectors) and then the final continuous EL spectrum was obtained, after subtraction of the dark background signal.

**X-ray scattering.** X-ray scattering measurements were performed on a high-resolution X-ray diffractometer. A 4.2 m synthetic graphite monochromator was used to select 1.54 Å radiation. The one of the pump in order to avoid effects of the polarization of the excitation beam was chosen to be 0.5 s and the transmitted intensity of the signal beam was recorded shot-by-shot (see Supplementary Fig. 13). Moreover, the fluence was corrected to have a similar flux of absorbed photons ($3 \times 10^{15}$ photons cm$^{-2}$) for all the measurements, taking into account the absorbance at the excitation wavelength and the photon energy. The probe beam was chosen to be transmitted through the sample and overlapped with the pump beam) and a reference beam. The signal and reference beams were detected separately using a pair of spectrophotographs (home-built prism spectrometers) equipped with 512 x 58 pixels back-thinned Silicon CCDs (Hamamatsu S07030-0906) and InGaAs arrays (Hamamatsu) for, respectively, visible and near-IR detection. The spectrophotographs were assembled by Entwicklungsbüro Streising, Berlin. Wave-length calibration was accomplished with a set of 10 nm bandpass filters. To improve the sensitivity, the pump pulses were chopped at half the amplifier frequency, and the transmitted intensity of the signal beam was recorded shot-by-shot and it was, finally, corrected for laser intensity fluctuations using the reference beam. The spectra were averaged 3000–4500 times at each time delay and the entire range of measured time delays was scanned 8–10 times. All the TA experiments were performed with a probe polarization at the magic angle with respect to the optical axis of the polarizer in order to avoid effects of the polarization of the excitation beam on the probe absorption intensity. Prior to the TA analysis, the spectra were corrected for the chirp of the white light (parameters obtained by measuring the pump-probe cross-correlation on a glass slide placed between crossed polarizers).

**X-ray scattering: GIWAXS and RSoXS.** GIWAXS measurements were performed at the 11-BM Complex Materials Scattering (CMS) beamline of the National Synchrotron Light Source II (NSLS-II) with a beam energy of 10 keV. The 2D scattering patterns were collected at an X-ray incidence angle of 0.12° with a range of measured time delays was scanned 8–10 times. All the TA experiments were performed with a probe polarization at the magic angle with respect to the optical axis of the polarizer in order to avoid effects of the polarization of the excitation beam on the probe absorption intensity. Prior to the TA analysis, the spectra were corrected for the chirp of the white light (parameters obtained by measuring the pump-probe cross-correlation on a glass slide placed between crossed polarizers).
Pro. sector averaged 1D scattering patterns of the polymer film were collected at beamline 11.0.1.2 following procedures described earlier61. BHF films were cast on PSS-coated glass substrates, floated in water, and transferred onto 100 nm Si3N4 windows (Norcada)62. The 2-D R-RoSoXS data were collected at beamline 11.1.0.2 at the Advanced Light Source using a Peltier cooled (~45 °C) in-vacuum (base pressure = 10−9 Pa) CCD detector (PI-MTE, Princeton Instruments, 2048 x 2048 pixels). 1-D scattering profiles were obtained from the reduction of the 2-D scattering patterns using a custom Nika analysis package and subsequently normalized for the instantaneous X-ray flux. The scattering intensity is affected by the distance traveled by the X-ray beam through the sample as well as the scattering volume. R-RoSoXS scattering intensities were therefore normalized for absorption and film thickness. Data were acquired at multiple energies in the range 283–284 eV to optimize material contrast over the entire thickness contrast, minimize beam damage, and avoid fluorescence background34,64. Material contrast at the C K-edge was calculated from transmission NEXAFS measured using a photodiode at the ALS beamline 6.3.2 on neat films transferred onto 100 nm SiN4 windows (Norcada). The NEXAFS spectra were normalized to the absorption spectrum of an identical blank SiN4 window. The spectra were analyzed using the QANT analysis package34.

Spectroscopic ellipsometry. The real (n) and imaginary (κ) parts of the complex optical constants were determined from variable angle spectroscopic ellipsometry (VASE) measurements on neat polymer (J61) and acceptor (m-ITIC) films cast on Si (see results in Supplementary Table 5). VASE was carried out with a M-2000-XI, J.A. Woollam Co., Inc., USA. The incidence angle was scanned from 45° to 75° in steps of 1°, and the photon energy varied from 0.74 to 5.87 eV. Modeling of the blend films was performed using the CompleteEASE software package. The film thickness and optical constants were fitted to a uniaxial B-Spline model. The ordinary values of the n and κ are reported here.

DFT calculations. In order to calculate the electron transfer parameters λ and J1,2,3,4,5,6,7,8,9 we performed density functional theory calculations as implemented in Gaussian 0988. In brief, we used the B3LYP89 functional and the 6-21G basis set for optimizing the molecular structures of monomers and donor-acceptor complexes and for determining the total energy. We calculated the transfer integral for which we used the larger 6-311G** basis for a better description of the electronic states. In order to obtain the relaxation energies, we firstly optimized the molecular structures of the donor and acceptor individually (see Supplementary Note 7), to obtain their equilibrium geometry (short-hand notation R0) and the related total energies E(R0). As displayed in Supplementary Figs. 18 and 19, both the m-ITIC central unit and the J61 polymer backbone are rather planar, i.e. torsion angles are below 5°. The attached phenyl rings (for m-ITIC) and thiophene rings (for J61), however, are pointing out of the backbone plane. These groups therefore increase the molecular distance when forming π–π stacks. Secondly, the negatively charged m-ITIC and the positively charged J61 structures were optimized, which results in the geometries of the ionic species (R+, respectively). Finally, a single point calculation of the uncharged molecular geometries R, were performed to get the total energies. The relaxation energies were then obtained from the differences λm→e = E(R+) − E(R−) for J61 and m-ITIC, respectively. The results are summarized in Supplementary Table 6. Note, that the different conformations of the polymer yield almost the same values for λm→e. This led us to the conclusion that the relaxation energy is mainly determined by local interaction of nearest and next-nearest atoms and is therefore independent from the global orientation of the backbone. Moreover, Supplementary Table 6 shows that turning one thiophene ring in each repeat unit from cis to trans orientation leads to an increase of about 126 meV in the total energy for the structure in Supplementary Fig. 19. Hence, the cis/cis orientation exhibits the smallest energy such that only this conformation is considered in the following. The relaxation energies, which are assigned mainly to intramolecular high-frequency modes due to the stiff backbone, of both donor and acceptor add to the intramolecular reorganization energy λ of the CT process. For the polymer, we take the relaxation energy for the structure consisting of two repeat units as similar to the size to the acceptor molecule, hence λ ≈ 1.61 meV.

For the simulation of donor–acceptor complexes to calculate the transfer integrals, the obtained molecular structures for m-ITIC and J61 were used to construct geometries with different lateral and vertical distances. We considered intermolecular distances ranging from 4.5 to 6.0 Å (see Supplementary Note 7), the results of which are depicted and discussed in the main text.

Data availability
Data in Figs. 1–4 is made publicly available (BIRS Repository, University of Bern, https://doi.org/10.7892/boris.139648).

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Additional information
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