# Color Determination from a Single Broadband Organic Photodiode

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Establishing the color of incident light is essential for many applications, such as machine vision, but generally requires either a dispersive component or multiple spectrally selective photodetectors. In contrast, here an incident spectrum is parametrized using a single broadband organic photodiode (OPD). This is achieved by exploiting the incident wavelength dependence of charge extraction caused by optically induced trap states in a metal oxide electron extraction layer, which results in an atypical spectral dependence of the reverse bias photocurrent density vs voltage (J-V) characteristics. Such dependence is augmented by confining the active layer within an optical microcavity to influence the light absorption profile and thus metal oxide trap state density. The average wavelength of an (approximately normally distributed) incident spectrum is then calculated to within  $\approx$ 5 nm by algorithmically minimizing the difference between a measured J-V curve and one determined from the overlap integral of a trial spectrum with previously acquired voltage bias dependent external quantum efficiency (EQE) spectra.

Obtaining spectral information about incident light, whether a spectrum, a color image, or simply the average wavelength, is highly desirable for many applications such as machine vision and chemical analysis.<sup>[1–4]</sup> Such "color information" requires wavelength discrimination and is provided in a conventional spectrometer by a dispersive component such as a prism or diffraction grating. While such components enable high spectral

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resolution, they generally add to the size and cost of the total system. An alternative approach is to employ multiple narrowband detectors with different spectral sensitivity; such detectors are either intrinsically narrow-band using for example optical microcavities,<sup>[5–9]</sup> or broadband with external color filters.<sup>[10,11]</sup> Although much simpler than dispersion based spectrometers, this approach still requires a multitude of devices thus increasing the total device area, and reduces sensitivity to low illumination intensities since each photodiode detects only a proportion of the incident spectrum.

Here, we demonstrate an alternative source of wavelength discrimination. Rather than detecting only a relatively narrow wavelength range (i.e., <100 nm), we instead manipulate how a single broadband (500–950 nm) photodiode responds to illumination at different wavelengths. We illus-

trate this concept using a solution processed organic photodiode (OPD). OPDs are currently attracting extensive interest<sup>[2,3,12–16]</sup> due primarily to their compatibility with large-area, low-cost production<sup>[17]</sup> onto lightweight flexible substrates, which facilitates applications such as wearable sensors,<sup>[18,19]</sup> smart packaging,<sup>[20,21]</sup> and certain medical technologies.<sup>[18,22-24]</sup> Such devices usually operate under an applied reverse bias,<sup>[15]</sup> and have wavelength sensitivity that can extend from the UV to the near infra-red (NIR).<sup>[25,26]</sup> Various approaches have been employed to induce spectral sensitivity in OPDs without external color filtering.<sup>[27]</sup> These include changing the chemical structure of the component species<sup>[28]</sup> and using optical cavities (particularly near the optical band edge).<sup>[5-9]</sup> Other approaches include charge-collection narrowing (CCN), in which only colors with sufficiently low absorption coefficients produce carriers close enough to the far electrode for efficient extraction,<sup>[29,30]</sup> and charge injection narrowing (CIN), which similarly relies on different absorption coefficients but in this case employs photomultiplication at the far electrode due to charge tunneling injection induced by interfacial trap filling.<sup>[31-33]</sup> However, conventional OPDs (and indeed inorganic photodetectors) cannot usually distinguish between incident light with an energy greater than the optical bandgap since all excitons rapidly relax to the lowest excited state (i.e., Kasha's Rule)<sup>[34]</sup> prior to charge separation and subsequent extraction.

To overcome this limitation, we introduce incident wavelength dependence by incorporating a metal oxide electron extraction layer (EEL)<sup>[35–37]</sup> between the organic active layer and the electron collecting contact. Such metal oxide layers can have incident



illumination wavelength (not just intensity) dependent trap state distributions that influence charge extraction.<sup>[35,38-42]</sup> This spectrally dependent charge extraction is experimentally observed as a dependence of the photocurrent density versus voltage (I-V)characteristics on wavelength (in addition to the usual intensity dependence). It can be further enhanced by incorporating the organic and metal oxide layers within an optical cavity<sup>[5,6,9]</sup> to manipulate the extent of light absorption by the metal oxide layer. Crucially, if this *I*–V variation with illumination wavelength (equivalent to the bias dependence of an external quantum efficiency (EQE) spectrum) is known across the entire incident spectra, there is in principle enough information in a single measured *I-V* characteristic to parameterize, but not fully determine, the incident spectrum. While extracting spectral information in this manner requires a simple minimization algorithm, prior characterization of the device, knowledge of the incident light intensity and sufficient time to perform a voltage sweep, our approach enables the average wavelength of an (approximately normally distributed) incident spectrum to be determined within  $\approx 5$  nm using a single broadband OPD.

We begin by outlining the OPD device architecture used to demonstrate our proposed spectral parameterization approach. **Figure 1**a shows a cross-sectional scanning electron microscope (SEM) image, indicating the multiple layers used to create the top illuminated device. Briefly considering each layer from the bottom upwards, ~100 nm of Au is evaporated onto a glass substrate (in principle replaceable with a flexible alternative) to serve as an electrical contact and a reflective back mirror. This

is followed by a metal oxide layer that induces the wavelength variation in reverse-bias J-V characteristics, here  $\approx 30$  nm of amorphous indium gallium zinc oxide ( $\alpha$ -IGZO).<sup>[43,44]</sup> IGZO is widely used for metal oxide thin film transistors (TFTs),<sup>[37,43-47]</sup> and here forms an EEL since its -4.2 eV conduction band<sup>[48,49]</sup> provides a downward energetic cascade (see energy level diagram<sup>[50-53]</sup> in Figure 1b) for electrons under reverse bias (when the Au electrode is negative relative to the Ag electrode, see charge carrier directions in Figure 1b).<sup>[15]</sup> Furthermore, its deep (-7.5 eV) valence band<sup>[43,48]</sup> suppresses unwanted hole injection, thus reducing dark current density  $J_d$ .<sup>[48,49]</sup> Crucially for this application, and in common with ZnO,<sup>[35,39,40]</sup> the IGZO trap state density is influenced by the incident light color<sup>[38,42]</sup> so can induce wavelength dependent electron extraction.

Next follows the active layer, a  $\approx 260$  nm thick spin coated film that is a 1:2 (by weight) blend of low bandgap diketopyrrolopyrrole (DPP) derived polymer donor poly{2,2'-[(2,-5-bis(2-hexyldecyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)dithiophene]-5,5'-diyl-alt-thiophen-2,5-diyl}) (PDP93T)<sup>[54]</sup> (structure Figure 1c inset, absorption spectrum in Figure 1e) and common fullerene derivative acceptor [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PC<sub>60</sub>BM).<sup>[55]</sup> Although the claimed electrochemical energy levels for conjugated species can vary by up to 0.5 eV depending on the measurement technique, we show in Figure 1b values acquired via square wave voltammetry (SWV).<sup>[52]</sup> The HOMO and LUMO were measured at approximately –4.9 and –3.1 eV for PDPP3T and –5.8 and –3.6 eV for PC<sub>60</sub>BM, consistent within 0.2 eV to values



**Figure 1.** Device structure and initial characterization. The device stack is shown as a a) cross-sectional SEM image and b) an energy level diagram, with typical OPD *J*–V characteristics c) under simulated solar illumination (blue) and dark conditions (black) (PDP93T structure inset). The modeled optical electric field  $|E(z)|^2$  distribution d) shows optical modes at ~540 and ~900 nm, apparent in the difference e) between PDP93T:PC<sub>60</sub>BM film absorption (green), the calculated fraction of absorbed photons in the device (grey shading) and corresponding EQE spectrum at –2 V applied bias (red).

Adv. Optical Mater. 2020, 8, 1901722

acquired with ultraviolet photoemission spectroscopy (UPS).[52] Combining these conjugated species in the ubiquitous bulkheteroiunction (BHI) architecture allows this energy level offset to facilitate charge separation at the donor-acceptor (D-A) interface, with free charges extracted via a bicontinuous networks.<sup>[12,56,57]</sup> PDPP3T is chosen here due to its low optical bandgap of ≈930 nm (≈1.3 eV)<sup>[28]</sup> that enables NIR detectivity. Furthermore, PDPP3T:PC<sub>60</sub>BM blends have been widely used in solar cells,[58-61] with the blend ratio and processing conditions used here previously optimized for maximum power conversion efficiency.<sup>[59]</sup> Above the active layer is ≈60 nm of evaporated molybdenum oxide (MoO<sub>3</sub>). This n-type semiconductor is widely used as a hole extraction layer (HEL),<sup>[51,62]</sup> despite approximate conduction and valence band energies of -5.5 and -8.6 eV, respectively;<sup>[53]</sup> indeed, it has been proposed that electron transfer from the organic semiconductor results in an Ohmic contact.<sup>[63,64]</sup> Finally,  $\approx 16$  nm of Ag form a semitransparent top electrode. The thicknesses of these upper layers are a compromise between light transmission and optical confinement (top contact transmission, reflection, and absorption spectra are shown in Figure S1 in the Supporting Information); higher reflection enhances cavity finesse but reduces light in-coupling.

Determining the real refractive indices and extinction coefficients over the relevant spectral range (500-1000 nm) with ellipsometry (see Figure S2 in the Supporting Information) enables the electric field intensity  $|E|^2$  to be calculated as a function of depth using optical modeling<sup>[7]</sup> (brief details in the Experimental Section, further discussion in the Supporting Information), thus guiding the choice of layer thickness to create a second order Fabry-Perot cavity. Our rationale for tailoring optical confinement is primarily to enhance the wavelength dependence of optically induced trap formation by varying the light absorption, and hence trap state density, in the metal oxide EEL. This spectral variation is clear from Figure S3 (Supporting Information), which shows the fraction of photons absorbed by each device layer at each wavelength. The spatial distribution of these modes can be seen from the modeled  $|E|^2$  in Figure 1d, with dominant modes at  $\approx 540$ and ≈900 nm (and a weaker mode at ≈670 nm) (we limit our investigation to the 500-1000 nm spectral range since this is where the optical modes are located, and furthermore where the charge extraction wavelength dependence, necessary for our color determination approach, is greatest). Layer thicknesses were carefully chosen to locate a mode at ≈900 nm, thus enhancing NIR absorption near the optical band edge. Figure 1e shows that these optical cavity modes cause the modeled spectral distribution of absorbed photons (calculated from the fraction of incident photons absorbed by each layer using the transfer matrix method, see the Experimental Section) to differ substantially from the thin film absorption spectrum. This difference in spectral distribution, not observed in a previous study on a similar device<sup>[48]</sup> with much thinner extraction layers and thus far less optical confinement, is supported by the experimentally measured EQE spectrum, which approximately maps the features of the modeled distribution. Differences between the EQE are attributed the real device having a lower cavity finesse than the model, likely due to rough surfaces, along with wavelength dependent charge collection efficiency (discussed below).

Before exploring and then utilizing the incident photon energy dependence of charge extraction, our next step is to confirm that the device functions satisfactorily as an OPD and that reproducible *I*–*V* characteristics can be obtained. Figure 1c shows that the device (when scanned at 50 mV s<sup>-1</sup>) exhibits some hysteresis in dark conditions, which we predominantly attribute to displacement current (charge accumulation within intrinsic traps the in metal oxide EEL may also contribute). The device has  $J_d \approx 6 \times 10^{-7}$  mA cm<sup>-2</sup> at -2 V applied bias, around five times lower than that recorded by Zhou et al. for a similar PDPP3T:PC70BM device<sup>[56]</sup> and amongst the lowest OPD I<sub>d</sub> values in recent literature comparisons.<sup>[12,15]</sup> This is achieved by minimizing extrinsic leakage pathways such as pinholes<sup>[65]</sup> by using an SU-8 edge cover layer and having a comparatively thick (≈260 nm) active layer.<sup>[25]</sup> Using the EQE spectrum (Figure 1e) together with  $I_{d}$  (both at -2 V) to calculate the common photodetector figures-of-merit<sup>[28]</sup> responsivity R = q EQE/E and shot noise limited (i.e., without considering frequency dependence)<sup>[66,67]</sup> specific detectivity  $D^* \approx R/\sqrt{2q J_d}$ gives maximum values of  $\approx 0.16$  A W<sup>-1</sup> and  $\approx 1.1 \times 10^{13}$  Jones at 550 nm, respectively (q is the electronic charge, E is energy). At the 900 nm optical mode close to the optical band edge  $R \approx 0.08$  A W<sup>-1</sup> and  $D^* \approx 6.0 \times 10^{12}$  Jones (Figure S4 in the Supporting Information shows full spectra for R and  $D^*$ ). Relative to other reported OPDs,<sup>[12,15,28,56,68]</sup> this device has a lower than average EQE (and thus *R*) but a shot noise limited *D*\* commensurate with the state-of-the-art due to the low  $J_d$ .

The all-important wavelength dependence in the *J*–*V* characteristics is illustrated in **Figure 2**a for the outlined IGZO/ PDP93T:PC<sub>60</sub>BM device. It shows a map of voltage sweeps under a series of illumination wavelengths (10 nm increments with a 10 nm bandwidth), acquired using a variable neutral density filter to ensure a constant photon flux  $\phi$  of  $\approx 2.15 \times 10^{15} \text{ s}^{-1} \text{ cm}^{-2}$  at each wavelength (see the Experimental Section). Given that EQE is defined as<sup>[69]</sup>

$$EQE(\lambda, V) = \frac{J(\lambda, V)}{q\phi(\lambda)}$$
(1)

the photocurrent density at each wavelength  $\lambda$  and applied voltage V is directly proportional to EQE, enabling the latter to be extracted from voltage transects. Acquiring EQE spectra using multiple *J*–V sweeps, rather than in the conventional manner of scanning the wavelength at a constant voltage bias, improves reproducibility since the forward bias applied at each wavelength appears to "reset" the device (see Figures S5 and S6 in the Supporting Information). EQE spectra acquired from illuminated *J*–V sweeps are shown for a selection of reverse biases in Figure 2b. Immediately apparent is the expected enhancement at the cavity modes where light absorption, and thus charge carrier generation, is greater. However, our proposed approach to color determination is underpinned not by differences in absolute EQE but instead by spectral variation in the shape of the *J*–V characteristics.

The spectral variation in bias dependence can be seen more clearly by considering the EQE ratio relative to 0.0 V applied bias (bottom panel). Comparing the reverse bias J-V characteristics at selected wavelengths (Figure 2c) shows this difference in shape (not just magnitude) with incident wavelength.







**Figure 2.** Wavelength dependence of J-V characteristics, during a scan from +4 to -2 V. Map of current density vs reverse bias a) voltages at different wavelengths (top), with EQE spectra at specific biases (bottom). b) shows normalized (at 550 nm, top) and relative EQE spectra (i.e., divided by the spectrum acquired at 0.0 V bias, bottom), while c) shows J-V characteristics at specific wavelengths (top), and the J-V curves relative to 500 nm (bottom).

Plotting the J-V curves relative to the (arbitrarily selected) 500 nm curve emphasizes this variation, with the four selected incident wavelengths resulting in different relative bias dependences. We note that the extent of spectral variation in J-V characteristics is not uniformly distributed, causing our approach to have greater sensitivity in the 650–850 nm range than below 650 nm. The possible origin of this variation, along with a proposed remedy, is discussed below.

In considering the origin of this wavelength variation in photocurrent bias dependence, we consider EQE as the product of the efficiencies of three separate processes, specifically light absorption  $\eta_{abs}(\lambda)$ , charge generation  $\eta_{gen}(V)$ , and collection  $\eta_{\rm col}(\lambda,V)$ .<sup>[69]</sup> We start with the assumption that absorption is independent of applied voltage (i.e., neglecting electroabsorption), and that charge generation (from a photogenerated exciton) is largely independent of wavelength (since excitons relax to lower energy charge transfer (CT) states prior to charge separation; we note that while there may be some slight wavelength variation due to different exciton diffusion rates to the D-A interface, this is unlikely to dominate and does not affect our spectral parameterization approach outlined below).<sup>[70]</sup> Thus,  $\eta_{col}(\lambda, V)$  must be predominantly responsible for the observed wavelength and voltage dependence of photocurrent (even if there is or can be different for absorption by the donor or by the acceptor in the blend. We assert that trap states within the metal oxide EEL causes this wavelength variation, since it is not apparent in PDPP3T:PCBM OPDs with a LiF/Al EEL (see Figure S7 in the Supporting Information).<sup>[28]</sup> As such, we propose in Figure 3a mechanism for the influence of photoinduced IGZO trap states<sup>[38]</sup> on charge extraction and hence *I*-V characteristics. Following light absorption and charge separation, electrons drift under the applied electric field F towards the Au electrode. However, some electrons are detained by the IGZO trap states (both intrinsic and photoinduced), creating a space charge layer (SCL) and thus an energetic barrier to extraction. The reduced electron mobility  $\mu_e$  relative to hole mobility  $\mu_h$  redistributes *F* so that it is greatest over the IGZO layer (to maintain charge neutrality, i.e.,  $F_e \mu_e = F_h \mu_h$ ). Applying a larger reverse bias voltage enables electrons to overcome this barrier, thus increasing photocurrent.



**Figure 3.** Schematic band diagram showing the influence of EEL traps on charge extraction. Under illumination, excitons (shading) are primarily generated in the polymer, before dissociating at a PDPP3T:PC<sub>60</sub>BM interface and thus producing holes (red) in the PDPP3T HOMO and electrons (blue) in the PC<sub>60</sub>BM LUMO. Charges drift in the applied field, with electrons accumulating in the IGZO trap states. This accumulation creates and extraction barrier and increases the effective field.

Our interpretation is supported by additional J-V characteristics with different scan parameters. Most straightforwardly, for J-V curves with 700 nm illumination (thus avoiding the dominant optical modes at ≈540 and ≈900 nm), a higher photon flux reduces extraction efficacy ( $\eta_{col}$ ), illustrated by flatter curve implying greater electron trapping and thus recombination (Figure S8, Supporting Information). This is attributed to an increased photogenerated trap state density and a higher proportion of traps being filled, both of which raise the extraction barrier. Furthermore, increasing the maximum applied forward bias to +4 V (Figure S5, Supporting Information) leads subsequently to more efficient charge extraction in reverse bias, attributed to the forward bias electric field both sweeping out trapped carriers and reducing trap state density due to bias stress.<sup>[71]</sup> Such a process should negate any previous device history (e.g., a different prior illumination color), thus making each scan independent (a more detailed discussion of factors influencing the data acquisition rate is presented in the Supporting Information).

The influence of initially applying a positive bias is especially clear in Figure S9 (Supporting Information), which maps J-V characteristics and thus EQE as a function of wavelength for down sweeps starting at -2 V and shows a plateau in the J-V characteristics between  $\approx$ 500 and  $\approx$ 720 nm. While this wavelength region broadly corresponds to increased charge generation from the optical modes, the same feature (and indeed J-V shape in Figure 2c), does not appear when illuminating at the  $\approx$ 900 nm optical mode. As such, the observed wavelength dependence is not purely a function of cavity mode location leading to increased charge density at the IGZO/BHJ interface, demonstrating that incident photon energy also matters.

We rationalize this photon energy dependence by invoking work by Chen et al., which investigated how illumination below the optical bandgap affected the threshold voltage  $V_{\rm th}$  of an IGZO TFT.<sup>[38]</sup> Two competing processes were identified, with blue ( $\approx$ 470 nm) and green ( $\approx$ 520 nm) illumination leading to a time-dependent negative  $V_{\rm th}$  shift while red ( $\approx$ 700 nm) and IR ( $\approx$ 915 nm) light caused a less pronounced (but faster) positive shift (see Figure S10 in the Supporting Information, adapted from Ref. [38]). The negative shift was attributed to high energy light forming hole trap states, while all illumination colors created electron trap states. It is these photogenerated trap states to which we attribute the wavelength dependency of the *J*–*V* characteristics, since their character depends on incident photon energy while their formation rate scales with light intensity and hence cavity mode overlap into the IGZO layer (Figure 1d).

This transition in trap state behavior with incident wavelength (Figure S10, Supporting Information) can be related to the observation that the greatest variation in bias dependence lies between 650 and 850 nm (Figure 2). While this leads to our color determination approach having spectrally variable sensitivity, the role of trap states suggests a possible mechanism to spectrally broaden the high sensitivity window. Since the properties of IGZO trap states are highly dependent on both composition and processing conditions,<sup>[37,44,72–74]</sup> varying these parameters may enable adjustment of spectral region where variation in charge extraction with illumination color is most pronounced. By combining devices with different spectral sensitivity profiles, and incorporating their total contribution into the fitting algorithm, sensitivity could thus be extended across a broader spectral region.

The demonstrated wavelength variation in the EQE bias dependency can then be exploited to extract spectral information. Our approach, represented as a flow chart in Figure 4a, fundamentally rests on the photocurrent being proportional to the overlap integral between the EQE spectrum and the incident photon flux,<sup>[69]</sup> that is

$$J(V) = q \int EQE(\lambda, V)\phi(\lambda) d\lambda$$
(2)

Equation (2) is well established, and widely used to calculate the short circuit current  $I_{sc}$  in organic photovoltaic (OPV) devices where  $\phi(\lambda)$  is typically an AM1.5G solar spectrum.<sup>[75,76]</sup> When the EQE bias dependency is included, Equation (2) clearly enables a *I–V* characteristic to be reproduced. However, it is important to note that if  $EQE(\lambda, V)$  is intensity dependent, as here, the total photon flux  $\int \phi(\lambda) d\lambda$  must be equal to the photon flux at each EQE data point to ensure that the device is under equivalent condition. This overlap integral approach is illustrated in Figure 4b, which shows the variation in EQE spectra over a series of voltage biases (again with constant light intensity per data point) along with a test light emitting diode (LED) spectrum (separately measured using a spectrometer) that we ultimately aim to parameterize from a measured I-V curve. Also shown are two hypothetical Gaussian peaks with the same area (i.e., light intensity), used to demonstrate the wavelength dependence of the *I-V* characteristic. Figure 4c shows the I-V curves calculated using Equation (2) with the EQE spectra in Figure 4b for both the measured LED spectrum and the two hypothetical spectra. A measured I-V characteristic for the device under LED illumination is superimposed, showing the similarity with that calculated by applying Equation (2) to the LED spectrum. Note that if there was no wavelength dependence to EQE(V), incident  $\phi(\lambda)$  with the same total flux would give the same shaped *I*-V characteristics.

To extract spectral information from a measured J-V characteristic, we work backwards to determine  $\phi(\lambda)$  that, when an overlap integral with EQE( $\lambda$ , V) is calculated, would reproduce the same *I*-*V* curve. We thus employ a standard Levenberg-Marquardt minimization algorithm<sup>[77]</sup> (with varied starting parameters to avoid local minima), evaluating Equation (2) using a set of previously acquired EQE( $\lambda$ , V) spectra (Figure 2b) against a varying trial  $\phi(\lambda)$  to minimize the weighted residual  $I_{res}(\lambda_0, \sigma)$ between measured and calculated J-V characteristics (see the Experimental Section). This approach requires the trial  $\phi(\lambda)$  to be parametrized, here as a Gaussian peak with central wavelength  $\lambda_0$  and standard deviation  $\sigma$ . Figure 4d shows  $J_{res}(\lambda_0, \sigma)$ , along with the parameters that correspond to the hypothetical Gaussian spectra in Figure 4b; notably,  $\lambda_0$  is far more tightly defined than  $\sigma$ . The global minimum in  $J_{res}(\lambda_0, \sigma)$  can be identified at  $\lambda_0$  = 733 nm and  $\sigma$  = 6.5 nm. Reconstructing the incident spectrum with the global minimum parameters (see Computational Methods in the Experimental Section) returns a spectrum located at a similar wavelength to the incident LED spectrum (Figure 4e), thereby demonstrating our central claim that spectral parameters can be extracted from a single OPD.

Finally, we explore factors that may influence the precision of incident color determination (defined here as the average ADVANCED SCIENCE NEWS \_\_\_\_\_\_ ADVANCED OPTICAL MATERIALS www.advopticalmat.de



**Figure 4.** Spectral characterization. a) A flow chart outlines how the incident spectrum is parametrized. b) EQE spectra (grey) over a wide range of reverse biases, overlaid with an LED spectrum centered at 730 nm and two hypothetical Gaussian spectra. c) Measured and calculated (from overlap integrals) *J*–*V* characteristics. d) Summed residuals between the measured *J*–*V* characteristic from LED illumination and those calculated for hypothetical Gaussian spectra with varying  $\lambda_0$  and  $\sigma$  (blue and red circles indicate parameters corresponding to hypothetical spectra in (a)). e) Comparison of LED incident spectra that are measured spectroscopically and calculated from the measured *J*–*V* characteristic.

wavelength of the incident spectra) using our approach. To achieve this, we first linearly interpolate our experimental EQE( $\lambda$ , V) data in wavelength to produce a realistic hypothetical data set with 1 nm wavelength increments. We then consider two possible sources of uncertainty that may influence the incident spectrum characterization. Most straightforwardly, the incident spectra may not be normally distributed, leading to variation between the simulated J-V from the overlap integrals with a trial Gaussian peak and the "measured" J-V curve. To test the effect of this discrepancy, we calculate the location and width of two incident spectra with skewed Gaussian distributions (**Figure 5**a). Perhaps surprisingly, our approach is relatively insensitive to the skew, with deviation in calculated central wavelength of <3 nm.

Secondly, the accuracy with which any incident spectrum can be parametrized clearly depends on the previously acquired J-Vcharacteristics used to calculate EQE spectra and thus overlap integrals. To simulate the effect of experimental uncertainty, each EQE( $\lambda$ , V) data point has a percentage of the original value (drawn from a random distribution) added or subtracted (see the Experimental Section). A hypothetical Gaussian incident spectrum is used on the interpolated original data to produce a J-V curve. The minimization approach with outlined in Figure 4a is then applied on the "disordered" data, with the average location of the calculated peak determined as a function of the applied disorder (width of the random distribution as a percentage). Figure 5b shows that narrower peak widths are more sensitive to disorder in the EQE( $\lambda$ , V) array, because the variation is averaged out in broader overlap integrals. Notably, a 50 nm wide peak can be located almost perfectly (within 1 nm) even with 10% disorder in EQE( $\lambda$ , V). However, a systematic shift in *J*-*V* curve shape and amplitude with wavelength, most likely due to a different light intensity, would clearly cause a shift in the calculated peak location. We suggest that this could be minimized by characterizing the device at a wide range of relevant light intensities and then determining which previously acquired data set was applicable by simultaneously recording light intensity using a second detector. Other factors that may influence the accuracy of color determination with our approach are device stability (demonstrated over 8 days with *I*–V measurements in Figure S11 in the Supporting Information) and background illumination. While both these influences are discussed further in the Supporting Information, we note that the outlined algorithmic approach to color determination is highly suitable for in situ calibration, similar to that employed in some OLED displays.<sup>[78]</sup> For example, a spectral correction factor could be generated by simply illuminating the device with a known spectrum and comparing with





**Figure 5.** Potential accuracy of spectral parameter extraction. Hypothetical skewed Gaussian incident spectra a) are used to calculate a J-V curve from the EQE overlap integral, from which a Gaussian spectrum is approximated as outlined in Figure 4a. b) Introducing random disorder in  $J(V, \lambda)$  characteristics, represented as standard deviations in EQE spectra, shows that broader peaks are far less sensitive to this disorder.

the calculated output, thus negating the effect of any long term device variation on color determination.

In summary, we have developed a PDPP3T:PC<sub>60</sub>BM OPD with a metal oxide (here  $\alpha$ -IGZO) EEL that imparts spectral variation to the *J*–*V* characteristics. This variation is attributed to the formation of photon energy dependent light-induced trap states that impede electron extraction, with the wavelength dependence augmented by an optical cavity. Such wavelength dependent charge extraction, in conjunction with previous characterization of **EQE**( $\lambda$ , *V*) at different light intensities, knowledge of the incident light intensity and application of a minimisation algorithm, enables the approximate spectral peak location to be obtained from the *J*–*V* characteristic of a single OPD with, in principle, a precision of <5 nm. Although reliant on a metal oxide interlayer, the proposed approach should be active layer agnostic and thus applications.

### **Experimental Section**

Device Fabrication: A patterned reflecting Au bottom mirror and contact (100 nm) was thermally evaporated onto  $3 \times 3$  cm glass substrates, followed by sputtering two IGZO layers with a total thickness of  $\approx$ 30 nm. An edge cover/pixel definition layer was deposited and photolithographically structured (exposure and development) to define the pixel active area. PDPP3T (from California Organic Semiconductors Inc.)

and PC<sub>60</sub>BM (from Nano-C) in a 1:2 weight ratio were dissolved in a solvent mixture of CHCl<sub>3</sub> and ortho-dichlorobenzene (o-DCB) (92.5% to 7.5% volume ratio) at concentrations of 6 and 12 mg mL<sup>-1</sup>, respectively. The solution was stirred at 1500 rpm at 90 °C for 4 h then spin-coated at 700 rpm. Devices were then left under  $\approx 1 \times 10^{-6}$  mbar vacuum for 4 h to remove residual solvent. Finally, MoO<sub>x</sub> and Ag (both from Alfa Aesar) were evaporated to form the semitransparent top contact.

OPD Characterization: The Absorption Spectrum of a 100 nm PDPP3T: PC<sub>60</sub>BM film was determined using a Varian CARY-5000 spectrophotometer, with transition T and reflection R subtracted via A = 100 - R - T. A sample MoO<sub>x</sub>/Ag film was measured using a Perkin Elmer Lambda UV/VIS/NIR 1200 spectrometer.  $n(\lambda)$  and  $k(\lambda)$ were determined using optical ellipsometry (at 75°) and Semilab -Spectroscopic Ellipsometry Analyzer (V1.5.1) software. The emission spectrum of a Thorlabs M730L5 LED was determined with an Avantes spectrometer. SEM images were acquired using a high-resolution FIB-SEM (FEI Nova Nanolab 200 DualBeam), with labeled thicknesses taken from the optical model that approximately produces the experimental EQE spectra. I-V characteristics were acquired with downward voltage sweeps from +4 to -2 V at a rate of 50 mV s<sup>-1</sup> (unless stated otherwise) using a Keithley 2400 source-measurement unit. Devices were kept in an enclosed nitrogen filled box during storage and measurement to avoid photo-oxidation. Color dependence was achieved using white light passed through an Oriel Cornerstone 130 monochromator with 10 nm bandwidth. Incident photon flux was kept constant using a silicon reference diode with a known EQE spectrum and a calibrated beam splitter, then adjusted for each color using neutral density filters. Dark current and one sun illumination (an approximate AM1.5G spectrum) measurements (Figure 1c) were taken with a separate configuration in a nitrogen filled glovebox, with J-V characteristics (from which  $J_d$  is extracted) were recorded on 1 mm  $\times$  1 mm devices at a scan rate of 10 mV s<sup>-1</sup>. EQE spectra were determined using  $2 \times 2$  mm devices due to the experimental constraints of the N<sub>2</sub> filled sample boxes, and calculated from color dependent /-V sweeps using Equation (1) to ensure consistency in device history for each wavelength (this method is contrary to the standard practice of sweeping wavelength at a constant bias).

*Computational Methods*: The 1D electric field intensity distribution at each wavelength was determined using both finite-difference time domain (FDTD) and transfer-matrix-method (TMM) algorithms (to increase numerical reliability)<sup>[79]</sup> with the commercial software package "Lumerical FDTD" (described in more detail in the Supporting Information). *J*–V characteristics were fitted using a standard Levenberg– Marquardt algorithm within the LMFIT Python package.<sup>[80]</sup> The incident Gaussian spectrum producing the *JV*-curve with the lowest residual,

specified by  $J_{res}(\lambda_0, \sigma) = \sum_{0V}^{-2V} (J_{meas}(V) - J_{calc}(V, \lambda_0, \sigma))$ , was identified by fitting with a range of starting values to avoid local minima. Simulated spectral parameterization was performed on the (interpolated to 1 nm increments)  $J(V,\lambda)$  array (Figure 2a). Disorder was introduced according to  $J_{dis}(V,\lambda) = J(V, \lambda)(1 + 0.01x)$ , where x is drawn from a normal distribution with width corresponding to "disorder%" in Figure 5b. The average calculated peak location and standard deviation was determined by applying overlap integral minimization approach to five iterations.

## **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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1901722 (7 of 9)

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# **Conflict of Interest**

The authors declare no conflict of interest.

## **Keywords**

charge extraction, indium gallium zinc oxide, organic photodiodes, spectral selectivity, trap states

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