Plastic Solar Cells: A Multidisciplinary Field To Construct Chemical Concepts from Current Research

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An important role of a chemical educator is to emphasize the relevance of chemistry and stimulate students who may have not found sciences interesting or pertinent. As many students show increasing interest in global climate change, sustainability, and the development of renewable energy sources, the field of solar cells offers an area where students may be motivated to learn the chemistry. To stress the importance of solar cells in today's society, it must be pointed out that every minute the sun delivers more energy to the surface of the earth than the entire world consumes in a year. This makes solar energy a potential source of virtually unlimited, clean, and free electricity, which is especially important if we take into account that earth's reserves of coal, oil, and gas are finite and likely to become resource-depleted in the course of this century (1).

One limitation to solar-cell technology has been the high cost of the materials, which has relegated its use to satellites and other high-tech applications (2). The development in the mid-1990s of solar cells based on organic plastics has offered the prospect to make solar power affordable for far broader uses. The development of this field[1] has only been possible through the collaborative efforts of synthetic chemists, physical chemists, physicists, engineers, and materials scientists. This emphasizes to the students the importance of multi-disciplinarity in research.
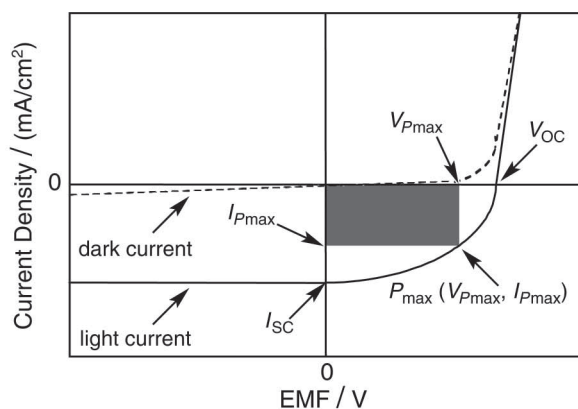
In this article we propose examples of plastic solar-cell technology to illustrate core concepts in chemistry. This can be of interest to the general public, teachers of organic chemistry or materials science, and undergraduate students owing to its pedagogical character. The principles of operation of a plastic solar cell (3) can be used to introduce key concepts such as the photovoltaic effect or the photoinduced electron transfer, which are fundamentally important to understand photosynthesis and the basic processes that govern most novel optoelectronic devices. From a spectroscopic perspective, the optical bandgap of the light-absorbing components can be correlated with their physical and electronic structure, which is going to determine its possible application in devices. From the materials science point of view, the principal concept of molecular design can be introduced showing how the evolution of the synthesis of organic molecules and polymers has provided materials with tailored properties (high quantum efficiency, mechanical flexibility, and the appropriate color or transparency) allowing the usefulness to be maximized. Finally, the field of organic photovoltaics provides good examples of the chemistry of fullerenes and conjugated polymers, materials of particular interest in current chemistry.

Characteristics of Organic Solar Cells

The ability of a material to produce electric current under illumination is called the photovoltaic (PV) effect. This process was discovered by Edmund Becquerel in 1839 (4) and constitutes the basis of solar cells. A PV cell can be defined as a device that converts incident light to electrical energy. Very simply, when the incident light (energy) is absorbed by the device, electrons are promoted to excited states and can produce, under some conditions, a motion of charges, that is, an electric current. This behavior can be graphically represented by the current–voltage (I–V) curve of the cell at a given illumination and temperature, in which some working parameters that determine the efficiency of the cell, are displayed (Figure 1) (5). I–V curves are usually recorded applying a variable load and tracing the current (6). Measurements are carried out both under illumination[2] and under the dark. Solar cells behave as large area diodes (7).[3] In such devices, when two materials with different work functions are brought into contact to form a junction (e.g., electrodes or active layers), the positive and negative charges redistribute instantaneously, establishing internal electric fields. As the concentration of electrons is much larger on the n side than on the p side, whereas the hole concentration is larger on the p side than the n, this difference makes electrons flow from the n region into the p region, and holes flow the other

Figure 1. Current–voltage (I–V) curves of an organic solar cell (in the dark, dashed line; illuminated, solid line). Under illumination, the characteristic intersections with the abscissa and the ordinate are the open-circuit voltage (V_{OC}) and the short-circuit current (I_{SC}), respectively. The maximum power output (P_{max}, with coordinates V_{Pmax} and I_{Pmax}) is determined by the point where the product of current and voltage is maximized. Division of P_{max} by the product of I_{SC} and V_{OC} yields the filling factor, FF.

way around. This flow of charge results in a region near the junction that is depleted of majority carriers, that is, of electrons on the n side and holes on the p side. As a result, an internal electric field ("built-in" potential) builds up, which opposes further diffusion across the junction and determines the rectifier action of the diode, as current can only flow in one direction across the junction. However, organic solar cells are not ideal diodes in the dark and under a bias a low-intensity current (usually in the μA range), the "dark current", can flow. Under illumination, when the voltage exceeds a threshold, the cell conducts.

When the solar cell is "short-circuited" (electrodes are connected and potential is zero) under illumination, the maximum current, the so-called short-circuit current (I_{SC}), can be measured. Under "open-circuit conditions" (intensity zero) no current flows and the voltage reaches a maximum according to Ohm's law: this value is the open-circuit voltage (V_{OC}). When an organic solar cell is used to generate power, the power output is given by the product of the current and voltage, IV. The point on the $I–V$ curve yielding the maximum value of this product is the maximum power point (P_{max}), which is inherently incapable of exceeding the product $I_{SC}V_{OC}$ ($P_{max} = I_{Pmax}V_{Pmax} < I_{SC}V_{OC}$). Another important parameter to define the solar cell performance is the filling factor, FF, defined as the ratio of the maximum power to the short and open-circuit values:

$$FF = \frac{V_{Pmax}\, I_{Pmax}}{V_{OC}\, I_{SC}} \qquad (1)$$

where FF is always less than 1, as I_{SC} and V_{OC} are never obtained simultaneously in actual use. The FF is a quality consideration, as it measures the "squareness" of the $I–V$ curve. For an ideal cell, the curve would be rectangular (FF = 1), but for real cells the FF is between 0.75 and 0.85 because of losses or shunt resistances. The external yield or energy conversion efficiency, η (often expressed as a percentage), is defined as the maximum power produced by the cell (P_{max}) divided by the incident power on the representative area of the cell (P_{light}):

$$\eta = \frac{P_{max}}{P_{light}} \qquad (2)$$

At this point, it is important to emphasize that the efficiency of a solar cell depends on the working temperature as well as on the "quality" of the illumination, that is, the total light intensity and the spectral distribution of the intensity. The last can be qualitatively understood considering that the efficiency of light absorption by the device is not the same when a strong (intense) or weak (diffuse) source of light is used or that light can not be properly absorbed when using an inappropriate illumination frequency. Therefore, it has been necessary to define standard measurement conditions to allow the comparison of solar cell performances between different laboratories. These conditions (for terrestrial solar cells) use a light intensity of 1000 W m^{-2} and a spectral distribution AM 1.5 global standard solar spectrum,[4] that is, the same distribution of frequencies as an incidental solar ray in a 48.2° angle. The working temperature is defined as 25 °C.

Structure and Principles of Operation of an Organic Solar Cell

Similarly to the $I–V$ curves, the principles of operation of all organic photovoltaic cells (8) are essentially the same in spite of the different device configurations (9). The cells consist of a single layer of a photovoltaic material sandwiched between two conductive contacts (electrodes) with different work functions (homojunction devices); one layer of an electron-donor material and another of an electron-acceptor material (heterojunction devices, Figure 2A) or a bulk-mixture of both (bulk-heterojunction devices, Figure 2C). To allow the interaction of light with the photovoltaic material, the device is built onto a transparent substrate (glass, plastic film) and one of the conducting contacts is also transparent,[5] so the material can absorb the incident sunlight photons and generate excitons. In an insulator or semiconductor, an exciton is an excited state that corresponds to a bound state of an electron, e$^-$, and an imaginary particle called an electron hole, h$^+$. To understand this definition, it can be useful to study the process of exciton formation (Figure 2B). Upon irradiation, an electron is excited to the conduction band of the material leaving behind a hole of opposite charge in the valence band (6, 10) (process 1 in Figure 2B). As the promoted electron and the hole have opposite electric charge, both remain bounded by a Coulomb force, which makes this state slightly more stable than a dissociated free electron and a hole. It is worth mentioning that only photons higher in energy than the band gap ($h\nu \geq E_g$) contribute to the photogeneration (the absorbed light has to be energetic enough to promote electrons) and the energy transferred to the exciton increases with E_g (i.e., the higher the energy content of the photon, the higher the energy of the exciton generated).

When the light-generated exciton reaches (mainly by diffusion) a dissociation site it separates into charges of different sign (process 2 in Figure 2B). The overall electric field between the two electrodes drives separated charge carriers towards the respective contacts (charge transport). This light-triggered transfer of one electron from a molecule to another is the photoinduced electron transfer. Finally, the charges are collected at the electrodes (process 3 in Figure 2B) to generate an electric current. In few words, the main processes in all organic photovoltaic cells involve (i) absorption of photons (exciton generation), (ii) generation of charge carriers (exciton dissociation), (iii) transport of charge carriers to the electrodes, and (iv) collection of charges (generation of electric current). In this way, the flow of absorbed photons is converted into a flow of dc power by the illuminated cell.

Whereas in homojunction devices exciton dissociation usually takes place at the junction with the electrodes, in heterojunction and bulk-heterojunction devices it takes place much more effectively at the donor–acceptor (D–A) interface, leading to a free electron in the acceptor material and a free hole in the donor (10). Since donor materials are more

likely to conduct holes and acceptor materials electrons, the last device architecture ensures the transport of charge carriers to the electrodes with only a small chance to recombine with their counterpart (e.g., bumping into each other, process 5, Figure 2B) as they do not have to diffuse through the same material (in opposition to homojunction devices), and connect with the correct electrode.

To increase the intimate contact between the donor and acceptor materials and provide a nearly complete transport of excitons to the D–A interface and thus exciton dissociation, different strategies have been developed, the most successful is the so-called bulk heterojunction. Conceptually, a bulk heterojunction is a multiple D–A junction in which the D–A interface is present everywhere in the material (see Figure 5Bii) in contrast to two layered heterojunction devices (Figures 2A and 5Bi) in which the D–A interface is limited to the surface between both layers. In an ideal situation, any point in the composite is within a few nanometers of a D–A interface (i.e., within the exciton diffusion length, the length excitons diffuse before they decay) and, if the network in the device is bicontinuous, the collection efficiency of charges of opposite sign can be equally efficient.

Organic photovoltaics is a multidisciplinary field in science and the advance of this technology has only been possible through the collaboration and involvement of chemists, physicists, and materials scientists. The role of physicists and materials scientists studying different configurations and processing techniques has proven to be critical for the improvement of the lifetime and the decrease in the costs of fabrication. However, the key factor in improving device performances lies in the development of materials specifically designed for organic photovoltaics. Therefore, the relevant task of theoretical chemists is to identify the characteristics of a successful material for organic photovoltaics, whereas the goal of synthetic chemists should be the design of synthetic strategies towards the preparation of these materials on a preparative scale. Thus, chemical synthetic tailoring of the desired properties in organic semiconductor materials is at the cutting edge of current research.

Design of a Successful Material for Organic Photovoltaics

As we have mentioned, after exciton dissociation the electric field drives the separated charge carriers toward their respective electrodes. The relation between the drift velocity, v_d, attained by these charge carriers and the electric field is the electron or hole mobility, $\mu = v_d / E$, where E is the magnitude of the electric field. Mobility gives an indication of the electron–hole scattering towards the electrodes: high values are required to ensure an effective generation of current. One important limitation to the use of organic materials in solar cells lies in their low intrinsic mobilities, which range typically between 10^{-7} and 10^{-3} cm^2 V^{-1} s^{-1} for hole-transporting materials and are even smaller for electron transporters. One of the reasons for the low mobility is the high disorder of most organic solids. Thus, one strategy to enhance the mobility involves polymers with ordered phases, for example, polythiophenes (11), and systems that can be arranged into
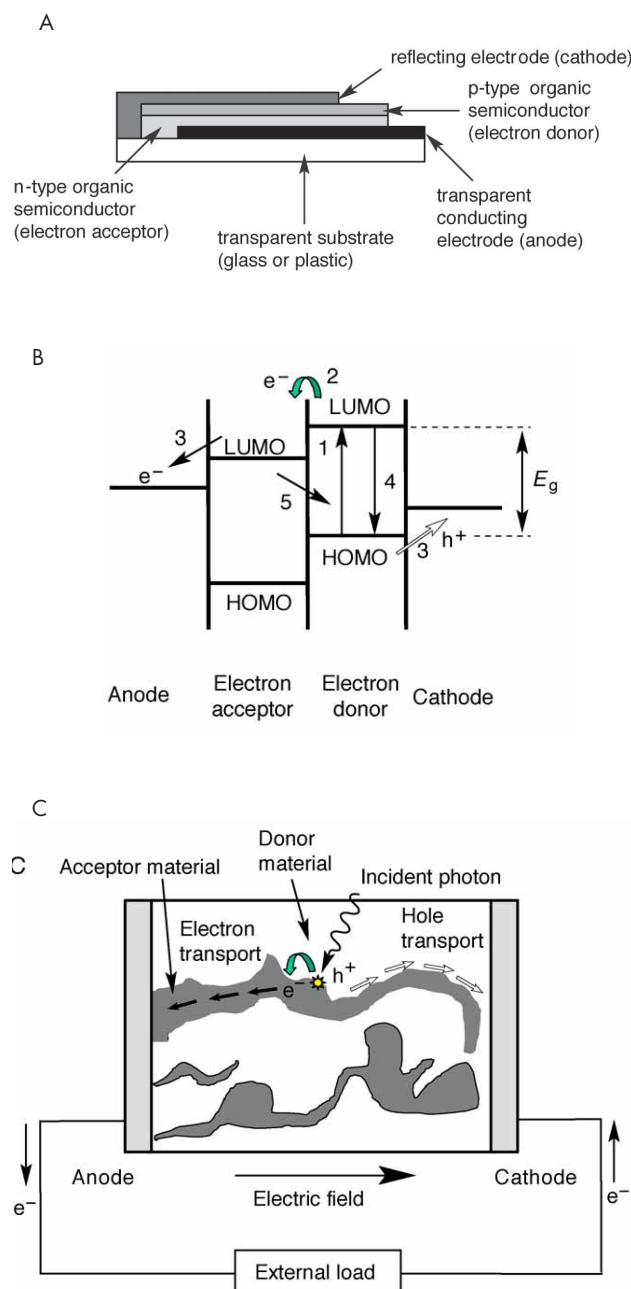

Figure 2. (A) Typical heterojunction organic solar cell architecture. (B) Schematic energy-band diagram of a donor–acceptor heterojunction. Following photoexcitation (1) an electron excitation from the HOMO to the LUMO of the donor generates an exciton. The exciton is then dissociated (2) at the p–n junction generating an electron lying in the LUMO of the electron-acceptor material and a hole in the HOMO of the electron-donor material. Charges of opposite sign migrate through the materials and transfer to the contacts (3). For efficient photocurrent generation charge separation (2) should efficiently compete with geminal recombination (4) while transfer to contacts (3) should compete with interfacial recombination (5). (C) Schematic bulk-heterojunction solar cell. p-Type (white) and n-type materials are intimately mixed together to form a dispersed heterojunction. Note arrows denoting hole movement are hollow.
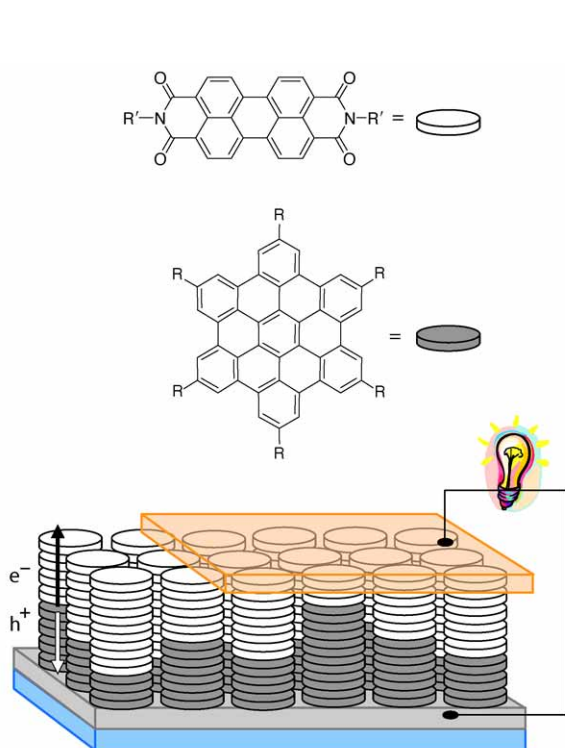
Figure 3. (A) Structure of hexaperibenzocoronene and perylene-bisimide bearing long alkyl chains. (B) Schematic representation of an idealized stacking of discotic molecules showing the migration of electrons and holes along the direction of highest mobility.

Figure 4. Slight modifications of the chemical structure of semiconducting polymers ("band gap engineering") make it possible to obtain materials with different absorptions.

ordered phases such as liquid crystals.[6] This strategy has been used by Müllen and coworkers (Figure 3) to combine the electron-donor discotic liquid crystal hexaperibenzocoronene and perylenebisimide derivatives (acceptors) to produce highly ordered thin films of planar donors and acceptors segregated vertically with a wide area of contact, ideal for charge transport. It is as if the π–π overlapping between planar-conjugated molecules created a vertical and continuous "highway" for the transport of carriers to the electrodes *(12)*. Alternatively, inorganic additives such as CdSe or TiO_2 *(13)* may be added to work as effective electron-transporting components as they can be patterned into an ordered continuous network increasing the electron mobility and transport *(14)*. This alternative has provided dye-sensitized solar cells with up to 10% efficiency *(15)*.

As shown in Figure 4, slight modifications in the chemical structure of semiconducting polymers produce materials with different bandgaps and therefore different absorptions (colors) *(16)*. This flexibility in chemical tailoring is essential for matching the absorption spectrum of the photoactive material to the solar emission spectrum. We cannot forget that we want the device not only to absorb light but also to convert as much solar light into electricity as possible (broad range of absorption wavelengths). Therefore, small bandgap materials (E_g ca. 1.1 eV) are more suitable for optimized efficiencies.

As an alternative to the syntheses of organic low-band gap materials, other strategies have been used to increase the
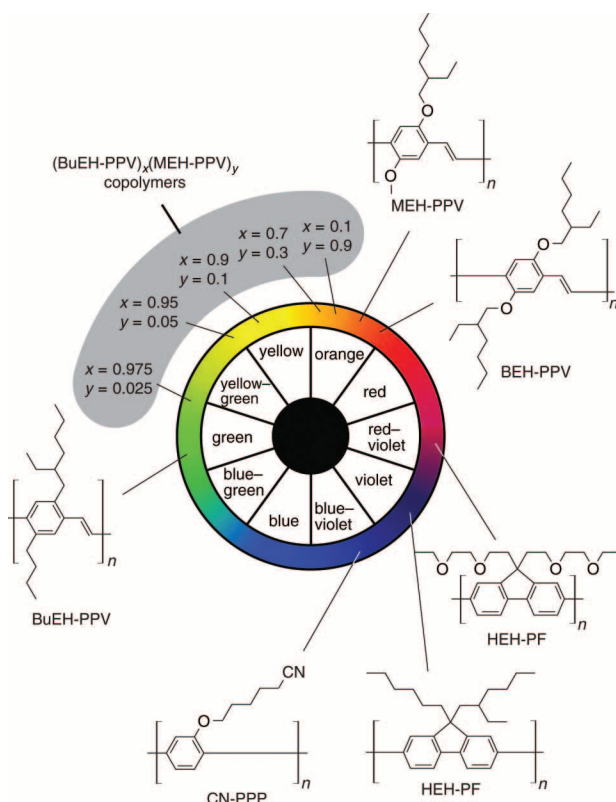
absorption of the active layer ("light harvesting"). One is to introduce a layer of a highly absorbing material, usually an organic dye, in the donor and the acceptor. The dye works as a light harvester providing that the light (energy) it absorbs can be transferred to the active material, thus increasing the global light absorption of the device *(17)*. Analogously, inorganic nanocrystals have been also used to increase the visible absorption, such as copper indium disulfide ($CuInS_2$) *(18)*.

The control over the morphology in dispersed heterojunction devices is a critical point, as effective exciton dissociation takes place at the interface. Owing to the different nature of the donor and acceptor materials, they tend to phase separate and reaggregate separately, creating isolated domains of donor and acceptors, which strongly decrease the interfacial area for the effective exciton dissociation. The degree of phase separation and domain size depends on the solvent used in the fabrication, speed of evaporation, and also on the solubility and miscibility of the donor and the acceptor, among other factors. Thus, a great deal of work has been performed by physicists and materials engineers to find the best combination of donor and acceptor systems in a variety of solvents and processing conditions, for example, different speeds of deposition on different device configurations to obtain optimized efficiencies. One example of the strong influence of the solvent used for the processing of the organic layer was reported in 2001. Two types of cells were made with identical layout, but with the photoactive layer spin cast from either chlorobenzene or toluene solutions. The power con-

version efficiency increased from 0.9% when the active layer was cast from toluene to 2.5% when chlorobenzene was used instead *(19)*. Atomic force microscopy (AFM) images of both films showed how the enhanced uniformity of the film obtained from chlorobenzene solutions could dramatically produce a change in the performance of the cell. Unfortunately, at present there is not real control over the morphology although some trends can be predicted.

One extensively investigated strategy to avoid phase segregation and ensure a large interfacial area between donor and acceptor is the covalent linkage of both units (Figure 5). We and others have investigated the synthesis and photophysics of D–A systems based on conjugated oligomers (fragments of polymers) covalently linked to the electron-acceptor [60]fullerene core and analyzed their applicability for the fabrication of photovoltaic devices (Figures 5A and 5Biii) *(20)*.

A similar strategy involves the covalent linkage of electron-acceptor moieties directly to donor polymer backbones. This is the so-called "double cable" approach due to their p- or n-type conduction properties, that is, electron transport through the "cable" formed by the acceptor units and hole transport through the polymeric chain "cable" (Figure 5Biv) *(21)*. This approach is intended to overcome phase segregation as both electroactive moieties are linked in the primary structure of the material. However, first reports on solar cells based on polythiophenes covalently linked to [60]fullerene moieties show only limited cell efficiencies, probably owing to the low fullerene content (C_{60} could be only attached to the 7% of repeating units), which can not provide efficient pathways for electron transport *(22)*.

Donor–acceptor diblock copolymers (Figure 5C) have also been proposed as materials for organic photovoltaics. As they are known to exhibit self-organized structures on the fractions of their block components (Figure 5D), domain sizes can be controlled down to the nanometer scale. Diblock copolymers containing oligophenylenevinylenes in the donor block and bearing pendant [60]fullerenes in the acceptor block (Figure 5C) have been employed in the fabrication of organic photovoltaics. The polymer structure results in the formation of a honeycomb structure on the micrometer scale *(23)*.

Finally, it must be pointed out that each of these approaches to optimize efficiencies requires not only a great effort for the synthesis of novel materials (chemists) but also in the optimization of the morphology in the solid blends for any novel combination of materials and the device architecture (physicists, engineers). Thus, it is important to consider that, of the wide variety of organic materials that have become available during the last decade, only a few have been extensively studied and the best materials have yet to be identified.

Conclusion

In summary, the field of organic photovoltaics constitutes a promising field of research that attracts attention from both academic and industrial researchers. The development of materials that absorb light in a broader range of the solar spectrum and a higher control on the morphology of organic thin films should be further explored as these evolve as key parameters to achieve good transport properties and efficiencies. The challenges still remain to achieve better light conversion efficiencies and fabricate devices with longer lifetimes
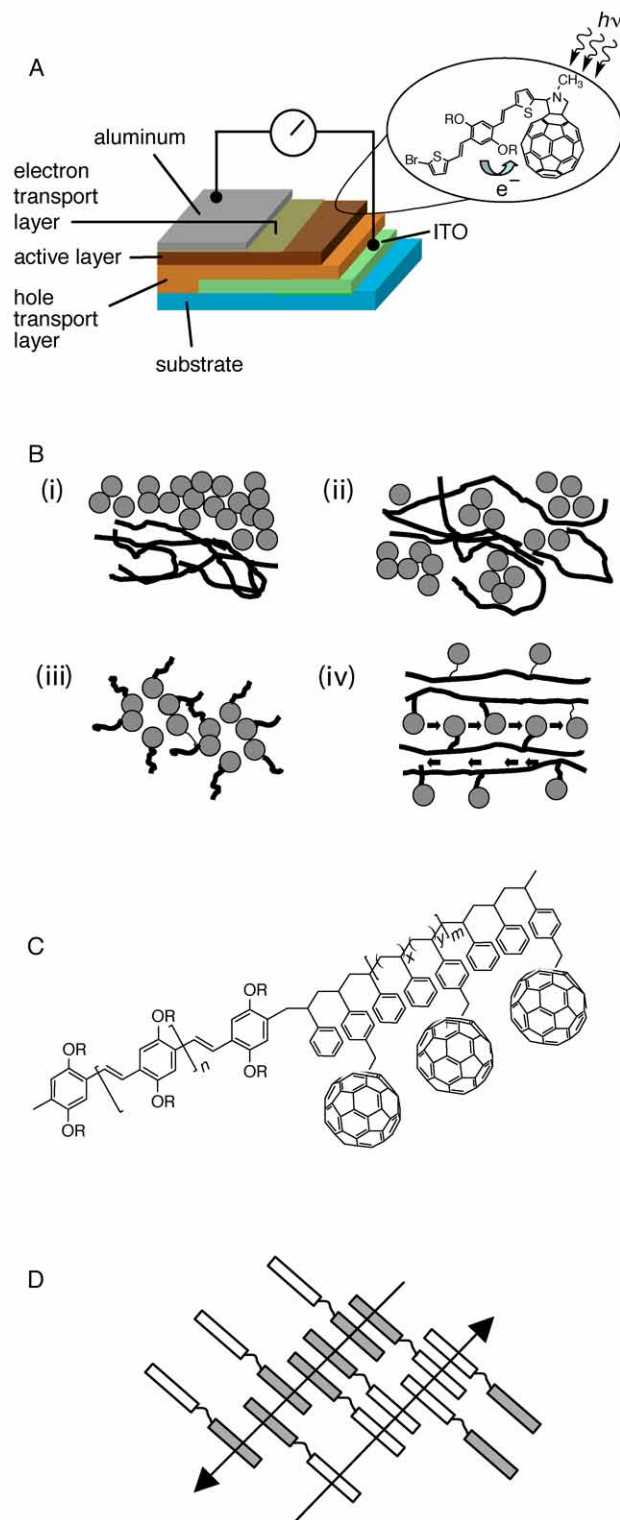

Figure 5. (A) Schematic representation of a solar cell using a conjugated oligomer covalently linked to a [60]fullerene core as active layer *(21)*. (B) Different morphologies of heterojunction cells. (i) Two-layered heterojunction of acceptors (circles) and polymers (lines); (ii) dispersed or bulk heterojunctions; (iii) conjugated oligomers covalently linked to acceptor moieties, and (iv) "double cable" polymers. The arrows in the "double cable" polymer scheme indicate the complementary p- or n-type conduction properties. (C) Structure of a block copolymer used for PV applications. (D) Idealized layered structure of a diblock copolymer, which is expected to facilitate electron and hole transport.

at low cost to enter the on-grid market. Only the collaborative work of synthetic chemists, physicists, and engineers will make it possible to obtain the wide use of organic photovoltaics in the next few years. The strategies for the design of novel materials with tailored properties owing to the almost unlimited flexibility and versatility of organic chemistry and the enhancement of the performance of the devices through the interdisciplinary collaboration between researchers of different fields may be incorporated into the chemistry curriculum as examples of the application of chemical principles to cutting edge research and technology to overcome limitations and to present chemistry as a central science for the development of other disciplines.

Acknowledgments

ᵂSupplemental Material

A background to organic photovoltaics, including a figure with the most representative molecular organic materials first used in photovoltaics devices, a schematic drawing of a solar cell with a blend of conjugated polymer and [60]fullerene, and a schematic showing the easy preparation of polymer films by different techniques are available in this issue of *JCE Online*.

Notes

1. A background to organic photovoltaics is available in the Supplemental Material.ᵂ

2. Illumination is supplied by Xe or Ar lamps, solar light simulators, and so forth with a calibrated light intensity and cooling the cell, as much of the incident light becomes heat.

3. A diode is a component that permits the flow of current in one direction but blocks it in the opposite (rectifier behavior).

4. Solar spectra are noted by an air mass (AM) value, which is a measure of the length of the path through the earth's atmosphere that the solar radiation travels. The value is calculated as $1/\cos z$, where z is the zenith angle between a line perpendicular to the earth's surface and a hypothetical line intersecting the sun. Thus, AM 1 describes the case in which the sun is directly overhead. The AM 1.5 spectrum is commonly used for testing photovoltaic devices meant for terrestrial use. AM 0 is the spectrum of sunlight outside the earth's atmosphere and is used for testing PV devices intended for use in space.

5. Transparent semiconductor tin doped indium oxide (ITO) is used in most optoelectronic devices as the anode, deposited by electron beam evaporation or sputtering techniques on different substrates.

6. Liquid crystals (LC, also called mesogens) are substances that exhibit a phase of matter combining properties of a conventional liquid (they may flow) and a solid crystal, as their molecules can be arranged and ordered as in a crystal. There are many different types of LC, depending on the different orientation of their molecules. For example, some disk-like molecules tend to stack and form columnar structures that can also arrange in different ways (e.g., hexagonal packing); these are the discotic liquid crystals.

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