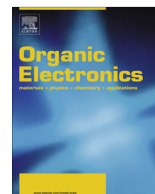




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## Narrow band green organic photodiodes for imaging



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## ABSTRACT

Accurate color reproduction using image sensors requires four narrow-band absorbing photodetectors (blue, green, yellow and red). Current photodetectors use a broadband photodetector in combination with color filters, which generally do not have sufficient wavelength discrimination for illuminant independent color recognition. We have developed a green-sensitive organic photodetector, in which color selection is achieved using a narrow-absorbing ketocyanine chromophore, coupled with a low finesse electro-optical cavity inducing further spectral narrowing. The optimized device contained a bulk heterojunction light-absorbing layer comprised of a ketocyanine dye blended with [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester. The photodetector had a response full width at half maximum of 80 nm centered around 525 nm, and an external quantum efficiency of 15% at –1.0 V, which is the highest so far reported for a narrow band green-absorbing organic photodetector. The performance of this detector is sufficient to meet the specifications required by machine vision systems.

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## 1. Introduction

The ability to accurately and independently capture the color of images of the illuminant is critical for many applications including robotics and machine vision. It has been theoretically shown that illuminant independent detection is possible if the photodetector is able to achieve spectral responses with full width-half-maxima (FWHM) of less than 100 nm [1]. The majority of photodiode detectors (whether inorganic or organic) are broadband and the typical approach to the color discrimination problem is to use color filters. In the case of the commonly used silicon-based photodetectors the problem is compounded by the fact that the silicon is not only used for the photodiode but also the electronic circuitry thus increasing the com-

plexity and manufacturing cost of high resolution detectors. A more elegant approach is to disconnect the detector electronics and photodiode components, and in particular develop photodiodes that only absorb over specific and chosen range of wavelengths. Such an approach is difficult to achieve with inorganic semiconductors due to their banded electronic structures leading to broad optical absorption but can in principle be achieved with photodiodes made from organic semiconductors with narrow absorption features.

Organic photodiodes typically comprise a thin ( $\approx 100$  nm) photo-active layer with strong optical absorption over the appropriate spectral range, sandwiched between two electrodes and electron and hole injection layers [2–6]. The devices are low finesse electro-optical cavities and hence their photo-response is not only related to the absorption of the photo-active layer, but also strongly governed by the optical field distribution within the cavity. The cavity properties (mode density, resonance

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frequency and Q-factor) depend on the refractive indices of all layers in the device as well as their thickness [7,8]. In general, the total light absorption over a broad spectral range can be maximized by considering these electro-optical effects, and particularly by optimizing the photo-active layer thickness [9,10]. For narrow band photodetectors, these effects are more subtle and the non-active layers (such as the transport layers and electrodes) can substantially perturb the spectral response.

In our previously reported approach to achieve the goal of photodiodes with a narrow FWHM optical response, we have used solution processable dendronised ketocyanine chromophores in typical bulk heterojunction (BHJ) device architectures [11,12], in which the ketocyanines have narrow absorption spectra and are stable, neutral, and strongly absorbing [13,14]. We have been able to achieve blue and green selective organic photodiodes with FWHM of the main absorptions of 130 nm and around 90 nm, respectively, providing the use of a 400 nm cut-off filter for the latter. However, one issue with these devices was even though the more weakly absorbing [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PC<sub>60</sub>BM) was used, the fullerene electron acceptor absorbed light, therefore, broadening out the photodiode response. One way to overcome this problem is for the donor and acceptor to absorb at similar wavelengths, which has been achieved for green absorbing photodiodes using the evaporable small molecules dicyanovinylterthiophene and *N,N*-dimethylquinacridone [5]. In fact, evaporable small molecule devices have been the most widely studied for wavelength selective organic photodiodes [3–5], although in many cases the FWHM is greater than that required for illuminant independent color discrimination.

As alluded to above, an alternative approach to controlling the absorption window is to manipulate the electro-optical cavity by engineering the device architecture. For example, the FWHM of the photoresponse of devices with the architecture ITO/P3HT/Al, where P3HT is poly(3-*n*-hexylthiophene), was found to be controlled by the thickness of the polymer layer, although the external quantum efficiencies (EQEs) of the devices were all below 0.1% [15]. The use of a grating in conjunction with a BHJ-based device containing a water interlayer has also enabled color selectivity [16]. Optical cavity effects have also been used to tune the photodiode spectral response across visible wavelengths [17]. For example, the maximum of the photoresponse of semi-transparent devices comprised of Al/MoO<sub>x</sub>/CuPc/C<sub>60</sub>/BCP/Ag, where CuPc is copper phthalocyanine and BCP is bathocuproine, was controlled through varying the thickness of the MoO<sub>x</sub> optical spacer [18]. However, in these devices, reflective electrodes (aluminum and silver) were used to ensure a high cavity Q-factor required for tuning the optical cavity mode to the desired wavelength, in which the semitransparent nature of such devices decreases the EQE dramatically due to inefficient light-coupling into the cavity.

In this manuscript, we show that by combining narrow-absorbing chromophores and optical cavity tailoring, it is possible to achieve very narrow FWHM spectral responses. In particular, we demonstrate how the photoresponse of a particular device design can be predicted through optical

modeling prior to fabrication, thus enabling rapid optimization of the photodiode structure. The strategy is illustrated for two different chromophores comprised of ketocyanine dyes (**1** and **2** in Fig. 1) specifically chosen to absorb green light with a narrow absorption band. An optimized device had a peak response at 525 nm and a state-of-the-art FWHM of 80 nm with the EQE being the highest reported thus far for such narrow band green sensitive photodiodes.

## 2. Materials and methods

### 2.1. Material synthesis

4-Bromobenzyl bromide, cyclopentanone, molybdenum oxide (MoO<sub>3</sub>) and 1,2-dichlorobenzene 99.99% (DCB) were obtained from Sigma–Aldrich and were used as received. [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PC<sub>60</sub>BM) and C<sub>60</sub> were purchased from ADS and were used as received. All solvents except tetrahydrofuran were freshly distilled prior to use. Acetonitrile was dried over calcium hydride overnight before distillation. *N,N*-Dimethylformamide was dried over magnesium sulfate overnight before distillation under reduced pressure. *t*-Butanol was distilled from calcium hydride. Column chromatography was performed with Davisil LC60A 40–63 micron silica gel. Thin layer chromatography (TLC) was performed using aluminum backed silica gel 60 F254 plates. <sup>1</sup>H and <sup>13</sup>C NMR were performed using Bruker Avance AV-300 or AV-500 MHz spectrometers in deuterated chloroform; AR H = phenyl H; IND H = indolenyl H; VIN H = vinyl H; CP H = cyclopentanone H. Coupling constants are given to the nearest 0.5 Hz. UV–visible spectroscopy was performed using a Cary 5000 UV–Vis spectrophotometer as either a thin film on quartz substrates or as a solution in dichloromethane. FT-IR spectroscopy was performed on solid samples using a Perkin–Elmer Spectrum 100 FT-IR spectrometer with ATR attachment. Melting points (MPs) were measured in a glass capillary on a Büchi B-545 melting point apparatus and are uncorrected. Microanalyses were performed using a Carlo Erba NA 1500 Elemental Analyzer. Electrospray ionization mass spectrometry (ESI-MS) was performed on a Bruker HCT 3D Ion Trap mass spectrometer. Thermal transitions were determined by using a Perkin–Elmer Diamond Differential Scanning Calorimeter. Thermal gravimetric analysis was undertaken using a Perkin–Elmer STA 6000 Simultaneous Thermal Analyzer. Thermal decomposition values [*T*<sub>d(5%)</sub>] were reported as the temperature corresponding to a 5% mass reduction.

#### 2.1.1. 2-[1-(3,5-Dibromobenzyl)-5-bromo-3,3-dimethylindolin-2-ylidene]acetaldehyde **4**

A solution of 6-bromo-2,3,3-trimethylindolenine **3** (2.65 g, 11.1 mmol) and 4-bromobenzyl bromide (2.76 g, 11.1 mmol) in anhydrous acetonitrile (11 mL) was added to a Schlenk tube and subjected to three freeze–pump–thaw cycles with backfilling with argon. The tube was then sealed and the mixture was heated at 80 °C for 2 days. The solution was allowed to cool and the solvent was removed *in vacuo*. The red solid was triturated with diethyl ether (3

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