

SUPPLEMENTAL MATERIAL

Relating chain conformation to the density of states and charge transport in conjugated polymers: The role of the β -phase in poly(9,9-dioctylfluorene)

Xingyuan Shi (侍兴源),^{1,*} Vojtech Nádaždy,² Aleksandr Perevedentsev,^{3,‡} Jarvist M. Frost,¹ Xuhua Wang,¹ Elizabeth von Hauff,⁴ Roderick C. I. MacKenzie,⁵ and Jenny Nelson^{1,†}

¹*Department of Physics and Centre for Plastic Electronics, Imperial College London, South Kensington Campus, SW7 2AZ London, United Kingdom*

²*Institute of Physics, Slovak Academy of Sciences, Dúbravská cesta 9, 845 11 Bratislava, Slovakia*

³*Department of Materials, Eidgenössische Technische Hochschule (ETH) Zürich, Vladimir-Prelog-Weg 5, 8093 Zürich, Switzerland*

⁴*Department of Physics and Astronomy, Vrije Universiteit Amsterdam, De Boelelaan 1081, 1081 HV Amsterdam, The Netherlands*

⁵*Faculty of Engineering, University of Nottingham, University Park, NG7 2RD Nottingham, United Kingdom*

[‡]*Present address: Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus de la UAB, 08193 Bellaterra, Spain*

*Corresponding author. x.shi12@imperial.ac.uk

†Corresponding author. jenny.nelson@imperial.ac.uk

CONTENTS

I.	Supplementary particulars of simulation.....	S3
A.	1-D tight-binding calculations of oligofluorenes	S3
B.	Device parameters for drift-diffusion modelling	S5
II.	Supporting information on the reconciliation of transport phenomena.....	S10
A.	On the significance of accounting for carrier relaxation in interpreting transport data	S10
B.	Evidence for carrier detrapping in previous reports of ToF hole transport in PFO	S10
C.	An alternative approach to determining the attempt-to-escape rate.....	S11
III.	Impact of conformational trap volume fraction on carrier transport.....	S12
IV.	Interplay between sub-bandgap DoS and band mobility on the photocurrent shape	S19
	References.....	S20

I. Supplementary particulars of simulation

A. 1-D tight-binding calculations of oligofluorenes

The effect of chain conformation on molecular orbital energies is modelled using a one-dimensional tight-binding model, as described in Sec. IV Part A of the main text. Each fluorene monomer is modelled as a single site of HOMO energy E that is coupled to each of its neighbours by a hole coupling element J , set to $J_0|\cos(\theta)|$ where θ is the inter-monomer torsion angle, assumed to be $\theta_0 = 45^\circ$ (or 135°) for the ordered, relaxed glassy phase chain. A β -phase segment is modelled by a series of monomers between which the torsion angle is set to 180° . To simulate disordered systems, the site HOMO energy can be distributed around the nominal value E_0 ($= -5.85$ eV) in a Gaussian distribution of width σ_E while the torsion angle in the glassy parts of the chain may be distributed by σ_θ around θ_0 . Solving the tight-binding Hamiltonian for an N -mer delivers the set of N eigenvalues and eigenvectors for the system. The highest-lying eigenvalue approximates the HOMO energy of the modelled chain, although the results do not agree exactly with density functional theory (DFT) calculations on the same systems because of the neglect of correlation effects in the tight-binding model. DFT calculations for HOMO energies of octamers in the relaxed ground state, the case of 45° torsion and the planarised case obtained using B3LYP/6-31G* are presented in Table S1 for comparison. These show that planarising an octamer introduces a hole trap approximately 0.2 eV deep. The model does allow much larger systems to be studied than with DFT and readily extends to chains of hundreds of sites thus allowing long conformational structures to be studied.

Figure S1 compares the results of these one-dimensional tight-binding calculations for the cases of a glassy 100-mer with no disorder in energy or torsion angle (blue) and the same system containing a segment of twenty monomers where the inter-monomer coupling is set to J_0 to represent a β -phase segment ($J_0 = 0.45$ eV). The subfigures plot the following quantities in the panels shown — top panel: probability density (i.e. $|\psi|^2$) for the lowest five eigenfunctions ψ ; second panel: value of the monomer site HOMO energy (E) at each site; third panel: value of the hole coupling to the next monomer (J) all as a function of monomer index; the bottom two panels show the density of states (DoS) obtained by

summing over all eigenvalues, first for the glassy chain (blue) and then for the β -embedded chain (red). The figure indicates that for the perfectly ordered one-dimensional system (blue) a DoS function is obtained showing the classic one-dimensional form centred at the monomer HOMO energy of 5.85 eV and of width approaching circa four times the maximum inter-monomer coupling (J_0). The red plots show that when the planarised segment is introduced, the lowest eigenvalues are localised in the planarised segment and the DoS develops isolated states of energy set well outside the range for the ordered system. The lowest energy hole states will act as hole traps, of depth, for the parameters used, of around 250 meV below the lowest state of the β -phase free system. Notice that this localisation is achieved without any variation in the site energy along the system.

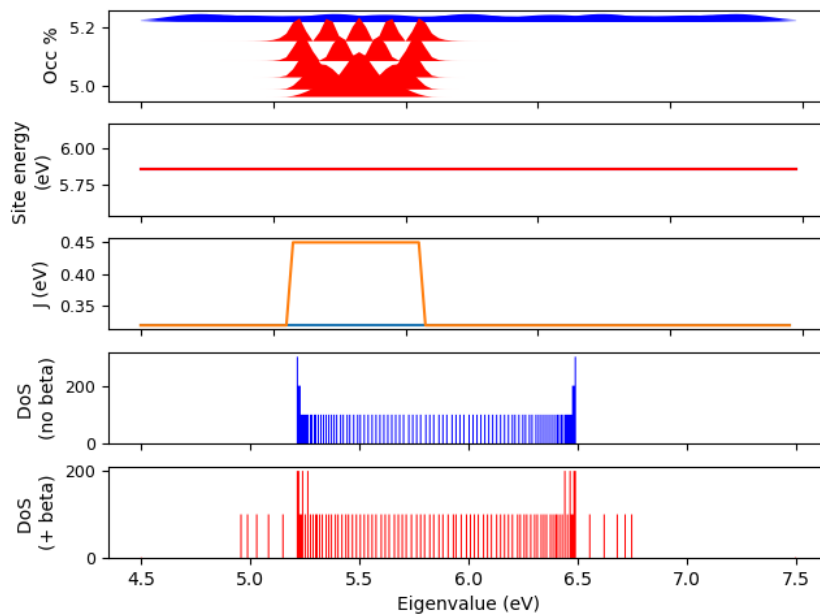


FIG. S1. **Top panel:** probability density (i.e. $|\psi|^2$) for the lowest five eigenfunctions ψ for the ordered β -phase free 100-mer chain (blue) and the ordered chain containing a 20-mer of β -phase (red). **Second panel:** site HOMO energies for the ordered β -phase free (blue) and β -phase embedded (red) chains. **Third panel:** inter-site torsion angles for the ordered β -phase free (light blue) and β -phase embedded (yellow) 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 ordered β -phase free chain (blue). **Bottom panel:** density of states obtained by summing over all eigenvalues for the ordered β -phase embedded chain (red). The x-axes of the bottom two panels present energy in the unit of electronvolt.

TABLE S1. HOMO energies calculated using density functional theory (B3LYP/6-31G*) for octamers of PFO, modelled with methyl units instead of di-octyl side chains, in the optimised geometry, planar geometry (torsion angles all constrained to 180°),

and in the case where all torsion angles are constrained to 45° . The effect of planarising the oligofluorene, relative to the case of 45° torsion angles, is to stabilise the HOMO by 200 meV.

Octamers of PFO	HOMO (eV)	LUMO (eV)
Optimised	-5.05	-1.44
Planar	-4.91	-1.44
45°	-5.11	-1.19

B. Device parameters for drift-diffusion modelling

When fitting the drift-diffusion model to the experimental data it was our objective to reproduce and rationalise the apparently different hole transport observed from varying measurement techniques using one unified set of device parameters. The symbols used to represent the different parameters are given in Table S2 below. Fermi-level positions at the contacts are set by varying the concentration of majority carriers at the interfaces (and relate to values of T , E_g , N_v and N_c) hence deducing injection barriers, ϕ , of contact levels relative to the bands—more detail is available in the gpvdm manual. The values for σ_h and N_v are constrained according to our experimental estimate of attempt-to-escape rate of 10^{11} Hz (as $\nu_0 = v_{th} \sigma_h N_v \approx 10^{11}$ Hz, where v_{th} is the thermal velocity, σ_h the hole capture cross section, and N_v the valence band effective density of states of free holes). Finally, the parameters were iterated to obtain the best fit of simulated transient and steady-state response to the experimental data (by primarily adjusting σ_h , N_v , σ_β , and the magnitude of the narrow Gaussian (β -phase), since other parameters are pretty much all fixed). All simulations were performed at $T = 295$ K.

We summarise the full drift-diffusion device parameter space in Tables S2 (for global device variables shared between ToF and hole-only device simulation), S4 (for ToF photocurrent simulation) and S5 (for hole-only J - V simulation). It is also well worth pointing out that since unipolar hole transport is investigated in our ToF and single-carrier device configurations, parameters relating to LUMO properties and carrier annihilation have very limited impact on the simulation (as tested during our numerical modelling process) and the determination of these values lies beyond the scope of this work.

TABLE S2. Global device parameters used for PFO ToF photocurrent and hole-only J - V simulation. Light-pink-shaded cells concern parameters for the HOMO and holes, light-green-shaded parameters concern the LUMO and electrons, and clear cells dedicate to parameters that are ‘neutral’. The ‘*’ mark placed next to some parameters denotes that such parameters are assigned as per intrinsic material properties of PFO, or our experimental findings, or instrumentation conditions. (The author is indebted to former Italian colleagues Dr. Davide Moia and Dr. Andrew M. Telford for colour coding scheme of the table.)

Symbol	Parameter description	Value
$N_{\text{HOMO}}^{\text{glassy}}$	Density of hole traps at the HOMO mobility edge, due to the glassy Gaussian component	$10^{28} \text{ m}^{-3} \text{ eV}^{-1}$
$\sigma_{\text{HOMO}}^{\text{glassy}}$ *	Disorder breadth (standard deviation) of the glassy Gaussian component	75 meV
E_{HOMO}^{β}	β -phase depth relative to the HOMO mobility edge	0.27 eV
N_{HOMO}^{β}	Density of hole traps at the β -phase peak	$5 \times 10^{26} \text{ m}^{-3} \text{ eV}^{-1}$
$\sigma_{\text{HOMO}}^{\beta}$	Disorder breadth (standard deviation) of the β -phase feature	45 meV
$N_{\text{HOMO}}^{\text{exp}}$	Density of hole traps at the HOMO mobility edge due to the common exponential tail	$5 \times 10^{26} \text{ m}^{-3} \text{ eV}^{-1}$
$E_{\text{ch}}^{\text{HOMO}}$ *	HOMO exponential tail characteristic energy	75 meV
$\sigma_{\text{h}}^{\text{HOMO}}$	HOMO hole capture cross section (free hole–trapped hole; carrier trapping)	$6 \times 10^{-21} \text{ m}^2$
$\sigma_{\text{e}}^{\text{HOMO}}$	HOMO electron capture cross section (free electron–trapped hole; SRH annihilation)	10^{-22} m^2
$\mu_{\text{h,free}}$ *	Free hole mobility	$6 \times 10^{-5} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$
N_{v}	Effective density of states for free holes	$4 \times 10^{27} \text{ m}^{-3}$
$E_{\text{LUMO}}^{\mu_{\text{c}}}$ *	LUMO mobility edge, relative to vacuum level	-2.6 eV
E_{g} *	Electrical bandgap	3.2 eV
N/A	Numerical sub-bandgap space	0.8 eV
N/A	Number of discretised trap intervals	80
N/A	Mesh points along the 1-D device space	50
ε_{r} *	Relative permittivity of medium	3
v_{th}	Thermal velocity for carriers	10^5 m s^{-1} [1,2]
T *	Device temperature	295 K
$N_{\text{LUMO}}^{\text{exp}}$	Density of electron traps at the LUMO mobility edge, due to the exponential tail	$10^{26} \text{ m}^{-3} \text{ eV}^{-1}$
$E_{\text{ch}}^{\text{LUMO}}$	LUMO exponential tail characteristic energy	40 meV
$\sigma_{\text{e}}^{\text{LUMO}}$	LUMO electron capture cross section (free electron–trapped electron; carrier trapping)	10^{-22} m^2
$\sigma_{\text{h}}^{\text{LUMO}}$	LUMO hole capture cross section (free hole–trapped electron; SRH annihilation)	10^{-22} m^2
$\mu_{\text{e,free}}$	Free electron mobility	$10^{-2} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$
N_{c}	Effective density of states for free electrons	$5 \times 10^{26} \text{ m}^{-3}$

TABLE S3. Additional device parameters for PFO ToF photocurrent simulation.

Symbol	Parameter description	Value
p_{left}	Hole density at the (left) majority p-contact	10^8 m^{-3}
n_{right}	Electron density at the (right) majority n-contact	10^2 m^{-3}
R_s	Series resistance of device	50Ω
R_p	Shunt resistance of device (blocked injection from contacts)	$10^{11} \Omega$
d	Active layer thickness (from profilometry measurements)	$1.8 \times 10^{-6} \text{ m}$
α	Absorption coefficient (at $\lambda_{\text{ex}} = 355 \text{ nm}$)	$1.35 \times 10^7 \text{ m}^{-1}$
dt	Numerical time increment	10^{-9} s
N/A	Laser pulse duration	$5 \times 10^{-9} \text{ s}$
N/A	dt multiplier	1.05

TABLE S4. Additional device parameters for PFO hole-only J - V simulation.

Symbol	Parameter description	Value
p_{left}	Hole density at the (left) majority p-contact	$4 \times 10^{27} \text{ m}^{-3}$
n_{right}	Electron density at the (right) majority n-contact	$5 \times 10^{-11} \text{ m}^{-3}$
R_s	Series resistance of device (inferred from IS measurements)	50Ω
R_p	Shunt resistance of device (from low-bias region of J - V)	$8 \times 10^8 \Omega$
d	Active layer thickness (from profilometry measurements)	$1.35 \times 10^{-7} \text{ m}$
dV	Numerical voltage increment	10^{-2} V

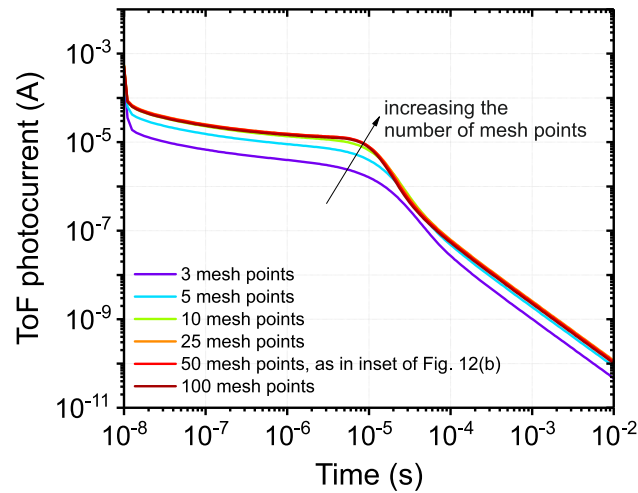


FIG. S2. A set of ToF photocurrent transients simulated by varying only the number of mesh points, between 3 and 100.

The results indicate that using 10 mesh points or more would be completely adequate to describe the device response.

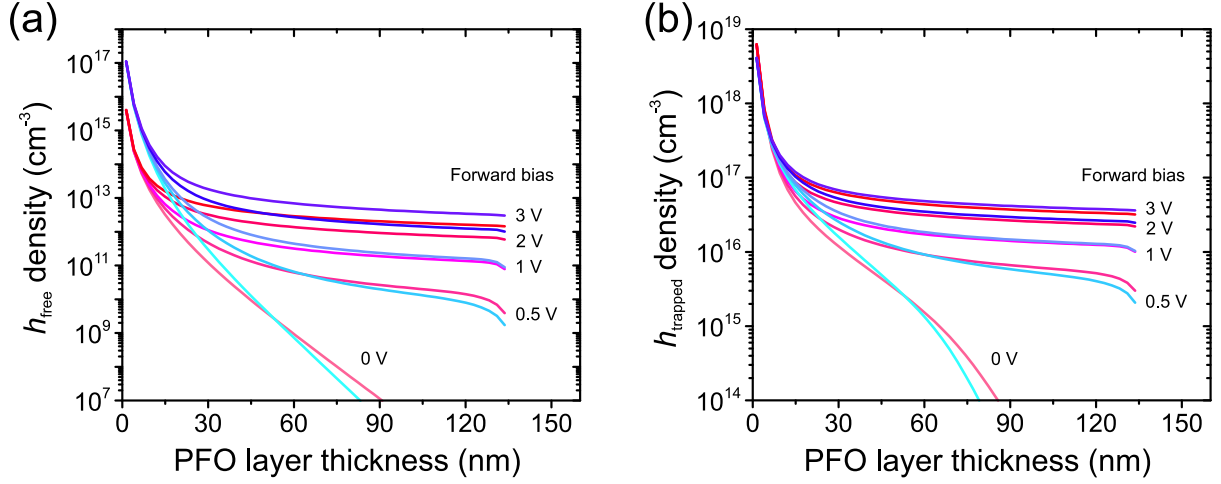


FIG. S3. Simulated profiles of **(a)** density of free holes (h_{free}) and **(b)** density of trapped holes (h_{trapped}) across the 135-nm glassy (blue-colour sets) and β -embedded (red-colour sets) PFO layers as used to model the hole-only transport measurements.

Figures S4(a), (b) and (c) respectively show simulated time-of-flight (ToF) hole transients with 1- μm , 5- μm and 8- μm β -phase embedded PFO layers, which we consider representative of the range of thickness (d) used for practical ToF devices. Across the wide range of d applied, clear pre-transit plateaux are visible in all hole transients. Figure S4(d) summarises the apparent ToF hole mobilities (μ_h), extracted from the transients using the two-tangent method in the usual manner, along with the 1.8- μm set (as in Fig. 11(b) of the main text). The data show minimal impact of d on the apparent ToF mobilities extracted, and hence support the relevance of the 1.8- μm ToF μ_h dataset in Fig. 11(b) for the PFO devices we studied.

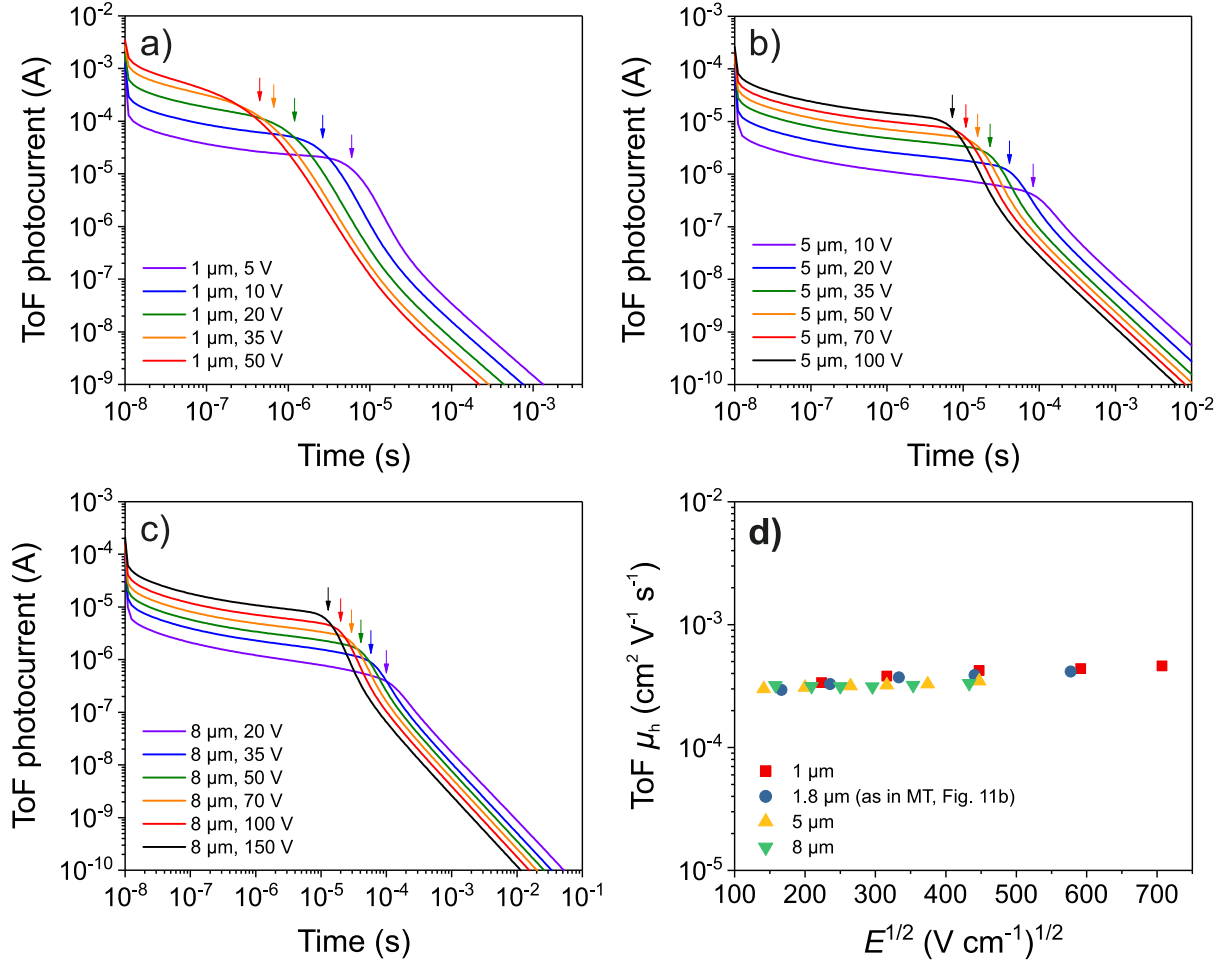


FIG. S4. Simulated time-of-flight (ToF) hole transients with (a) 1 μm , (b) 5 μm and (c) 8 μm β -phase embedded PFO active layer settings. See figure legend for voltage bias applied for each trace. Arrows denote apparent transit times for respective traces, using which we extract ToF hole mobilities (μ_h). Panel (d) summarises the simulated ToF μ_h (including the 1.8- μm set as in the main text of our submission): the results indicate a very marginal difference across the active layer thicknesses.

II. Supporting information on the reconciliation of transport phenomena

A. On the significance of accounting for carrier relaxation in interpreting transport data

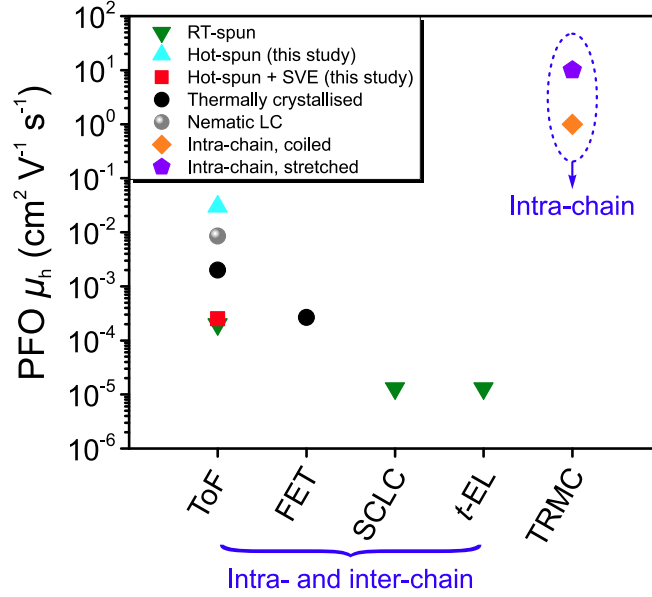


FIG. S5. A survey of μ_h values reported for PFO using different experimental probes and/or different device processing protocols (see legend). The data are taken from Refs. [3–6] for time-of-flight photocurrent (ToF), [7] for bottom-gate top-contact field-effect transistor (FET), [8] for space-charge-limited current (SCLC), [9] for electroluminescence transient method (t -EL). The above data concern bulk transport (involving both intra- and inter-chain processes). Time-resolved microwave conductivity (TRMC) results on dilute solutions (on intra-chain transport) are also presented [10–12].

B. Evidence for carrier detrapping in previous reports of ToF hole transport in PFO

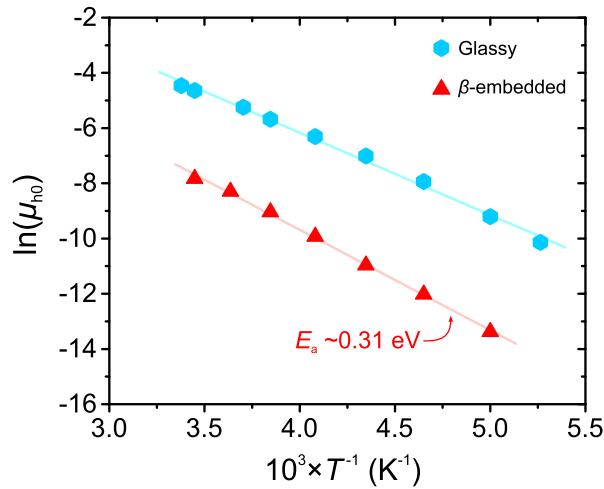


FIG. S6. Arrhenius analysis of the temperature-dependent zero-field hole mobilities (μ_{h0}) of β -phase embedded and glassy HMW ToF devices (values as reported in Fig. 21) by plotting $\ln(\mu_{h0})$ versus T^{-1} . An activation energy (E_a) of ~ 0.31 eV is

estimated for the β -phase embedded sample from the fitted slope. Shown also is an E_a of ~ 0.25 eV for the glassy case from a somehow ‘forced’ and relatively inferior Arrhenius fit.

Figure S6 shows that the zero-field hole mobility extracted from the temperature- and field-dependent plots of ToF hole mobility for the β -phase embedded device (the bottom set in Fig. 2(b) of the main text) varies with temperature as though it is thermally activated with an activation energy of ~ 0.31 eV. This activation energy is close to the estimated depth of the defect due to the β -phase and is consistent with transport being thermally activated by detrapping from that defect. The same activated behaviour was previously reported in Ref. [32] and assigned to charge release from polaron states. The new evidence presented in this paper suggests that the behaviour previously reported could in fact have resulted from the presence of β -phase unaware or failed to identify at that time. The lower E_a of ~ 0.18 eV for the annealed (120 °C for 15 hours), semi-crystalline samples in Ref. [4] may indicate that crystallisation has effectively removed β -phase, which would be expected from the phase behaviour of PFO [13,14], that β -phase is dissipated when $T > \text{ca. } 380$ K. If the activation is partially caused by detrapping–trapping events from the β -phase defect, then the polaron binding energy cannot be estimated from the ToF data and is very likely to be lower than previously proposed (~ 0.19 eV [4] and in Ref. [15]).

C. An alternative approach to determining the attempt-to-escape rate

Having established that the temporal position of the knee in ToF transients of β -embedded PFO is mediated by the conformational defect, we turn to an alternative approach (other than the method applied in Sec. III Part A of the main text) to estimate the attempt-to-escape rate ν_0 . Using our estimated trap depth of ~ 0.3 eV for the β -phase conformer, and the transit time fitted at finitely high bias (obtained by the asymptotic fitting of transit time toward infinite $E^{1/2}$ as illustrated in Fig. S7) signifying an intrinsic carrier retention time of ~ 1.35 μs (with infinitely high drift velocity) due to β -phase trap, we derive $\nu_0 \approx 1.2 \times 10^{11}$ Hz using Eq. (2) of the main text by having $E^* = 0.3$ eV, $t = 1.35$ μs and $T = 290$ K). Note that this number is in excellent agreement with our previous estimate of $\nu_0 \approx 1 \times 10^{11}$ Hz obtained by matching inflection features in the DoS extracted from HDR transients measured at

different temperatures (see Sec. III Part A of the main text), adding confidence to the estimate of the attempt-to-escape frequency.

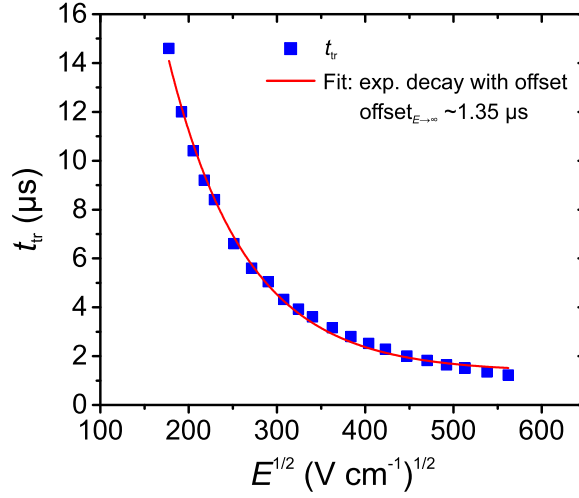


FIG. S7. Alternative route to estimating the attempt-to-escape frequency ν_0 from the extraction of the intrinsic carrier retention time due to β -phase conformational traps, achieved via asymptotic fitting of the bias-dependent transit times towards infinitely high field using a mono-exponential decay function with offset.

III. Impact of conformational trap volume fraction on carrier transport

The present Section serves as an example showing how the population of structural traps and resultant microstructure could affect transport behaviour including estimated mobility and carrier dispersion. All the results presented in the main text have been obtained using a high-molecular-weight (HMW) batch PFO where the β -phase fraction is limited to $\sim 4.6 \pm 0.4\%$. To investigate the effect of higher volume fractions (vol%) of β phase, we extended the study using a low-molecular-weight (LMW) version PFO (see Table I in Appendix A of the main text for molecular weight profiles), thanks to higher molecular/chain mobility and reduced chain entanglement of the LMW material to form higher vol% of β -phase upon a controlled solvent vapour exposure processing.

Using the Raman mode analysis outlined in Appendix E of the main text, we estimated vol% of embedded β -phase to be $\sim 6 \pm 0.1\%$ for LMW devices.

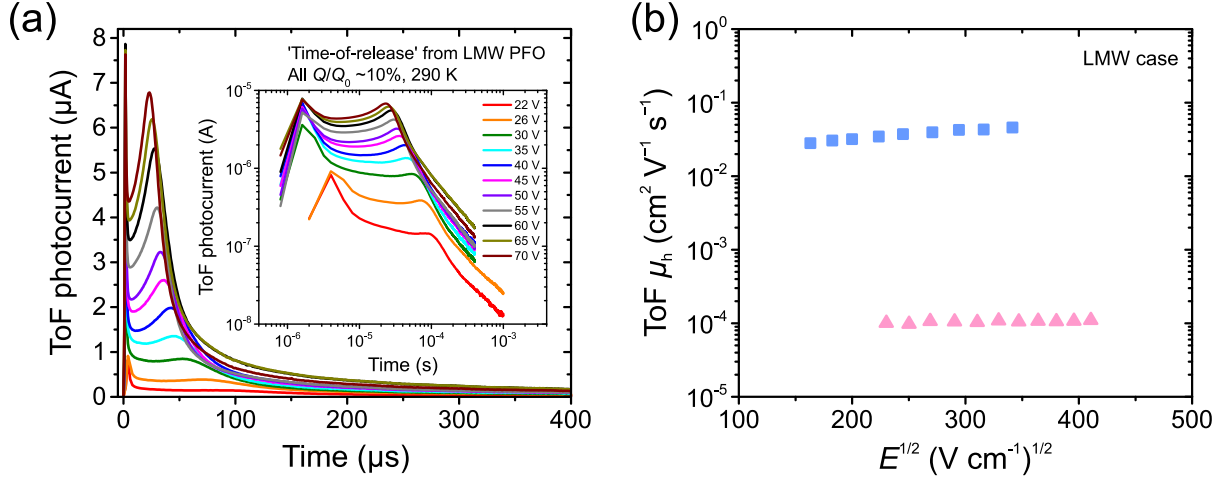


FIG. S8. (a) ‘Time-of-release’ transients from the β -phase embedded LMW ToF devices obtained as a function of applied electric field. The inset shows the equivalent data in double-log scale. (b) Poole-Frenkel plot of the ToF mobility (at 290 K) for glassy (■) and β -phase (▲) inferred from LMW PFO devices. The carrier transit time for each LMW β -embedded ToF transient was extracted from the peak position of the cusp since the conventional tangents method would not be applicable in this case due to the shape of the transients.

From Fig. S8(b), the RT μ_h of LMW glassy PFO agrees very well with that of its HMW counterpart (see Fig. 2(b) of the main text). With the heavy cusps evident in the LMW β -embedded ToF traces (see Fig S8(a)), it is not feasible to determine carrier transit time from the ordinary tangent approach. Instead, we have chosen to assign the t_{tr} to the peaks of the cusps. The RT-cast β -embedded ToF μ_h obtained in this way is $\sim 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, agreeing with past results from e.g. β -embedded (via SVE), and RT-cast devices reported by Yap, Kreouzis and Foster [5,6,16]. With the fraction of optically injected charge, Q/Q_0 , controlled at $\sim 10\%$ of the geometric charge held on the device contacts, we ensure that the occurrence of cusps is not due to space-charge effect distorting the electrostatic profile exerted by the applied bias, but rather to do with intrinsic carrier dynamics within the PFO layer.

The occurrences of cusps in ToF transients were previously observed by Ochse *et al.* [17], Im *et al.* [18], Laquai *et al.* [19], more recently by Liu *et al.* [20], as well as Foster [16] on β -embedded PFO devices. In Refs. [17–19] where extrinsic charge generation layers (CGL) were employed, the authors ascribed the cusp phenomena at high temperatures (beyond ca. 300 K) in their studies to the temperature-dependent offset between the equilibrium energy for transport within the active layer and the quasi-equilibrium carrier injection level from the CGL, and argued that this offset will increase by elevating

the measurement temperature. Here we demonstrate such cusp behaviour can also arise from a disordered medium per se.

On a side note, the parallel decaying tails in the inset of Fig. S8(a) again support the validity of our assumption based on the multiple-trapping model, which states that carrier redistribution due to iterative trapping–detrapping, hence distortion to the mapped DoS is minimised at high biases.

Figure S9 shows the comparison of hole transport dispersion in HMW and LMW PFO by ToF method.

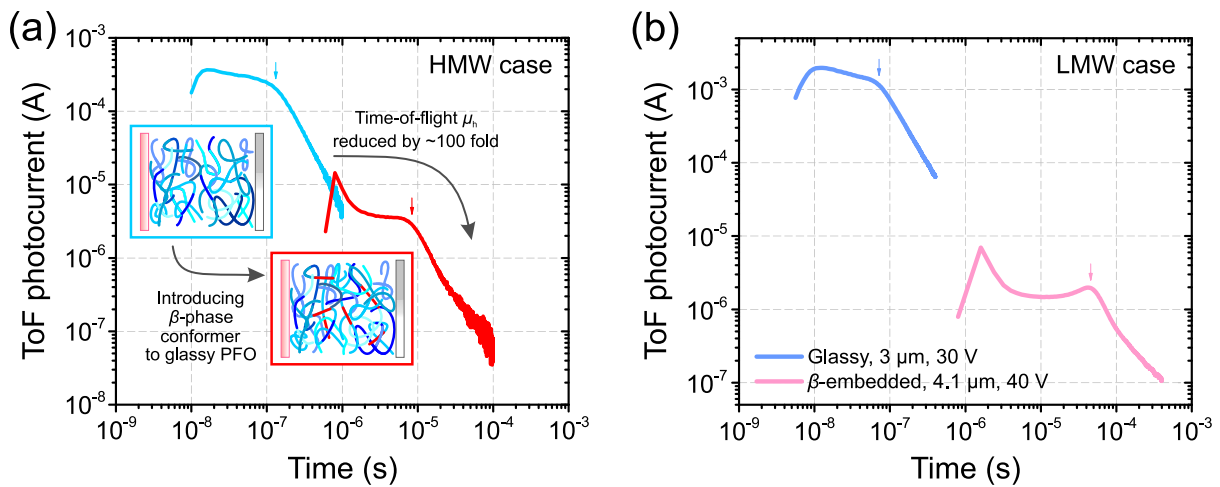


FIG. S9. Comparison of hole photocurrent transients measured in **(a)** HMW (reproduced from Fig. 2(a) of the main text for ease of comparison) and **(b)** LMW PFO ToF devices, demonstrating the degree of dispersiveness of the curves in the different cases. In (a) the HMW $\pm \beta$ ToF traces were obtained at a controlled condition of 10 V ($E^{1/2} \approx 235 \text{ V}^{1/2} \text{ cm}^{-1/2}$), 290 K, and in (b) the LMW $\pm \beta$ ToF traces were obtained at a controlled condition of $E^{1/2} \approx 316 \text{ V}^{1/2} \text{ cm}^{-1/2}$ (due to difference in thickness), 290 K. LMW β -embedded device shows occurrence of cusp (“time-of-release”) and a smaller W than its HMW β -embedded counterpart. Cartoons in (a) show $\pm \beta$ -phase ToF layers sandwiched between ITO (left, pink colour) and aluminium (right, silver colour) contacts (not to scale). The diverse blue shades of the polymer chains symbolise the distribution in charge transport site energies, with the extended and planarised β -phase chain segments highlighted in red.

In Fig. S9(b) both glassy and β -phase embedded LMW PFO devices were probed at electric field $\sim 316 \text{ V}^{1/2} \text{ cm}^{-1/2}$ (their layer thicknesses are different hence different bias voltage were applied). Figure S9(a) and (b) are plotted using the same respective scales for x- and y-axes (however with different ranges for the y-axes), thus allowing hole transport dispersion to be directly compared by the naked eye. It is visually clear in Fig. S9(b) that for the LMW devices, due to the cusps (an indication of temporal distribution of photocurrent), β -phase embedded PFO shows a lower degree of transport dispersion than

the glassy device. In addition, subtle differences in the post-transit tail slope could be observed when comparing high and low MW counterparts, where in the LMW scenario both glassy and β -phase embedded devices show less steep post-transit decays relative to their HMW counterparts. We therefore hypothesise that the extent of disorder differs with molecular weight distributions of polymers and, empirically, lower MW would lead to greater degrees of disorder.

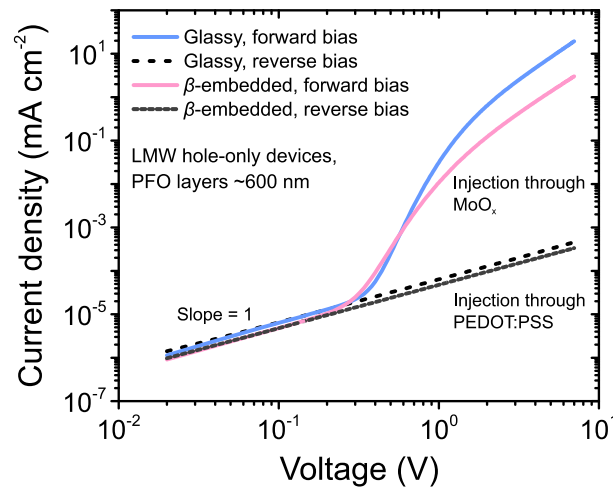


FIG. S10. Steady-state J - V response for asymmetric hole-only devices configured as ITO/PEDOT:PSS/ $\sim$ 600-nm-thick glassy and β -phase embedded LMW PFO layers/MoO_x/Au. Voltage ranges from 20 mV to 7 V in 20 mV scan steps. The dc hole mobility reduction due to β -phase appears to be marginally greater than in the HMW case.

In terms of LMW J - V behaviour presented in Fig. S10, the difference of a factor of $\sim$ five in the high forward bias current density is marginally larger than that in the HMW case (cf. Fig. 3(a) of the main text). Again, this is consistent with the picture of having a larger fraction ($\sim 6 \pm 0.1\%$ for LMW versus $\sim 4.6 \pm 0.4\%$ for HMW) of β -phase embedded, whilst the fraction of β -phase does not reach the threshold for percolation.

Another very effective way of the differentiating in the degree of dispersive transport is via the use of impedance spectroscopies ($-\text{Im}[Z]-f$ and $-\Delta B-f$ methods), as we show below.

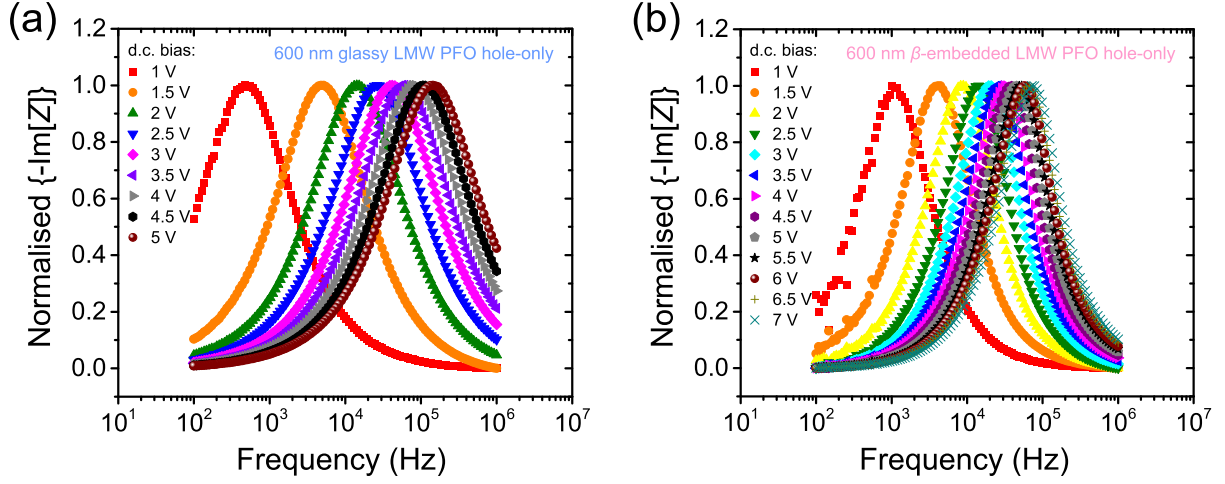


FIG. S11. Normalised $-\text{Im}[Z]$ - f spectra of ~ 600 -nm asymmetric LMW PFO hole-only devices: (a) glassy, and (b) β -phase embedded. At each given dc bias, we reciprocate the frequency peak of the $-\text{Im}[Z]$ spectrum to a dc hole transit time, from which a corresponding steady-state hole mobility can be derived [21]. Note the difference in the $-\text{Im}(Z)$ - f breadth, signifying that the β -phase embedded device possesses less dispersion in hole transport than the pristine glassy devices. We present the field-dependent μ_h set in Fig. S14 after the correction for V_{bi} .

Note the apparent difference in the breadth of the $-\text{Im}[Z]$ - f feature of normalised impedance spectra of glassy and β -phase embedded LMW PFO devices. This gives us a qualitative representation of the degree of hole transport dispersion: the ‘breadth’ of the $-\text{Im}[Z]$ versus $\log_{10}(f)$ plots in Fig. S11 indicates that the degree of hole transport dispersion [21] is smaller for the β -phase embedded than the glassy LMW layers. The higher degree of hole transport dispersion in the pristine glassy case hinders the use of $-\Delta B$ - f method [22,23] to estimate dc mobility, as peaks could not be found in the $-\Delta B$ - f spectra (as shown in Fig. S12).

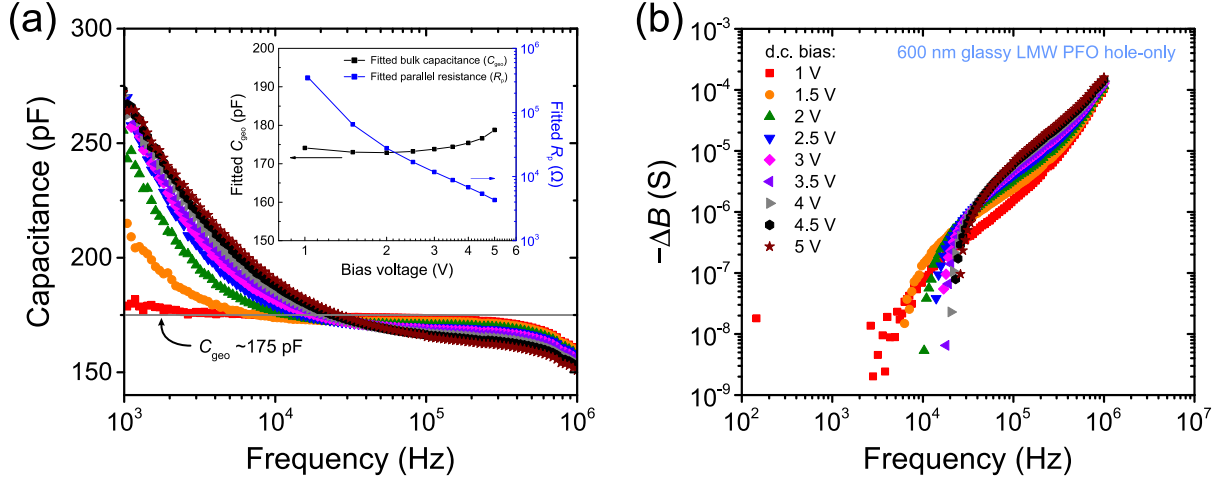


FIG. S12. LMW glassy hole-only device probed by $-\Delta B$ - f technique. The high hole transport dispersion leads to no peaks in the $-\Delta B$ - f spectra as shown in subplot (b), hence rendering this method inappropriate for determining dc mobility in this scenario.

On the contrary, due to a much lower transport dispersion, the LMW β -phase embedded hole-only device probed by the same $-\Delta B$ - f technique displays characteristic concave dips in the C - f plot (Fig. S13(a)), from which peaks in the $-\Delta B$ - f spectra (Fig. S13(b)) can be derived hence in turn the corresponding dc μ_h [22].

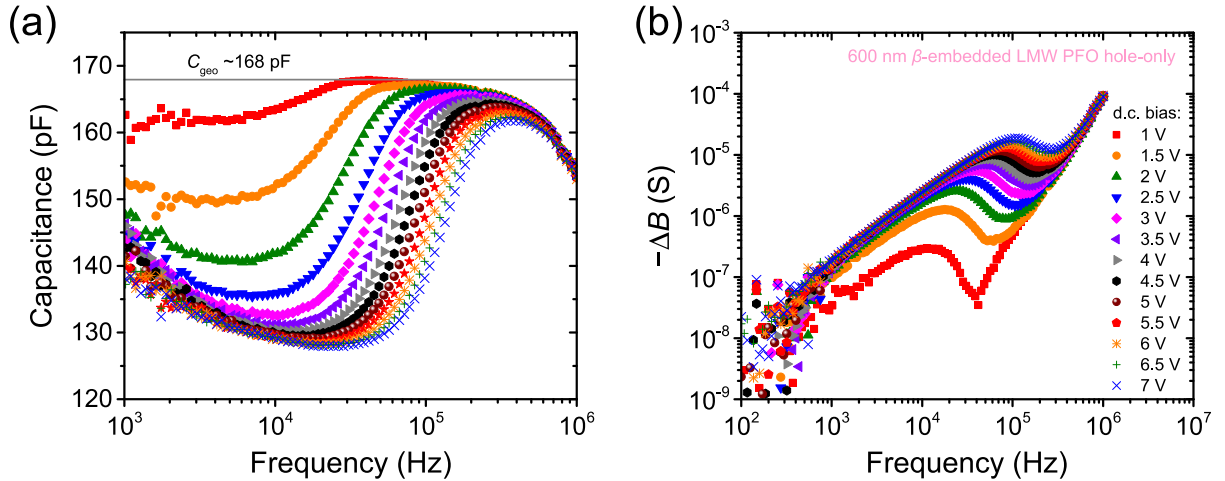


FIG. S13. LMW β -embedded hole-only device probed by $-\Delta B$ - f technique. The lower hole transport dispersion leads to characteristic peaks in the $-\Delta B$ - f spectra as shown in subplot (b), allowing this method to be used to determine dc mobility in this scenario. We present the field-dependent μ_h set in Fig. S14 after the correction for V_{bi} .

The bias-dependent peaks could be correlated with the field-dependence of dc hole mobility—this allows extraction of PF plots from impedance spectroscopies [21]. The results are presented in Fig. S14.

It is noteworthy from Fig. S14 that the hole mobility for the LMW ‘1hrSVE’ (β -phase embedded) devices is lower than their glassy counterparts—a finding that is in excellent agreement with results from HMW devices (as in Fig. 4 of the main text). Also, the transport dispersion is lower as well, as evidenced from comparison of both $C(f)$, and $-\text{Im}(Z)$ plots above (Figs. S11–S13; this observation appears to be consistent with our LMW time-resolved transport data indicated in Fig. 9(b)).

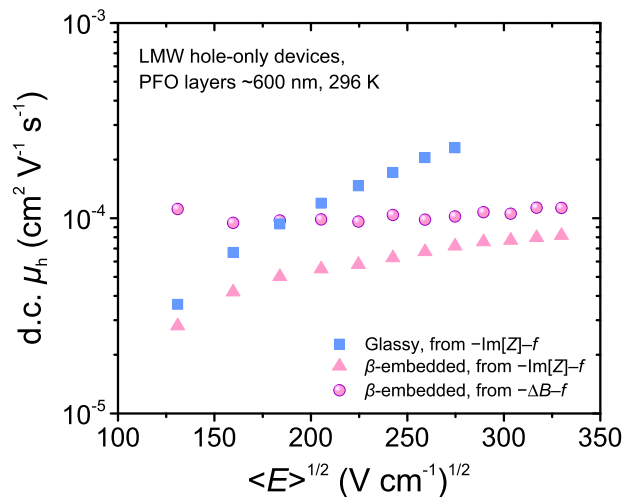


FIG. S14. Poole-Frenkel plot summary of the field-dependent $\pm \beta$ steady-state μ_h values derived from impedance spectroscopic probes into LMW PFO hole-holy devices: glassy via $-\text{Im}(Z)-f$ (■), β -embedded via $-\text{Im}(Z)-f$ (▲) and β -embedded via $-\Delta B-f$ (●).

The above LMW devices mobility values agree well with those of HMW counterparts (that is, cf. Fig. 4 of the main text). There is some slight discrepancy between the dc mobility inferred from the $-\text{Im}(Z)-f$ and $-\Delta B-f$ methods for β -embedded hole-only device, especially at the low electric field region. However, the relative differences in dc mobility magnitude and field dependence for the two systems are preserved.

We finish the Section by remarking that this HMW versus LMW hole transport study is, to the best of our knowledge, a first-time clear experimental demonstration of the impact of a specific conformational disorder on the *dispersion* of carrier transport.

IV. Interplay between sub-bandgap DoS and band mobility on the photocurrent shape

Here we address the interplay between carrier transport across the device and carrier retention due to localised trap states. We show how these two processes affect the overall shape of photocurrent transients depending on the numerically assigned energetic depth of distinct defect states and band mobility. We perform this generalisation to help readers better understand their own experimental data.

In Fig. S15(a) based on a single mono-exponential tail DoS ($E_{\text{ch}} = 60$ meV), we introduce an additional sub-bandgap Gaussian feature (breadth 45 meV) locating either 0.25 eV (‘shallow’; magnitude $5 \times 10^{19} \text{ cm}^{-3} \text{ eV}^{-1}$) or 0.5 eV (‘deep’; magnitude $5 \times 10^{17} \text{ cm}^{-3} \text{ eV}^{-1}$) away from the HOMO mobility edge. In either case the additional narrow Gaussian protrudes the local mono-exponential DoS level. How such feature manifests itself in the simulated ToF transient is shown in Fig. S15(b). In these simulations the value of free carrier (band) μ_{h} was kept at $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. All other modelling parameters were preserved as in Tables S2 and S3. The numerical hole DoS is illustrated in Fig. S15(a). From Fig. S15(b) we note that the shallow Gaussian case qualitatively resembles the effect of β -phase embedded PFO device in the present study (see Fig. 9 of the main text), due to concurring events of (i) detrapping of carriers from the shallow DoS bump and (ii) the end of mobile carrier transit with a much reduced average velocity (compared to the no-bump case) that is slowed down by the repetitive, pseudo-balanced trapping–detrapping processes when $t < t_{\text{tr}}$. It is also evident that, additional to a gentle knee signifying the carrier transit time, the deep Gaussian case associates with a prominent ‘hump’ in the post-transit regime (hence an overall ‘double-kink’ hole transient). Such hump at the long-time limit signifies a clear thermal release process, rather than convolving with the temporal onset of the fast carrier transit knee. The true carrier transit time, is largely unaffected in this case, since the temporal interaction/overlap between events of (i) free carriers to traverse the device and (ii) the average time of carrier retention within the sharp defect states, is well separated due to the large depth of the Gaussian feature. Additionally, we note that for the single mono-exponential tail DoS input, the simulated ToF transient obeys a dispersion shape as described by Scher and Montroll [24], with $\alpha \sim 0.42$.

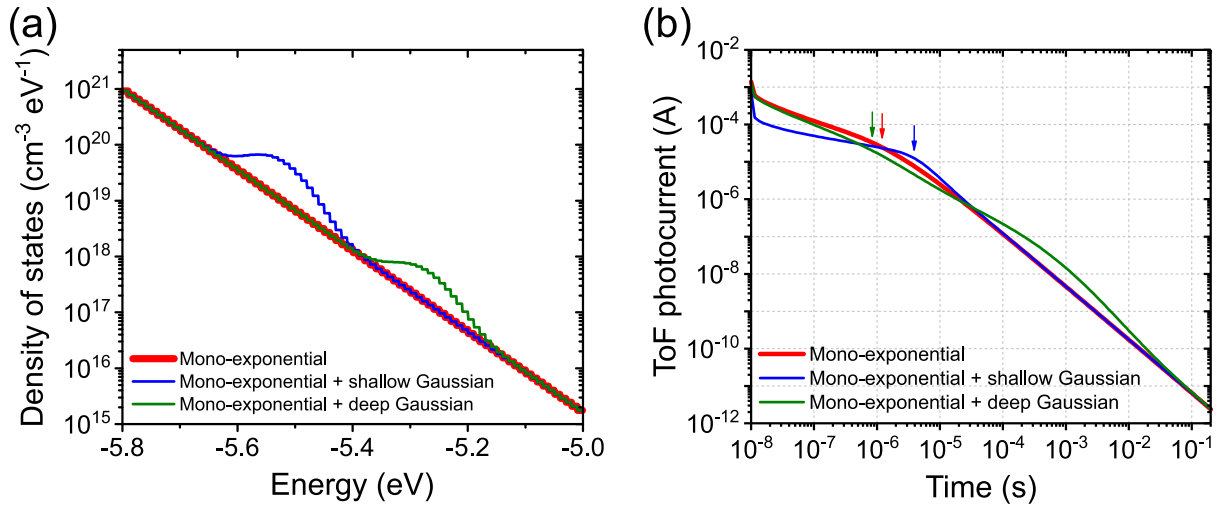


FIG. S15. (a) Numerical DoS inputs of either including or excluding (—) a sub-bandgap Gaussian feature protruding the mono-exponential HOMO tail states. The extra Gaussian can situate either at 0.25 eV (‘shallow’; —) or 0.5 eV (‘deep’; —) depth. (b) The corresponding simulated photocurrent transients, with (— and —) and without (—) such extra ‘bump’ in the DoS. Apparent transit times are marked by downwards arrows. The band μ_h used for this set of simulation was 0.1 cm² V⁻¹ s⁻¹ and, bias of 10 V. See legend for details.

-
- [S1] B. E. Pieters, *PhD Thesis*, TU Delft, The Netherlands, 2008.
- [S2] M. A. Green, *Intrinsic concentration, effective densities of states, and effective mass in silicon*, J. Appl. Phys. **67**, 2944 (1990).
- [S3] M. Redecker and D. D. C. Bradley, *Mobility enhancement through homogeneous nematic alignment of a liquid-crystalline polyfluorene*, Appl. Phys. Lett. **74**, 1400 (1999).
- [S4] T. Kreouzis, D. Poplavskyy, S. M. Tuladhar, M. Campoy-Quiles, J. Nelson, A. J. Campbell, and D. D. C. Bradley, *Temperature and field dependence of hole mobility in poly(9,9-dioctylfluorene)*, Phys. Rev. B **73**, 235201 (2006).
- [S5] B. K. Yap, R. Xia, M. Campoy-Quiles, P. N. Stavrinou, and D. D. C. Bradley, *Simultaneous*

- optimization of charge-carrier mobility and optical gain in semiconducting polymer films*, Nat. Mater. **7**, 376 (2008).
- [S6] M. Redecker, D. D. C. Bradley, M. Inbasekaran, and E. P. Woo, *Nondispersive hole transport in an electroluminescent polyfluorene*, Appl. Phys. Lett. **73**, 1565 (1998).
- [S7] L.-L. Chua, J. Zaumseil, J.-F. Chang, E. C.-W. Ou, P. K.-H. Ho, H. Sirringhaus, and R. H. Friend, *General observation of n-type field-effect behaviour in organic semiconductors*, Nature **434**, 194 (2005).
- [S8] H. T. Nicolai, G. A. H. Wetzelaer, M. Kuik, A. J. Kronemeijer, B. de Boer, and P. W. M. Blom, *Space-charge-limited hole current in poly(9,9-dioctylfluorene) diodes*, Appl. Phys. Lett. **96**, 172107 (2010).
- [S9] T. van Woudenberg, J. Wildeman, P. W. M. Blom, J. J. A. M. Bastiaansen, and B. M. W. Langeveld-Vos, *Electron-Enhanced Hole Injection in Blue Polyfluorene-Based Polymer Light-Emitting Diodes*, Adv. Funct. Mater. **14**, 677 (2004).
- [S10] P. Prins, F. C. Grozema, F. Galbrecht, U. Scherf, and L. D. A. Siebbeles, *Charge Transport along Coiled Conjugated Polymer Chains*, J. Phys. Chem. C **111**, 11104 (2007).
- [S11] P. Prins, F. C. Grozema, B. S. Nehls, T. Farrell, U. Scherf, and L. D. A. Siebbeles, *Enhanced charge-carrier mobility in β -phase polyfluorene*, Phys. Rev. B **74**, 113203 (2006).
- [S12] M. J. Bird, O. G. Reid, A. R. Cook, S. Asaoka, Y. Shibano, H. Imahori, G. Rumbles, and J. R. Miller, *Mobility of Holes in Oligo- and Polyfluorenes of Defined Lengths*, J. Phys. Chem. C **118**, 6100 (2014).
- [S13] S. H. Chen, A. C. Su, and S. A. Chen, *Noncrystalline Phases in Poly(9,9-di-n-octyl-2,7-fluorene)*, J. Phys. Chem. B **109**, 10067 (2005).
- [S14] C. Liu, Q. Wang, H. Tian, J. Liu, Y. Geng, and D. Yan, *Morphology and Structure of the β Phase Crystals of Monodisperse Polyfluorenes*, Macromolecules **46**, 3025 (2013).

- [S15] R. U. A. Khan, D. Poplavskyy, T. Kreouzis, and D. D. C. Bradley, *Hole mobility within arylamine-containing polyfluorene copolymers: A time-of-flight transient-photocurrent study*, Phys. Rev. B **75**, 035215 (2007).
- [S16] S. Foster, *PhD Thesis*, Imperial College London, United Kingdom, 2013.
- [S17] A. Ochse, A. Kettner, J. Kopitzke, J. H. Wendorff, and H. Bässler, *Transient photoconduction in discotic liquid crystals*, Phys. Chem. Chem. Phys. **1**, 1757 (1999).
- [S18] C. Im, H. Bässler, H. Rost, and H. H. Hörhold, *Hole transport in polyphenylenevinylene-ether under bulk photoexcitation and sensitized injection*, J. Chem. Phys. **113**, 3802 (2000).
- [S19] F. Laquai, G. Wegner, C. Im, H. Bässler, and S. Heun, *Nondispersive hole transport in carbazole- and anthracene-containing polyspirobifluorene copolymers studied by the charge-generation layer time-of-flight technique*, J. Appl. Phys. **99**, 033710 (2006).
- [S20] S.-W. Liu, C.-C. Lee, W.-C. Su, C.-H. Yuan, C.-F. Lin, K.-T. Chen, Y.-S. Shu, Y.-Z. Li, T.-H. Su, B.-Y. Huang, W.-C. Chang, and Y.-H. Liu, *Downscaling the Sample Thickness to Sub-Micrometers by Employing Organic Photovoltaic Materials as a Charge-Generation Layer in the Time-of-Flight Measurement*, Sci. Rep. **5**, 10384 (2015).
- [S21] D. C. Tripathi, A. K. Tripathi, and Y. N. Mohapatra, *Mobility determination using frequency dependence of imaginary part of impedance ($\text{Im } Z$) for organic and polymeric thin films*, Appl. Phys. Lett. **98**, 033304 (2011).
- [S22] S. W. Tsang, S. K. So, and J. B. Xu, *Application of admittance spectroscopy to evaluate carrier mobility in organic charge transport materials*, J. Appl. Phys. **99**, 013706 (2006).
- [S23] K. K. H. Chan, S. W. Tsang, H. K. H. Lee, F. So, and S. K. So, *Charge transport study of semiconducting polymers and their bulk heterojunction blends by capacitance measurements*, J. Polym. Sci. Part B Polym. Phys. **51**, 649 (2013).
- [S24] H. Scher and E. W. Montroll, *Anomalous transit-time dispersion in amorphous solids*, Phys.

Rev. B **12**, 2455 (1975).