Relating Chain Conformation to the Density of States and Charge Transport in Conjugated Polymers: The Role of the $\beta$-phase in Poly(9,9-dioctylfluorene)

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Charge transport in $\pi$-conjugated polymers is characterized by a strong degree of disorder in both the energy of conjugated segments and the electronic coupling between adjacent sites. This disorder arises from variations in the structure and conformation of molecular units, as well as the weak intermolecular binding interactions. Although disorder in molecular conformation can be expected to influence the density of states (DOS) distribution—and hence, optoelectronic properties of the material—until now, there has been no direct study of the relationship between a distinct conformational defect and the charge transport properties of a conjugated polymer. Here, we investigate the impact of introducing an extended, planarized chain geometry, known as the “$\beta$-phase,” on hole transport through otherwise amorphous films of poly(9,9-dioctylfluorene) (PFO). We show that while $\beta$-phase introduces a striking drop of about a hundredfold in time-of-flight (TOF) hole mobility ($\mu_h$) at room temperature, it reduces the steady-state $\mu_h$ measured from hole-only devices by a factor of less than about 5. In order to reconcile these observations, we combine high-dynamic-range TOF photocurrent spectroscopy and energy-resolved electrochemical impedance spectroscopy to extract the hole DOS of the conjugated polymer. Both methods show that the effect of the $\beta$-phase content is to introduce a sharp sub-bandgap feature into the DOS of glassy PFO lying about 0.3 eV above the highest occupied molecular orbital. The observed energy of the conformational trap is consistent with electronic structure calculations using a tight-binding approach. Using the obtained DOS with a drift-diffusion model capable of resolving charge carriers in both time and energy, we show how the seemingly contradictory transport phenomena obtained via the time-resolved, frequency-resolved, and steady-state methods are reconciled. The results highlight the significance of energetic redistribution of charge carriers in affecting transport behavior. This work demonstrates how charge-carrier mobility in organic semiconductors can be controlled via molecular conformation, and it resolves a long-standing debate over how different (equilibrium versus nonequilibrium) transport techniques reveal electronic properties of disordered solids in a unified manner.

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I. INTRODUCTION

Dating from early research into amorphous inorganic semiconductors [1–5] to recent studies on $\pi$-conjugated molecular semiconducting materials [6–13], there has been consistent interest in understanding the impact of localized, sub-bandgap states on charge transport in disordered electronic materials. Organic semiconductors are particularly interesting on account of the strong interaction between the electronic states and vibrational modes of the materials, which makes energetic disorder almost...
There is as yet no consensus on how to relate charge transport phenomena—including charge-carrier mobility, field dependence of mobility, and degree of carrier transport dispersion—to the sub-bandgap DOS using experimental methods. The challenge of relating transport properties to these localized states is complicated by the fact that (i) different methods can deliver different values of charge-carrier mobility even for the same material systems processed via identical protocols and that (ii) the particular origin and form of the sub-bandgap DOS in a disordered semiconductor is not normally uniquely known. Lack of knowledge of the DOS makes it impossible to predict the charge transport behavior using any transport model that is capable of accounting for the presence of energetic disorder and/or trap states.

In order to address these challenges, materials systems are needed where the sub-bandgap DOS is well defined and tunable in a controlled manner. In the case of organic semiconductors, variations in the energy of electronic states may arise from effects including chemical defects, impurities, supramolecular structural variations and polymorphs, dynamic disorder due to thermal fluctuations, or intermolecular electrostatic and polarization interactions. In general, the exact origin of trap states at any given depth is not known. It is typical for the sub-bandgap DOS profile to appear exponential over a range of energies although without any clear physical reason. In the case of conjugated polymers, one important source of site energy distribution is conformational disorder due to variation in intrachain torsion and the resulting variations in the extent of $\pi$-conjugation along the polymer backbone. Several experimental and modeling studies have addressed the impact of molecular conformation on electronic structure and transport properties. However, despite sound models for the dependence of electronic structure on conformation, the large conformational phase space of conjugated polymers has made it difficult to relate the DOS and, ultimately, the recorded electronic transport properties explicitly to the presence of any conformer, even when certain conformers are deliberately introduced.

In the present work, we select the conjugated polymer, poly(9,9-dioctylfluorene) (PFO), for detailed study. PFO expresses several polymorphs, one of which, termed the $\beta$-phase (see Fig. 1), features an extended, planar-zigzag chain conformation that can be reproducibly introduced into amorphous (or “glassy”) phase PFO layers via exposure to solvent vapors, and whose presence can readily be identified spectroscopically via its UV-Vis absorption, photoluminescence, and Raman scattering “fingerprints.” Moreover, the hole mobility ($\mu_h$) in PFO is reported to be a strong function of the phase of the polymer, and recent studies showed that glassy PFO exhibits a room-temperature (RT) time-of-flight (TOF) $\mu_h$ that is apparently 2 orders of magnitude higher than that of the same medium contaminated with $\beta$-phase.

FIG. 1. (a) The chemical structure of PFO. Each of the di-8-octyl side chains attached to the central carbon atom (C$_8$) of a monomer is abbreviated as C$_4$H$_{17}$. (b) Molecular geometries of an oligofluorene (side chains represented by methyl groups for clarity) in the minimum potential energy, glassy conformation with dihedral angles $\theta$ of about 45° or 135° (top, cyan) and in the $\beta$-phase conformation, with $\theta \approx 180^\circ$ (bottom, magenta).
We show how the DOS of the polymer can be determined using two independent methods, namely, high-dynamic-range (HDR) TOF photocurrent measurements and energy-resolved electrochemical impedance spectroscopy (ER-EIS), and that the impact of introducing β-phase into the polymer is to induce a sharp sub-bandgap feature in the DOS some 0.3 eV above the highest occupied molecular orbital (HOMO) of the glassy polymer. We show that the effect of the β-phase conformer on different charge transport measurements (including transient, frequency-resolved, and steady-state) can be explained quantitatively in terms of the DOS due to this conformational defect. Furthermore, we demonstrate how apparent differences in transport data from the complementary set of (opto)electrical probes can be resolved using a time- and energy-resolved device model [11] that allows for the energetic redistribution of charge carriers.

This work provides a first demonstration that knowledge of a particular conformational defect can be related quantitatively to the effect on transport measurements, meaning that the effect of conformational defects on charge transport properties of a conjugated polymer can, in principle, be predicted. This enables the charge transport properties of conformationally disordered polymer materials to be modeled. In addition, the explanation of apparently different observations of transport in terms of a single picture of the density of states shows how, when appropriate models of charge transport are used, different measurement methods can be reconciled. This finding resolves a long-standing controversy over the ability of different methods to faithfully probe the charge transport properties of a disordered solid.

II. IMPACT OF THE β-PHASE ON HOLE TRANSPORT IN PFO

A. Temperature-dependent time-of-flight charge-carrier mobility

TOF hole mobility measurements on optically thick PFO devices prepared in the two different forms (glassy and β-phase embedded) reveal a clear trend in mobility with microstructure. Figure 2(a) shows double-logarithmic plots of the transient hole photocurrent measured at RT (about 290 K) for about 1.8-μm-thick PFO films sandwiched between hole-blocking indium tin oxide (ITO) and aluminium (Al) electrodes under an applied bias of 10 V (i.e., at an electric field of about $5.6 \times 10^4$ V cm$^{-1}$). Such identical conditions mean that transient hole transport for the different devices can be directly compared from the carrier transit times $t_{tr}$ defined here as the intersection of the asymptotes to the current plateau and the trailing edge of the transient in the double-logarithmic plot. A reduction of about a hundredfold in TOF hole mobility upon generating β-phase into fully glassy layers is evident. Figure 2(b) presents TOF $\mu_h$ measured as a function of temperature and electric field in devices of structure ITO/PFO $\beta$-embedded (red line) HMW PFO devices.

FIG. 2. (a) Representative TOF photocurrent transients for glassy (blue line) and β-phase embedded (red line) HMW PFO devices. All films had very comparable thickness ($\sim 1.8$ μm), and measurements were performed under identical conditions ($V_\text{bias} = 10$ V, i.e., at $E \approx 5.6 \times 10^4$ V cm$^{-1}$; and $T = 290$ K). For each case, the carrier transit time $t_{tr}$ (indicated by an arrow) was extracted by locating the point of intersection of two tangents (omitted for clarity) fitted to the pre- and post-transit regimes of the transient on the double-logarithmic scale. The variation in onset of the initial spike reflects the different choices of the temporal resolution or window to best capture the photocurrent transients. No manual offset was applied to the transients, and the photocurrent levels are absolute. (b) Poole-Frenkel plots of TOF hole mobility ($\mu_h$) as a function of the square root of applied electric field, measured at different temperatures for HMW TOF devices made with pristine glassy PFO (top set, open hexagons) and with PFO containing β-phase structural minority introduced by exposure to toluene vapor for an hour (bottom set, filled triangles). Gaussian disorder model analysis of these data is presented in Appendix F. The temperatures measured were— in order of increasing $\mu_h$— 190, 200, 215, 230, 245, 260, 270, 290, and 296 K for the glassy set; and 200, 215, 230, 245, 260, 275, and 290 K for the β-phase embedded set.
devices; \(\sim 4 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\) at RT). UV-Vis absorption and photoluminescence measurements were carried out to ensure that the chosen processing routes yielded PFO films in the required microstructures (see Appendix D). Each TOF \(\mu_h^0\) value in Fig. 2(b) was estimated by ascribing a transit time to the point of intersection of two tangents fitted to the short-time (“pretransit”) and long-time (“posttransit”) parts of each photocurrent transient on the double-logarithmic scale, thus marking the so-called “knee” position [see Fig. 2(a) for representative TOF transients]. The TOF \(\mu_h\) obtained in this way is reduced by around 2 orders of magnitude through the introduction of only about 4.6 \pm 0.4 vol\% of \(\beta\)-phase (as estimated in Appendix E). This observation is in accordance with the impact of \(\beta\)-phase on TOF \(\mu_h^0\) reported in Ref. [70]. The magnitude of this effect is dependent upon the molecular-weight properties of the polymer used, with the low-molecular-weight (LMW) material leading to a larger fraction (\(\sim 6 \pm 0.1\) vol\%) of \(\beta\)-phase dispersed in the PFO film and a slightly larger impact on the reduction of \(\mu_h\) [see the Supplemental Material (SM) [72], Sec. III, Fig. S8(b); for clarity, we present all hole transport data on LMW PFO in the SM [72], whereas only high-molecular-weight (HMW) results are included in the main text). Figure 2(b) also indicates that the sensitivity of TOF \(\mu_h\) to electric field is greater for the glassy, high-mobility device. Previously, different field dependences have been assigned to the degree of configurational disorder [6] that leads to differences in the spread of \(\sigma\) values for the energetic disorder \(\sigma_{\text{GDM}}\)—defined as the standard deviation (or breadth) of a Gaussian distribution of (spatially uncorrelated) site energies—for the \(\beta\)-phase embedded device (\(\sigma_{\text{GDM, } \beta\text{-embedded}} \approx 85 \text{ meV}\)) than for the glassy device (\(\sigma_{\text{GDM, glassy}} \approx 75 \text{ meV}\)). It also yields a high-temperature limit of TOF \(\mu_h^0 \left(\mu_{h(0)}^{\beta\text{-embedded}}\right)\) for the pristine glassy device of about 0.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\), which is referred to, in the framework of the GDM, as the effective free-hole mobility through glassy phase PFO (for further clarification, see Appendix F). We use this \(\mu_{h(0)}^{\beta\text{-embedded}}\) value as an initial input for numerical device modeling (see the SM [72], Sec. I, Part B) and note that its magnitude is compatible with experimental estimates (on the order of about 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\) for the ac intrachain mobility along randomly coiled PFO chains in dilute solutions [52,73].

### B. Steady-state \(J - V\) response from glassy and \(\beta\)-phase embedded PFO hole-only devices

In order to test the consistency of our observed effect of \(\beta\)-phase on hole transport in PFO, we study the same systems with a second, steady-state technique. Steady-state dark current density–voltage (\(J - V\); sometimes referred to as space-charge-limited current) measurements probe hole transport in a unipolar device structure with at least one Ohmic hole-injecting contact. Ultrathin (about 5–10 nm) MoO\(_x\) interlayers prior to top-contact metallization were previously shown to achieve Ohmic hole injection into the very deep-lying HOMO of PFO, a level that is otherwise inaccessible via conductive polymer poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) [74].

![FIG. 3.](image)

(a) Double-logarithmic steady-state current density–voltage (\(J - V\)) plots for devices of structure ITO/PEDOT:PSS/PFO (∼135 nm)/MoO\(_x\)/Au made with glassy (blue curves) and \(\beta\)-phase embedded (red curves) layers. The measurements were taken at 295 K in the dark. Forward-bias response is illustrated by solid lines and refers to hole injection through the Au/MoO\(_x\) Ohmic contact. Reverse-bias response (dashed lines) refers to hole injection through the ITO/PEDOT:PSS blocking contact. (b) Plots of the corresponding slopes of all dual-logarithmic-scale traces shown in subplot (a) against the logarithm of voltage [slope = \(d(\log_{10} J)/d(\log_{10} V)\)]. The purple line at a slope of 2 marks the behavior of trap- and barrier-free space-charge-limited conduction at high bias, which is predicted by the Mott-Gurney theory.
Figure 3(a) shows steady-state $J − V$ curves for hole-only devices of asymmetric structure ITO/PEDOT:PSS/PFO ($\sim 135$ nm)/MoO$_3$/Au, prepared with glassy and $\beta$-phase embedded PFO layers. Both devices exhibit clear current rectification behavior. The distinction between the steady-state current density levels in the high-bias, drift-dominant regime when holes are injected from the Au/MoO$_3$ contact (i.e., forward bias) suggests that there is a systematic difference in $\mu_h$ between the glassy and $\beta$-phase embedded layers. However, it is a factor of about 2–4 rather than the 2-orders-of-magnitude difference probed by TOF. Here, we do not attempt to obtain mobility values directly from these curves since it has been previously shown [75,76] that the mobility extracted from dark $J − V$ data by the commonly adopted Mott-Gurney law [77] is not reliable when—as in the present case—both a significant distribution of electronic traps and contact asymmetry (hence a built-in potential, $V_{bi}$) are present in the devices.

C. Mobility extracted from hole-only devices using impedance spectroscopy

An alternative route to determining $\mu_h$ in single-carrier devices, as put forward by Tripathi et al. [37], Martens et al. [78], and Tsang et al. [34], is to examine the frequency-resolved impedance or admittance response. Both techniques are able to provide insights into the degree of transport dispersion from the spectra obtained. Figure 4 is obtained under forward bias by recording the frequency-dependent imaginary component of the impedance spectra [i.e., $-\text{Im}(Z)$ versus frequency; see Appendix C, Part 4 and Appendix G, Part 1] for the same glassy and $\beta$-phase embedded hole-only devices as in Part B. The data show that the mildly field-dependent glassy-state $\mu_h$ of around $6 \times 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$ to $1 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ drops by a factor of about 2–5 upon inclusion of $\beta$-phase conformers. As with the steady-state dark $J − V$ response, $\beta$-phase reduces $\mu_h$, and the effect is again relatively moderate in comparison with the TOF results. Interestingly, the same set of impedance measurements on the LMW batch PFO systematically indicate a more pronounced impact of $\beta$-phase on hole transport, particularly in lowering the degree of transport dispersion—a finding that is consistent with the time-resolved photocurrent transients (see the SM [72], Sec. III, for details).

The value for the hole-only device mobility estimated from impedance spectroscopy in the $\beta$-phase embedded case agrees reasonably well with a prior report by Nicolai et al. [74] of $1.3 \times 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$, based on analysis of dark $J − V$ measurements on room-temperature spin-coated PFO films. We expect films prepared as described in that report to contain $\beta$-phase according to such film deposition protocol, although not explicitly stated by the authors, since prolonged solvent evaporation during the deposition process promotes chain relaxation during solidification and hence the formation of $\beta$-phase [79].

In summary, $J − V$ and impedance spectroscopy measurements on hole-only devices reveal that glassy PFO exhibits a higher steady-state hole mobility than $\beta$-phase embedded PFO by a factor of about 2–5. In contrast, TOF suggests the mobility of glassy PFO is around a hundredfold higher than that of $\beta$-phase embedded PFO. As we show below, our analysis suggests that a small fraction of $\beta$-phase chains dispersed within amorphous PFO should introduce trap states that penalize the hole mobility. However, the influence of these trap states on transport, in practice, appears to be very different depending upon which experimental technique is used. We also note a molecular-weight dependence of the impact of the induced $\beta$-phase fraction on mediating hole transport. To resolve the apparently contradictory observations, we next address the forms of the hole DOS in glassy PFO in the absence or presence of $\beta$-phase.

III. PROBING THE HOLE DOS FOR GLASSY AND $\beta$-PHASE EMBEDDED PFO

A. Extracting DOS from high-dynamic-range time-of-flight measurements

To probe the hole DOS in PFO, we first adapt the TOF technique where the dynamic range for photocurrent transients is extended to span around 7 to 8 orders of
magnitude and, in turn, 6 orders in time up to about 10 ms (see Appendix C, Part 2 for method details). Such high-
dynamic-range measurements allow the DOS to be probed
over several tenths of an electronvolt (about 0.5–0.55 eV in
the present study) relative to the transport level of charge
carriers, provided that the internal field is sufficiently high
and carrier retrapping can be neglected. The rationale is
outlined as follows.

Transient current measurements are one of the most
widely used means to relate transport to DOS. Based on
the multiple-trapping model, Tiedje and Rose [2], and
Orenstein and Kastner [3] related dispersive current tran-
sients, commonly observed in TOF photocurrent measure-
ments, to the thermal release of trapped carriers out of a
distribution of localized states as time elapses. Seynhaeve
et al. extended the theory to estimate the band-tail dis-
tribution of hydrogenated amorphous silicon (a-Si:H) from
experimental TOF data [4]. Such a model was later adapted
by others [9,11,80] to probe the DOS in organic bulk-
heterojunction photovoltaic devices. In this treatment, the
time-dependent photocurrent $i(t)$ is determined by the
thermally activated release of charge carriers from trap
states, whose DOS distribution is given by $g(E')$. By
mapping trap depth $E'$ onto release time $t$, we obtain $g(E')$
from the photocurrent,

$$g(E') = \frac{i(t)}{q f_{\text{loc}} V k_B T},$$

(1)

where $q$ is the elementary charge, $f_{\text{loc}}$ the fraction of
localized states occupied immediately after the laser exci-
tation, $V$ the device volume, and $k_B T$ the thermal en-
ergy; $E'$ represents the demarcation depth—relative to the trans-
port level—of the energy level up to which the DOS is filled
at time $t$ with negligible detrapping events. In deriving
Eq. (1), it is assumed that the rate of carrier release is
controlled by thermal activation; hence, one can map the
time at which a carrier is released from a trap state onto the
depth at which the carrier was detained as

$$E'(t) = k_B T \ln(\nu_0 t),$$

(2)

where $\nu_0$ is the attempt-to-escape frequency. Note that the
logarithmic dependence of energy on time means that a
HDR photocurrent is needed to probe localized states deep
in the gap. It should be stressed that the approximation to
the DOS delivered from Eq. (1) only holds in the long-time
limit (the so-called “post-transit regime”), where the TOF
photocurrent is dominated by the detrapping of carriers via
thermal activation [2,4,80]. It is assumed that, provided the
internal field is high enough, retrapping would be minimal
in this regime and that carrier loss by recombination is
negligible (which is fair since TOF investigates unipolar
transport) and the $f_{\text{loc}}$ stays frozen at site energies greater
than the time-evolving demarcation energy $E'$. Since the
magnitude of $f_{\text{loc}}$ is generally not known, Eq. (1) delivers a
relative DOS distribution. It is also assumed that the sub-
bandgap DOS distribution remains unchanged over the
temperature range probed and that trap states are empty
prior to laser excitation due to ultralow dc dark current level
(<25 pA) recorded for the TOF devices within the bias
range applied. In this study, we apply the HDR TOF
method to probe the distribution of hole-trap states in PFO.

Figure 5(a) shows HDR hole transients from HMW PFO
TOF devices prepared in the glassy state with and without
the $\beta$-phase conformational heterogeneity introduced. To
convert $i(t)$ to a DOS with an energy scale determined relative
to the transport level [Eq. (2)], we must fix a value
for the attempt-to-escape frequency $\nu_0$. Note that the choice
of $\nu_0$ affects only the absolute position of the DOS on the
energy scale but not the relative position or shape. We
estimate $\nu_0 \approx 10^{11}$ Hz from temperature-dependent HDR
transient measurements by adjusting $\nu_0$ until particular
features in the post-transit half of the transient curves
coincide when plotted against energy [see vertical dashed
lines in Fig. 5(a), downwards arrows in Fig. 5(b), and the
figure caption for details]. We further show, in the SM [72],
Sec. II, Part C, that an estimate of $\nu_0$ on the same order
could be derived using an alternative analysis. Following
Eq. (2), this value of $\nu_0$ translates the dynamic range of our
HDR transients to a sub-bandgap depth of about 0.5–
0.55 eV. The DOS curves mapped out in this way are
plotted in Fig. 5(b). Figure 5(b) also shows that the shape of
the glassy-state DOS extracted from the post-transit regime
photocurrent is not dependent on the external bias voltage,
suggesting that recombination does not affect the shape of
the mapped DOS for the range of voltages studied and that
carrier redistribution into deep localized states due to
retrapping events is negligible. Furthermore, the temper-

ature independence of the DOS confirms that no thermally
induced microscopic phase transition takes place within the
photoconductive layer in the narrow temperature range over
which the measurements can be compared. (Extracted DOS
can be compared only over a narrow temperature range
because the upper limit is fixed by the need to avoid phase
transitions near the glass transition temperature of the
polymer, $T_g \sim 53^\circ$C [71], and hence low-temperature
measurements were performed in cryogenic conditions.)
The energy-space map of the set of transients can thus be
considered a realistic approximation to the DOS, and it
supports the idea that we are working in a regime where
Eq. (2) is valid.

Comparing the mapped hole DOS for glassy and
$\beta$-phase embedded devices in Fig. 5(b), we can see that
while both devices show a similar, approximately expo-
nential tail of states at high depth (>ca. 0.42 eV), the $\beta$-
phase embedded device alone exhibits an additional sharp
feature at about 0.3 eV above the transport level (direction
referred according to electron energy). An exponential tail
of states, where $g(E)$ varies according to $g(E) \propto \exp
(E/E\text{ch}), with E\text{ch} being the characteristic energy of the tail of states, has been inferred from various attempts to measure the DOS of a conjugated polymer [9,11,45,80]. Such a g(E) profile is consistent with a conformationally disordered and entangled polymer [56]. The characteristic energy observed here (E\text{ch} ∼ 75 ± 5 meV) is similar to values reported for other conjugated polymers. The clear extra peak or cliff that is visible only in the case of the β-phase embedded device suggests the presence of an additional, relatively well-defined distribution of defect states.

**B. Thin-film DOS mapping using energy-resolved electrochemical impedance spectroscopy**

As a complementary measurement of the effect of β-phase on the hole DOS, we use a sensitive spectroscopic method for DOS mapping in organic semiconductors, namely, energy-resolved electrochemical impedance spectroscopy (ER-EIS) [81,82]. This method has previously been applied to the determination of HOMO and LUMO positions, electronic bandgap, and characteristic energy of the HOMO band tail, as well as to the characterization of defect state evolution in the bandgap of poly(3-hexylthiophene) (P3HT) induced upon degradation in air [83] or by varying layer thickness [84], and defect states in poly(silylene) materials induced by ultraviolet-light degradation [85]. Recently, the ER-EIS method, along with structural information, was used to characterize the energetic position and density of midgap trap states of the PbS nanocrystal thin film [86].

Representative ER-EIS spectra of the HOMO branch of thin glassy PFO films with and without β-phase are shown in Fig. 6. The energy scale was recalculated from the applied bias voltage to electronvolt using the −4.66-eV energy of the Ag/AgCl reference electrode vs vacuum level. Note that this calibration yields HOMO energies that are deeper than those for the same polymer thin films measured using photoelectron spectroscopy and cyclic voltammetry (about 5.6–5.8 eV) [14,87,88]. The g(E) scales inversely proportional to the measured charge-transfer resistance R\text{CT} (see Appendix C5) and is calibrated to the DOS scale by assuming the maximum of the HOMO level. Note that this calibration yields HOMO energies that are deeper than those for the same polymer thin films measured using photoelectron spectroscopy and cyclic voltammetry (about 5.6–5.8 eV) [14,87,88]. The g(E) scales inversely proportional to the measured charge-transfer resistance R\text{CT} (see Appendix C5) and is calibrated to the DOS scale by assuming the maximum of the HOMO branch to be on the order of about 10^{21} \text{ cm}^{-3} \text{ eV}^{-1} [89,90]

In the spectra, we recognize, for both samples, a peak in the DOS at −6.4 eV, with an additional feature (peak or slight shoulder) localized approximately 0.3 eV above the DOS maximum at ca. −6.1 eV. This band of states is more pronounced for the PFO film with intentionally introduced β-phase, which indicates its origin could be related to the presence of β-phase. If so, then the glassy sample in this...
ground-state backbone conformation is nonplanar, with a dihedral angle $\theta$ of around 45° or 135° between the adjacent monomer planes; therefore, the electronic coupling is not maximized. In the $\beta$-phase conformer, a number of consecutive monomers lie in a coplanar configuration ($\theta = 180^\circ$). Although such low-entropy geometry is metastable in the solid state with its total energy lying above the ground state, this conformation stabilizes the energies of charge carriers along the polymer chain.

We model the effect of such conformational features on the hole DOS as follows. First, we estimate the electronic coupling $J_0$ between the HOMO orbitals of consecutive, maximally coupled monomers using the counterpoise method [42,91] to be $J_0 = 0.45 \text{ eV}$. Then, having confirmed that the coupling varies with torsion angle like $J = J_0 |\cos \theta_0|$, we set up a tight-binding Hamiltonian representing a one-dimensional (1D) long chain with nonzero off-diagonal elements representing the hole coupling $J$ between each pair of neighboring monomers. For chains (or segments) in the ground-state conformation, these have the value $J = J_0 |\cos \theta_0|$, where $\theta_0$ is the equilibrium intermonomer torsion of 45° (or 135°). The diagonal elements represent the monomer site energies as seen by a hole and are identical at a value that we denote as $E_0$ (calculated to be $-5.85 \text{ eV}$ relative to vacuum using density functional theory on a monomer, using the B3LYP/6-31G* functional-basis set combination) for a chain of identical monomers. To represent a degree of energetic and conformational disorder, the site energies and angles $\theta$ can be distributed around the equilibrium values. The $\beta$-phase segments are modeled as sequences with uniform site energy, also at $E_0$, and a maximum $J = J_0$ corresponding to $\theta = 180^\circ$.

Figure S1 of the Supplemental Material [72] shows that a perfectly ordered chain with constant intermonomer torsion ($\theta_0$ of 45°) leads to a DOS with the characteristic form for a one-dimensional band (sharp maxima in the DOS at the extremes of the distribution). Introducing energetic or conformational disorder (or both) broadens the DOS to introduce tail states below the onset of the DOS (see Fig. 7). The effect of introducing an ordered $\beta$-phase segment of length $N$ (we use $N \geq 20$, guided by experimental evidence in Ref. [92]) is, in contrast, to introduce distinct states lying well below the onset of the one-dimensional band (see the SM [72], Sec. I, Fig. S1, for the effect of a $\beta$-phase segment of length 20 on the DOS of an ordered 100-mer). Figure 7 depicts the same phenomena calculated for a system that contains disorder of width $\sigma = 0.05 \text{ eV}$ in the site HOMO energies and disorder of $\sigma_\theta = 0.1$ radians in the torsion angles of the glassy parts. In the disordered system, the feature in the density of states due to the $\beta$-phase is still prominent and is separated by around 0.25 eV from the HOMO of the $\beta$-phase free chain.

The energetic position of the $\beta$-phase DOS onset compares well with the position of the feature introduced experiment must also contain a certain trace amount of $\beta$-phase, which is likely due to a combination of the low film thickness (~40 nm) used for ER-EIS measurements, the effect of the rough ITO surface in seeding $\beta$-phase development, and the high sensitivity of the ER-EIS technique. The floor-level DOS deep in the bandgap is estimated as $10^{16}$–$10^{17} \text{ cm}^{-3} \text{ eV}^{-1}$. This value is in good agreement with values determined from the TSC technique on a polyfluorene-type material by Renaud et al. [29].

IV. SIMULATING THE EFFECT OF $\beta$-PHASE ON THE DENSITY OF STATES AND HOLE TRANSPORT

We have seen that introducing $\beta$-phase into glassy PFO layers results in (i) a reduction in $\mu_h$, to a varied extent for different measurements, and (ii) a prominent feature in the sub-bandgap space of the hole DOS as probed using transient photocurrent and electrochemical impedance spectroscopies. In order to relate the observations directly to the presence of the $\beta$-phase conformer, here we take a theoretical approach, via first modeling the effect of $\beta$-phase on the hole DOS and then simulating the electrical response of a device in different conditions.

A. The effect of $\beta$-phase on the hole DOS from 1D tight-binding simulation

In many $\pi$-conjugated polymers, the extension and stabilization of the electronic states are strongly coupled to the torsion angle $\theta$ between planes of consecutive monomers. In PFO, as with all other polymers featuring a phenyl-phenyl linkage between monomers, the

FIG. 6. Density-of-states curves of the HOMO branch measured by ER-EIS for thin films (~40 nm) of glassy (blue) and $\beta$-phase embedded (red) PFO. The $\beta$-phase embedded sample shows a distinct satellite peak around 0.3 eV above the HOMO peak of the glassy sample. The faint shoulder visible in the glassy sample around the position of the $\beta$-phase feature is likely due to contamination with a minute amount of $\beta$-phase developed during preparation of the glassy sample.
FIG. 7. Top panel: Probability density (i.e., |ψ|^2) for the lowest five eigenfunctions ψ for an energetically and torsionally disordered β-phase free 100-mer chain (blue), and a disordered chain containing a 20-mer of β-phase (red), with the energetic disorder width 0.05 eV and the torsional disorder width 0.1 radians. Note that the lowest eigenfunctions for the system containing the β-phase segment are localized in the planarized segment. Second panel: Site HOMO energies for the disordered β-phase free (blue) and β-phase embedded (red) chains. Third panel: Intersite (intermonomer) electronic couplings for the disordered β-phase free (light blue) and β-phase embedded (orange) chains. The x axes of the first three panels present the spatial extent along the 100-mers. Fourth panel: Density of states obtained by summing over all eigenvalues for the disordered β-phase free chain (blue). Bottom panel: Density of states obtained by summing over all eigenvalues for the disordered β-phase embedded chain (red). The x axes of the bottom two panels present energy in units of electronvolts.

into the experimental DOS by the β-phase and confirms that the β-phase segments will act as intrachain trap states for holes. The stabilization of the hole energy in the β-phase segment is a direct result of the increased electronic coupling within the planarized segment and of the segment length. Density functional theory calculations of the hole energy confirm that planarization could stabilize the HOMO of a fluorene octamer by around 0.20 eV relative to that of the glassy conformer (see the SM [72], Sec. I, Part B, Fig. S2). This is a lower limit as longer segments will be more strongly stabilized, and it is consistent with results from the tight-binding model.

B. Numerical DOS and the reproduction of transport phenomena

We now investigate the effect of such changes in the DOS on time-resolved and steady-state transport using a continuum device model. When we consider the comparison of HDR photocurrent transients and extracted DOS maps in Fig. 5, we hypothesize that the transient knee of the β-phase embedded device at around 2 μs, which determines the value of the hole transit time used to calculate TOF mobility, may be significantly influenced by the release of charge carriers from and the recapture of carriers into trap levels introduced by the presence of β-phase. This process is likely to persist until the drop in photocurrent occurs upon the charge packet reaching the counter electrode, which is compatible with the usual interpretation of TOF transients. The effects of charge transit and detrapping thus need to be resolved. It is, however, difficult to convert TOF transients around the knee into a DOS profile directly using Eqs. (1) and (2) because the knee lies close to the pretransit region where Eqs. (1) and (2) are not valid. Furthermore, Eqs. (1) and (2) often predict broader features in the DOS than really exist, due to the assumption that there is no thermal broadening effect on the demarcation energy E’ as in Eq. (2). Therefore, to relate the photocurrent transient to the underlying DOS distribution, a more complex model is needed.

To help us interpret the TOF transients and other electrical measurements, we adapt an open-source 1D numerical drift-diffusion model named General-Purpose Photovoltaic Device Model [93]. This model solves the bipolar drift-diffusion equations in the time domain to take account of charge-carrier transport across the device, and Poisson’s equation to account for electrostatic effects [11]. We approximate the motion of mobile charge carriers using two parabolic bands, one to represent the effective DOS for free electrons and the other to represent the effective DOS for free holes. Position space is discretized using 50 evenly spaced, finite-difference mesh points (a value that is adequate to generate device response with high numerical accuracy; as shown in the SM [72], Sec. I, Part B, Fig. S2). To account for energy-dependent charge-carrier trapping and recombination, at each mesh point (i.e., a 0D energy “slice”), we introduce a set of 80 discretized trap levels spanning 0.8 eV (i.e., 10 meV per interval) beneath the LUMO and another set of such trap levels above the HOMO; at each level, the DOS for that energy interval is defined, and each trap level at an individual mesh point can be occupied by the relevant charge carriers up to the limit of the DOS for that interval. For each trap interval, we solve the Shockley-Read-Hall rate equations in the time domain. Thus, we are able to resolve the flow of carriers across the device, as well as the charge density in both position and energy spaces as a function of time without assuming quasiequilibrium to describe the occupancy of states. This and similar approaches have previously been applied to organic semiconductor devices to model experimental data, including steady-state J − V measurements [94,95], small-signal ac response [96], ultrafast pump-probe measurements [97], and other nonequilibrium transient transport phenomena [95,98].

To first model the hole DOS for glassy PFO, we combine an exponential tail of E_{ch} = 75 meV, as suggested by the long-time limit of the DOS mapped from the HDR TOF transients, and a Gaussian centered around the transport...
energy level with a breadth of 75 meV. The peak magnitude of the Gaussian and the trap density of the exponential tail at the band edge are varied until good fits are obtained for the glassy TOF and steady-state $J - V$ results. We note that such a composite DOS has previously been proposed in the literature for other material systems [7,11–13,99–101]. The DOS of the $\beta$-phase embedded PFO was then modeled by superimposing a narrower Gaussian of $5 \times 10^{20}$ cm$^{-3}$ eV$^{-1}$ peak height and 45 meV breadth, centered at 270 meV above the hole transport level. In obtaining these $\beta$-phase-related parameters, the depth of this feature was first assigned as 0.3 eV relative to the HOMO mobility edge, related parameters, the depth of this feature was first assigned as 0.3 eV relative to the HOMO mobility edge.

The $\beta$-phase feature is centered at 270 meV above the transport level, featuring a breadth of 45 meV and a $5 \times 10^{20}$ cm$^{-3}$ eV$^{-1}$ peak height. The graphs are plotted as piecewise-constant functions to represent the discretization in energy space of the DOS distributions that are used in the numerical model.

Figure 9 compares experimental HDR TOF transients with transients simulated using the energy-resolved drift-diffusion model with the aforementioned numerical DOS functions, under the same conditions as the experiment (including, e.g., temperature, applied bias, and film thickness). The model closely reproduces the positions of features in the glassy PFO experimental TOF curves and the long-time slope. Upon addition of the narrow Gaussian representing $\beta$-phase to the model, the simulated TOF transient develops a peak at around 2 $\mu$s, exactly as is observed experimentally. We also note from Fig. 9 that the simulated photocurrent transient curves cross beyond about 10 $\mu$s, in contrast to the experimental data. We postulate that this different behavior may result from different levels of carrier occupancy in the experimental case due to unintentional variations in the laser pulse intensity, whereas in the simulation case, laser pulse photon flux is kept the same. The crossing observed in the simulated case is

![Figure 8](image1.png)

**FIG. 8.** Numerical hole DOS functions proposed in the drift-diffusion modeling, for glassy PFO (blue curve) and PFO containing $\beta$-phase (red curve), respectively. This set of model DOS is a simplified picture of realistic distributions; however, it nonetheless captures the key features. As an approximation due to relatively low content of $\beta$-phase, a direct superposition for constructing the $\beta$-embedded DOS is applied. The numerical $\beta$-phase feature is centered at 270 meV above the transport level, featuring a breadth of 45 meV and a $5 \times 10^{20}$ cm$^{-3}$ eV$^{-1}$ peak height. The graphs are plotted as piecewise-constant functions to represent the discretization in energy space of the DOS distributions that are used in the numerical model.

![Figure 9](image2.png)

**FIG. 9.** Simulated (dashed lines) and experimental (solid lines) HDR TOF transients for glassy (blue) and $\beta$-phase embedded (red) HMW PFO devices at RT. The experimental traces are reproduced from Fig. 5(a). The model reproduces positions of transient features and trends for both device types. The $\beta$-phase is introduced by adding a Gaussian sub-bandgap state as depicted in Fig. 8 and with no other parameter changed relative to the glassy case. Note that the transients are taken at different applied biases for the two systems.
expected because the additional band of states in the DOS of the \( \beta \)-embedded device resulting from the \( \beta \)-phase defect means that fewer carriers are generated in the deep tail than in the glassy device, resulting in a lower level of transient photocurrent in the long-time limit. We stress that the only differences between the two simulations in Fig. 9 are (i) the addition of the narrow Gaussian deep trap feature and (ii) change of the bias voltage according to the respective experimental settings. No other simulation parameters were altered. The appearance of this strongly delayed knee in the modeled curve as seen in the experimental one suggests that the experimental feature is very likely caused by charge-carrier transport events involving the \( \beta \)-phase trap levels. The model includes charge-carrier trapping, detrapping, and transport; thus, it is likely to be due to a combination of these effects. Extraction of a transit time from the simulated curves while assuming that this knee is due to charge-carrier collection leads to an estimate of mobility for the \( \beta \)-phase embedded device that is around 2 orders of magnitude lower than for the glassy device, as found experimentally and demonstrated below.

Figure 10 shows the simulated steady-state dark \( J \)–\( V \) curves for comparison with the experimental data in Fig. 3, obtained using exactly the same model for the material parameters as those used to model the TOF results, and via allowing for the different contact barriers (one Ohmic contact for dark \( J \)–\( V \) rather than two blocking contacts for TOF) and different PFO layer thickness of the hole-only devices relative to the TOF devices (135 nm for dark \( J \)–\( V \) rather than 1.8 \( \mu \)m for TOF). The \( J \)–\( V \) curves are obtained from the steady-state dark current response of the modeled device to a sweep of forward-bias voltage. Remarkably, the steady-state model predicts that \( \beta \)-phase has only a mild effect on the \( J \)–\( V \) response relative to the glassy case, exactly as seen experimentally in Fig. 3, even though the same model of the two materials reproduces a dramatic effect on the TOF photocurrent transients.

Figure 11(a) presents a Poole-Frenkel form summary of the \( \mu_h \) values extracted from TOF devices and impedance spectroscopic measurements on hole-only devices. Figure 11(b) plots the corresponding simulated results where the \( \mu_h \) of hole-only devices are extracted from the simulated steady-state \( J \)–\( V \) response. The simulated TOF \( \mu_h \) values are extracted by analyzing the modeled transients identical to the approach applied for the experimental transients, while the simulated dc \( \mu_h \) values for hole-only devices are derived by multiplying the band \( \mu_h \) assigned to the model by the ratio of free to total (i.e., free

![Graph](image_url)
plus trapped) charge density (as proposed by Refs. [2,103]), at a mesh point right next to the hole-extracting electrode along the 1D device space (see the SM [72], Sec. I, Fig. S3 for simulated spatially resolved profiles of densities of free and trapped charge carriers within the hole-only devices). The model reproduces the experimental results well in terms of both magnitude of effects and trends. Notably, the simulated TOF transients for the $\beta$-phase embedded device lead to an apparent $\mu_h$ up to 2 orders of magnitude lower than that of the glassy case, while the simulated dark steady-state response leads to a mobility reduction of only a factor of about 2–3. We further note that the value of the TOF $\mu_h$ extracted from the numerical simulation is not sensitive to the active layer thickness, as shown in Fig. S4 of the SM [72]. The discrepancy in the $\mu_h$-field-dependence slopes from hole-only devices between Figs. 11(a) and 11(b) (with simulated ones showing a stronger field dependence than the experimental counterparts) may primarily be due to the fact that the diffusion contribution of holes was not excluded in extracting the experimental $\mu_h$ (a, strictly speaking, drift-only term), hence giving rise to values higher than realistic $\mu_h$ especially in the low-field range where carrier diffusion prevails over drift. The observation may also be caused by a minor discrepancy in the estimated $V_{hi}$ from $C-V$ characteristics of the hole-only devices (see Appendix G, Part 2) relative to the actual value, thus leading to a slight over-correction for the field dependence.

V. RECONCILING THE CONTRADICTORY EFFECTS OF $\beta$-PHASE ON HOLE TRANSPORT

A. Significance of accounting for carrier relaxation in interpreting transport phenomena

We have established that a consistent picture of the density of states due to the $\beta$-phase conformational defect
can account for the different effects on PFO device response from different (transient, impedance, and steady-state) transport probes. It remains to establish how electronic transport (and apparent mobility) is related to carrier dynamics in the different measurements. To do this, we first simulate TOF transients with and without \( \beta \)-phase at a controlled external bias of 10 V and temperature of 295 K. We plot the carrier distribution within the sub-bandgap states at particular time points, by considering a slice at the 5th out of a total 50 mesh points of the device (counting from the anode toward the cathode). Figure 12(a) plots the hole density in the DOS for such a slice of a glassy device at times spaced logarithmically from 10 ns to 1 ms after photoexcitation. Beyond about 1 \( \mu s \) (i.e., after \( t_a \sim 120 \) ns), the carrier distribution shows a relatively sharp edge distinguishing occupied from unoccupied states and minimal carrier redistribution into deep traps due to retrapping, as theory predicts for a post-transit photocurrent transient under a strong field [2,4]. In contrast, when the Gaussian band of localized states associated with the \( \beta \)-phase is present in the DOS [Fig. 12(b)], there is no sharp edge to the carrier distribution until more than 10 \( \mu s \) (i.e., after \( t_a \sim 9 \) \( \mu s \)), and at earlier times, a significant fraction of the states lying between 0.2 and 0.35 eV above the band edge is populated. It is the charge-carrier interaction with these trap states—through trapping and release—that controls the onset of the kneelike feature (\( t_a \sim 9 \) \( \mu s \)). The pretransit plateau corresponds to a window of time during which repetitive charge retrapping and detrapping occur from the \( \beta \)-phase defect such that the population of mobile holes is mostly maintained (apart from a small carrier redistribution into deep tail states), as illustrated in the inset to Fig. 12(b). This leads to the much-delayed arrival of the fastest charge carriers at the counter electrode relative to the \( \beta \)-phase-free (glassy) case.

This analysis allows us to resolve the difference between the mobilities measured using transient and steady-state methods for the same material system. The DOS for the glassy and \( \beta \)-phase embedded devices are largely similar and differ only in the presence—for the \( \beta \)-phase embedded case—of a small density of trap states concentrated at a level around 0.3 eV above the hole transport edge. The contribution to current at each point in the device is controlled by the density of free holes at that point. The density of free holes is controlled in turn by the activation of the most energetic (relatively “hot”) charge carriers in the sub-bandgap DOS to the transport level with the result that current is higher when the activation barrier is lower (DOS filled to a higher level) or when the carrier population at the highest filled level is higher. To understand the differences in the effect of \( \beta \)-phase on the measured mobility, we need to understand the difference in the transient and steady-state measurements.

In steady-state conditions, such as in dark \( J-V \) measurements, the filling of the density of states varies across the device while a uniform current density is maintained by variations in the local electrostatic potential. The effect of \( \beta \)-phase is to increase the DOS in a certain energy window above the transport level such that for any charge-carrier density, sufficient to fill the DOS up to or beyond the \( \beta \)-phase defect level, more of the charge carriers are located further from the hole transport level; the density of free holes is lower, and therefore the current is lower. The presence of the \( \beta \)-phase defect has a noticeable effect on DOS filling within the hole-only devices under forward bias, as illustrated by plots of the occupied DOS in Fig. 12(c), indicating that the profile of trapped carriers in the \( \beta \)-phase embedded hole-only device is overall “cooler” than that of the glassy device. This effect suppresses the density of free holes in the bulk of the device by a factor of between about 2 and 10 (depending on position; see the SM [72], Sec. I, Fig. S3) relative to the glassy case, and it affects the electric-field distribution as shown in Fig. 12(d). The overall effect is thus to reduce the hole mobility.

The transient photocurrent measurement made by TOF differs in a few respects. First, because of the low optical excitation density and the absence of electrically injected charges, the level of DOS filling is not only much lower but it also varies more strongly across the optically thick layer (especially soon after the photogeneration of carriers). Second, the excess charge carriers are not fully relaxed in the DOS during the timescale of the measurement—their energetic distribution starts overall hot and progressively cools down, leading to an effective carrier mobility that decays with time. Third, mobility is therefore estimated from the time-dependent photocurrent, which is effectively a reflection of the change in the occupied DOS with time, rather than from an average photocurrent that reflects different levels of occupancy. Because the time-dependent photocurrent is sensitive to features in the DOS, and the DOS filling level does not change strongly across the bulk of the device once it has entered the post-transit regime, a strong change in photocurrent corresponds to a distinct sub-bandgap DOS peak (like the \( \beta \)-phase) as the DOS empties by carrier detrapping. In addition, when such a distinct feature is present (and provided it is relatively shallow), the carriers undergo a much larger amount of repetitive trapping-detrapping events during the prolonged pretransit time, thus leading to more redistribution of carriers into deeper traps [compare carrier redistribution in Figs. 12(a) and 12(b)]. The analysis of TOF transients is based on the idea that the induced photocurrent drops when charge carriers reach the opposite electrode; thus, a qualitative change in photocurrent is associated with a transit time. However, the presence of peaks in the DOS can lead to significant changes in the photocurrent due to capture and release of trapped carriers. These effects produce changes in the shape of the photocurrent such as a clear and strongly delayed kneelike feature; hence, the apparent experimental observation of “nondispersive” [104], or even seemingly “trap-free” [105],
transport. It is noteworthy that due to the reciprocity between time and frequency, a profound influence of phase on carrier dynamics is also visible in the frequency-resolved capacitance–voltage response of the hole-only devices (see Fig. 24 in Appendix G). In addition, thanks to a higher volume content of phase induced, the LMW devices amplify the effect of phase by featuring strong “cusps” in their TOF transients, as shown in Fig. S8(a) of the Supplemental Material [72]. This observation supports the idea that the photocurrent feature reflects charge-carrier trapping and release events associated with the distinct conformational defect. In the case of the phase feature in PFO, the effect on the photocurrent transient of the charge-carrier interaction with the phase defect is to shift the transit time to longer times, thus leading to a substantially lower value of the estimated mobility. This result demonstrates that all photocurrent transients, in general, reflect a combination of charge-carrier trapping, detrapping, recombination, and transport processes, and therefore, it is difficult to rely on simple analytical models to interpret the device response, especially in the presence of nontrivial density-of-state distributions. We further note that the assumed relationship between photocurrent evolution and mobility that is normally used for TOF is not always appropriate when there are strong peaks in the sub-bandgap DOS. (For more details, see Sec. IV of the SM [72], where we generalize the interplay between such sub-bandgap DOS and band mobility on the photocurrent shape.) If a true estimate of the effect of phase on steady-state hole transport in a device were needed, the analysis used here for the steady-state measurements should yield a more realistic estimate, while the large effect inferred from the TOF method is overestimated. We also reiterate that the TOF transient at any given time depends on the instantaneous carrier distribution profile within the DOS, which is a function of charge-carrier dynamics, the carriers’ history, and the given DOS. Therefore, a detailed numerical model is required to understand the precise shape of the transient in both early- and late-time limits, especially when the DOS shape is complex.

Next, we comment on the difference in magnitude between the hole mobilities inferred from glassy PFO devices using the TOF method (TOF $\mu_h = 2-4 \times 10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$) and using the impedance method (steady-state $\mu_h = 0.6-1 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$) since neither measurement is affected by the phase defect. Higher mobility values have previously been reported using TOF when compared to vertical-mode steady-state techniques, in disordered molecular materials [106–108]. The reason is likely to be that in a disordered system, the fastest carriers that determine the appearance of a transit time in TOF (we recall their time-dependent carrier mobility through progressive thermalization) are normally much faster than the mean velocity that would characterize the carrier velocity distribution for the same device in the steady state.

This discussion reveals clearly the critical effect of the choice of measurement technique on the meaning of an extracted mobility value. Figure S5 of the Supplemental Material [72] summarizes how the reported $\mu_h$ in PFO varies by orders of magnitude depending on the measurement technique as well as the preparation of the sample. The variations in the values of $\mu_h$ reported previously for PFO are likely to result partly from the unintentional presence of different phases (such as the phase) in the devices, as well as the different assumptions underlying analyses for different techniques. This observation underlines the fact that the value of a mobility measurement is only meaningful in the context of the assumptions underlying the measurement technique used. For example, a steady-state measurement is relevant for mobility in a device that is operated in the steady state under similar injection levels, while a value of mobility measured under conditions far from the intended operating conditions of interest may not be meaningful.

**B. Multiple-trapping versus polaronic conduction:**

**Insights from previous studies of hole transport in PFO**

Finally, we consider our results in the context of prior reports of the hole transport in PFO. Before doing that, we briefly consider the different models of microscopic charge transport. We have used a multiple-trapping model where charge-carrier activation is controlled by the energy difference between a charge carrier in a trap state and the transport level. In the case of organic semiconductors, it is also common to use a polaronic transport model where charges must overcome a polaron binding energy, as well as any difference in site energy, in order to move. This additional activation energy due to polaron binding, in the weak-coupling limit [109], is given by $\lambda/4$, where $\lambda$ is the reorganization energy. In this limit, $\lambda$ is large compared to the electronic coupling between transport sites and comparable with or larger than the disorder in transport-site energy. The presence of a significant polaron binding energy would affect the temperature dependence of mobility but would not affect the relationship between the shape of the DOS and the photocurrent transient at a given temperature. Our results may be consistent with polaronic transport, but since we work within a narrow temperature range of 16 K, we cannot conclude from our data whether polaronic transport is relevant or not.

Several previous works placed the TOF $\mu_h$ of room-temperature “as-cast” films of PFO at around, or marginally over, $2 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ [69,104,110]. Judging from the device preparation conditions used, it is very likely that those films contained phase [79]. In support of this idea, the previously reported TOF $\mu_h$ hole mobilities agree well with the value presented here for phase embedded PFO. Kreouzis and co-workers [69] assigned the transport in RT as-cast (nonannealed) PFO layers to a polaronic hopping mechanism [111] on account of the thermally activated
nature of the zero-field hole mobility \( [\ln(\mu_{h})] \propto T^{-1}] \), wherein the activation energy \( E_a \) would be enhanced by the reorganization energy. In contrast, uncorrelated hopping within a Gaussian DOS would have yielded a TOF \( \mu_{\text{h}} \) varying like \( \ln(\mu_{h}) \propto T^{-2} \) [6] rather than \( \ln(\mu_{h}) \propto T^{-1} \). We can now tentatively explain this observation in terms of the effect of \( \beta \)-phase. The \( E_a \) obtained from the analysis of the previously reported TOF of as-cast PFO is around 0.3 eV [69]. This value closely matches the estimated depth (~0.3 eV) of the sub-bandgap \( \beta \)-phase defect in this study, and the \( E_a \) for our \( \beta \)-phase embedded device as shown in the Arrhenius plot in Fig. S6 of the SM [72]. It is therefore plausible that the transport behavior reported in Ref. [69] was dominated by the thermal activation of holes out of \( \beta \)-phase traps, rather than by a combination of Gaussian disorder and polaron activation; also, the size of the polaron binding energy, if present, may be smaller than deduced in that study. See the SM [72], Sec. II, Part B for more discussions.

VI. CONCLUSIONS

In this study, we have attempted to understand and address the impact of conformational defects on the density of states and charge transport in \( \pi \)-conjugated polymers, taking the fully extended, planar-zigzag \( \beta \)-phase segment in amorphous PFO as an example. By applying a HDR TOF photocurrent technique, we have probed the density of trap states extending far (up to \( \sim 0.55 \) eV) above the hole transport level of the polymer, and we have shown that the DOS is affected by the presence of the \( \beta \)-phase conformer through the addition of a set of hole states approximately 0.3 eV above the hole transport level. The validity of the DOS obtained by HDR TOF is confirmed using a complementary technique based on energy-resolved electrochemical impedance spectroscopy. Moreover, the energetic position and sharpness of the defect states is consistent with the simulated effect of backbone planarization on the HOMO energy in oligofluorenes.

We have also exploited the PFO system with the presence or absence of \( \beta \)-phase to reconcile apparent disagreement in hole mobility values extracted using different experimental techniques. Specifically, we found that while the hole mobility probed by the TOF photocurrent appears to be up to 2 orders of magnitude lower for \( \beta \)-phase embedded than for neat glassy PFO, the steady-state value based on hole-only devices is only a factor of 2–5 times lower. We rationalize this by using a macroscopic device model whereby charge carriers are resolved in terms of energy as well as position and time. We show that within this model, the different observations from time-resolved and steady-state probes can be reconciled. The underlying reason for the seemingly contradictory phenomena is the different levels of carrier relaxation or occupation within the localized states, as well as the different interpretation of currents in terms of mobility for the different measurements. To the best of our knowledge, this work accomplishes the first quantitative demonstration of a direct relationship between conformational disorder, sub-bandgap DOS distribution, and charge transport behavior in a molecular electronic material. This study also highlights the importance of applying energy-resolved models to properly analyze and interpret transient, out-of-equilibrium electronic phenomena in disordered semiconductors featuring a significant density of sub-bandgap localized states.

A somewhat surprising result of this study is that conformational variants that encourage charge-carrier delocalization (such as the \( \beta \)-phase in PFO) can inhibit rather than assist charge transport. This phenomenon is a consequence of the limited density of \( \beta \)-phase segments that can be introduced into high-molecular-weight PFO, which prevent charge percolation through the \( \beta \)-phase alone, and the twisted nature of the optimum ground-state conformation that results from the phenyl-phenyl linkage of the polymer. The impact of conformational variation on transport in polymers with more planar ground-state geometry would be less significant [19]. The \( \beta \)-phase content can be increased to some extent in low-molecular-weight polymers, as shown here, but to an insufficient degree for percolation, thus leading to an even stronger penalty on mobility.

This work demonstrates how electronic transport can be controlled via molecular conformation in organic semiconductors. Another general implication from this study is that charge-carrier mobility, as a figure of merit from experimental probes, must depend heavily on the measurement conditions and carrier concentration, and on how charge carriers reflect the DOS as they transit across a disordered solid. In the specific case of PFO, this knowledge could, in principle, be exploited by tuning of charge transport through judicious control of the \( \beta \)-phase content. Such optimization could have potential benefits in balancing hole and electron mobility in OLEDs, as well as in simultaneously optimizing luminescence quantum yield and the spectral definition of the blue emission. In a broader context, findings of this study can also be applied to areas concerning (i) electronic transport or charge transfer within other (macro)molecular systems, where conformational freedom plays a role, and (ii) the arrival of a unified picture of the impact of structural and energetic disorder on transport behavior in disordered semiconductors observed using different transport techniques.

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APPENDIX A: MATERIALS

HMW and LMW PFO materials, synthesized via the Suzuki coupling reaction, were sourced from Sumitomo Chemical/Cambridge Display Technology (CDT). The polymers underwent extensive postsynthesis purification to remove ionic impurities and catalyst residues, and they were used as received. HPLC-grade toluene (≥99.8%, VWR Chemicals) was used as solvent throughout the PFO sample and device fabrication. Conductive polymer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS; work function ~5.2 eV; Heraeus Clevios™ P VP Al 4083) was selected as the interlayer on indium-tin oxide (ITO) for creating asymmetric PFO hole-only devices. Ultrathin (~5 nm) layers of molybdenum oxide (MoO₃; purity ≥99.5%; Sigma-Aldrich) were thermally evaporated atop polymer active layers to establish Ohmic contacts for hole-only devices. Pellets of aluminium (Al; purity 99.999%; top metallization for time-of-flight devices) and gold (Au; 99.99%; top metallization for hole-only devices) for thermal evaporation were obtained from Kurt J. Lesker® Company.

To extract molecular-weight properties of the PFO polymers used in this study, polystyrene-equivalent gel permeation chromatography (GPC) measurements were carried out with a Viscotek instrument comprising a pump and a degasser (GPCmax VE2001), a detector module (Viscotek 302 TDA), and three columns (2×PLGel Mix-C and 1×ViscoGEL GMHHRN 18055). PFO solutions (including 0.1 vol% toluene as an end marker) were prepared in chloroform with 1.2 mg mL⁻¹ concentration. To promote polymer dissolution, the solutions were heated at 50°C for 15 minutes. They were subsequently filtered [112] to remove any possible extrinsic dust or particulates. The columns were held at 35°C, with a solution flow rate of 1 mL min⁻¹ set for the GPC measurements. Raw detection curves for the high- and low-MW PFO solutions are presented in Fig. 13, indicating monomodal distributions of both batches and the concurrent onset of the toluene end marker. The offset in GPC peaks visualizes the relative difference in the MW profiles of the two polymers, which are therefore dubbed HWM and LWM, respectively.

OMNISEC software (Viscotek) was employed to analyze the data using conventional calibration. Because of the higher chain stiffness of PFO, its absolute molecular weight is a factor of 2.7 lower than the polystyrene-equivalent value [62]. The number of repeat units for the average chain length from each PFO batch was estimated from the corresponding stiffness-corrected absolute values of number-average molecular weight ($M_n$) and by factoring in the molecular weight of a PFO monomer (~388 Da). The results, along with polystyrene-equivalent weight- ($M_w$) and number-average ($M_n$) molecular weights, as well as the corresponding polydispersity indices (PDI = $M_w/M_n$), are summarized in Table I.

FIG. 13. Gel permeation chromatography (GPC) detection curves for both HMW (blue line) and LMW (red line) PFO solutions (1.2 mg mL⁻¹ in chloroform with 0.1 vol% toluene as the end marker). Monomodal molecular distributions for both PFO batches are evident. Note that $M_w$ and $M_n$ values for both materials, as listed in Table I, were extracted from the GPC curves based on conventional polystyrene-equivalent calibration.

FIG. 14. False-color sketch of the solvent vapor exposure apparatus. The red stage represents the hot-plate surface kept at 50°C during the process to promote evaporation of toluene (light blue) from a small petri dish placed atop. The lime-green pieces represent the substrates with glassy PFO layers cast uppermost. These samples are lifted above the hot-plate surface by about 1 cm using thermal-insulating plastic vial lids as stands. This way, we prevent direct thermal contact and thus any potential film crystallization into the α'-phase [113]. An enclosed chamber is achieved by placing a larger, upturned petri dish onto the hot-plate surface. The continuous vapor exposure period is set to one hour; the process is hence abbreviated as 1hrSVE.
APPENDIX B: SAMPLE AND DEVICE FABRICATION

1. Substrates

(a) Spectrosil® B fused-silica substrates (12 × 12 mm²; thickness ~1 mm; UQG Optics) were used to realize PFO thin-film samples for optical spectroscopies.

(b) For TOF and hole-only devices, as well as samples for energy-resolved electrochemical impedance spectroscopy (ER-EIS), glass/indium-tin oxide (glass/ITO) substrates (12 × 12 mm²; ITO layer thickness of about 150–250 nm; ITO work function of about 4.7 eV; total thickness of about 1 mm; PsiOTec) were used. Sheet resistance of the prepatterned ITO stripe (covering the central 8 × 12 mm² area) was about 10–15 Ω/□ [see Fig. 15(a) for the substrate pattern]. PEDOT:PSS interlayers (~30 nm) were treated on top (via spin coating at 3000 rpm for 60 s followed by drying at 120°C for 6 min) in the case of making hole-only devices.

Below, we provide fabrication protocols for the PFO samples and devices investigated in the present work.

FIG. 15. Schematic top views of (a) the bare glass/ITO substrate and (b) finished devices thereon. In panel (a), the 12 × 12 mm² glass substrate is partially covered by an 8 × 12 mm² ITO stripe (grey). The thickness of the ITO layer varies from 150 to 250 nm depending on batches of manufacture. The total thickness of the substrate is about 1 mm; in panel (b), six top electrodes (sky blue) are deposited via thermal evaporation under high vacuum (∼10⁻⁶ mbar) through a shadow mask, thereby forming six indivial devices (pink). The overlap between the top contact and ITO stripe defines the effective geometric area for each single device (~4.5 mm²). Electrical connection to the bottom ITO electrode is established by applying conductive silver paste (orange) at either edge of the ITO stripe after physically removing the local active layer. Such a configuration allows for characterization of six devices on one substrate and hence comparison of their property-performance uniformity.

2. Glassy PFO film deposition

A solution of HMW PFO (7 mg ml⁻¹ in toluene) was spin coated onto thoroughly cleaned and O₂-plasma-treated fused-silica substrates at 1200 rpm, yielding PFO thin films with thickness of about 65 nm for UV-Vis absorption measurements. To fabricate “baseline” isotropic glassy PFO films with maximally suppressed β-phase and crystalline chain segments, both the solution and substrates were placed on a hot plate set at 95°C (below the boiling point of toluene, ~111°C, to avoid bubbling) for at least 3 minutes immediately prior to spin coating: The total duration of steps, including (i) transfer of the preheated substrate to the vacuum chuck, (ii) pipetting hot PFO solution onto the substrate, (iii) closing the spin coater lid, and (iv) initiating the spin, was controlled to be less than 8 s. We refer to the above process as “hot spin coating” for PFO films.

Optically thick (~1.8 μm) HMW glassy PFO photoconductive layers in TOF devices were prepared according to the hot spin-coating procedures described above, except from spin coating 30 mg ml⁻¹ viscous HMW PFO solutions in toluene at 800 rpm for 60 s, followed by a 30-s “smoothing” step at 2000 rpm, onto cleaned, O₂-plasma-treated glass/ITO substrates. Moreover, for these thick films, an aluminium vacuum chuck was also employed and preheated to about 95°C, in order to promote maximally rapid solvent evaporation and thereby prevent chain relaxation during solidification [79] to form the β-phase. Likewise, LMW PFO photoconductive layers (~3–4.1 μm) were also cast following hot spin coating, however using 700–1200 rpm and a higher solution concentration of ~70 mg ml⁻¹.

For the preparation of hole-only devices, glassy PFO layers were similarly cast onto PEDOT:PSS precoated ITO/glass substrates.

Prior to the deposition of top contacts, in order to generate β-phase embedded (or “β-embedded” for short) variants, the hot-spun glassy PFO layers were further processed according to procedures described below.

3. Inducing the β-phase by exposing glassy PFO layers to solvent vapors

To induce planarized β-phase conformers into pristine glassy PFO layers (of both optically thin and thick), postdeposition solvent vapor exposure (SVE) was performed, as illustrated in Fig. 14. See figure caption for detailed procedures. Note that this 1-hour treatment was for
a period significantly longer than the period of about 10 minutes estimated by Caruso and Anni in achieving the saturated formation of β-phase chain segments in 400-nm toluene-vapor-exposed films [64].

Subsequent to film deposition and “1hrSVE” postdeposition treatments, the films were desiccated over several hours to remove any residual trapped solvent. Film thickness was determined using a DektakXT™ surface profilometer.

4. Thermal evaporation of top contacts

For the TOF devices, about 100-nm-thick Al counter electrodes were deposited via thermal evaporation at \( \leq 10^{-6} \) mbar through a shadow mask onto optically thick PFO films, yielding stacked structures with a geometric device area of about 4.5 mm\(^2\) defined by the electrode overlap regions (see Fig. 15 for details).

The hole-only devices feature likewise geometric layouts while using ultrathin (~5 nm) MoO\(_x\) interlayers further capped by about 100-nm Au as top metallization.

APPENDIX C: SETUPS OF
(OPTO)ELECTRICAL PROBES

1. Time-of-flight photocurrent charge-carrier motility

Photogeneration of the charge carriers was delivered by pulsed frequency-tripled Nd:YAG laser excitation \( (\lambda_{ex} = 355 \text{ nm}; \text{pulse width } \sim 5 \text{ ns}; \text{Quantel}) \) through the ITO front anode. A Keithley high-voltage source-measure-unit (SMU) 237 was used for applying a variable dc bias voltage across TOF devices. Typical dc dark current levels are less than 25 pA at 50-V bias for the PFO TOF devices, indicating excellent blocking properties of the chosen contacts. Photocurrent transients were recorded using a Tektronix® TDS 3052 digital storage oscilloscope (or scope for short) with its 0.5-GHz full-bandwidth setting. Neutral-density filters were applied to limit the intensity of the incident laser beam to \( Q/Q_0 < 10\% \) (and less than 15% in the HDR measurement scenario), where \( Q_0 \) is the bias-dependent amount of charges held across the contacts of the sandwichlike TOF devices and \( Q \) the population of photogenerated charges. Figure 16 shows a schematic of the TOF photocurrent setup.

To capture fast transients featuring, e.g., sub-100-ns transit time, 50 \( \Omega \) channel termination was chosen (which matches the 50 \( \Omega \) coaxial cable characteristic impedance) and with a 50 \( \Omega \) source impedance fitted onto the Keithley SMU 237 for optimized electrical response. Data acquisition was externally triggered by the laser Q-switch synchronization signal. When necessary, transients were recorded with a 256- or 512-averaged sampling mode for an enhanced signal-to-noise ratio (SNR).

During the TOF measurement at room temperature (typically at about 295 K), devices were housed inside a hermetic, pure nitrogen filled and electrically grounded metal enclosure (fitted with a fused-silica optical window to allow for optical excitation) for (i) sample preservation against degradation and (ii) electromagnetic interference rejection.

Temperature-dependent (cryogenic) TOF measurements were carried out using an OptistatDN liquid nitrogen cryostat (Oxford Instruments) adapted with miniature 50 \( \Omega \) coaxial cables (RG178B/U; Lapp Kabel) for electrical signaling.

2. Reconstruction of HDR TOF photocurrent transients

Concerning TOF post-transit photocurrent analysis, the logarithmic dependence of energy on time implies that acquisition of HDR photocurrent with a large time span is essential for estimating the profile of localized states lying deep in the bandgap. As for the passive resistive sensing approach, it relies on a terminating variable resistor to convert current transients into time-varying voltage signals proportional to the choice of sensing resistance. In order to obtain transients with extended time and dynamic range, one can progressively assign increasing values of sensing resistance by varying a resistor wired in parallel with the RC approach, it relies on a terminating variable resistor to convert current transients into time-varying voltage signals proportional to the choice of sensing resistance. In order to obtain transients with extended time and dynamic range, one can progressively assign increasing values of sensing resistance by varying a resistor wired in parallel with the 1-M\( \Omega \) termination of the scope. It can be expected that applying higher resistance is advantageous for probing deeper into the post-transit regime due to higher measurement sensitivity and better SNR. However, an enlarged RC time constant of the setup would, meanwhile, suppress the ability to capture high-frequency features that a photocurrent carries, typically following its initial onset. By carefully balancing the interplay between measurement sensitivity and the speed of system response, and overlaying (“stitching” together) individual photocurrent sections obtained from incremented resistor values, we are able to reconstruct a single piece of TOF photocurrent transient with extended dynamic range. We employ a
commercially available variable resistor (VT1, Thorlabs) for our passive-mode HDR photocurrent measurements. The VT1 unit features a feedthrough configuration to the BNC inputs of the scope. Having the variable resistor set (50, 100, 500, 1 k, 5 k, 10 k, and 50 k ohms) fully integrated within its miniaturized metal housing, this unit provides a superior electromagnetic shielding. When necessary, further higher resistance values can be applied using fixed sub-styline terminators FT104 (100 kΩ) and FT254 (250 kΩ) (both from Thorlabs) paired with a BNC T-connector. Along with adjusting the sensing resistances, we also exploit the finite horizontal (500 points in fast sampling mode) and vertical (9-bit, i.e., 512 points) resolutions of the digital scope, as we note that acquisition sampling mode) and vertical (9-bit, i.e., 512 points) resolutions of the digital scope, as we note that acquisition of photocurrent sections by tuning “volts/div” and “time/ div” settings properly for a given sensing resistance could also benefit the reconstruction of a whole HDR transient.

Figure 17 provides an example of such reconstructed HDR photocurrent transients, where its constituent sections are distinguished by multicolors, with each color corresponding to a value of sense resistor chosen to collect the data. Spanning circa 7 orders of magnitude in current levels and 6 orders of magnitude in time, this pieced HDR transient preserves both the early timescale features (sub-100-ns region) and the signal fidelity in the long-time limit.

3. Current density–voltage measurements on single-carrier devices

A Keithley SMU 236 automated via a LabVIEW computer interface was used to record the $J − V$ response of a series of single-carrier devices of structure ITO/PEDOT: PSS/PFO/MoO$_3$/Au, with the PFO active layers prepared in either fully glassy or $β$-phase embedded states. The typical voltage scan step is 20 or 25 mV. The devices were kept in the dark and inert N$_2$ atmosphere during measurements.

4. Mobility determination from frequency-dependent imaginary part of the impedance

Frequency-resolved probes were further applied to single-carrier devices, in order to extract charge-carrier mobilities and compare degrees of transport dispersion for a given device configuration with either the presence or absence of the molecular conformational traps. The hole-only devices are assumed as locally linear, causal, and time-invariant (LTI) systems. A frequency-variable small-signal ac perturbation (50 mV$_{pp}$ to ensure local linearity) was applied on top of a set of discrete dc bias voltages during the measurements. The variable dc bias dictates the “background” spatial charge-carrier density and electrostatic profiles across a device.

A portable electrochemical impedance analyzer CompactStat (Ivium Technologies B.V.) was used with measurement interface IVIUMSOFT software v2.454. Impedance spectroscopies on asymmetric hole-only devices were performed based on a two-electrode setup, that is, having the counter electrode (CE) and the reference electrode (RE) wired onto the blocking device contact, while the working electrode (WE) and the sense terminal (S) joint are connected with the opposite contact capable of providing Ohmic injection of carriers.

The steady-state (dc) charge-carrier mobility $μ_e/h$ can be determined from the $− \Im[Z] − f$ data as [37]

$$μ_e/h = \frac{d^2 f_{peak}}{γV_{dc}}$$

where $d$ is the active layer thickness, $V_{dc}$ a set of discrete dc bias voltages that tracks along the steady-state $J − V$ curve [114], $f_{peak}$ the peak frequency of each $− \Im[Z]$ versus log$_{10}(f)$ spectrum at a given dc bias, and $γ$ a numerical factor that relates the time constant $τ_c$ (i.e., $1/f_{peak}$) from the frequency-resolved $− \Im[Z]$ data [115] to the dc transit time ($τ_{dc}$) of carriers. The value of $γ$ is not clearly determined in the literature [34,37,78,116] and has been identified as a variable depending on the degree of transport dispersion [37], typically ranging from about 0.35 to 0.6. By recognizing that the actual selection of this prefactor $γ$ value will by no means significantly affect the magnitude of estimated mobility, we have chosen $γ = 0.5$ for all measurement scenarios where the $− \Im[Z] − f$ method was applied.

Additional to the aforementioned $− \Im[Z] − f$ method for steady-state carrier mobility extraction, we have also exploited a negative differential susceptance ($− ΔB − f$)
method [34,78,116,117] to characterize and directly compare transport dispersion among hole-only devices nominally prepared from the same material, however treated via varied processing routes. The determination of carrier mobility using the \(-\Delta B - f\) method relies on the ability to locate the characteristic concave “dips” in the \(C - f\) spectra, a phenomenon that only occurs in low-dispersive transport. However, the degree of transport—hence the applicability of the method—can be mediated by the inclusion or exclusion (abbreviated as “+/-”) of certain sub-bandgap trap states relating to specific polymorph(s) of a given material system. Such an example is demonstrated in Figs. S11–S14 of the SM [72], where hole transport in LMW \(+/-\) \(-\beta\) hole-only devices is concerned. When the \(-\Delta B - f\) method was applied for mobility extraction, we adopted \(\gamma = 0.56\), as proposed by Tsang et al. for disordered molecular semiconductors with low carrier dispersion [34].

All impedance spectroscopic data were analyzed using ZVIEW software v3.4d.

5. Energy-resolved electrochemical impedance spectroscopy (ER-EIS)

This recently developed method is capable of mapping the DOS in organic semiconductors over wide energy ranges [81,82]. The ER-EIS method is based on the interaction between the organic film and electrolyte via reduction-oxidation (redox) reactions. This reaction, which is similar to the capture-extraction process of an electron with the DOS in organic semiconductors, results in a recombination current \(j_{\text{rec}}\). The desired DOS function of electronic transport and defect states, \(g(E)\), can be derived directly from the measured charge-transfer resistance of a semiconductor-electrolyte interface, \(R_{CT}\), at the position of the Fermi energy \(E_F\) and at a frequency where the redox reactions determine the real part of the impedance [82]:

\[
[R_{CT}(E_F)]^{-1} = S \frac{\partial j_{\text{rec}}}{\partial V} = q^2 k_{\text{ET}} S[A] g(E_F), \tag{C2}
\]

where \(q\) is the elementary charge, \(k_{\text{ET}}\) the charge-transfer rate constant (assumed energy-independent), \(S\) the sample area, and \([A]\) the concentration of the electrolyte redox species in the interphase region of the solid-liquid contact.

The DOS function \(g(E)\) in a semiconductor at the electrochemical potential, \(E_F = q V_{\text{app}}\), can be expressed in terms of \(R_{CT}\) measured at the given applied dc voltage \((V_{\text{app}})\) as [81,82]

\[
g(E_F) = (q^2 k_{\text{ET}} S[A] R_{CT})^{-1}. \tag{C3}
\]

The \(R_{CT}\) is experimentally measured by the harmonic perturbation \(dV\) with a proper frequency. Such small-signal amplitude \(dV\) superimposed on an external dc bias \(V_{\text{app}}\) thus provides direct information about the electronic DOS at the energy adjusted by varying \(V_{\text{app}}\).

A Solartron Analytical 1260 impedance/gain-phase analyzer was used for the ER-EIS experiments. The frequency was set to 0.5 Hz, the amplitude of ac voltage was 100 mV, and the average scan rate of the dc voltage ramp was 10 mV s\(^{-1}\). The measurements were performed in a glove box with protective \(N_2\) atmosphere (with oxygen and moisture below 20 ppm and 2 ppm, respectively) using a common three-electrode electrochemical cell with volume of about 200 \(\mu\)L and a working electrode area of about 12 \(\text{mm}^2\). Solution of 0.1-M TBAPF\(_6\) in acetonitrile was used as the supporting electrolyte. The potential of the working electrode with respect to the reference Ag/AgCl electrode was controlled via a home-built potentiostat. Pt wire was used as the counter electrode. The energy recorded relative to the reference Ag/AgCl electrode can be referred to the local vacuum level given that the Ag/AgCl energy departs from the vacuum value by 4.66 eV.

APPENDIX D: SPECTROSCOPIC SIGNATURES OF GLASSY AND \(\beta\)-PHASE EMBEDDED PFO FILMS

We examine photophysical properties of prepared PFO films to confirm that the chosen processing protocols indeed yield the required solid-state microstructures. UV-Vis absorption spectra were recorded using a dual-beam Shimadzu UV-2600 spectrophotometer equipped with a diffuse reflectivity (integrating sphere) attachment, which allows the spectra to be corrected for reflection and scattering losses. Photoluminescence (PL) spectra were recorded using a Jobin Yvon Horiba FluoroMax-3 spectrofluorometer in reflection geometry (with an angle of incidence of about 75° to minimize reabsorption effect). The PL excitation was chosen at 385 nm.

Figure 18(a) shows the obtained UV-Vis absorption spectra. Glassy PFO films exhibit a typical, inhomogeneously broadened absorption spectrum (peaking at about 381 nm) that arises from a stochastic distribution of intermonomer torsion angles for the ensemble of kinetically trapped, nonequilibrium chain conformations obtained following hot spin coating [79] (and hence a broad distribution of electronic coupling between adjacent polymer repeat units). The absorption spectrum for \(\beta\)-phase embedded PFO films displays the characteristic redshifted peak at about 432 nm, attributed to the \(S_0 \rightarrow S_1\) 0-0 transition for the extended, planar-zigzag-type \(\beta\)-phase chain segments [65,118]. The \(\beta\)-phase absorption peak is especially well defined because (i) \(\beta\)-phase is understood to form with a certain minimum segment length [92], and (ii) the \(\beta\)-phase formation process—namely, co-crystallization with a small-molecular solvent [119]—inherently requires
a distinct molecular geometry in terms of both the backbone and the side-chain arrangements [120,121].

Figure 18(b) shows PL spectra of the +/− β TOF films normalized to their respective $S_1 \rightarrow S_0$ 0-0 vibronic peaks. The spectra emphasize the (i) redshifts, (ii) sharpened linewidths, and (iii) reduced apparent Huang–Rhys factors [122] of the vibronic transitions upon planarization of backbone (glassy $\rightarrow$ β-phase), which in turn promotes intrachain electronic coupling and delocalization of the excited state. Note that for β-phase embedded films, due to efficient excitation energy transfer, the PL emission originates almost entirely from those minority chain-extended species, with only a slight shoulder at about 420 nm signifying the $S_1 \rightarrow S_0$ 0-0 transition peak of glassy-state PFO.

Furthermore, site-selective PL measurements confirmed that the glassy PFO films are maximally free from either crystalline or β-phase chain segments (see Fig. 19 and caption for details)—an important feature for our charge transport study.

APPENDIX E: ESTIMATING VOLUME FRACTION OF INDUCED β-PHASE BY RAMAN SCATTERING

Figure 20 illustrates the approach we took to estimating the volume fraction (vol%) of the β-phase present in the β-phase embedded TOF layers by quantifying the relative intensity of a Raman mode that features a characteristic dependence on the β-phase fraction [125]. Note that for these thick layers, conventional analysis of the β-phase fraction based on optical transmission measurements (as applicable to thin films) is problematic due to their excessively large optical depth.

Previously reported Raman spectroscopy measurements on PFO films (see Ref. [67]) have revealed a linear relation between the relative intensity of selected Raman peaks and the β-phase fraction, albeit for PFO of somewhat lower molecular weight. Notably, the Raman intensity ratio $r_R$ of
To this end, Raman spectra were recorded for glassy and β-phase embedded TOF films using instrumental settings identical to those in Ref. [67] and are shown in Fig. 20. The corresponding Raman intensity ratios \( r_R \) of the 1581-cm\(^{-1} \) mode relative to the 1606-cm\(^{-1} \) mode were then placed on the previously reported fit line in order to assess the β-phase fraction (see inset of Fig. 20).

For the β-phase embedded HMW PFO TOF film, a value of about 0.126 was found for \( r_R \); this analysis yields an estimate of \( \sim 4.6 \pm 0.4\% \) for the β-phase fraction. Gratifyingly, for the glassy PFO TOF film (\( r_R = 0.102 \)), the β-phase fraction is estimated to be \(-0.2\% \), which closely matches the nominal 0% value.

We estimated, in the same manner, about \( 6 \pm 0.1\% \) β-phase content for LMW layers subjected to the controlled 1hrSVE treatment (see Fig. 14 for processing details).

### APPENDIX F: ENERGETIC-DISORDER BREADTH ANALYSIS BASED ON THE GAUSSIAN DISORDER MODEL

It is a fairly common practice in the literature on disordered low-mobility organic photoconductive media to extract disorder parameters within the framework of the GDM [6]. The GDM assumes the DOS profiles to be of Gaussian type with standard deviation (aka breadth) \( \sigma_{\text{GDM}} \). The analysis would allow us to compare results with previously published data on similar (e.g., polyfluorene-type) materials. In addition, although the GDM formalism is not directly consistent with our device model (as presented in Sec. IV, Part B), it serves to evaluate free-hole mobility in the case of glassy devices that feature active layers with microstructural homogeneity and isotropy.

The GDM analysis as shown in Fig. 21 yields a slightly higher value for the energetic disorder of the β-phase embedded device (\( \sigma_{\text{GDM, } \beta\text{-embedded} \approx 85 \text{ meV} } \)) than for the

![FIG. 20. Estimation of β-phase vol% in HMW TOF (i.e., optically thick) layers using glassy (blue line) and β-phase embedded (red line) Raman spectra. A grey arrow indicates the spectral position of the 1581 cm\(^{-1} \) mode. The inset shows the previously reported [67] experimental data and linear fit (filled circle and dashed line, respectively) for the Raman intensity ratio \( r_R \) of the 1581 cm\(^{-1} \) mode relative to the 1606 cm\(^{-1} \) mode as a function of the β-phase fraction. The corresponding \( r_R \) values extracted from the Raman spectra of glassy (blue open circle) and β-phase embedded (red open circle) TOF PFO films are placed on the fit line to provide estimates for their respective β-phase fractions.

![FIG. 21. Analysis of temperature-dependent HMW PFO TOF hole mobility data based on the GDM. The plots show zero-field hole mobility \( \mu_0 \) versus \( T^{-2} \) for the estimation of energetic disorder breadth \( \sigma \) and high-temperature-limit \( \mu_0 \) based on GDM fitting of the experimental TOF \( \mu_0 \) data as in Fig. 2(b): (a) for the glassy device and (b) for the β-phase embedded device.

\( r_R = 4.68 \times 10^{-3} \times |\beta\text{-phase fraction}()| + 0.103 \) (E1)

While the generality of this relation in terms of, for instance, molecular weight of PFO is not explicitly determined to date, it was nevertheless deemed appropriate for estimating the β-phase fraction in thick PFO layers used in TOF devices.
neat glassy device ($\sigma_{\text{GDM, glassy}} \approx 75$ meV). A broadened disorder breadth for the $\beta$-phase embedded PFO would be expected, due to the presence of conformational deep trap states. However, it should be stressed that for the above analysis, the Gaussian form of DOS is a significant simplification to the realistic DOS distributions in these materials, and therefore the derived values of $\sigma$ should be treated with reservation. It also provides a high-temperature limit of $\mu_{\beta}(T \rightarrow \infty)$ for the glassy device of about 0.6 cm$^2$ V$^{-1}$ s$^{-1}$, which we assign as the effective “free” hole mobility (or the band edge $\mu_{\beta}$) above the HOMO mobility edge in the framework of the multiple-trapping model. We believe $\mu_{\beta}(T \rightarrow \infty)$ could provide a guide to the magnitude of hole mobility in a scenario that always features abundant thermal activation to populate carriers up in the mobile band. Although we recognize that the physical significance of the effective free charge mobility from the GDM is not clear, it was simply used as a guide to the magnitude of free-hole mobility of the mobile band through the amorphous PFO medium. This value—which is of order of 1 cm$^2$ V$^{-1}$ s$^{-1}$—is compatible with time-resolved-microwave-conductivity-assessed intrachain mobility along coiled PFO chains in dilute solution [52,73]. Traditionally, the estimate of $\mu_{\beta}$ in the high-temperature limit has been correlated with the degree of electronic coupling (aka overlap integral) between transport sites for material systems comparison. Here, we argue that this is not always applicable, especially for active layers bearing structural heterogeneities (e.g., in the case of $\beta$-phase embedded PFO).

**APPENDIX G: IMPEDANCE SPECTROSCOPIES OF PFO HOLE-ONLY DEVICES WITH OR WITHOUT $\beta$-PHASE**

Impedance spectroscopies on the HMW PFO hole-only devices with and without the inclusion (+/−) of the $\beta$-phase were performed using a frequency-variable (100-Hz to 1–2-MHz) 50-mV $p_p$ small-signal ac perturbation at discrete forward dc biases. The (arguably simplistic) equivalent circuit applied to model the system behavior is provided as an inset of Fig. 22, along with example Nyquist plots of a series of low-bias data sets probed from the $\beta$-embedded device, is shown in the main figure. The complete experimental data, arranged in the form of the negative imaginary part of the impedance versus frequency ($-\text{Im}[Z] − f$), on both the $+/−\beta$ devices, are presented in Fig. 23.

The circuit model, a simplified Randles circuit [127,128] (Fig. 22 inset) is chosen since it yields well-fit semicircles as a function of forward dc bias (Fig. 22). This choice allows us to evaluate hole-only device parameters such as series resistance $R_s$, geometric capacitance $C_{\text{geo}}$, etc. In reality, the equivalent circuit would surely be more sophisticated than the simplified Randles treatment since, for instance, the charge-trapping effect is not taken into account by such a circuit model, nor does the model include any semiempirical circuit elements such as constant phase elements (CPE) to account for nonideal capacitive behavior originating from, e.g., dispersive carrier transport. However, we note that often “less is more”: From these unconstrained fits—obtained without restricting any of the three components in the equivalent circuit to produce an individual optimal semicircle fit to the impedance data set at each dc bias—we found $R_s \sim 50–100$ $\Omega$ (useful later for hole-only device modeling), $C_{\text{geo}} \approx 830–870$ pF [129]. In addition, as expected from the superlinear forward-bias $J − V$ response [as shown in Fig. 3(a)], the overall conductivity across the device rockets (as $R_p$ rapidly drops) with increased voltage bias.

1. Normalized $-\text{Im}[Z]$–frequency response

Figure 23 plots, side by side, the acquired $+/−\beta$ impedance spectroscopy data in the normalized $-\text{Im}[Z]$ versus $\log_{10}(f)$ presentation. By performing numerical simulation of $C − f$ and $-\text{Im}[Z] − f$ characteristics that takes into account various degrees of transport dispersion, Tripathi et al. demonstrated that the $-\text{Im}[Z] − f$ method is resilient even to the presence of high dispersive transport; hence, it affords reliable determination of dc mobility [37]. In addition, the relative degree of dispersion can be compared by inspecting the relative breadth of the $-\text{Im}[Z]$ spectra among different systems, with a narrower $-\text{Im}[Z] − f$ distribution corresponding to a lower dispersion. Concerning Fig. 23, no discernible difference in either the FWHM or the overall shape of the $+/−\beta$ normalized $-\text{Im}[Z]$ spectra is present—we note that this observation is gratifyingly consistent with the similar transport dispersions ($W_{\text{glassy}} \approx W_{\beta\text{-embedded}} \approx$...
extracted from TOF photocurrent transients, as shown in Fig. 2(a). We therefore apply Eq. (C1) based on the $-\text{Im}\left[\frac{1}{Z}\right]$ method \cite{37} to extract field-dependent steady-state (dc) hole mobility ($\mu_h$) for $+/-\beta$ hole-only devices.

2. Capacitance–voltage characteristics

There remains an additional requirement for correcting the dc biases for the built-in voltage $V_{bi}$ of the asymmetric hole-only devices in order to work out their respective field-dependent dc mobility values. To this end, we turn to capacitance–voltage ($C-V$) measurements \cite{38,131}. The experimental $C-V$ characteristics are provided in Fig. 24.

We identify, from Fig. 24(b), the occurrence of a (first) characteristic capacitive peak around the $V_{bi}$ region under forward bias. This peak is associated with the competition between the drift and diffusion current components near the MoO$_x$/PFO interface: The diffusion term causes an increase \cite{132} in charge-carrier density when the dc bias closely approaches $V_{bi}$, while the drift term sweeps away the accumulated carriers thereby reducing the capacitance \cite{38,131,133}. At further increased forward-bias voltages, the hole current motion across the device proceeds towards the drift-dominant, space-charge-limited regime, while the capacitance rolls off towards three-quarters (0.75) of the geometric capacitance $C_{geo}$ \cite{38,131,134}. Moreover, the frequency-dependent capacitance response of semiconductor diodes in the presence of localized defect states \cite{22,40,135,136} has been well documented in the literature. In conjunction with probing the intrinsic $C-V$ caused by the gradual transition from diffusion- to drift-governed transport, because of the frequency-tunable small-signal ac modulation, the $C-V$ measurements inherently capture an extra capacitance contribution from charges thermally released from trap states. We present the underlying reasons as follows.

Given the reciprocity between time and frequency, we recall from Eq. (2) that the maximum frequency, at which the trapped carriers are still able to interact with the ac modulation and thus contribute to the junction capacitance,
is given by the trap-depth-dependent carrier emission rate [137]. The \( C - V \) spectra probed via a frequency-variable ac perturbation (1–100 kHz for the present measurement as in Fig. 24) therefore reflect the landscape of sub-bandgap DOS by modulating the occupancy of the defect states (or ODOS): A higher-frequency small signal interacts with trap levels in closer vicinity to the HOMO transport level, and it interrogates further into the sub-bandgap space as its frequency decreases [138].

As for the glassy hole-only device [shown in Fig. 24(a)], the capacitance in the forward-bias regime is more pronouncedly affected by the aforementioned charge-trapping effect [139], hence hampering the assessment of \( V_{bi} \). Despite the different trap-mediated forward-bias capacitance response between +/- \( \beta \) devices, under reverse bias where hole injection is effectively blocked, the devices otherwise signify the geometric capacitance [134], with \( C_{geo} \) for both devices of about 810 pF: This implies an identical thickness of the two device variants and agrees with surface profilometry measurements.

Following the above rationale, we extract, from Fig. 24(b), \( V_{bi} \) of \( \beta \)-embedded hole-only devices by locating the potential at which the capacitance value in the forward-bias regime equals the geometric capacitance \( C_{geo} \) inferred from the reverse-bias regime [131], provided that the value is no longer a function of further increased frequency of the 50-mV\(^{pp}\) small-signal ac perturbation (i.e., from, namely, either the 6.309-kHz or 10-kHz trace). The \( V_{bi} \) is thus estimated to be about 0.47 V.

Figure 25 summarizes the estimated \( \mu_h \) data prior to and after accounting for \( V_{bi} \).


[112] Using Chromafil® PTFE filters (Macherey-Nagel GmbH & Co. KG) of 1- or 0.45-μm pore sizes for HMW and LMW materials, respectively.


[114] Thereby granting this method the inherent capability of extracting field-dependent carrier mobility.

[115] The $f_{\text{peak}}$ equivalently manifests at the “top” of the (near) semicircles in a Nyquist plot (e.g., Fig. 22).


[117] With $-\Delta B(f) = -f(C - C_{\text{geo}})$, where $C_{\text{geo}}$ is the geometric capacitance of the device.


[122] In other words, the increase of the recorded ratios of $S_1 \rightarrow S_0$ 0-0 vibronic transition relative to the 0-1 and 0-2.


[125] This characteristic dependence is largely attributable to the mode’s sensitivity to enhanced electronic polarizability arising from the planarized β-phase chain segments.

[126] A main peak of about 1606 cm$^{-1}$ is assigned to a symmetric in-plane C–C ring-stretching mode [92].


[128] The Warburg diffusion element $Z_\sigma$ is omitted in such simplified Randles circuit, as we expect a drift-dominated behavior within the devices under the given measurement settings, including (i) small-signal frequency ≥100 Hz and (ii) the lowest applied dc bias voltages ≥ $V_{\text{bi}}$ (the reader is referred to the incoming $C = V$ measurement results for the estimation of $V_{\text{bi}}$).

[129] Similar to $C_{\text{geo}}$ values inferred from $C - f$ measurements, vide infra (Fig. 24).

[130] Commonly read as $W = (t_{1/2} - t_{0})/t_{1/2}$, where $t_{1/2}$ is the time at which the current decreases to half of its plateau value [6].


[132] Primarily due to a reduction in local band bending close to the contact.


[137] Note that \( R_{\text{escape}} = \nu_0 e^{-\left(E/k_B T\right)} \); hence, the deepest trap level still capable of responding to an ac small signal with angular frequency \( \omega = 2\pi f \) is given by \( E^*(\omega) = k_B T \ln(\nu_0 \omega^{-1}) \).

[138] Therefore, greater capacitance contributions from defects at lower modulation frequencies, as in Fig. 24.

[139] In the case of a glassy device, the conspicuous trap-mediated characteristics arise from not having an energetically deep-lying and distinct distribution of localized sub-bandgap states, as in the case of the \( \beta \)-embedded device. Alternatively, to intrinsically circumvent the trapping effect, high-quality diodes realized by nearly trap-free active layers (made from, e.g., conjugated small molecules via vapor deposition) would be required [38].