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Hole-Transport in Low-Donor-Content Organic Solar Cells

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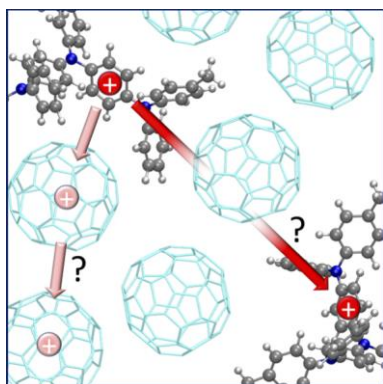
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Abstract

Organic solar cells with an electron donor diluted in a fullerene matrix have reduced density of donor-fullerene contacts, resulting in decreased free-carrier recombination and increased open-circuit voltages. However, the low-donor concentration prevents the formation of percolation pathways for holes. Notwithstanding, high (> 75 %) external quantum efficiencies can be reached, suggesting an effective hole-transport mechanism. Here, we perform a systematic study of the hole mobilities of 18 donors, diluted at ~6 mol% in C₆₀, with varying frontier energy level offsets and relaxation energies. We find that hole transport between isolated donor molecules occurs by long-range tunneling through several fullerene molecules, with the hole mobilities being correlated to the relaxation energy of the donor. The transport mechanism presented in this study is of general relevance to bulk-heterojunction organic solar cells where mixed phases of fullerene containing a small fraction of a donor material or vice versa are present as well.

TOC Graphic



Main text

Low-donor-content organic solar cells (OSCs) have an active layer consisting of a small-molecule electron donor diluted at approximately 5 wt% in fullerene, resulting in a large average distance between donor molecules of about 2.5 nm and a reduced donor-acceptor interface area. Originally introduced by Tang and co-workers in 2011,¹ it has been found that the reduced donor-acceptor contacts in such solar cells results in less free-carrier recombination and thus increased open-circuit voltages as compared to OSCs with substantially higher donor content.² On the other hand, due to the low donor content, continuous networks of adjacent hole-transporting molecules that span across the blend layer cannot be formed and thus inefficient hole transport might be expected.

Despite this, rather high internal quantum efficiencies (IQE) and external quantum efficiencies (EQE) over 75% in the strongly absorbing spectral region of the fullerene can be reached, even for transparent donors (e.g. TAPC).¹ This raises the intriguing question of what the exact hole-transport mechanism at such low donor contents is.

Similarly, in efficient bulk heterojunction (BHJ) OSCs,^{3,4} mixed donor:fullerene phases containing a small fraction of the donor material or a small fraction of fullerenes can also occur, despite more equal overall ratios. It is unclear how charges, generated on those isolated donor or acceptor domains, can still reach the electrodes; however, overall IQEs can, in the best cases, be over 90%, suggesting that such charges are indeed harvested.⁵ Low-donor-content solar cells are therefore interesting model systems to understand transport across isolated, mixed phases. We point out that vacuum deposited molecules are more finely intermixed than in solution processing, making vacuum deposited low-donor-content OSCs a better model system for studying transport in isolated phases.

In this paper, we elucidate the hole-transport mechanism in thin films of C_{60} where the donor is diluted below the percolation limit (~ 6 mol%, except where stated otherwise) and investigate whether C_{60} plays a direct role by hosting the holes or just by mediating the hole-transport. We demonstrate that the holes are not traveling in the C_{60} phase, instead they tunnel from donor to donor. The hole mobility shows a strong correlation with the simulated and measured relaxation energy of the donor. Based on this finding, an empirical law for estimating the hole mobility in low-donor-content organic solar cells is formulated. More generally, the

transport mechanism presented in this study explains why in certain mixed phases of BHJ solar cells, charges are still efficiently collected, despite the absence of a clear percolation network.

In order to analyze the hole-transport mechanism, we consider two main scenarios. The first one assumes that holes move by means of thermally assisted jumps from the highest occupied molecular orbital (HOMO) of the donor to the HOMO of the neighboring C₆₀. Since it is known that C₆₀ is able to transport holes,⁶⁻⁹ holes might then be transported in the fullerene phase, until they are trapped at another donor molecule. This scenario would be a “trap and release” transport mechanism via C₆₀, where the donors act as the traps, which would be consistent with the finding that mobilities for holes are lower than those for electrons in these blends.¹⁰ A similar mechanism has been proposed to explain the hole mobility for MDMO-PPV:PCBM solar cells.⁹

The alternative scenario presumes tunneling of the holes from one donor to another donor through the C₆₀ host.¹¹ A schematic representation of the two proposed mechanism can be found in Figure S6 in the Supporting Information (SI). To distinguish between the two scenarios in low-donor-content devices, we designed a series of experiments, supported by simulations, in which we studied a series of 18 different donor molecules regarding their transport behavior and characteristic energies involved in the processes.

The hole mobilities of the low-donor-content active layers were first determined using single-carrier devices. Current-voltage (I-V) curves were measured to obtain the hole mobility through a fit with the Murgatroyd model in the space-charge-limited-current (SCLC) region,¹² as described in the SI Section 2. The mobility values at room temperature and the molecular structures of the used donor molecules are presented in Table S1 in the SI. The measured I-V curves of the single-carrier devices are symmetric (Figure S1 in the SI), which excludes significant injection and extraction barriers at the contacts.

In case of a trap and release transport mechanism via C₆₀, we would expect the hole mobility to decrease with increasing donor content, because the trap density would be increased. Figure 1, therefore, shows the concentration dependence of the hole mobilities of selected systems. We find, however, that the mobility *increases* with increasing donor content in the devices over the whole concentration range studied, indicating that the trap-and-release model is unlikely or certainly not the dominant mechanism.

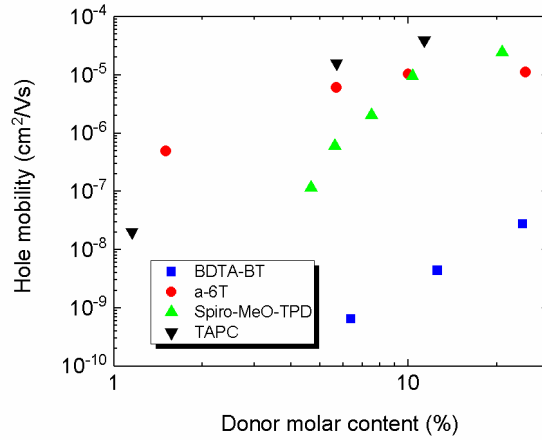


Figure 1 Hole mobilities obtained via SCLC measurements as a function of the donor molar content for 4 different donors.

A second piece of evidence that holes are not significantly transported on C_{60} is the missing correlation of the mobility with the donor HOMO energy. In the case of hole activation to the fullerene HOMO, we would expect that the trap depth E_{tr} , i.e. the energy difference between the HOMO of the donor and the HOMO of the fullerene

$$E_{tr} = E_{HOMO}(D) - E_{HOMO}(C_{60}) \quad (1)$$

would be reflected in the transport activation energy (E_a) for the hole mobility, possibly even as a proportionality between both energies. Moreover, E_{tr} , which is in the order of 1 eV, should dominate any activation behavior of the hole transport within the fullerene phase, if present. To determine whether this is the case, the temperature-dependence of the hole mobility was obtained from I-V curves of single carrier devices for 10 different donor: C_{60} combinations. Within the analyzed temperature range, the hole mobilities of these materials exhibit an Arrhenius behavior¹³ as depicted in Figure 2(A). From the Arrhenius fit of the temperature-dependent mobility measurements, the transport activation energy E_a is extracted and plotted in Figure 2(B).

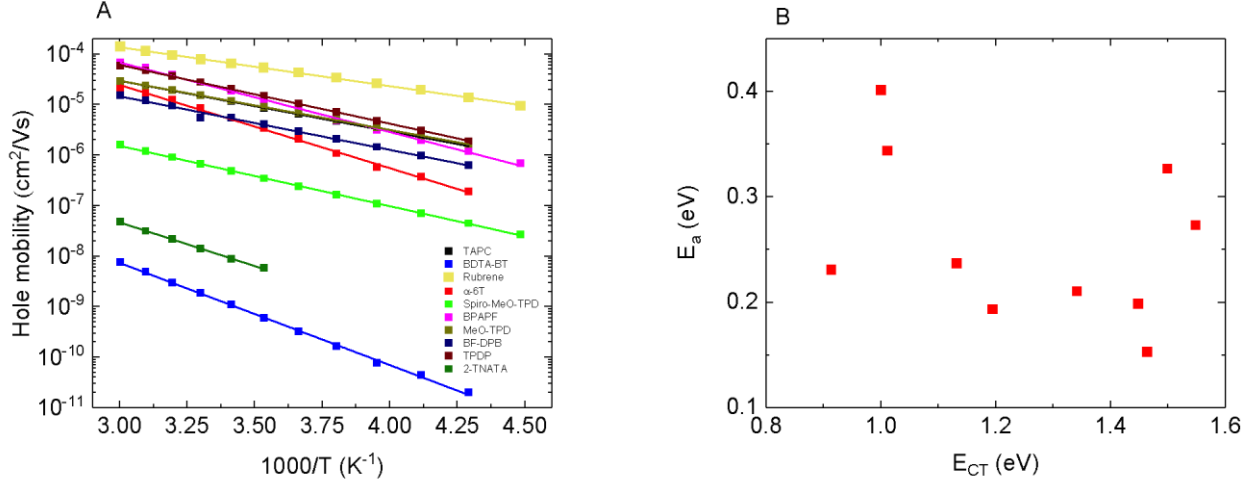


Figure 2 (A) Arrhenius plot of the temperature dependent hole mobility for 10 different donor materials, measured in hole-only devices. (B) Activation energy for the hole transport (E_a) versus E_{CT} , showing that these quantities are uncorrelated.

In order to compare E_a with the trap depth E_{tr} , we have to extract the HOMO energy levels of the donor materials in the host. For this purpose, we study the charge-transfer (CT) state energy E_{CT} , which is determined by the relative positions of $E_{HOMO}(D)$ and the lowest unoccupied molecular orbital (LUMO) of the acceptor $E_{LUMO}(C_{60})$. $E_{HOMO}(D)$ is expected to correlate with E_{CT} after adding the electron-hole binding energy Δ

$$E_{HOMO}(D) \cong E_{LUMO}(C_{60}) - E_{CT} - \Delta \quad (2)$$

Access to E_{CT} is provided through sensitively measured EQE (sEQE) spectra, revealing the CT absorption bands of photovoltaic devices. From a fit of the low-energy tail of the CT absorption band, E_{CT} is obtained.¹⁴ E_{CT} is directly related to E_{tr} via:

$$E_{tr} \cong E_{gap}(C_{60}) - E_{CT} - \Delta \quad (3)$$

where $E_{gap}(C_{60})$ is the transport gap of C_{60} . We assume Δ to vary only weakly between donors when the acceptor is chosen to be C_{60} .¹⁵ As shown in Figure 2(B), we find no proportionality between E_a and E_{CT} , implying that there is also no correlation between E_a and E_{tr} . This analysis

shows that the “donor trap” energy is not significantly reflected in the hole mobility activation and thus further corroborates that trap-and-release is not the dominant mechanism for hole transport.

It remains to investigate if the second transport scenario, based on a tunneling process from donor to donor, can explain the hole transport mechanism in low-donor-content OSCs. A suggestion that this tunneling can even be enhanced by the “barrier” molecules in between donors has been made by Nenashev and coworkers,¹⁶ Symalla, Massé and coworkers.^{11,17} The authors of Refs. ¹¹ and ¹⁷ used *ab initio* modeling to study charge transport in multicomponent emissive host-guest layers used in organic light-emitting diodes (OLEDs), in which this layer consists of a small concentration (3%–10% molar) of a phosphorescent dye embedded in a host matrix. They argue that charge transport between distant sites in such systems is mediated via the coherent process of molecular superexchange, in which again the energy difference E_{tr} is relevant¹⁸⁻²⁰ (cf. SI, section 5). The similarity of the systems, suggests the same mechanism could explain efficient hole transport in low-donor-content solar cells.

Firstly, we notice that the scaling of the hole mobility with the donor concentration in Figure 1 is consistent with tunneling between the donor molecules, given that higher donor concentrations will lead to reduced tunneling distances. We next study whether the energies of the involved transport levels $E_{HOMO}(D)$ and $E_{HOMO}(C_{60})$ are consistent with the superexchange mechanism, by investigating the correlation with the energy difference E_{tr} in two ways. We first compare the hole mobilities to E_{CT} as obtained above. The second approach is to calculate the donor ionization potential (*IP*) within density functional theory (DFT) and correlate that with the hole mobilities. As we combine the donor molecules always with C_{60} , only the *IP* of the donor molecules is relevant since the *IP* of C_{60} is constant.

In Figure 3(A), the hole mobility is plotted as a function of IP_D , with the latter determined by DFT calculations in the solid state. Due to the diversity of the donor materials used, the mobility varies considerably (from $6.61 \cdot 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for rubrene to $6.44 \cdot 10^{-10} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for BDAT-BT). Also the calculated donor *IP*s vary by about 1 eV. Surprisingly, however, only a weak correlation can be found between the donor *IP* and the hole mobility. Plotting the mobility versus E_{CT} does not show a clear correlation either.

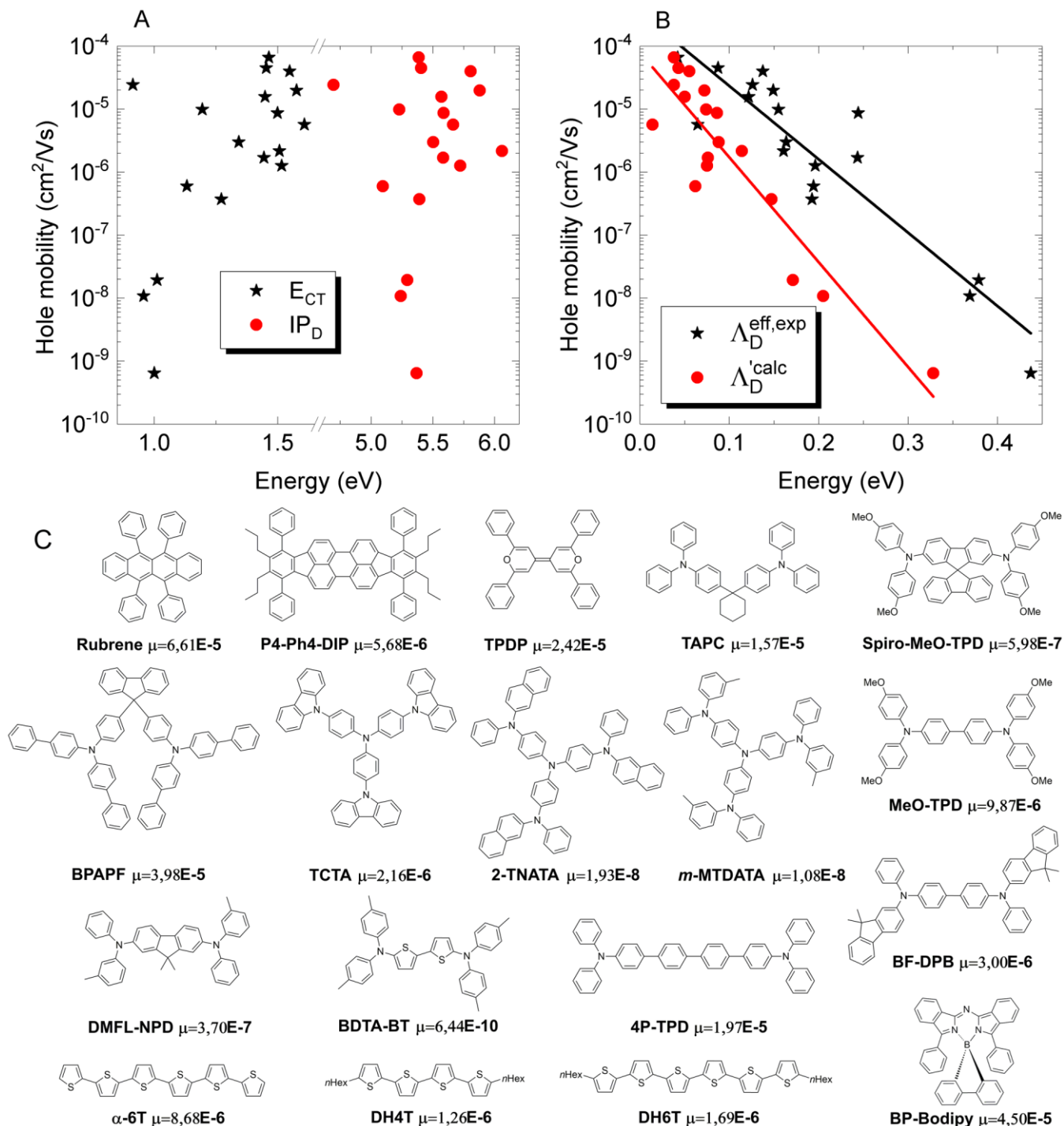


Figure 3 Hole mobility in low-donor-content OSCs for varying donor materials at room temperature. (A) Hole mobility versus ionization potential (IP) and E_{CT} . (B) Hole mobility versus calculated (Λ_D^{calc}) and experimental ($\Lambda_D^{\text{eff,exp}}$) donor relaxation energy. Relaxation energies are determined as described in the main text. (C) Molecular structure of the donor materials used in this study. Hole mobilities values are reported after the names, in cm^2/Vs .

In contrast, the hole mobility clearly correlates with the amount of molecular deformation of the donor upon charging, which is given by its relaxation energy as can be seen in Figure 3(B) (see also Figure S2 and Figure S3 in the SI for a comparison of mobilities of materials with similar E_{CT} or similar $\Lambda_D'^{calc}$). Here, the reduced gas-phase relaxation energy of the donor $\Lambda_D'^{calc}$ is obtained from DFT simulations omitting high-frequency vibrational modes (see Methods Section).²¹ The following empirical relation for the mobility is extracted:

$$\mu(T = 293 \text{ K}) = \mu_{\infty} e^{-A\Lambda_D'^{calc}} \quad (4)$$

with $A = 0.038 \pm 0.004 \text{ meV}^{-1}$ and $\mu_{\infty} = 8 \cdot 10^{-5} \pm 4 \cdot 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, allowing us to predict the hole mobility in this system from the calculated relaxation energy of the donor.

Alternatively, the relaxation energy of the donor can also be measured by sEQE, denoted as Λ_{DA}^{exp} of the donor:C₆₀ CT state. Note that in contrast to $\Lambda_D'^{calc}$, this quantity is expected to contain contributions from the reduced hole relaxation energy of the donor as well as the reduced electron relaxation energy of C₆₀.²¹ To correct for the latter, we subtract the negative polaron relaxation energy of C₆₀, i.e. 38 meV from the measured CT state reorganization energy according to ref.²² and obtain the effective relaxation energy $\Lambda_D^{eff,exp}$ of the donor presented by black symbols in Figure 3(B). It should be noted that $\Lambda_D^{eff,exp}$ might contain additional contributions from the relaxation of the surrounding environment, the contribution of which, however, should be essentially constant (the matrix being C₆₀ for all the studied samples). Performing the same fit with eq (4) we obtained $A' = 0.026 \pm 0.003 \text{ meV}^{-1}$ and $\mu_{\infty}' = 3 \cdot 10^{-4} \pm 2 \cdot 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Independently of whether we take the relaxation energies from DFT simulations or sEQE measurements, we can predict the hole mobility in this system at the considered donor concentration.

The dependence of the hole mobility with the relaxation energy of the donor was confirmed using a second experimental technique to determine the mobility. Dark-injection transient mobility measurements^{23,24} were performed for a selected number of donor:C₆₀ samples. The results are presented in Figure S4 and Figure S5 in the SI and show excellent agreement with the findings based on SCLC mobility values.

This important trend confirms that the holes indeed reside on the donor molecules and that the observed transport activation is strongly correlated to the deformation of the molecular structure of the donors. We also note that, at the average distance between neighboring donors of ~ 2.5 nm, transfer integrals H_{AC} between two donor molecules A and C are small (according to calculations in ref. ^{11,17} on the order of 0.1-1.0 meV), while the calculated relaxation energy for our donors series is on average 96 meV and is only comparably small for P4-Ph4-DIP (14 meV). Since the transfer integrals are much smaller than the relaxation energy of the donor molecules, it is meaningful to consider polaronic effects on transport,^{25,26} expressed by eq (4).

The strong influence of Λ_D on the mobility shown in Figure 3 might still potentially hide an additional dependence of the mobility on the HOMO energy difference E_{tr} or on energetic disorder. E.g., for the superexchange one expects the transfer rates and thus the mobility prefactor to scale with $1/E_{tr}^2$, as shown in the SI Section 5. Removing the strong Λ_D dependence from the mobility by defining $\eta = \mu / (\mu_\infty e^{-A\Lambda_D'^{calc}})$, we can study whether any correlation having the form of $\eta \propto H_{AC}^2 \propto 1/E_{tr}^2$ is remaining.

Figure 4 shows a plot of η against E_{tr} . Clearly the variation in the corrected mobilities among the different donors is strongly reduced by many orders of magnitude upon taking into account the effect of Λ_D . For η , we do not find a clear correlation with E_{tr} . In the series investigated in this work, we find that E_{tr} varies by a factor of two among different donors (see change of E_{CT} in Figure 2(B)), which should influence the charge-transfer rate and, thus, η by a factor 4. The absence of a clear correlation makes us conclude that the involved transfer integrals H_{AC} are not clearly correlated with E_{tr} which indicates that the superexchange mechanism is not dominant for our systems, unless there is a strong variation in the nearest-neighbor transfer integrals $H_{D-C_{60},0}$ when comparing different donors. This result therefore indicates conventional tunneling at the basis of Marcus type hopping.

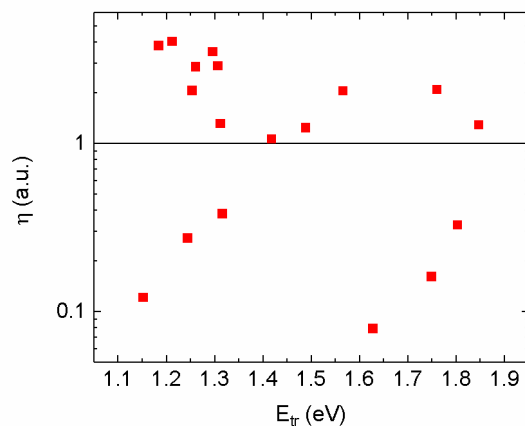


Figure 4. Corrected mobility η vs the energy difference between the HOMO of the donor and the HOMO of the fullerene E_{tr}

In conclusion, we examined donor:C₆₀ blends with 18 different electron donating molecules at ~6 mol% content with varying frontier energy level offsets and varying donor relaxation energies. Efficient hole transport is seen even though a low amount of donor, below the percolation threshold, is present in the active layer. The transport of holes is thermally activated, as demonstrated by an Arrhenius-type behavior in the analyzed temperature range. The temperature dependence of the hole mobility is dominated by the relaxation energy of the donor material as measured by sEQE and simulated by DFT. These results connect a molecular parameter (relaxation energy) with a macroscopic material property (mobility). Concerning the distinction of tunneling versus trap-and-release mechanism, we have clear evidence that holes do not hop onto the C₆₀ molecules, thus excluding trap-and-release as a major transport mechanism. Our results indicate a direct tunneling transport from donor to donor, without mediation by C₆₀. Tunneling, which is expected to depend only weakly on the donor's HOMO energy, is consistent with our measurements where no correlation of mobility with the donor IP was found.

Observation of reasonable hole mobility ($10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) for low-relaxation-energy donor blends, despite the high C₆₀ content, provides a further reason for the success of fullerenes as electron acceptor in organic BHJ solar cells.

The results shown herein are also relevant for BHJ solar cells. In fact, our findings imply that, despite the absence of a clear percolation network of donor molecules, holes are effectively transported through the active layer.

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Supporting information: Further details on the donor materials employed, on the hole only devices and mobility calculation, on the dark injection measurements, on superexchange transfer rate and Experimental Methods and Computational Methods

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