Highly Sensitive Organic Phototransistors Fabricated from PCPDTBT:PCBM Blend

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Abstract. Organic phototransistors (OPTs) play a crucial role in various light sensing and imaging applications. In this work, we have fabricated highly sensitive Poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b,3,4-b’]dithiophene)-alt-4,7(2,1,3-benzothiadiazole)] (PCPDTBT)/(6,6)-phenyl-C61-butyric acid methyl ester (PCBM) blended thin film based OPTs using ribbon-floating film transfer method. A high charge carrier mobility (μ) of 0.002 cm²V⁻¹s⁻¹ and an I_on/I_off of 6 × 10⁴ was showcased by the blended polymer thin film based OPT as compared to its pristine polymer thin film based counterpart which had a μ of 0.001 cm²V⁻¹s⁻¹ and an I_on/I_off of 9 × 10³. Further, the blended polymer thin film based OPT demonstrated a high photosensitivity of 6.6 × 10³ and a photoresponsivity of 0.13 A/W towards white light which were much superior than those of many of the previously reported polymer thin film based OPTs. The results hold crucial significance towards the development of cost effective blended polymer thin film based OPTs.

1. Introduction
Photodetectors serve as an indispensable part of numerous imagers and sensors, artificial vision, plastic fiber based transceivers and in the cardiovascular monitoring systems in the healthcare domain[1–4]. Owing to the flexibility of organic semiconductors, the photodetectors based on these organic semiconductors have become a lucrative substitute to the inherently rigid inorganic Si-based photodetectors[5,6]. The former is being employed in cardiovascular monitoring systems in the medical domain to record the feeble light signals[7]. Among the three types of organic photodetectors i.e, organic photodiodes (OPDs), organic photoconductors and organic phototransistors (OPTs)[8–12], the OPTs have showcased low device dark currents and high signal to noise ratios (SNRs)[13,14], leading to their superior performance.

OPTs sensitive to different regions of the electromagnetic spectrum have been widely explored in the recent past. However, there has been a tremendous consumer demand for high performance white light sensing devices. Hence, numerous attempts have been made by researchers towards the fabrication of highly sensitive OPTs. Wang et al. used fluorographene (FG) nanosheets to modify the interface between the organic semiconductor layer and the gate dielectric layer and demonstrated high
performance white light sensitive OPTs with a photoresponsivity (R) of 21.83 AW⁻¹ and a photosensitivity (P) of 1.85 × 10⁴[15]. Perylenebis(dicarboximide)s (PDIs) multifiber-based white light sensitive OPT was fabricated by Gemayel et al. which showcased a high R value of 4.08 ± 1.65 × 10⁵ AW⁻¹[16]. The OPTs based on polymer/nanoparticle composites and polymer/small molecule blends were explored with the aim to achieve efficient device performance[17,18]. In this report, we have fabricated highly sensitive polymer/small molecule blend based OPTs which have demonstrated high P and R values towards white light. A low band-gap copolymer Poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta [2,1-b;3,4-b']dithiophene)-alt-4,7(2,1,3-benzothiadiazole)] (PCPDTBT) was blended with a small molecule [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) to develop the thin films using ribbon-floating film transfer method (ribbon-FTM)[19,20]. The formed thin films were highly oriented and were employed as the active layers of the fabricated OPTs. The OPT employing PCPDTBT/PCBM blend as the active layer showcased superior performance over the one with pristine PCPDTBT as its active layer. The performance of the fabricated OPTs was found to be superior than many of the previously reported similar OPTs. The results thus showcase highly sensitive blended polymer thin film based OPTs for use as light sensors.

2. Experimental

2.1. Materials

PCPDTBT and PCBM were procured from Sigma Aldrich and were used as received. The polymer solutions were prepared in anhydrous Chloroform. Electronic grade Ethylene Glycol (EG) and Glycerol (Gl) were used as the substrates for developing polymer thin films.

2.2. Sample preparation

1.2 cm × 1.2 cm sized glass samples were ultra-sonically cleaned in Acetone, Iso-propyl alcohol (IPA) and de-ionized (DI) water for five minutes each. Their surfaces were then made hydrophobic through hexamethyldisilazane (HMDS) treatment. 3 (w/v)% solutions of pristine PCPDTBT and PCPDTBT:PCBM (3:1) blend were prepared in anhydrous Chloroform. Thin films of these solutions were then formed on EG:Gl (3:1) hydrophilic substrate mixture pooled in a rectangular tray. This mixture was chosen as it yielded film with maximum polymer orientation. For coating the thin films, ribbon-FTM process was employed[19]. It involved dropping of polymer solution at the hydrophilic substrate/ PTFE slider interface which spreaded forward and formed a long floating thin film after an eventual vaporization of the polymer solvent. A detailed explanation of the ribbon-FTM process and the mechanism of polymer film formation has been provided in our previous reports[19,20]. The floating pristine and blended polymer thin films were then transferred on the glass samples. Subsequently, the coated samples were annealed at 70 °C in an inert Argon glove box prior characterization.

2.3. OFET Fabrication

For device fabrication, 300 nm thick Si/SiO₂ wafers were used. These were cleaned in Acetone, IPA and DI-water via ultra-sonication for two minutes each. Subsequently, their surfaces were modified with HMDS. The maximally oriented polymer films formed on EG:Gl (3:1) mixture were coated on the Si/SiO₂ wafers to form the active layers of the OFETs. The coated samples were annealed inside an Argon filled glove at 70 °C for half an hour. These were then coated with Au source (S) and drain (D) electrodes of 50 nm thickness. The electrodes were deposited using thermal evaporation such that the direction of the formed transistor channel was along the polymer orientation direction as shown in Figure 1a. The fabricated bottom gate top contact (BGTC) type organic field effect transistors (OFETs) thus had an Lₘ = 20 μm and W = 2 mm. Figure 1b shows a schematic illustration of these OFETs.
2.4. Characterization Instruments

A UV-Vis-NIR spectrophotometer (JASCO V-570) was used to measure the absorption spectra of the thin films. A Glan Thomson prism was used to measure the polarized absorption spectra of the samples. A Keithley 2612A sourcemeter unit was used to measure the electrical characteristics of the OFETs. A solar simulator was used for OPT photo-response measurements.

3. Results and Discussion

3.1. Polarized absorption spectroscopy

Absorption spectroscopy is a powerful tool which provides information about the strength of macromolecular order, extent of polymer effective $\pi$-conjugation and the absorbing species contained in the film[21,22]. To observe the effect of blending PCBM with PCPDTBT, absorption spectrum of pristine PCPDTBT thin film was measured and compared with that of the blended film. Figure 2a shows the respective absorption spectra of the two films. As can be observed, a higher absorption intensity between 300 nm to 350 nm indicative of the PCBM moiety was clearly visible in the absorption spectrum of the PCPDTBT:PCBM (3:1) blended film[23]. Furthermore, two peaks around 410 nm and 740 nm corresponding to the CPDT and BT units of the PCPDTBT copolymer were clearly visible in both the films[24]. It was thus observed that blending PCBM with PCPDTBT had led to an increase in the overall absorption range of the latter which is highly desired for white light sensing. Furthermore, the effect of blending PCBM on the orientation characteristics of the PCPDTBT film was observed through polarized absorption spectroscopy[20]. Linearly polarized light was obtained using a Glan Thomson prism and it was made to fall on the samples. Furthermore, the plane of polarization of the incident light was sequentially made parallel (\( \parallel \)) and perpendicular (\( \perp \)) to the orientation direction of the polymer chains in the films. As can be observed from Figures 2b and 2c, intensified film absorption was observed in the \( \parallel \) direction. The absorption intensity reduced in the \( \perp \) direction. The extent of reduction in the absorption varied between the two films.

Figure 2. a) Normalized and b), c) polarized absorption spectra of the pristine and blended PCPDTBT thin films.
Dichroic ratio (DR), a measure of the degree of polymer orientation in the films, was estimated for a quantitative analysis using the equation\[25\]:

$$DR = \frac{\text{Maximum absorption at } \lambda_{\text{max}(I)}}{\text{Absorption at } \lambda_{\text{max}(\perp)}}$$ (1)

A high DR of 4.1 was obtained for the pristine PCPDTBT thin film. DR was slightly decreased to 3.96 upon blending PCBM with PCPDTBT as in the case of the blended film. Blending of PCBM was thus found to have a minimal effect on the orientation of the polymer chains.

3.2. OFET Characterization

To investigate the influence of PCPDTBT/PCBM blending, two types of OFETs were fabricated which employed pristine PCPDTBT and PCPDTBT/PCBM (3:1) blended thin films as their active layers. The OFETs were characterized in vacuum. Figures 3a and 3b show the electrical characteristics of the two types of OFETs. The OFET performance parameters were estimated for the two devices and these have been tabulated as Table 1. It was observed that blending of the polymer with PCBM resulted in an improvement in the overall device performance with the PCPDTBT/PCBM blend based OFET demonstrating a higher charge carrier mobility (\(\mu\)) of 0.002 cm\(^2\)V\(^{-1}\)s\(^{-1}\) and an \(I_{\text{on}}/I_{\text{off}}\) of \(6 \times 10^4\) over its pristine polymer thin film based counterpart which had a \(\mu\) of 0.001 cm\(^2\)V\(^{-1}\)s\(^{-1}\) and an \(I_{\text{on}}/I_{\text{off}}\) of 9 \times 10^3. The results thus reflect that blending of the polymer with PCBM enhanced the OFET performance.

![Figure 3.a) Transfer and b) Output characteristics of the pristine PCPDTBT and PCPDTBT:PCBM (3:1) blended thin film based OFETs.](image)

Table 1. Estimated performance parameters of the two types of OFETs.

| OFET Type                | Mobility (\(\mu\)) (cm\(^2\)V\(^{-1}\)s\(^{-1}\)) | Threshold Voltage (\(V_{\text{TH}}\)) (V) | On-off ratio (\(I_{\text{on}}/I_{\text{off}}\)) |
|--------------------------|-----------------------------------------------|------------------------------------------|-----------------------------------------------|
| Pristine PCPDTBT thin film based | 0.001                                         | 0                                        | 9 \times 10^3                                |
| PCPDTBT:PCBM blend based  | 0.002                                         | 8                                        | 6 \times 10^4                                |

To observe the effect of PCPDTBT/PCBM blending on the photo-response of the fabricated OFETs, these were illuminated with white light from a solar simulator with an incident power...
intensity of 100 mWcm$^{-2}$. Figure 4a depicts the variations in the OPT drain source currents ($I_{DS}$) upon illumination with white light.

For quantitative analysis regarding the suitability of the fabricated OFETs as OPTs, two parameters indicative of an OPT performance, namely, $P$ and $R$ were obtained using the equations[26,27]:

$$P = \frac{I_{\text{Photo}} - I_{\text{Dark}}}{I_{\text{Dark}}}$$  \hspace{1cm} (2)

$$R = \frac{I_{\text{Photo}} - I_{\text{Dark}}}{P_{\text{in}}A}$$  \hspace{1cm} (3)

The photosensitivity plots of the two OPTs are depicted in Figure 4b. As can be observed, blending of PCPDTBT with PCBM resulted in an enhancement in the OPT photosensitivity. The PCPDTBT/PCBM (3:1) blend based OPT had a higher $P$ value of $6.6 \times 10^3$ over its pristine polymer thin film based counterpart which had a $P$ value of $1.4 \times 10^3$. The increased $P$ value resulted from the lower dark current values in case of the PCPDTBT/PCBM (3:1) blend based OPT. Furthermore, the performance of the fabricated OPTs was compared with other similar OPTs as indicated in Table 2.

As can be observed from Table 2, the performance of the pristine PCPDTBT was at par with those of other pristine polymer based OPTs fabricated from P3HT, BAS-PPE polymers etc[28,29]. Furthermore, blending a small amount of PCBM in the polymer resulted in a superior performance OPT with a high $P$ of $6.6 \times 10^3$. In spite of having an inherently lower charge carrier mobility of 0.002 cm$^2$V$^{-1}$s$^{-1}$ as compared to other high mobility polymers like P3HT ($\mu = 0.01-0.07$ cm$^2$V$^{-1}$s$^{-1}$)[28], the blended polymer based OPT fabricated in this work showcased a superior photo-response. This can be attributed to the highly aligned polymer chains in this OPT and the presence of the small molecule (PCBM) which facilitated an efficient dissociation of the photo-generated excitons in the active layer of the OPT. The results thus showcase efficient blended polymer based OPTs which have great potential for use in light sensing applications.

![Figure 4](image-url)

Figure 4.a) Variations in the $I_{DS}$ values of the pristine PCPDTBT and PCPDTBT:PCBM (3:1) blended thin film based OPTs upon white light illumination. b) OPT photosensitivity plots.

| OPT Active Layer Constituent | Incident wavelength, Intensity ($\lambda$, $P_{\text{in}}$) (nm, mWcm$^{-2}$) | Mobility ($\mu$) (cm$^2$V$^{-1}$s$^{-1}$) | $P$ (a.u) | $R$ (A W$^{-1}$) | Ref |
|-----------------------------|-------------------------------------------------|---------------------------------|--------|----------------|----|
| P3HT                        | White light, 51                                 | $0.01-0.07$                     | $3.8 \times 10^3$ | 245            | [28] |
4. Conclusions

Highly sensitive blended polymer thin film based OPTs have been fabricated using ribbon-FTM. PCPDTBT was blended with a small molecule, PCBM, to form thin films to be used as active layers of the fabricated OPTs. The formed films were highly oriented with a maximum DR of 3.96. A comparison of the performance of the blended polymer based OPT with that of the pristine polymer based OPT revealed a superior performance by the former with a high \( \mu \) of 0.002 cm\(^2\)V\(^{-1}\)s\(^{-1}\) and an \( \text{I}_{\text{on}}/\text{I}_{\text{off}} \) of \( 6 \times 10^4 \). Furthermore, the PCPDTBT/PCBM blended thin film based OPT showcased a high \( P \) of \( 6.6 \times 10^3 \) and an \( R \) of 0.13 AW\(^{-1}\) towards white light (\( P_{\text{in}} = 100\text{mWcm}^{-1} \)) marking its high suitability towards white light sensing applications.

Acknowledgements

V.S would like to thank the department of science and technology (DST), India for providing financial support to the project entitled “Development of Low Voltage High Sensitivity Organic Photosensitive Transistors for Near Infrared Light Sensors”, project number: EMR/2016/008018. N.Y is thankful to Japan Student Service Organization (JASSO) for providing scholarship for this work at Kyushu Institute of Technology (KIT), Japan. V.S would like to thank Director, IIT Indore for his constant support.

References

[1] Xu H, Liu J, Zhang J, Zhou G, Luo N and Zhao N 2017 Flexible Organic/Inorganic Hybrid Near-Infrared Photoplethysmogram Sensor for Cardiovascular Monitoring Adv. Mater. 29 1–6
[2] Martino N, Ghezzi D, Benfenati F, Lanzani G and Antognazza M R 2013 Organic semiconductors for artificial vision J. Mater. Chem. B 1 3768–80
[3] Park S, Fukuda K, Wang M, Lee C, Yokota T, Jin H, Jinno H, Kimura H, Zalar P, Matsuhisa N, Umezu S, Bazan G C and Someya T 2018 Ultraflexible near-infrared organic photodetectors for conformal photoplethysmogram sensors Adv. Mater. 30 1–8
[4] Wu Z, Zhai Y, Yao W, Eedugurala N, Zhang S, Huang L, Gu X, Azoulay J D and Ng T N 2018 The Role of Dielectric Screening in Organic Shortwave Infrared Photodiodes for Spectroscopic Image Sensing Adv. Funct. Mater. 28 1–9
[5] Colace L, Masini G, Galluzzi F, Assanto G, Capellini G, Di Gaspare L, Palange E and Evangelisti F 1998 Metal-semiconductor-metal near-infrared light detector based on epitaxial Ge/Si Appl. Phys. Lett. 72 3175–7
[6] Tang L, Kocabas S E, Latif S, Okyay A K, Ly-Gagnon D S, Saraswat K C and Miller D A B 2008 Nanometre-scale germanium photodetector enhanced by a near-infrared dipole antenna Nat. Photonics 2 226–9
[7] Lee Y H, Kweon O Y, Kim H, Yoo J H, Han S G and Oh J H 2018 Recent advances in organic sensors for health self-monitoring systems J. Mater. Chem. C 6 8569–612
[8] Jansen-van Vuuren R D, Armin A, Pandey A K, Burn P L and Meredith P 2016 Organic Photodiodes: The Future of Full Color Detection and Image Sensing Adv. Mater. 28 4766–802
[9] Liu X, Lin Y, Liao Y, Wu J and Zheng Y 2018 Recent advances in organic near-infrared photodiodes J. Mater. Chem. C 6 3499–513
[10] Ren X, Yang F, Gao X, Cheng S, Zhang X, Dong H and Hu W 2018 Organic Field-Effect Transistor for Energy-Related Applications: Low-Power-Consumption Devices, Near-Infrared Phototransistors, and Organic Thermoelectric Devices Adv. Energy Mater. 8 1–27

[11] Sun Z, Li J and Yan F 2012 Highly sensitive organic near-infrared phototransistors based on poly(3-hexylthiophene) and PbS quantum dots J. Mater. Chem. 22 21673–8

[12] Dong H, Zhu H, Meng Q, Gong X and Hu W 2012 Organic photoresponse materials and devices Chem. Soc. Rev. 41 1754–808

[13] Ma L, Chen B, Guo Y, Liang Y, Zeng D, Zhan X, Liu Y and Chen X 2018 NIR polymers and phototransistors J. Mater. Chem. C 6 13049–58

[14] Xu H, Li J, Leung B H K, Poon C C Y, Ong B S, Zhang Y and Zhao N 2013 A high-sensitivity near-infrared phototransistor based on an organic bulk heterojunction Nanoscale 5 11850–5

[15] Wang L, Xie X, Zhang W, Zhang J, Zhu M, Guo Y, Chen P, Liu M and Yu G 2014 Tuning the light response of organic field-effect transistors using fluorographene nanosheets as an interface modification layer J. Mater. Chem. C 2 6484–90

[16] Gemayel M El, Treier M, Musumeci C, Li C, Mu K and Samor P 2012 Ja211515B.Pdf

[17] Qi Z, Cao J, Li H, Ding L and Wang J 2015 High-performance thermally stable organic phototransistors based on PSeTPTI/PC61BM for visible and ultraviolet photodetection Adv. Funct. Mater. 25 3138–46

[18] Mok S M, Yan F and Chan H L W 2008 Organic phototransistor based on poly(3-hexylthiophene)/ TiO2 nanoparticle composite Appl. Phys. Lett. 93 2006–9

[19] Tripathi A S M, Kumari N, Nagamatsu S, Hayase S and Pandey S S 2019 Facile fabrication of large area oriented conjugated polymer films by ribbon-shaped FTM and its implication on anisotropic charge transport Org. Electron. 65 1–7

[20] Tripathi A S M, Gupta R K, Sharma S, Nagamatsu S and Pandey S S 2020 Molecular orientation and anisotropic charge transport in the large area thin films of regioregular Poly(3-alkylthiophenes) fabricated by ribbon-shaped FTM Org. Electron. 81

[21] Korovyankov O J, Österbacka R, Jiang X M, Vardeny Z V. and Janssen R A 2001 Photoexcitation dynamics in regioregular and regiorandom polythiophene films Phys. Rev. B - Condens. Matter Mater. Phys. 64 2351221–6

[22] Spano F C 2005 Modeling disorder in polymer aggregates: The optical spectroscopy of regioregular poly(3-hexylthiophene) thin films J. Chem. Phys. 122 1–15

[23] Cook S, Ohkita H, Kim Y, Benson-Smith J J, Bradley D D C and Durrant J R 2007 A photophysical study of PCBM thin films Chem. Phys. Lett. 445 276–80

[24] Schulz G L, Fischer F S U, Trefz D, Melnyk A, Hamidi-Sakr A, Brinkmann M, Andrienko D and Ludwigs S 2017 The PCPDTBT Family: Correlations between Chemical Structure, Polymorphism, and Device Performance Macromolecules 50 1402–14

[25] Tripathi A S M, Pandey M, Sadakata S, Nagamatsu S, Takashima W, Hayase S and Pandey S S 2018 Anisotropic charge transport in highly oriented films of semiconducting polymer prepared by ribbon-shaped floating film Appl. Phys. Lett. 112

[26] Ljubic D, Liu W, González-Espinoza C E, Hu N X, Wu Y and Zhu S 2017 Binary Blends of Polymide and Benzothienobenzothiophene for High-Performance Solution-Processed Organic Phototransistors Adv. Electron. Mater. 3 1–10

[27] Noh Y Y, Kim D Y, Yoshida Y, Yase K, Jung B J, Lim E and Shim H K 2005 High-photosensitivity p-channel organic phototransistors based on a biphenyl end-capped fused bithiophene oligomer Appl. Phys. Lett. 86 84–7

[28] Pal T, Arif M and Khondaker S I 2010 High performance organic phototransistor based on regioregular poly(3-hexylthiophene) Nanotechnology 21

[29] Xu Y, Berger P R, Wilson J N and Bunz U H F 2004 Photoresponsivity of polymer thin-film transistors based on polyphenyleneethynylene derivative with improved hole injection Appl. Phys. Lett. 85 4219–21
[30] Hamilton M C and Kanicki J 2004 Organic polymer thin-film transistor photosensors *IEEE J. Sel. Top. Quantum Electron.* 10 840–8

[31] Hamilton M C, Martin S and Kanicki J 2004 Thin-film organic polymer phototransistors *IEEE Trans. Electron Devices* 51 877–85