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Spectrally Selective Printable Organic Photodetectors: En Route to High-Performance Wearable Color Imagers

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ABSTRACT

Spectrally selective printable organic photodetectors are uniquely placed to deliver easy-to-fabricate, high-performance color imagers. Herein, we discuss our breakthroughs in spectrally selective printable organic photodetectors with cutting-edge performance and their monolithic stacking into multi-color sensors, which pave the way for high-performance color imagers that could be seamlessly integrated into wearables.

1 Introduction

Low-cost color imagers—which consist of arrays of spectrally selective photodetectors that can concurrently acquire 2D maps of an illuminant in different colors bands—are in high demand for a wide range of wearable applications, ranging from pattern recognition for an interactive experience of our daily objects and environments, to analytical applications, navigation, data communication, and security, to mention but a few [1]–[3]. Printable organic semiconductors are uniquely placed to play a key role in wearable color imagers: not only can they be processed through facile methods [4]–[6] on a wide range of substrates, thereby allowing flexible-/stretchable form factors; additionally, they can deliver a spectrally selective photoresponse throughout the visible range and beyond without the use of color filters [7], [8]. Therefore, printable organic semiconductors could potentially overcome the cost constraints and the mechanical and performance limitations of conventional (i.e., filter-based) color imager technologies, catalyzing the advent of wearable color imagers with enhanced sensitivity, resolution, and functionalities. Furthermore, in contrast to other emerging printable optoelectronic technologies [9]–[12], organic semiconductors are carbon-based materials and thus provide an environmentally friendly avenue for next-generation image sensors [13].

To have a disruptive impact, however, a remaining challenge has been to realize printable spectrally selective organic photodetectors with high sensitivity, as well as their monolithic, solution-based integration into a vertical device stack to achieve enhanced spectral capabilities and functionality. Herein we illustrate the strategies we have adopted to overcome these challenges, thereby demonstrating color-selective, printable organic photodetectors with cutting-edge performance.

2 High-Performance Narrowband-Absorption-Type Printable Organic Photodetectors

Driven by the overarching goal of realizing easy-to-fabricate color sensors, we investigated printable organic photodetectors based on the narrowband-absorption-type (NBA) configuration, which is the most promising from a manufacturability perspective because it relies on a photoactive layer that absorbs only in the target spectral range—thereby leading to appreciable photocurrent only within the spectral region where the photoactive layer has a large absorption coefficient [3], [14]. In other words, NBA photodetectors are inherently filter-free and provide a spectrally selective photoresponse that is hardwired in the photoactive layer, which makes them largely insensitive to process parameter variations—a particularly attractive property in the context of solution-based manufacturing, where process parameter variations are wider than in conventional semiconductor manufacturing. Importantly, this favorable property is unique among the various strategies devised to date to achieve spectrally selective organic photodetectors. Indeed, alternative approaches rely on internal filtering mechanisms and are thus more complex to implement and more sensitive to process parameter variations [3]. A grand challenge in printable NBA photodetector research to date, however, has been to achieve high peak responsivity together with high spectral selectivity, due to the trade-off typically observed between these two quantities.

To realize highly responsive color-selective NBA photodetectors, we investigated photoactive layers based on the donor-acceptor bulk heterojunction concept, which is conducive to efficient photogeneration. The commonplace adoption of fullerenes as the electron-accepting moiety, however, is known to lead to poor spectral selectivity because of the shallow absorption tail exhibited by fullerenes through the visible range. To overcome this challenge, we explored fullerene-free strategies for red- and green-selective photodetectors. Specifically, to realize printable NBA photodetectors for the red spectral range, we adopted a blend comprising SBDTIC, an acceptor-donor-acceptor benzodithiophene-based molecule, as the non-fullerene acceptor [14]. This choice was motivated by the spectrally selective absorption of SBDTIC in the red

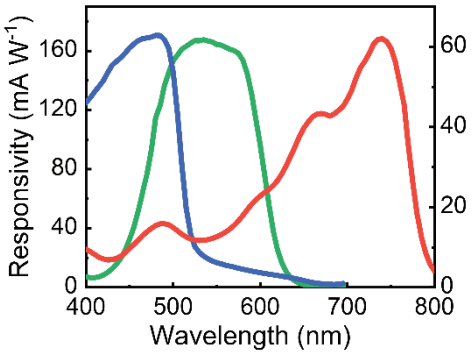

Fig. 1 Spectral responsivities of green- and far-red-selective non-fullerene-based photodetectors and blue-selective F8T2:PC$_{61}$BM photodetector [14]–[16].

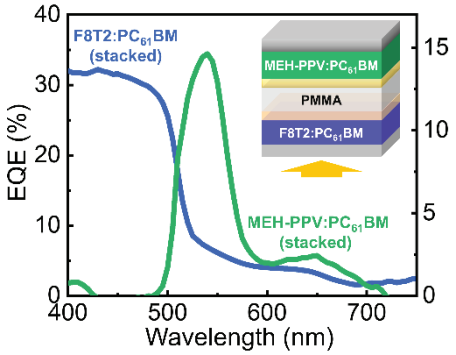

Fig. 2 EQE spectra of solution-processed monolithic stack of green- and blue-selective photodetectors [16].

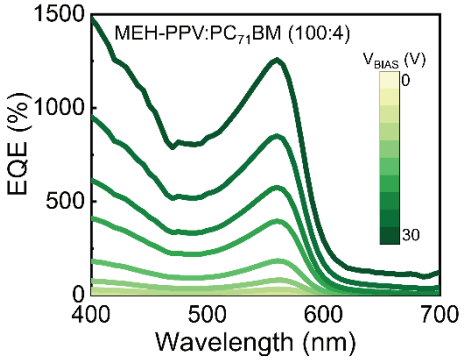

Fig. 3 EQE spectra of an MEH-PPV:PC71BM (100:4) photodetector at various bias voltages.

range. In blends with Poly-TPD, a poly(triarylamine) compound transparent throughout the visible range, the resultant photodetectors exhibited pronounced spectral selectivity to red and far-red photons (Fig. 1) alongside particularly low dark currents. Moreover, these photodetectors delivered a peak specific detectivity of $1.42 \cdot 10^{13}$ Jones, which is cutting-edge for printable NBA photodetectors selective to the far-red range [14].

We also pursued a non-fullerene-based approach to high-performance green-selective NBA photodetectors [15]. In this case, we adopted a blend comprising a donor and a non-fullerene acceptor both narrowly absorbing in the green spectral range. The resultant photodetectors exhibited a strong photoresponse in the green spectral range (Fig. 1) and a peak external quantum efficiency (EQE) of 40 %—the highest to date for printable green-selective NBA photodetectors—while also achieving the highest spectral selectivity [15].

To realize efficient blue-selective NBA photodetectors, however, the adoption of fullerenes is not problematic because of their appreciably stronger absorption in the blue spectral range. Therefore, we investigated F8T2:PC$_{61}$BM photodetectors, achieving a strong photoresponse in the blue spectral range (Fig. 1) along with one of the highest peak EQE for printable blue-selective NBA photodetectors [16].

3 Solution-Based Monolithic Stacking of Multi-Color Organic Photodetectors

To capitalize on the unique spectral capabilities of printable organic photodetectors, it is ideal to vertically stack photodetectors responsive in different spectral regions to realize filter-free pixels with multi-color sensitivity. Indeed, this concept could potentially enable color imagers with higher sensitivity, resolution, and color accuracy compared to conventional technologies [16]. However, until recently, a major challenge in organic photodetectors research was to realize this architecture through solution-based methods. We recently overcame this challenge by demonstrating the first solution-based monolithic integration of vertically stacked printable organic photodetectors capable of independently and concurrently sensing green and blue photons [16]. To achieve this, we adopted printable F8T2:PC$_{61}$BM and MEH-PPV:PC$_{61}$BM blends as photoactive layers (Fig. 2). We additionally employed a solution-deposited insulating spacer to allow the independent biasing and photocurrent readout of the two stacked photodetectors [16]. Moreover, to minimize the transmission losses for photons traversing the stack, we adopted ultrathin metal electrodes [16]. This first-ever demonstration of a solution-processed vertically stacked device architecture delivered favorable spectrally selective responses in the blue and green ranges (Fig. 2), thereby illustrating the potential of this approach toward the realization of filterless imagers covering multiple spectral bands in the visible range and beyond.

Within a multi-layer device stack such as the one we developed, a certain degree of optical losses is expected as light travels into it. Consequently, we also investigated the possibility of realizing green-sensitive MEH-PPV-based devices with photocurrent gain, potentially leading to an apparent EQE greater than 100 % [3]. We

reasoned that, in a stacked device architecture, photocurrent gain could potentially be used to boost the responsivity of the devices deeper in the device stack, thereby mitigating the optical losses in place. Therefore, we studied photodetectors based on an MEH-PPV photoactive layer also comprising a small amount of $PC_{71}BM$. Given the energy level alignment between the two moieties and the dominant hole-transport character of MEH-PPV, we conjectured that isolated $PC_{71}BM$ domains within an MEH-PPV layer could serve as electron traps, which could then be used to trigger a photocurrent gain mechanism. Following this lead, we realized sandwich-type devices comprising MEH-PPV:$PC_{71}BM$ layers with a 100:4 blending ratio. These MEH-PPV:$PC_{71}BM$ devices delivered a strong photoresponse with a reverse bias voltage V_{BIAS} > 20 V, achieving an apparent peak EQE of 1256 % in the green spectral range with V_{BIAS} = 30 V (Fig. 3). This finding substantiates the opportunity provided by organic photodetectors with a photocurrent gain to overcome the optical losses inherent in vertical device stacking, thereby pointing the way for future efforts toward high-performance printable organic color imagers covering a large number of spectral bands within a stacked device architecture.

4 Conclusions

Herein, we have discussed the materials and device strategies we have investigated to enhance the performance and functionality of spectrally selective printable organic photodetectors. On the one hand, printable NBA photodetectors based on non-fullerene acceptors have delivered cutting-edge sensitivity and spectral selectivity. On the other hand, the first solution-based realization of a monolithic device stack of organic photodetectors demonstrates the viability and potential of this architecture for high-performance color imagers, whose sensitivity could be enhanced via a photocurrent gain. Therefore, these breakthroughs mark a significant step toward the application of printable organic photodetectors for easy-to-fabricate, high-performance wearable color imagers.

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