Solution-based fullerene-free route enables high-performance green-selective organic photodetectors

Yang Cao¹, Jianjun Mei¹, Kai Xia¹, Ting Zhao¹, Jing Zhao¹, Nicola Gasparini² and Vincenzo Pecunia¹,³,*

¹ Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Institute of Functional Nano & Soft Materials, Soochow University, 199 Ren’ai Road, Suzhou, 215123 Jiangsu, People’s Republic of China
² Imperial College London, Department of Chemistry and Centre for Plastic Electronics, London W12 0BZ, United Kingdom
³ School of Sustainable Energy Engineering, Simon Fraser University, 5118–10285 University Drive, Surrey, V3T 0N1 BC, Canada

E-mail: vincenzo.pecunia@sfu.ca

Keywords: narrowband organic photodetectors, non-fullerene acceptors, green-selective photodetectors, narrowband-absorption-type photodetectors, solution-processed photodetectors

Abstract
Ongoing developments in machine vision, wearables, and the Internet of Things have led to strong demand for easy-to-fabricate, color-selective photodetectors. Narrowband-absorption-type (NBA) printable organic photodetectors provide an attractive solution, given their spectral robustness and fabrication simplicity. However, a key remaining challenge to realizing their potential is to concurrently achieve high photoconversion efficiency and spectral selectivity. Herein, this challenge is tackled by investigating a non-fullerene-based route to green-selective, solution-based photodetectors. Soluble phthalocyanine acceptor PhO-Cl₆BsubPc is considered due to its high absorption selectivity to green photons. Blends with soluble quinacridones are pursued to realize the ideal of a donor:acceptor layer selectively absorbing the target photons throughout its volume. A latent-pigment route to the solution-based deposition of linear trans-quinacridone (QA) enables well-intermixed QA:PhO-Cl₆BsubPc layers. Green-selective photodetectors with cutting-edge performance are thus realized, achieving a 25% increase in external quantum efficiency compared to all prior solution-based NBA implementations, as well as a nearly five-fold enhancement of the green-to-blue spectral rejection ratio. The merit of this approach is further illustrated by comparison with the corresponding fullerene-based photodetectors. By demonstrating an approach to solution-based NBA photodetectors with cutting-edge photoconversion efficiency and spectral selectivity, this study represents an important step toward printable, high-performance organic color sensors and imagers.

1. Introduction

Organic semiconductors offer a formidable opportunity for next-generation narrowband photodetectors that can meet the spectral, functional, and cost requirements of a wealth of emerging application areas—including the Internet of Things, computer vision, wearables, and health and wellness monitoring, to mention but a few [1–5]. Such potential firstly builds on the tunability of their optoelectronic properties via chemical tailoring, which enables the realization of narrowband photodetectors with diverse spectral characteristics in the ultraviolet, visible, and near-infrared spectral regions [1, 6]. Additionally, organic narrowband photodetectors based on solution-processed photoactive layers are particularly appealing, as they can capitalize on the high throughput and versatility of additive deposition methods such as printing and coating [1, 7–10], in addition to a more favorable sustainability profile compared to emerging, solution-based semiconductor technologies containing toxic heavy metals (e.g. lead halide perovskites and heavy-metal-based quantum dots) [11–16]. Therefore, solution-based organic narrowband photodetectors are uniquely positioned to deliver spectrally-selective light sensors and imagers that are both low-cost and
with diverse form factors (e.g. mechanically flexible), hence suitable for ubiquitous deployment, as demanded by a wealth of emerging application domains.

Due to their optoelectronic versatility, organic semiconductors enable narrowband photodetection through a variety of strategies, which can be grouped into three main classes: narrowband-absorption-type (NBA) [1, 17, 18]; filtered (including input optical filtering and internal filtering via charge collection narrowing, charge injection narrowing, or exciton dissociation); and microcavity-resonance-based [19–22]. Among these strategies, NBA photodetection has been mainstream due to its appealing trade-off between simplicity and performance, which is of fundamental importance for the realization of easy-to-make optoelectronics alternative to silicon-based technologies [6, 19, 23]. Specifically, an NBA photodetector consists of a sandwich-type device stack comprising a thin (~100 nm) organic semiconductor layer, which selectively absorbs photons within the target spectral range [1, 17, 18] (figure 1(a)). Therefore, NBA photodetectors are uniquely filter-free, as they do not require any component of the device stack to suppress the photoresponse outside the target spectral range through deliberate loss mechanisms—i.e. optical filtering, carrier recombination, and/or exciton annihilation, as in charge collection narrowing, charge injection narrowing, and exciton dissociation narrowing [19–22]. Indeed, an NBA photodetector could ultimately allow all photons in the target spectral range to be absorbed and contribute to the photoreponse (figures 1(a) and (b)), which is potentially conducive to high photoconversion efficiencies and speed of response, as well as an angle-independent behavior. Furthermore, given the simplicity of their device architecture and the robustness of their spectral response in the presence of process parameter variations (i.e. their spectral response is ‘hardwired’ in the materials used; see figures 1(a) and (b)), NBA photodetectors are highly appealing in terms of manufacturability, especially in combination with solution-based fabrication methods. By contrast, approaches based on internal filtering (i.e. charge collection narrowing, charge injection narrowing, and exciton dissociation narrowing) deliver narrowband responses that are not hardwired in the photoactive material used—indeed, these approaches rely on broadband absorbers [21, 24–27]. Based on the operational, fabrication, and architectural simplicity of NBA photodetectors, it is not surprising that the only implementations to date of imagers comprising narrowband organic photodetectors—demonstrated with commercially relevant imager architectures by Samsung, Sony, and Japan Broadcasting Corporation [28–30]—rely on the NBA configuration.

Despite their considerable appeal, a recurrent challenge in the realization of high-performance NBA photodetectors has been to achieve adequate spectral selectivity—i.e. a strong photoreponse in the target spectral range combined with a weak photoreponse elsewhere. This property is quantified in terms of the spectral rejection ratio SRR, which is defined as the ratio between the peak external quantum efficiency (EQE), $EQE_{p}$, and the EQE at a representative wavelength $\lambda_{ext}$ outside the target spectral range: $SRR = EQE_{p}/EQE(\lambda_{ext})$ (figure 1(b)) [1]. The spectral selectivity challenge faced by NBA photodetectors is exemplified by the reports to date on their green-responsive embodiments, which have attracted considerable commercial and research interest due to the importance of green light detection (wavelength range: $\lambda \cong 400–500$ nm) for color sensing and imaging—as evidenced by the research efforts of Samsung, Sony, and Japan Broadcasting Corporation [28, 30, 31]. Indeed, this challenge is yet to be overcome with

![Figure 1. (a) Sketch of the NBA approach to green-selective light detection with organic semiconductors, featuring a photoactive layer that ideally absorbs only green photons. This example refers to a dual-absorber D:A configuration, comprising a donor and an acceptor both designed to absorb photons within the target spectral range. (b) Representative normalized EQE spectrum of a green-selective organic photodetector, alongside the absorbance spectrum of the photoactive layer. The arrow labeled $SRR_{G,B}$ refers to the ratio between the peak EQE and the EQE at $\lambda_{ext} = 400$ nm, thereby illustrating the spectral rejection ratio with respect to blue photons. Similarly, $SRR_{R,B}$ refers to the spectral rejection ratio with respect to red photons ($\lambda_{ext} = 650$ nm). (c) Aggregate plot of the normalized EQE spectra of representative literature implementations of NBA, green-sensitive/selective organic photodetectors based on solution-processed photoactive layers (gray traces: individual implementations; green solid traces: upper and lower bounds; green dashed trace: average of all spectra) [17, 33, 34, 36–38, 40, 46]. The red circles and gray arrows highlight their large spurious response in the blue spectral range.](image-url)
solution-processed implementations [17, 32–40], which are of paramount technological interest. Firstly, the peak EQE values of solution-processed, green-responsive, NBA photodetectors to date are below 32% and typically around 10% (table S1), indicating that only a minor fraction of the incident green photons are converted into photocurrent [17, 32–40]. Moreover, all the implementations to date exhibit a comparatively strong yet undesired photoresponse in the blue spectral range—at a minimum, $\leq 30\%$–60\% of the peak photoresponse (see figure 1(c))—which severely limits their spectral selectivity [17, 32–40]. Consequently, the lack of a viable solution-based route to high-performance, green-selective, NBA photodetectors has represented a major hurdle to the commercial exploitation of printable organic color sensors and imagers.

It is noteworthy that the solution-processed, green-responsive, NBA photodetectors reported to date have delivered limited spectral selectivity and in-band photoconversion efficiency regardless of their material configurations of the photoactive layers [17, 32–40]. This is unsurprisingly so with fullerene-based bulk heterojunctions [17, 34, 40]. Indeed, while fullerenes have been widely used in organic optoelectronics due to their excellent electron-accepting character, their broad absorption tail through the visible spectral range leads to a highly undesired parasitic photoresponse outside the target spectral region in NBA photodetectors (amounting to $\sim$40\%–60\% of the in-band photoresponse) [17, 41–45], thereby severely limiting the spectral rejection ratio (e.g. see figures 1(c) and S1) [1, 6, 17]. Alternative solutions explored to date—involving single-component photoactive layers or blends with non-fullerene acceptors [17, 32–40]—have only garnered limited success, typically delivering low in-band EQE (i.e. low EQE within the target spectral range) and a comparatively large but undesired photoresponse outside the target spectral range (e.g. see figure S1). Nonetheless, in light of their synthetic and spectral flexibility, non-fullerene acceptors provide a vast compositional space largely unexplored in the narrowband photodetector domain.

With the aim of advancing solution-processable NBA photodetectors toward their full potential, herein we investigate a fullerene-free route to overcome the spectral selectivity challenge of NBA photodetectors for green-selective light sensing. Specifically, we explore the capabilities of solution-processed blends combining a green-absorbing subphthalocyanine derivative as a non-fullerene acceptor and a quinacridone-based donor also absorbing in the green spectral range. We identify a latent-pigment strategy for the solution-based processing of a green-absorbing donor to enable the solution-based fabrication of bulk heterojunctions with high photoconversion efficiency in the green spectral range. We discuss the performance of the resultant photodetectors, establishing that our materials and device strategies lead to solution-processed photodetectors with the highest photoconversion efficiency and spectral rejection ratio compared to the prior relevant literature. We contrast this result with the performance arising from the use of a fullerene acceptor in bulk heterojunctions with the same donor. By achieving cutting-edge performance in terms of both in-band photoconversion efficiency and spectral selectivity, we demonstrate the opportunity provided by non-fullerene acceptors for the realization of high-performance solution-based NBA photodetectors toward printable color sensors and imagers.

2. Results and discussion

With a view to realizing efficient solution-processed green-selective photodetectors, we reasoned that the most direct strategy would be to pursue the narrowband dual-absorber D:A approach [18], which involves the use of a bulk heterojunction comprising a donor (D) and an acceptor (A) both selectively absorbing in the green spectral range (figure 1(a)). Indeed, this strategy would inherently boost the absorption coefficient of the photoactive layer in the green spectral range, while the D:A bulk-heterojunction form of the photoactive layer could provide a high photogeneration efficiency. With this approach, a comparatively thin photoactive layer would suffice to absorb green photons, thereby helping reduce recombination losses by keeping the collection distance (i.e. the distance that photocarriers must travel to reach the electrodes) to a minimum.

For the narrowband dual-absorber D:A approach to be effective, however, it is essential to select adequate donor and acceptor materials [18], as any significant degree of spectral mismatch between the two inevitably leads to the broadening of the spectral response of the resultant photodetector. Therefore, we sought to identify a solution-processable non-fullerene acceptor selectively absorbing in the green spectral range. Drawing from the developments in non-fullerene-acceptor-based organic photovoltaics, we considered that a number of soluble small molecules of the boron-subphthalocyanine family could potentially meet this requirement. Boron subphthalocyanines are cone-shaped molecules comprising a central boron atom, three nitrogen-bridged isodindoline units, and a variety of peripheral and axial substituents (e.g. see figure 2(a)) [47, 48]. Their ability to function as electron acceptors typically requires the introduction of peripheral halogen substituents (e.g. see figure 2(a)) [49–51]. Concurrently, the axial ligand (e.g. see figure 2(a)) can be critical to achieving sufficient solubility for the use of boron subphthalocyanines in solution-deposited photoactive layers [52–54].
Based on the considerations above, we selected phenoxy-hexachloro-boron subphthalocyanine (PhO-Cl$_6$BsubPc) as a non-fullerene acceptor. PhO-Cl$_6$BsubPc is a soluble molecule featuring chlorines as the peripheral substituents (in the third and fourth outside positions on the isoindoline groups) and a phenoxy ligand at the axial position (figure 2(a)). Our choice was firstly motivated by its green absorbing capability and promising performance in organic solar cells [50, 55, 56]. Additionally, we considered that the straightforward synthesis of subphthalocyanines [56–58] makes them attractive for use in device applications, given that the adoption of compounds with low synthetic complexity is advantageous for the future scaling up of organic optoelectronics [59, 60].

Films of PhO-Cl$_6$BsubPc spin-coated from a chloroform solution manifested a narrow and strong absorption band in the green spectral range (figure 2(b)). This absorption band was associated with a particularly large peak absorption coefficient of $\alpha_p = 2.7 \times 10^5$ cm$^{-1}$ at a wavelength of $\lambda_{\alpha_p} = 582$ nm and a full width at half maximum amounting to $\text{FWHM}_\alpha = 85$ nm, as determined via absorption spectrophotometry (figure S2). This absorption band corresponds to the typical Q-band of boron phthalocyanines; hence, it can be assigned to the $S_1-S_0$ (i.e. HOMO-LUMO) transition [61]. We determined via Tauc analysis (figure S2) that the corresponding optical gap amounted to 2.04 eV, consistent with the literature [56].

In regard to the selection of suitable donors, we sought to identify compounds with narrowband absorption in the green spectral range, consistent with the narrowband dual-absorber D:A approach. We specifically opted for small molecule options, given the broadband absorption character of polymeric systems [62] arising from their characteristic conformational disorder [63, 64]. We reasoned that a viable solution could be offered by quinacridone-based small molecules due to their green-absorbing behavior—see figure 2(a) for the structure of the parent molecule linear trans-quinacridone (QA), which features a five-ring-fused core with two pairs of amine and carbonyl groups. While QA and derivatives have been investigated as donors in green-selective vacuum-deposited photodetectors [65–76], to the best of our
knowledge, their use in the solution-processed counterparts has not been reported to date. Importantly, QA is insoluble in common organic solvents due to its strong hydrogen-bonding interactions [77]. Therefore, we originally considered combining PhO-Cl\textsubscript{6}BsubPc with N,N'\textsuperscript{-}dimethylquinacridone (N,N'\textsuperscript{-}DMQA) or N,N'\textsuperscript{-}di(n-butyl)-quinacridone (N,N'\textsuperscript{-}DBQA), which feature the structure of QA functionalized with methyl or n-butyl groups, respectively, at the nitrogen sites (figure S3). Indeed, the N,N'\textsuperscript{-}dialkylation of QA is known to enhance its solubility [77–79]. While both N,N'\textsuperscript{-}DMQA and N,N'\textsuperscript{-}DBQA present good spectral overlap with PhO-Cl\textsubscript{6}BsubPc (figure S3), neither were found suitable for high-performance, solution-processed organic photodetectors selective to the green spectral range. On the one hand, we found that N,N'\textsuperscript{-}DMQA had too low a solubility in common organic solvents to be able to spin-coat films with a thickness suitable for device fabrication. On the other hand, N,N'\textsuperscript{-}DBQA had adequate solubility but delivered N,N'\textsuperscript{-}DBQA:PhO-Cl\textsubscript{6}BsubPc films with non-ideal morphology and particularly low EQE (figure S3).

To circumvent the challenge, we reasoned that, in principle, it would be appealing to use the parent molecule QA in blends with PhO-Cl\textsubscript{6}BsubPc. Indeed, in contrast to N,N'\textsuperscript{-}dialkylated QA derivatives, QA presents carbonyl and amine groups (figure 2(a)), which lead to the formation of N–H...O hydrogen bonds in QA films [77, 80]. Given that chloro-boron subphthalocyanines can also participate in hydrogen/halogen bonding (through their imine nitrogens, phenoxo oxygen, and chlorines) [81, 82], we envisaged that QA could potentially deliver good intermixing in QA:PhO-Cl\textsubscript{6}BsubPc blends via intermolecular interactions between the donor and the acceptor, which would be advantageous for efficient photoconversion.

Given the insolubility of QA in common organic solvents [77], however, it was not possible to deposit QA:PhO-Cl\textsubscript{6}BsubPc blends by mixing the component molecules in solution. Therefore, we considered the adoption of a 'latent-pigment' route for the solution-based deposition of QA:PhO-Cl\textsubscript{6}BsubPc films [83]. This approach involves the initial use of a soluble molecule closely related to the insoluble one of interest, into which it can be converted through a heating step after deposition. Specifically, we resorted to tert-butylcarboxyl-(t-BOC-)substituted quinacridone (t-BOC-QA) as the latent pigment for QA (figure 2(a)), following prior reports on the solution-based preparation of QA films for transistors and solar cells [84–86]. Indeed, in t-BOC-QA, the t-BOC groups at the N,N' positions inhibit hydrogen bonding, thereby rendering the molecule soluble in common organic solvents.

Spin-coated films of t-BOC-QA manifested an absorption band in the blue range, consistent with the reduced π–π intermolecular interaction resulting from the sterically hindering t-BOC groups (figure 2(c)). Once we annealed the t-BOC-QA films at suitable temperatures, however, their absorption spectra underwent a sizeable bathochromic shift (figure 2(c)). In particular, this spectral change was observed for annealing temperatures above ~170 °C, while no additional major changes occurred for annealing temperatures above 210 °C. This observation was in line with thermogravimetric analysis (TGA) data from t-BOC-QA films (see the extrapolated onset temperatures of the corresponding TGA curve in figure 2(d)) and consistent with the literature [84–86]. Such spectral shifts correspond to the full conversion of t-BOC-QA into QA for annealing temperatures in the range of 210 °C–230 °C, as also confirmed by the consistency of the resulting optical gap (2.07 eV; see figure S2) with the literature value for pristine QA [87, 88]. The absorption spectra of the resultant QA films (figures 2(b) and (c)) confirmed their narrowband-absorption character in the green spectral range. Alongside a vibronic structure, the dominant absorption band peaked at 566 nm, leading to a favorable spectral overlap with PhO-Cl\textsubscript{6}BsubPc films (figure 2(b)).

The ability to deposit QA from solution through the latent-pigment route allowed us to explore the solution-based deposition of QA:PhO-Cl\textsubscript{6}BsubPc blends. In particular, we proceeded by first spin-coating solutions of t-BOC-QA and PhO-Cl\textsubscript{6}BsubPc in chloroform and subsequently annealing the resultant films in order to convert their t-BOC-QA domains into QA (figure 2(a)). The bathochromic shift associated with the use of QA as opposed to the N,N'\textsuperscript{-}dialkylated counterparts enabled a better spectral match with PhO-Cl\textsubscript{6}BsubPc (figure S3), resulting in QA:PhO-Cl\textsubscript{6}BsubPc (1:1) films with a full width at half maximum of their absorbance amounting to $FWHM_{\alpha} = 91$ nm (figure 2(b)), hence leading to minimal spectral broadening compared to the standalone PhO-Cl\textsubscript{6}BsubPc films. The resultant absorption spectrum of such QA:PhO-Cl\textsubscript{6}BsubPc films largely resembled that of PhO-Cl\textsubscript{6}BsubPc (figure 2(b)), which can be attributed to the favourable spectral overlap between QA and PhO-Cl\textsubscript{6}BsubPc and the larger absorption coefficient of the latter (figure S2).

For a preliminary assessment of the compatibility of QA and PhO-Cl\textsubscript{6}BsubPc for the realization of donor-acceptor bulk heterojunctions, we first characterized the ionization potentials of spin-coated PhO-Cl\textsubscript{6}BsubPc and QA thin films via ultraviolet photoelectron spectroscopy. We found that the HOMO levels of the PhO-Cl\textsubscript{6}BsubPc and QA films were at 5.69 and 5.16 eV, respectively, below the vacuum level (figure 2(c)). Therefore, in consideration of the corresponding optical gaps, a type-II heterojunction would be formed in QA:PhO-Cl\textsubscript{6}BsubPc film (figures 3(a) and (b)) [1, 89]. In particular, the energy offset between the LUMO levels, $\Delta E_{\text{LUMO}}$, amounted to 0.66 eV, while the HOMO energies differed by $\Delta E_{\text{HOMO}} = 0.53$ eV.
This confirmed the potential suitability of QA and PhO-Cl6BsubPc to serve as a donor-acceptor pair within a bulk heterojunction and provide a sufficient driving force for exciton dissociation at their interface [90]. To shed further light on this aspect, we characterized the photoluminescence spectra of thin films of QA, PhO-Cl6BsubPc, and QA:PhO-Cl6BsubPc (1:1). While the single-component films were strongly luminescent (with emission spectra in line with radiative exciton recombination) (figure 2(f)), the luminescence of the 1:1 films was considerably quenched, thereby pointing to the possibility of efficient exciton dissociation at the QA | PhO-Cl6BsubPc interface. This finding was also consistent with the good intermixing of the component materials in QA:PhO-Cl6BsubPc layers (figure 2(g); root-mean-square film roughness of 1.2 nm), which is generally expected to facilitate the photoconversion process. Interestingly, the quenching effect was stronger when the QA:PhO-Cl6BsubPc films were illuminated at a wavelength $\lambda_{\text{exc}} = 420$ nm (which is selectively absorbed by QA), denoting greater quenching efficiency for excitons generated in the QA domains (figure 2(f)).

Based on the positive indications above, we pursued the realization of photodetectors featuring QA:PhO-Cl6BsubPc blends. In particular, we adopted a sandwich-type device structure with a QA:PhO-Cl6BsubPc film placed between ITO | PEDOT:PSS (serving as the anode plus hole transport layer assembly) and LiF | Al (serving as an electron-selective cathode).

The EQE spectra of such photodetectors manifested a narrowband character, covering a spectral range largely following the absorbance spectrum of the QA:PhO-Cl6BsubPc blend (figure 3(c)). The EQE peak of such photodetectors was centered around $\lambda_{\text{EQE}} = 510$ nm at $V_{\text{BIAS}} = 0$ V ($V_{\text{BIAS}} = V_{\text{Al}} - V_{\text{ITO}}$) (figure 3(c)). Interestingly, $\lambda_{\text{EQE}}$ differed from the absorption peak of the QA:PhO-Cl6BsubPc films, i.e. 581 nm (see above). We trace this difference to the different dissociation efficiency for excitons generated in the QA and PhO-Cl6BsubPc domains, as also suggested by the PL spectra (figure 2(f)). Indeed, given that QA also absorbs at wavelengths lower than those of the PhO-Cl6BsubPc absorption band, a higher exciton dissociation efficiency in the QA domains would enhance the photoresponse at such wavelengths, leading to an apparent blue shift of the photoresponse compared to the absorption spectrum of the blend. This could also explain the EQE peak shifting from $\lambda_{\text{EQE}} = 510$ nm at $V_{\text{BIAS}} = 0$ V to $\lambda_{\text{EQE}} = 525$ nm once $V_{\text{BIAS}} = 1.4$ V was reached, which suggests the enhancement of the dissociation efficiency for excitons generated in PhO-Cl6BsubPc domains with increasing electric field [89].

The QA:PhO-Cl6BsubPc photodetectors exhibited a strong photoresponse in the green spectral range, reaching a peak EQE, $EQE_p$, of 40% at $V_{\text{BIAS}} = 1.4$ V. Notably, this is the highest photoconversion efficiency
for NBA green-selective photodetectors comprising a solution-processed photoactive layer [17, 33, 34, 36–38, 46, 91, 92] (see figure 3(d) and table S1), marking a more than twofold increase with respect to most of the literature and a 25% enhancement compared to the best prior result. Moreover, the QA:PhO-Cl\textsubscript{6}BsubPc photodetectors delivered a responsivity $R = \frac{I_{ph}}{P_{opt}}$ (where $I_{ph}$ is the photocurrent and $P_{opt}$ the incident optical power density) of up to 168 m\text{A} W\textsuperscript{-1} in the green spectral range (figure S4), which is the highest reported so far for solution-processable green-selective NBA photodetectors [17, 33, 34, 36–38, 46, 91, 92], in line with their cutting-edge EQE. Concurrently, their on-off ratio was up to five orders of magnitude (figure S4), benefiting from a particularly low dark current. This behaviour enabled a specific detectivity in the shot-noise limit (calculated as $D^* = \frac{R/(2qI_D)}{1/2}$, where $I_D$ is the measured dark current) between 2 × 10\textsuperscript{12} and 1.2 × 10\textsuperscript{13} Jones (figure S4), which is state-of-the-art for organic photodetectors [1].

While an appreciable photoresponse (12%) in the green spectral range was also observed at $V_{BIAS} = 0.0$ V (figure 3(c)), it is apparent that the application of a small reverse bias voltage considerably boosted $EQE_p$. In general, this can be traced to the enhancement of the exciton dissociation efficiency and the charge collection efficiency with the application of an electric field [89].

It is worth noting that we achieved an $EQE_p$ of 40% after considerable device optimization. Firstly, we studied the impact of varying the blending ratio between QA and PhO-Cl\textsubscript{6}BsubPc. We found that photodetectors with a 1:1 blending ratio delivered appreciably larger EQE than those with 1:1.5 and 1:1.5 ratios (figure S5), therefore indicating that the 1:1 ratio is optimal for photoconversion. Additionally, we assessed the impact of the temperature at which the QA:PhO-Cl\textsubscript{6}BsubPc films were annealed. While the absorbance spectra of such layers did not change for annealing temperatures between 210 °C and 230 °C, the EQE was highest for an annealing temperature of 210 °C (figure 3(e)). Atomic force microscopy (AFM) revealed that the QA:PhO-Cl\textsubscript{6}BsubPc films became rougher as the annealing temperature increased within this range, with the domain size concurrently becoming larger (figure S6). Therefore, we trace the higher EQE of the 1:1 QA:PhO-Cl\textsubscript{6}BsubPc photodetectors to their superior morphology and intermixing of the donor and acceptor domains, which are indeed key contributors to the photoconversion efficiency of a bulk-heterojunction layer [89].

Alongside a strong in-band photoresponse, a key requirement for color-selective photodetectors is the ability to reject out-of-band photons—i.e. blue and red photons for green-selective photodetection. To assess the compliance of our QA:PhO-Cl\textsubscript{6}BsubPc photodetectors to this requirement, we first determined the full width at half maximum of their EQE spectra, $FWHM_{EQE}$, which quantifies the spectral spread of their photoresponse. We thus found that our QA:PhO-Cl\textsubscript{6}BsubPc photodetectors delivered a $FWHM_{EQE}$ down to 131 nm (figure 3(e)), which is in line with the NBA photodetector literature [1].

Importantly, the full width at half maximum of the EQE spectrum only partially captures the ability of a photodetector to selectively respond to photons within a certain wavelength range. Indeed, many green-responsive photodetectors in the literature achieve a $FWHM_{EQE}$ in a similar range but concurrently deliver a strong out-of-band photoresponse (figure 1(c)). Therefore, we quantified the spectral rejection ratios $SRR_{G,B} = EQE(\lambda_{p,EQE})/EQE(\lambda = 400 \text{ nm})$ and $SRR_{G,R} = EQE(\lambda_{p,EQE})/EQE(\lambda = 650 \text{ nm})$ of our QA:PhO-Cl\textsubscript{6}BsubPc photodetectors, where the wavelengths $\lambda = 400$ nm and 650 nm were selected due to their being representative of the blue and red spectral regions.

As shown in figure 3(f), our QA:PhO-Cl\textsubscript{6}BsubPc photodetectors delivered a green-to-red spectral rejection ratio, $SRR_{G,B}$, of 45 at $V_{BIAS} = 0.0$ V and monotonically increasing to 107 as the voltage reached $V_{BIAS} = 1.4$ V, which denotes a robust rejection of red photons. This attribute primarily results from the optical gaps of the component semiconductors in the blend, which are sufficiently large to prevent appreciable absorption of red photons. Indeed, green-sensitive photodetectors strongly rejecting red photons are straightforward to realize by selecting organic semiconductors with suitable optical gaps, as also demonstrated in the literature (see figure S1 and table S1).

On the other hand, it has been challenging to date to achieve solution-processed, green-selective photodetectors with a large spectral rejection ratio with respect to blue photons (see figures 1(c) and (f)). In this regard, our QA:PhO-Cl\textsubscript{6}BsubPc photodetectors achieved an $SRR_{G,B}$ of 7.6 at $V_{BIAS} = 0.0$ V and up to 17.6 at $V_{BIAS} = 1.4$ V. As shown in figure 3(d), this result corresponds to a nearly five-fold enhancement compared to any prior implementation of green-selective NBA organic photodetector based on solution-processed photoactive layers [17, 33, 34, 36–38, 46]. Importantly, such a large spectral rejection ratio with respect to blue photons is achieved alongside the highest peak EQE to date compared to all the prior relevant literature (i.e. green-selective NBA photodetectors based on solution-processable photoactive layers).

Interestingly, the application of a reverse bias voltage enhanced the spectral performance of the QA:PhO-Cl\textsubscript{6}BsubPc photodetectors, leading to a reduction of $FWHM_{EQE}$ and an increase in both $SRR_{G,B}$ and $SRR_{G,R}$ (figure 3(e)). The enhancement of $FWHM_{EQE}$ and $SRR_{G,B}$ with $V_{BIAS}$ agrees with the indications discussed earlier regarding the greater contribution to the photoresponse from photons absorbed in the
PhO-Cl₆BsubPc domains as the reverse bias voltage is increased. On the other hand, the increase in $SRR_{GR}$ may arise from the greater impact of the applied electric field on the photoconversion process associated with electronic states above/near the optical gap as opposed to tail states.

The record-high $EQE_p$ and $SRR_{GB}$ values achieved by the QA:PhO-Cl₆BsubPc photodetectors in comparison to all the prior relevant literature reflect the merits of the narrowband dual-absorber D:A approach (i.e. the use of a donor and an acceptor both selectively absorbing in the green spectral range; see figure 1(a)), which can enable a strong photoresponse and good spectral selectivity (i.e. low sensitivity to blue and red photons in the present case). Specifically, our photodetectors thrive on this approach because of two key factors: (a) the selection of a suitable non-fullerene acceptor with particularly limited out-of-band absorbance—which boosts the spectral rejection ratio—and the affinity between the donor and the acceptor, enabling good intermixing and a high photoconversion efficiency—i.e. a strong in-band photoresponse. Therefore, these properties could provide the design criteria for the future development of high-performance printable NBA photodetectors throughout the visible spectral range and beyond.

While the characterization above was carried out on freshly fabricated devices, we separately assessed the aging behaviour of our QA:PhO-Cl₆BsubPc photodetectors by measuring their $EQE$ at room temperature in air at discrete times over a period of 15 days (figure S7). The peak $EQE$ remained essentially constant for more than 24 hours but subsequently underwent a slow reduction, reaching approximately half of its original value on day 15. Given that the photodetectors investigated herein were not optimized for device longevity, this constitutes an encouraging result, especially in light of relevant investigations from the literature. Indeed, while QA boasts favourable stability [87], boron subphthalocyanines have varying levels of optoelectronic stability in air depending on the axial substituents, with some embodiments providing greater robustness than the phenoxy substituent used herein [93]. Therefore, it can be envisaged that future synthetic efforts targeting different axial substituents for boron subphthalocyanines could enable improved stability for our highly sensitive green-selective photodetectors. Further optimization routes worth pursuing toward greater device longevity include additive incorporation to passivate water-induced charge traps [94], encapsulation layers to reduce exposure to air species [95], and hole transport layers alternative to PEDOT:PSS [96].

Further insight into our fullerene-free approach to green-selective photodetectors can be gleaned by contrasting these devices with photodetectors relying on the fullerene acceptor phenyl-C₆₁-butyric-acid-methyl-ester (PCBM) as opposed to PhO-Cl₆BsubPc (i.e. photodetectors comprising a QA:PCBM photoactive layer). The energy level diagram of the QA-PCBM pair also reveals a staggered configuration with large energy offsets (figure 4(a)), thereby being conducive to a donor-acceptor bulk heterojunction with the potential for efficient photogeneration. Photodetectors made with QA:PCBM photoactive layers, however, delivered appreciably lower $EQE$ compared to the QA:PhO-Cl₆BsubPc counterparts. Their peak $EQE$ amounted to 12.0% at $V_{BIAS} = 1.5$ V (figure 4(b)), which is more than three-fold lower than that of QA:PhO-Cl₆BsubPc photodetectors. We trace the lower $EQE$ of the QA:PCBM devices to the non-ideal morphology of their photoactive layer, whose significant roughness (figure 4(c)) is expected to negatively impact the photoconversion process [89]. The sharp difference between this morphology and the one observed from QA:PhO-Cl₆BsubPc layers may relate to the different levels of intermolecular interactions between donor and acceptor in the QA:PhO-Cl₆BsubPc and QA:PCBM layers: while PhO-Cl₆BsubPc possesses groups that may form hydrogen/halogen bonds with QA [81, 82], in general, fullerenes do not offer this opportunity (to the same extent or at all, depending on their functionalization) primarily because of their bulky buckyball structures. Given that small-molecule photoactive layers are

Figure 4. (a) Energy levels of the various layers in a QA:PCBM photodetector. (b) EQE spectra of a QA:PCBM photodetector as a function of the applied reverse bias (the dashed line represents the normalized absorption spectrum of the QA:PCBM blend). (c) AFM image of a QA:PCBM film.
optimal for narrowband photodetection via the NBA approach (cf broadband nature of polymer semiconductors), our findings point to the attractiveness of non-fullerene acceptors for realizing the full potential of this approach in solution-based devices. Another key aspect that emerges from the EQE spectra of the QA:PCBM photodetectors is the absence of spectral selectivity, given that the photoresponse in the blue spectral range is comparable to that in the green spectral range (i.e. their FWHM is ill-defined and their $SRR_{GB} < 2$). This property reflects the broad absorption tail of PCBM through the visible range (see figure S8), as indeed the EQE spectrum of the QA:PCBM photodetectors closely follows the absorbance spectrum of the QA:PCBM layer (dashed line in figure 4(b)).

Applications involving color-selective light detection also require adequate speed of response to capture a time-varying illuminant. Therefore, we characterized the response of our QA:PhO-Cl$_6$BsubPc photodetectors to square light pulses in the green spectral range (figure 5(a)). The resultant rise and fall times fell in the range of 20–30 $\mu$s regardless of the applied optical power (figure 5(b)). This speed of response is more than adequate to meet the requirements of real-world applications involving color-selective light detection (typically demanding responses faster than the millisecond range), which confirms the practical potential of our approach.

3. Conclusion

To realize the full potential of NBA organic photodetectors for easy-to-make and high-performance color sensors, herein we investigated the capabilities of printable, fullerene-free photoactive layers for color-selective photodetection. With a focus on green-selective photodetectors, we studied photoactive layers comprising printable subphthalocyanine PhO-Cl$_6$BsubPc as a non-fullerene acceptor, which we adopted in virtue of its straightforward synthesis and high absorption selectivity to green photons. Specifically, we sought to realize photoactive layers combining PhO-Cl$_6$BsubPc with soluble green-selective quinacridone donors as a way of ensuring efficient photoconversion and robust rejection of out-of-band photons. While off-the-shelf $N,N'$-dialkylated quinacridones were found to be problematic due to solubility issues or poor intermixing in the solid state, a latent-pigment route came to the rescue: by converting a soluble quinacridone into QA via a simple annealing step, we could solution-deposit QA:PhO-Cl$_6$BsubPc thin films with pronounced absorption selectivity to green photons and adequate intermixing. Embedded within a sandwich-type device structure, this approach enabled us to realize green-selective NBA photodetectors with cutting-edge photoconversion efficiency (up to 40%) and green-to-blue spectral rejection ratio (up to 17.6). Importantly, this constitutes a 25% enhancement in photoconversion efficiency and a nearly five-fold increase in spectral selectivity compared to all the relevant solution-processed NBA photodetector literature. A comparison with fullerene-based photodetectors obtained by replacing PhO-Cl$_6$BsubPc with PCBM allowed us to clarify the merits of our fullerene-free approach. Indeed, QA:PCBM photoactive layers exhibited poor film morphology, delivering photodetectors with appreciably lower photoconversion efficiency and no spectral selectivity. We therefore revealed that the strength of the solution-based fullerene-free approach realized with QA:PhO-Cl$_6$BsubPc builds on the synergy of two factors: the spectral flexibility and selectivity of both donor and acceptor, enabling photoactive layers wherein both donor and
acceptor domains contribute to spectrally-selective photoconversion; and the ability to tailor the chemistry of the donor and acceptor to enable intermolecular interactions resulting in good intermixing in thin films, as achieved with the latent-pigment route for QA in combination with PhO-Cl$_6$BsubPc.

Overall, this work illustrates the potential of the fullerene-free approach to printable, NBA photodetectors for high-performance color sensing. Additionally, this work offers indications for donor and acceptor design that could help translate this approach to other spectral regions in the visible range and beyond. Therefore, the insights and cutting-edge performance provided by our study illustrate the opportunity offered by fullerene-free NBA organic photodetectors for printable color sensors and imagers that can meet the performance requirements of emerging applications.

4. Experimental section

4.1. Materials
t-BOC-QA was synthesized according to the procedure detailed in [83, 97] using the following materials: QA (97%; Sigma Aldrich), tetrahydrofuran (≥99.0%, AR; Yonghua Chemical Co.), di-(t-butyl)-dicarbonate (98%; Beijing Coincidence Technology Co.), and N,N'-dimethylaminopyridine (99%; Shanghai Aladdin Biochemical Technology Co.). For all other experiments, the following chemicals were purchased and used without further purification: N,N'-DMQA (96%; TCI Chemicals), N,N'-DBQA (98%; SunaTech Inc.), PhO-Cl$_6$BsubPc (99.99%; Lumtec), PCBM (>99.5%; Lumtec), PEDOT:PSS (Clevios P VP Al 4083; Heraeus), chloroform (≥99.8%, HPLC; Yonghua Chemical Co.), acetone (≥99.5%, AR; Sinopharm Chemical Reagent Co.), isopropanol (≥99.7%, AR; Yonghua Chemical Co.), LiF (99.99%; Zhongnuoxincai, Beijing Technology Co.), Al (99.999%; Zhongnuoxincai, Beijing Technology Co.), ITO-coated glass substrates (South China Science & Technology Co.), and glass substrates (Guangzhou Lighting Glass Co.).

4.2. Solution preparation
Solutions of N,N'-DBQA, t-BOC-QA, PhO-Cl$_6$BsubPc, and PCBM were prepared by dissolving their powders in chloroform (20 g l$^{-1}$) within a nitrogen-filled glove box. Solutions of t-BOC-QA:PhO-Cl$_6$BsubPc, N,N'-DBQA:PhO-Cl$_6$BsubPc, and t-BOC-QA:PCBM were obtained by mixing the solutions of the component materials in the desired ratio. All the solutions were stirred for 3 h at 40 °C before use.

4.3. Device Fabrication
ITO-coated glass substrates were washed in an ultrasonic bath by sequentially placing them in acetone, isopropanol, and deionized water (10 min for each step). The substrates were then dried with ultrapure nitrogen gas and subsequently underwent an oxygen plasma treatment for 15 min (using a Harrick PDC-002 system). Afterward, the PEDOT:PSS ink was filtered (using PTFE filters with a 0.45 µm pore size) and spin-coated on the substrates (500 rpm for 15 s, 3000 rpm for 30 s). The samples were then annealed on a hot plate at 150 °C for 10 min. The photoactive layer solution (t-BOC-QA:PhO-Cl$_6$BsubPc, N,N'-DBQA:PhO-Cl$_6$BsubPc, or t-BOC-QA:PCBM) was then spin-coated (2000 rpm for 25 s, 1000 rpm for 15 s) onto the samples. The samples comprising t-BOC-QA were then annealed on a hotplate at 210 °C (unless stated otherwise) for 15 min. The samples comprising N,N'-DBQA were annealed on a hotplate at 50 °C for 10 min. Finally, a 1.0 nm-thick LiF layer and a 90 nm-thick Al layer were thermally evaporated onto the samples through a shadow mask at a pressure below 2.0 × 10$^{-6}$ mbar.

4.4. Characterization
Absorption spectrophotometry was conducted using a UV–vis–NIR LAMBDA 950 system (PerkinElmer); the samples for such measurements were prepared by spin-coating the organic thin films of interest onto quartz substrates. Steady-state photoluminescence spectra were acquired using an FL3 fluorometer (HORIBA Scientific). TGA measurements were conducted with a thermogravimetric analyzer TGA 1 (Metter Toledo). The thickness and morphology of organic films were acquired with a Veeco Multimode V atomic force microscope (Bruker) in tapping mode using a silicon cantilever (Nanoworld, NCH). Current–voltage characteristics were measured in air with a Keithley 6420 source meter. EQE spectra were measured with a custom-built setup comprising an Omni-A2005i monochromator (Zolix), a power meter (Thorlabs, PM200), and a calibrated silicon photodiode (Thorlabs, S120VC). Transient photocurrent measurements were run with a custom-built setup relying on a 528 nm light-emitting diode controlled with a USB-6001 data acquisition device (National Instruments). During such measurements, the current signal from the photodetectors under test was amplified with a DHPCA-100 amplifier (FEMTO).
Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

Acknowledgments

C Y and V P contributed equally to this work. The authors are grateful to Professor Xiao-Jun Wang (Jiangsu Normal University) for the synthesis of t-BOC-QA. V P acknowledges financial support from the National Natural Science Foundation of China (61805166).

Author contributions

Y C carried out the bulk of the fabrication and characterization experiments. J M, K X, T Z, and J Z contributed to materials and/or device characterization experiments. Y C, J M, and K X contributed to data analysis. N G contributed to the discussion of the results. V P conceived and supervised the project, designed the experiments, contributed to data analysis, and wrote the manuscript. All authors revised the manuscript.

Conflict of interest

The authors declare no conflict of interest.

ORCID iDs

Nicola Gasparini  https://orcid.org/0000-0002-3226-8234
Vincenzo Pecunia  https://orcid.org/0000-0003-3244-1620

References

[1] Pecunia V 2019 Organic Narrowband Photodetectors: Materials, Devices and Applications (Bristol: IOP Publishing)
[2] Simone G, Dyson M J, Meskers S C J, Janssen R A J and Gelinck G H 2020 Adv. Funct. Mater. 30 1904205
[3] Chow P C Y and Someya T 2020 Adv. Mater. 32 1902045
[4] Yang D and Ma D 2019 Adv. Opt. Mater. 7 1800522
[5] Pecunia V, Fattori M, Abdinia S, Sirringhaus H and Cantatore E 2018 Organic and Amorphous-Metal-Oxide Flexible Analogue Electronics (Cambridge: Cambridge University Press)
[6] Jansen-van Vuuren R D, Armin A, Pandey A K, Burn P L and Meredith P 2016 Adv. Mater. 28 4766
[7] Brossard F S F, Pecunia V, Ramsay M J, Meskers S C J, Janssen R A J and Gelinck G H 2017 Adv. Mater. 29 1704425
[8] Deckman J, Lechéne P B, Pierre A and Arias A C 2018 Org. Electron. 36 139
[9] Lan Z, Lee M-H and Zhu F 2022 Adv. Intell. Syst. 4 2100167
[10] Pace G, Grimaldi A, Sampietro M, Natali D and Cairoini M 2017 Semicond. Sci. Technol. 30 104006
[11] Gong I, Darling S B and You F 2015 Energy Environ. Sci. 8 1953
[12] Pecunia V, Occhipinti L G and Hoyo R L Z 2021 Adv. Energy Mater. 11 2100698
[13] Perumal Veeramalai C, Feng S, Zhang X, Pammi S V N, Pecunia V and Li C 2021 Photon. Res. 9 968
[14] Konstantatos G n.d. Colloidal Quantum Dot Optoelectronics and Photovoltaics ed G Konstantatos and E H Sargent (Cambridge: Cambridge University Press) pp 173–98
[15] Pammi S V N, Tran V, Maddaka R, Eom J, Jung J S, Jeong H, Kim M, Pecunia V and Yoon S G 2020 Adv. Opt. Mater. 8 2000845
[16] Pammi S V N, Maddaka R, Tran V-D, Eom J-H, Pecunia V, Majumder S, Kim M-D and Yoon S G 2020 Nano Energy 74 104872
[17] Jansen-van Vuuren R D, Pivrikas A, Pandey A K and Burn P L 2013 J. Mater. Chem. C 1 3532
[18] Xia K, Li Y, Wang Y, Porilla L and Pecunia V 2020 Adv. Opt. Mater. 8 1902056
[19] Pecunia V 2019 J. Phys. Mater. 2 042001
[20] Siegmund B et al 2017 Nat. Commun. 8 15421
[21] Armin A, Jansen-van Vuuren R D, Kopidakis N, Burn P L and Meredith P 2015 Nat. Commun. 6 6343
[22] Liu M et al 2021 J. Phys. Chem. Lett. 12 2937
[23] Zhao T, Xia K, Natali D and Pecunia V 2022 Adv. Opt. Mater. 10 2200862
[24] Arca F, Sramek M, Tedde S F, Lugli P and Hayden O 2013 IEEE J. Quantum Electron. 49 1016
[25] Miao J, Zhang F, Du M, Wang W and Fang Y 2018 Adv. Opt. Mater. 6 1800601
[26] Xie B, Xie B, Zhang K, Yin Q, Hu Z, Yu G, Huang F and Cao Y 2020 Nat. Commun. 11 2871
[27] Siegmund B et al 2017 Nat. Commun. 8 15421
[28] Sakai T, Takagi T, Imamura K, Mineo K, Yakushiji H, Hashimoto Y, Aotake T, Sadamitsu Y, Sato H and Aihara S 2021 ACS Appl. Electron. Mater. 3 3085
[29] Han M G et al 2016 ACS Appl. Mater. Interfaces 8 26143
[30] Togashi H et al 2019 2019 IEEE Int. Electron Devices Meeting (IEDM) (IEEE) pp 16.6.1–4
[31] Lim Y et al 2020 ACS Appl. Mater. Interfaces 12 51688
[32] Aihara S, Hirano Y, Tajima T, Tanioka K, Abe M, Saito N, Kamata N and Terunuma D 2003 2003 IEEE Workshop on CCD and Advanced Image Sensors p 8
