Mitigating Dark Current and Improving Charge Collection for High-
Performance Near-Infrared Organic Photodiodes via P-doping Strategy

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Keywords: organic photodiode, near-infrared photodetector, p-doping, dark current, high-
detectivity

Abstract

Organic photodetectors (OPDs) have gained increasing interest for their remarkable opto-
electronic performances and compatibility with flexible devices. However, the commonly
occurring high dark current and low detectivity severely reduces the performance and hinders
commercialization of near infrared photodetectors. Here, we introduce a universal strategy of a
p-doped hole transport layer to realize highly sensitive photodetectors. The dark current is
significantly reduced by mitigating the reverse charge injection. As a result, the optimized OPD
consisting of PM6:Y6 as active layer and 1 nm F₆TCNQ p-doped PBTTT as a hole transport
layer exhibits an ultra-low dark current of 0.2 nA cm⁻², which is one the best performed near
infrared OPDs ever reported and comparable to commercialized silicon photodetectors. A
maximum specific detectivity of 6.02×10¹³ Jones at 800 nm is achieved with improved charge
collection efficiency and reduced trap states. And the potential commercial application in image
sensing is presented by integrating optimized OPDs into high-pixel-density arrays, further
demonstrating the significance of the improved detection characteristics in capturing high-quality sample images with this technology. The insights provided in our study have profound implications for the design and optimization of high-performance OPDs spanning the ultraviolet to near-infrared range.

1. Introduction

Solution-processed advanced OPDs have great potential in a variety of technologies and applications, including image sensing, machine vision and wearable health monitoring,[1-3] which have gained popularity over their inorganic counterparts due to the excellent optoelectronic and mechanical properties.[4, 5] The phase-separated bulk heterojunction (BHJ) composed of donor polymers and acceptor small molecules sandwiched between charge extraction layers is the most widely used device structure for both organic solar cells and OPDs. Different from the organic solar cells that operated under forward bias in photovoltaic mode for energy conversion, OPDs typically operate under reverse bias for photodetection. Therefore, minimizing the dark current density ($J_d$) while retaining high photocarrier extraction efficiency under light illumination is essential for enhancing vital performance metrics including the signal-to-noise ratio (SNR), linear dynamic range (LDR), and specific detectivity ($D^*$).[6] The intrinsic $J_d$ is primarily due to the charge carrier injection from the contacts into the semiconductor under a reverse voltage bias, or thermally generated charges in the bulk of the photoactive layer.[7-10] Whereas thermal generation typically makes a limited contribution to $J_d$ owing to the relatively large bandgap (>1 eV) of organic materials. Hence, inserting electron-blocking layers and hole-blocking layers between the contact-BHJ interfaces to enhance the energy barrier for undesired charge injection is a common strategy for reducing the dark current.[11-14] Despite the success of these charge-blocking layers, the external quantum efficiency (EQE) of these devices remains unchanged or is even reduced [15] owing to the
relatively large energy barrier at the blocking layer/photoactive layer interface caused by the interfacial dipole or the prolonged transport path.

Molecular doping is widely employed to regulate charge carrier concentration and thereby electronic transport properties in organic semiconductors (OSCs).[16] This process involves introducing a redox-active organic or inorganic molecule as a dopant. These dopants, by accepting electrons (p-type doping) or donating them (n-type doping) to OSCs, generate free holes or electrons within these materials. The ability to modulate electronic properties through molecular doping, combined with ease of processing, makes OSCs broadly interesting across organic electronics and energy applications. Recently, doped semiconducting polymers have become promising materials for solar cells,[17, 18] organic light-emitting diodes (OLEDs),[19, 20] organic field-effect transistors (OFETs),[21-23] and thermoelectric materials.[24, 25] Impressive advances in understanding doping mechanisms and developing techniques for sequential processing have enabled better control of doping efficiency.[26, 27]

Inspired by these developments, we demonstrate a p-doped hole transport layer (HTL) using poly(2,5-bis(3-hexadecylthiophen-2-yl)thieno[3,2]thiophene) (PBTTT) doped with F$_4$TCNQ, effectively reducing $J_d$ and enhancing the EQE in near-infrared OPDs. Utilizing strong oxidation capability of F$_4$TCNQ, we achieved efficient p-doping of PBTTT through a sequential doping process. Employing Mott-Shockley analysis and dark current simulation revealed that the reduced $J_d$ resulted from diminished trap-induced injection current density. Further analysis of energy level alignment showed that doping shifts the lowest unoccupied molecular orbital (LUMO) energy levels upward due to the interfacial dipole effect, increasing the electron injection barrier under reverse bias and thereby reducing $J_d$. Intriguingly, we observed doping-induced broadening of the density of states (DOS) in the highest occupied molecular orbital (HOMO) region, attributed to the formation of a partially filled polaron band. This larger DOS overlap between doped PBTTT and the donor in the photoactive layer further enhances collection efficiency. Additionally, an optimal doping concentration enhances
conductivity, charge carrier mobility, and morphology smoothness, significantly improving charge transport and extraction at the anode side, resulting in significantly enhanced device performance. The optimized OPD device exhibits exceptional photodetection performance, including a $J_d$ of 0.2 nA cm$^{-2}$ and a maximum specific detectivity of $6.02 \times 10^{13}$ Jones at 800 nm, positioning it among the top high-performance OPDs for visible to near-infrared photodetection.

Replacing $F_4$TCNQ with another p-type dopant, HATCN, we further investigated to confirm the universality of this doping strategy. Moreover, the potential for commercial application in image sensing was convincingly demonstrated by integrating high-performance OPDs into high-pixel-density image arrays, eliminating the need for patterned sensing layers. These breakthroughs underscore the critical role of molecular doping in the design and enhancement of high-performance OPDs.

2. Results and discussion

2.1. Materials and device structure

The structure of the device is illustrated in Fig. 1a. The active layer of our OPDs contains a BHJ system that comprises a polymer donor PM6 blend with Y6(Fig. S1). The staggered bandgap alignment of PM6 and Y6 demonstrates efficient charge separation following photogeneration of excitons (type-II heterojunction). An inverted architecture was adopted for the fabrication of the OPDs. The poly(ethyleneimine) ethoxylated (PEIE) layer, serving as a low-work function electron-transport layer, and the BHJ active layer were sequentially solution-processed onto an indium tin oxide (ITO) glass substrate. For electron-blocking layer, we utilized a prototypical hole-transport molecular PBTTT p-doped with $F_4$TCNQ (Fig. 1b), followed by the thermally evaporated molybdenum oxide and silver electrode.
Fig. 1. (a) Schematic structure of the OPD device. (b) The molecular structures of PBTTT and F$_4$TCNQ. (c) The HOMO and LUMO level of PBTTT and F$_4$TCNQ, the values are used from literature report.[28] (d) UV-Vis absorption spectra of PBTTT films doped by F$_4$TCNQ with different thicknesses.

Fig. 1c shows the values of the HOMO and LUMO level of PBTTT and F$_4$TCNQ. The charge transfer reaction between these two materials is energetically favorable, as evidenced by the higher HOMO level of PBTTT compared to the LUMO level of F$_4$TCNQ. This alignment facilitates easy electron transfer from PBTTT to F$_4$TCNQ. Additionally, the extent of solid-state ordering in doped conjugated semiconductors is significantly influenced by the molecular structures and the doping methods used. Sequential doping, in particular, has been found to better preserve film morphology and enhance conductivity compared to other methods.[26] The key point of the method is firstly fabricating a high-quality film of host material, followed by the introduction of dopant molecules into the film. Hence, in this study, the PBTTT film was pre-deposited using a water transfer printing method, with the detailed procedure available in
the Supporting Information. The doping process was executed by evaporating F₄TCNQ molecules onto the PBTTT layer, allowing them to diffuse into the film.

Molecular doping in conducting polymers not only generates mobile charge carriers but also introduces impurities that can alter carrier trapping mechanisms or energy band structures. Excessive dopant molecules sometimes hinder the carrier transport. To optimize the doping level, we varied the thicknesses of F₄TCNQ from 0 nm to 5 nm during thermal evaporation. The absence of charge transfer reaction between F₄TCNQ and PBTTT was confirmed by UV-visible absorption spectroscopy measurements. As depicted in Fig. 1d, the pristine PBTTT film displayed a distinct π-π* transition peak near 550 nm. However, in the spectra of p-doped PBTTT films, there was a noticeable decrease in the intensity of this peak. With the doping thickness increasing, notable absorption features emerged at approximately 768 nm and 864 nm, corresponding to the F₄TCNQ anions. These features, along with typical sub-band gap absorption indicative of polaron formation, confirmed charge transfer during the doping process. Additionally, a comprehensive X-ray photoelectron spectroscopy (XPS) scan was conducted to assess the diffusion depth of F₄TCNQ. Fig. S2 illustrates the nitrogen 1s peak variation with sputtering depth, demonstrating that F₄TCNQ molecules effectively diffuse from the surface into the bulk, thereby serving as efficient charge transfer dopants.

2.2. Dark current suppression and photodetection performance
Fig. 2. The detection property of the photodetector: (a) Characteristic \( J-V \) curve of the OPDs under illumination (125 \( \mu \)W cm\(^{-2} \), 800 nm) and in the dark. (b) The wavelength and EQE of the optimized device as a function of voltage bias. (c) Responsivity and (d) Detectivity as a function of wavelength. (e) The noise spectral density of OPDs under a reverse bias of -1 V. (f) Linear dynamic range.

**Fig. 2a** presents the current density-voltage \( (J-V) \) characteristics of the OPDs measured in the dark and under illumination. The dark current density was investigated as function of the doping thickness of \( F_4 \)TCNQ, with the \( J_d-V \) characteristics detailed in **Fig. S3**. The \( J_d \) of pristine device was 6.04×10\(^{-9} \) A cm\(^{-2} \) at -2 V which is lower than the value reported in the previous work,[31, 32] attributable to the enhanced electron blocking performance of the PBTTT layer. The \( J_d \) reached its minimum for the device doped at 1 nm (2.08×10\(^{-10} \) A cm\(^{-2} \) at -2 V), nearly two orders of magnitude lower than the control device. Furthermore, under increasing reverse bias voltage, the dark current in the doped-1 nm PBTTT-based device rose more gradually compared to the control device (**Fig. S3c**). This observation underscores the effectiveness of the doped electron blocking layer (EBL) in reducing \( J_d \). However, increasing the \( F_4 \)TCNQ doping thickness beyond 1 nm led to a rise in \( J_d \), mainly due to a higher density of traps or uncontrolled impurities in \( F_4 \)TCNQ at higher concentrations. Remarkably, these \( J_d \) are among the lowest...
value reported for visible and near infrared photodiodes,[32-34] highlighting the superior
electron injection blocking capabilities of the doped interlayer.

In order to investigate the photodetection response of the photodetectors, we carefully
measured the photocurrent under various incident wavelength (Fig. S4). Fig. 2b shows the
wavelength and EQE of the optimized device as a function of voltage bias. The responsivity
(\(R\)) and specific photodetectivity (\(D^*\)) are two important figure-of-merits of the OPDs. \(R\)
indicates how efficiently an OPD responds to light illumination and is defined as

\[
R = \frac{(I_{ph} - I_{dark})}{P_{in} A} \tag{1}
\]

where \(I_{ph}\) is the photocurrent, \(I_{dark}\) is the dark current, \(P_{in}\) the incident light intensity, and \(A\) the
device area(0.0314 cm\(^2\)). As shown in Fig. 2c, \(R\) peaks at a wavelength of approximately 780
nm, achieving 0.50 A W\(^{-1}\) at an applied bias of -1 V. This performance signifies efficient charge
carrier extraction, rendering the device well-suited for near infrared light detection.

Additionally, it is noteworthy that the \(R\) of the optimized OPD remains relatively stable when
the reverse bias voltage is increased from 0 V to -1 V (Fig. S4b). This stability suggests that
the device already exhibits effective carrier transport and extraction even at zero voltage bias.

Detectivity (\(D^*\)) is the crucial parameter of photodetector, which describes the smallest
detectable signal. It can be expressed to

\[
D^* = R \frac{A}{\sqrt{2qI_{dark}}} \tag{2}
\]

where \(q\) is elementary charge (1.6\times 10^{-19} \text{ C}), \(R\) is the responsivity. Fig. 2d displays the
calculated \(D^*\) as a function of wavelength. Notably, the effective suppression of dark current
without sacrificing photocurrent led to a high detectivity value of 6.02\times 10^{13} Jones at 800 nm,
measured at a reverse bias of -1 V. These measured \(D^*\) values are among the highest reported
for near-infrared organic or perovskite thin-film photodetectors.[35-37] It is also noteworthy
that the calculated \(D^*\) values of our OPDs are comparable to those of commercial silicon
photodiodes (Si PDs) in the 600 to 900 nm wavelength range (≈ 10^{12}-10^{13} Jones), exemplified
by the Hamamatsu S1226-18BK (Fig. S5a). Meanwhile, according to the comparison of the $J_d$
as a function of EQE from previously reported OPDs (Fig. S5b), a superior enhanced
performance was further evidenced owing to the doped interlayer.

To precisely ascertain the total noise current, the noise currents of the optimized OPD were
experimentally measured across various frequencies and are depicted in Fig. 2d. For the OPDs
with 1 nm doped HTL, a notably low noise current of less than 10^{-11} A Hz^{-1/2}, was observed at
frequencies ranging from 1 to 100 Hz. This noise current diminishes further at higher
frequencies, and is an order of magnitude lower than that of the undoped device. The shot noise
($i_s$) can be calculated by the expression:

$$i_s = \sqrt{2 q I_{dark}}$$ (3)

The calculated shot noise current is only 2.19 fA Hz^{-1/2}, which is much smaller than the
measured noise current, indicating that the noise is dominated by the 1/f noise (flicker noise),
especially at low frequency. Linear dynamic range (LDR) gives a range within which the
photocurrent versus intensity is a linear function. It could be extracted through

$$LDR = 20 \log \frac{J_{max}}{J_{min}}$$ (4)

$J_{max}$ and $J_{min}$ are the maximum and minimum photocurrent densities which deviate from
linearity. As shown in Fig. 2e, device had a linear response covering almost eight orders of
magnitude under the 780 nm monochromatic illumination, which yields a large LDR of 156 dB.
Thus, the relatively low dark current attributes to the large LDR. The transient photocurrent of
the optimized OPD device at -1 V under a NIR light modulation frequency of 20 Hz is shown
in Fig. S6a. A rise time (output signal changing from 10 to 90% of the peak output value) of
120 µs and fall time (output signal varying from 90 to 10%) of 100 µs were obtained. The -3
dB cutoff frequency ($f_{-3dB}$) is another important parameter for evaluating the applicable
bandwidth of photodetectors, which is defined as the frequency at which output amplitude
decreases by 3 dB. However, due to equipment constraints, the actual $f_{-3\text{dB}}$ value for our OPDs was not measured. As shown in Fig. S6b, we summarize several representative parameters of recent literatures.[32, 38-40] Based on the observed trends, an $f_{-3\text{dB}}$ exceeding 10 kHz is anticipated, which would be adequate for applications in image sensors and clinical diagnostics. Moreover, the doping strategy employed in the blocking layers has shown potential for broader application in photodetectors with various active layers. We applied this doping approach to other BHJ sensing layers, resulting in effective dark current suppression in these systems as well (Fig. S7). Furthermore, to broaden the scope of this doping strategy in reducing $J_d$, we experimented with doping PBTTT layers using other p-type dopants such as HATCN, achieving similar results. For the HATCN-doped PBTTT layer, the reverse $J_d$ decreased by more than an order of magnitude (Fig. S7d).

2.3. Mechanisms of p-doping improving device performance

![Fig. 3. (a) $C$-$f$ characteristics of the devices. (b) $C$-$V$ characteristics, and (c) Mott-Schottky plot (dashed lines represent the linear fitting). (d) Corrected current density-voltage curves.](image)

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For a better understanding on the difference in the dark current and EQE between devices, we performed the capacitance-frequency ($C$-$f$) measurements and the capacitance-voltage ($C$-$V$) measurements. The $C$-$f$ measurements were employed to evaluate trap density, which uses the small applied AC bias alternately traps and releases carriers from states near the Fermi energy. When the frequency of the applied AC signal is low enough, only states shallower than the trap energy can respond fast enough to the ac field to contribute to the capacitance, resulting in a step in the $C$-$f$ spectrum.[41] As shown in the $C$-$f$ plot (Fig. 3a), the plot reveals a distinct step at lower frequencies in the devices, with the doped device showing a lower capacitance compared to the pristine device. This indicates a relatively higher trap density in the pristine device. Consequently, the $C$-$f$ measurement result is consistent with the trend of the frequency response, and the change reflects the nature of the defect state in the film as a function of charge filling. In addition, we further performed the capacitance-voltage ($C$-$V$) measurements (Fig. 3b) and corresponding Mott-Shockley analysis (Fig. 3c). This analysis is predicated on the assumption that free carriers are completely depleted in the space charge region at the p-n junction.[42] The Mott-Shockley plot of $C^{-2}$-$V$ yields a straight line, whose slope reflects the trap density. The trap density ($N_A$) is defined by

$$N_A = \frac{-2}{q\varepsilon_0\varepsilon_rA^2} \left( \frac{dV}{dC^{-2}} \right) #(5)$$

where $\varepsilon_r$ is the relative dielectric constant of the BHJ film (assuming $\varepsilon_r = 3$), $\varepsilon_0$ is the vacuum permittivity, and $A$ is device area. Compared with the $N_A$ of pristine device ($1.26\times10^{15}$ cm$^{-3}$), the doped device displayed a significantly lower $N_A$ of $7.3\times10^{14}$ cm$^{-3}$. Meanwhile, the the lower trap density is consistent with the suppressed $J_d$ and enhanced EQE of the doped PBTTT device compared to pristine device. The results of the above Mott-Shockley analysis reveal that doped PBTTT interlayer can manifest the diminished impurity concentration inside the device.
To further figure out the underlying mechanism of the $J_0$ reduction, the corrected current density-voltage ($J_{\text{corr}}-V_{\text{rev}}$) characteristics (Fig. 3d) is analyzed according to the following equation:

$$J_{\text{corr}} = J - \frac{V_{\text{rev}} - J R_S}{R_{\text{sh}}} \tag{6}$$

where $J$ is the absolute value of the apparent current density, $V_{\text{rev}}$ is the absolute value of the applied reverse bias. $R_S$ and $R_{\text{sh}}$ are the area-normalized series resistance and shunt resistance, respectively, as extracted from the differential resistance.[43] In the doped device, the $J_{\text{corr}}-V_{\text{rev}}$ curve remains relatively flat until $V_{\text{rev}}$ reaches 0.2 V, and the dark current below this voltage is likely due to saturated generation current under full depletion conditions.[44] As the reverse bias increases to 0.24 V, the slope of the logarithmic $J_{\text{corr}}-V_{\text{rev}}$ curve surpasses 2, characteristic of space charge limited current (SCLC) with trap presence, signifying a dominance of charge injection in this regime.[7] Conversely, the pristine device enters the SCLC region at a lower onset voltage of about 0.12 V, less than that of the doped device. Hence, the $J_{\text{corr}}-V_{\text{rev}}$ characteristics imply that the elevated dark current in the pristine device primarily arises from carrier generation. Given that thermal generation current is significant only in semiconductors with smaller bandgaps,[10] we associate the generation current in the pristine device with trap-induced generation current, corroborating the Mott-Shockley analysis. Additionally, the doped device exhibits a higher $R_{\text{sh}}$ of $3.8 \times 10^{9}$ Ω cm², compared to $2.0 \times 10^{7}$ Ω cm² in the pristine device (as presented in Fig. S8). These findings suggest that the doped blocking layers effectively reduce both trap-induced generation current at low reverse bias and trap-assisted charge injection at high reverse bias, while also diminishing shunt leakage. Consequently, these modifications render OPDs more suitable for high detectivity applications.
Fig. 4. (a) The UPS spectra of the HOMO regions and (b) the secondary-electron cutoff region for different doping thickness. (c) Energy level diagram of the OPD. (d) Double logarithmic $J-V$ characteristics in hole-only devices. (e) The resistance of the doped PBTTT films as a function of the thickness of $F_4$TCNQ molecules. (f) The AFM of doped PBTTT films.

The influence of $F_4$TCNQ doping on the energy levels of PBTTT was initially investigated through ultraviolet photoelectron spectroscopy (UPS) evaluations. **Fig. 4a** displays the UPS spectra for the HOMO region. With increasing doping thickness, a significant band energy shift in both the onset (HOMO$_{on}$) and peak (HOMO$_{peak}$) of the HOMO emission was observed. The work function was calculated based on the relationship between the secondary electron cutoff energy and the incident photon energy, as depicted in **Fig. 4b**. For PBTTT and PBTTT:$F_4$TCNQ (1 nm doping), the HOMO$_{on}$ values were determined to be 0.75 eV and 0.3 eV, respectively. Given PBTTT's optical band gap of 1.68 eV, its LUMO level is estimated at -3.1 eV, aligning with previously reported values.[28] Consequently, the LUMO level of the 1 nm doped PBTTT film is extrapolated to be -2.8 eV. **Fig. 4c** illustrates a schematic of the energy levels in OPD devices, showing that even a minimal amount of $F_4$TCNQ doping results in an upward shift of
PBTTT's LUMO. This shift increases the energy barrier for electron injection under reverse voltage bias, thereby reducing the $J_d$.

Having elucidated the mechanism of reduced $J_d$ in doped devices, we further investigated the EQE and $R$ enhancement of these devices. The evolution of HOMO of doped PBTTT is shown in Fig. S9 through UPS data, to better visualize the HOMO region's evolution with varying doping thicknesses. Notably, HOMO$_{\text{peak}}$ broadened considerably as the F$_4$TCNQ thickness increased, reaching near doubling of the DOS width in the HOMO region at approximately 1 nm, compared to the pristine device. Consequently, this increase in DOS overlap between PBTTT and the donor within the photoactive layer led to an improvement in the efficiency of photogenerated carrier transfer (Fig. S10). This, in turn, contributed to the enhanced performance of the devices.

The hole mobilities of PBTTT films both with and without (w/o) F$_4$TCNQ films were assessed from a current density-voltage ($J$-$V$) analysis. Fig. 4d presents the double-logarithmic $J$-$V$ curves for hole-only devices with a structure of ITO/PEDOT:PSS/PBTTT(with and w/o F$_4$TCNQ)/MoO$_3$/Ag. The hole mobility ($\mu$) was extrapolated from the $J$-$V$ data of the SCLC region by using $J = 9\varepsilon_0\varepsilon_r\mu V^2/8d^3$, where $\varepsilon_0 (= 8.85 \times 10^{-14}$ F cm$^{-1}$) is the permittivity of free space, $\varepsilon_r (=3)$ is the dielectric constant of the PBTTT film,[45] and $d (= 15$ nm) is the thickness of the PBTTT film. The PBTTT:F$_4$TCNQ film with 1 nm doping exhibited a hole mobility of 2.77$\times$10$^{-3}$ cm$^2$V$^{-1}$s$^{-1}$, which is an order of magnitude higher than 9.15$\times$10$^{-4}$ cm$^2$V$^{-1}$s$^{-1}$ observed in the pristine PBTTT film. This finding suggests that doping PBTTT with F$_4$TCNQ significantly enhances the hole transport and collection efficiency at the interface, thereby improving overall device performance.

Fig. 4e presents the resistance measurements of PBTTT films. An efficient charge transfer was verified through the current-voltage characteristics (Fig. S11). Notably, doping with F$_4$TCNQ led to a significant reduction in the resistance of PBTTT films, decreasing it by six orders of magnitude. The surface morphologies of these doped PBTTT films were analyzed.
using atomic force microscopy (AFM), as depicted in Fig. 4f. The pristine layer is seen to contain various peaks, indicating molecular terracing and the presence of large grains. In contrast, F₄TCNQ doping appeared to diminish and smooth these surface features. This observation is supported by the surface roughness root mean square (RMS) values, which decreased from 1.95 nm in the neat PBTTT to 1.36 nm in PBTTT:F₄TCNQ films with 1 nm doping level. Such alterations in surface morphology, attributed to the addition of F₄TCNQ, mitigated grain boundary effects, thereby facilitating improved charge carrier transport within the film.

2.4. Imager integrating TFT backplane

Fig. 5. Imager integrating TFT backplane and p-doped photodiodes. (a) The schematic illustration of image sensing process, the pattern used for sensing is PKU logo. (b) Schematic view of a single pixel. (c) The photograph of the final near infrared imaging detector. (d) The image of the PKU logo captured by the photodetector array.
Due to the excellent capability of monolithic integration over a complementary metal-oxide-semiconductor (CMOS) or TFT-based pixel circuits, OPDs offer new opportunities for image sensing.[46-48] Moreover, their high opto-electric responses and low dark current associated with moderate carrier mobility enable large-area, high-pixel count displays and image arrays without patterning the active layer.[49, 50] We demonstrated a high-pixel-density imaging with an organic photodiode image array. For image process (as shown in Fig. 5a), we first printed a piece of transparent PET film with a specified pattern (PKU logo), then an near-infrared LED was used to illuminate it and project onto an OPD array. The schematic structure of single pixel of OPD arrays was demonstrated in Fig. 5b. The bottom of the chip is ITO pixel electrode, we then fabricated the ETL/sensing layer/HTL/top electrode covering the entire sensing area, which is the same of device fabrication process. Fig. 5c is the photograph of the organic image sensor. The left black part of this sensor is flexible printed circuit, and it is bonded with the TFT chip to provide an efficient read out circuitry which is essential for high quality imaging. The active pixel size, defined by the bottom ITO pixel pad, was 200 µm × 200 µm. As illustrated in Fig. 5d, the image captured by the OPD array can clearly reflect the original picture. These weak signals within the common rows and columns of an exposed pixel could be an indication of electrical or optical crosstalk. Meanwhile, this results further validate a critical role for molecular doping in fabrication of OSC devices for high resolution imaging.

3. Conclusion

In summary, we have successfully demonstrated high-performance near-infrared OPDs through p-doping strategy. The F₄TCNQ doped PBTTT can form a favorable energy level alignment at interface, resulting in the reduction of the $J_\text{d}$, from $6.04 \times 10^{-9}$ A cm$^{-2}$ to $2.08 \times 10^{-10}$ A cm$^{-2}$ at -2 V. We also found that doping improved the hole mobility of the interlayer, resulting in enhanced charge transport and collection efficiency. Interestingly, the larger overlap of DOS between PBTTT and donor within the photoactive layer, further increasing the photogenerated...
charge carrier transfer efficiency. All these factors contributed to significantly improved device
performance, which exhibited high responsivities (0.50 A W\(^{-1}\) at 780 nm under -1 V), a large
LDR of 156 dB, and a high detectivity over 10\(^{13}\) Jones. Consequently, the champion device can
be applied in high-pixel-density image array, and achieve a simple array structure with precise
pitch and without patterning the sensing layer. A clear image has been successfully captured
through bonding with the TFT backplane. Meanwhile, the doping strategy is also applicable to
other p-type dopants, and could be an efficient way to construct near-infrared OPDs with high
responsivity and low noise for practical application at room temperature.
Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements:

This study was supported through the National Natural Science Foundation of China(62204006, 62304013), Development and Reform Commission of Shenzhen Municipality(XMHT20220106002), Shenzhen Fundamental Research Program(No. GXWD20201231165807007-20200810113811001), Shenzhen Science and Technology Program(GJHZ20210705143400002).

Appendix A. Supplementary data

Supplementary data to this article can be found online.

References


This work delivers a universal strategy of a p-doped hole transport layer (HTL) to realize highly sensitive NIR photodetectors. Benefiting from the suppression of reverse charge injection and reduction of interfacial trap density, a ultralow dark current and high external quantum efficiency can be obtained when using doped HTL layer. This p-doping strategy provides new insights into the design of high-performance photodetectors with potential applications by simultaneously offering the merits of high sensitivity, high imaging resolution, light-weight and low cost.