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Filterless Narrowband visible Photodetectors

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Abstract

Wavelength selective light detection is crucial for many applications such as imaging and machine vision. Narrowband spectral responses are required for colour discrimination and current systems use broadband photodiodes combined with optical filters. This approach increases architectural complexity, and limits of the quality of colour sensing. Here we report filterless, narrowband red, green, and blue photodiodes with tuneable spectral responses. The devices have simple planar junction architectures with the photoactive layer being a solution processed mixture of either an organohalide perovskite or lead halide semiconductor, and a neutral or cationic organic molecule. The organic molecules modify the optical and electrical properties of the photodiode and facilitate narrowing charge collection narrowing of the device's external quantum efficiency. These red, green, and blue photodiodes all possess full-width-at-half-maxima of <100 nm and performance metrics suitable for many imaging applications.

Photodetectors are the mainstay of imaging systems, environmental surveillance, communication and biological sensing.^{1, 2, 3, 4} In general, photodetectors can be classified as spectrally broadband^{5, 6, 7} or narrowband^{8, 9, 10} depending on the width of their spectral response window. Spectral discrimination in state-of-the-art commercial photodetectors is currently realised using broadband inorganic semiconductor photodiodes in combination with a dichroic prism or set of optical filters.^{11, 12, 13} However, this approach increases photodetector architectural complexity and cost, and is a major limitation in achieving higher pixel densities in imaging systems.^{12, 14} Furthermore, the use of input filtering creates additional optical interfaces, decreases the image sharpness, negatively impacts colour constancy, and also imposes UV-stability challenges.^{12, 15, 16} These problems are the main motivations for finding new ways to achieve narrowband light detection without the need for input optical filtering.

A number of alternative strategies are emerging for colour discrimination and these include: i) the use of truly narrowband absorbers such as organic semiconductors and nano-crystals^{17, 18, 19} in the photodiode active layer; ii) splitting the light into its component colours⁹; and iii) optical manipulation of the light absorption within the active layer¹². These approaches are yet to demonstrate the appropriate set of performance metrics for any meaningful applications, i.e., spectrally tuneable narrowband responses having full-width-at-half-maxima (FWHM) <100 nm, in combination with low noise, high speed and large linear dynamic range.¹⁰ Recently, Armin *et al.* established a method for achieving narrowband spectral responses in red and near infrared (NIR) photodiodes exploiting broadband absorbing organic semiconductors.¹⁰ This method was based upon manipulating the internal quantum efficiency (IQE) of the photodiode *via* charge collection narrowing (CCN). Paradoxically, the CCN concept utilises the relatively poor charge transport properties of organic semiconductors in thick bulk heterojunction photodiodes. These devices are engineered such that only volume generated photocarriers are collected and hence produce current. Volume photogeneration occurs for incident light energies around the optical gap of the junction material combination (a blend of an organic semiconductor acceptor and donor) and delivers a narrow IQE in the tail of the optical absorption. Although in principle manipulating the electro-optics in this way is a generic, architecturally-driven approach, the implementation of CCN still relies upon having materials with the appropriate optical gap, absorption and electrical transport properties. These considerations have so far limited this promising concept to red and NIR narrowband organic semiconductor photodiodes.

In this paper we report narrowband red, green and blue photodiodes all with FWHM <100 nm. This is achieved using the CCN concept in organohalide perovskites and mixed lead halide semiconductors where we engineer two absorption onsets controlled by varying the blend ratio of halides in the semiconductors^{20, 21, 22}; and/or by the addition of high concentrations of an organic (macro)molecule in the composite film that forms the junction. In so doing we have been able to simultaneously control the optical and electrical transport properties of the photodiode, and produce a unique set of fully tuneable narrowband responses across the entire visible spectrum and into the NIR.

Charge Collection Narrowed Photodiodes

The working principles of the charge collection narrowing concept (CCN) have been discussed in detail by Armin *et al.*¹⁰. We re-iterate the basic principles here for clarity, and particularly point out the current limitations of CCN photodiodes. Consider first the simplest of photodiode architectures shown in the inset of **Figure 1**: a photoactive layer (the junction) sandwiched between a transparent anode [Indium tin oxide (ITO)/ Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS)] and cathode stack (C60/LiF/Ag). These materials are typical of those used to engineer efficient hole and electron extraction and suppress dark current in organic^{7, 10} and the first organohalide perovskite broadband photodiodes²³. In such a simple architecture CCN is realised because the junction is optically and electrically “thick”, i.e., has a high optical density and long transit time for photogenerated carrier extraction. The principle is demonstrated for a hypothetical junction with absorption (α) as shown in **Figure 1** that has two distinctly different optical density regimes: high α where the incident light intensity falls off exponentially within the junction (the Beer-Lambert regime); and low α where the incident light propagates within the junction and is subject to interference (the cavity regime). In the Beer-Lambert regime, photogenerated carriers are produced in the vicinity of the transparent conducting electrode, and we term this **surface generation**. In the cavity regime photogenerated carriers are produced throughout the junction including in the vicinity of the metallic electrode, and we term this **volume generation**.

Comparing these two cases, the surface generated carriers will be subject to significant recombination losses due to the higher local carrier concentration and imbalanced transit times for the electrons and holes. Thus, the charge collection efficiency (η_{coll}) is suppressed resulting in low (if not zero) external quantum efficiency (EQE, dashed line in **Figure 1**) in the Beer-Lambert region. Recombination losses will be lower for volume generated carriers and the EQE is maintained in the cavity regime. For the wavelengths longer (photons lower in energy) than the optical gap of the junction, the absorption coefficient decreases to zero sharply where the photo-response vanishes. Finally, if two absorption onsets can be engineered as shown in **Figure 1**, then the narrowband response can be optimized and completely controlled *via* the CCN electro-optical mechanism. The width of the response window is typically reported as the full-width-at-half-maximum (FWHM) $\approx \lambda_{\text{onset1}} - \lambda_{\text{onset2}}$.

It is worth noting that this theoretical optimisation using two relatively sharp absorption onsets has not been considered before. The closest example being the aforementioned narrowband red and NIR bulk heterojunction (BHJ) organic photodiodes reported recently by Armin *et al.*¹⁰ In this case, the position of the peak response (λ_{max}) and window (FWHM) are defined by the relatively diffuse optical gap of the bulk heterojunction organic semiconductor blend. This is currently limited by the gap of the fullerene (electron acceptor) component at ~ 700 nm. Thus, blue, green or yellow narrowband CCN organic semiconductor photodiodes, which are required for full colour imaging, have remained a substantial challenge. Furthermore, the broadness of the absorption edge due to energetic disorder in organic semiconductors²⁴ makes it difficult to deliver the sharp response onsets and narrow

FWHM required for filter-free discriminative colour sensing. Hence, new photoactive materials with tuneable optical and electrical properties and efficient charge generation quantum yield are required to overcome these limitations, and thus demonstrate the generic power of the CCN concept over the entire red-green-blue (RGB) spectral range.

Organohalide Lead Perovskites as Tuneable Photoactive Layers

Organohalide lead perovskites have recently emerged as high efficiency photovoltaic materials with power conversion efficiencies (PCEs) as high as 20%.^{25, 26, 27, 28} These hybrid semiconductors exhibit optoelectronic properties similar to those of typical inorganic direct band gap materials, notably: high charge carrier mobility; long electron/hole pair diffusion length; high dielectric constants; low binding energy and very high absorption coefficient.^{29, 30, 31} In addition, they can be solution processed^{32, 33} and possess optical gap tuneability^{20, 21, 22}, similar to organic semiconductors. The field of organohalide perovskite photovoltaics has rapidly expanded to other optoelectronic platforms, in particular light sensing²³ and even light emission²². With respect to light sensing, properties such as high carrier generation quantum yield (delivering high specific detectivities), low recombination losses (resulting in large linear dynamic range²³) and high charge carrier mobilities (resulting in high response frequency^{23, 34}) are very attractive features. Broadband organohalide perovskite photodetectors based on photoresistors^{35, 36} and transistors³⁷ have been realized with high sensitivity. More recently, high detectivity and high speed organohalide perovskite broadband photodiodes have been reported by few groups^{23, 34, 38, 39, 40}. In all cases, these devices rely upon the broad absorption of organohalide lead perovskites.

The optical gap of organohalide lead perovskites can be tuned over a broad range by changing the blend ratio of the constituent halides, for example iodide/bromide/chloride^{20, 21}. **Figure 2a** shows absorption spectra of iodide/bromide mixed halide materials ($\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$) with varying halide ratio to demonstrate the principle. This tunability can be used to deliver the necessary control over λ_{onset1} , but is not sufficient for realizing separate red, green, and blue CCN photodiodes, which requires the lower wavelength onset to be likewise manipulated (λ_{onset2}). However, if both absorption onsets could be controlled then the task of utilising CCN to achieve a narrowband spectral response is reduced to achieving the appropriate electrical properties in the junction, i.e., differentiation between volume and surface photocarrier generation as in organic semiconductor photodiodes. We will return to this particular challenge later. To control the lower wavelength absorption onset we found that the introduction of compatible organic (macro)molecules to form composite films could be used to engineer λ_{onset2} . An example of how this approach and combination of materials can be used to produce a narrowband red response is shown in **Figure 2b** for the case of $\text{CH}_3\text{NH}_3\text{PbI}_2\text{Br}$ doped with Rhodamine B (approximate concentration $\sim 7\text{wt}\%$ calculated from its molar concentration of 0.09 M in the precursor as described in the **Methods** section). We will discuss this combination as an exemplar of the principle. In this composite film the $\text{CH}_3\text{NH}_3\text{PbI}_2\text{Br}$ provides an λ_{onset1} at 700 nm. A clear λ_{onset2} then emerges at ~ 610 nm, and below that wavelength the absorption coefficient of the film is a *combination of the Rhodamine B and perovskite*. Critically, the X-ray diffraction (XRD) spectra of the composite film shown in **Figure 2c** demonstrates that the tetragonal crystal structure of the

CH₃NH₃PbI₂Br is preserved when mixed with the Rhodamine B. However, the inclusion of Rhodamine B was found to decrease the crystal size and improve the film quality as indicated by the width of XRD peaks shown in **Figure 2c**, and depicted in the Scanning Electron Microscopy (SEM) images in **Figure S1**. Furthermore, high crystallinity and the tetragonal structure, which is characteristic of the organohalide perovskites, was found to be preserved for all the halide ratios studied as shown in **Figure S2**.

We turn now to the effect of the Rhodamine B on the electrical properties of the composite film. Organohalide perovskites with polycrystalline morphologies of the type utilised in high efficiency solar cells have recently been shown to possess largely non-excitonic photocarrier generation³¹. Lin *et al.*³¹ asserted that this behaviour in CH₃NH₃PbI₃ was a result of a high static dielectric constant producing a low exciton binding energy. As such, at room temperature, electron-hole pairs are spontaneously created upon photoexcitation. Evidence is however emerging that the local morphology (crystallite size for example) may play a role in controlling the relative branching ratio of excitonic and non-excitonic photoexcitations [reference].

In a system with predominantly non-excitonic dynamics, efficient charge carrier photogeneration can be delivered with no need for a bulk or linear heterostructure. The simplest possible metal-insulator-metal or (*p*-insulator-*n*) linear homojunction architectures can therefore be used to create solar cells. This is also an advantageous feature for CCN photodiodes as it negates the need for an acceptor:donor (*np*) heterojunction as in the case of organic semiconductor-based devices. **Figure 2b** clearly shows that the fundamental optical gap of the organohalide perovskite is unaffected by the Rhodamine B in the film, which is consistent with the crystal structure. **Figure S3** presents measurements of the static dielectric constant obtained using Charge Extraction with Linearly Increasing Voltage (CELIV).⁴¹ We find the Rhodamine B-CH₃NH₃PbI₂Br composite film to have a static dielectric constant of 45, suggested that the material should be largely non-excitonic and therefore (as we show below) deliver efficient homojunction photodiodes.

Realization of Narrowband Red Organohalide Perovskite Photodiodes

Based upon the rationale outlined above we selected a Rhodamine B and CH₃NH₃PbI_{3-x}Br_x combination to deliver a narrowband red photodiode with response between ~600 nm and 700 nm (defined by $\lambda_{\text{onset}2}$ and $\lambda_{\text{onset}1}$, respectively). The 700 nm absorption edge was obtained with a precursor molar ratio of methylammonium iodide (MAI):PbI₂:PbBr₂ 1:0.5:0.5 resulting in CH₃NH₃PbI₂Br. By performing transfer matrix simulations (the optical constants [*n*, *k*] of the composite material are shown in **Figure S4** and were obtained using spectroscopic ellipsometry according to a method we previously reported³¹), the optical field distribution in the photodiode junction was predicted⁴².

Figure 3a shows results from these transfer matrix simulations for a relatively “thick” junction photodiode (~500 nm) for four wavelengths: 350 nm, 450 nm and 550 nm in the Beer Lambert regime; and 650 nm in the cavity regime. Based upon these results a device with ~500 nm junction should, at least from an optical perspective, deliver a narrowband CCN-derived response in the red. We next fabricated linear homojunction photodiodes

(structure as per **Figure 1** inset) with differing junction thicknesses (150 nm - thin to 490 nm - thick) in order to confirm the optical findings and also test whether the electrical properties of the Rhodamine B-organohalide perovskite composite film could deliver charge collection narrowing. In this regard, **Figure 3b** shows EQEs at -0.5 V (a typical, low operating reverse bias voltage for photodiodes). As predicted, for the thinnest junction (150 nm) all incident wavelengths create volume photocarrier generation, which are collected with reasonable efficiency because of the relatively short extraction distance for both electrons and holes. Therefore, this device shows no colour discrimination and is effectively broadband. Increasing the junction thickness produces more surface generation for wavelengths shorter than λ_{onset2} . In the limit, the 490 nm junction delivers a sub-100 nm narrowband response with onsets almost precisely at the design onsets. Of particular note is the sharpness of λ_{onset2} and λ_{onset1} , the latter derived from the organohalide perovskite absorption edge, and the relatively flat EQE between 600 nm and 700 nm indicative of the shape of the absorption in that region (**Figure 2b**). The tunability of the optical gap of the mixed organohalide perovskites is demonstrated by the EQEs in **Figure 4a**. By changing the halide ratio the narrowband response can be pushed out into the NIR and the FWHM also further tuned (from ~40 nm to 200 nm).

At this point, it is important to recall that the CCN mechanism originates from the recombination of surface generated charges either geminately or non-geminately.¹⁰ In efficient organohalide perovskite solar cells the carrier mobilities are thought to be very high^{23, 34} and bimolecular recombination very low.³¹ This means, that even in thick junctions (for example 500 nm), the carrier collection efficiency (η_{coll}) is almost 100%. This would preclude the CCN mechanism since all photogenerated carriers, even those surface generated, would be collected. Hence, in our thick junction narrowband Rhodamine B-CH₃NH₃PbI₂Br photodiodes, some element of the collection efficiency (mobility and/or recombination rate) has been modified. To examine these factors we first measured current density-voltage (*J-V*) curves for the red narrowband device under red, green and blue illumination (provided by a light emitting diodes) all at an irradiance of (~50 mW/cm²). These results are shown in **Figure 3c**, and we observe similar fill factors (*FF*) of between 40-50% in all cases regardless of the excitation wavelength. This implies that the transport efficiency of the long-lived carriers is maintained, but the dramatic drop in short circuit current density for blue and green wavelengths relative to red suggests higher carrier recombination or poorer charge generation.

To further probe the recombination dynamics (and particularly the recombination order) we performed intensity dependent photocurrent (IPC)^{43, 44} measurements – again with blue (405 nm), green (532 nm) or red (650 nm) illumination. The deviation from linearity of the IPC response has been reported to occur at the intensity (and hence carrier density) at which bimolecular recombination becomes dominant^{43, 44}. **Figure 3d** shows the results of these IPC measurements on the narrowband red device. Blue and green wavelengths induce deviation an order of magnitude earlier than the red illumination. This confirms that higher order non-geminate (nonlinear) recombination is present in the Beer-Lambert regime ($\lambda < 600$ nm). Moreover, significantly lower responsivity, *R*, in the linear regime (as seen from the offset in

the logarithmic plot of **Figure 3d**) for blue and green wavelengths versus red indicates the presence of higher geminate (first order) recombination losses. These recombination results, when viewed alongside the results of **Figures 2** and **3** highlight one very important feature of the composite film approach – we are able to simultaneously control the electrical and optical properties of the junction material to deliver the desired spectral responses. Paradoxically, the narrowband selectivity is achieved by making the junction transport properties worse – not a common strategy in optoelectronics.

Having established the basic principles of achieving a narrowband red photodiode, we now move on to fully characterize its light detection properties. The dark current density (J_d) is one of the most important indicators of the noise figure of merit for photodetectors. **Figure 4b** shows the measured J_d of the optimized Rhodamine B-CH₃NH₃PbI₂Br composite device at -0.5 V, which was $<5 \times 10^{-8}$ A/cm². By measuring the noise spectral density from the Fourier transform of the current versus time (see **Supplementary Information Figure S5**), the noise current (i_{noise}) was found to be ~ 100 fA/ $\sqrt{\text{Hz}}$ from 0 V to -1 V. The noise equivalent power (NEP) can be obtained from **equation (1)**⁷ and was found to be ~ 2 pW/ $\sqrt{\text{Hz}}$.

$$\text{NEP} = \frac{i_{\text{noise}} \cdot \sqrt{B}}{R} = \frac{hc \cdot i_{\text{noise}} \cdot \sqrt{B}}{\text{EQE} \cdot e \cdot \lambda} \quad (\text{W}). \quad (1)$$

The specific detectivity can be calculated based on **equation (1)**⁷ from the measured noise so that:

$$D^* = \frac{\sqrt{A \cdot B}}{\text{NEP}} = \frac{e \cdot \lambda \cdot \sqrt{A} \cdot \text{EQE}}{hc \cdot i_{\text{noise}}} \quad \left(\sqrt{\text{Hz}} \frac{\text{cm}}{\text{W}} \right), \quad (2)$$

where λ is the detection wavelength, e the electron charge, A the device area (here 0.2 cm²), h Planck's constant and c the speed of light in vacuum. The calculated D^* at the detection frequency of the EQE (120 Hz) is shown in **Figure 4c** with values reaching $\sim 2 \times 10^{11}$ Jones ($\sqrt{\text{Hz}} \frac{\text{cm}}{\text{W}}$) in the photodiode response window. Overall these performance metrics compare very favorably with state-of-the-art narrowband filter-based visible light photodetectors but with far superior tunability, FWHM, and photo-response suppression outside the design window. It is also worth noting that these red narrowband photodiodes were actually quite stable contrary to current expectations of organohalide perovskite devices. Using basic encapsulation techniques (see **Methods**) the photodiodes maintained their performance after four months stored in air surviving more than twenty measurement sets during that time. Example EQEs are shown in **Figure S6**. Given the supposed instabilities of organohalide perovskites, this is promising from a real application perspective.

Blue and Green Narrowband Photodiodes

The principles outlined for red narrowband photodiodes can be extended to the blue and green regions of the visible spectrum. The same challenges exist in this regard: materials to deliver appropriate and tuneable absorption onsets, and control of junction recombination dynamics. Clearly Rhodamine B, given the position of its absorption onset (~ 630 nm), is not appropriate and for blue and green devices we used PEIE (polyethylenimine, 80%

ethoxylated) to deliver composite films with the appropriate properties. There is a subtle difference between the roles of Rhodamine B in the red photodiodes and PEIE in the green and blue photodiodes. In the case of the latter, absorption onsets can be solely adjusted by changing the halide ratio in the semiconductor. PEIE only absorbs in the UV and hence does not play an optical role – it is used to manipulate the crystallite size and overall degree of disorder and hence control the junction electrical properties to realise CCN.

From **Figure 2a** it can be seen that an appropriate mixed organohalide perovskite ($\text{CH}_3\text{H}_3\text{PbI}_x\text{Br}_{3-x}$) could deliver the correct λ_{onset1} for a green photodiode, but not shorter wavelengths. To realize a blue device we used a non-organohalide mixed lead halide system ($\text{PbI}_x\text{Br}_{2-x}$) and tuned the optical gap by controlling the ratio of PbI_2 and PbBr_2 in the same way as for the organohalide perovskites. Addition of PEIE did not change the basic structure of the $\text{PbI}_x\text{Br}_{2-x}$ in the composite film although (as in the case of Rhodamine B) the crystal size decreased and there was an increase in overall disorder of the film, which is required for CCN to operate (XRD spectra of **Figure S7**).

Films containing PEIE and $\text{CH}_3\text{H}_3\text{PbI}_x\text{Br}_{3-x}$ or $\text{PbI}_x\text{Br}_{2-x}$ at the optimised ratios also had high static dielectric constants, ~ 35 and 19 , respectively as measured by CELIV (**Figure S3**). We could therefore realistically expect that these material combinations will also display largely non-excitonic charge generation physics and therefore be suited to a homojunction architecture. Thus, the blue and green photodiodes were optimized in the same way as described for the red device with an identical structure. The approximate Rhodamine B and PEIE concentrations, the halide ratios, and junction thicknesses for the final RGB “suite” of photodetectors is provided in **Table 1**. The precursor solution compositions to achieve these junction structures are provided in the **Methods** section. In **Figure 5a** we present the absorption coefficients of the red, green, and blue device material combinations, and the junctions were optimised to deliver FWHM of ~ 100 nm in the response windows 600 nm – 700 nm; 500 nm – 600 nm; and 400 nm – 500 nm. **Figure 5a** also shows the normalised EQE for the RGB suite of photodetectors confirming the desired photo-responses were achieved, and noting the blindness of each outside its design spectral window. We also note that the exact λ_{max} and FWHM of the blue and green photodiodes can be further tuned by adjusting the optical gap of the semiconductor, and hence λ_{onset1} .

Figure S8 presents the reverse bias voltage dependence of the EQE for each of the optimised photodiodes. Whilst, as previously noted, the red photodiodes show virtually no bias dependence, the blue and green devices do. This is indicative of poorer charge collection efficiencies in the latter. However, all three RGB photodetectors deliver $>10\%$ EQE at modest reverse bias operating voltage (-1 V), again advantageous from a practical point of view for applications such as cameras. The dark current densities and specific detectivities at λ_{max} are summarised in **Table S1**. Once again we observe the superiority of the red photodiode, but note the respectable performance of the blue and green devices, which we believe are the first truly narrowband photodetectors for these spectral regions. Additional performance metrics are presented in **Figures 5b**. The measured linear dynamic ranges (LDRs) at low reverse bias operating voltage (-0.5 V) for the red photodiode (as indicated in **Figure 3d**) was over 6 orders of magnitude (conventionally expressed as $\text{LDR} = 120$ dB)^{2, 3, 7} and green and

blue devices exhibited ~5 orders of magnitude of linear response. These are state-of-the-art for any narrowband detectors.

Finally, another important metric for photodetectors is their temporal or frequency response, which defines the speed of image capture, or data acquisition rate in applications such as surveillance. The frequency response is dictated by the charge carrier transit time and the capacitance-resistance (RC) characteristic time of the system⁷. Although the charge carrier transit time is expected to be extremely short in organohalide perovskites (and indeed lead halides) due to high charge carrier mobilities^{23, 45}, their large dielectric constants increases the cell capacitance and therefore limits the response speed²³. **Figure 5c** shows the frequency responses of the optimized photodiodes at -0.5 V. The green device shows a $f_{-3\text{dB}}$ of ~144 kHz, and the red and blue photodiodes have a slightly higher $f_{-3\text{dB}} = 297$ kHz and 345 kHz, respectively. Such frequencies responses are far above those values required for imaging applications. However, we should emphasize that these frequency responses are close to the RC limited bandwidth (f_{RC}), which can be calculated by **equation (3)**⁷.

$$f_{\text{RC}} = \frac{1}{2\pi RC} \quad (\text{Hz}) \quad (3)$$

To assess this limit, the RC -time was quantified from the current density decay of the devices (an example is shown for the blue photodiode in **Figure S9**). The red, blue, and green photodiodes showed $RC = 0.4$ - 0.7 μs , corresponding to $f_{\text{RC}} = 400$ - 200 kHz. The measured rise times (t_r) and fall times (t_f) can be seen in **Figure S8d, e** and **f** with $t_r = 3.0$ μs , 6.9 μs and 1.8 μs , and $t_f = 1.9$ μs , 3.0 μs and 1.5 μs for the red, green and blue devices, respectively. Such high-speed responses are similar to commercial broadband visible inorganic semiconductor photodiodes. However, in our current case these values were obtained based on a device area of 0.2 cm^2 , i.e., orders of magnitude larger than the pixel size required for imaging sensors. Therefore, the frequency response of these composite photodiodes could ultimately be transit-time-limited instead of RC -limited as calculated previously by Lin *et al.*²³ and experimentally shown by Dou *et al.*³⁴ and Fang *et al.*⁴⁶

Conclusion

In conclusion, we have demonstrated the first truly narrowband, filterless set of red, green, and blue photodetectors with tuneable photo-responses and FWHM <100 nm. The devices utilise organohalide perovskites and mixed lead halides as solution processable semiconductors. The optical and electrical properties of the photoactive films are controlled by the addition of an organic component. Two absorption onsets are engineered, with the positions by optical gap tuning of the semiconductor, and choice of the organic (macro)molecular component of the composite film. These onsets are sharp and establish the optical conditions for realising charge collection narrowing (CCN) – the creation of two spectral regimes: Beer-Lambert and cavity dominated. The basic crystal structure of the organohalide perovskites and mixed lead halides within the composite films are the same as in the neat semiconducting materials, although the crystal size is decreased and hence there is an increase in the overall film disorder. All the composite films have high static dielectric constants suggesting they possess non-excitonic charge generation physics, i.e., are suited for

the simplest possible homojunction photodiode architectures. The added organic components in the composite films act to increase free carrier recombination, allowing only volume-generated carriers to be collected and thus achieving the electrical requirements for CCN. The strategy therefore relies upon making the film transport properties worse rather than better, an unusual approach in optoelectronics. The transport efficiencies of neat organohalide perovskites of the type used in solar cells are simply too high to achieve CCN. The red, green, and blue photodiodes were fully characterised and delivered state-of-the-art narrowband performance metrics: low dark current, high specific detectivities, large LDRs and fast frequency responses that will likely be transit-time rather than RC -limited in practical applications. Critically, all the photodiodes were highly selective for their design windows with sharp photo-response rises and falls. This is very promising for purer illuminant independent colour recognition and contrast. Our results further emphasise the potential of organohalide perovskite and related materials for low cost, next generation optoelectronics. The strategy we introduce has generic utility to control the physical, optical, chemical and processing properties of solution processed and indeed evaporated semiconductors for multiple applications.

Author contributions

QL characterized the perovskite films and fabricated the devices. QL and AA tested the devices and all authors interpreted the data. PLB and PM supervised the project. All Authors contributed to the preparation of the manuscript. All authors have given approval to the final version of the manuscript.

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Figure captions:

Figure 1 | Working principles of charge collection narrowed (CCN) photodiodes. The absorption coefficient of an arbitrary active layer with separate high and low absorption (α) regions (solid blue line). In the high α region, the Beer-Lambert law dominates the light absorption and carriers are mainly generated near the transparent electrode (we term this surface generation). This increases the recombination and reduces the charge collection efficiency (η_{coll}) due to strongly imbalanced electron/hole transport. In the low α region, cavity effects influence the light absorption significantly for optically thick junctions, and carriers are generated in the volume of the active layer (volume generation). The EQE can be shaped by manipulating the η_{coll} , i.e., the IQE¹⁰. The full-width-at-half-maximum (FWHM) can be controlled by tuning the two onsets of α and reported as the FWHM $\approx \lambda_{\text{onset1}} - \lambda_{\text{onset2}}$. The inset shows the simple homojunction photodiode structure: a photoactive layer between a cathode and anode.

Figure 2 | Optical gap tunability and addition of an organic (macro)molecular component to organohalide perovskite semiconductors. (a) The optical gap of the organohalide perovskite can be tuned by changing the ratio of PbI_2 and PbBr_2 during film preparation. This approach can be used for adjusting the absorption onset 1 (λ_{onset1}) of the narrowband CCN photodiodes of **Figure 1**. (b) Addition of Rhodamine B allows the absorption onset 2 (λ_{onset2}) to be adjusted. (c) Comparison of X-ray Diffraction (XRD) spectra for organohalide perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_2\text{Br}$) with or without Rhodamine B. The films containing Rhodamine B possess attenuated diffraction intensity (~ 20 times lower) and broader peaks. This indicates that, by adding Rhodamine B, the growth of larger crystals is hindered and the crystal size is much smaller compared with neat organohalide perovskite films.

Figure 3 | Working mechanism and performance of the red narrowband CCN photodiodes. (a) Optical field distributions in the red narrowband photodiodes (film thicknesses: 500 nm $\text{CH}_3\text{NH}_3\text{PbI}_2\text{Br}$ and 60 nm C60) for four wavelengths: i) $\lambda < 600$ nm (in the Beer-Lambert region), photons cannot penetrate the whole of the film and carriers are surface generated; ii) $700 \text{ nm} > \lambda > 600 \text{ nm}$ (in the cavity region), volume generated photocarriers. (b) External Quantum Efficiencies (EQE) of narrowband red CCN photodiodes with various junction thicknesses at a reverse bias operating voltage of -0.5 V. The thinnest junction delivers an almost broadband response because surface and volume generated carriers are collected. By increasing the junction thickness, surface generation and volume generation are distinguished and the EQE at shorter wavelengths (in the Beer-Lambert region) is suppressed. (c) Current density-voltage (J - V) measurements of the red narrowband CCN photodiodes under different illumination colours with similar irradiances ($\sim 50 \text{ mW/cm}^2$). All J - V s show Fill Factors of $\sim 50\%$, indicating similar charge transport efficiency for the longer lived carriers. (d) Intensity dependent photocurrent (IPC) measurements of red narrowband photodiodes (zero bias) under various irradiance intensities and three different laser wavelengths. Deviation of the photocurrent from linearity as a function of input irradiance indicates the onset of significant bimolecular recombination and occurs

greater than an order of magnitude earlier for blue and green wavelengths (surface generated carriers).

Figure 4 | Device performance and bandwidth tunability of red narrowband photodiodes. (a) EQEs of the red narrowband photodiodes fabricated with different ratios of PbI_2 and PbBr_2 at -0.5 V. The high wavelength edge of the photoresponse window can be controlled by the semiconductor optical gap (λ_{onset1}). (b) Light and dark J - V curves of the devices from (a). The dark current at -0.5 V is $<5 \times 10^{-8}$ A/cm². (c) Measured specific detectivity (D^*) of an optimized red narrowband photodiode at -0.5 V (1.9×10^{11} Jones with FWHM <80 nm).

Figure 5 | Device performance summary of red, green, blue narrowband CCN photodiodes. (a) EQE spectra at -0.5 V of optimized narrowband photodiodes and related junction absorption coefficients clearly showing how the CCN concept can be realized across the visible spectrum. (b) Linear dynamic range (LDR) of the optimized narrowband photodiodes measured at -0.5 V. The red photodetector shows a linear response of >6 orders of magnitude versus irradiance intensity, whereas the green and blue photodetectors exhibit ~ 5 orders of magnitude of linear response. (c) Frequency response (speed) of optimized narrowband RGB photodiodes at -0.5 V. The green photodetector shows $f_{\text{3dB}} \sim 144$ kHz, and the red and blue photodetectors f_{3dB} of ~ 297 kHz and 345 kHz, respectively – all more than sufficient for most imaging applications.

Table 1 | Typical organic component concentrations, compositions and junction thicknesses for the final RGB “suite” of photodetectors.

	Organic component	Organic component concentration (wt.%)	Composition	Junction thickness (nm)
Red photodiodes	Rhodamine B	~ 7	$\text{CH}_3\text{NH}_3\text{PbI}_2\text{Br}$	500~600 nm
Green photodiodes	PEIE	~ 0.75	$\text{CH}_3\text{NH}_3\text{PbIBr}_2$	500~600 nm
Blue photodiodes	PEIE	~ 0.75	$\text{PbI}_{1.4}\text{B}_{0.6}$	400~500 nm

Methods

Materials: Lead iodide (PbI_2 , 99.999% trace metals basis), lead bromide (PbBr_2 , 99.999% trace metals basis) and lead chloride (PbCl_2 , 99.999% trace metals basis) were purchased from Sigma Aldrich. Methylammonium iodide (MAI, MS101000-10) and methylammonium bromide (MABr, MS301000-05) were purchased from Dyesol Pty Ltd. PEDOT:PSS was obtained from Heraeus (Clevios P Al4083). [6,6]-Phenyl-C61-butyric acid methyl ester (PC60BM) and C60 were purchased from ADS. Polyethylenimine, 80% ethoxylated solution (PEIE, 37 wt.% in water) and Rhodamine B (83689, for fluorescence) were purchased from Sigma Aldrich. All commercial products were used as received, unless otherwise stated.

Device Fabrication: The photodetectors were fabricated on commercial indium tin oxide (ITO) patterned glass electrodes ($15 \Omega/\text{sq}$; Kintec) in a class 1000 clean room. The ITO electrodes were cleaned in a detergent solution (Alconox) bath at 70°C for 10 min, followed by sonication in sequence with Alconox, Milli-Q water, acetone, and 2-propanol (IPA) for 10 min each. The cleaned substrates were dried with nitrogen before being coated with 30 ± 5 nm PEDOT:PSS by spin-coating at 5000 rpm for 30 s. The PEDOT:PSS coated substrates were heated on a hot plate at 170°C for 20 min. After cooling, the substrates were transferred to a nitrogen-filled glove box for device fabrication ($\text{O}_2 < 1$ ppm, $\text{H}_2\text{O} < 1$ ppm).

Active layers were spin-coated onto the PEDOT:PSS layer using the following methods:

(i) **Red photodetectors** contained Rhodamine B and different ratios of PbI_2 and PbBr_2 to tune the band gap of the mixed halide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Br}_{3-x}$. Typically, the molar concentration of MAI was kept at 1 M (160 mg/mL). The sum of the molar concentrations of PbI_2 and PbBr_2 was also kept at 1 M for consistency. Thus, the ratio of PbI_2 and PbBr_2 (varying from 1:0, 0.75:0.25, 0.5:0.5 to 0.25:0.75) determined the optical gap of the $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Br}_{3-x}$. The molar concentration of Rhodamine B was maintained at 0.09 M (~7 wt%). Independent of the PbI_2 : PbBr_2 ratio, casting solutions were prepared in γ -butyrolactone and spin-coated at 1000 rpm for 120 s followed by 4000 rpm for 40 s to create the active layers.

(ii) **Green photodetectors** contained PEIE and different ratios of PbI_2 and PbBr_2 to tune the optical gap of the mixed halide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_x\text{Br}_{3-x}$. Typically, 469 mg PbI_2 and 66 mg PbBr_2 were dissolved in *N,N*-Dimethylformamide (DMF) (1 mL) to create a 1.2 M $\text{PbI}_{1.7}\text{Br}_{0.3}$ solution. A 37 wt.% PEIE solution in deionized water was diluted by DMF to 5 wt%, and 30 μL of this 5 wt% PEIE solution was added into 170 μL of the $\text{PbI}_{1.7}\text{Br}_{0.3}$ solution and stirred for 30 min. The PEIE: $\text{PbI}_{1.7}\text{Br}_{0.3}$ solution was then spin-coated at 700 rpm for 180 s onto the PEDOT:PSS pre-prepared substrates. The films were then dipped into a 15 mg/mL MABr IPA solution for 15 min during which the colour of the film gradually changed from yellow to red. The films were rinsed with IPA to remove excess MABr. The perovskite composition within the composite film was estimated from the optical gap (~600nm) to be $\text{CH}_3\text{NH}_3\text{PbIBr}_2$.

(iii) **Blue photodetectors** contained PEIE and different ratios of PbI_2 and PbBr_2 to tune the optical gap of $\text{PbI}_x\text{Br}_{3-x}$. Typically, 354 mg PbI_2 and 121 mg PbBr_2 were dissolved in DMF (1 mL) to create a 1.1 M $\text{PbI}_{1.4}\text{Br}_{0.6}$ solution. 30 μL of the 5 wt% PEIE solution was added into

170 μL of the $\text{PbI}_{1.4}\text{Br}_{0.6}$ solution and stirred for 30 min. The PEIE: $\text{PbI}_{1.4}\text{Br}_{0.6}$ solution was spin-coated at 1000 rpm for 180 s to create the active layer.

After deposition, the active layers were heated at 100 °C for 10 min on a hot plate in a nitrogen-filled glove box. Then 60 nm of C60 was evaporated to form the hole-blocking layer to reduce the photodiode dark current. Finally, 1 nm of LiF and 100 nm of Ag were deposited by thermal evaporation under a 10^{-6} mbar vacuum with an appropriate mask (0.2 cm² for each device) to form the cathode and complete the device. All photodiodes were encapsulated for device performance measurements. A standard encapsulation protocol was used, namely: epoxy resin (XNR 5516Z-B1, Nagase ChemteX Corporation) was screened onto the edges of a capping glass plate, which was then placed onto the photodiodes firmly before being illuminated under UV light for 10 min.

Characterization: Optical absorption spectra were collected using a Cary 5000 UV-Vis spectrophotometer and near normal incidence reflectance measurements were obtained using a FilmTek 2000M TSV thin film measurement system. The crystallinity of the films was characterized using X-ray Diffraction (XRD). All XRD Spectra were obtained on a Bruker Advance D8 X-Ray Diffractometer equipped with a LynxEye detector, Cu tube ($\text{CuK}\alpha = 1.5418 \text{ \AA}$) and operated at 40 kV with a 2θ scan range of 10-70°. The surface morphology of the perovskite films and cross-sectional structure of the photodiodes were imaged using a Hitachi SU3500 scanning electron microscopy (SEM) with an accelerating voltage of 10 keV and a Jeol JSM-7100F field-emission scanning electron microscopy (FESEM) (Jeol JSM-7100F) with an accelerating voltage of 2 keV. Film thicknesses were determined using a surface profilometer (Veeco Dektak 150). The capacitance of the devices was measured using the Charge Extraction by Linearly Increasing Voltage (CELIV) technique⁴¹.

Device Performance Measurements: The current density–voltage (J - V) characteristics were recorded using an Agilent B1500A Semiconductor Analyzer with a scan speed of 0.01 V/s. Light J - V curves were recorded with a NSPR510CS Nichia red LED (625 nm), 3 W high power star emitter – green (520-530 nm) and blue (460-470 nm) illumination. External Quantum Efficiency (EQE) spectra and the near normal incidence reflectance of the devices were recorded with a PV Measurements Inc. QEX7 system, which was calibrated with a NREL certified photodiode without light bias. Frequency response measurements were obtained using a NSPR510CS Nichia red LED (625 nm), 3 W high power star emitter – green (520-530 nm) and blue LED (460-470 nm) modulated with an Agilent 33250A arbitrary wave function generator. The photocurrent responses of the photodiodes were recorded using a digital storage oscilloscope (LeCroy Waverunner A6200). Linear dynamic ranges (LDRs) were determined using laser diodes at 650 nm and 405 nm and a second harmonic Nd:YAG laser (Laserver) operating continuously at 532 nm as the illumination source with a series of neutral density filters purchased from Thorlabs and Holmarc used to vary the light intensity. The light intensity was calibrated using a standard photodiode simultaneously to compensate for intensity fluctuations and the current response was recorded using an Agilent B1500A Semiconductor Analyzer.