

# The Role of Acceptor Properties on the Hole Transport Mechanism in Low-Donor-Content Organic Solar Cells

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donor concentrations. We found an unexpected correlation between the hole mobility and the energy offset between the donor HOMO and the acceptor LUMO (instead of the acceptor HOMO), with the mobility increasing as the offset decreases. Such a correlation is supported by molecular modeling suggesting a contribution from the acceptor LUMOmediated superexchange mechanism. These results corroborate our experimental observation, hinting at a previously neglected mechanism of transport, which depends on the coupling between the donor HOMO and the acceptor LUMO.



## ■ INTRODUCTION

Over the last decades, the demand for clean energy has become increasingly large.<sup>1</sup> The undeniable correlation between climate changes and carbon emission<sup>2,3</sup> puts pressure on the development of innovative technologies capable of supplying not only high efficiency, but also cheap and versatile solutions. In such a context, organic solar cells (OSCs) find a broad application field in complementing the conventional inorganic solar cell technology by covering niches where using the latter becomes challenging due to their mechanical properties. Plastic OSCs can be applied in facades, curved surfaces as well as semitransparent windows.<sup>4,5</sup>

Thanks to the intensive research performed over the last years,<sup>6,7</sup> the understanding of the means of operation in organic semiconductors has raised the conversion efficiency of OSCs to over 19%,<sup>6</sup> and brought them from a lab-scale to a commercial stage.<sup>5</sup> Nonetheless, there is still room for improvement, and several fundamental charge transfer and transport mechanisms are yet to be understood. State-of-the-art OSCs make use of a donor–acceptor (D–A) structure, where mobile holes and electrons are transported after being generated by exciton splitting at the D–A interface. While this transport process is mostly taken for granted, particular cases are challenging to describe. It was believed that to obtain an efficient charge extraction, both holes and electrons should find

percolation paths formed by the donor and acceptor material, respectively. However, in 2011, Tang et al. reported a class of devices showing that this might not be exactly the case for every D–A structure.<sup>8</sup> The so-called low-donor-content OSCs delivered considerable performance, while using low donor concentration (TAPC, 5 vol %), for which a percolation path is not expected to be formed. The low-donor OSCs became an important model system for studying different properties due to the diminished morphological impact caused by the low donor concentration.<sup>9–12</sup> However, the complete understanding of the operation mechanism in these systems is still under debate.<sup>13–16</sup> In order to improve charge carrier mobility ( $\mu$ ), one of the most important aspects in organic optoelectronic devices,<sup>17</sup> a complete picture of this phenomenon is required.

Since the publication of these results by Tang et al., different groups sought an explanation of the working mechanism of low-donor-content OSCs. Atomistic nonequilibrium molecular

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Figure 1. Hole mobility versus (a)  $HOMO_D-HOMO_A$  and (b)  $HOMO_D-LUMO_A$  in devices comprising 18 mol % donor content. (c) Hole mobility versus the  $HOMO_D-LUMO_A$  energetic difference in devices comprising different donor contents. All measurements were performed at 300 K. See Supporting Information Figure 18 for different temperatures. (d) Energy levels of MeO-TPD compared against all acceptors used. Taken from refs 23–29.

dynamics (MD) simulations revealed that, at 5 wt %, percolation can be achieved only if a hopping distance of 1.2-1.5 nm is considered.<sup>18</sup> Alike, it was suggested that a tunneling-like long-range hopping on the order of 4 nm is present, where holes can tunnel from donor-to-donor sites through several fullerene molecules. Based on this process, around 80-100% of photogenerated holes are extracted depending on the applied bias. A smaller portion, 0-20%, might transfer into the fullerene phase and be efficiently extracted, given the fullerene's ambipolar behavior.<sup>13</sup> For that, an energy barrier must be overcome, which is assisted by a Fowler-Nordheim tunneling process.<sup>14</sup> However, some studies suggest different mechanisms, especially at concentrations below 2 wt %. Kaiser et al. developed a model using kinetic Monte Carlo (kMC) simulations aiming to reproduce the experimental data of low-donor OSCs.<sup>15</sup> Their results suggest that at these low concentrations, it is very unlikely that long-range hopping is responsible for the hole mobilities achieved experimentally. Instead, the authors were able to explain their data on the basis of hole back transfer, where holes are transferred back to the fullerene phase and extracted efficiently. The authors argue, therefore, that most of the holes are extracted through the fullerene matrix, while a much smaller amount would be extracted by long-range hopping, mostly at concentrations higher than 2 wt %. An alternative explanation for the charge transport at very low concentrations is that donor sites act as trapping level, in dark.<sup>16</sup> However, applying this interpretation to single carrier devices, it seems unlikely that holes would be injected into the acceptor's HOMO, given that a considerable hole mobility can be measured even for relatively low HOMO level materials, as will be shown in the Results section.

From the suggested mechanisms presented above, we expect that the hole mobility would either: (i) for tunneling and hole back transfer, decrease as the offset between the HOMO of the donor  $(HOMO_D)$  and the HOMO of the acceptor  $(HOMO_A)$ increases, as it would translate into a larger energy barrier to tunnel through or a deeper trap to escape from; (ii) for longrange hopping, be rather insensitive to any donor-acceptor energy offset, as well as for optical release. While the authors emphasize that this regime might change for higher concentrations, it is worth mentioning that Spoltore et al. investigated 18 donors blended at 6 mol % with C<sub>60</sub> and found no clear trend correlating the hole mobility to the energy offset.<sup>19</sup> Instead, the hole mobility was linked to the donor relaxation energy, indicating that the charges reside in the donor molecules. According to ref 19, the absence of correlation between the energy offset and the hole mobility points to conventional tunneling at the basis of Marcus-type hopping. While this might be the case, comparing the same donor blended at the same concentration with two different acceptors will certainly lead to different hole mobilities, as is shown in the present paper. Therefore, the acceptor does influence the hole mobility in low-donor-content OSCs. Whether holes face different energy barriers for different acceptors in the process of hole back transfer or are affected in another fashion by the molecular parameters of each donor remains an open question. Here, we investigate the influence of the acceptor properties on hole transport in diluted systems. We find that the interaction between the HOMO<sub>D</sub> and the LUMO<sub>A</sub> plays a key role in determining the hole mobility, whereas the energy barrier HOMO<sub>D</sub>-HOMO<sub>A</sub> seems to be less relevant.

#### RESULTS

Hole Mobility Assisted by  $HOMO_D$ -LUMO<sub>A</sub> Superexchange. In order to analyze how the acceptor affects hole transport in low-donor-content bulk heterojunctions (BHJ), we fabricated a set of hole-only devices using MeO-TPD blended with 6 different acceptors. Additionally, 6 concen-



**Figure 2.** Hole mobility versus (a)  $HOMO_D - HOMO_A$  and (b)  $HOMO_D - LUMO_A$  in devices comprising 6 mol % m-MTDATA diluted into three different acceptor matrices. (c) Hole mobility versus the  $HOMO_D - LUMO_A$  energetic difference in devices comprising different donor contents. (d) Hole mobility of devices comprising ~14 mol % of  $F_n$ -ZnPc diluted into  $C_{60}$ . All measurements were performed at 300 K. See Supporting Information Figures 23 and 32 for different temperatures.

trations were used for each acceptor, spanning from 2 to 20 mol % to ensure that the described transport mechanism is valid in the region of interest for low-donor devices. To achieve the single carrier character in our devices, we employed heavily *p*-doped hole transport layers (BF-DPB:F<sub>6</sub>-TCNNQ, 10 wt %, 20 nm) in both top and bottom contacts, namely, ITO and Ag, respectively. These hole transport layers are known to provide ohmic contacts with good electron blocking and hole injection.<sup>20</sup> The electrical similarity of both top and bottom contacts can be inferred from the symmetrical *JV* curves achieved for all concentrations, as shown in Supporting Information Figures 11–32.

Vacuum-processing is especially well-suited for this study, since the concentration can be precisely tuned and the dispersion of donor molecules in the acceptor matrix is expected to be homogeneous, thereby avoiding aggregation. The absence of aggregation features in the diffractogram acquired by grazing-incidence wide-angle X-ray scattering (GIWAXS) and discussed within Supporting Information Supporting Information Note 2 supports this expectation.

Based on the tunneling and trap-and-release models described in the introduction, hole transport within this concentration range is expected to depend exponentially on the donor concentration.<sup>14-16</sup> While an increase in the hole mobility has already been reported when the donor concentration becomes higher,<sup>21,22</sup> the influence of the acceptor's energy levels has not been investigated so far. In Figure 1, such an effect is visualized. Surprisingly, our data reveal an opposite trend to that suggested by the tunneling or trap-and-release models. As shown in Figure 1a, the hole mobility shows no clear relation to the energy offset  $E_{H-H}$  = HOMO<sub>D</sub>-HOMO<sub>A</sub>. Instead, it seems that the mobility is correlated to the acceptor LUMO (LUMO<sub>A</sub>), see Figure 1b,d (see also Supporting Information, paragraph 8). Even though the energy offset  $E_{H-H}$  is the largest for MeO-TPD:HATNA- $\text{Cl}_{6}$ , the mobility is one of the highest, suggesting that  $E_{\text{H-H}}$  is

not the most important parameter for hole transport. On the other hand, the energy difference  $E_{\rm H-L} = \rm HOMO_D$  - LUMO<sub>A</sub> for this material combination is the lowest, pointing to a correlation between the  $E_{\rm H-L}$  and the hole mobility; that is, the lower  $E_{\rm H-L}$  the higher the hole mobility. A similar behavior is observed for all concentrations above ~4 mol %, becoming clearer when approaching the high concentration limit at 18 mol % in our study (see Figure 1c). Therefore, we do not exclude a different mechanism at concentrations below and close to ~4 mol %, but the very low carrier mobility values at low concentrations make it difficult to draw firm conclusions on the mechanisms at play.

Apart from MeO-TPD, we also investigated the hole mobility of blends comprising three other donors, namely, TAPC, TPDP, and m-MTDATA, each blended with at least three different acceptors at varying concentrations within the same range as the one used for MeO-TPD. The donor:acceptor combinations were chosen so that a variety of energy offsets were obtained. All combinations show a similar trend to that of MeO-TPD. In fact, for m-MTDATA, the prominent role of  $E_{H-L}$  becomes even more pronounced, as shown in Figure 2. When going from Cl<sub>6</sub>-SubPc to HATNA-Cl<sub>6</sub> as acceptor,  $E_{H-H}$  increases (see Figure 2a), which is expected to cause a reduction in hole mobility, but instead, the hole mobility increases by at least 1 order of magnitude. Such an odd behavior is reflected in the correlation of mobility with  $E_{\rm H-L}$  presented in Figure 2b. While  $E_{\rm H-L}$  decreases when going from Cl<sub>6</sub>-SubPc to HATNA-Cl<sub>6</sub>, the hole mobility increases. As shown in Figure 2c, the same effect is observed for all concentrations above ~4 mol %.

Additional experiments using fluorinated zinc phthalocyanines ( $F_n$ -ZnPc) as donors diluted in  $C_{60}$  show equivalent results. In the  $F_n$ -ZnPc: $C_{60}$  devices, the only characteristic varying from n = 0 to n = 8 is the  $E_{H-L}$  energy offset, as the energy gap of  $F_n$ -ZnPc does not change upon fluorination.<sup>30</sup> In Figure 2d, the hole mobilities for three of these systems are shown. Similarly to what is observed in the other systems presented so far, the hole mobility decreases as the fluorination is increased, which represents an increase in the  $E_{H-L}$  energy offset. In contrast, the energy offset  $E_{H-H}$  decreases, but this does not translate into an improved mobility. All systems presented here were also measured at varying temperatures ranging from 220 to 320 K. The data are shown in Supporting Information Figures 18, 23 and 32. Within this temperature range, the same behavior discussed so far is observed.

Seeking an explanation for the decreasing mobility with increasing  $E_{H-L}$ , we reviewed the literature on charge transport in organic blends. Apart from the well-known hopping mechanism, it has been shown that a coexisting transport phenomenon might handle the charge transport,<sup>31</sup> especially when the transporting sites are far apart from each other. In the so-called superexchange regime, charges reside virtually in the electronic states of hosting molecules while they are transported among guest molecules. A similar effect was shown for organic light-emitting diodes (OLEDs),<sup>32</sup> where small concentrations of the emitter molecules are dispersed in the host matrix, which is usually a wide-gap organic semiconductor. The superexchange mechanism enhances the rate of emitter-to-emitter hopping, especially if the emitter behaves as a deep trap in the host gap. The increased hopping rate allows for charge transport in systems with reduced or absent percolation paths.

We hypothesize that the holes move by exploiting a superexchange process involving the LUMO<sub>A</sub> as a virtual state, thereby allowing charge transport even at low donor concentrations. Since superexchange depends on the energy separation between the involved energy levels, it is reasonable to assume that, as the HOMO<sub>D</sub> and LUMO<sub>A</sub> become energetically closer to each other, the effective (acceptormediated) intermolecular coupling between the donor molecules becomes stronger, leading to improved transport properties.

We tested this hypothesis against molecular modeling simulations. Specifically, we first performed classical MD simulations to build acceptor amorphous matrices, where donor molecules were dispersed with m/m concentrations of around 6 mol %, as shown in Supporting Information Figure 4. To reduce computational costs, we limited our simulations to MeO-TPD blended with 3 different acceptors, namely, HATNA-Cl<sub>6</sub>, HATNA, and C<sub>60</sub>. In the following, we assume that the donors (D) show an alternated pattern with the acceptors (A), which is supported by the radial distribution functions (RDFs) between D molecules, calculated from MD simulations and reported in the Supporting Information Figure 1. The RDFs show a well-defined peak at 7.5 Å when  $C_{60}$  is the A associated with DAD-like interactions (i.e., one A bridging two D). In the RDFs, we also note the presence of a peak at shorter distances (at 5 Å in the case of  $C_{60}$ ) that reflects the presence of D molecules in direct contact (DD-like interactions) and additional features at larger distances corresponding to longer range DAAD, DAAAD, etc., interactions. We posit also that the charge transport properties at intermediate concentrations (6 mol % and above) are dominated by DAD pathways, which is reasonable since (i) the DD contacts are due to some degree of local D aggregation that likely results in the formation of isolated and, therefore, nonconducting domains; and (ii) the effective coupling rapidly decreases with the average distance between D molecules, thus pathways such as DAAD, DAAAD, etc., are likely inefficient.

In this scenario, assuming an orthogonalized basis set of isolated D and A levels and weak interactions so that the lowest hole eigenstate energy of the full system equals that of the D, the effective electronic coupling between two D molecules separated by one A (in a DAD pathway) is given  $by^{33}$ 

$$V_{\rm DD}^{\rm eff} = V_{\rm DD}^{\rm direct} + \sum_{\rm MO_i \in A} \frac{V_{\rm DA}^{\rm H} M_{\rm O_i} V_{\rm DA}^{\rm MO_i \, \rm H}}{E_{\rm D}^{\rm H} - E_{\rm A}^{\rm MO_i}}$$
(1)

where  $V_{\text{DD}}^{\text{direct}}$  denotes the direct hole coupling between the D molecules,  $V_{\text{DA}}^{\text{H} \text{ MO}_i}$  denotes the coupling between the HOMO<sub>D</sub> (where the hole resides) and any mediating (either occupied or unoccupied) molecular orbital (MO<sub>i</sub>) of A,  $E_D^{\text{H}}$  denotes the HOMO<sub>D</sub> energy, and  $E_A^{\text{MO}_i}$  denotes the *i*th MO energy on A. In eq 1, the second term includes all the superexchange pathways.

In a superexchange mechanism, the hole transport proceeds as sketched in Figure 3, with pathways mediated by the virtual



Figure 3. Schematic representation of the superexchange process.

involvement of either occupied (a) or unoccupied (b) MO on A. Quantitative estimates of the effective electronic couplings would require the application of a partition-based method applied to the full energy spectrum and retaining electronic polarization effects together with the relative phase of the various pathways (i.e., of interference effects).33 While such calculations can be done in model cocrystals or alternated DA copolymers, it is out of reach for the amorphous systems at hand. Still, one can reasonably assume that, thanks to the energy penalty at the denominator of eq 1, the HOMO<sub>A</sub> and/ or LUMO<sub>A</sub> would provide the largest contributions to the effective couplings. It is commonly assumed that for hole transport, the  ${\rm HOMOs}_{\rm A}$  should be the leading virtual states. If this holds, then we would expect the effective coupling and the hopping rates, which scale as  $(V_{DD}^{eff})^2$ , and thus the hole mobility, to increase with a reduced energy mismatch  $E_{H-H}$ . As detailed above, this is not what is seen experimentally. Conversely, we hypothesize that LUMOs<sub>A</sub> are the leading superexchange pathways, which is supported by data reported in Figures 1 and 2, showing good correlation between measured values of  $\mu$  and  $E_{H-L}$ .

By means of density functional theory (DFT) calculations, we computed the transfer integrals between the energy levels of interest, that is, the HOMO<sub>D</sub> with both LUMO<sub>A</sub> and HOMO<sub>A</sub>, considering the closest molecular pairs (see Methods and Supporting Information Note 1). The results are shown in Figure 4 (see also Supporting Information Figure 2 for raw data). For the three systems, as the molecules get closer to each other, the HOMO<sub>D</sub>-LUMO<sub>A</sub> electronic couplings tend to be on average larger than the corresponding HOMO<sub>D</sub>-HOMO<sub>A</sub> couplings, thus corroborating our hypoth-

Figure 4. Transfer integral (J) for MeO-TPD blended with three different acceptors considering the HOMO<sub>D</sub>-HOMO<sub>A</sub> and HOMO<sub>D</sub>-LUMO<sub>A</sub> electronic coupling.

esis that holes are more likely to use  $LUMO_A$  as a virtual bridge orbital in a superexchange mechanism.

The results shown in Figure 4 are somewhat surprising. For two interacting equivalent molecules in a cofacial arrangement, we would expect the HOMO-HOMO interactions to be stronger than their HOMO-LUMO counterparts because of the presence of an additional nodal plane in the LUMO. We tentatively assign the reversal in this trend found here to the more diffuse (spatially extended) character of the LUMOs<sub>A</sub>, affording a better spatial overlap with the HOMO<sub>D</sub>. Moreover, a correlation between the HOMO<sub>D</sub>-LUMO<sub>A</sub> electronic interactions and the ground state total energy of the pairs is also possible; hence, the most stable configurations sampled in our MD simulations might also be those that maximize these couplings. Additional calculations are required to assess the universal character of our findings. In any case, to qualitatively assess the proposed theory, we define the following proxy to the effective coupling:

$$V_{\rm DD}^{\rm super,L} = \frac{|V_{\rm DA}^{\rm HL}|^2}{E_{\rm D}^{\rm H} - E_{\rm A}^{\rm L}}$$
(2)

where we only retain the  $LUMOs_A$  in eq 1 and neglect the direct hole coupling between the D molecules. The amorphous blend structure yields a distribution of  $V_{DD}^{\text{super},L}$ , possibly turning into "hot spots" for charge percolation. To account for this inhomogeneity, we computed an average value of  $V_{DD}^{\text{super,L}}$ considering the top 90% of the full distributions (shown in Figure 3), in order to get reasonable statistics. We also corrected the computed MO energies by adjusting the calculated mean values of the distributions according to their experimental counterparts in Figure 1d. By doing this, we obtained an effective averaged coupling  $\langle V_{\rm DD}^{\rm super,L} \rangle$  of 2.5 meV for C<sub>60</sub>, 0.25 meV for HATNA, and 0.43 meV for HATNA-Cl<sub>6</sub>. The predicted trend closely follows that of the measured hole mobility in Figure 1a,b, that is,  $\mu(C_{60}) > \mu(HATNA-Cl_6) >$  $\mu$ (HATNA). Most importantly, these results support the picture in which HATNA-Cl<sub>6</sub> performs better than HATNA as a hole mediator, which is consistent with their respective  $E_{\rm H-L}$ energy mismatch values. However, the reality is more complex as, at intermediate D concentrations, the direct hole coupling (the first term in eq 1) could also contribute. As a matter of fact, the calculated mean values of the full  $V_{\text{DD}}^{\text{direct}}$  distributions (reported in Supporting Information Figure 3) amount to 0.42 meV for C<sub>60</sub>, 0.26 meV for HATNA, and 0.36 meV for HATNA-Cl<sub>6</sub>. Within the rough theoretical models used here, these values are thus on par with the superexchange couplings; namely, the two terms in eq 1 have comparable magnitudes. Interestingly, both direct and superexchange interactions decrease along the series  $C_{60}$  > HATNA-Cl<sub>6</sub> > HATNA. While this might be accidental, it could also reflect the

propensity for the MeO-TPD molecules to homogeneously disperse into the three A films investigated by modeling. Visual inspection of the produced amorphous structures indeed seems to indicate a more intimate mixing of MeO-TPD in HATNA, which at equivalent D concentration might somewhat hinders percolation. More work is definitively required to test this hypothesis.

#### CONCLUSIONS

We have investigated the hole transport mechanism in a set of low-donor-content BHJs. By varying the concentration of donor molecules dispersed into different acceptor matrices, we observed that the hole mobility is correlated with the HOMO<sub>D</sub>-LUMO<sub>A</sub> energy offset. This finding contradicts the expected behavior in low-donor-content systems predicted by the tunneling and trap-release transport mechanisms suggested so far. Most of these mechanisms assume that the hole mobility is correlated with the HOMO<sub>D</sub> - HOMO<sub>A</sub> energy difference and would, therefore, increase as these energy levels become close. Apart from our experimental results showing exactly the opposite trend, DFT calculations of the transfer integrals between the HOMO<sub>D</sub> and both acceptor energy levels show that the coupling between HOMO<sub>D</sub> and LUMO<sub>A</sub> is larger (on average) than that between HOMO<sub>D</sub> and HOMO<sub>A</sub>. These simulations indicate that holes may exploit LUMO<sub>A</sub> as virtual states in a superexchange process, allowing hole transport even when percolation paths are not formed. However, the calculations also show that, at intermediate donor concentrations, direct interactions between the donors are also possible. In view of the observed dependence between the measured hole mobility and HOMO<sub>D</sub>-LUMO<sub>A</sub> energy offset values, we conclude that either the acceptor LUMO-mediated superexchange paths dominate or the differences among the acceptor hosts are mostly related to the fine degree of donor-acceptor molecular mixing (in which case the observed correlation above would be accidental). Of course, it is also possible (and even likely) that the two effects (enhanced superexchange pathways and improved percolation) concur to the observed ranking.

#### METHODS

**Device Preparation.** The materials used in the device are presented in Supporting Table 7. To construct the devices, organic molecules were thermally evaporated on glass substrates covered by prestructured ITO contact (32  $\Omega \square^{-1}$ , Thin Film Devices) at ultrahigh vacuum (pressure <  $10^{-7}$  mbar). Before deposition, substrates are cleaned for 15 min in different ultrasonic baths with NMP solvent, deionized water, and ethanol followed by O<sub>2</sub> plasma for 10 min. Organic materials were purified 2–3 times via sublimation. The overlap of the bottom and top contact (Al, 100 nm, Kurt J. Lesker) defines the device's active area (6.44 mm<sup>2</sup>). After evaporation, samples are directly transferred to a glovebox with an

inert atmosphere, where they are encapsulated with a cover glass, fixed by UV hardened epoxy glue. A moisture getter (Dynic Ltd.) is inserted between the top contact and the glass to hinder degradation.

JV Characteristics. Dark JV characteristics were measured with a high-resolution SMU (Keithley SMU 2635) at varying temperatures in a vacuum cryostat. The temperature range was set from 220 to 320 K with steps of 10 K. Every measurement data point was acquired after steady-state conditions were achieved. The measurement is controlled by the software SweepMe! (https://sweep-me.net/).

**Hole Mobility Calculation.** The temperature-dependent JV curves were fitted according to the Murgatroyd law,<sup>34</sup> frequently used to determine the mobility in organic materials under the space-charge limited current (SCLC):<sup>35,36</sup>

$$J_{\rm SCLC} = \frac{9}{8} \varepsilon_0 \varepsilon \mu_{\rm h} \frac{V^2}{d^3} \exp\left(0.89\beta \sqrt{\frac{V}{d}}\right)$$
(3)

where  $\varepsilon_0$  is the vacuum permittivity,  $\varepsilon$  is the material dielectric constant,  $\mu_h$  is the hole mobility, V is the voltage, d is the device thickness, and  $\beta$  is a fitting parameter accounting for the field dependence of the current described by the Poole–Frenkel effect. The mobility was determined in both the negative and positive regions of the curves. For most devices, this leads to the same mobility values. The highest value was taken in cases where the mobility is different and caused by slightly asymmetrical curves. The only fitting parameters were the mobility and the constant  $\beta$ .

**GIWAXS.** GIWAXS experiments were performed at beamline XRD1 at ELETTRA, Italy. The beam energy for all measurements was 12.39 keV, and the dimensions of the beam were  $200 \times 200 \ \mu$ m. A Dectris Pilatus 2 M area detector was used to record the images. The sample-to-detector sample distance for all samples was 400 m and was verified together with the position of the beam on the detector by measuring a LaB<sub>6</sub> reference. The incidence angle was 0.12°. For the MeO-TPD:HATNA-Cl<sub>6</sub> samples, five images with 60 s exposure were recorded per sample and then integrated to get the final image presented in the paper. For MeO-TPD:Cl<sub>6</sub> and MeO-TPD:Cl<sub>6</sub>–SubPc, the samples were rotated by 360° while being exposed to the beam for 120 s so that the whole area of the samples was probed. The data was analyzed using WxDiff.

**MD and DFT Calculations.** Classical MD simulations, run with the NAMD software,<sup>37</sup> were carried out to reproduce three amorphous samples with a low-donor content (around 6 mol %). These simulations were performed using a united atom force field (UAFF), previously developed for the morphological study of emissive OLED layers in crystalline or glassy phases where hydrogen atoms are implicitly modeled (see Supporting Information Note 1 for further details).<sup>38</sup> At the end of the MD simulations, molecular pairs were selected according to geometrical criteria and extracted from the last MD snapshot. The selection was based on the closest atom–atom distances, which should be less than 5 Å. Transfer integrals were computed at the DFT PBE0/def2-SVP level of theory for the chosen pairs by using the dimer projection method. Such calculations were performed using ORCA 4.2.<sup>39</sup>

## ASSOCIATED CONTENT

## **1** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.3c02263.

Procedure used for the MD simulations and DFT calculations; data and analysis of GIWAXS diffractograms; concentration and temperature-dependent JV curves of each donor blended with varying acceptors; and chemical properties of materials (PDF)

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#### **Author Contributions**

J.K., D.S., and J.B. designed the experiments. G.L. and D.B. performed the MD simulations and the DFT calculations. F.T. and M.H. measured GIWAXS and analyzed the data, supervised by S.C.B.M. Also, J.K., S.X., and J.W. prepared the samples. J.K. measured the electric properties and analyzed the data. K.V., K.L., D.B., and D.S. supervised the entire project. All the authors contributed to the writing and discussions presented in this paper.

### Notes

The authors declare no competing financial interest.

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