Mid-gap Trap State Mediated Dark Current in Organic Photodiodes

Christina Kaiser

Swansea University

Oskar Sandberg

Swansea University

Stefan Zeiske

Swansea University

Sam Gielen

Hasselt University, Institute for Materials Research (IMO)

Wouter Maes

Hasselt University, Institute for Materials Research (IMO)

Koen Vandewal

Institute for Materials Research (IMO-IMOMEC), Hasselt University, Wetenschapspark 1, Diepenbeek 3590, Belgium <https://orcid.org/0000-0001-5471-383X>

Paul Meredith

Swansea University

Ardalan Armin (✉ ardalan.armin@swansea.ac.uk)

Swansea University <https://orcid.org/0000-0002-6129-5354>

Article

Keywords: organic photodiodes, electronics, nanoscience

Posted Date: July 26th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-710876/v1>

License: This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Mid-gap Trap State Mediated Dark Current in Organic Photodiodes

Christina Kaiser¹, Oskar J. Sandberg^{1*}, Stefan Zeiske¹, Sam Gielen², Wouter Maes², Koen Vandewal², Paul Meredith¹, Ardalan Armin^{1*}

¹Sustainable Advanced Materials (Sêr-SAM), Department of Physics, Swansea University, Singleton Park, Swansea SA2 8PP, United Kingdom

²Hasselt University, Institute for Materials Research (IMO), Agoralaan 1 – Building D, 3590 Diepenbeek, Belgium and IMEC, Associated Lab IMOMECE, Wetenschapspark 1, 3590 Diepenbeek, Belgium

*Email: ardalan.armin@swansea.ac.uk; o.j.sandberg@swansea.ac.uk

Abstract

Photodiodes are ubiquitous in industry and consumer electronics. New applications for photodiodes are constantly emerging, such as the internet of things and wearable electronics that demand different mechanical and optoelectronic properties from those provided by conventional inorganic devices. This has stimulated considerable interest in the use of next generation semiconductors, particularly the organics, which provide a vast palette of available optoelectronic properties, can be incorporated into flexible form factor geometries, and promise extremely low cost, low embodied energy manufacturing from earth abundant materials. The sensitivity of a photodiode to low light intensities (typically important in these new applications) depends critically on the dark current. Organic photodiodes, however, are characterized by a much higher dark current than expected for thermally excited band-to-band transitions. Here, we show that the lower limit of the dark current is given by recombination via mid-gap trap states. This new insight is generated from temperature dependent dark current measurements of narrow-gap photodiodes for the near-infrared. Based on Shockley-Read-Hall statistics, a diode equation is derived which can be used to determine an upper limit for the specific detectivity and to explain the general trend observed for the light to dark current ratio as a function of the experimental open-circuit voltage for a series of organic photodiodes. A detailed understanding of the origins of noise in any detector is fundamental to defining performance limitations and thus is critical to materials and device selection, design and optimisation for all applications. Our work establishes these important principles for organic semiconductor photodiodes for the near-infrared.

Introduction

Organic semiconductors present promising complementary absorbers to inorganic semiconductors for photodetection, in particular in the wavelength range between 1 and 2 μm . This spectral window is interesting for bioimaging¹, optical telecommunication² and machine vision³. The advantages of organic semiconductors include monolithic integrability with silicon read-out circuitry^{4,5}, reduced material and manufacturing costs from earth abundant feedstocks, and inherent material properties like flexibility, bandgap tunability and light weight.⁶ Combining these properties with state-of-the-art device performance and operational lifetimes is expected to result in disruptive innovations, particularly in the field of consumer electronics,⁷ such as previously demonstrated with organic light emitting diodes.

In the past decade, advances in the absorber materials and device architectures used in organic photodetectors (OPDs) based on donor (D):acceptor (A) bulk heterojunction (BHJ) blends have delivered significant performance improvements. The operational spectral window of OPDs has been expanded from the visible range up to wavelengths of 1700 nm, however, with the best specific detectivities (D^*) above 1500 nm only reaching modest levels of $10^9 \text{ cmHz}^{1/2}/\text{W}$.^{8,9} The longer wavelength range has remained unattainable¹⁰ despite the implementation of optical and electrical¹¹ amplification that can boost the external quantum efficiency (EQE) to as high as 2000 %.¹² The main obstacle for achieving higher D^* has proven to be the large dark current density J_D , or more precisely the electrical shot noise produced by it, at typical operational bias (-0.5 to -2 V). For OPDs operating at zero bias voltage, a similar problem still exists due to the thermal noise which is related to parasitic and dynamic resistance of the diode.

In efficient organic photodiodes, the main source of J_D in reverse bias is leakage current, or the so-called shunt current density J_{shunt} , arising from imperfections related to device fabrication and material processing. In general, J_D of a photodiode is given by the Shockley diode equation

$$J_D = J_0(V, T) \left(\exp \left[\frac{q(V - J_D R_s)}{kT} \right] - 1 \right) + \frac{V - J_D R_s}{R_{\text{shunt}}}, \quad (\text{eq. 1})$$

where $J_0(V, T)$ is the dark saturation current density and R_s the series resistance, while R_{shunt} is the shunt resistance associated with J_{shunt} . R_s generally limits J_D in forward bias but is negligible at smaller voltages. In reverse bias, the dark current simplifies as $J_D = -J_0(V, T) + J_{\text{shunt}}$, being strongly affected by the shunt current $J_{\text{shunt}} = V/R_{\text{shunt}}$. The dark saturation current density $J_0(V, T)$ is a material dependent parameter, determined by thermally activated charge generation-recombination processes in the active layer. For an ideal diode, J_0 is independent of the applied voltage. Under these conditions, band-to-band recombination dominates and the activation energy of J_0 is expected to be equal to the bandgap energy. In organic BHJ photodiodes, this bandgap corresponds to the charge transfer energy (E_{CT}), which is closely related to the difference between the frontier molecular orbital energy levels of D and A. In the presence of additional recombination mechanisms, however, J_0 is increased and

generally depends on the voltage. Such a voltage dependence is commonly described in terms of a diode ideality factor (n) deviating from unity ($J_0(V, T) \exp(qV/kT) \propto \exp(qV/nkT)$). For organic photodiodes, typically $J_0 \ll |J_{\text{shunt}}|$. However, optimizing the morphology of the BHJ blend active layer and the device stack can reduce J_{shunt} relative to J_0 . Furthermore, as the bandgap energy decreases, J_0 is known to increase relative to J_{shunt} . In narrow-gap organic semiconductor blends designed for near-infrared photodetection, it was observed recently that J_D in reverse bias shows almost ideal diode behaviour,¹³ allowing for J_D to be fitted with eq. 1. A comparison of J_0 from the fitting with the radiative dark saturation current $J_{0,R}$ (expected from the Shockley-Queisser limit) further led to the conclusion that non-radiative mechanisms must dominate the J_D generation. However, the origin of the large dark current has remained unclear.^{14,15}

The magnitude of J_D and the dark saturation current in organic photodiodes are typically explained by either non-optimized device layouts or properties of the active layer. Non-optimized device layouts result in parasitic currents such as J_{shunt} due to pinholes in the active layer, injection currents due to misaligned energy levels at the semiconductor/metal interface¹⁵ and lateral currents¹⁶. In the second category, material properties such as energetic disorder and the presence of trap states are assumed to be responsible for the large J_D . In this regard, a possible origin is non-radiative band-to-band generation-recombination via CT states, which has been shown to increase exponentially with decreasing E_{CT} .^{13,17} Another major source of J_D can be generation-recombination via trap states, typically described in terms of Shockley-Read-Hall (SRH) statistics. In organic semiconductors, the presence of trap states has been previously shown via sensitively measured photothermal deflection spectroscopy as well as intensity dependent photocurrent measurements for a large set of fullerene and non-fullerene blends.¹⁸ Recently, the effect of mid-gap trap states has also been observed in the sub-gap EQE¹⁹ directly and by impedance spectroscopy.²⁰

In this work, we provide evidence that the dark saturation current in organic photodiodes is dominated by recombination via mid-gap trap states. To minimize the influence of the shunt, we use narrow-gap BHJs with a relatively high $J_0(V, T)$ such that at low reverse bias $J_0 > |J_{\text{shunt}}|$. Based on temperature dependent current density-voltage (J - V) measurements, we then find that the thermal activation energy (E_a) of J_D equals half the bandgap energy. A diode equation is derived that analytically describes the recombination via mid-gap trap states by incorporating SRH statistics. Based on the proposed diode model describing $J_0(V, T)$, several implications for organic photodiodes can be formulated: First, an upper limit of D^* can be calculated, which, in the case of the studied BHJs, is within one order of magnitude of the experimental D^* . Second, the shot noise and thermal noise can be determined for $J_0(V, T)$, demonstrating new reverse bias voltage characteristics and higher noise currents at zero voltage than expected for band-to-band recombination only. Third, the SRH-based diode equation helps to explain a general trend observed between J_D and the photocurrent density J_{SC} as a function of the

open-circuit voltage (V_{OC}), indicating that the dark recombination current in narrow-gap blends is mid-gap trap mediated.

Methods

Dark current density-voltage (J - V). The dark J - V characteristics were measured with a Keithley 2450 source meter. The device under test (DUT) was mounted in a temperature controlled Linkam sample stage, which was connected to a Linkam T96 temperature controller and a LNP96 liquid nitrogen pump.

External quantum efficiency (EQE). EQE measurements were performed using a homebuilt setup including a Perkin Elmer UV/VIS/NIR spectrometer (LAMBDA 950) as a source of monochromatic light. The light was chopped at 273 Hz and directed onto the device under test (DUT). The resulting photocurrent was amplified by a low noise current amplifier (FEMTO DLPCA-200) and measured with a Stanford SR860 lock-in amplifier. To decrease the noise floor of the setup, the DUT was mounted in an electrically shielded Linkam sample holder and an integration time of 30 s on the lock-in amplifier was used for detecting wavelengths above 1500 nm. NIST-calibrated Si and GaAs photodiodes by Newport were used as calibration references. The commercial reference Ge and two InGaAs photodiodes were purchased from Thorlabs with part numbers FDG03, F010D and FGA21, respectively.

Short-circuit current density versus open-circuit voltage (J_{SC} - V_{OC}). A custom-built continuous wave laser operating at 520 nm was used for J_{SC} - V_{OC} measurements. The incident light intensity was stepwise increased by a motorized two-wheel attenuator from Standa (10MCWA168-1) containing different optical density filters. A Keithley 2450 source-meter unit was used to record the short-circuit current and open-circuit voltage at each incident light intensity.

Device fabrication. Bulk heterojunction organic photodiodes were prepared using the inverted architecture glass/ITO/ZnO/PEIE/active layer/MoO₃/Ag. All chemical definitions and abbreviations are provided in the **Supplementary Note 1**. Prior to device processing, the ITO-coated substrates were cleaned via sonication in soap water, demineralized water, acetone and isopropanol, followed by a UV/O₃ treatment for 10 min. ZnO interlayers were spin-coated from a solution of Zn(OAc)₂·2H₂O (0.239 g, Merck) and ethanolamine (0.121 g, Merck) in 2-methoxyethanol (4 mL, Merck). The ZnO layers were annealed at 300 °C for 10 min to obtain a layer thickness of ~30 nm. PEIE interlayers were spin-coated from a solution of PEIE (0.1 mL, Merck) in isopropanol (35 mL) and thermally annealed at 100 °C for 10 min. The photoactive layer was deposited from a solution of narrow-gap polymer (the donor - D) and PC₇₁BM (Merck) in solvent with mass ratios of 1 to 3, respectively, and total concentrations of 64, 48 and 32 mg/mL for PTTBAI (in *o*-dichlorobenzene with 7 v/v% of 1,8-diiodooctane (DIO)), PBTQ(OD) (in *o*-dichlorobenzene with 3 v/v% of DIO) and PTTQ(HD) (in chloroform with 3 v/v% of DIO), respectively. The solution was stirred overnight at 60 °C to ensure

complete dissolution, and spin-coated on top of PEIE. The spin-speed was 800 and 1500 rpm for 451 and 250 nm thicknesses, respectively, for the PTTBAI active layer, 700 and 1100 rpm for 407 and 139 nm, respectively, for the PBTQ(OD) devices and 1100 rpm for 250 nm for the PTTQ(HD) based devices. The devices were finished by evaporation of top electrodes MoO₃ (10 nm) and Ag (100 nm), defining an active area of 4 mm².

Results

Figure 1 | Sub-gap EQE features and donor absorption. **a**, Sensitive EQE spectra of the studied D:PC₇₁BM blends showing strong absorption of the narrow-gap donor polymers in the NIR. PBDB-T:PC₇₁BM is added as a wide-gap blend for comparison, showing CT state (dotted green line) and mid-gap trap state (dashed green line) absorption features that can be fitted with Gaussian functions. **b**, Frontier molecular orbital energy levels as previously¹³ obtained from cyclic voltammetry for PBTQ(OD), PTTBAI and PTTQ(HD) and ultraviolet photoelectron spectroscopy for PBDB-T.²¹

To clarify the dominant recombination mechanism in organic photodiodes, we varied the D polymer in D:PC₇₁BM blends, where PC₇₁BM acts as the electron-accepting component (A). To this end, three narrow-bandgap polymers with different bandgap energies were used to fabricate D:PC₇₁BM photodiodes with different active layer thicknesses. The respective External Quantum Efficiency (EQE) spectra are shown in **Figure 1a** on a logarithmic scale, illustrating the bandgap edges and the sub-gap spectral range, which can be used to identify and quantify the presence of radiative channels below the gap responsible for dark current generation. For comparison, we also show the sub-gap EQE of the wider-gap blend PBDB-T:PC₇₁BM. Additional EQE spectra with different D:PC₇₁BM layer thicknesses are shown in **Figure S1** illustrating how optical interference affects the low-energy tail of the EQE.^{22,23} The HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energy levels of the narrow-gap donor materials were previously obtained from cyclic voltammetry (CV) as reported in literature,¹³ and are shown in **Figure 1b**. For comparison, the solution and thin film absorption spectra are given in **Figure S2**.

The EQE measurements were performed down to roughly 0.5 eV (≈ 2500 nm) over a dynamic range of 90 dB. For PBTQ(OD):PC₇₁BM and PTTQ(HD):PC₇₁BM, the spectral range of PC₇₁BM absorption above 1.65 eV (≈ 750 nm) can be clearly distinguished from the narrow-gap polymer absorption at lower energies. Four orders of magnitude below the above-gap EQE, organic semiconductors generally show trap state absorption, as previously reported.²⁴ It has been suggested that conventional D:A blends, corresponding to effective bandgaps of 1.3 eV and above, display both charge transfer and mid-gap trap state absorption at sub-gap energies¹⁹, which, unless overshadowed by interference effects, can be fitted with Gaussian functions to obtain the CT state energy (E_{CT}) and the mid-gap trap state energy (E_t). The EQE spectrum of a PBDB-T:PC₇₁BM device in Figure 1a is an example of such a system, showing a pronounced CT state and mid-gap trap state shoulders in the sub-gap.

In the narrow-gap blends, E_{CT} is expected to be very close to the singlet exciton energy ($E_{SE,D}$) of the neat donor polymer, where E_{CT} can be estimated from the gap between donor HOMO and acceptor LUMO, while $E_{SE,D}$ can likewise be estimated from the HOMO-LUMO gap of the donor. Based on the experimental CV energy levels (Figure 1b), similar offsets of roughly 0.3 eV between E_{CT} and $E_{SE,D}$ are found for all of the narrow-gap D:PC₇₁BM blends. Combined with the intrinsically low oscillator strength of CT absorption, the CT absorption shoulder is expected to be masked by the donor singlet exciton absorption. Moreover, the absorption of mid-gap trap states cannot be experimentally discerned from the EQE of the narrow-gap systems, likely because the respective energies are outside the energy range of the experimental apparatus.

From the EQE spectra it is possible to calculate the thermodynamic limit of J_0 , namely the radiative dark saturation current $J_{0,R}$, via detailed balance:²⁵

$$J_{0,R} = q \int_0^{\infty} \text{EQE}(E) \varphi_{BB}(E) dE, \quad (\text{eq. 2})$$

where $\varphi_{BB}(E)$ is the temperature dependent black body spectrum. In practice, the reliable evaluation of eq. 2 is limited by the upper and lower integration bounds set by the experimental apparatus,¹⁹ thus providing a lower limit of $J_{0,R}$. The calculated $J_{0,R}$ is demonstrated in **Figure S3**, where, for example, the narrow-gap blend PTTBAI:PC₇₁BM is characterized by $J_{0,R} = 3.1 \times 10^{-16}$ A/cm². This is to be compared to the corresponding experimental J_D value of $J_D(-0.1 \text{ V}) = 7.8 \times 10^{-9}$ A/cm², measured at -0.1 V, where J_{shunt} is expected to be minimal. Hence, even when the EQE in the spectral range of mid-gap trap states is included down to 0.6 eV, the calculated $J_{0,R}$ is still 6 to 7 orders of magnitude below the experimental J_D (at low reverse bias). This high offset between $J_{0,R}$ and J_D is commonly observed in organic photodiodes, but underlying reasons are still debated. Provided that the contribution from shunt currents is small at this voltage, the dark saturation current density is found to be strongly dominated by non-radiative generation-recombination mechanisms. Indeed, Gielen et al. have shown

that for the same narrow-gap D:PC₇₁BM blends studied here, the experimental J_D at low bias voltages, i.e. -0.1 V, is barely influenced by J_{shunt} , hence $J_D(-0.1 \text{ V}) \approx J_0$.¹³ It was further suggested that for narrow-gap blends, $J_D(-0.1 \text{ V})$ decreases exponentially with increasing E_{CT} .

Figure 2 | Extracting E_a from temperature dependent J - V measurements. **a**, The natural logarithm of $J_D(-0.1 \text{ V})$ in function of $1/kT$ can be fitted by a linear function with slope E_a for temperatures above 260 K ($1/kT < 45 \text{ eV}^{-1}$). The narrow-gap D:PC₇₁BM photodiodes, where D is PTTQ(HD), PTTBAI or PBTQ(OD), were fabricated with typically two different active layer thicknesses (green and red points). **b**, For narrow-gap organic D:PC₇₁BM blends, $E_a \approx 0.5 E_g$, whereas for commercial inorganic photodiodes, $E_a \approx E_g$. The bandgap was obtained from the optical gap $E_{\text{opt},1}$ from (i) solution absorption and $E_{\text{opt},2}$, (ii) thin film absorption of the neat donor film, (iii) the electronic bandgap E_{CV} from cyclic voltammetry and (iv) E_{CT} from the blend as the intercept of the measured EQE_{pv} and calculated EQE_{EL}.

To gain more insight into the dominant (non-radiative) recombination mechanism behind J_0 , we conducted temperature dependent J - V measurements. Assuming that $J_D(-0.1 \text{ V}) \approx J_0$, noting that the dark saturation current density takes the form $J_0 = J_{00} \exp(-E_a/kT)$, the corresponding activation energy E_a may be determined. Here, E_a equals the effective energy barrier of the dominating thermal excitation process in the dark, while J_{00} is a prefactor. For a CT state mediated band-to-band generation-recombination process, $E_a = E_{\text{CT}}$, while for a mid-gap state mediated generation-recombination process we expect $E_a \approx E_{\text{CT}}/2$.

Figure 2a shows $J_D(-0.1 \text{ V})$ as a function of $1/kT$ in the so-called Arrhenius plots for the different D:PC₇₁BM blends and device thicknesses. It was found that the voltage sweep direction and the input impedance of the source measure unit can have an impact on the J - V curve, in particular at low current levels near voltages around $V = 0$. Therefore, the current was measured continuously under applied bias while changing temperature to ensure that trapped charge carriers have sufficient time to be released and reach the electrodes. The corresponding Arrhenius plots at different bias are presented in **Figure S4**. To minimize the effects of shunts (high reverse bias) and noise (voltages near zero), however, we chose to consider -0.1 V . As shown in Figure 2a, the natural logarithm of J_D at -0.1 V is linearly dependent on $1/kT$ for temperatures above 260 K. For temperatures below 260 K, deviations from linearity are either caused by the inability to measure currents below 10^{-12} A or the dominance of other current channels such as J_{shunt} or surface recombination with weaker temperature dependences. In the high temperature limit, PTTBAI:PC₇₁BM (and PBTQ(OD):PC₇₁BM) photodiodes at two different active layer thickness show similar E_a with a difference of only 0.08 eV (and 0.02 eV) between the two thicknesses.

Figure 2b shows the obtained E_a as a function of several energy level gaps (E_g). We include the optical gap from thin-film absorption of the neat donor ($E_{\text{opt},2}$) and E_{CT} as the intercept of the measured EQE_{PV} and calculated EQE_{EL} of the photodiodes. Moreover, the electronic bandgap E_{CV} from cyclic voltammetry and the optical gap from solution absorption of the neat donor ($E_{\text{opt},1}$) are included. Despite the known uncertainties^{14,26} of obtaining the correct bandgap energy, the general correlation is $E_a \approx 0.5 E_g$ as observed for all narrow-gap organic D:A blends. This is to be compared with the results from temperature dependent J - V measurements of three commercial NIR photodetectors comprising germanium (Ge), strained and unstrained indium gallium arsenide (InGaAs) included in Figure 2b (for details see **Figure S5-S7** and **Table S1**), where E_a equals the bandgap energy, as expected.

The observation that E_a equals half of the related bandgap energy for the organic semiconductor blends suggests that the dark saturation current in these systems is mediated by generation and recombination via mid-gap trap states in reverse bias. In general, the dark saturation current in eq. 1 can be expressed by the sum of the components related to band-to-band recombination (J_0^{bb}) and mid-gap state mediated recombination (J_0^{SRH}) currents:

$$J_0(V) = J_0^{\text{bb}} + J_0^{\text{SRH}}(V) + J_0^{\text{inj}}(V), \quad (\text{eq. 4})$$

where for completeness we also include additional injection current components J_0^{inj} related to surface recombination (and generation) at the electrodes. In organic semiconductor blends, we expect the band-to-band component to be independent of voltage, following $J_0^{\text{bb}} \propto \exp(-E_{\text{CT}}/kT)$. The activation energy of J_0^{inj} , on the other hand, is expected to be predominantly given by the injection barrier of

minority carriers at the electrodes.²⁷ Given that $E_a \approx E_{CT}/2$, our results point towards $J_0(V) \approx J_0^{SRH}(V)$.

In order to evaluate the voltage dependence of $J_0^{SRH}(V)$, an analytical expression of the related dark current is derived for organic photodiodes based upon Shockley-Read-Hall (SRH) statistics (see the **Supplementary Note 2**). We obtain

$$J_0^{SRH}(V) \approx J_{0,SRH} \frac{2kT}{q[V_{bi} - V]} \ln \left[\frac{1 + 2B \exp\left(-\frac{qV}{2kT}\right)}{1 + 2B \exp\left(-\frac{qV_{bi}}{2kT}\right)} \right], \quad (\text{eq. 5})$$

where V_{bi} is the built-in voltage, while $J_{0,SRH}$ and B are related to the SRH lifetimes and trap energies for holes and electrons. For mid-gap trap states, we expect $J_{0,SRH} = qdN_0 \exp(-E_g/(2kT)) / \tau_{SRH}$, where d is the active layer thickness, N_0 is the available density of states for free charge carriers, and $\tau_{SRH} = \tau_n + \tau_p$ is the effective SRH lifetime, whereas $B = (\sqrt{\tau_n/\tau_p} + \sqrt{\tau_p/\tau_n})/2$. Here, τ_n and τ_p are the SRH lifetime for electrons and holes, respectively. The corresponding trap-mediated dark recombination current can be expressed as $J_{SRH}(V) = J_0^{SRH}(V) \left[\exp\left(\frac{qV}{kT}\right) - 1 \right]$. In forward bias, near flat-band conditions ($V \sim V_{bi}$), this current density simplifies as $J_{SRH}(V) \approx 2BJ_{0,SRH} \exp(qV/2kT)$, consistent with an ideality factor of 2. In reverse bias, in turn, we expect $J_{SRH}(V) \approx J_{0,SRH} V/[V_{bi} - V]$, saturating to $J_{SRH}(V) \rightarrow J_{0,SRH}$ at large reverse bias. We note that the derived SRH-mediated dark recombination current density presents an excellent and analytically tractable approximation for the expression originally proposed by Sah et al. describing the recombination current.²⁸

In accordance with eq. (5), we expect the dark saturation current to depend on the voltage. However, we note that the experimental dark current in forward bias quickly becomes limited by the series resistance and/or transport limitations at voltages above 0.2 V in narrow-gap blends. To overcome these resistive limitations and thus obtain a more accurate estimate for $J_{SRH}(V)$, we performed light intensity dependent J_{SC} and V_{OC} measurements. Here, V_{OC} is the open-circuit voltage at which the total current under illumination is zero, $J_{tot}(V_{OC}) = -J_{SC} + J_D(V_{OC}) = 0$, while J_{SC} is the short-circuit current density being proportional to the light intensity. Hence, since $J_D(V_{OC}) = J_{SC}$, by varying the light intensity and plotting the related J_{SC} as a function of V_{OC} , the dark J - V in the forward bias can be reproduced, but without the effect of transport limitations or series resistance (since $J_{tot} = 0$).²⁹ The experimental dark J - V characteristics along with the associated J_{SC} - V_{OC} plots are shown in **Figure 3a** for the PTTBAI:PC₇₁BM, PBTQ(OD):PC₇₁BM and PTTQ(HD):PC₇₁BM photodiodes.

A good fit of the dark J - V in reverse bias and the J_{SC} - V_{OC} plot in forward bias is obtained for all systems using $J_D = J_0^{SRH}(V) \left(\exp\left(\frac{qV}{kT}\right) - 1 \right)$ with J_0^{SRH} given by eq. (5) and assuming $B = 1$. These results further corroborate the assertion that the dark saturation current is dominated by bulk processes mediated via mid-gap trap states. The corresponding $J_{0,SRH}$ values as extracted from the fits are shown

in **Table S2**, allowing for the effective SRH lifetimes τ_{SRH} to be calculated. Assuming a typical value of $1 \times 10^{20} \text{ cm}^{-3}$ for N_0 , we find τ_{SRH} for PTTBAI, PBTQ(OD) and PTTQHD to be 0.3, 0.1 and 1 μs , respectively. We note that J_0^{bb} from the band-to-band recombination converges to values much lower than $J_0^{\text{SRH}}(V)$ and hence, can be neglected in reverse and forward bias. In contrast, $J_{\text{shunt}}(V)$ dominates the dark J - V at high reverse bias. This is demonstrated, first, in the dark J - V fits in Figure 3a and, secondly, in Figure S4, where $E_a(V)$ is shown to decrease with increasing reverse bias. For example, $E_a(-1 \text{ V}) = E_{\text{CT}}/2 - 0.09 \text{ eV}$ for PTTBAI and $E_a(-1 \text{ V}) = E_{\text{CT}}/2 - 0.04 \text{ eV}$ for PBTQ(OD). It can be concluded that $J_D \approx J_0^{\text{SRH}}$ holds true, at least for small voltages close to zero, including $V = -0.1 \text{ V}$.

Figure 3 | Experimental dark J - V characteristics and upper D^* limit. a, Deconvolution of the experimental dark J - V curves of narrow-gap D:PC₇₁BM photodiodes into mid-gap trap mediated J_{SRH} and J_{shunt} . Forward bias is taken from $J_{\text{SC}} - V_{\text{OC}}$ measurements to avoid series resistance. **b,** D^* approximated from i_{shot} of J_{SRH} at -1 V and the experimental noise current spectrum at -1 V . BLIP is the Background Limited Infrared Performance.

Based on the above findings, a new efficiency limit for photodiodes based on organic BHJ blends can be obtained. The performance of a photodetector is given by the specific detectivity $D^* = R\sqrt{A\Delta f} \times (i_{\text{noise}})^{-1}$, where R is the responsivity, i_{noise} is the measured noise current and Δf is the frequency bandwidth. As shown in the literature, i_{noise} can be well approximated by its shot noise

component i_{shot} at small bias. i_{shot} of any signal S is $i_{\text{shot}} = \sqrt{2qS\Delta f}$. Then, assuming absorber materials that are dominated by recombination via mid-gap trap states, the lower limit of D^* corresponding to $\text{EQE} = 1$ for $E \geq E_a$ and $\text{EQE} = 0$ for $E \leq E_a$ (i.e. R of an ideal photodiode) can be approximated by $D^* = R \times (\sqrt{2qJ_{\text{SRH}}(V)})^{-1}$. **Figure 3b** compares this calculated D^* at -1 V with the experimental D^* previously obtained by Gielen et al. from the measured noise current at -1 V and 3 kHz. Herein, the experimental D^* is generally close to the calculated D^* with a maximum offset of roughly 1 order of magnitude for PTTQ(HD):PC₇₁BM. From the fit shown in Figure 3a, PTTQ(HD):PC₇₁BM has the largest relative contribution of J_{shunt} to the total J_D at -1 V, which can be the origin of the relatively high experimental noise current. To improve D^* for this particular system, J_{shunt} should be decreased. Known strategies for reducing J_{shunt} include employing selective charge blocking layers, thick junctions and optimizing the device layout to decrease lateral leakage currents.

Furthermore, since photodetectors are generally operated under reverse bias, the voltage and V_{bi} dependence of J_{SRH} must be considered when calculating the expected noise current or analysing experimental noise measurements. In the **Supplementary Note 3**, we discuss thermal noise i_{thermal} and i_{shot} of J_{SRH} and J^{bb} . At 0 V, the net current is zero, but i_{thermal} of J_{SRH} and J^{bb} are non-zero with $i_{\text{thermal}}(J_{\text{SRH}}) > i_{\text{thermal}}(J^{\text{bb}})$. In reverse bias, i_{shot} of J_{SRH} increases with voltage, while i_{shot} of J^{bb} is expected to increase with increasing reverse bias until $J^{\text{bb}} \approx J_0^{\text{bb}}$ for $V \ll 0$. In contrast, due to the voltage dependence of J_0^{SRH} , a stronger voltage dependence at small reverse bias is expected when recombination via mid-gap state dominates, depending on the effective V_{bi} , i.e. $J_0^{\text{SRH}}(V) \approx J_{0,\text{SRH}}$ is reached for larger V , when the effective V_{bi} is high. However, the total i_{shot} in the limit $V \ll 0$ must be the sum over band-to-band recombination and SRH recombination via mid-gap trap states, hence, $i_{\text{noise,shot}}^2 = 2(J_0^{\text{bb}} + J_{0,\text{SRH}})q\Delta F$.

Finally, we note that the dark saturation current density exhibits distinctly different voltage dependence in forward and reverse bias when trap-mediated SRH recombination dominates. Based on eq. 5, the principal voltage dependence of $J_0^{\text{SRH}}(V)$ in the forward bias is of the form $J_0^{\text{SRH}}(V) \propto \exp(-qV/2kT)$, while $J_0^{\text{SRH}}(V)$ saturates to a constant value for voltages far into the reverse bias. Therefore, we expect the ratio between the dark saturation current densities in the forward bias, at a voltage V_F , and in the reverse bias, at a voltage V_R , to scale as $J_0^{\text{SRH}}(V_F)/J_0^{\text{SRH}}(V_R) \propto \exp(-qV_F/2kT)$. This is in contrast to the case when band-to-band recombination dominates the dark saturation current, where J_0 is typically independent of the voltage and $J_0^{\text{SRH}}(V_F)/J_0^{\text{SRH}}(V_R) = 1$. Hence, $J_0(V_F)/J_0(V_R)$ may be used as a proxy for the dominant recombination mechanism. To reliably determine $J_0(V_F)/J_0(V_R)$, the influence of resistive effects needs to be avoided. To this end, we again make use of J_{SC} vs V_{OC} data, allowing for the corresponding dark current density in forward bias ($V_F = V_{\text{OC}}$) to be obtained via $J_D(V_{\text{OC}}) = J_{\text{SC}}$.

Subsequently, the ratio between the dark saturation current densities in forward and reverse bias can be calculated via

$$\frac{J_{SC}}{|J_D(V_R)|} = \frac{J_0(V_{OC})}{J_0(V_R)} \times \left[\exp\left(\frac{qV_{OC}}{kT}\right) - 1 \right], \quad (\text{eq. 6})$$

for $V_R < -3kT/q$, noting that the dark current density is approximately given by $J_D(V_R) \approx -J_0(V_R)$ in the reverse bias. Herein, to minimize the J_{shunt} contribution to the total J_D in the reverse bias, J_D is evaluated at $V_R = -0.1$ V.

Figure 4 | General trend in performance metrics of narrow-gap photodiodes dominated by SRH recombination.

Calculated ratio of J_{SC} to $J_0(V_R)$ (a), and calculated ratio of $J_0(V_{OC})$ to $J_0(V_R)$ (b), plotted as a function of V_{OC} on a semi-logarithmic scale, where $J_0(V_R) \approx J_D(V_R)$ and $V_R = -0.1$ V for all fullerene-based devices (empty circles, data taken from literature¹³). Blue, orange and purple circles represent J_{SC} - V_{OC} data of the studied narrow-gap photodiodes at different light intensities. Red lines represent an analytical limit taking only into account band-to-band recombination. Black and green lines show the theoretical limits of SRH recombination via mid-gap trap states, where $V_{bi} = V_{OC}$ and $V_{bi} \gg V_{OC}$, respectively.

In **Figure 4a**, the experimentally-obtained $J_{SC}/|J_D(V_R)|$ is shown as a function of V_{OC} for the narrow-gap photodiodes investigated in this work (closed symbols), alongside literature known photodiodes (open circles),¹³ assuming $V_R = -0.1$ V. The theoretical limit, as expected based on eq. 6, when band-to-band recombination dominates the dark saturation current [$J_0(V_{OC})/J_0(V_R) = 1$] is indicated by the red line in Figure 4. Most photodiodes are generally well below this limit, consistent with previous findings by Gielen et al.¹³ The theoretical behavior, expected for SRH recombination via mid-gap states dominating the dark saturation current, is indicated by the black line for the case $V_{OC} \rightarrow V_{bi}$ when $J_0^{SRH}(V_{OC}) \rightarrow 2J_{0,SRH} \exp(-qV_{OC}/2kT)$ in eq. 5. Comparing with the experimental data, it can be seen that the general trend is indeed consistent with SRH recombination via mid-gap traps dominating J_0 in narrow-gap systems where $V_{OC} < 0.7$ V. This is further corroborated by the experimentally obtained $J_0(V_{OC})/J_0(V_R)$, estimated using eq. 6 in **Figure 4b**, showing that narrow-gap systems follow the trend

predicted by mid-gap state mediated recombination. We note that the scatter around the black line can be partly attributed to the fact that $V_{OC} \neq V_{bi}$ in general, and a weak additional voltage dependence is thus expected in accordance with eq. 5. For systems with relatively wide gaps ($V_{OC} > 0.7$ V), in turn, a deviation from the trend is seen. However, such a deviation is to be expected considering that the V_{OC} increases linearly with the effective bandgap E_{CT} (independent of whether band-to-band or SRH recombination dominates at open-circuit). Subsequently, high V_{OC} blends are characterized by very low J_0 levels, with $J_D(V_R)$ inevitably becoming dominated by parasitic shunts (J_{shunt}), overshadowing the true J_0 in these systems.

Conclusions

To conclude, we have undertaken a detailed study on the origin of the dark current in near-infrared photodetectors based upon next generation organic semiconductors. Specifically, we utilised temperature dependent dark J - V measurements on narrow-gap organic semiconductor blend photodiodes to show that the thermal activation of the dark current at small reverse bias equals half the bandgap, i.e., $E_a \approx 0.5E_g$. The dominant dark recombination mechanism is therefore mid-gap trap mediated. We derive a new expression for the dark current mediated by mid-gap trap states using SRH statistics. In this new expression, the dark saturation current J_0^{SRH} is voltage dependent and therefore can strongly affect the reverse bias dark current and its shot noise depending on the build-in voltage. In this light, we calculate a revised upper limit of D^* for the studied narrow-gap blends based on J_0^{SRH} that was obtained from a fit to the dark J - V characteristics. Lastly, we show that for a large set of narrow-gap organic photodiodes, the J_{SC} to $J_D(-0.1$ V) ratio as a function of voltage roughly describes a trend expected when considering SRH recombination via mid-gap trap states.

References

- (1) Guo, Z.; Park, S.; Yoon, J.; Shin, I. Recent Progress in the Development of Near-Infrared Fluorescent Probes for Bioimaging Applications. *Chem. Soc. Rev.* **2014**, *43* (1), 16–29. <https://doi.org/10.1039/C3CS60271K>.
- (2) Clark, J.; Lanzani, G. Organic Photonics for Communications. *Nat. Photonics* **2010**, *4* (7), 438–446. <https://doi.org/10.1038/nphoton.2010.160>.
- (3) Yoon, S.; Sim, K. M.; Chung, D. S. Prospects of Colour Selective Organic Photodiodes. *J. Mater. Chem. C* **2018**, *6* (48), 13084–13100. <https://doi.org/10.1039/c8tc04371j>.
- (4) Kwon, J.; Takeda, Y.; Shiwa, R.; Tokito, S.; Cho, K.; Jung, S. Three-Dimensional Monolithic Integration in Flexible Printed Organic Transistors. *Nat. Commun.* **2019**, *10* (1), 1–10. <https://doi.org/10.1038/s41467-018-07904-5>.
- (5) Park, K. S.; Baek, J.; Park, Y.; Lee, L.; Hyon, J.; Koo Lee, Y. E.; Shrestha, N. K.; Kang, Y.; Sung, M. M. Heterogeneous Monolithic Integration of Single-Crystal Organic Materials. *Adv. Mater.* **2017**, *29* (6). <https://doi.org/10.1002/adma.201603285>.
- (6) Jansen-van Vuuren, R. D.; Armin, A.; Pandey, A. K.; Burn, P. L.; Meredith, P. Organic Photodiodes: The Future of Full Color Detection and Image Sensing. *Adv. Mater.* **2016**, 4766–4802. <https://doi.org/10.1002/adma.201505405>.
- (7) Ren, H.; Chen, J.; Li, Y.; Tang, J. Recent Progress in Organic Photodetectors and Their Applications. *Adv. Sci.* **2021**, *8* (1), 2002418. <https://doi.org/10.1002/advs.202002418>.
- (8) Kaiser, C.; Schellhammer, K. S.; Benduhn, J.; Siegmund, B.; Tropiano, M.; Zeika, O.; Ortmann, F.; Meredith, P.; Armin, A.; Vandewal, K. Manipulating the Charge Transfer Absorption for Narrowband Light Detection in the Near-Infrared. *Chem. Mater.* **2019**, *31* (22), 9325–9330. <https://doi.org/10.1021/acs.chemmater.9b02700>.
- (9) Tang, Z.; Ma, Z.; Sánchez-Díaz, A.; Ullbrich, S.; Liu, Y.; Siegmund, B.; Mischok, A.; Leo, K.; Campoy-Quiles, M.; Li, W.; Vandewal, K. Polymer:Fullerene Bimolecular Crystals for Near-Infrared Spectroscopic Photodetectors. *Adv. Mater.* **2017**, *1702184*, 1702184. <https://doi.org/10.1002/adma.201702184>.
- (10) Li, Q.; Guo, Y.; Liu, Y. Exploration of Near-Infrared Organic Photodetectors. *Chem. Mater.* **2019**, *31* (17), 6359–6379. <https://doi.org/10.1021/acs.chemmater.9b00966>.
- (11) Lan, Z.; Lei, Y.; Chan, W. K. E.; Chen, S.; Luo, D.; Zhu, F. Near-Infrared and Visible Light Dual-Mode Organic Photodetectors. *Sci. Adv.* **2020**, *6* (5), 1–10. <https://doi.org/10.1126/sciadv.aaw8065>.
- (12) Wang, W.; Du, M.; Zhang, M.; Miao, J.; Fang, Y.; Zhang, F. Organic Photodetectors with Gain and Broadband/Narrowband Response under Top/Bottom Illumination Conditions. *Adv. Opt. Mater.* **2018**, *6* (16), 1–8. <https://doi.org/10.1002/adom.201800249>.
- (13) Gielen, S.; Kaiser, C.; Verstraeten, F.; Kublitski, J.; Benduhn, J.; Spoltore, D.; Verstappen, P.; Maes, W.; Meredith, P.; Armin, A.; Vandewal, K. Intrinsic Detectivity Limits of Organic Near-Infrared Photodetectors. *Adv. Mater.* **2020**, *32* (47), 2003818. <https://doi.org/10.1002/adma.202003818>.
- (14) Vandewal, K.; Benduhn, J.; Nikolis, V. C. How to Determine Optical Gaps and Voltage Losses in Organic Photovoltaic Materials. *Sustain. Energy Fuels* **2018**, 538–544. <https://doi.org/10.1039/C7SE00601B>.
- (15) Simone, G.; Dyson, M. J.; Weijtens, C. H. L.; Meskers, S. C. J.; Coehoorn, R.; Janssen, R. A. J.; Gelinck, G. H. On the Origin of Dark Current in Organic Photodiodes. *Adv. Opt. Mater.* **2020**, *8* (1), 1901568. <https://doi.org/10.1002/adom.201901568>.

- (16) Zheng, Y.; Fischer, A.; Sergeeva, N.; Reineke, S.; Mannsfeld, S. C. B. Exploiting Lateral Current Flow Due to Doped Layers in Semiconductor Devices Having Crossbar Electrodes. *Org. Electron.* **2019**, *65* (July 2018), 82–90. <https://doi.org/10.1016/j.orgel.2018.10.040>.
- (17) Benduhn, J.; Tvingstedt, K.; Piersimoni, F.; Ullbrich, S.; Fan, Y.; Tropiano, M.; McGarry, K. A.; Zeika, O.; Riede, M. K.; Douglas, C. J.; Barlow, S.; Marder, S. R.; Neher, D.; Spoltore, D.; Vandewal, K. Intrinsic Non-Radiative Voltage Losses in Fullerene-Based Organic Solar Cells. *Nat. Energy* **2017**, *2* (6), 17053. <https://doi.org/10.1038/nenergy.2017.53>.
- (18) Zeiske, S.; Sandberg, O. J.; Zarrabi, N.; Li, W.; Meredith, P.; Armin, A. Direct Observation of Trap-Assisted Recombination in Organic Photovoltaic Devices. *Nat. Commun.* **2021**, *12* (1), 3603. <https://doi.org/10.1038/s41467-021-23870-x>.
- (19) Zarrabi, N.; Sandberg, O. J.; Zeiske, S.; Li, W.; Riley, D. B.; Meredith, P.; Armin, A. Charge-Generating Mid-Gap Trap States Define the Thermodynamic Limit of Organic Photovoltaic Devices. *Nat. Commun.* **2020**, *11* (1), 5567. <https://doi.org/10.1038/s41467-020-19434-0>.
- (20) Kublitski, J.; Hofacker, A.; Boroujeni, B. K.; Benduhn, J.; Nikolis, V. C.; Kaiser, C.; Spoltore, D.; Kleemann, H.; Fischer, A.; Ellinger, F.; Vandewal, K.; Leo, K. Reverse Dark Current in Organic Photodetectors and the Major Role of Traps as Source of Noise. *Nat. Commun.* **2021**, *12* (1), 551. <https://doi.org/10.1038/s41467-020-20856-z>.
- (21) Zhao, W.; Li, S.; Zhang, S.; Liu, X.; Hou, J. Ternary Polymer Solar Cells Based on Two Acceptors and One Donor for Achieving 12.2% Efficiency. *Adv. Mater.* **2017**, *29* (2), 1604059. <https://doi.org/10.1002/adma.201604059>.
- (22) Kaiser, C.; Zeiske, S.; Meredith, P.; Armin, A. Determining Ultralow Absorption Coefficients of Organic Semiconductors from the Sub-Bandgap Photovoltaic External Quantum Efficiency. *Adv. Opt. Mater.* **2020**, *8* (1), 1901542. <https://doi.org/10.1002/adom.201901542>.
- (23) Armin, A.; Kassal, I.; Shaw, P. E.; Hamsch, M.; Stolterfoht, M.; Lyons, D. M.; Li, J.; Shi, Z.; Burn, P. L.; Meredith, P. Spectral Dependence of the Internal Quantum Efficiency of Organic Solar Cells: Effect of Charge Generation Pathways. *J. Am. Chem. Soc.* **2014**, *136* (32), 11465–11472. <https://doi.org/10.1021/ja505330x>.
- (24) Zeiske, S.; Kaiser, C.; Meredith, P.; Armin, A. Sensitivity of Sub-Bandgap External Quantum Efficiency Measurements of Solar Cells under Electrical and Light Bias. *ACS Photonics* **2019**, *7* (1), 256–264. <https://doi.org/10.1021/acsp Photonics.9b01531>.
- (25) Shockley, W.; Queisser, H. J. Detailed Balance Limit of Efficiency of P-n Junction Solar Cells. *J. Appl. Phys.* **1961**, *32* (3), 510–519. <https://doi.org/10.1063/1.1736034>.
- (26) Bredas, J. L. Mind the Gap! *Mater. Horizons* **2014**, *1* (1), 17–19. <https://doi.org/10.1039/c3mh00098b>.
- (27) Sandberg, O. J.; Armin, A. On the Effect of Surface Recombination in Thin Film Solar Cells, Light Emitting Diodes and Photodetectors. *Synth. Met.* **2019**, *254* (June), 114–121. <https://doi.org/10.1016/j.synthmet.2019.06.008>.
- (28) Sah, C. T.; Noyce, R. N.; Shockley, W. Carrier Generation and Recombination in P-N Junctions and P-N Junction Characteristics. *Proc. IRE* **1957**, *45* (9), 1228–1243. <https://doi.org/10.1109/JRPROC.1957.278528>.
- (29) Tvingstedt, K.; Deibel, C. Temperature Dependence of Ideality Factors in Organic Solar Cells and the Relation to Radiative Efficiency. *Adv. Energy Mater.* **2016**, *6* (9), 1–13. <https://doi.org/10.1002/aenm.201502230>.
- (30) Zhang, Z.; Miao, G.; Song, H.; Li, D.; Jiang, H.; Li, Z.; Chen, Y.; Sun, X. High in Content InGaAs Near-Infrared Detectors: Growth, Structural Design and Photovoltaic Properties. *Appl. Phys. A* **2017**, *123* (4), 219. <https://doi.org/10.1007/s00339-017-0835-3>.

Acknowledgements

This work was funded through the Welsh Government's Sêr Cymru II Program 'Sustainable Advanced Materials' (Welsh European Funding Office – European Regional Development Fund). C.K. is recipient of a UKRI EPSRC Doctoral Training Program studentship. N.Z. is funded by a studentship through the Sêr Cymru II Program. P.M. is a Sêr Cymru II Research Chair and A.A. is a Rising Star Fellow also funded through the Welsh Government's Sêr Cymru II 'Sustainable Advanced Materials' Program (European Regional Development Fund, Welsh European Funding Office and Swansea University Strategic Initiative). This work was also funded by UKRI through the EPSRC Program Grant EP/T028511/1 Application Targeted Integrated Photovoltaics. S.G. acknowledges the Research Foundation – Flanders (FWO Vlaanderen) for granting him a PhD fellowship. K.V. and W.M. are grateful for project funding by the FWO (G0D0118N, G0B2718N and GOH3816NAUHL).

Author Contributions

A.A. and P.M. provided the overall leadership of the project. O.J.S. and A.A. conceptualized the idea. C.K. and A.A. designed the experiments. C.K. fabricated the devices, performed most measurements and analysed the data. O.J.S developed the theoretical model. C.K., O.J.S., A.A. and K.V. interpreted the data. S.Z. performed the IPC measurements and S.G. assisted with device fabrication. W.M. provided the materials. All co-authors contributed to the development of the manuscript which was initially drafted by C.K.

Supplementary Information

Mid-gap Trap State Mediated Dark Current in Organic Photodiodes

Christina Kaiser¹, Oskar J. Sandberg^{1*}, Stefan Zeiske¹, Sam Gielen², Wouter Maes², Koen Vandewal², Paul Meredith¹, Ardalan Armin^{1*}

¹Sustainable Advanced Materials (Sêr-SAM), Department of Physics, Swansea University, Singleton Park, Swansea SA2 8PP, United Kingdom

²Hasselt University, Institute for Materials Research (IMO), Agoralaan 1 – Building D, 3590 Diepenbeek, Belgium and IMEC, Associated Lab IMOMECA, Wetenschapspark 1, 3590 Diepenbeek, Belgium

*Email: ardalan.armin@swansea.ac.uk; o.j.sandberg@swansea.ac.uk

Figure S1 | Sensitively measured EQE spectra of narrow-gap D:PC₇₁BM photodiodes.

Figure S2 | Thin film and solution absorption (**a** and **b**, respectively) of the investigated narrow-gap donor polymers.

Figure S3 | Radiative saturation current density $J_{0,R}$ calculated from detailed balance showing strong dependence on the low-energy EQE shoulder. The lower integration bound $E_{\min}$ is often extended beyond the experimental limit (here $E_{\min}$ is between 0.5 to 0.6 eV) by a Gaussian fit to the CT state (dashed green line) and mid-gap trap state (dotted green line) absorption features, as shown for PBDB-T:PC₇₁BM. The experimental $J_D(-0.1 \text{ V})$ is typically 6-7 orders of magnitude above the calculated $J_{0,R}$ when $E_{\min} = 0.6 \text{ eV}$.

Figure S4 | Temperature dependent dark J - V characteristics and Arrhenius plots of J_D at different voltages for the PBTQ(OD):PC₇₁BM (a) and the PTTBAI:PC₇₁BM (b) photodiode. E_a (eV) is largest for $V = -0.05$ V and decreases for larger reverse bias or in forward bias by up to 0.09 eV for PTTBAI:PC₇₁BM.

Figure S5 | Dark current as a function of temperature for three commercial IR photodetectors. Note that the strong voltage dependence of $J_D(V)$ of the strained InGaAs photodetector apparent at low temperatures was previously attributed to recombination via trap mediated tunneling.³⁰

Figure S6 | Arrhenius plot of J_D at different voltages for three commercial IR photodetectors.

Figure S7 | Optical bandgap (E_{opt}) inferred for the onset of the responsivity spectrum of three commercial photodiodes, with $E_{\text{opt}} = 0.73$ eV for indium gallium arsenide (InGaAs; Thorlabs part number FDG03) and germanium (Ge; Thorlabs part number FDG03) and $E_{\text{opt}} = 0.46$ eV for strained InGaAs (Thorlabs, part number FD10D). Responsivity data were taken from the Thorlabs website.

Table S1 | E_a determined from Arrhenius plots of J_D for commercial inorganic photodetectors. Optical bandgap (E_{opt}) determined from the responsivity data provided by the manufacturer. E_a is in excellent agreement with E_{opt} , except for the conventional InGaAs photodiode.

Material	E_{opt} (eV)	E_a (eV) @ -0.05 V	E_a (eV) @ -0.1 V	E_a (eV) @ -0.9 V
Ge	0.732	0.730	0.726	0.759
InGaAs strained	0.460	0.534	0.463	0.363
InGaAs	0.725	0.866	0.866	0.866

Table S2 | Fit parameters $J_{0,\text{SRH}}$, R_{shunt} and V_{bi} extracted from the experimental dark J - V curves in reverse bias and J_{SC} - V_{OC} in forward bias using eq. 5 from the main text under the assumption that $B = 1$. Experimental V_{OC} from light J - V measurements under 1 sun illumination. τ_{SRH} calculated from $J_{0,\text{SRH}}$ via $\tau_{\text{SRH}} = qdN_0 \exp(-E_g/(2kT)) / J_{0,\text{SRH}}$.

Donor (D)	V_{OC} [V]	$J_{0,\text{SRH}}$ [A/cm ²]	R_{shunt} [Ω /cm ²]	V_{bi} [V]	τ_{SRH} [μ s]
PTTBAI	0.44	4.88 E-8	1.2 E7	0.38	0.31
PBTQ(OD)	0.40	3.35 E-8	2.9 E8	0.49	0.11
PTTQ(HD)	0.27	5.91 E-7	2.5 E5	0.10	1.20

Supplementary Note 1: List of materials

Short Name	Systematic Name
Ag	silver
DIO	1,8-diiodooctane
ITO	indium tin oxide
MoO ₃	molybdenum trioxide
PEIE	polyethylenimine ethoxylated
PTTBAI	alternating copolymer (P) of TT : thieno[3,2- <i>b</i>]thiophene and BAI : 7,14-bis(4-(2-octyldodecyl)thiophen-2-yl)diindolo[3,2,1- <i>de</i> :3',2',1'- <i>ij</i>][1,5]naphthyridine-6,13-dione
PBTQ(OD)	alternating copolymer (P) of B : benzene and TQ(OD) : 6,7-bis(5-(2-octyldodecyl)thiophen-2-yl)-4,9-di(thiophen-2-yl)-[1,2,5]thiadiazolo[3,4- <i>g</i>]quinoxaline
PTTQ(HD)	alternating copolymer (P) of T : thiophene and TQ(HD) : 6,7-bis(5-(2-hexyldecyl)thiophen-2-yl)-4,9-di(thiophen-2-yl)-[1,2,5]thiadiazolo[3,4- <i>g</i>]quinoxaline
PC ₇₁ BM	[6,6]-phenyl-C ₇₁ -butyric acid methyl ester
ZnO	zinc oxide
Zn(OAc) ₂ ·2H ₂ O	zinc acetate dihydrate

Supplementary Note 2: Derivation of dark current in the presence of Shockley-Read-Hall recombination

We consider an organic diode device consisting of contacts that are assumed to be ohmic for holes at the anode ($x = 0$) and electrons at the cathode ($x = d$), with the thickness of the active organic layer being given by d . The recombination rate between free electrons and holes, of densities n and p , inside the active layer is assumed to be dominated by trap-assisted recombination. The corresponding trap-mediated dark current density is given by

$$J = q \int_0^d \mathcal{R}_{\text{SRH}} dx, \quad \text{eq. (S1)}$$

where $\mathcal{R}_{\text{SRH}}$ is the net recombination-generation rate taking place via traps. In the Shockley-Read-Hall (SRH) formalism, $\mathcal{R}_{\text{SRH}}$ takes the form

$$\mathcal{R}_{\text{SRH}} = \frac{c_n c_p N_t (np - n_i^2)}{c_n (n + n_1) + c_p (p + p_1)}. \quad \text{eq. (S2)}$$

Here, N_t is the trap density, while c_n and c_p are the capture coefficient for a free electron and hole to find an available trap site, respectively. Furthermore, $n_1 = N_c \exp\left(\frac{E_t - E_c}{kT}\right)$ and $p_1 = N_v \exp\left(\frac{E_v - E_t}{kT}\right)$, with E_c and E_v being the conduction and valence level, while E_t is the energy of the traps and kT is the thermal energy; N_c and N_v are the available density of states for free electrons and holes, respectively. Note that $n_1 p_1 = n_i^2 \equiv N_c N_v \exp\left(-\frac{E_g}{kT}\right)$, where $E_g = E_c - E_v$ is the electrical energy level gap.

In general, the carrier densities are given by $n = N_c \exp\left(\frac{E_{Fn} - E_c}{kT}\right)$ and $p = N_v \exp\left(\frac{E_v - E_{Fp}}{kT}\right)$, where E_{Fn} and E_{Fp} are the corresponding quasi-Fermi levels. For Ohmic contacts, the applied voltage may be approximated as $V = (E_{Fn} - E_{Fp})/q$, where q is the elementary charge; hence, $np = n_i^2 \exp\left(\frac{qV}{kT}\right)$. For not too high injection current levels, the electrical potential outside the contact regions is to a good approximation linear with x . Under the conditions, we expect:

$$n \approx n_{\text{cat}} \exp\left(-\frac{q[V_{\text{bi}} - V]}{kT} \left[1 - \frac{x}{d}\right]\right) \quad \text{eq. (S3)}$$

$$p \approx p_{\text{an}} \exp\left(-\frac{q[V_{\text{bi}} - V]}{kT} \frac{x}{d}\right) \quad \text{eq. (S4)}$$

for $V \leq V_{\text{bi}}$, where n_{cat} and p_{an} are the virtual electron and hole density at the cathode and anode contact, respectively, whereas V_{bi} is an effective built-in voltage which accounts for the energy-level bending at the anode and cathode contacts: $qV_{\text{bi}} = kT \ln\left(\frac{p_{\text{an}} n_{\text{cat}}}{n_i^2}\right)$. Then, making use of $np = n_i^2 \exp\left(\frac{qV}{kT}\right)$, the dark current for $V < V_{\text{bi}}$ can be expressed as

$$J(V) = J_0(V) \left[\exp\left(\frac{qV}{kT}\right) - 1 \right] \quad \text{eq. (S5)}$$

with

$$J_0(V) = q c_n c_p N_t n_i^2 \int_0^d \frac{dx}{c_n (n + n_1) + c_p (p + p_1)}. \quad \text{eq. (S6)}$$

This integral can be approximated by making use of the following regional approximation. At the anode side, the hole density dominates in the SRH recombination rate. In this region, the contribution from

electrons may be neglected. On the other hand, on the cathode side the reverse is true. In this region electrons dominate and the contribution from holes to the SRH rate is negligibly small. Hence,

$$\begin{aligned} c_p p &\gg c_n n, \quad x < x_{1/2} \\ c_p p &\ll c_n n, \quad x > x_{1/2} \end{aligned} \quad \text{eq. (S7)}$$

where $c_p p(x_{1/2}) = c_n n(x_{1/2})$ at $x = x_{1/2}$, or equivalently, $p(x_{1/2}) = \sqrt{\frac{c_n}{c_p}} n_i \exp\left(\frac{qV}{2kT}\right)$. At flat-band conditions, $V = V_{bi}$, we then expect $c_p p_{an} = c_n n_{cat}$ and $p_{an} = \sqrt{\frac{c_n}{c_p}} n_i \exp\left(\frac{qV_{bi}}{2kT}\right)$.

Based on the above regional approximation, Equation (S7), the integral $J_0(V)$ may be split into two simpler integrals:

$$J_0(V) \approx q c_n c_p N_t n_i^2 \left[\int_{x_{1/2}}^d \frac{dx}{c_n n + c_n n_1 + c_p p_1} + \int_0^{x_{1/2}} \frac{dx}{c_p p + c_n n_1 + c_p p_1} \right] \quad \text{eq. (S8)}$$

Then, after making use of Equations (S3) and (S4), Equation (S8) can be evaluated as

$$J_0(V) = J_{0,\text{SRH}} \frac{2kT}{q[V_{bi}-V]} \times \ln \left[\frac{1+2B \exp\left(-\frac{qV}{2kT}\right)}{1+2B \exp\left(-\frac{qV_{bi}}{2kT}\right)} \right] \quad \text{eq. (S9)}$$

allowing for the total trap-mediated current density in the dark to be obtained for $V \leq V_{bi}$ via Equation (S5). Here, $B \equiv \frac{1}{2} \left(\sqrt{\frac{\tau_p}{\tau_n}} \frac{n_1}{n_i} + \sqrt{\frac{\tau_n}{\tau_p}} \frac{p_1}{n_i} \right)$, with $\tau_n \equiv \frac{1}{c_n N_t}$ and $\tau_p \equiv \frac{1}{c_p N_t}$ being the related lifetimes for electrons and holes, respectively, while

$$J_{0,\text{SRH}} = \frac{q n_i^2 d}{\tau_p n_1 + \tau_n p_1} \quad \text{eq. (S10)}$$

is the actual reverse-bias dark saturation current density in the presence of trap-assisted recombination.

Finally, we note that in the case of mid-gap trap states ($n_1 \approx p_1 \approx n_i$), the associated dark current density at large forward bias (but well below V_{bi}) and at high reverse bias can be approximated by

$$J \approx J_{0,\text{SRH}} \times \begin{cases} \frac{2BkT}{q[V_{bi}-V]} \exp\left(\frac{qV}{2kT}\right), & V \gg \frac{2kT}{q} \\ \frac{V}{q[V_{bi}+|V|]}, & -V \gg \frac{2kT}{q} \end{cases} \quad \text{eq. (S11)}$$

respectively, where $J_{0,\text{SRH}} = q n_i d / (\tau_p + \tau_n)$. On the other hand, in the limit $V \rightarrow V_{bi}$ (flat-band conditions), the dark current density [Equation (S5) and Equation (S9)] approaches

$$J \rightarrow \frac{2B J_{0,\text{SRH}}}{2B + \exp\left(\frac{qV_{bi}}{2kT}\right)} \left[\exp\left(\frac{qV_{bi}}{2kT}\right) - 1 \right]. \quad \text{eq. (S12)}$$

Supplementary Note 3: Noise currents

$$J = \frac{V}{R_{\text{shunt}}} + J_0^{\text{bb}} \left[\exp\left(\frac{qV}{kT}\right) - 1 \right] + J_0^{\text{SRH}} \left(\exp\left(\frac{qV}{kT}\right) - 1 \right) \quad \text{eq. (S13)}$$

$$J = \frac{V}{R_{\text{shunt}}} + J_0^{\text{bb}} \left[\exp\left(\frac{qV}{kT}\right) - 1 \right] + J_{0,\text{SRH}} \frac{2kT}{q[V_{\text{bi}} - V]} \ln \left[\frac{1+2B \exp\left(-\frac{qV}{2kT}\right)}{1+2B \exp\left(-\frac{qV_{\text{bi}}}{2kT}\right)} \right] \left(\exp\left(\frac{qV}{kT}\right) - 1 \right) \quad \text{eq. (S14)}$$

$$R_p = \left(\frac{dJ}{dV} \right)_{V=0}^{-1} = \left[\frac{1}{R_{\text{shunt}}} + \frac{J_0^{\text{bb}} q}{kT} + \frac{2J_{0,\text{SRH}}}{V_{\text{bi}}} \ln \left\{ \frac{1+2B}{1+2B e^{-\frac{qV_{\text{bi}}}{2kT}}} \right\} \right]^{-1} \quad \text{eq. (S15)}$$

a) Thermal noise

$$i_{\text{noise,th}}^2 = \frac{4kT}{R_p} \Delta F = 4kT \Delta F \left[\frac{1}{R_{\text{shunt}}} + \frac{J_0^{\text{bb}} q}{kT} + \frac{2J_{0,\text{SRH}}}{V_{\text{bi}}} \ln \left\{ \frac{1+2B}{1+2B e^{-\frac{qV_{\text{bi}}}{2kT}}} \right\} \right] \quad \text{eq. (S16)}$$

$$\text{At } V = 0 : \quad i_{\text{noise,th}}^2 = \frac{4kT}{R_{\text{shunt}}} \Delta F + 4J_0^{\text{bb}} q \Delta F + 8kT \frac{J_{0,\text{SRH}}}{V_{\text{bi}}} \ln \left\{ \frac{1+2B}{1+2B e^{-\frac{qV_{\text{bi}}}{2kT}}} \right\} \Delta F \quad \text{eq. (S17)}$$

$$\text{For } V \ll 0 : \quad R_p = \left(\frac{dJ}{dV} \right)^{-1} = R_{\text{shunt}} \rightarrow i_{\text{noise,th}}^2 = \frac{4kT}{R_{\text{shunt}}} \Delta F \quad \text{eq. (S18)}$$

b) Shot noise

$$i_{\text{noise,shot}}^2 = 2Jq\Delta F \quad \text{eq. (S19)}$$

$$\text{At } V = 0 : \quad J = 0 \text{ and } i_{\text{noise,shot}}^2 = 0 \quad \text{eq. (S20)}$$

$$\text{For } V \ll 0 : \quad J = J_0^{\text{bb}} + J_{0,\text{SRH}} \rightarrow i_{\text{noise,shot}}^2 = 2(J_0^{\text{bb}} + J_{0,\text{SRH}})q\Delta F \quad \text{eq. (S21)}$$