Contorted Hexabenzocoronenes with Extended Heterocyclic Moieties Improve Visible-Light Absorption and Performance in Organic Solar Cells

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Supporting Information

ABSTRACT: The large band gaps of existing contorted hexabenzocoronene derivatives severely limit visible-light absorption, restricting the photocurrents generated by solar cells utilizing contorted hexabenzocoronene (cHBC). To decrease the band gap and improve the light-harvesting properties, we synthesized cHBC derivatives having extended heterocyclic moieties as peripheral substituents. Tetrabenzofuran-ayildibenzocoronene (cTBFDBC) and tetrabenzothienodibenzocoronene (cTBTDBC) both exhibit broader absorption of the solar spectrum compared to cHBC, with peak absorbances on the order of 10^5 cm^−1 in the near-ultraviolet and in the visible. Planar-heterojunction organic solar cells comprising cTBFDBC or cTBTDBC as the donor and C_70 as the acceptor surpass those having cHBC in photocurrent generation and power-conversion efficiency. Interestingly, devices containing cTBFDBC/C_70 exhibit the highest photocurrents despite cTBTDBC having the smallest band gap of the three cHBC derivatives. X-ray reflectivity of the active layers indicates a rougher donor−acceptor interface when cTBFDBC is employed instead of the other two donors. Consistent with this observation, internal quantum efficiency spectra suggest improved charge transfer at the donor−acceptor interface when cTBFDBC—as opposed to cTBTDBC or cHBC—is used as the donor.

1. INTRODUCTION

Molecular semiconductors are exciting candidates for use in organic photovoltaics due to their production scalability, nontoxicity, and structural versatility.¹ While planar aromatic molecules have been extensively studied,¹ a growing number of nonplanar compounds beyond fullerenes have utility as photoactive ingredients in organic photovoltaics (OPV).²⁻⁸ Among these, contorted hexabenzocoronene (cHBC) derivatives are synthetically accessible and chemically stable and have shown promising performance in OPV devices both as electron donors⁹⁻¹² and as electron acceptors.³ When utilized as electron donors, the concavity of cHBC derivatives allows complexation with fullerene acceptors,¹¹⁻¹³ leading to improved OPV performance relative to devices that utilize their planar counterparts.⁹ More recently, it has been shown that cHBC derivatives can also be utilized as electron acceptors if the energy levels are appropriately tuned via halogenation.³ Despite progress, there exists one major drawback to these materials; cHBC derivatives do not strongly absorb light beyond 450 nm. This absorption mismatch with the solar spectrum thus limits their performance when employed in OPVs.³⁻⁹⁻¹²⁻¹⁴

Nuckolls and co-workers replaced four of the six peripheral benzenes in cHBC with heterocyclic thiophenes to yield contorted dibenzotetrathienocoronene (cDBTTC).¹⁵ Bulk-heterojunction (BHJ) devices utilizing a soluble derivative of cDBTTC as the electron donor and [6,6]-phenyl C_71 butyric acid methyl ester (PC_70BM) as the electron acceptor outperform equivalent devices using a soluble derivative of cHBC as the donor; the 14% improvement in photocurrent and 10% enhancement in power-conversion efficiency is attributed to cDBTTC’s modest red shift in absorption (near 400 nm) compared to that of cHBC.¹¹⁻¹² Another approach utilized a core-expanded analogue of cHBC, contorted octabenzocircumbiphenyl (cOBCB),¹⁶ with PC_70BM, leading to higher yet photocurrent (24% improvement) and power-conversion efficiency (20% improvement) compared to those of similar devices that use cHBC as the donor.¹¹⁻¹⁶ This increase in photocurrent relative to devices comprising cHBC and cDBTTC was attributed to improvements in visible-light absorption by cOBCB, which extends out to 500 nm. To
further extend the spectral overlap with solar irradiation and to impart tunability to their optoelectronic properties, we need an improved understanding of the structure–property relationships that govern this class of materials.

Noting the versatility in molecular design\textsuperscript{14–17} and aiming to further improve light absorption, we designed and synthesized two cHBC derivatives having benzofurann and benzothiophene as peripheral substituents. By utilizing extended heterocyclic moieties on the periphery of cHBC, we have effectively lowered the band gap of these materials by simultaneously extending the conjugated core and introducing heteroatoms. The benzo-furan- and benzothiophene-containing cHBC derivatives reported here exhibit substantially enhanced absorption of visible light relative to cHBC, with optical band gaps that are narrower than those of any previously reported cHBC derivatives.\textsuperscript{3,9,14–16,18} When paired with C\textsubscript{70} in OPV devices, this improved absorption by cTBFDDBC and cTBTDBC leads to enhancements in photocurrent of 41% and 28% relative to devices using cHBC as donor, respectively.

2. EXPERIMENTAL SECTION

2.1. Absorption and Emission. Absorption spectra were collected on an Agilent Cary 5000 UV–vis–NIR spectrophotometer (Agilent Technologies, Inc., Santa Clara, CA). Evaporated thin films of cHBC derivatives on glass slides were measured, along with ca. 1 \micro{m} solutions of cHBC derivatives in \textgreek{DCD} in quartz spectrophotometer cells having a 10 mm path length. Emission spectra were collected on the same solutions using a Hitachi F-7000 fluorescence spectrophotometer. Optical band gaps were extracted from the thin-film spectra according to literature methods.\textsuperscript{19}

2.2. UPS and IPES. Ten nanometer thick films of cHBC derivatives were evaporated in a thermal evaporator located in a nitrogen-filled glovebox and transported to the measurement vacuum system in nitrogen. Ultraviolet photoelectron spectroscopy (UPS) and inverse photoelectron spectroscopy (IPES) measurements were performed at room temperature, in a dedicated ultrahigh vacuum chamber with a base pressure of <2 \times 10\textsuperscript{−10} Torr. UPS was performed using a Specs gas discharge lamp operating with helium, yielding helium I photons at 21.22 eV. The energy resolution in UPS was 0.15 eV. IPES was performed in isochromat mode using a home-built setup,\textsuperscript{20} with an energy resolution of 0.45 eV.

2.3. Solar Cells. Glass substrates prepatterned with indium tin oxide (ITO; 10 \text{Ω/square}, Colorado Concept Coatings LLC, Loveland, CO) were cleaned by sonication in deionized water, acetone, and isopropyl alcohol and dried with nitrogen. The substrates were then immediately transferred to a nitrogen glovebox for device fabrication. Five nanometers of MoO\textsubscript{3} (Sigma-Aldrich, St. Louis), 20 \text{nm} of cHBC, 40 nm of C\textsubscript{70} (Nano-C, Inc., Westwood, MA), and 5 nm of bathocuproine (BCP; Sigma-Aldrich) were evaporated sequentially at a pressure of 2 \times 10\textsuperscript{−6} Torr. Then 100 nm of Al was evaporated through patterned masks to define an active area of 0.18 cm\textsuperscript{2}. The thickness of each donor was individually optimized for device efficiencies: 25 ± 1 nm for cHBC, 23 ± 1 nm for cTBFDDBC, and 20 ± 1 nm for cTBTDBC. The devices were placed under AM1.5G 100 mW/cm\textsuperscript{2} illumination in a nitrogen-filled glovebox and the current density–voltage (\textit{J–V}) characteristics were acquired with a Keithley 2400 source measurement unit. For each donor, 12–18 devices were fabricated and tested. The devices were then annealed in the glovebox on a hot plate at 160 °C for 10 min before retesting. Annealing for 10–30 min at 160 °C did not significantly alter the device performance. External quantum efficiency (EQE) measurements were performed using a 300 W xenon arc lamp (Newport Oriel, Irvine, CA) with filtered monochromatic light from a Cornette 260 1/4 M double grating monochromator (Newport 74125). Spectral response simulations incorporating the measured optical constants of each layer (Figure S1 of the Supporting Information) in the device stack and the measured reflectance of the completed devices were performed using the transfer matrix formalism to yield the internal quantum efficiency (IQE) spectra.\textsuperscript{21} The exciton diffusion lengths of the active layers were adjusted so the simulated external quantum efficiency spectra match those measured. The internal quantum efficiency is the measured external quantum efficiency divided by the modeled donor/acceptor absorption. The C\textsubscript{70}/BCP interface was given an exciton-blocking boundary condition, whereas the MoO\textsubscript{3}/donor and donor/C\textsubscript{70} interfaces were given exciton-quenching boundary conditions, with the latter treated as a dissociative (photocurrent-producing) interface.\textsuperscript{22,23}

2.4. X-ray Reflectivity (XRR). Single and bilayer films comprising the individual active constituents and each active layer, respectively, were deposited onto polished silicon substrates and tested before and after annealing at 160 °C for 10 min with processing conditions identical to those used during OPV device fabrication. XRR measurements were taken on a Bruker D8 Discover with a Cu K\alpha source equipped with a parallel beam G{"o}t{\"o}bel mirror, 0.11 mm divergence slit, and scintillation detector. Diffuse reflection measurements were subtracted from the raw data to obtain the true specular reflection over 5 decades of intensity. We fit the experimental data with GenX\textsuperscript{24} by modeling the samples as homogeneous layers with variable interfacial roughness/widths.

2.5. Grazing Incidence X-ray Diffraction (GIXD). Four-layer stacks on ITO identical to each device were annealed with laminated Al electrodes that were subsequently removed for structural characterization to mimic device processing conditions. GIXD experiments were conducted at the G1 station (9.95 ± 0.05 keV) of the Cornell High Energy Synchrotron Source. The beam was chosen to be 0.05 mm tall and 1 mm wide. The width of each sample was 5 mm. The X-ray beam was aligned above the film’s critical angle but below that of the substrate, at a 0.18° incident angle with the substrate. X-ray scattering was collected with a two-dimensional charge-coupled device (CCD) detector, positioned 111.5 mm from the sample. All GIXD images have been background-subtracted.

3. RESULTS AND DISCUSSION

Figure 1 shows the chemical structures of the parent compound cHBC, contorted tetraphenylbenzodibenzo[1,4]coronene (cTBFDBC, 1a), and contorted tetraphenylbenzodibenzo[1,4]coronene (cTBTDDBC, 1b).

![Chemical structures of contorted hexabenzenocoronec (cHBC), contorted tetraphenylbenzodibenzo[1,4]coronene (cTBFDBC, 1a), and contorted tetraphenylbenzodibenzo[1,4]coronene (cTBTDDBC, 1b).](https://example.com/figure1.png)
Scheme 1. Synthesis of cTBFDBC (X = O; 1a) and cTBTDBC (X = S; 1b)

Figure 2. Thin-film absorption spectra (top) of cHBC (black), cTBFDBC (blue), cTBTDBC (red), and C70 (dashed, black). Energy levels (bottom) of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals of the constituents determined by ultraviolet photoelectron (UPS) and inverse photo-emission (IPES) spectroscopies, respectively. The measured energy levels reported here for cHBC are consistent with literature values. The energy levels of C70 were obtained from the literature.

gradual conversion to the boronic acid counterparts during the reaction allows coupling to compete favorably with boronic acid decomposition, thus leading to higher synthetic yields, particularly in the case of 2-benzofuranylboronic acid MIDA ester. Using this approach, we are able to achieve >80% yields for both 5a and 5b. Ring closing via photocyclization in toluene leads to 1a and 1b. Unlike the syntheses of many cHBC derivatives, Scholl cyclization is not needed to fully ring-close the precursors to yield 1a and 1b, likely due to a reduction in peripheral sterics with the introduction of five-membered rings. Following photocyclization, the products were purified in a tube furnace via horizontal physical-vapor transport (PVT). cTBFDBC and cTBTDBC and their respective precursors were confirmed by 1H nuclear magnetic resonance (NMR) and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS); these data are reported in the Supporting Information with accompanying figures. In general, the solubility of cTBFDBC and cTBTDBC in organic solvents is lower than that of cHBC. Like cHBC, however, both cTBFDBC and cTBTDBC are air-stable and exhibit excellent thermal stability. While the benzothiophene moiety is an extensively used building block for organic semiconductors, benzofuran is an attribute to strongly allowed β-bands, occurring at 377, 366, and 355 nm, respectively. The emission maxima of cHBC, cTBFDBC, and cTBTDBC, which we attribute to strongly allowed β-bands, occur at 372 and 399 nm, respectively. The emission maxima of cHBC, cTBFDBC, and cTBTDBC occur at 493, 506, and 524 nm, respectively, nearly overlap with the emission maxima of these molecules at 506 and 524 nm, respectively, indicating that the symmetry-forbidden transitions in cHBC are accessible in cTBFDBC and cTBTDBC, and are available to participate in light absorption. These desymmetrized transitions originate with the addition of benzofuran and benzothiophene moieties on four of the six peripheral aromatic rings of cTBFDBC and cTBTDBC, respectively. For comparison, cDBTTC, a heterocyclic cHBC...
obtained from the literature are also provided.\textsuperscript{30} The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of cHBC, cTFBDBC, and cTBTDBC with respect to the vacuum level were measured to be 5.5, 5.3, and 5.4 eV, respectively, and 2.5, 2.6, and 2.9 eV, respectively. Consistent with the trend seen in the optical band gaps, the electronic band gap is the largest for cHBC (3.0 eV), followed by cTFBDBC (2.7 eV) and cTBTDBC (2.5 eV). Compared to the parent compound, using extended heterocyclic moieties as peripheral substituents leads to band gap reductions of 0.3 and 0.5 eV for cTFBDBC and cTBTDBC, respectively. This decrease in band gap is greater than that previously reported in HBC derivatives with peripheral halogenation, where the band gap only varies by as much as 0.2 eV.\textsuperscript{3} This difference likely stems from an increase in the conjugation length afforded by the addition of benzofuram and benzothiophene moieties in cTFBDBC and cTBTDBC, respectively. Relative to cHBC, the reduction in band gap in cTFBDBC occurs at the expense of the HOMO energy level more than the LUMO energy level, while in cTBTDBC the band gap reduction primarily occurs in the LUMO energy level.

Vacuum-deposited planar-heterojunction devices were fabricated to compare the performance of cHBC, cTFBDBC, and cTBTDBC as electron donors in solar cells. We retained the same device architecture and employed the same hole- and electron-transport layers as well as electron acceptor for meaningful comparison. We chose the planar-heterojunction architecture so constituent miscibility and blend morphology are not variables in our comparison.\textsuperscript{38,39} Relevant device parameters before and after thermal annealing at 160 °C for 10 min averaged across 12–18 devices for each donor are summarized in Table 1. The J–V characteristics of champion devices of each donor are shown in Figure 3a–c as open and filled squares, respectively. Like previously reported BHJ devices utilizing other cHBC derivatives as donors paired with fullerene acceptors,\textsuperscript{11,12,16} we observed high open-circuit voltages relative to the quintessential poly(3-hexylthiophene)/phenyl-C_{60}-butyric acid methyl ester device.\textsuperscript{40} At 1.02 ± 0.01 V, the (V_{oc}) of the cHBC/C_{70} devices is the largest among the as-evaporated devices. This observation is consistent with cHBC/C_{70} having

<table>
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<tr>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>PCE (%)</th>
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<tbody>
<tr>
<td>cHBC/C_{70}</td>
<td>1.02 ± 0.01</td>
<td>2.7 ± 0.1</td>
<td>0.57 ± 0.02</td>
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<tr>
<td>cTFBDBC/C_{70}</td>
<td>1.05 ± 0.01</td>
<td>2.9 ± 0.1</td>
<td>0.64 ± 0.01</td>
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<td>3.7 ± 0.1</td>
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<td>0.81 ± 0.01</td>
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<tr>
<td>cTFBDBC/C_{70}</td>
<td>0.86 ± 0.01</td>
<td>3.3 ± 0.2</td>
<td>0.60 ± 0.02</td>
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<tr>
<td>cTBTDBC/C_{70}</td>
<td>0.90 ± 0.01</td>
<td>3.7 ± 0.1</td>
<td>0.65 ± 0.01</td>
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\textsuperscript{*}The average and standard deviation values reported here for each type of device are from a set of 12+ devices. The device yield on annealing was 100\% in all cases. All devices were measured under 100 mW cm$^{-2}$ AM1.5G simulated solar illumination. The device area was 0.18 cm$^2$.\textsuperscript{41,42}
the largest energy level difference between the HOMO of the donor and the LUMO of C70.41 Increases in donor absorption due to band gap narrowing in cTBDFDBC and cTBTDBC relative to cHBC are coupled with reductions in the energy level difference of 0.2 and 0.1 eV, respectively, leading to reductions in $V_{oc}$ accordingly. As-evaporated devices utilizing cTBDFDBC or cTBTDBC as the donor display enhanced photocurrents and power-conversion efficiencies relative to those using cHBC. We also observed significantly higher fill factors ($FF = 0.57 - 0.69$) in our devices compared with any other cHBC-based devices.$^{3,11,12,16}$ This enhancement in FF compared to previous cHBC devices is expected, given that planar-heterojunction devices generally exhibit fewer shunt pathways compared to BHJ devices.$^{42,43}$ Importantly, this observation also points out that contorted materials do not inherently suffer from excessive interfacial electronic coupling$^{13,44}$ and recombination when paired with fullerenes.

Annealing the devices at 160 °C for 10 min leads to improvements in all device parameters regardless of donor choice. Together, the improvements in $J_{sc}$, $V_{oc}$, and FF on annealing lead to enhancements in power-conversion efficiency of 25–30% for devices with each donor (summarized in Table 1).

To understand the role that the active-layer morphology plays on the improvements in device performance with annealing, we utilized GIXD and XRR. Figure S5 shows the GIXD images for the device stacks (less the aluminum interfaces in the bilayer) at 160 °C. The (100), (200), (010), and (110) reflections of C70 have been indexed in the orthorhombic crystal structure reported by Vaughan et al. with lattice parameters $a = b = 10.15$ Å and $c = 27.85$ Å and angles $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$. While weak scattered intensities centered about $q = 0.5$ Å$^{-1}$ can be observed in Figures S5c,d, these intensities are attributed to nearest-neighbor correlations in the cTBDFDBC layer; similar observations have been reported for cHBC films.$^{32}$ Therefore, besides the reflections associated with crystalline C70, the diffraction patterns are void of features that indicate long-range order. Further, the diffraction patterns of the annealed samples are the same as those of the as-evaporated samples. Thus, all three donor layers are unchanged on annealing at 160 °C for 10 min. This observation is not inconsistent with the work of Hiszpanski et al., who found that as-evaporated cHBC films are amorphous and require annealing at temperatures as high as 240 °C to induce large-scale crystallization.$^{29}$ That the diffraction images before and after annealing are indistinguishable further indicates that each multilayer stack retains its as-evaporated morphology on annealing. Thus, differences in crystallinity of the constituents cannot account for the device performance enhancements on annealing.

We used XRR to examine the buried donor–acceptor (D–A) interfaces in bilayer films identical to the active layers in the devices. The reflectivity traces of the films and their modeled electron density profiles are shown in Figures S6a and S6b–e, respectively. The top surfaces of these films were found to be molecularly smooth (root mean square roughness <1 nm). The modeled electron densities of the cHBC, cTBDFDBC, cTBTDBC, and C70 thin films are $0.40 \pm 0.01$, $0.41 \pm 0.01$, $0.42 \pm 0.01$, and $0.49 \pm 0.01$ electrons/Å$^3$. For comparison, the electron densities extracted from single-crystal structures of cHBC,$^{9}$ cTBDFDBC, and C70 are $0.46, 0.47$, and $0.54$ electrons/Å$^3$, respectively. The thin films are lower in electron density compared to their single-crystal counterparts because they lack long-range order. Since the electron densities of the donor and acceptor films vary by more than 10%, XRR can resolve the compositional variation across the buried donor/acceptor interfaces in the bilayer films.$^{46,47}$ The reflectivity traces of the bilayer films and their modeled electron density profiles are shown in Figure 4a and 4b–d, respectively. The reflectivity traces of the as-evaporated and annealed bilayer films are identical, indicating that the bilayer structure is retained on annealing in each case. Additionally, the thickness estimated from the electron density profiles of each bilayer film, shown in Figure 4b–d, is consistent with the thicknesses of the donor and acceptor layers separately measured by profilometry and ellipsometry. Both observations indicate that the donor–acceptor interface in each case is well-defined, and this interface is retained on thermal annealing. That the donor and acceptor layers in each case do not undergo mixing when annealed at 160 °C for 10 min is surprising given the extensive literature that describes the interdiffusion of PCBM and polymer donors in the active layers of polymer solar cells.$^{48–52}$ Our observation thus highlights the limited miscibility C70 has with the cHBC derivatives, even when they are amorphous. That the donor–

![Figure 3. $J−V$ characteristics in the dark (triangles) and under illumination (squares) of (a) cHBC/C70, (b) cTBDFDBC/C70, and (c) cTBTDBC/C70 bilayer devices as-evaporated (open symbols) and after annealing (filled symbols) at 160 °C for 10 min.](image-url)
acceptor interfaces are retained in our bilayer films indicates that intermixing is not responsible for the improvements in device performance; we are left to surmise that improvements in device characteristics must stem from better active layer-electrode contacts on thermal annealing.40,53−55 While the XRR measurements show that the D−A interface in each bilayer is unchanged on annealing, comparing the interfaces of the bilayer films comprising different donors reveals subtle differences. In the reflectivity traces shown in Figure 4a, the interference fringes in the reflectivity traces of the cHBC/C70 and cTBTDBC/C70 samples persists beyond \( q_z = 2.5 \text{ nm}^{-1} \), while the fringes in the reflectivity trace of the cTBFDBC/C70 stack dampen before \( q_z = 2.5 \text{ nm}^{-1} \). This subtle difference in the reflectivity traces of our bilayer films translates to a slightly broader interface in cTBFDBC/C70 (Figure 4c inset) compared to the other two bilayer films (Figure 4b,d insets). The slight interfacial broadness depicted in cTBFDBC/C70 is observed both in the as-evaporated bilayer film, as well as in the thermally annealed film, and can be ascribed to a slightly rougher D−A interface compared to those in cTBTDBC/C70 and cHBC/C70. Given that the surfaces of the donors are equally smooth before the deposition of C70 (Figures S6a−c), the broader D−A interfacial width observed in the cTBFDBC/C70 bilayer relative to the cHBC/C70 and cTBTDBC/C70 bilayers must be specific to interfacial interactions between cTBFDBC and C70. Accordingly, we believe this rougher D−A interface is responsible for the enhanced performance of cTBFDBC/C70 devices, in light of the morphological invariance across the three donor/acceptor pairs.

To further elucidate, we show the EQE spectra of devices comprising each donor in Figure 5a. The EQE of the reference cHBC/C70 device (black) reaches 27% at wavelengths near 400 nm where both HBC and C70 absorb, while the contribution from C70 peaks at 17% at 530 nm. The EQE of cTBFDBC/C70 (blue) and cTBTDBC/C70 (red) devices exceed 35% and 30% near 400 nm, respectively, where both donor and C70 are actively absorbing. The red-shifted absorption maximum of cTBTDBC relative to cHBC (Figure 2) enhances the EQE of the cTBTDBC/C70 device (red) between 400 and 450 nm relative to the reference device (black), leading to an EQE above 30% at 430 nm. Despite a blue-shift in the absorption maximum of cTBFDBC relative to cHBC (Figure 2), the EQE of the cTBFDBC/C70 device (blue) exceeds 35% at 404 nm—this is the highest EQE of the three devices. In addition to these enhancements in EQE near 400 nm, devices comprising cTBFDBC/C70 and cTBTDBC/C70 exhibit improved light harvesting at all wavelengths compared to those
comprising cHBC/C$_{70}$. The EQE of the cTBFDBC/C$_{70}$ and cTBTDBC/C$_{70}$ devices reaches 32% at 510 nm and 26% at 528 nm, respectively, stemming from photoabsorption by the desymmetrized transitions that are forbidden in cHBC.

The absorption profile of cTBFDBC is a less ideal match with the solar radiation spectrum than cTBTDBC, yet devices comprising cTBFDBC consistently outperform those containing cTBTDBC in photocurrent when paired with C$_{70}$. Further, the diffusion lengths for these two donors in our model are comparable, suggesting differences in exciton diffusion are not responsible for differences in device performance. To elucidate the origin of these performance differences arising from the donor choice, we determined the internal quantum efficiency (IQE) spectra shown in Figure S5. At wavelengths of 400–550 nm, the cTBTDBC/C$_{70}$ device outperforms the cHBC/C$_{70}$ and cTBTDBC/C$_{70}$ devices in terms of IQE. At wavelengths greater than 600 nm, where only C$_{70}$ absorbs, the IQE spectra of the cHBC/C$_{70}$ and cTBTDBC/C$_{70}$ devices overlap. This comparison indicates that cTBTDBC harvests absorbed photons more efficiently than the parent cHBC when paired with C$_{70}$ in devices, and that C$_{70}$ is equally effective in both devices. The cTBFDBC/C$_{70}$ device outperforms the cHBC/C$_{70}$ and cTBTDBC/C$_{70}$ devices in IQE by about 5–15% at all wavelengths, including at wavelengths longer than 600 nm where C$_{70}$ is the only active absorber. Consistent with having a rougher D–A interface, this wavelength-independent boost in IQE suggests improved exciton dissociation and charge transfer at the D–A interface when cTBFDBC—as opposed to cTBTDBC or cHBC—is used as the donor.

Interestingly, the IQE spectra in Figure S5b are not spectrally flat; the IQE is higher at wavelengths that correspond to strong donor absorption than at wavelengths where only C$_{70}$ absorbs. This spectral asymmetry is especially pronounced in the IQE of the cTBFDBC/C$_{70}$ device where the maximum IQE is 47% at 390 nm. We speculate this wavelength-dependent IQE stems from the overlap between donor emission (Figure S3) and C$_{70}$ absorption (Figure 2) that allows for efficient Förster resonance energy transfer of excitons from cTBFDBC to C$_{70}$. Accordingly, we observe an enhancement in IQE at wavelengths corresponding to donor absorption relative to wavelengths corresponding to C$_{70}$ absorption. That the cTBFDBC/C$_{70}$ device has the highest IQE is consistent with cTBFDBC exhibiting the highest QY of the three donors.

4. CONCLUSIONS

We have designed, synthesized, and characterized benzoferan- and benzothiophene-containing cHBC derivatives, finding that these molecules significantly outperform cHBC in terms of visible-light absorption and are therefore better candidates as donors in OPV devices. We attribute the improvements in optoelectronic properties seen in cTBFDBC and cTBTDBC to a simultaneous decrease in molecular symmetry and an increase in conjugation relative to the parent compound. While CHBC derivatives have been shown to be promising active materials for organic solar cells due to their high open-circuit voltages, and recently their ability to function as acceptors, this is the first time that devices using these materials have been fabricated that have high fill factors. While this improvement is attributed to the planar-heterojunction architecture of our devices (compared to previous BHJ devices), these results allow us to conclude that devices comprising contorted CHBC derivatives do not intrinsically suffer from low fill factors. Further, via XRR we probed the donor–acceptor interfaces of bilayer thin films comprising three different contorted donors and C$_{70}$ and found C$_{70}$ to be immiscible with our cHBC derivatives under the annealing conditions used here. The stability of the donor and acceptor phases and the robustness of the active-layer architecture in our devices have profound implications for small-molecule organic solar cells as well as other multilayer devices, such as OLEDs.

ASSOCIATED CONTENT

5 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.5b04503.

Notes

The authors declare no competing financial interest.

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Molecules


Contorted Aromatic Molecules.
S. ;Y ager, K. G. ;T oney, M. F. ;L oo, Y. -L. ;N uck olls, C. A


Optical Processes in Semiconductors


S. ;Y ager, K. G. ;T oney, M. F. ;L oo, Y. -L. ;N uck olls, C. A


Optical Processes in Semiconductors


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