Helical Nanoribbons for Ultra-Narrowband Photodetectors

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Supporting Information

ABSTRACT: This Communication describes a new molecular design that yields ultranarrowband organic photodetectors. The design is based on a series of helically twisted molecular ribbons as the optoelectronic material. We fabricate charge collection narrowing photodetectors based on four different helical ribbons that differ in the wavelength of their response. The photodetectors made from these materials have narrow spectral response with full-width at half maxima of <20 nm. The devices reported here are superior by approximately a factor of 5 to those from traditional organic materials due to the narrowness of their response. Moreover, the active layers for the helical ribbon-based photodetectors are solution-cast but have performance that is comparable to the state-of-the-art narrowband photodetectors made from methylammonium lead trihalide perovskite single crystals. The ultranarrow bandwidth for detection results from the helical ribbons’ high absorption coefficient, good electron mobility, and sharp absorption edges that are defined by the twisted molecular conformation.

This study describes a family of twisted molecular ribbons as electronic materials for ultranarrowband organic photodetectors. Narrowband photodetectors have broad applications in color discrimination, imaging, and security systems.1,2 One of the key parameters for a narrowband photodetector is the full-width at half-maximum (FWHM) of spectral response: ultranarrowband photodetectors have important applications in optical systems where either only specific wavelengths need to be detected or a high spectral resolution is required, thus such a detector should respond to as narrow a wavelength region as possible, and therefore this FWHM should be small. The conventional strategy to create narrowband photodetectors is to combine band-pass filters with broadband photodiodes.1 However, the complicated architecture of the resulting photodetector increases the cost and limits their application in high pixel density detectors. Alternative methods involve using narrowband absorbers such as organic molecules and inorganic nanocrystals,3 or manipulating the internal quantum efficiency via charge collection narrowing (CCN) (The working principle of the CCN photodetector will be detailed below).4 The state-of-the-art narrowband photodetectors have been made using methylammonium lead trihalide perovskite single crystals, and they show a spectral response of <20 nm (FWHM).5 Compared with lead-based perovskite materials, organic materials have some advantages such as lightweight and less toxicity. However, the FWHM of spectral response in organic CCN photodetectors is usually greater than 50 nm.6 Until the present work, it has proven difficult to achieve narrowband response with a FWHM of <20 nm using organic materials.7,8

A family of organic optoelectronic materials would serve well in CCN photodetectors if they could be made with the following properties: (1) they should have as sharp an absorption edge as possible; (2) they should have as high an extinction coefficient as possible; and (3) they should have an absorption edge that is tunable across the visible spectrum. In addition to these optical properties, these materials must behave as carrier-transporting semiconductors. The optical materials must have sharp-edged, strong absorptions because the CCN device is designed such that only those photons whose energies are close to the absorption edge are allowed to penetrate the active layer to a depth that will allow both carriers to reach their respective electrodes (see Figure 2A).4 Tunability of the absorption edge is a necessity for multicolor detection.

Figure 1A displays the molecular structures of the perylene diimide (PDI) ribbons used here as the electron acceptors in the photodetector. We utilized the previously described dimer (hPDI2), trimer (hPDI3), and tetramer (hPDI4); in these compounds, the PDI subunits are fused with ethylene bridges.11 We also recently found a robust method to make a longer version of these helical ribbons (hPDI3-Pyr-hPDI3), by fusing an electron-rich subunit (a dialkoxy-pyrene) with two hPDI3 subunits.12 This longer hPDI3-Pyr-hPDI3 ribbon has a bathochromically shifted absorbance relative to its shorter cousins.11,12 In previous studies, we have shown that each of these ribbons have nonplanar conformations due to the cove edges.11 For example, Figure 1B shows the helical conformation of the donor–acceptor helical ribbon hPDI3-Pyr-hPDI3. These ribbons have high optical absorptivity, good electron mobility, and sharp absorption edges. We have previously demonstrated that helical PDI ribbons are among the best electron acceptors in organic solar cells with high power conversion efficiencies.12–15 By incorporating these four ribbons into a CCN device architecture, we here prepare a set of four photodetectors, each of which shows a wavelength-specific, ultranarrow spectral response (FWHM of ~20 nm). The narrowness of the photosensitivity exceeds that achieved with traditional organic materials by over a factor of 5.4,5,7,9,16

Figure 2A shows a schematic of a CCN photodetector. The active layer of the CCN photodiode is thick enough that it can modulate the exciton and carrier distribution. Due to the
thickness and high absorption coefficients of the active layer, photons with energies corresponding to wavelengths higher than the band gap are completely absorbed at the surface adjacent to the transparent electrode. The carriers that are generated will not produce current due to the highly imbalanced electron- and hole-diffusion lengths that make it unlikely that both carriers reach the respective electrodes. Only incident light near the absorption edge penetrates to the appropriate depth in the active layer that both the resulting electron and hole can move to their target electrodes; this causes the photodetector to exhibit photoresponse only near the absorption edge.5

We fabricated photodetector devices by combining the hPDI ribbons and the commercial wide-band gap polymer, poly(9,9-dioctylfluorene-alt-benzothiadiazole) (F8BT).17,18 The Supporting Information contains the method for device fabrication. F8BT has a blue-shifted absorption spectrum complementary to that of the hPDI ribbons (Figure 2B). We can quantify the sharpness of the absorption edge in the ribbons by measuring the FWHM of the lowest-energy absorption band. As shown in Figure 2B, the lowest-energy absorption bands for the ribbons have a FWHM of 20—30 nm, which is much smaller than that of typical conjugated polymers (70—100 nm).5 Films of these ribbons maintain the sharp absorption edges characteristic of the molecularly dispersed materials, presumably because the nonplanar molecular structure inhibits agglomeration and crystallization. Importantly, the absorption edges of the four ribbons differ, varying from the band edge of hPDI2 (570 nm) to that of hPDI3-Pyr-hPDI3 (650 nm).

Table 1 summarizes the key parameters for each of the helical molecular ribbon devices. The Supporting Information contains a discussion of the responsivity (R) and specific detectivity (D*s) of these devices. Overall, the responsivity and specific detectivity are comparable to those of perovskite single crystal photodetectors.6 Figure 2C displays the normalized

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>FWHM (nm)</th>
<th>Peak R (mA/W)</th>
<th>Peak D* (Jones)</th>
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<tr>
<td>hPDI2</td>
<td>575</td>
<td>22</td>
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<tr>
<td>hPDI3</td>
<td>600</td>
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<td>7.3</td>
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<tr>
<td>hPDI4</td>
<td>615</td>
<td>16</td>
<td>3.4</td>
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<tr>
<td>hPDI3-Pyr-hPDI3</td>
<td>645</td>
<td>20</td>
<td>1.1</td>
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Figure 1. (A) Structures of the helical ribbons. (B) Energy minimized molecular model from DFT calculations for hPDI3-Pyr-hPDI3. Carbon = gray, nitrogen = blue, oxygen = red. Hydrogen atoms have been removed to clarify the view. A methyl group was substituted for each of the side chains in the calculations.

Figure 2. (A) Schematic of a CCN photodetector. The dashed line is a conceptual boundary between above-bandgap region and near-band edge region. Brightness gradient in the active layer indicates the light penetration depth with respect to different wavelengths. (B) Normalized film absorption spectra of the compounds used in the active layer. (C) Normalized EQE spectra of narrowband photodetectors made from the helical ribbons.
external quantum efficiency (EQE) spectra for all of the photodetectors. Each of the CCN devices made from the helical, molecular ribbons has a photosresponse only near the corresponding absorption edge (Table 1). More importantly, all of the devices show exceptionally narrow spectral response with FWHMs of ~20 nm. It is important to note that the state-of-art organic narrowband photodetectors have FWHMs of ~100 nm for visible light detection.\(^5\) The FWHM of our photodetectors, which are from spin-cast films, is comparable to that of the best narrowband photodetectors made from perovskite single crystal active layers.\(^6\)

We next discuss the origins of the high performance CCN devices with this new molecular system. Most importantly, as mentioned above, these ribbons have sharp absorption edges that define the ultranarrow detection bands. We postulate this is due to the rigidity of the chromophores in the ribbons; most small molecules and polymers (FWHM of 70–100 nm) used in photodetectors, having much more rotational freedom, have much broader absorption edges.\(^5\) To emphasize the origin of the sharp absorption feature, we compare absorption spectra of hPDI2 and a dimeric uncyclized-PDI that contains an uncyclized ethylene bridge (uPDI2, Figure 3A). uPDI2 displays a much broader lowest-energy absorption band than hPDI2 (FWHM of 70 nm, Figure 3B) because the conjugated cores of the hPDIs do not contain any rotatable carbon–carbon single bonds and have very narrow distributions of accessible conformations at room temperature (Figure 1B). In contrast, owing to the rotatable bonds, uPDI2 has a more flexible backbone, which is commonly seen in other organic semiconducting materials, that allows access to more molecular geometries. We conclude that the sharpness of the band edge for the helical ribbons originates from their fused but twisted molecular structures.

In addition, the spectroscopic transitions do not shift, broaden, or change their shape upon going from a solution to a film. Highly crystalline films have a broader distribution of density of states relative to amorphous films due to Frenkel exciton band formation by stronger intermolecular coupling.\(^19,20\) For example, the lowest-energy absorption band for the flat PDI monomer, which can aggregate, shifts upon film formation as shown in Figure 3D.

A further advantage of these helical, molecular ribbons over traditional materials is that they have very high oscillator strengths for their lowest-energy transitions. Fullerenes, which are the most commonly used electron acceptors in solar cells and photodetectors, have low oscillator strengths and a long absorption band tail in the visible region.\(^21\) Figure 3B compares the broad absorption edge for PC\(_{71}\)BM with that of hPDI2. These lowest energy transitions for these ribbons have very high absorptivity. The molar extinction coefficients are more than 1 × 10\(^5\) M\(^{-1}\) cm\(^{-1}\) for each of the molecular ribbons (Figure S6).\(^11,12\) Sufficient absorbance at energies above the absorption edge is essential for narrowband CCN photodetection. To emphasize this, we made the F8BT:hPDI2 CCN photodetectors with two different active-layer film thicknesses (780 and 1140 nm). We observe multiple high-energy transitions in the EQE spectrum that correspond to the small peaks in the transmission spectrum in the device having 780 nm-thick active layer (Figure 4A), but when film thickness is increased to 1140 nm, all the photons with energy greater than the absorption edge are absorbed (Figure 4B). The photosresponse occurs precisely at the absorption edge (575 nm, blue trace in Figure 4B). It is important to note that previously reported polymer:fullerene photodetectors, which have drastically inferior detection bandwidth, require 3–5 \(\mu\)m thick active layers in order to absorb completely light above absorption-edges.\(^7,8\) The high absorption coefficients of these helical ribbons allow us to reduce the thickness of the active layer to \(\sim 1 \mu\)m for all of the devices referred to in Figure 2C. Notably, the thickness is about 3 orders of magnitude smaller than that
of perovskite single crystals used in narrowband photodetectors.\(^6\)

Furthermore, the helical molecular ribbons employed here have high electron mobility. The micrometer thick active layers that characterize CCN photodetectors typically are inefficient photocurrent collectors. Carrier mobility is a key parameter with respect to reducing carrier recombination, and our previous studies have shown that these ribbons have high electron mobilities in thin-film filed-effect transistors.\(^{11}\) We measure the electron in the F8BT:hpPDI2 blend films by the space-charge-limited current (SCLC) method.\(^{22}\) The electron mobility is calculated to be \(3.9 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\) (Figure S7), which is similar to that of PC\(_{71}\)BM-based blended films.\(^{23,24}\) The high electron mobility of the helical ribbons allows them to function well in a thick bulk heterojunction device.

In summary, we present here a new molecular blueprint for ultranarrowband organic photodetectors. Our CCN photodetectors are based on four different helical ribbons that differ in the wavelength of their response. The photodetectors made from these materials have narrow spectral response with FWHM of <20 nm. The ultranarrow bandwidth for detection results from the helical ribbons high absorption coefficient, good electron mobility, and sharp absorption edges that are defined by the fused but twisted molecular structure. These materials augur well for applications in color discrimination, imaging, and security systems. Our results indicate that the CCN effect is a general effect for organic bulkjunction devices. It is also applicable to other nonfullerene systems.\(^{25}\) We will be able to improve further the device performance by synthesizing \(p\)-type ribbon-like molecules that structurally and optically match the PDI ribbons.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available on free charge of the ACS Publications website at DOI: 10.1021/jacs.6b13089.

Device fabrication, characterization, supplementary figures, and carrier mobility measurements (PDF)

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**Notes**

The authors declare no competing financial interest.

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