

Discotic liquid crystals for solar cells

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The light-induced electron-hole generation, separation and migration are important processes for the conversion of light to electric or chemical energy (solar cells; photosynthesis), the latter being the basis of life on earth. Most of the world's current energy supplies are based on fossil energy sources and only a little is provided by hydropower, biomass and nuclear energy. The exponential growth of CO₂ level in the atmosphere is leading to the threat of a worldwide climate change. Also, there will be limited availability of fossil energy sources in the long term. Exploitation of nuclear energy does not appear to be socially acceptable, universally. The problem of energy provision, particularly in the Third World, remains unsolved. The alternative energy sources are the renewable energy sources. The overflowing solar energy is the most promising source for future sustainable production of fuel and electricity.

The photovoltaic effect, the direct conversion of light energy into electricity by solar cells, is known since 1839 but until the mid-twentieth century it remained mostly a laboratory curiosity. The space programme (scientific, commercial and military satellites) gave tremendous impetus to the development of solar cells. The oil crisis of 1973 forced many countries to look for alternative sources of energy and interest in photovoltaics as a terrestrial source of power increased greatly.

Solar cells with high efficiency are usually fabricated from inorganic semiconductors. Flat-plate photovoltaic technology of today is based mainly on single or polycrystalline silicon solar cells. However, the technology is too expensive for many applications to be viable. Organic thin-film solar cells are very attractive for flat-plate terrestrial applications because they can be fabricated using potentially low-cost methods, which can process large area substrate in an economic way.

Photovoltaic devices employing organic semiconductors are usually of two types, Schottky and *p/n*-type. In a Schottky cell the organic *p*-conductor is usually sandwiched between two electrodes of different work function, while in an organic double layer *p/n*-cell a layer of *n*-

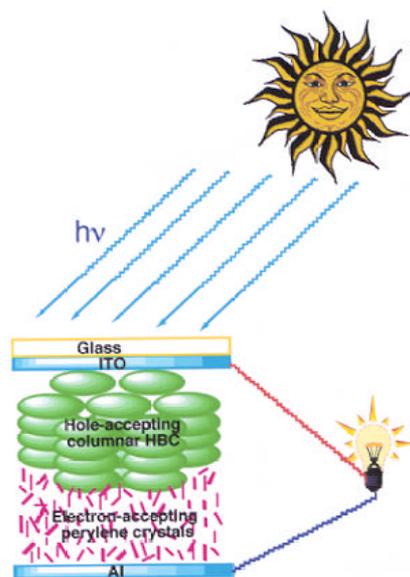


Figure 1. Schematic diagram of a bilayer photovoltaic solar cell.

conductor and a layer of *p*-conductor are sandwiched between two electrodes. These devices consisting of molecular or polymeric organic compounds as active part of solar cells, exhibit very low power conversion efficiencies (below 1%). The photosensitivity of semiconducting organic materials can be enhanced by blending donor and acceptor molecules to optimize photoinduced charge separation. Blends of conjugated polymers and fullerene (C₆₀) were utilized to prepare solar cells with external quantum efficiencies (EQEs) of 5–10%. Yu *et al.*¹ achieved EQE of 29% for a blend of a hole-transporting polymer with the electron acceptor C₆₀. The efficiency was further improved by blending a soluble methanofullerene into the conjugated polymer film. Shaheen *et al.*² recently reported a photovoltaic device having EQE of 50% and power conversion efficiency of 2.5%. An organic–inorganic heterojunction device based on ZnO and single crystalline pentacene doped with bromine gives solar-energy conversion efficiencies up to 4.5%.

In general, crystalline molecular organic materials exhibit better transport properties than their polymeric counterparts. However, single crystals are difficult and

costly to process, a disadvantage which can be overcome by utilizing discotic liquid crystals, because their columnar structure resembles the aromatic stacking in single crystalline conductors. Schmidt-Mende *et al.*³ recently used hexabenzocoronene-based discotic liquid crystals as hole-transporting layer to construct an efficient organic photovoltaic solar cell.

The supramolecular assemblies of disc-shaped molecules lead to the formation of discotic liquid crystals, discovered in Bangalore in 1977 by Chandrasekhar and his colleagues^{4,5}. Mesophases formed by these molecules are primarily columnar (Figure 2). In the columnar phase, the discs are stacked one on top of another to form columns (Figure 2). The separation between the aromatic cores is of the order of 3.5 Å.

Discotic liquid crystals have very high charge carrier mobility in columnar mesophases which offers potential applications as organic charge transport materials in a variety of devices such as one-dimensional conductors, photoconductors, field-effect transistors, photovoltaic solar cells, etc. Both *p*-type discotic liquid crystals such as triphenylene, dibenzopyrene and hexabenzocoronene (Figure 3 *a–c*), and *n*-type discotic liquid crystals such as tricycloquinazoline, anthraquinone and perylene (Figure 3 *d–f*), are known.

Gregg *et al.*⁶ studied photovoltaic effects in symmetrical cells filled with discotic liquid crystalline porphyrin complexes. Photovoltaic effect comparable

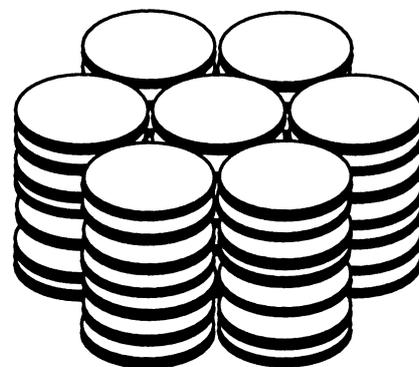


Figure 2. Schematic representation of columnar phase.

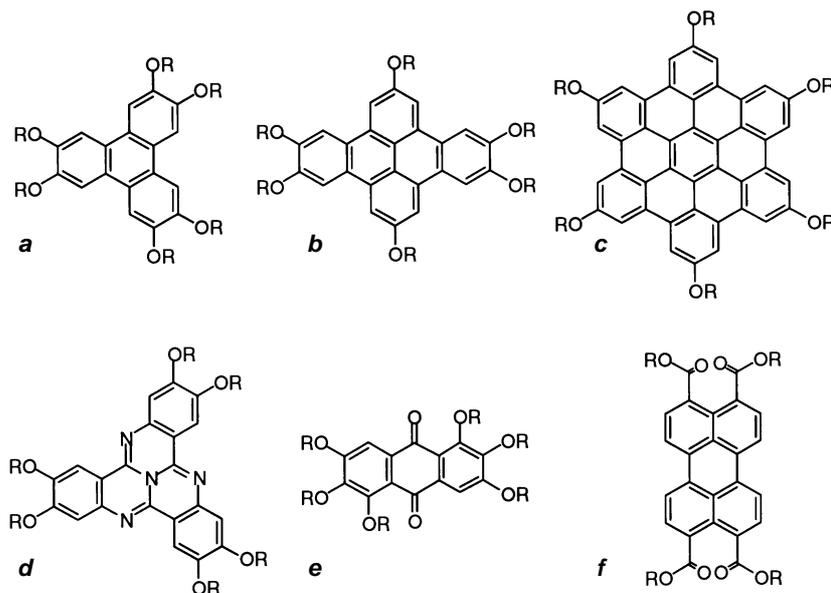


Figure 3. Chemical structure of *p*-type (a–c) and *n*-type (d–f) discotics.

with that of some of the better organic solar cells was found. However, the authors did not study the charge mobility in the mesophase itself, but utilized the liquid crystalline properties to fill the cell and to promote macroscopic order which, on cooling, provided polycrystalline films. Schmidt-Mende *et al.*³ constructed a *p/n*-type photovoltaic solar cell using discotic liquid crystalline hexabenzocoronene as the hole-transporting layer and a perylene dye as electron transporting layer (see Figure 1). A chloroform solution of crystalline dye perylene *N,N'*-bis(1-ethylpropyl)-3,4,9,10-perylene-bis(dicarboximide) (perylene) and room temperature discotic liquid crystal hexadodecylphenylhexabenzocoronene (HBC) were spin-coated onto indium tin oxide. Photodiodes were prepared by the evaporation of Al onto HBC: perylene blend films. Perylenes are known to possess high electron mobilities and have been used as electron acceptors in devices. The hexabenzocoronene-based discotic liquid crystals have the highest hole mobility ever reported for a discotic liquid crystal. The device made by Schmidt-Mende *et al.*³ exhibits EQEs up to 34% and power efficiencies of up to ~2%. These efficiencies are comparable with the best ones reported for organic photovoltaic devices. Efficient photo-induced charge transfer between the hexa-

benzocoronene and perylene and facile charge transport through vertically segregated perylene and hexabenzocoronene *p*-systems are primarily responsible for these efficiencies.

Although single crystalline organic materials and inorganic semiconductors exhibit better efficiencies, their processability is difficult and expensive. The device of Schmidt-Mende *et al.*³ is based on simple solution processing and utilization of the self-organization of discotic liquid crystalline and crystalline organic materials for the charge transport. These results in conjunction with several other recent studies on charge and energy migration in discotic liquid crystals⁷ lead us closer to a long-desired goal of achieving cheaper, clean, eco-friendly energy for the benefit of mankind. The topic is of great importance to developing countries.

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Discotic Liquid Crystals. Discotic liquid crystals (DLCs) have been well recognised as one-dimensional organic semiconductors.[12–21] Because of their excellent charge transport property, DLCs have been extensively applied to prepare bulk hetero junction (BHJ) solar cells. DLCs derived from porphyrin,[22,23] phthalocyanine, [24–32] triphenylene (TP) [33–35] and hexabenzocoronene [36–45] have been used as hole transporting layer while perylene and C60 derivatives have commonly been used as electron transporting materials. 6 - Discotic liquid crystals. S. Chandrasekhar. Publisher: Cambridge University Press. Since the early investigations of Lehmann and others elucidating the relationship between liquid crystalline behaviour and chemical constitution, the accepted principle was that the molecule has to be rod-like in shape for thermotropic mesomorphism to occur, but it has emerged during the last decade that compounds composed of disc-like molecules may also exhibit stable mesophases. Some typical discotic molecules are shown in fig. 6.1.1. Generally speaking, they have flat (or nearly flat) cores with six or eight (or sometimes four) long chain substituents, commonly with ester or ether (but rare