Herein, we detail how to grow one crystalline organic semiconductor on another epitaxially and thereby provide a method to tune the electronic nature of the $p$–$n$ junction in organic photovoltaics (OPVs). While OPVs are attractive as materials for conversion of sunlight into electrical energy,\textsuperscript{[1]} higher conversion efficiencies\textsuperscript{[2]} are needed for OPVs to become a viable technology.\textsuperscript{[3–6]} Regardless of the type of OPV, either a bilayer\textsuperscript{[7]} or bulk-heterojunction (BHJ)\textsuperscript{[8]} (Figure 1 A), the interface between the hole and electron transporting films is the critical locus for exciton formation and dissociation.\textsuperscript{[8–11]} In inorganic materials, the interface between two semiconductors is crucially important in determining and controlling the electrical properties of these materials and is controlled by a heteroepitaxial growth of one crystalline material on another. We show here that $p$-type and $n$-type organic semiconductors can be designed to have nested shapes that create an epitaxial growth that achieves higher conversion efficiencies and open circuit voltages in these devices to within 10\% of the theoretical limit. We utilize the class of molecules known as contorted hexabenzocoronenes (HBCs, Figure 1 B) because they are established $p$-type semiconductors\textsuperscript{[12–14]} and are also photoconductive.\textsuperscript{[15, 16]} This HBC has an unusual shape in that it is contorted and doubly-concave.\textsuperscript{[12]} The size and shape of this molecule are complementary to buckminsterfullerene (C$_{60}$), which is a well-known $n$-type semiconductor (Figure 1 C). It is this potential for shape and electronic complementarity between these two molecular structures that led us to investigate them in the context of heteroepitaxial growth.

We first focused on whether HBC and C$_{60}$ formed co-crystalline, supramolecular assemblies. Two experiments, one from solution (Figure 2 A) and one from the gas phase (Figure 2 B) show that the materials form co-crystals. Large purple-gray crystals were produced from a saturated solution of C$_{60}$ and HBC in chlorobenzene.

The molecular structure determined from the solution-grown crystals reveals that HBC and C$_{60}$ spontaneously formed an interdigitated supramolecular complex (complex 1). The three-dimensional structure of HBC comprises two opposing concave aromatic faces, wherein a C$_{60}$ had nestled into each face (Figure 2 A). It is important to note that a number of organic molecules have been specifically designed to form complementary interactions with C$_{60}$ and have yielded co-crystals.\textsuperscript{[17–20]} However, few of these molecules are suitable candidates for the formation of a $p$–$n$ junction.\textsuperscript{[17]}

The crystal of 1 comprises C$_{60}$, HBC, and chlorobenzene (2:1:1), wherein HBC and C$_{60}$ organize into a repeating pattern of ABAABA as shown in Figure 2 A. Each HBC has two C$_{60}$ nearest neighbors, and each C$_{60}$ has one HBC nearest neighbor and one C$_{60}$ nearest neighbor. The C$_{60}$ is centered over one of the
six-membered rings on the edge of the coronene core of HBC; in this instance, the vertical π–π distance is 3.00 Å.

We were also able to co-crystallize these molecules without solvent using horizontal physical vapor transport. We placed HBC and C₆₀ powders in the hot zone (550 °C) of a horizontal, gradient-temperature furnace. Crystals (complex 2) formed in the cold zone of the furnace (330 °C). The composition of 2 was 1:1 HBC:C₆₀ (Figure 2B).

The assembly of HBC and C₆₀ in 2 is different from 1. The HBC and C₆₀ organize in an ABAB repeating pattern in 2 (Figure 2B). In this structure there are two crystallographically inequivalent HBC sites. Every HBC has two C₆₀ nearest neighbors with the C₆₀ having two non-identical HBC neighbors. Each C₆₀ is centered directly in the middle of the core six-membered ring in one type of HBC at a π–π distance of 2.93 Å. Each C₆₀ is also centered over another HBC just outside one of the bonds of the core six-membered ring at a π–π distance of 3.07 Å. The HBC molecules in 2 are organized in sheets (Figure 2B). Even though there are two inequivalent HBC sites, they are assembled into a rectangular array with a center-to-center distance of 11.36 Å. Every HBC molecule has a 3.63 Å close carbon-to-carbon contact with four neighboring HBCs.

The C₆₀ molecules in 2 form columns (Figure 2B). The center-to-center distance between the columns is 9.88 Å, which is one of the shortest C₆₀–C₆₀ distances reported to date. The fullerenes assemble in a zigzag pattern with a 111° bend (center-to-center) at each C₆₀. The columns are spaced 15.87 Å apart from one another. A spacing of 9.88 Å is within the range of previously reported values for C₆₀–C₆₀ spacings in the pure crystal, but 15.87 Å is significantly larger than those values, indicating that C₆₀ forms columns in 2.

The solution-grown crystals of 1 were large enough that we were able to directly measure the resistance of single crystals using evaporated silver electrodes (Figure 3). These crystals are insulating, which is expected as both HBC and C₆₀ individually are semiconductors. The resistance was significantly reduced after the same species was kept in vacuum at room temperature for twelve days. We presume that this is due to the slow evaporation of chlorobenzene. Illumination of the devices causes a 1,000-fold decrease in resistance. Crystals of 2 were not large enough to measure in single-crystal devices.

We made OPV devices to test our hypothesis that the large decrease in resistance in the crystals is due to charge transfer between the n- and p-type molecules. We chose an OPV bilayer architecture (Figure 4A) rather than a BHJ architecture because it is easier to optimize the former. We used an electrode pattern that allowed for rapid and reproducible electronic characterization of over 200 devices at a time. Standard electrode materials were deliberately used for all devices for direct comparison to literature values. We measured the electrical characteristics of these devices in the dark, and then again when they were exposed to a 1.5 AM solar-simulated light source (power density = 1 sun, 100 mW cm⁻²). The devices were open to air during the measurements unless otherwise noted.

The illumination-dependent current-density/voltage characteristics of an HBC/C₆₀ device appear in Figure 4B: a short-circuit current density (Jₛᶜ) of 3.32 mA/cm², open-circuit voltage (Vₒᶜ) of 0.88 V, and a fill factor of 0.27 yield an efficiency of 0.77%. These values are not high enough to be viable in technology, but are very good given the poor absorbance of the HBC and the high Vₒᶜ in the device. It charts a path to more efficient devices that would shift the absorbance of the HBC to absorb more broadly in the solar region of the spectrum. As support for this, the normalized external quantum efficiency (EQE) spectra show the highest value for the relative efficiency near 390 nm. This is close to the maximum in the absorbance of the HBC thin film (Figures S1 and S2, Supporting Information).

The efficiency of a photovoltaic device is proportional to the magnitude of the Vₒᶜ. To a first approximation, the theoretical
maximum $V_{OC}$ for our devices is the energy difference between the highest occupied molecular orbital (HOMO) of HBC at ~5.5 eV and the lowest unoccupied molecular orbital (LUMO) of C$_{60}$ at ~4.5 eV. Our $V_{OC}$s approach this difference of 1.0 V. These are among the highest values reported for OPVs.\[3\]

The efficiency of a photovoltaic device is also directly proportional to the $J_{SC}$. Upon illumination, the current density of the HBC/C$_{60}$ devices clearly increases, regardless of the applied bias. This is consistent with our observations of photoconductivity\[15, 16\] in HBC films and HBC/C$_{60}$ co-crystals (Figure 3).

The device performance observed here is unexpectedly good given that the absorbance of HBC overlaps poorly with the simulated solar spectrum (Figure 4 C). When the devices were irradiated at 422 nm near the maximum of the normalized EQE spectrum, we observed conversion efficiencies of up to 5.7 % (Figure 4 D).\[25\] There is only a slight change in the average $V_{OC}$ of these devices upon moving from solar to UV LED illumination (Figure 4 B, 4D). The performance of HBC/C$_{70}$ devices is essentially the same as that of HBC/C$_{60}$ devices (Figure S3, Supporting Information). All the devices were operated in ambient atmosphere without any encapsulation.

We have seen that HBC and C$_{60}$ form a tight molecular complex. We have also seen that bilayer OPV devices using these two compounds have good functional performance. We have previously used grazing incidence X-ray diffraction (GIXD) to detect co-crystalline regions within polymer/fullerene BHJs\[26\] and herein we use the same technique to analyze the HBC/C$_{60}$ interface. We collected GIXD data from HBC-coated silicon substrates after stepwise depositions of C$_{60}$ onto the HBC (25 nm). We increased the thickness ($x$ nm) of the C$_{60}$ layer from 0 nm to the optimal device thickness of 40 nm (Figure 5).

The film of pure HBC shows weak crystalline order; a weak (100) reflection at $Q = \sim$ 0.5 Å$^{-1}$, labeled “A” in Figure 5, is largely confined to the vertical direction ($Q_z$) and indicates that the HBC molecules are oriented within a 5–10° tilt from the surface normal, while the breadth of the peak indicates small crystallite domains. The broad peak centered at $Q = \sim$ 1.5 Å$^{-1}$ is dominated by the signal from the SiO$_2$ substrate which overwhelms that of any HBC reflections. When 3–6 nm of C$_{60}$ is deposited on top of the HBC film, the intensity of peak A increases significantly along the vertical, and C$_{60}$ peaks ($Q = \sim$ 0.75 (peak B), 1.24 and 1.5 Å$^{-1}$) also appear. However, in the absence of an interaction between HBC and C$_{60}$, the (100) reflection from pure HBC should be damped rather than enhanced by a thin C$_{60}$ layer at grazing incidence. Instead, we find that while the intensity of the C$_{60}$ peaks increase linearly with increasing film thickness for all deposition steps, the intensity of peak A increases for thin C$_{60}$ films ($x \leq$ 6 nm), that is, at the interfacial region, before decreasing as it becomes buried by the C$_{60}$ (see Figure 5 inset). The increase in intensity of peak A suggests the C$_{60}$ introduces an additional degree of order at the bilayer in-
interface. Since reflections due to complex 2 appear in the Q-region of A while C_{60} reflections do not (Figure 5), we anticipate that, under the present conditions, deposition of C_{60} on the HBC surface would result in the formation of some small co-crystalline regions at the interface. This interpretation is supported by the shift of the (111) reflection of C_{60} (peak B) from its nominal position (0.73 Å⁻¹) to lower Q (0.7 Å⁻¹), toward the co-crystal reflections, for the 3 nm C_{60} film, as well as the width of peak A, which is roughly consistent with a 3 nm interface layer.

To further probe the local electronic and geometric structure of the HBC/C_{60} interface, it was investigated with surface-sensitive X-ray photoelectron (XPS) and near-edge X-ray absorption spectroscopy (NEXAFS). For this experiment, the interface was modeled by depositing 2 nm C_{60} on a 10 nm HBC film on ITO. The spectral differences between the C_{60} (2 nm)/HBC(10 nm) bilayer and pristine (10 nm) films of either HBC or C_{60} then afforded insight into the unique interaction between the shape complementary donor and acceptor molecules. XPS probing the C 1s region (Figure S4, Supporting Information) provides direct evidence for an electronic interaction between C_{60} and HBC in the deposited films. Specifically, relative to the pure HBC and C_{60} films, the bilayers have a shift to higher binding energy by 0.2 eV, a change in peak shape, and a narrowing in peak width. Such features are consistent with charge transfer at donor-acceptor interface, which affects the ability of the system to screen and stabilize the core-ionized final state, thereby altering the shape, width, and energy of the photoemission peak. This supports the presence of an intimate interaction between the donor and acceptor molecules.

Surface-sensitive, polarization-dependent NEXAFS, shown in Figure S4 (Supporting Information), indicates that the electronic interaction between acceptor and donor is accompanied by a physical ordering of the molecules at the HBC/C_{60} interface. In the total electron yield (TEY) signal, which probes the bulk of the 10 nm films, no polarization dependence is observed, indicating the lack of a preferred molecular orientation in the film. However, an anisotropy in bond geometry is uniquely observed for the HBC/C_{60} bilayer in the Auger electron yield (AEY) signal, which probes the ~1–2 nm near-surface region; that is, the HBC/C_{60} interface. From the polarization dependence of the integrated π⁺ resonances, we estimate that the HBC molecules interacting with C_{60} are oriented at an average tilt angle of ~40° with respect to the surface plane. If the HBC ordering is related to a spontaneous assembly of the molecular partners at the bilayer interface into complex 2, this HBC tilt angle orients the (110) plane of the co-crystal parallel to the surface plane. In this geometry, X-rays diffracted from the (110) plane of complex 2 would contribute intensity confined to the Q direction at Q = 0.48 Å⁻¹ and thereby explain the increase in peak A in the GIXD data at the HBC/C_{60} interface (Figure 5). The data suggests that there is sufficient solid-state and surface mobility of the molecular partners for coalescence into an ordered state at the interface that can be modeled by the “ball and socket” structure shown in Figure 2.

The sequential deposition of the two shape-complementary molecules thus does produce an interface that is at least partially organized. Do the OPVs benefit from this molecular organization? To assess this we tested p-type molecules that lack the doubly-concave distortion from planarity of our HBC but is otherwise very similar. Flat hexa-peri-hexalubenzocoronene (flat-HBC) is an excellent candidate for comparison to the HBC under investigation (contorted-HBC) (Figure S5, Supporting Information). These two molecules have similar electronic structures, band gaps, molecular weights, chemical formulas, evaporation temperatures, molecular dimensions, and UV/Vis absorption spectra in thin films (Figure S2, Supporting Information). The most obvious difference between flat-HBC and our contorted-HBC is shape: one is perfectly flat while the other is severely distorted from planarity. While the contorted-HBC is shape-complementary to fullerenes, the flat-HBC is not.

Devices made with the two HBC molecules behaved quite differently under simulated solar irradiation. Devices based on contorted-HBC are more efficient than those based on flat-HBC (0.55 % versus 0.07 %). The former also have higher Voc_{CS} than the latter (0.84 V versus 0.19 V, Figure S3, Supporting Information). This supports the notion that shape complementarity contributes to the higher Voc_{CS} values for contorted-HBC.

Notably, under UV-LED irradiation, contorted-HBC device outperformed flat-HBC by more than two orders of magnitude (average efficiencies of η = 3.36 % versus 0.03 %, Figure S6, Supporting Information). The emission spectrum of the UV-LED covers the longest-wavelength absorbance shoulder for thin films of both HBCs (Figures 2C and S2, Supporting Information). Although contorted-HBC devices had Voc_{CS} similar to those of flat-HBC devices under solar irradiation, the Voc_{CS} of contorted-HBC devices were over ten times greater than flat-HBC (0.80 V versus 0.07 V) under UV light. These results further support our assertion that the shape-complementary interface is essential for peak device performance.

In summary, we reported that shape complementarity improves the donor/acceptor interface and, consequently, the photovoltaic properties of bilayer OPVs. We showed that contorted-HBC forms intimate complexes with the fullerenes. We also showed that differences in complementarity directly translate to differences in OPV performance. Better shape complementarity improves the interface between donor and acceptor materials in our devices and leads to some of the highest Voc_{CS} reported to date, with a maximum of 0.95 V. We also observe efficiencies of up to 5.7 % in ambient atmosphere for narrow-width UV irradiation and 1.04 % for solar illumination. This data indicates that our OPV cells may be ideally partnered with longer wavelength absorbing layers to achieve higher efficiency solar cells.

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[25] Average UV LED data: efficiency = 3.4 %; $J_{oc} = 0.16 \text{mA cm}^{-2}$; $V_{oc} = 0.80 \text{V}$; FF = 0.23.

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