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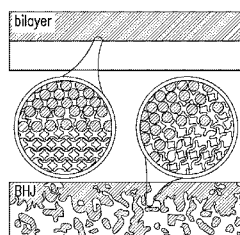


FIG. 1A

(57) Abstract: Systems and methods for hierarchical assembly of nanostructured organic heterojunctions for photovoltaic devices are described. Particularly, an apparatus for converting light energy to electrical energy is provided. An apparatus includes one or more organic photovoltaic devices. Photovoltaic devices include a cathode in electrical contact with the apparatus and an anode in electrical contact with the apparatus. Photovoltaic devices further include an acceptor layer having molecules forming a supramolecular network on a substrate and a donor layer having fullerene molecules bonded onto the supramolecular network.



HIERARCHICAL ASSEMBLY OF NANOSTRUCTURED ORGANIC HETEROJUNCTIONS FOR PHOTOVOLTAIC DEVICES

SPECIFICATION

CROSS-REFERENCE TO RELATED APPLICATIONS

5 The present application claims priority to U.S. Provisional Application No. 61/266,345, filed on December 3, 2009, and U.S. Provisional Application No. 61/349,569, filed on May 28, 2010, the disclosures of which are explicitly incorporated in their entirety by reference herein.

BACKGROUND

10 Bulk heterojunction (BHJ) active layer architectures can be employed in efficient organic photovoltaics (OPVs). This type of structure can include an interpenetrating network of p-type semiconducting molecules as the electron donors and n-type semiconducting molecules as the electron acceptors. The resulting device can exhibit an extensive interface for separation of photogenerated excitons, thereby
15 yielding higher efficiencies. However, one challenge is controlling the formation and size of the donor and acceptor domains within the BHJ. Addressing these challenges can lead to further improvements in device performance.

SUMMARY

 Hierarchical assembly of nanostructured organic heterojunctions for
20 photovoltaic devices are described. Particularly, an apparatus for converting light energy to electrical energy is provided. For example, the apparatus includes one or more organic photovoltaic devices. Photovoltaic devices can include a cathode in electrical contact with the apparatus and an anode in electrical contact with the apparatus. Photovoltaic devices can further include an acceptor layer having
25 molecules forming a supramolecular network on a substrate and a donor layer having fullerene molecules bonded onto the supramolecular network.

 An organic photovoltaic device is also provided. In one embodiment, an organic photovoltaic device includes a cathode, an anode, an acceptor layer having molecules forming a supramolecular network on a substrate, and a donor layer having
30 fullerene molecules bonded onto the supramolecular network.

A method for generating an organic photovoltaic device is also provided. In one embodiment, the method includes forming an anode layer of molecules arranged as a supramolecular network on a substrate, thermally evaporating a donor layer of fullerene molecules on the anode layer, and electrically connecting an anode and cathode to the assembly of the anode and donor layers.

Some embodiments include a class of molecules, dibenzotetrathienocoronenes (DBTTCs), shown below. These molecules can be used for hierarchical self-assembly at the molecular level and stack into columnar superstructures that in turn form a supramolecular network of cables on indium tin oxide (ITO) and ITO/poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS). This network can function as a scaffold for the molecular recognition and directed assembly of buckminsterfullerene (C_{60}). The templated growth of the C_{60} film creates a nanostructured p-n heterojunction, which can enable more efficient conversion of sunlight into electricity.

In some embodiments, the molecules are members of a class of polycyclic aromatic molecules known as contorted hexabenzocoronones (HBCs). These molecules can include three fused interpenetrating pentacene subunits that form a doubly concave shape due to steric interactions at the periphery of the molecule. These molecules form columnar nanostructures in self-assembled monolayers, cables, and liquid crystalline phases, with concomitant field effect mobilities of up to $1 \text{ cm}^2/\text{V}\cdot\text{s}$. The embodiments also include a class of contorted structures that have four of their benzo rings exchanged for fused thienyl rings. The unsubstituted DBTTC 1A and the hexyl-substituted DBTTC 1B can be prepared, for example, through the high yield (> 90%) procedure outlined in Scheme 1 (shown below), which proceeds in three steps and, in certain embodiments, utilizes only commercially available reagents. The 1,1,8,8-tetrabromobisolefin can be coupled with the appropriate thienyl boronic esters under Suzuki-Miyaura reaction conditions to yield the bis-tetrasubstituted olefins 2A and 2B (Scheme 1). The synthesis can be completed with a Katz-modified Mallory photocyclization.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 illustrates (A) a depiction of ball-and-socket interfaces in bilayer and bulk heterojunction devices; (B) a chemical model of the contorted-HBC;

and (C) the correlation between depiction (top) and molecular structure from the co-crystal of HBC and C₆₀ (bottom).

Figure 2 illustrates the organization of HBC and C₆₀ in co-crystals of C₆₀ and HBC (A) from solution as complex 1 (*left*) and (B) from the gas phase as complex 2 (*right*).

Figure 3 (A) is a labeled photograph of a single-crystal device of complex 1 and (B) is a graph showing the inverse temperature vs. sheet resistance of the device.

Figure 4 illustrates (A) an exemplary schematic of the OPV device architecture; (B) J-V characteristics of contorted-HBC OPVs; (C) absorbance spectrum of a thin film of *contorted*-HBC overlaid with the emission of the UV LED light source and the solar spectrum; and (D) J-V characteristics of *contorted*-HBC OPVs in the dark and illuminated with UV LED light source at 422 nm and an intensity of 1.5 mW/cm².

Figure 5 illustrates exemplary GIXD measurements according to exemplary embodiments of the described subject matter.

Figure 6 illustrates external Quantum Efficiency (EQE) spectrum of a contorted-HBC/C₆₀ device and EQE of a C₆₀ device without the HBC layer.

Figure 7 illustrates overlaid thin-film absorption spectra of contorted-HBC and flat-HBC along with the emission spectrum of the UV LED light source.

Figure 8 depicts exemplary graphs according to exemplary embodiments of the described subject matter.

Figure 9 depicts exemplary graphs (A) and (B) according to exemplary embodiments of the described subject matter.

Figure 10 depicts exemplary chemical structures of contorted-HBC and flat-HBC.

Figure 11 illustrates an exemplary contorted-HBC/C₆₀ device and illustrates I-V characteristics compared to those of a flat-HBC/C₆₀ device when illuminated under a UV LED.

Figure 12 illustrates an exemplary schematic of the HPVT.

Figure 13 is an exemplary graph of data according to exemplary embodiments of the described subject matter.

Figure 14 is an exemplary picture from CrystalMaker™ π - π distance measurements on complex 2.

Figure 15 (A) illustrates an exemplary chemical structure of 1A and 1B. (B) illustrates a schematic representation of an exemplary nanostructured OPV.

Figure 16 illustrates crystal structure of the hexyl-substituted DBTTC 1B. Hydrogen atoms and hexyl side chains are not shown for clarity. (A) A columnar stacking arrangement is observed along the [100] plane in the crystal. (B) Armchair conformation of 1B observed in the crystal. (C) Butterfly-shaped conformation of 1B observed in the crystal. The lines on the bottom in (B) and (C) indicate the contortion of the central pentacene moiety.

Figure 17 illustrates physical characterization of thermally annealed (150 °C) films of 1B on bare ITO. A typical tapping mode AFM image is shown in (A), and the angle-dependent C1s NEXAFS spectrum is shown in (B). A 2-D CCD image from a representative GIXD measurement is illustrated in (C). The corresponding integrated intensity along Q_z and Q_y , as well as the simulated powder diffraction pattern, is illustrated in (D).

Figure 18 illustrates tapping mode AFM images of films from 1B that were (A) unannealed, (B) annealed at 100 °C, and (C) annealed at 150 °C.

Figure 19 (A) is an exemplary schematic illustration of the nanostructured OPV architecture. (B) illustrates the corresponding energy levels, reported with respect to vacuum, for the donor and acceptor materials. (C) illustrates exemplary J-V curves for a DBTTC device, both with and without illumination, at 100 mW/cm².

Figure 20 illustrates an exemplary synthesis scheme for DBTTC according to exemplary embodiments of the described subject matter.

DETAILED DESCRIPTION

The disclosed subject matter pertains to systems and methods for hierarchical assembly of nanostructured organic heterojunctions for photovoltaic devices. One aspect of the disclosed subject matter relates to methods and systems for assembling photovoltaic universal joints, including, for example, ball-and-socket interfaces in molecular photovoltaic cells.

The disclosed subject matter illustrates methods for epitaxially growing one crystalline organic semiconductor on another and thereby provides 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, higher conversion efficiencies can enhance the viability of OPVs. Regardless of the type of OPV, and for either a bilayer and bulk-heterojunction (BHJ) (see, e.g., Figure 1A), the interface between the hole and electron transporting films is the locus for exciton formation and dissociation. In inorganic materials, the interface
5 between two semiconductors is useful in determining and controlling the electrical properties of these materials and is controlled by a heteroepitaxial growth of one crystalline material on another. 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 voltage in these devices, (e.g., within 10% of
10 the theoretical limit). In one embodiment, the class of molecules known as contorted hexabenzocoronenes (HBCs) (see, e.g., Figure 1B) can be used because they are p-type semiconductors and are also photoconductive. This HBC has an unusual shape in that it is contorted and doubly-concave. The size and shape of this molecule are complementary to buckminsterfullerene (C_{60}), which is one n-type semiconductor
15 (see, e.g., Figure 1C). It is this shape and electronic complementarity between these two molecular structures that makes them useful in heteroepitaxial growth.

One embodiment illustrates that HBC and C_{60} form co-crystalline, supramolecular assemblies. Two examples, one from solution (Figure 2A) and one from the gas phase (Figure 2B) show that the materials form co-crystals. Large
20 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 includes two
25 opposing concave aromatic faces, wherein a C_{60} had nestled into each face (Figure 2A). A number of organic molecules have been designed to form complementary interactions with C_{60} and have yielded co-crystals.

The crystal of 1 includes C_{60} , HBC, and chlorobenzene (2:1:1), in which HBC and C_{60} organize into a repeating pattern of ABAABA as shown in Figure
30 2A. 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 about 3.00 Å.

The molecules were co-crystallized without solvent using horizontal physical vapor transport. HBC and C₆₀ powders were placed 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).

Figure 2b demonstrates that the assembly of HBC and C₆₀ are different in **2** than in **1**. The HBC and C₆₀ organize in an ABAB repeating pattern in **2** (Figure 2B), according to one non-limiting embodiment. 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 columns is about 9.88 Å, a very short C₆₀-C₆₀ distance. The fullerenes assemble in a zigzag pattern with a 111° bend (center-to-center) at each C₆₀. The columns are spaced about 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; thus C₆₀ forms columns in **2**.

The solution-grown crystals are large enough to allow direct measurement of the resistance of single crystals using evaporated silver electrodes (see, e.g., Figure 3). These crystals are insulating, 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 12 days. Without being bound by a particular theory, it is believed that this is due, at least in part, to the slow evaporation of chlorobenzene. Illumination of the devices causes a 1,000-fold decrease in resistance.

This decrease in resistance implies an increase in the carrier density. This can be due to charge transfer between the n- and p-type molecules, e.g., exciton

splitting. OPV devices were constructed to illustrate this concept. An OPV bilayer architecture (see, Figure 4A) was selected over a BHJ architecture since it is easier to optimize OPV bilayers. An electrode pattern was used that allowed for rapid and reproducible electronic characterization of over 200 devices at a time. Standard electrode materials were used for all devices for direct comparison. The electrical characteristics of these devices were measured 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/cm²). The devices were open to air during the measurements unless otherwise noted.

The illumination-dependent current density/voltage characteristics of an HBC/C₆₀ device are shown in Figure 4B: A short-circuit current density (J_{SC}) of 3.32 mA/cm², open-circuit voltage (V_{OC}) of 0.88 V, and a fill factor of 0.27 yield an efficiency of 0.77%.

Figure 3B illustrates the inverse temperature vs. sheet resistance relationship of the device measured before annealing (triangles), after annealing (circles), with illumination (red), and without illumination (blue).

The efficiency of a photovoltaic device is proportional to the magnitude of the V_{OC} . To a first approximation, the theoretical maximum V_{OC} for 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 C₆₀ at ~4.5 eV. The V_{OC} 's approach this difference of 1.0 V.

The efficiency of a photovoltaic device is also directly proportional to the J_{SC} . Upon illumination, the current density of the HBC/C₆₀ devices increases, regardless of the applied bias. This is consistent with the observed photoconductivity in HBC films and HBC/C₆₀ co-crystals (see, e.g., Figure 3).

Although the absorbance of HBC overlaps poorly with the simulated solar spectrum, the device performed unexpectedly well (Figure 4C). When the devices were irradiated at 422 nm near the maximum of the normalized EQE spectrum, conversion efficiencies of up to 5.7% were observed (see Figure 4D).

There is only a slight change in the average V_{OC} of these devices upon moving from solar to UV LED illumination (see Figures 4B, 4D). The performance of HBC/C₇₀ devices is essentially the same as that of HBC/C₆₀ devices. All the devices were operated in ambient atmosphere without any encapsulation.

HBC and C₆₀ form a tight molecular complex and bilayer OPV devices using these two compounds have good functional performance. Grazing Incidence X-ray Diffraction (GIXD) can be used to detect co-crystalline regions within polymer/fullerene BHJs. The same technique can be used to analyze the HBC/C₆₀ interface. GIXD data was collected from HBC-coated silicon substrates after stepwise depositions of C₆₀ onto the HBC (25 nm). The thickness (x nm) of the C₆₀ layer was increased from 0 nm to the optimal device thickness of 40 nm (Figure 5).

Figure 4 illustrates (A) an exemplary schematic of the OPV device architecture: PEDOT:PSS (25nm), HBC (25nm), C60 (40nm), Aluminum (60nm). The surface area of the device is 0.16 cm²; (B) illustrates J-V characteristics of *contorted*-HBC OPVs in the dark and illuminated with 1.5 AM solar simulated light source; (C) depicts absorbance spectrum of a thin film of *contorted*-HBC overlaid with the emission of the UV LED light source and the solar spectrum; and (D) depicts J-V characteristics of *contorted*-HBC OPVs in the dark and illuminated with UV LED light source at 422 nm and an intensity of 1.5 mW/cm².

The film of pure HBC shows weak crystalline order; a weak (100) reflection at $Q = \sim 0.5 \text{ \AA}^{-1}$, 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 $Q \sim 1.5 \text{ \AA}^{-1}$ is dominated by the signal from the SiO₂ substrate which overwhelms that of any HBC reflections. When 3-6 nm of C₆₀ is deposited on top of the HBC film, the intensity of peak A increases significantly along the vertical, and C₆₀ peaks ($Q = \sim 0.75$ (peak B), 1.24 and 1.5 $\text{\AA}^{-1}$) also appear. However, in the absence of an interaction between HBC and C₆₀, it would be expected that the (100) reflection from pure HBC would be dampened rather than enhanced by a thin C₆₀ layer at grazing incidence. Instead, it has been found that while the intensity of the C₆₀ peaks increase linearly with increasing film thickness for all deposition steps, the intensity of peak A *increases* for very thin C₆₀ films ($x \leq 6 \text{ nm}$), i.e., at the interfacial region, before decreasing as it becomes buried by the C₆₀ (see Figure 5 inset). The increase in intensity of peak A indicates that the C₆₀ introduces an additional degree of order at the bilayer interface. Since reflections due to complex 2 appear in the Q-region of A while C₆₀ reflections do not (Figure 5), under the present conditions, deposition of C₆₀ on the HBC surface can result in the formation of some small co-crystalline regions at the interface. This is supported by

the shift of the (111) reflection of C₆₀ (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 C₆₀ 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/C₆₀ interface, a surface-sensitive X-ray Photoelectron (XPS) and Near Edge X-ray Absorption Spectroscopy (NEXAFS) was performed. For this demonstration, the interface was modeled by depositing 2 nm C₆₀ on a 10 nm HBC film on ITO. The spectral differences between the C₆₀ (2 nm)/HBC(10 nm) bilayer and pristine (10 nm) films of either HBC or C₆₀ demonstrate the unique interaction between the shape complementary donor and acceptor molecules.

XPS probing the C 1s region provides direct evidence for an electronic interaction between C₆₀ and HBC in the deposited films. Specifically, relative to the pure HBC and C₆₀ 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 the 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 indicates that the electronic interaction between acceptor and donor is accompanied by a physical ordering of the molecules at the HBC/C₆₀ 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/C₆₀ bilayer in the Auger electron yield (AEY) signal, which probes the ~1-2 nm near-surface region; i.e. the HBC/C₆₀ interface. From the polarization dependence of the integrated π^* resonances, the HBC molecules interacting with C₆₀ are estimated to be 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_z direction at Q = 0.48 Å⁻¹ and thereby explain the increase in peak A in the GLXD data at the HBC/C₆₀ interface (Figure 5). The data indicates 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 produces an interface that is at least partially organized. P-type molecules are used that lack the doubly-concave distortion from planarity of the HBC but are otherwise very similar. Flat hexa-peri-hexabenzocoronene (*flat*-HBC) can be compared to the HBC in this illustration (*contorted*-HBC). These two molecules have similar electronic structures, band-gaps, molecular weights, chemical formulas, evaporation temperatures, molecular dimensions, and UV-visible absorption spectra in thin films. A difference between *flat*-HBC and the *contorted*-HBC is shape: one is flat while the other is 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 differently under simulated solar irradiation. Devices based on *contorted*-HBC are more efficient than those based on *flat*-HBC (0.55% versus 0.07%). Devices based on *contorted*-HBC also have higher V_{OC} 's than the latter (0.84 V versus 0.19 V). This supports the notion that shape complementarity contributes to the higher V_{OC} 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 $\eta = 3.36\%$ versus 0.03%). The emission spectrum of the UV-LED covers the longest-wavelength absorbance shoulder for thin films of both HBCs (see Figure 4C). Although *contorted*-HBC devices had V_{OC} 's similar to those of *flat*-HBC devices under solar irradiation, the V_{OC} 's 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 the assertion that the shape-complementary interface is essential for peak device performance.

Figure 5 illustrates GIXD measurements (2-D images on the left and integrated intensity on the right) for films of C_{60} (40 nm), bilayers of increasing thickness of C_{60} on HBC, and pure HBC (25 nm). HBC, complex 2 and C_{60} reflections obtained from powder samples are also shown. Integrated intensities of the diffraction pattern are normalized by the maximum peak height; 2-D images for $x=0-10$ nm share the same intensity scale while $x=20$ nm has a larger upper limit due to the thickness of the film (see inset for peak intensity). Peak A corresponds to

diffraction intensity which increases in intensity at the HBC/C₆₀ interface before disappearing under the C₆₀ signal. Note: the sharp peak appearing at $Q=1.53 \text{ \AA}^{-1}$ in the 10 nm C₆₀ data corresponds to the (222) reflection of pure C₆₀.

Shape complementarity can improve the donor/acceptor interface and, consequently, the photovoltaic properties of bilayer OPVs. It has been shown that *contorted*-HBC forms intimate complexes with the fullerenes. It has also been shown that differences in complementarity directly translate to differences in OPV performance. Better shape complementary improves the interface between donor and acceptor materials and leads to some of the highest V_{OC}'s known to date, with a maximum of 0.95 V. Efficiencies of up to 5.7% were observed in ambient atmosphere for narrow width UV irradiation and 1.04% for solar illumination. This data indicates that the OPV cells can be partnered with longer wavelength absorbing layers to achieve higher efficiency solar cells.

An approach toward higher efficiency organic photovoltaic devices (OPVs) can be used according to the subject matter described herein. Complementarity in shape between the donor (contorted hexabenzocoronene, HBC) and acceptor (buckminsterfullerene, C₆₀) molecules resulted in OPVs that perform surprisingly well. In ambient atmosphere, the OPVs exhibit conversion efficiencies (η) of 5.7 % under ambient UV irradiation and over 1% under ambient solar illumination, with open circuit voltages (VOC) of 0.95V, within 10% of the theoretical maximum of 1.0 V. These OPVs have been illustrated with grazing incidence x-ray diffraction, x-ray photoelectron spectroscopy, and near edge x-ray absorption spectroscopy to confirm the presence of heteroepitaxial growth of C60 on HBC. This exploitation of host-guest chemistry at the organic/organic interface demonstrates an exemplary embodiment for OPV device design.

Some embodiments of the presently disclosed subject matter provide air stable organic photovoltaics from small molecules acene derivatives. Photovoltaics can play a role in satisfying the long-term global demand for cheap and renewable energy. Within the broad and diverse photovoltaic field, organic small molecules can be used. Indeed, small molecules can be easy to synthesize and purify, are monodisperse, exhibit high carrier mobilities, and can be processed directly from solution. The described subject matter illustrates the molecular design of organic small molecules for device stability in ambient atmosphere and provides photovoltaics that are not only efficient but are also stable in the presence of oxygen. The

molecules include derivatized pentacenes and other extended acene systems as the p-type donor materials in bilayer device architectures. By modifying the 6 and 13 positions of pentacene molecules with aromatic substituents, typical pentacene degradation pathways that adversely affect device performance are minimized. Such derivatized pentacenes afford not only stable device operation in ambient atmosphere but can also provide, for example, energy conversion efficiencies greater than 1 %. Other embodiments illustrate larger polycyclic aromatic ring systems such as HBC, which include three fused and interpenetrating pentacene moieties. Devices that feature HBC as the donor material display unexpectedly high efficiencies in air, which is surprising given the poor overlap between the solar spectrum and the absorbance of HBC. In addition, substitution of the HBC ring system with long alkyl chains provides improved solution processability and simplified device fabrication. Therefore, HBC derivatives are suitable as donor materials in bulk heterojunction device structures. Solar cells manufactured from the materials described herein do not require encapsulation, allowing for facile device fabrication. Consequently, the described materials provide for the manufacture of photovoltaics with improved air-stability.

Some embodiments relate to photovoltaic universal joints including ball-and-socket interfaces in molecular photovoltaic cells.

Contorted hexabenzocoronene and derivatives (*contorted*-HBC) and hexa-peri-hexabenzocoronene (*flat*-HBC) were synthesized according to literature procedures (see, e.g., S. Xiao, Q. Miao, S. Sanaur, K. Pang, M. L. Steigerwald, C. Nuckolls, *Angew. Chem. Int. Ed.* 2005, 44, 7390–7394 and S. Xiao, J. Tang, T. Beetz, X. Guo, N. Tremblay, T. Siegrist, Y. Zhu, M. L. Steigerwald, C. Nuckolls, *J. Am. Chem. Soc.* 2006, 128, 10700–10702). C₆₀ (Catalog No: BU-603; CAS: 99685-96-8) and C₇₀ (Catalog No: BU-703; CAS: 115383-22-7) were obtained from BuckyUSA, Inc. Anhydrous chlorobenzene (Catalog No: 284513; CAS:108-90-7) was obtained from Sigma-Aldrich. PEDOT:PSS was obtained under the name Baytron P (Catalog No: 01016141; CAS: 7732-18-5) from H.C. Stark.

The thicknesses of all thin films were calibrated via atomic force microscopy of either a masked off edge and/or a stretched film. All thermal depositions were performed under a pressure of $\sim 1 \times 10^{-6}$ torr at an average rate of ~ 1.0 Å/sec.

Patterned indium-tin oxide glass substrates were cleaned thoroughly by sonication in acetone and isopropyl alcohol, dried under a stream of nitrogen, and UV-ozone etched for five minutes. PEDOT:PSS was spun at 5000 rpm for 60 seconds and the film was subsequently baked at 200 °C for 30-45 minutes. The unmodified *contorted*-HBC or *flat*-HBC were thermally evaporated to a thickness of 25 nm. Solution processable HBC derivatives were spincoated from a 2-4 mg/mL toluene solution at 1000 rpm. Either C₆₀ or C₇₀ was then thermally evaporated to a thickness of ~40 nm. The substrates were taken out of ultra-high vacuum (UHV) and moved to a nitrogen atmosphere where they were masked and placed under UHV again. Aluminum was deposited to a thickness of ~60 nm.

Finished devices possessed an area of 0.16 cm². They were moved to ambient atmosphere and measured with Keithley 2602/2400 sourcemeters under both dark conditions and under illumination with a solar simulated light source. Ultra-violet light emitting diodes (LEDs) were obtained from NEBO™. All illumination sources were calibrated using a silicon photodiode.

The optical power of the UV source was measured with a silicon photodiode. Light was incident on the detector, and the current induced was recorded. The area of the photodetector was 1 cm² yielding units of A/cm². The spectrum of the light source was then taken using a spectrometer and this spectrum was normalized (to set the integral to unity) and point-wise multiplied by the responsivity curve of the photodetector to compensate for nonlinearities in the current response. The resulting integration is the power conversion factor for the light source, in Watts/Amp. This value directly converts the previous photovoltaic response to the optical power of the light source.

Saturated solutions of C₆₀ and HBC in chlorobenzene were combined (5 mL each) and the resulting mixture was allowed to sit in an unsealed small vial sealed within a larger container. Long purple-gray needles (1-3 mm) formed within three weeks, with minimal evaporation of chlorobenzene (<10%).

Complex 2 crystals were grown using horizontal physical vapor transport (HPVT), as shown in Figure 11. A quartz tube was wrapped with heating coils to provide a temperature gradient. This gradient was measured prior to crystal growth (see Figure 12). The HBC and C₆₀ powders were placed 5-8 inches apart in the hottest region of the furnace. By flowing ultra-high-purity argon carrier gas through the furnace, crystals grew in the colder region of the furnace (330 °C).

Silver contacts (~100nm thickness) were deposited on crystals of complex 1 by using a thermal evaporator to form two electrodes with a 300 μ m gap between them. Steady state current was measured with a Keithley 6517A. In order to minimize transient currents, a bias voltage was applied for ten seconds before each current measurement. Sheet resistance at various temperatures was evaluated in order to extract activation energies. All measurements were performed in vacuum.

Distance measurements and images from the crystal structures of complexes 1 and 2 were generated using CrystalMaker™ 7.2 (which can be obtained from CrystalMaker Software Ltd. at <http://www.crystallmaker.com>). Close contacts were obtained by measuring the distance between two carbon nuclei on adjacent molecules. The π - π distances between HBC and C₆₀ were calculated by creating a plane between the three sp²-carbons in HBC closest to C₆₀, measuring the distance between that plane and the center of C₆₀, and then subtracting the calculated radius of that C₆₀. The radius of each C₆₀ was calculated by taking the mean distance of each carbon to the center of the molecule.

An example of a π - π distance calculation is shown in Figure 14. A plane was generated through the three carbons on HBC closest to C₆₀ (in this case it was three from the center six-membered ring on HBC). All carbons of the C₆₀ were selected and a centroid was calculated. A distance of 6.439 Å was found from that centroid to the plane, centered directly on the six-membered ring. A mean nuclear radius of that C₆₀ was generated as part of the centroid calculation output (3.5139 Å). To obtain the π - π distance (2.93 Å), the mean radius was subtracted from the center-to-plane distance (6.439 – 3.514 = 2.925). To find the π - π distance between the two C₆₀'s in complex 1, 2 mean radii (10.008 - 2 x 3.5139 = 2.98 Å) were subtracted from the distance between the two C₆₀ centroids.

Samples were prepared by cutting silicon wafers (with native oxide) to a size of approximately 1 x 1 cm. Silicon substrates were cleaned by sonication in acetone and isopropyl alcohol followed by drying in a stream of nitrogen gas. HBC was thermally evaporated to a thickness of 25 nm using the same deposition conditions as for the photovoltaic devices. Subsequently, C₆₀ layers of various thicknesses were evaporated onto the silicon substrates. All samples were made in duplicate to ensure consistency. Samples were packaged within two sealed mylar bags under a nitrogen atmosphere and then shipped to the Stanford Synchrotron Radiation Lightsource (SSRL), where the measurements were performed.

Grazing Incidence X-ray Diffraction (GIXD) measurements were performed at the Stanford Synchrotron Radiation Lightsource on beam line 11-3 at a photon energy of 12.7 keV. The incident x-ray beam, k_{in} , has a grazing incidence angle with the sample surface. A 2D MAR345 image plate detector (pixel size 0.15 mm), positioned a distance L from the sample, records the scattered beam, k_{out} . This is converted into an image of the reciprocal space (Q-space) with the scattering expressed as a function of the scattering vector $Q=k_{out}-k_{in}$. Here, the sample-to-detector distance L , calibrated with a LaB_6 polycrystalline standard, was 398.6 mm. The incidence angle was chosen as 0.1° , slightly above the critical angle for total external reflection from the organic film surface. This reduces any background scattering from the substrate and gives a large diffracting volume. The samples were kept under a helium atmosphere during measurement to minimize damage to the films from the intense x-ray beam and eliminate X-ray scattering from air. A linear background, defined by regions before and after the diffraction peaks, was subtracted from the reciprocal space map. A dark (blank) image scan was also subtracted from the measurements to help isolate weaker signals from the samples.

Samples were prepared by cutting indium tin oxide (ITO) to a size of approximately 12 mm x 5 mm. ITO substrates were cleaned by sonication in acetone and isopropyl alcohol followed by drying in a stream of nitrogen gas. Pure films of HBC and C_{60} , respectively, were thermally evaporated to a thickness of 10 nm on the ITO using the same deposition conditions as for the photovoltaic devices. To model the C_{60} -HBC interface, 2nm of C_{60} was deposited on separate 10 nm HBC films, prepared under the same conditions. All samples were made in duplicate to ensure consistency. Samples were packaged within two sealed mylar bags under a nitrogen atmosphere and transported to the Stanford Synchrotron Radiation Lightsource (SSRL), where the measurements were performed.

C 1s region XPS and XAS measurements were performed at the Stanford Synchrotron Radiation Lightsource on beam line 13-2. Beamline 13-2 has a spherical grating monochromator and an energy range of 250-1100 eV, and the focused beam has a spot size of $0.01 \times 0.075 \text{ mm}^2$. It is equipped with an elliptically polarizing undulator (EPU) that can be used in three different polarization modes: elliptical, horizontal and vertical; circular polarization was accomplished by summing spectra for elliptical polarization with opposite elliptical distortion. The BL13-2 station is designed for surface and solid state demonstrations with ultra-high vacuum

compatible samples up to 10 mm in diameter. The main chamber has an electron spectrometer (SES-R3000, VG-Scienta) for photoemission spectroscopy and X-ray absorption spectroscopy.

XAS spectra were simultaneously measured in both total (TEY) and Auger electron yield (AEY) modes. The reference absorption intensity (I_0) of the incoming x-ray beam, measured on a gold coated mesh positioned just after the refocusing optics, was measured simultaneously and used to normalize the spectra to avoid any artifacts due to beam instability. TEY was obtained by the sample drain current (sampling depth > 5nm). In AEY mode, the electron spectrometer was tuned to a kinetic energy window of 230-240 eV, which was chosen obtaining information restricted to the near-surface (~1-2 nm) region. All spectra were recorded in the photon energy range 280-310 eV with energy resolution better than 100 meV. The energy scale was calibrated using photoemission lines of a reliable peak from the second and third order diffracted photon, here the C1s of our C₆₀ reference sample. The spectra were normalized by fitting the data points before the absorption edge by a straight line taken as zero, and normalizing the maximum intensity of the s* resonance (at ~300 eV) to 1.

XPS spectra were measured with energy resolution better than 100 meV. The XPS binding energy scale spectra taken at photon energy 600 eV was shifted 2.3 eV to higher binding energy; using the calibrated shift between the monochromator at 310 eV and actual energy (determined by higher order photoemission lines of the C₆₀ C1s peak).

With regard to Figure 6, lines representing EQE-HBC/C₆₀ device and EQE-C₆₀ only device are guides to the eye. The spectra has been normalized and represents relative values. The normalized absorbance of HBC and C₆₀ thin films are also shown for comparison.

With regard to Figure 8, current vs. voltage graphs show the average device characteristics for 1) *contorted*-HBC/C₆₀ dark current and illuminated current. 2) *contorted*-HBC/C₇₀ dark current and illuminated current. 3) *flat*-HBC/C₆₀ dark current and illuminated current.

Figure 9 illustrates (A) C 1s region XPS measured at photon energy 600 eV for: C₆₀(10nm)/ITO, HBC (10nm)/ITO, and C₆₀(2nm)/HBC(10nm)/ITO; and (B) depicts polarization dependent XAS of HBC(10nm)/ITO, C₆₀(10nm)/ITO, and C₆₀(2nm)/HBC(10nm)/ITO measured in Total Electron Yield (TEY) mode. The

surface-sensitive Auger Electron Yield (AEY) XAS of C₆₀(2nm)/HBC(10nm)/ITO is also shown. A schematic of the C₆₀-HBC bilayer interface is inset.

Figure 13 shows the temperature (in degrees Celsius) of the gradient in the quartz tube plotted as a function of displacement along tube (in inches).

5 Some embodiments include the hierarchical assembly of nanostructured organic heterojunctions for photovoltaic devices.

The bulk heterojunction (BHJ) active layer architecture can be used in efficient organic photovoltaics (OPVs). In some embodiments, this type of structure includes an interpenetrating network of p-type semiconducting molecules as the
10 electron donors and n-type semiconducting molecules as the electron acceptors.

The resulting device possesses an extensive interface for separation of photogenerated excitons, thereby yielding higher efficiencies. However, controlling the formation and size of the donor and acceptor domains within the BHJ can increase device performance.

15 In some embodiments, an exemplary class of DBTTC molecules, shown in Figure 15A, can be used to control the formation and size of the donor and acceptor domains within the BHJ. These molecules have been designed for hierarchical self-assembly at the molecular level and stack into columnar superstructures that in turn form a supramolecular network of cables on ITO and
20 ITO/PEDOT:PSS. This network functions as a scaffold for the molecular recognition and directed assembly of C₆₀. The templated growth of the C₆₀ film creates a nanostructured p-n heterojunction as depicted in the embodiment of Figure 1B, which enables more efficient conversion of sunlight into electricity.

According to one aspect of the invention, the following description
25 includes an exemplary design, synthesis, and structure of DBTTC exemplary molecules including contorted HBCs, which are members of a class of polycyclic aromatic molecules. They include three fused interpenetrating pentacene subunits that form a doubly concave shape due to steric interactions at the periphery of the molecule. These molecules form columnar nanostructures in self-assembled
30 monolayers, cables, and liquid crystalline phases, with concomitant field effect mobilities of up to ~1 cm²/V·s. Since such structured HBC films have also demonstrated one-dimensional photoconductivity, they can be suitable for organic photovoltaics. Contorted HBCs can form a shape-complementary complex with the

n-type acceptors, such as C₆₀ and C₇₀, yielding an intimate, self-assembled donor/acceptor interface.

Some embodiments include a prepared class of contorted structures that have four of their benzo rings exchanged for fused thienyl rings. The unsubstituted DBTTC **1A** and the hexyl-substituted DBTTC **1B** were prepared through the high yield (> 90%) procedure illustrated in Figure 20, which proceeds in three robust steps and utilizes commercially available reagents. The 1,1,8,8-tetrabromobisolefin were coupled to the appropriate thienyl boronic esters with Suzuki-Miyaura reaction conditions to yield the bis-tetrasubstituted olefins. The synthesis was then completed with a Katz-modified Mallory photocyclization.

To elucidate the molecular conformation of DBTTC and its structure in the solid state, crystals of **1B** were grown from dichloromethane/hexanes. Figure 16 depicts several of the molecules from this structure. The DBTTC is made up of two anthradithiophene units fused with a central pentacene moiety. In Figure 16A, the core of the molecule stacks into a columnar arrangement along the [100] axis within the crystal. The DBTTC molecules also have intimate nearest neighbor contacts with *intermolecular* carbon-to-carbon distances that are as small as ~3.4 Å and sulfur-to-carbon distances that are as small as ~3.6 Å. While not being bound by any particular theory, it is believed that the fused thiophene units likely facilitate such intimate π - π stacking interactions.

The sterically smaller thiophenes on the periphery of DBTTC can reduce the congestion between adjacent aromatic rings as compared to HBC. One consequence of the alleviated congestion around the exterior is the “flattening” of **1B** relative to the contorted HBC. A second consequence is the existence of two distinct polymorphs of **1B** within the crystal. In one conformation (Figure 16B), the three intersecting subunits of the DBTTC adopt a motif that is similar to the previously reported HBC derivatives. In the other conformation (Figure 16C), the molecule resembles a butterfly with the pentacene subunit forming the body and the anthradithiophene subunits forming the wings.

Some embodiments illustrate the electrochemistry and spectroscopy of DBTTC. The electrochemical and spectroscopic properties of DBTTC can provide insight into its potential as a p-type donor molecule. A solution-phase cyclic voltammogram of **1B** provides three oxidative waves at potentials of 1.1 V, 1.5 V, and

1.6 V, as well as a single reductive wave at -1.7 V. The cathodic to anodic peak ratios indicate that all three oxidative waves are quasi-reversible (the reductive wave is irreversible), so **1B** is electrochemically stable in several oxidation states. These measurements enable the energy of the highest occupied molecular orbital (HOMO) to be estimated as 5.1 eV below vacuum, the energy of the lowest unoccupied molecular orbitals (LUMO) to be estimated as 2.3 eV below vacuum, and the bandgap to be estimated as 2.8 eV. In its totality, the cyclic voltammetry indicates the potential of DBTTC as an electron donor in a photovoltaic device.

The solution and thin-film UV-visible absorbance spectra of **1B** are also provided. In solution, there are two strong absorptions at 355 nm and 372 nm, as well as corresponding shoulders at 343 nm and 395 nm, respectively, which have been previously assigned to the dominant "radialene" resonance structure of the six-benzene coronene core. A set of weaker absorptions between 400 and 490 nm can be associated with the radialene π - π^* triplet states. A corresponding thin film absorbance spectrum is broadened and generally red-shifted with a main peak at ~ 370 nm but few other apparent features. This type of spectrum is a hallmark of π - π stacking and strong intermolecular interactions among the DBTTC chromophores.

Some embodiments of the disclosed subject matter relate to DBTTC nanostructure formation on ITO.

Inspired by the crystal structure in Figure 16 and the red-shifted thin-film absorbance, films of **1B** were characterized. Solution-processed, annealed films of **1B** were examined on ITO with Atomic Force Microscopy (AFM) in non-contact mode (Figure 17A). It was found that films from **1B** were not uniform, but instead included a network of "cables." These cables are highly anisotropic: the length was on the order of ten microns, the width was on the order of a micron, and the height was on the order of a hundred nanometers. This network covered the entire substrate and appeared three dimensional, with the cables protruding from the surface.

The orientation of **1B** was determined on ITO with Near Edge X-Ray Absorption Fine Structure (NEXAFS). Films from **1B** display a pronounced angular-dependence of the intensity of the π^* resonance in the NEXAFS spectrum (Figure 17B). This resonance is strongest near normal incidence, when the electric field is parallel to the substrate. The π^* orbitals of **1B** are therefore preferentially oriented in the plane of the substrate, with a high degree of edge-on orientation, which is

consistent with alignment of the molecular columns along the long axis of the cables. From NEXAFS, the average molecular tilt angle of $\sim 64^\circ$ with respect to the substrate for **1B**.

The crystallinity of the DBTTC films with Grazing Incidence X-Ray Diffraction (GIXD) is illustrated. Figure 17C shows the GIXD data for **1B** on bare ITO, overlaid with the simulated DBTTC powder diffraction pattern. The 2-D images reveal that the diffraction intensity is confined to the lateral (Q_x or in-plane) and vertical (Q_z or out-of-plane) reflections, respectively. The Q_z pattern is dominated by intensity from the [1-10] reflection ($Q = 0.365 \text{ \AA}^{-1}$) and a peak corresponding to diffraction from the [100] plane is also present ($Q = 0.334 \text{ \AA}^{-1}$), albeit with weaker intensity. However, the intensity ratio of these peaks is inverted in Q_x , where the [100] and [001] reflections dominate the in-plane diffraction intensity, while the [1-10] reflection has relatively weak intensity. In addition, the [001], [1-10], and [10-1] reflections, which all contribute to the signal along Q_x , are absent from Q_z . These GIXD observations, in concert with the NEXAFS and AFM data, support the presence of a three-dimensional and crystalline network of cables from **1B**.

Some embodiments provide controlled growth of DBTTC nanostructures on ITO/PEDOT:PSS.

Three-dimensional cable networks can also be formed on PEDOT:PSS coated ITO, which is commonly utilized for OPVs. GIXD, AFM, and NEXAFS measurements all indicated that the cables formed on PEDOT:PSS covered the entire surface and were very similar to those on bare ITO. Therefore, coarse control was gained over the size and density of the fibers on the technologically relevant PEDOT:PSS surface.

It was found that controlled heating was helpful for the growth of an aligned cable network. Figure 18 shows non-contact mode AFM images of films from **1B** on PEDOT:PSS coated ITO substrates with and without annealing. Unannealed films are morphologically flat with an rms roughness of $\sim 1 \text{ nm}$ (Figure 18A). Films annealed at 100°C feature some isolated cable-like structures but otherwise also display a flat morphology (Figure 18B). However, films annealed at 150°C feature a nearly ideal network of anisotropic cables. Notably, the cables in Figure 18 are smaller than those on bare ITO, with widths of hundreds of nanometers and heights of ~ 10 to $\sim 30 \text{ nm}$. This observation is further supported by the GIXD

measurements, in which the broadening of the peaks on PEDOT:PSS indicates smaller crystalline domain sizes relative to bare ITO. The size and alignment of the cables in Figure 18C is therefore effective for the formation of an ordered heterojunction, as depicted in Figure 16B. The corresponding cross sectional profiles
5 in Figure 18 are shown for each image.

Some embodiments of the disclosed subject matter relate to the construction of photovoltaic devices from the DBTTC network.

To complete the active layer for a photovoltaic device, an electron acceptor (C_{60}) was thermally evaporated onto the supramolecular, three-dimensional network formed from **1B**. The DBTTC network templates the growth and self-
10 assembly of the buckminsterfullerene, which completely covers the surface of the fibers. The C_{60} also fills in the gaps between the fibers, thereby yielding mixed films that are smooth and homogeneous, relative to the pristine nanostructures of Figure 18C.

15 An exemplary structure of a completed photovoltaic device with an aluminum cathode is illustrated in Figure 19A, with the energy band diagram depicted in Figure 19B. The corresponding typical J-V characteristics exhibit nearly ideal diode behavior (Figure 19C). A short circuit current density J_{sc} of 13.1 mA/cm^2 , open circuit voltage V_{oc} of 0.50 V, and fill factor FF of 0.46 yield a champion power
20 conversion efficiency of 3.0 %. These values are fully consistent with the corresponding EQE spectrum, which resembles both the HBC and C_{60} thin-film spectra and reaches values of $\sim 60 \%$ to $\sim 80 \%$ over the wavelength range between 350 nm and 550 nm. Notably, this power conversion efficiency is close to the state-of-the art for BHJ organic photovoltaics from small molecules.

25 To assess the importance of the nanostructured morphology, devices were fabricated with unannealed and thermally deposited donor layers from **1B**. These donor layers are flat and can therefore model a planar donor/acceptor interface in a bilayer OPV. Such a device architecture possesses a reduced interfacial area relative to a nanostructured device and a concomitant lower power conversion
30 efficiency. Efficiencies of $>1\%$ for the bilayer devices were found, representing a >3 -fold reduction from the values reported above. This observation emphasizes the crucial role of the nanostructured donor morphology.

BHJs can be developed from small molecules as the p-type donor material, with reported peak efficiencies of $\sim 4 \%$. Indeed, solution-processable small

molecules have demonstrated several advantages over their polymeric counterparts. They can often be easily synthesized and purified, thereby sidestepping device reproducibility problems associated with broad polymeric molecular weight distributions, batch to batch polymer variability, and contamination with reaction side products. Furthermore, small molecules typically possess high carrier mobilities due to their propensity for organization into highly ordered, crystalline domains. All of these features make small molecules highly attractive targets.

The described subject matter includes the electronic and self-assembly properties of small molecules for OPVs. DBTTC yields a donor layer that is made up of a supramolecularly assembled three-dimensional network of one-dimensional cables. This network possesses a large effective interfacial surface area, thereby serving as an effective scaffold for the templated self-assembly of C₆₀ molecules. The resulting active layer can be free of, or at least relatively free of, the bottlenecks and dead-ends that can accompany thermodynamically formed BHJs, for example small regions of donor material embedded in a larger regions of acceptor material, thereby enabling efficient transport of charge to the anode and cathode along both the DBTTC nanostructures and the templated C₆₀ overlayer. Consequently, this morphology represents a quality nanostructured BHJ, thereby yielding high power conversion efficiencies of ~ 3 %. Indeed, a clear and general path toward even higher power conversion efficiencies can be demonstrated via improved control over the size and topology of the DBTTC nanostructures.

The foregoing merely illustrates the principles of the disclosed subject matter. Various modifications and alterations to the described embodiments will be apparent to those skilled in the art in view of the teachings herein. It will thus be appreciated that those skilled in the art will be able to devise numerous techniques which, although not explicitly described herein, embody the principles of the disclosed subject matter and are thus within the spirit and scope thereof.

CLAIMS

1. An apparatus for converting light energy to electrical energy comprising one or more organic photovoltaic devices, the one or more photovoltaic devices comprising:
 - 5 a cathode in electrical contact with the apparatus;
 - an anode in electrical contact with the apparatus;
 - an acceptor layer comprising molecules forming a supramolecular network on a substrate; and
 - 10 a donor layer comprising fullerene molecules bonded onto the supramolecular network.
2. The apparatus of claim 1, wherein the fullerene molecules are selected from the group consisting of C60 and C70.
3. The apparatus of claim 1, wherein the molecules forming supramolecular networks on the substrate are selected from dibenzotetrathienocoronene molecules and contorted hexabenzocoronones.
 - 15
4. The apparatus of claim 1, wherein the bonding includes thermal evaporation.
5. The apparatus of claim 1, wherein the substrate is selected from ITO and ITO/PEDOT:PSS.
6. The apparatus of claim 1, wherein the dibenzotetrathienocoronene molecules form anisotropic cables.
 - 20
7. The apparatus of claim 1, wherein the power conversion efficiency of the one or more organic photovoltaic devices is greater than or equal to 3.0%.
8. An organic photovoltaic device, comprising:
 - a cathode;
 - 25 an anode;

an acceptor layer comprising molecules forming a supramolecular network on a substrate; and

a donor layer comprising fullerene molecules bonded onto the supramolecular network.

- 5 9. The apparatus of claim 8, wherein the fullerene molecules are selected C60 and C70.
10. The apparatus of claim 8, wherein the molecules forming supramolecular networks on the substrate are selected from dibenzotetrathienocoronene molecules and contorted hexabenzocoronones.
- 10 11. The apparatus of claim 8, wherein the bonding includes thermal evaporation.
12. The apparatus of claim 8, wherein the substrate is selected from ITO and ITO/PEDOT:PSS.
13. The apparatus of claim 8, wherein the dibenzotetrathienocoronene molecules form anisotropic cables.
- 15 14. The apparatus of claim 8, wherein the power conversion efficiency of the one or more organic photovoltaic devices is greater than or equal to 3.0%.
15. A method for generating an organic photovoltaic device, comprising:
- forming an anode layer of molecules arranged as a supramolecular network on a substrate;
- 20 thermally evaporating a donor layer of fullerene molecules on the anode layer; and
- electrically connecting an anode and cathode to the assembly of the anode and donor layers.
16. The apparatus of claim 15, wherein the fullerene molecules are selected from C60 and C70.
- 25

17. The apparatus of claim 15, wherein the molecules forming supramolecular networks on the substrate are selected from dibenzotetrathienocoronene molecules and contorted hexabenzocoronones.
18. The apparatus of claim 15, wherein the bonding includes thermal evaporation.
- 5 19. The apparatus of claim 15, wherein the substrate is selected from ITO and ITO/PEDOT:PSS.
20. The apparatus of claim 15, wherein the dibenzotetrathienocoronene molecules form anisotropic cables.
21. The apparatus of claim 15, wherein the power conversion efficiency of the
10 organic photovoltaic device is greater than or equal to 3.0%.

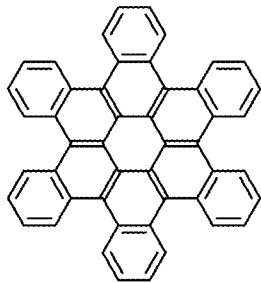


FIG. 1B

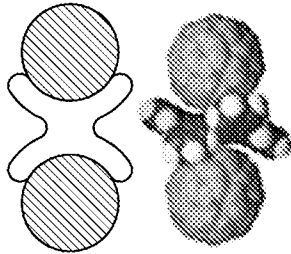


FIG. 1C

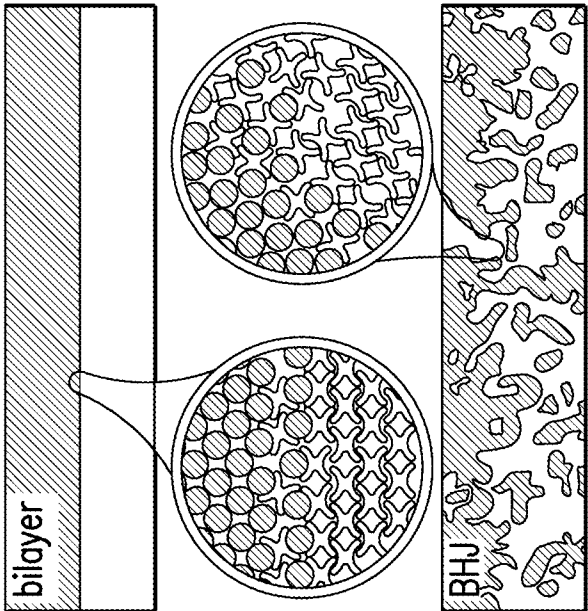


FIG. 1A

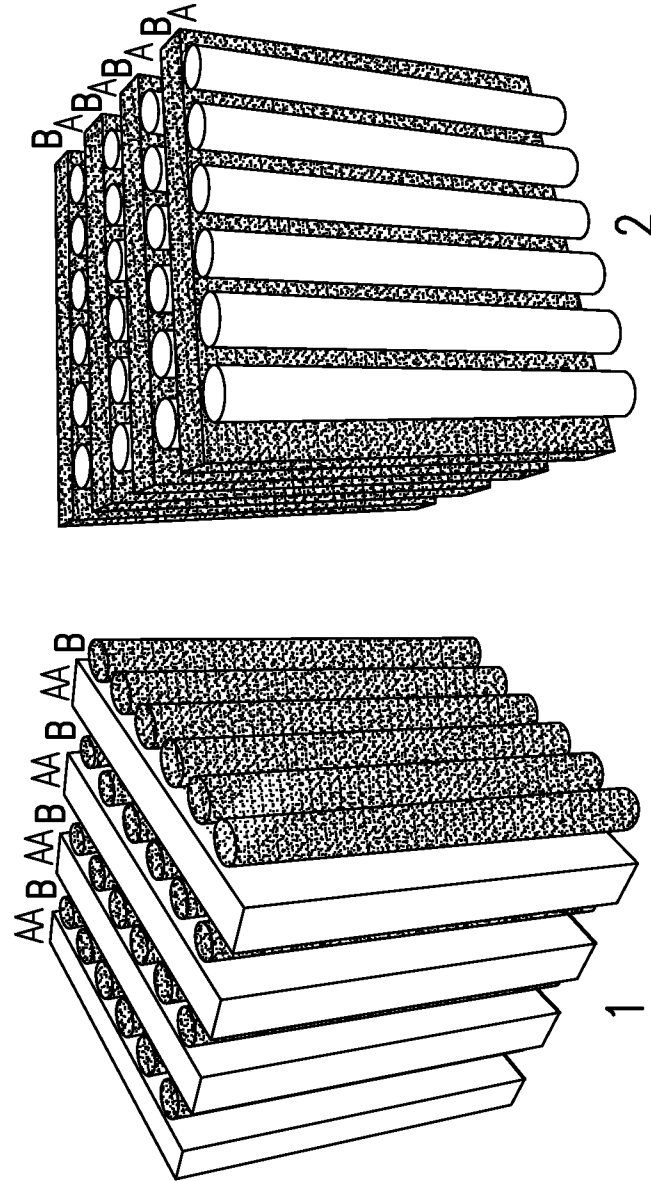


FIG. 2A

FIG. 2B

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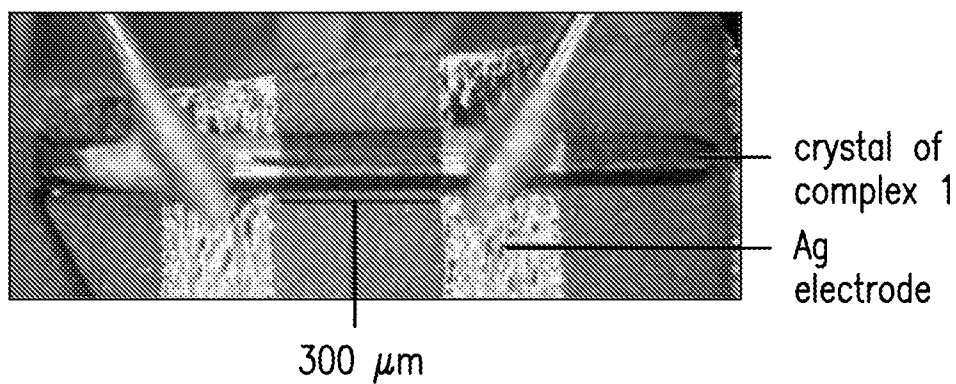


FIG. 3A

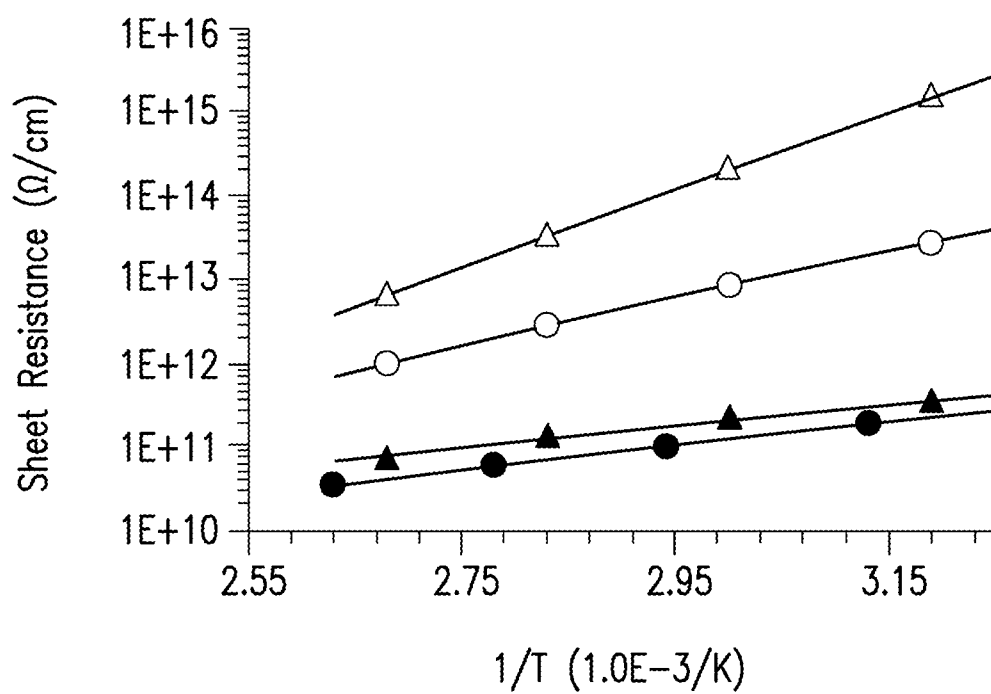


FIG. 3B

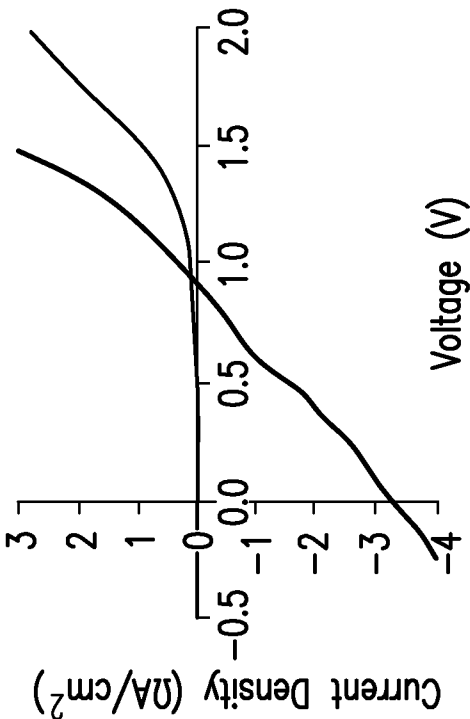


FIG. 4B

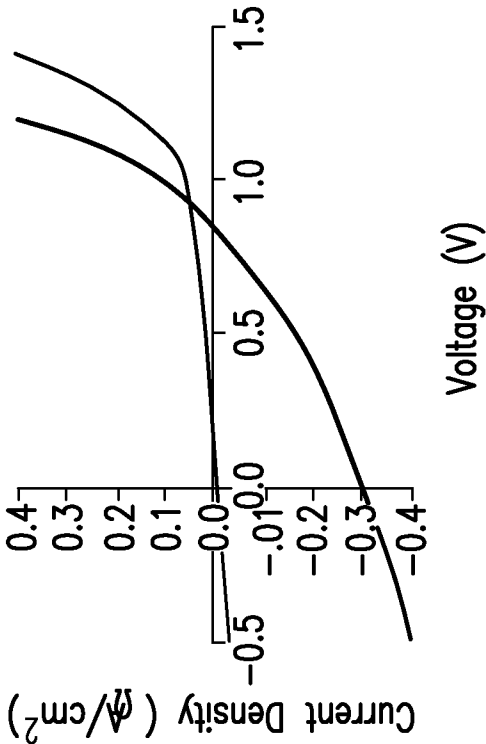


FIG. 4D

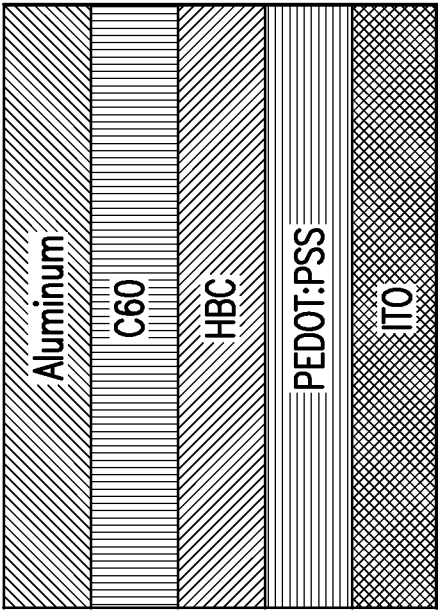


FIG. 4A

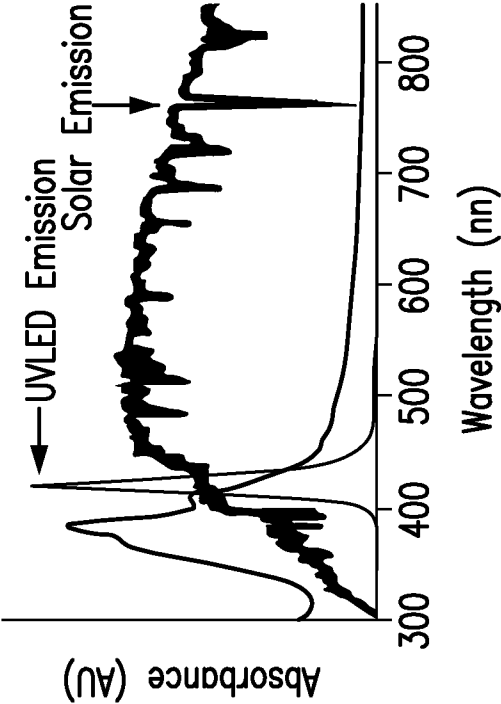


FIG. 4C

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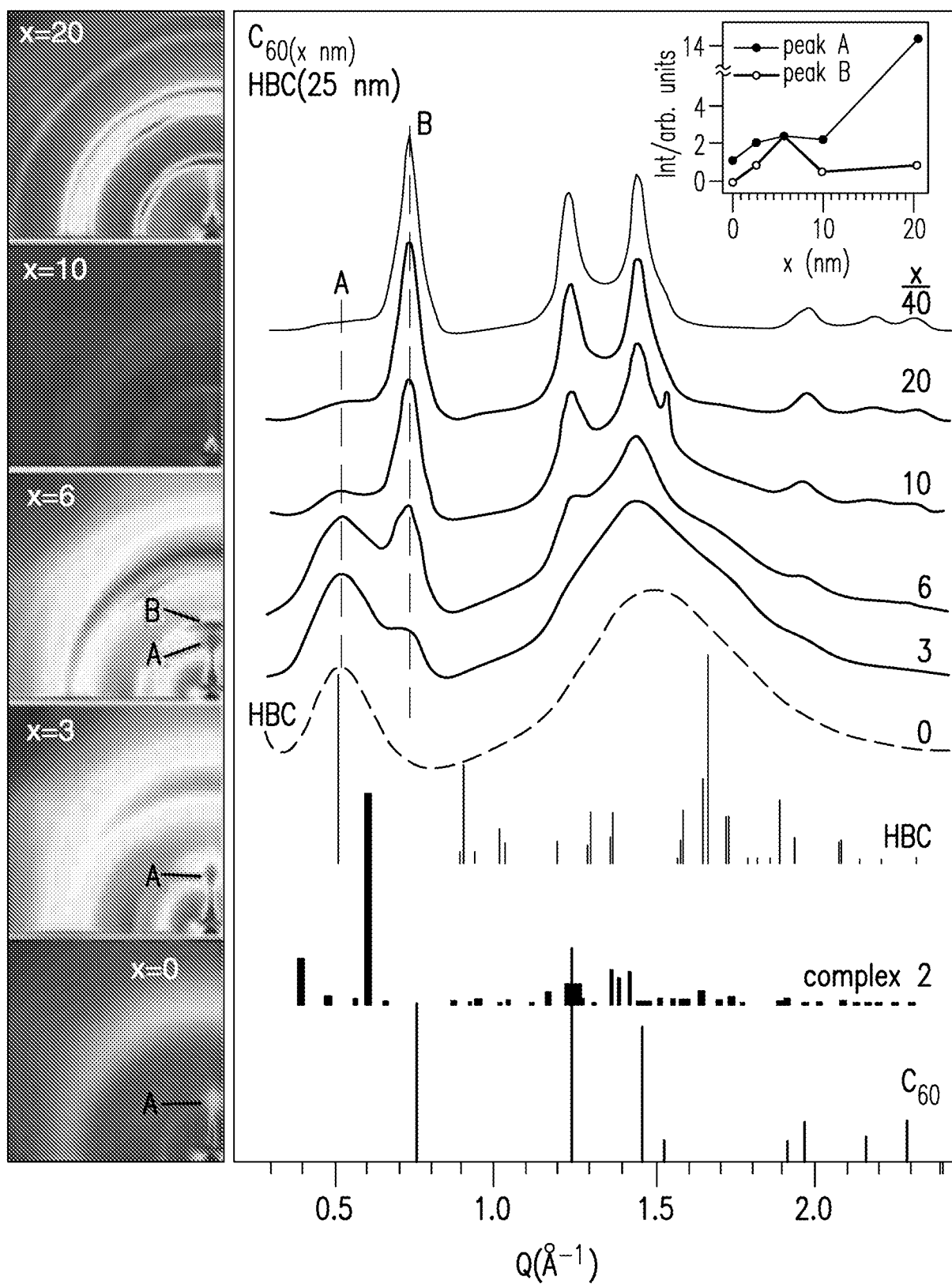


FIG. 5

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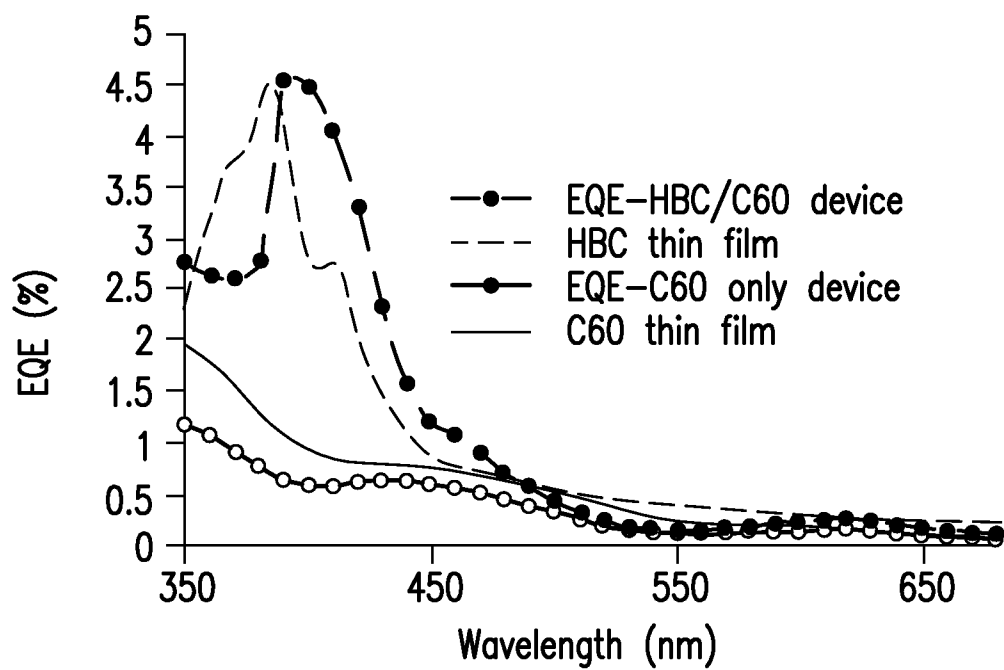


FIG. 6

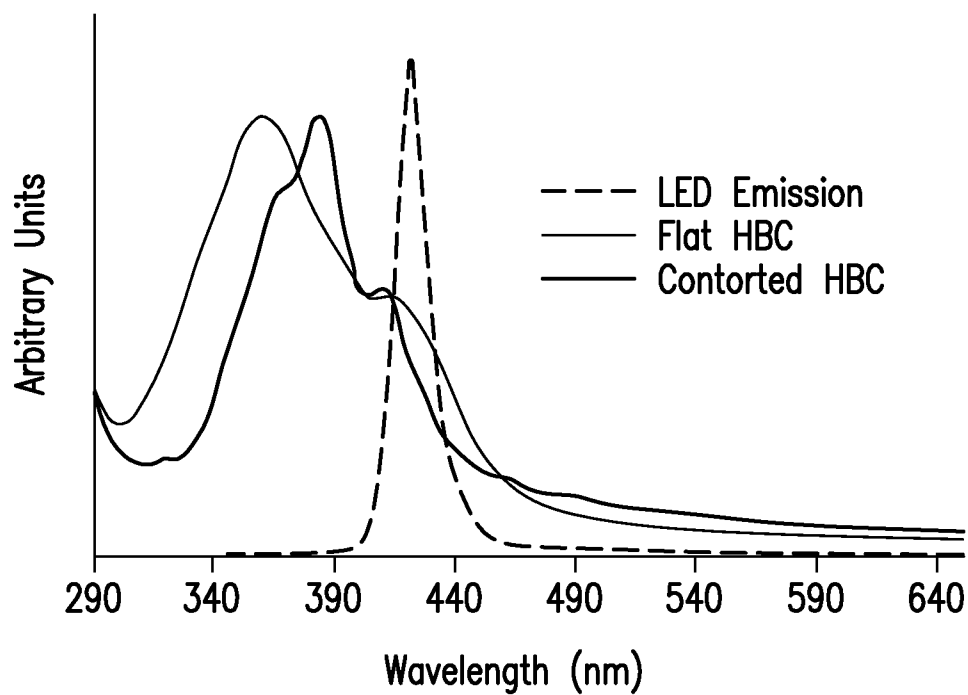


FIG. 7

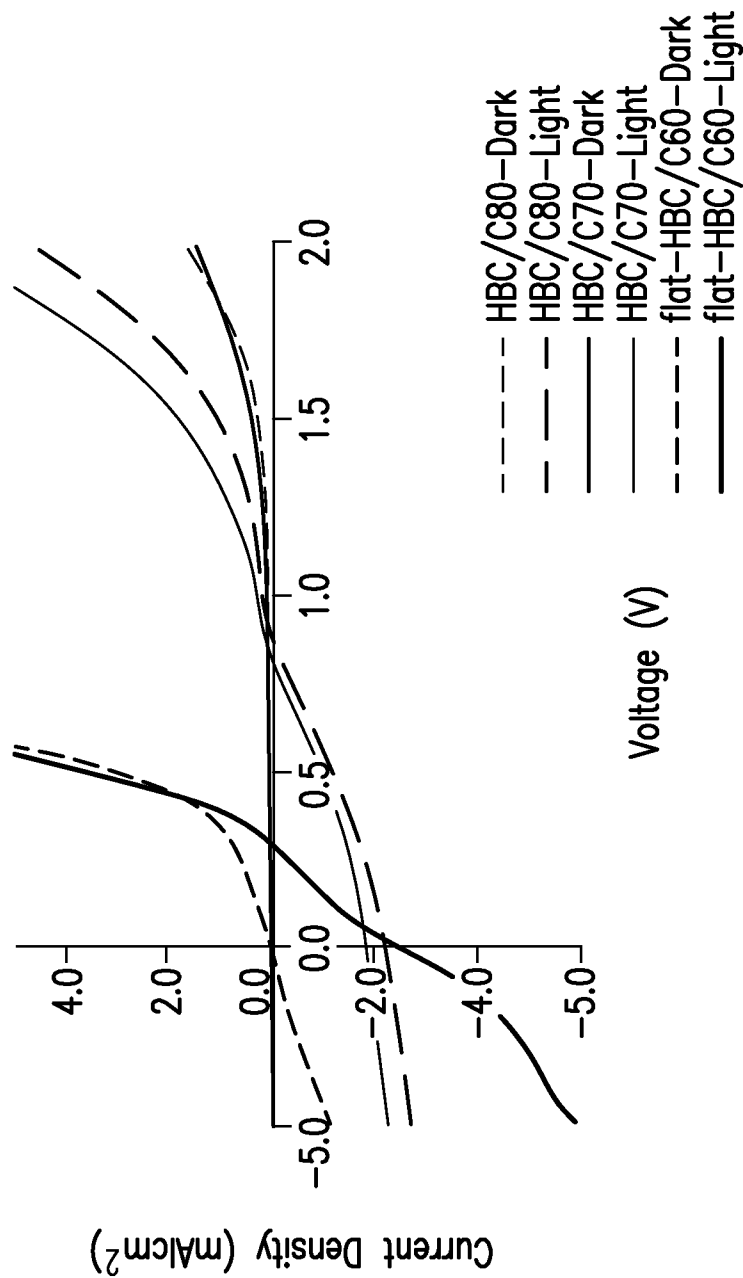


FIG. 8

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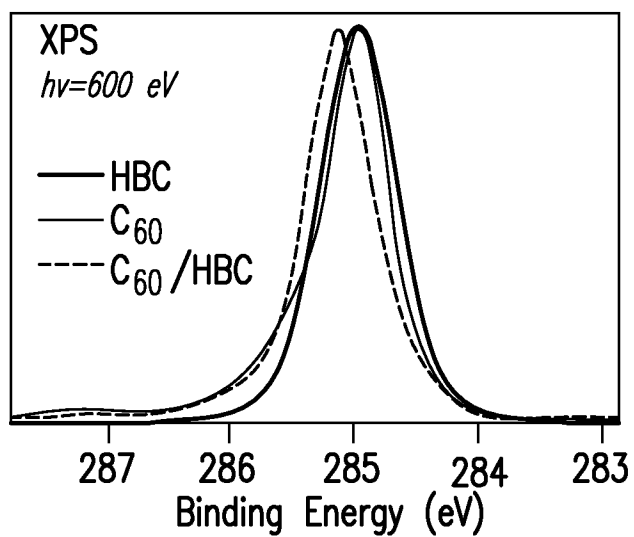


FIG. 9A

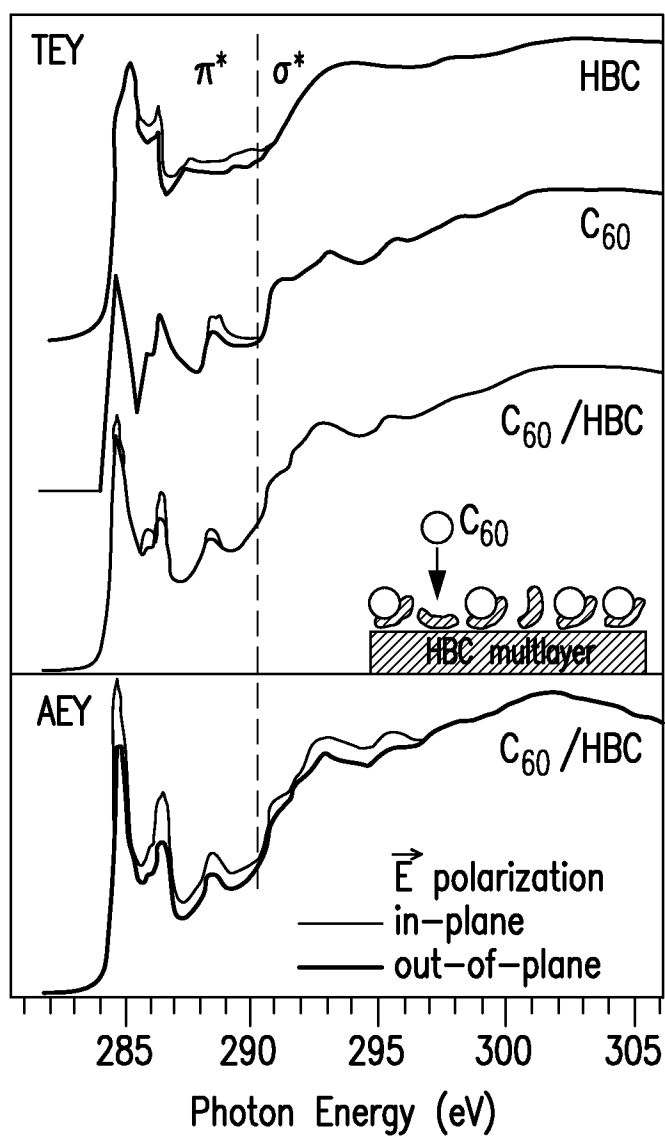


FIG. 9B

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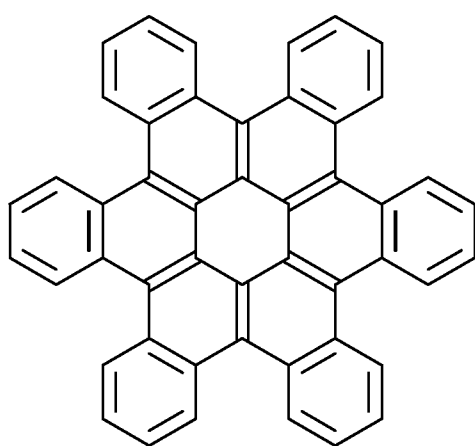
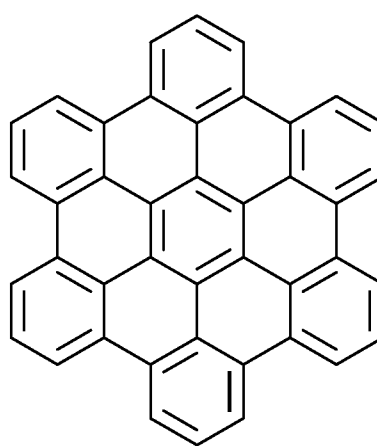
*contorted-HBC**flat-HBC*

FIG.10

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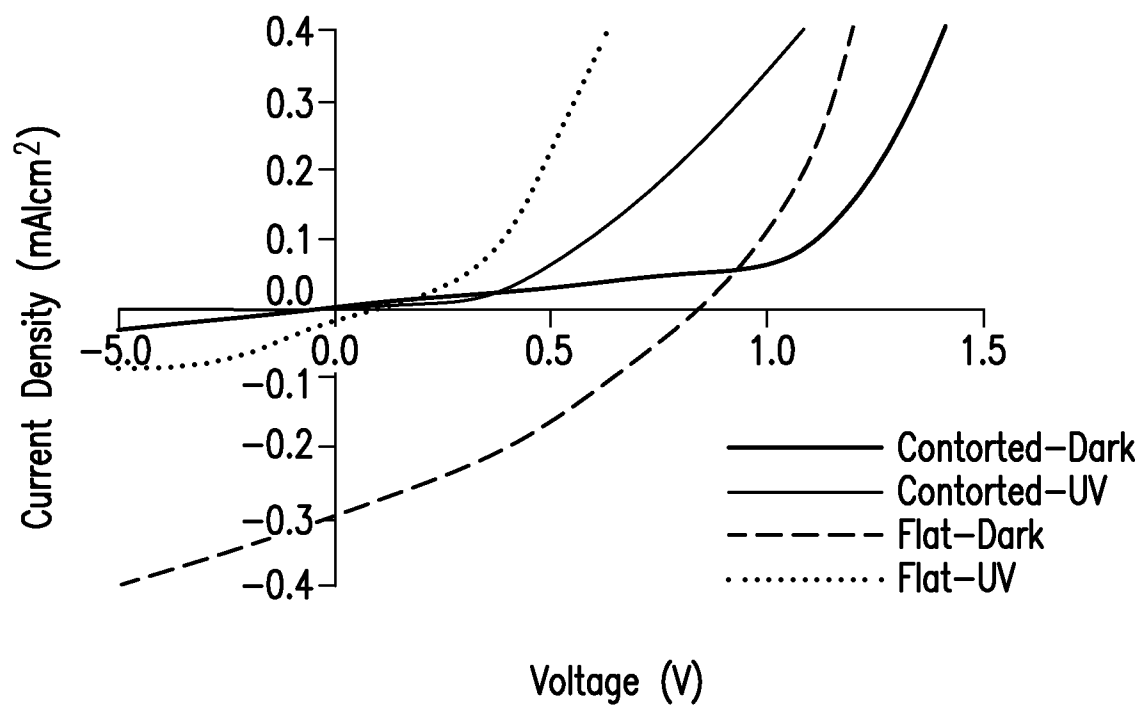


FIG. 11

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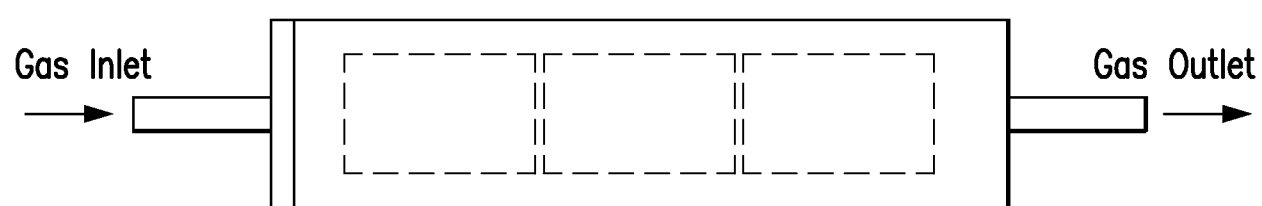


FIG. 12

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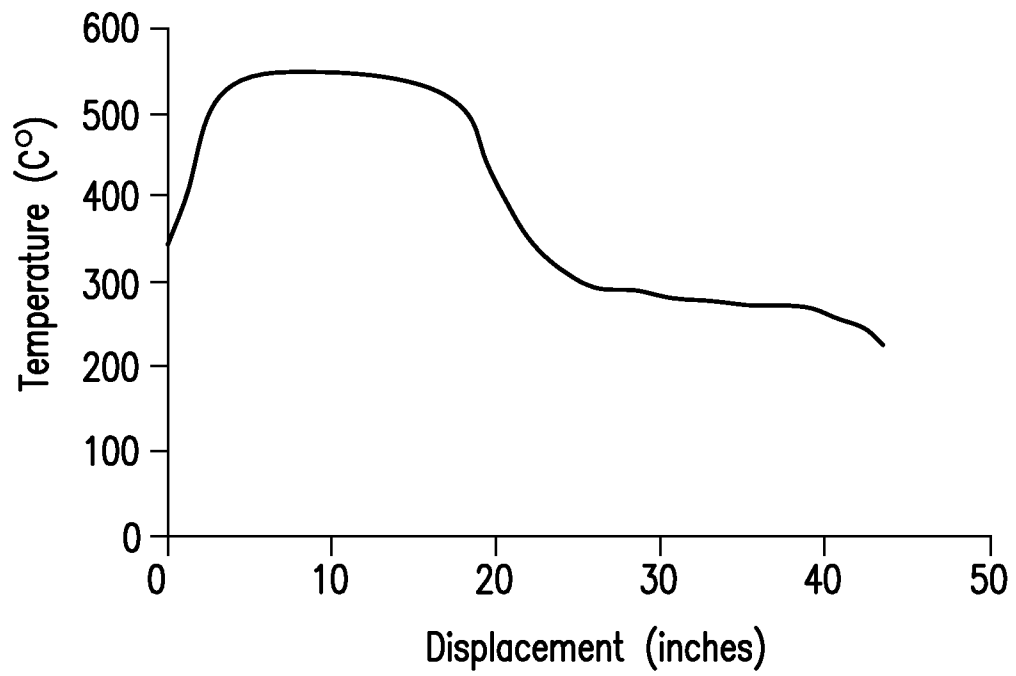


FIG. 13

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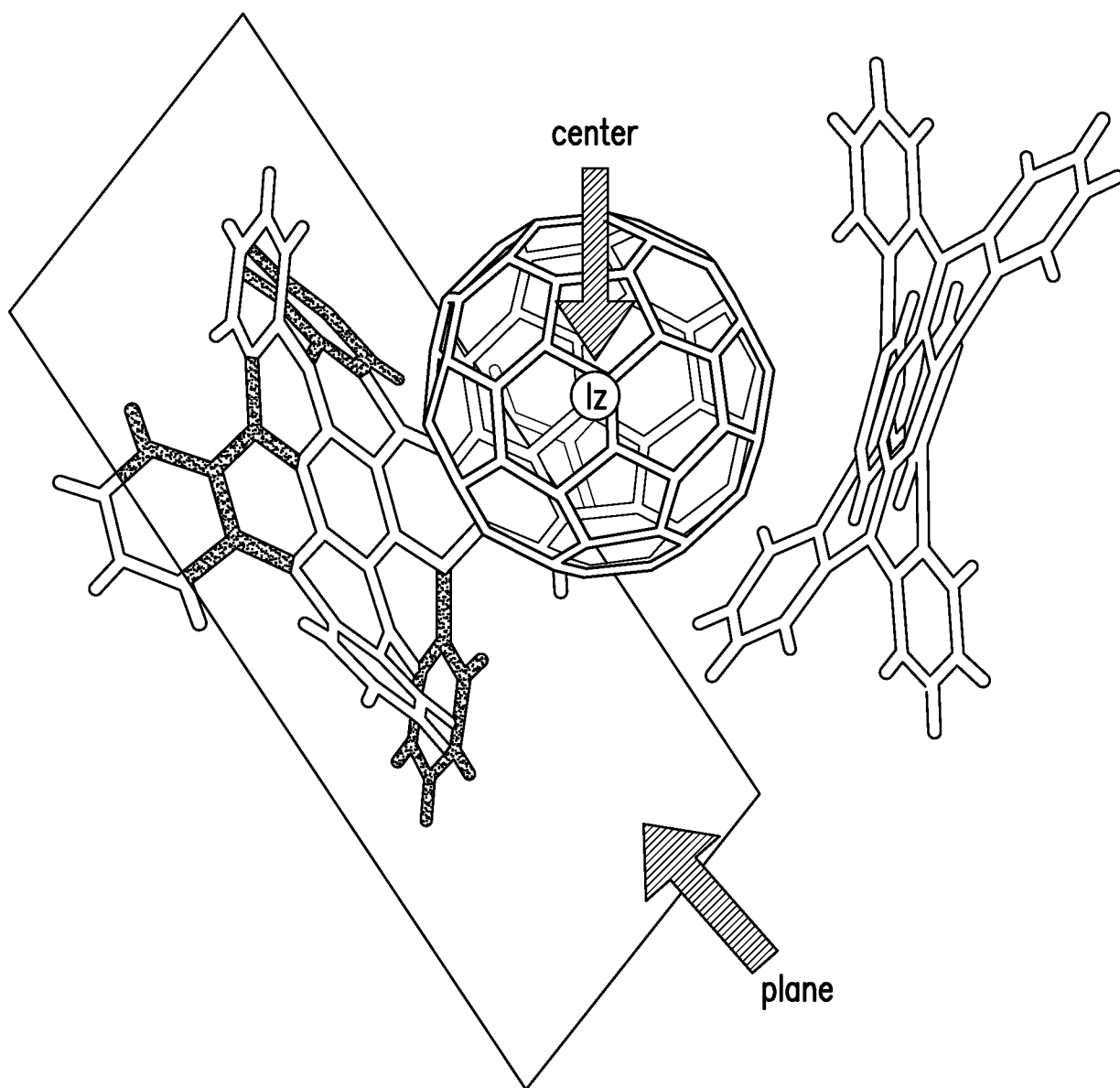
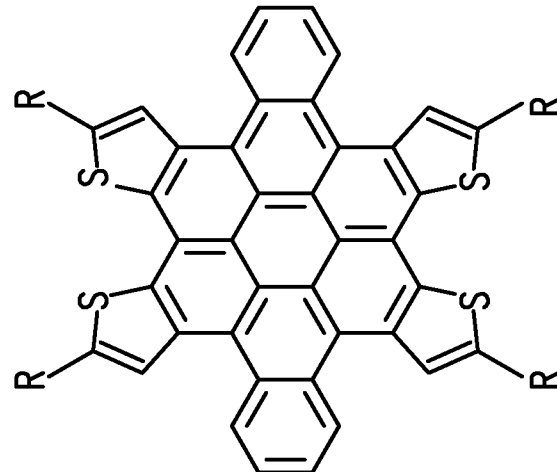


FIG. 14



1A: R=H
1B: R=C₆H₁₃

FIG. 15A

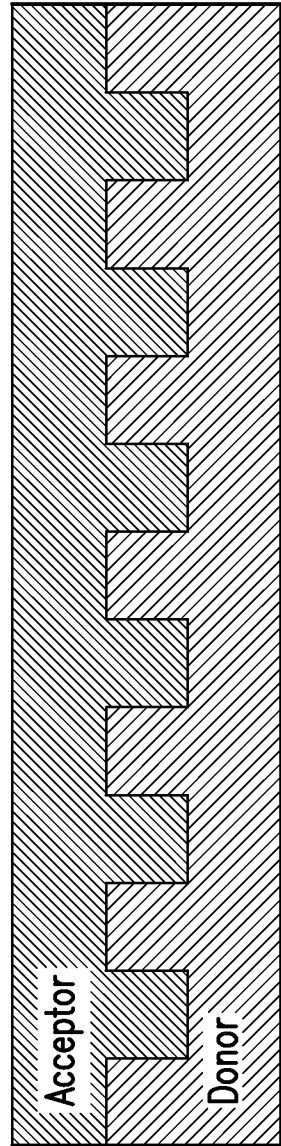


FIG. 15B

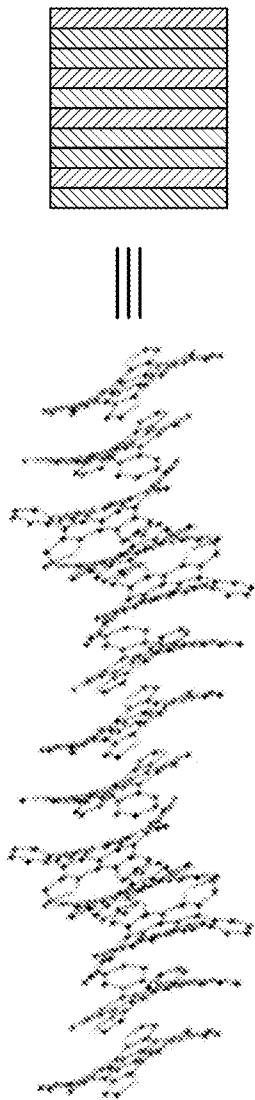


FIG. 16A

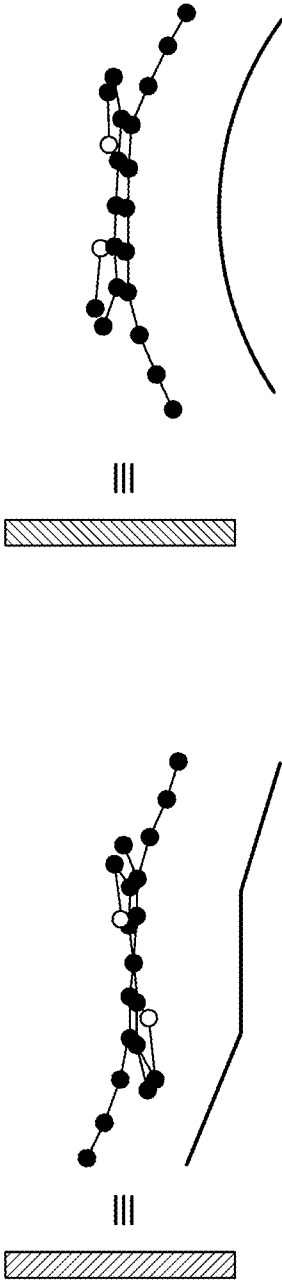


FIG. 16B

FIG. 16C

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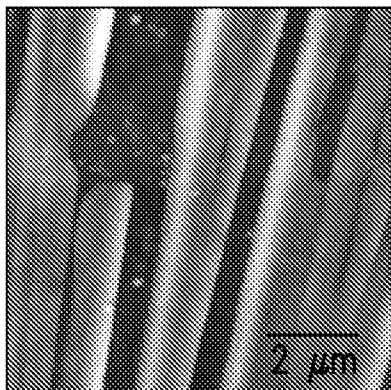


FIG. 17A

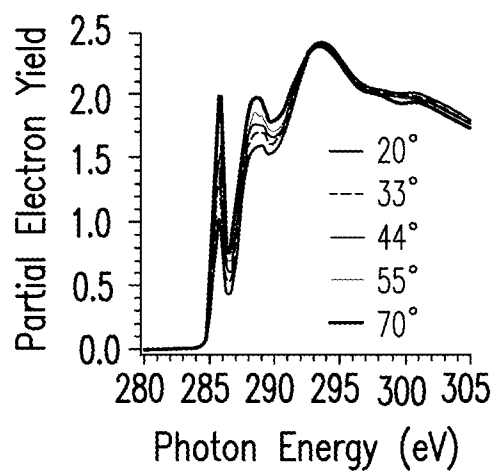


FIG. 17B

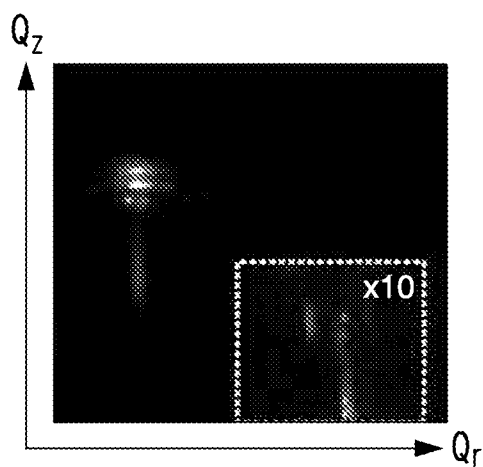


FIG. 17C

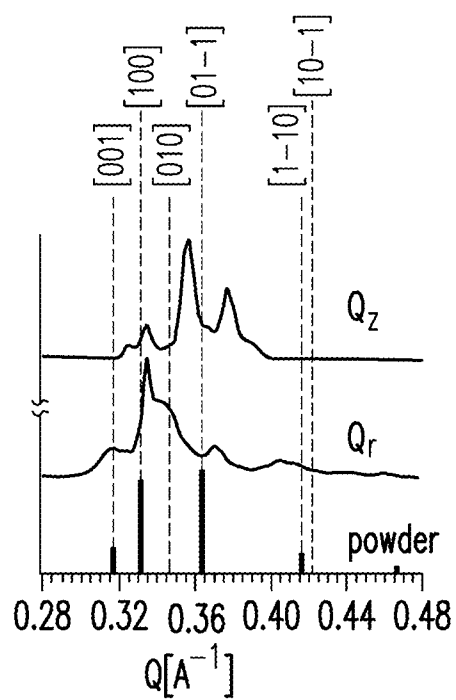


FIG. 17D

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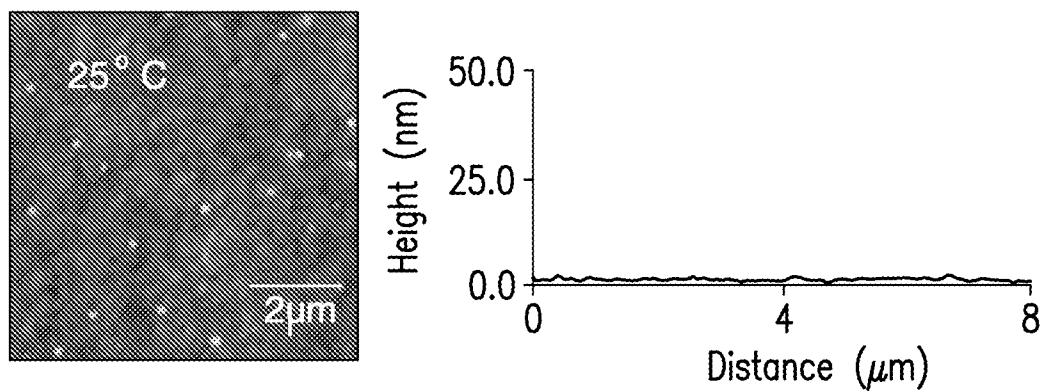


FIG. 18A

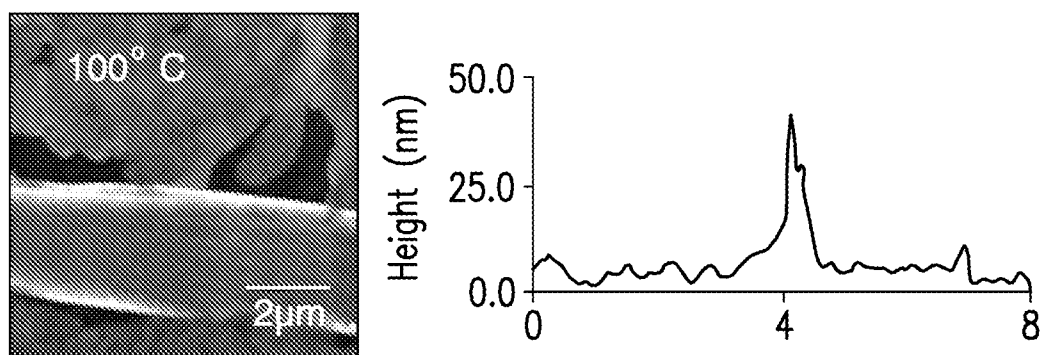


FIG. 18B

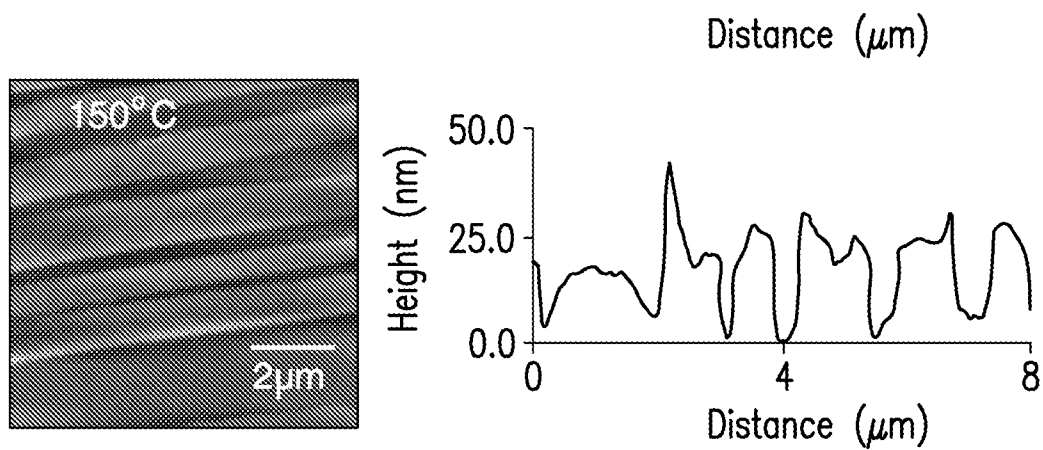


FIG. 18C

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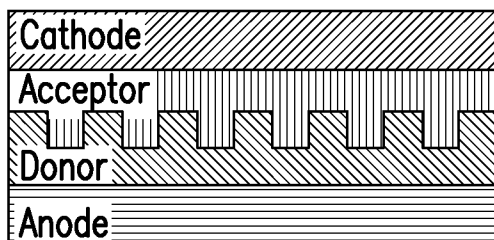


FIG. 19A

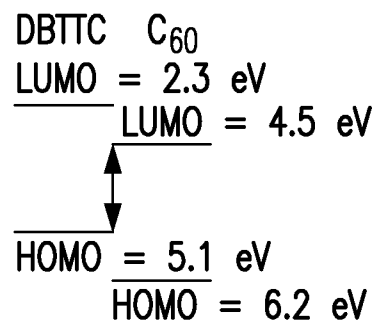


FIG. 19B

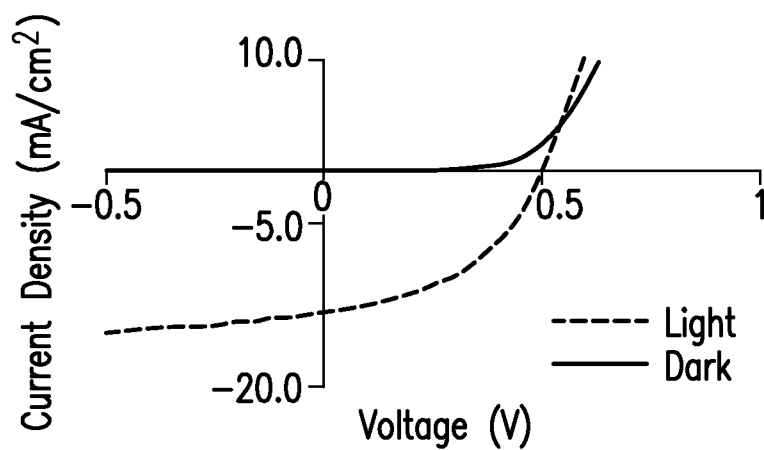


FIG. 19C

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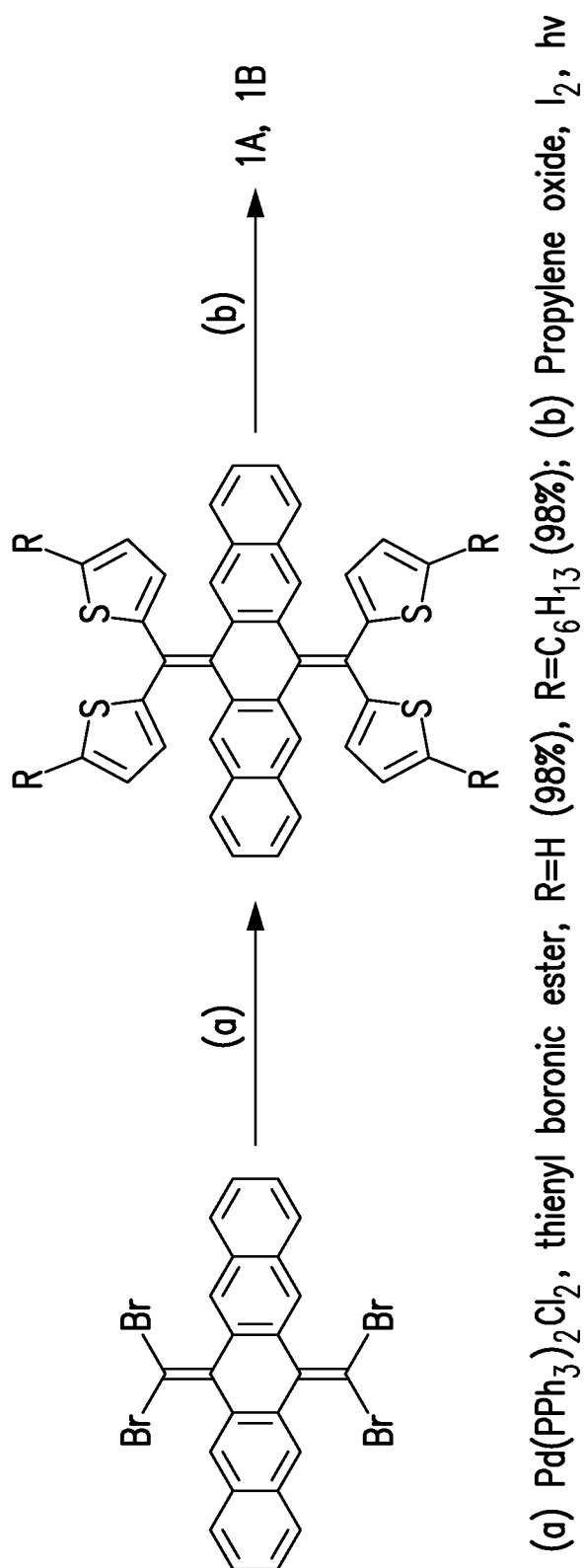


FIG. 20

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 10/58698

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - H01L 31/00 (2011.01)

USPC - 136/263; 252/500; 977/734

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: H01L 31/00 (2011.01)

USPC: 136/263; 252/500; 977/734

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

USPC: 136/260; 257/E31.003 (Keyword limited; search terms below)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PubWEST(PGPB, USPT, JPAB, EPAB); Google Scholar; Google Patents

Search terms: photovoltaic organic fullerene\$2 ITO PEDOT PSS hexabenzocoronene\$4 anode cathode donor acceptor layer\$2 electric\$5 and substrate\$2 efficiency thermal evaporation nanostructur\$3 anisotropic cable\$2

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2008/0223445 A1 (Marks et al.) 18 September 2008 (18.09.2008), especially, para [0003], [0011], [0013], [0018], [0024], [0049], [0053], [0071]	1-21
Y	US 2007/0095391 A1 (Sun) 03 May 2007 (03.05.2007), especially, para [0022], [0055]	1-21
Y	US 2007/0292601 A1 (Nuckolls et al.) 20 December 2007 (20.12.2007), especially, para [0014]	3, 10, 17
Y	US 2007/0184574 A1 (Ohno et al.) 09 August 2007 (09.08.2007), especially, para [0004], [0051], [0192]	6, 13, 20
Y	US 2009/0061721 A1 (Isa) 05 March 2009 (05.03.2009), especially, para [0088], [0147]	6, 13, 20

☐ Further documents are listed in the continuation of Box C.


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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

17 January 2011 (17.01.2011)

Date of mailing of the international search report

07 FEB 2011

Name and mailing address of the ISA/US

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