Ultrathin Polymer Nanofibrils for Solar-Blind Deep Ultraviolet Light Photodetectors Application


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Supporting Information

ABSTRACT: Solar-blind deep ultraviolet photodetectors (DUVPDs) based on conventional inorganic ultrawide bandgap semiconductors (UWBS) have shown promising application in various civil and military fields and yet they can hardly be used in wearable optoelectronic devices and systems for lack of mechanical flexibility. In this study, we report a non-UWBS solar-blind DUVPD by designing ultrathin polymer nanofibrils with a virtual ultrawide bandgap, which was obtained by grafting P3HT with PHA via a polymerization process. Optoelectronic analysis reveals that the P3HT-‖PHA nanofibrils are sensitive to DUV light with a wavelength of 254 nm but are virtually blind to both 365 nm and other visible light illuminations. The responsivity is 120 A/W with an external quantum efficiency of up to 4970%, implying a large photoconductive gain in the photoresponse process. The observed solar-blind DUV photosresponse is associated with the resonant mode due to the leakage mode of the ultrathin polymer nanofibrils. Moreover, a flexible image sensor composed of 10 × 10 pixels can also be fabricated to illustrate their capability for image sensing application. These results signify that the present ultrathin P3HT-‖PHA nanofibrils are promising building blocks for assembly of low-cost, flexible, and high-performance solar-blind DUVPDs.

KEYWORDS: Optoelectronic device, polymer nanostructures, leakage mode, virtual ultrawide bandgap semiconductor, image sensor

Solar-blind deep ultraviolet photodetector (DUVPD) is a sort of optoelectronic device that can detect photonic irradiation with wavelengths in the range of 200–280 nm. As a complement to visible and infrared light (IR) photodetectors (PDs), DUVPDs are of paramount importance and have recently received extensive attention for their promising applications in military surveillance, target detection and acquisition, missile launch detection, chemical analysis, and flame detection. For example, DUVPDs have exhibited great potential in biological and medical analysis because DUV photons can be strongly absorbed by DNA molecules, inducing significant damage. In addition, highly responsive solar-blind DUVPDs that are immune to interference from ambient visible or UVA and UVB lights are crucial to track ballistic missile. Therefore, solar-blind DUVPDs have been widely employed in some space-based warning systems.

Benefiting from the rapid advance of semiconductor technology, various high-performance DUVPDs with different device geometries have been developed in the past decades. Generally, these devices are made of ultrawide bandgap semiconductors (UWBS), such as Ga2O3, ZnMg1−xO, diamond, and AlxGa1-xN, which are normally characterized by a bandgap of around 5 eV or even larger value. Various studies have demonstrated that the UWBS-based DUVPDs can attain excellent DUV sensitivity, including a large on/off ratio, relatively low dark-current, high responsivity, and high rejection ratio. Despite these obvious advantages, these inorganic UWBS DUVPDs have their own shortcomings. For instance, the majority of the above UWBS materials are usually grown by sputtering, plasma-enhanced chemical vapor deposition (PECVD), molecular beam epitaxy (MBE), or even metal–organic chemical vapor deposition (MOCVD), which means the synthesis process is complicated, and the fabrication cost is relatively high. Moreover, the rigid nature of these materials limits their application in flexible and wearable devices. From the perspective of mechanical properties, semiconducting polymer materials are suitable for the assembly of flexible optoelectronic devices, which may find applications in wearable medical device and telehome healthcare system. Unfortunately, the majority of conjugate polymer

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materials have narrow bandgaps, making them more sensitive to visible and near-infrared radiation rather than the DUV region.20,21

Here, we report on a highly sensitive a non-UWBS solar-blind DUV PD made of ultrathin poly(3-hexylthiophene)-poly(hexadecyloxyallene) (P3HT-b-PHA) nanoparticles with virtual ultrawide bandgap which are synthesized by a simple transfer-etching solution method. Like UWBS, the poly(3-hexylthiophene)-poly(hexadecyloxyallene) (P3HT-b-PHA) can absorb DUV light and generate excitons for the selective absorption of shell part (-PHA) in 200−300 nm region. At the same time, the resultant photogenerated carriers can be easily transported by the semiconducting P3HT. Device analysis revealed that the ultrathin P3HT-b-PHA nanoparticles were highly sensitive to illumination with a wavelength of 254 nm but were virtually blind to both 365 nm and other illumination in the visible region. Such a solar-blind DUV sensitivity was related to the leakage mode of the ultrathin polymer nanoparticles according to modeling based on finite difference time-domain (FDTD). Furthermore, flexible DUV sensors on a PET substrate with 10×10 pixels have been fabricated, and their ability to capture a still DUV image under bending strains has been successfully demonstrated. These results, along with the relatively simple fabrication process, corroborate that the ultrathin P3HT-b-PHA nanoparticles are of potential importance in future DUV optoelectronic devices and systems.

**Results and Discussion.** The device configuration of the nanofibrillar polymer-based DUV PD and the molecular structure are illustrated in Figure 1a. The P3HT-b-PHA block copolymer nanoparticles in this study were synthesized through a one-pot sequential polymerization method, as shown in Figure S1 (see SI for detailed information). To confirm the chemical structures of the triblock copolymers, 1H nuclear magnetic resonance (NMR) spectroscopy was performed. The 1H NMR data in Figure 1b shows two strong peaks at a (6.98 ppm) and b (2.80 ppm), which can be attributed to the protons of thiophene ring and hexyl side chain of the P3HT block. Moreover, the proton signals at c (5.95, 5.80 ppm), d (3.60 ppm), and e (2.50 ppm) are all due to the group of the PHA block. According to further gel permeation chromatography (GPC) analysis shown in Figure 1c, the number-average molecular weight (Mn) of the as-synthesized homopolymer P3HT(80) and diblock copolymer are determined to be 13.3 and 35.7 kDa, respectively, corresponding to a diblock copolymer structure of P3HT(80)-b-PHA(80). Figure 1d compares the normalized UV−vis absorption spectra of both P3HT (black line) and P3HT-b-PHA (red line) films, from which one can easily find that besides the absorption of P3HT in the 400−600 nm region the P3HT-b-PHA shows an extra absorption at 200−300 nm due to the presence of the PHA block.
to the characteristic absorption of PHA. Without question, such a strong absorption in the DUV region is highly beneficial for the detection of DUV light illumination. By a transfer-etching method (Figure S2), the P3HT-b-PHA material was further transformed to large-scale ultrathin P3HT-b-PHA nanofibrils with a diameter of approximately 15 nm, according to the TEM image in Figure 1a.

It should be noted that during the transfer-etching process, the diameter of P3HT-b-PHA nanofibrils were kept nearly unchanged, whereas their density was substantially increased when the concentration of P3HT-b-PHA in the blending solvent was increased. Figure 1e and Figure S3 show the atomic force microscopy (AFM) images of P3HT-b-PHA nanofibrils which were obtained by selecting different concentrations of 0.75, 1.50, and 3.00 mg/mL as precursors. (For convenience, the as-derived samples are labeled as PP-0.75, PP-1.5, and PP-3, respectively.) With increasing P3HT-b-PHA concentration, the density of the nanofibrils increases dramatically. Figure S4 illustrates the diameter distribution of the nanofibrils obtained from simulation (Figure S5). The diameters for all three samples are all distributed in the range of 10–20 nm with nearly the same average value. To study the electrical properties of the P3HT-b-PHA nanofibrils, organic field effect transistor (OFET) devices with a bottom-gate and top-contact (BGTC) geometry were fabricated. Figure S6 plots the output characteristics of the nanofibril OFETs. The increase in electrical conduction with gate voltage reveals the typical characteristics of the nanofibril OFETs with a p-type channel. By using the linear part of the $I_D$–$V_G$ curve in Figure 1f, the hole mobilities of all the three devices are calculated and summarized in Table S1. Compared with the other two samples, the P3HT-b-PHA device assembled from PP-1.5 exhibits the highest mobility (0.04 cm²/(V s)), the smallest subthreshold (SS, 2.24) and lowest threshold voltage ($V_{th}$, $-5.67$ V). Notably, when illuminated by DUV light ($540$ μW/cm²) with a wavelength of 254 nm, the three devices all exhibit marked sensitivity (Figure 1g). The $I_{light}/I_{dark}$ ratio reaches as high $4.73 \times 10^3$ for the PP-1.5 device, representing the highest value in comparison with the other two devices.

The observed sensitivity to DUV illumination can be understood as follows: due to the unique molecular structure, the shell part (-PHA) absorbs the incident DUV light and generate excitons, which drift to the core–shell interface and separate into electrons and holes with the assistance of an external bias, as illustrated by Figure 2a. During this process, the photocurrent is determined by the gate voltage (Figure 2b); when bias voltage changes from 0 to $-80$ V, the photocurrent increases accordingly. Meanwhile, the $I_{light}/I_{dark}$ ratio increases dramatically due to the sharp decrease in dark

Figure 2. (a) Schematic illustration of the operation mechanism of P3HT-PHA nanofibrils DUVPD under light illumination. (b) Transfer curves of the PP-1.5 in dark and different DUV (254 nm) light intensities. (c) The $I_{light}/I_{dark}$ of the PP-1.5-based device under 254 nm radiation. (d) Time-dependent photosresponse behavior of the DUVPD under light illumination with different intensities. (e) Responsivity and specific detectivity as a function of gate voltage. (f) EQE as a function of gate voltage. (g) The evolution of photocurrent under illumination with different wavelengths. (h) Spectral response of the device based on PP-1.5.
Table 1. Comparison of the Key Parameters of the Present Device and Other Devices with Similar Structures

<table>
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<tr>
<th>materials and structures</th>
<th>wavelength (nm)</th>
<th>(I_{\text{light}}/I_{\text{dark}}) ratio</th>
<th>(R) [A·W(^{-1})]</th>
<th>(D^*) [cm·Hz(^{1/2})·W(^{-1})]</th>
<th>EQE [%]</th>
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<tr>
<td>P3HT-PHA nanofibrils</td>
<td>254</td>
<td>4000</td>
<td>120</td>
<td>(4.2 \times 10^4)</td>
<td>4.97 \times 10^4</td>
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<td>graphene-(\beta)-Ga(_2)O(_3)</td>
<td>254</td>
<td>39.3</td>
<td>9.9 \times 10^4</td>
<td>1.96 \times 10^4</td>
<td>2</td>
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<tr>
<td>(\beta)-Ga(_2)O(_3)</td>
<td>251</td>
<td>9.7</td>
<td>6.29 \times 10^12</td>
<td>10</td>
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<tr>
<td>graphene-microcrystalline diamond</td>
<td>220</td>
<td>1.4</td>
<td>(1 \times 10^{13})</td>
<td>30</td>
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<td>220</td>
<td>5 \times 10^8</td>
<td>10.5</td>
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<td>1 \times 10^9</td>
<td>0.00016</td>
<td>11</td>
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<td>1.0 \times 10^6</td>
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<td>2.92 \times 10^4</td>
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current (Figure 2c). Further photoresponse under different intensities ranging from 3 to 70 \(\mu\)W/cm\(^2\) in Figure 2d reveals that the device can be readily switched between on and off states under different light intensities with good reproducibility between several exposure durations. Moreover, with increasing illumination intensity the photocurrent also increase. It should be noted that when repeatedly illuminating the device with the same light intensity, both the photocurrent and dark current illumination intensity the photocurrent also increase. It should be observed that when bias voltage changes from 0 to \(-80\) V, the responsivity, detectivity and EQE increase accordingly. Specifically, at a bias voltage of \(-80\) V these values reach 120 A/W, \(4.2 \times 10^4\) cm·Hz\(^{1/2}\)·W\(^{-1}\), and 49700%, respectively. Table 1 compares some key device parameters (e.g., \(I_{\text{light}}/I_{\text{dark}}, R, D^*\), and EQE) of the present P3HT-PHA nanofibrils (PP-1.5) device and other solar-blind DUVPDs composed of UWBS. It is clear that these parameters are slightly poorer than DUVPDs based on a ZnO–Ga\(_2\)O\(_3\) hybrid structure. Nonetheless, they are not only better than DUVPDs composed of graphene-\(\beta\)-Ga\(_2\)O\(_3\) heterojunction, \(\beta\)-Ga\(_2\)O\(_3\) thin film, graphene-microcrystalline diamond, and S-doped diamond but also than those made of some newer materials such as MoS\(_2\) and CsPbX\(_3\) quantum dots. Such a relatively good device performance, together with the easy synthesis process, renders our polymer photodetector potentially important for future low-cost optoelectronic devices and systems. One more thing that should be mentioned is that the present ultrathin nanofibril device has a relatively poor ambient stability. The photocurrent will experience a noticeable reduce when exposed in ambient condition without any special treatment. Despite this, we believe the device stability can be retained if any passivation treatment or package work were employed.

The solar-blind DUV light sensitivity of the ultrathin nanofibrils device is completely different from devices assembled from P3HT-b-PHA thin film with a thickness of approximately 80 nm. Figure 3a illustrates the schematic structure of the P3HT-b-PHA thin film device fabricated by a simple spin-coating method, as depicted in Figure S7. Figure S8 shows the output and transfer curves of the P3HT-b-PHA thin film FET. On the basis of the linear part of the \(I_{D}-V_{g}\) curve, the hole mobility was calculated to be \(\sim 10^{-4}\) cm\(^2\)/(V·s), four hundred times lower than that of P3HT-b-PHA nanofibrils. This relatively high hole mobility is related to the special synthetic process. When P3HT-b-PHA is mixed with PMMA, the flexible PMMA matrix creates a flexible surrounding environment, which is beneficial for forming a highly ordered molecule stack. This process can greatly facilitate charge transport; therefore, the mobility of P3HT-b-PHA increases dramatically. Apart from the huge difference in carrier mobility, the P3HT-b-PHA thin film device also exhibits a different spectral property. The spectral response in Figure 3c revealed that in contrast to the P3HT-b-PHA nanofibril device the thin film PD exhibits broadband sensitivity in the range of 200–800 nm. It exhibits obvious sensitivity not only to 254 nm illumination in the DUV region but also to illumination in UVA and visible light regions. In fact, such a remarkable difference in spectral sensitivity is
absorption curves of the P3HT-b-PHA thin film under different light illumination, the gate voltage and drain voltage are kept at −80 V and −10 V, respectively. (c) Spectral response of the device made of P3HT-b-PHA thin film. (d) Comparison of the experimental absorption curves of the P3HT-b-PHA thin film and nanofibrils.

Figure 3. (a) Schematic illustration of the thin film PD. (b) Photoreponse behavior of the 80 nm thin film PD under different light illumination, the gate voltage and drain voltage are kept at −80 V and −10 V, respectively. (c) Spectral response of the device made of P3HT-b-PHA thin film. (d) Comparison of the experimental absorption curves of the P3HT-b-PHA thin film and nanofibrils.

consistent with the experimental UV–vis absorption curve in which the P3HT-b-PHA thin film shows strong absorption in both the DUV and 450–650 nm regions, whereas the absorption of P3HT-b-PHA nanofibrils at 450–650 nm is considerably reduced (Figure 3d).

To shed light on the observed difference in photoreponse, the optical properties of both P3HT-PHA nanofibrils and thin film were theoretically simulated and compared using FDTD method. (The optical constant of P3HT-PHA was obtained from the experiment, which is provided in Figure S9.) In the simulations, the diameter of the P3HT-PHA nanofibrils is 15 nm, and the thickness of P3HT-PHA thin film is set to be 80 nm. The P3HT-PHA film can absorb light not only in DUV region but also in the visible and UVA regions (Figure 4b). Further simulation finds that the P3HT-PHA nanofibrils only absorb DUV light. Specifically, the absorption characteristic is highly dependent on the incident polarizations. The nanofibrils can hardly absorb x-polarized light but they can absorb y-polarized light in the DUV region (Figure 4a). This difference between the two structures originates from the resonance between the one-dimensional nanostructure and polarized light.36 To further investigate the physical mechanism and the absorption difference of the P3HT-PHA nanofibrils in both visible and ultraviolet bands, the electric fields of the nanofibrils at the wavelengths of 254, 365, 550, and 650 nm under y-polarization incidence are extracted and shown in Figure 4c–f, respectively. It is obvious that under 254 nm illumination, the incident electric field can be trapped along the nanofibrils efficiently by exciting the TM01 resonant mode due to the leakage mode.57 However, with increasing incident wavelength (Figure 4c–f), the intensities of the trapped electric fields in the nanofibrils decreases, as depicted in Figure 4g. In fact, this evolution in the electric field of the resonant mode is understandable considering that with the increase of incident wavelength, the excited capacity of the resonant mode (TM01) due to the leakage mode will be reduced (for a nanofibril with a diameter of 15 nm, its cutoff wavelength is only 118 nm. Therefore, only the TM01 mode exists under illuminations of 254, 365, 550, and 650 nm). In fact, similar phenomenon was also observed in other ultrathin nanofibrils with diameters of 10 and 6 nm (Figure S10).

The ability to record image information with high resolution is of paramount importance in commercial imaging devices, such as cameras, fax machines, and so forth. To explore the possible application of P3HT-b-PHA nanofibril-based solar-blind DUVPD, a flexible image sensor with 10 × 10 pixels was fabricated (Figure 5a). During device fabrication, 30 nm thick aluminum strips were evaporated onto the plastic substrate poly(ethylene terephthalate) (PET) to serve as gate electrodes, and perfluoro(1-butylvinyl ether) polymer (CYTOP) was spin-coated as the dielectric layer. P3HT-1.5 nanofibrils were then formed by the process above, followed by the deposition of source/drain electrodes. All pixels on the PET substrate show pronounced sensitivity to 254 nm illumination. Figure 5b shows the representative source-drain current as a function of bias voltage, from which one can see that the photocurrent of the PP-1.5 nanofibrils device increase gradually when the light intensity increases from 17 to 540 μW/cm². Figure 5c shows the image produced by projecting a “UV” optical pattern onto the P3HT-b-PHA nanofibrils PD array without bending, collecting, and displaying the photocurrent distribution in the computer. It is obvious that the character “UV” was successfully projected onto the nanofibrils image sensor. As a matter of fact, the image was still clear even when the device was bent at an angle of 5° (Figure 5d). Nonetheless, when choosing either 365 nm or white light as projection light, no obvious “UV” projection was obtained (Figure 5e,f). This result confirms that the present P3HT-b-PHA nanofibril PD array can be used for solar-blind DUV imaging applications.

In summary, a non-UWBS solar blind DUV phototransistor was developed based on ultrathin P3HT-b-PHA nanofibrils with virtual ultrawide bandgap which is characterized by a shell part (-PHA) that can absorb DUV light and generate excitons, which the P3HT-b-PHA thin film shows strong absorption in both the DUV and 450–650 nm regions, whereas the absorption of P3HT-b-PHA nanofibrils at 450–650 nm is considerably reduced (Figure 3d).

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and the shell part (-P3HT) that is beneficial for charge transport. The polymer nanofibrils derived by a simple transfer-etching method have an average diameter of approximately 15 nm, with a hole mobility as high as 0.04 cm²V⁻¹s⁻¹. A PD based on the P3HT-b-PHA nanofibrils exhibits excellent solar-blind sensitivity; it is highly sensitive to 254 nm illumination with a responsivity of 120 A/W but is nearly blind to illumination from 365 nm to the visible light region. This spectral response is associated with the leakage mode of the ultrathin polymer nanofibrils according to FDTD simulation. Flexible DUV sensors on a PET substrate with 100 pixels have been fabricated, and their ability to capture a still DUV image under bending strain have been successfully demonstrated. The totality of the above study suggests that the present solution-processed polymer nanofibrils are ideal building blocks for the assembly of highly sensitive and flexible DUVPDs, which may find potential applications in future low-cost wearable optoelectronic devices and systems.

**Experimental Section. Materials Synthesis and Characterization.** Poly(methyl methacrylate) (PMMA) (Mw ~ 996 kDa) and chlorobenzene (CB) were purchased from Sigma-Aldrich. The CYTOP was purchased from AGC Asahi Glass. In this study, P3HT-b-PHA was synthesized by a one-pot sequential polymerization, which has been reported previously.²³,²⁴ To prepare the P3HT-b-PHA nanofibrils, P3HT-b-PHA and PMMA were separately dissolved in chlorobenzene and dichlorobenzene, respectively, and mixed at optimum concentrations of P3HT-b-PHA (0.75, 1.50, and 3.00 mg/mL) and PMMA (3 wt %). The mixed solutions were then spin-coated onto clean silicon substrates at 2000 rpm for 60 s in a glovebox. After drying overnight in a vacuum oven to remove the solvent, the silicon wafer samples were immersed in deionized water to strip the thin film from the silicon surface. The as-obtained films were rinsed in deionized water and transferred to SiO₂/Si substrates or PET substrates, and finally transitioned to P3HT-b-PHA nanofibrils by rinsing with ethyl acetate to remove the PMMA matrix. The morphologies and the thickness of the polymer thin films were investigated using tapping-mode atomic force microscopy (AFM) (Nanoscope, Veeco Instrument Inc.). Field-emission transmission electron microscopy (TEM) observations were conducted on a high-resolution JEM-2100F field-emission transmission electron microscope. The samples for TEM characterization were obtained by peeling off the spin-cast films on silica substrates and subsequently transferring those onto 200 mesh copper grids. The UV-vis spectroscopy (UV-vis) measurements were performed on a UNIC 4802 UV/vis double beam spectrophotometer.

**Device Fabrication and Analysis.** In the study, two kinds of device geometries were fabricated and investigated. The first device geometry is a bottom-gate P3HT-b-PHA nanofibril transistor on SiO₂/Si, in which the source and drain were fabricated by thermally evaporating a 30 nm thick gold electrode with the assistance of a shadow mask (the channel width is approximately 100 μm). To construct the flexible bottom-gate P3HT-b-PHA nanofibril transistor, ribbon-like Al electrodes were first evaporated on a PET substrate to serve as gate electrodes. CYTOP solvent was then spin-coated on the gate electrodes as the dielectric layer onto which a film of P3HT-b-PHA nanofibrils was then transferred by the above solution approach. Finally, the source-drain electrode arrays were deposited on the nanofibrils by a second thermal evaporation. The PET electrical characteristics were measured by a Keithley 4200-SCS instrument in the ambient atmosphere. The field-effect mobility of the devices was obtained in the saturation regime from the highest slope of the \( I_D \) versus \( V_G \) plots by using eq 4

\[
I_D = \frac{WC}{2L} \mu (V_G - V_f)^2
\]
where $I_D$ is the drain—source current, $V_D$ is the gate voltage, $V_P$ is the drain—source voltage, $C_T$ is the capacitance per unit area, and $L$ and $W$ are the channel length and width, respectively. The optoelectronic properties of the solar-blind DUVPD were studied by a Keithley 4200-SCS instrument equipped with a monochromatic LED light source, from which the incident DUV light was directly focused and guided onto the device. Prior to device analysis, the power intensity of the incident light was calibrated by a power meter (Thorlabs GmbH., PM 100D). Unless otherwise specified, all the measurements were carried out at room temperature.

**Numerical Simulation.** All numerical simulations were performed using the custom-programmed FDTD algorithm. In the calculations, the plane wave propagated along the $z$-axis with a power of 1 W, and the wavelength range was set in the range of 215–800 nm. Periodic boundary conditions were set in the $x$- and $y$-directions of the unit structure to simulate an infinite number of nanowire structures and an infinite length of nanowires in the simulations. Meanwhile, the 400 nm thickness of the perfectly matching layer was set at the top and bottom of the structure to avoid nonphysical reflections of outgoing electromagnetic waves. The absorption value was obtained based on the sum of the incident power minus transmitted and reflected power under the principle of energy conservation. In addition, the air permittivity was 1 in all simulations.

**Associated Content**

- Supporting Information
  - The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.9b04410.
  - Additional information, figures, and table (PDF)

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**Notes**
- The authors declare no competing financial interest.

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**References**


Supporting information for

Ultrathin Polymer Nanofibrils for Solar-Blind Deep Ultraviolet Light Photodetectors Application

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Chemical structures and reactions...
Figure S1. Scheme of the synthesis route of P3HT, P3HT-b-PHA, and block copolymers.

Synthesis

1. Synthesis of monomer 2 hexadecyloxyallene

1-(Prop-2-yn-1-yloxy)hexadecane: To a suspension of KOH (16.8 g, 0.30 mol) in 100 mL DMSO was added 5.4 mL propargyl alcohol (5.60 g, 0.10 mol) at 0 ºC. After stirring for 30 min, cetyl bromide (31.5 mL, 0.10 mol) was added at 0 ºC. Stirring was continued for 10 h at room temperature. The resulting brown suspension was diluted with 200 mL water and extracted with diethyl ether (3 × 50 mL). The combined organic layer was washed with water (2 × 20 mL) and brine (2 × 20 mL), dried over Na₂SO₄, filtered and concentrated in vacuo. The yellowish, oily liquid was purified by flash chromatography (petroleum ether) gave 1-(prop-2-yn-1-yloxy)hexadecane as a colorless liquid.

Hexadecyloxyallene: At room temperature, KOBu⁻ (2.40 g, 21.4 mmol) was added batch-wise into a solution of 1-(prop-2-yn-1-yloxy)hexadecane (5.00 g 17.9 mmol) in 100 mL THF within 30 min. The suspension was stirred at room temperature for 5 h, then filtered through a celite pad and washed with ether (50 mL). Combined solution was concentrated under reduced pressure and purified by flash chromatography (0.5~0.8% diethyl ether in petroleum ether) to afford 3 as a colorless oil (4.10 g, 82%).

2. Synthesis of the di-block copolymer P3HT-b-PHA

The general approaches to the preparation of the P3HT-b-PHA rod-coil di-block copolymers are shown in Fig S1, the copolymers were synthesized in one-pot via two sequential living polymerizations of 2,5-dibromo-3-hexylthiophene (1), hexadecyloxyallene (2). A 50 mL flask was charged with 2,5-dibromo-3-hexylthiophene (0.25 g, 0.80 mmol) and a stir bar. The flask was then evacuated on a vacuum line and flushed with dry nitrogen. After this evacuation-flush procedure repeated this three times, dry THF (10.0 mL) and tert-butylmagnesium chloride (0.40 mL, 2.0 M solution in THF) were successively introduced by a syringe. The reaction mixture was allowed to stir at room temperature for 2 h, followed by the addition of Ni(dppp)Cl₂ (9.20 mL,
13.3 μmol, [1]₀/[Ni]₀ = 80) to generate macroinitiator Ni(II)-terminated P3HT (poly-1₈₀). The polymerization process was monitored by gel permeation chromatography (GPC) analysis of small aliquots taken out from the reaction solution at appropriate time intervals. Subsequently, hexadecyloxyallene (0.40 g, 1.46 mmol) was dissolved in dry THF (5 mL) under nitrogen atmosphere and added into reaction mixture ([2]₀/[Ni]₀ = 80). After stirred at 50 ºC for 10 h, the resulting mixture solution was subsequently cooled down to room temperature. A small aliquot was then taken out for analysis until the molecular weight of di-block copolymer Ni(II)-terminated P3HT-b-PHA (poly(1₈₀-2₈₀)) ceased to increase.

**Figure S2.** Scheme of transfer-etching method for synthesizing the P3HT-b-PHA nanofibrils device.
Figure S3. AFM images of P3HT-b-PHA nanofibrils formed by the transfer-etching process.

Figure S4. The calculated diameter distribution of nanofibrils.
**Figure S5.** The (a-c) false color OrientationMap extracted from the original image. Each pixel’s orientation corresponds to an orientation on the attached color wheel. (d-f) Orientation Distribution extracted from the Orientation Map. The radial axis indicates the count of pixels of a given orientation. A diametrical black line segment indicates the average orientation, and the full-frame value of $S_{2D}$ is indicated at bottom left. (g-i) Decay of the orientational order parameter, $S_{2D}$, as a function of frame size. Fitted model parameters are indicated at upper right.
Figure S6. Output characteristics of PHA-0.75, PHA-1.5, PHA-3 based OFET devices.

Calculation of the mobility of the PHA-1.5m

The hole mobility ($\mu$) can be determined from the relation:

$$I_D = \frac{WC_i}{2L} \mu (V_G - V_T)^2$$

Where $I_D$ is the drain–source current, $V_G$ (-80V~20 V) is the gate voltage, $V_D$ (-80 V) is the drain–source voltage, $C_i$ ($1.09 \times 10^{-8}$) is the capacitance of dialect layer in per unit area, and $L$ and $W$ are the channel length (1000 μm) and width (100 μm), respectively. The highest drain–source current ($-3.6 \times 10^{-5}$ A) is obtained from PHA-1.5m and the highest $\mu$ is calculated to be 0.04 cm$^2$V$^{-1}$s$^{-1}$.
Table S1. Field-effect characteristics of PP-0.75, PP-1.5, PP-3 based field-effect transistors.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration</th>
<th>$\mu_{\text{FET}}$, $[\text{cm}^2\text{V}^{-1}\text{s}^{-1}]$</th>
<th>On/off ratio</th>
<th>SS[ log$I_{ds}$]</th>
<th>$V_{th}$[V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP-3</td>
<td>3 mg/ml</td>
<td>0.0059(±0.0006)</td>
<td>1.67×10^4</td>
<td>3.35</td>
<td>-6.38</td>
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<tr>
<td>PP-1.5</td>
<td>1.5 mg/ml</td>
<td>0.040(±0.008)</td>
<td>1.69×10^5</td>
<td>2.24</td>
<td>-5.67</td>
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<tr>
<td>PP-0.75</td>
<td>0.75 mg/ml</td>
<td>0.0025(±0.0002)</td>
<td>8.46×10^3</td>
<td>3.79</td>
<td>-6.96</td>
</tr>
</tbody>
</table>

Figure S7. The illustration of method to prepare P3HT-b-PHA thin film and the corresponding AFM image.

Figure S8. Output (a) and transfer curves (b) of the P3HT-b-PHA thin film transistor in dark and under different UVC (254 nm) light intensities.
The study of $n, k$ of the P3HT-b-PHA sample:

$n, k$ value measurement: both P3HT-b-PHA nanofibrils and film are deposited on glass through the process described above. Dual rotating-compensator Mueller matrix ellipsometer (MME, ME-L ellipsometer, Wuhan Eoptics Technology Co., Wuhan, China) was used to collect the ellipsometric data of the thin film samples. With dual rotating-compensator configuration, the full Mueller matrix elements can be obtained in a single measurement. The spectral range is from 200 nm to 1000 nm. The two arms of the instrument and the sample stage can be rotated to change the incidence angle and azimuthal angle in the experiments and both of these angles in experiment is 65°. The optical constant of the studied materials as well as the film thickness can be extracted from the measured ellipsometric data, by performing a weighted least-squares regression analysis method (Levenberg-Marquardt algorithm). In the data analysis, the optical constant of the studied materials can be characterized by superimposing the general oscillator models (such as Lorentz model, Tauc-Lorentz model, Gaussian model etc.), which can characterize the samples in this work precisely. This is done by linearly adding the general oscillator models to the polo model, which is a zero-broadening oscillator.
**Figure S9.** The refractive index (n) and extinction coefficient (k) of P3HT-b-PHA in the spectral range from 215 nm to 800 nm.

**Figure S10.** The intensity ratios of the leakage modes between the incident wavelengths of 254nm and 356nm in several nanofibrils with different diameters, such as 6nm, 10nm, 15nm, 20nm, and 25nm, respectively.