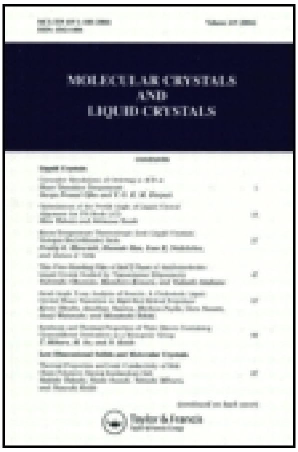

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Toward Organic Photovoltaic Cells Based on the Self-Assembly of Discotic Columnar Liquid Crystals

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Two key parameters for the performance of an organic photovoltaic cell are the exciton diffusion length and the charge carrier mobility. Considering these parameters, columnar liquid crystals, with strong pi-orbital overlap between neighbouring cores, are promising materials. We describe our strategy towards the synthesis of both donor- and acceptor-type materials exhibiting a hexagonal columnar mesophase at the operating temperature range of the cell, including room temperature. We present the alignment behaviour of these materials when submitted to a thermal annealing, and, in particular, an approach to obtain thin open films with homeotropic orientation.

Keywords Columnar liquid crystals; discotic molecules; donor–acceptor materials; photovoltaic devices; pi interactions; solar cells

1. Introduction

The term "organic semiconductor", currently applied to many different types of materials, was initially coined to designate specifically certain molecular crystals (naphthalene, anthracene, etc.) presenting properties similar to inorganic semiconductors. If in the beginning, the photoconductivity of organic crystals was not used either because of their weak photosensitivity or a spectral domain restricted to the ultraviolet, numerous photoconductive "small molecules" were nevertheless developed since the seventies. These molecules, incorporated in a polymer insulating matrix, are commonly used in photocopiers and laser printers [1]. Dyes such as phthalocyanines or perylene derivatives, widely used for the manufacture of photoconductive layers, can also be integrated into organic photovoltaic cells (OPVC).

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Although the feasibility of organic solar cells was demonstrated from the seventies onwards, the relevance of their development became clear only recently in the more general frame of the development of renewable energies. The main advantages of organic components over their inorganic counterparts are their compatibility with flexible substrates, the quasi-infinite designing possibilities of active materials, and the use of relatively simple large-area and possibly low-cost deposition techniques [2]. Despite continuous improvement in the OPVC power conversion efficiency (the best values being of the order of 5%), research is still needed to get a better understanding of their operation and to develop new materials for higher efficiencies. In this paper, we will describe our research aiming at realizing OPVCs based on the self-assembly of discotic columnar liquid crystals.

2. The Functioning of an OPVC

An organic photovoltaic cell generally consists of a multilayer structure of ~100 nm thickness, composed mainly of a donor and an acceptor material. The relative donor or acceptor character of a material is defined with respect to the electronegativity scale. The more electronegative a material is, the more its acceptor character is emphasized because it has more power to attract electrons. A material possessing a large electron affinity value (of the order of 4 eV) is then generally called "acceptor"; it is considered as "donor" if its ionization energy is weak (typically 5 eV).

The first stage of organic photovoltaic conversion (Fig. 1) is the absorption of photons in the organic film(s). The transition towards the lowest unoccupied molecular orbital (LUMO) energy level leads to the formation of a hole which remains connected to the electron by mutual electrostatic attraction; the electrically neutral electron-hole couple is called exciton. Whereas in inorganic semiconductors, the binding energy of excitons is very weak (14.7 meV for silicon) and the thermal energy is sufficient at ambient temperature to separate both charges, this energy generally reaches values of the order of 200 meV in organic semiconductors. During their lifetime, excitons diffuse over a more or less large distance which depends on the material. Their dissociation may occur if they reach the donor/acceptor interface, electrons being then attracted by the acceptor material and the holes by the donor

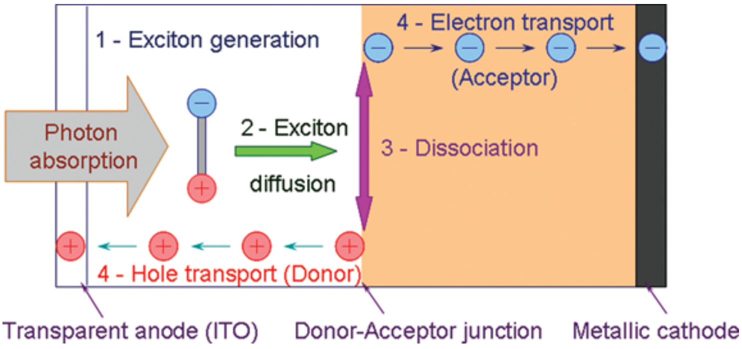

Figure 1. Schematic description of organic photovoltaic cell (OPVC) operation. (Figure appears in color online.)

one. Finally, the charge carriers generated at the interface reach the electrodes and the circuit outside the cell.

3. Columnar Liquid Crystals as Active Photovoltaic Materials

Two key parameters for the performance of an OPV cell are thus the exciton diffusion length (L_D) and the charge carrier mobility (μ). As most polymeric or small-molecule organic materials currently used as active layers in OPVCs are in an amorphous glassy or nanocrystalline state, their values of both L_D and μ are several orders of magnitude lower than those of single crystals of polycyclic aromatics, notably L_D generally being smaller than the necessary layer thickness for quasi-quantitative light absorption (about 50 nm) [3]. Using single crystalline layers, therefore, without doubt would be an efficient way to improve the performances of OPVCs, but the fabrication of such single-crystalline organic layers of the required dimensions with no carrier-trapping grain boundaries on the path of the charges and excitons is difficult and does not permit the use of simple solution processing or high-throughput evaporation procedures.

Liquid crystals (LCs) offer a compromise approach due to their good transport properties combined with a propensity for controllable growth of large oriented domains in thin films. They combine in this respect some of the positive features of amorphous materials and macroscopic single crystals: whereas crystallization is usually a process that is hard to control due to the effect of supercooling, leading to fast and inhomogeneous growth after kinetically retarded nucleation, liquid crystalline domains can be grown slowly and at thermodynamic near-equilibrium upon slow cooling through the liquid-to-LC phase transition. Well-oriented large-domain layers are thus more easily feasible than with crystalline materials. As concerns the transport properties, the intermediate degree of ordering within LCs as compared to liquids and to crystals means that their values of L_D and μ can be far superior to those measured in amorphous materials and, in some cases, approach the values obtained in single crystals [4], depending both on the geometrical and electronic make-up of the individual molecules and on the supramolecular order in the liquid crystalline phase.

For optoelectronic devices, columnar LCs formed by discotic molecules represent one of the most promising type of self-organized material. Such liquid-crystalline phases consist of columns of stacked disks, with the columns forming a two-dimensionally crystalline array, whilst some fluidity is maintained within the columns. For their use in OPVCs, the column-forming molecules are extended polycyclic aromatic pi-electron systems surrounded by flexible aliphatic side chains. The close contact between the stacked aromatic cores in the center of each column enables excitons or charge carriers to hop easily from molecule to molecule over large distances along the column because of the good pi-orbital overlap between neighbouring cores. The transport properties tend thus to be anisotropic, and if uniform orientation of the columns can be achieved with the columns perpendicular to the plane of the layer, good trough-layer exciton and charge transport can be obtained. L_D has been found to span 70 nm along the columns in triphenylene LCs [5], similar to the average thickness of an absorptive layer in an organic solar cell. μ attains values of 10^{-3} to $10^{-1}\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$ in various columnar triphenylene materials [6], which is about four orders of magnitude higher than in polycrystalline pentacene films [7].

Columnar mesophases can be subdivided into two groups: highly symmetrical ones where the disks are on average perpendicular to the column axis (which means that if the columns are oriented perpendicular to a surface, the disks are parallel to this surface), and phases of lower symmetry where the disks within a column are tilted with respect to the column axis. Tilted phases most often consist of columns with different tilt directions, which means that it is impossible for all disks to adopt an orientation perpendicular to a given surface. Such tilted phases, generally of rectangular or oblique column lattice symmetry, therefore have a strong tendency to adopt the so-called planar orientation, with the column axes parallel to the surface. Only the more symmetrical non-tilted phases, of hexagonal symmetry, tend to adopt the so-called homeotropic orientation, i.e., with their columns perpendicular to the surface, as this allows the terminal disks to lie flat on the solid substrate. As this is the needed orientation for efficient through-layer charge carrier and exciton transport, only hexagonal columnar phases are of strong interest for OPV applications.

To construct an OPVC based on this approach, both donor- and acceptor-type materials exhibiting a hexagonal columnar mesophase are required, and this phase should be thermodynamically stable at the operating temperature range of the cell, including room temperature. Mesogens that exhibit their LC phase at room temperature are rare. Therefore, the materials used by the display industry in the fabrication of LCDs are mixtures of several compounds in order to suppress the melting temperature well below room temperature. Mixing several mesogens of different aromatic make-up and side chains is feasible as long as only the birefringence and viscoelastic properties of the resulting mixed material are important, as it is the case in nematic display cells. Nevertheless, as the transport properties are closely dependent on the relative molecular orbital energies of neighbouring molecules, mixing different compounds is unproblematic in the case of electronic applications, such as for OPVCs, only if their electronic properties are near identical. Thus homogeneous mixing of different chromophores should be avoided in favour of mixing of different electronically equivalent regio- or stereo-isomers where differences are restricted to the electronically less relevant molecular periphery. Especially the use of several racemic aliphatic chains turns out to be an efficient approach to suppress crystallization at room temperature.

The overwhelming majority of established polycyclic aromatic columnar LCs bears alkyl, alkoxy or alkanoyloxy side chains as flexible substituents, which impart a relatively electron-rich or donor-type character to the chromophore. In view of this lack of acceptor-type columnar LC materials, we have developed a new class of columnar LCs with variable electronic properties in recent years, namely the alkyl ester and imido-ester derivatives of various polycyclic arene-oligocarboxylic acids [8]. Electron-withdrawing carbonyl substituents seemed to have been particularly neglected in the earlier works on columnar LCs: whereas columnar $Ar(OC(=O)R)_n$-type ester derivatives of phenols were amongst the first columnar LCs discovered in the late seventies [9], the inverse structure $Ar(C(=O)OR)_n$ had not been scrutinized for columnar liquid-crystallinity. We found that in contrast with the most established families of columnar LCs, these materials exhibit a columnar mesophase at high temperature even with very short alkyl chains such as ethyl. With longer and racemically branched alkyl chains such as 2-ethylhexyl, sufficient disorder is introduced to suppress the domain of the crystalline state below room temperature and thus to obtain a liquid crystalline state that is stable at ambient conditions and over large temperature ranges. Examples of such room temperature columnar LCs are the

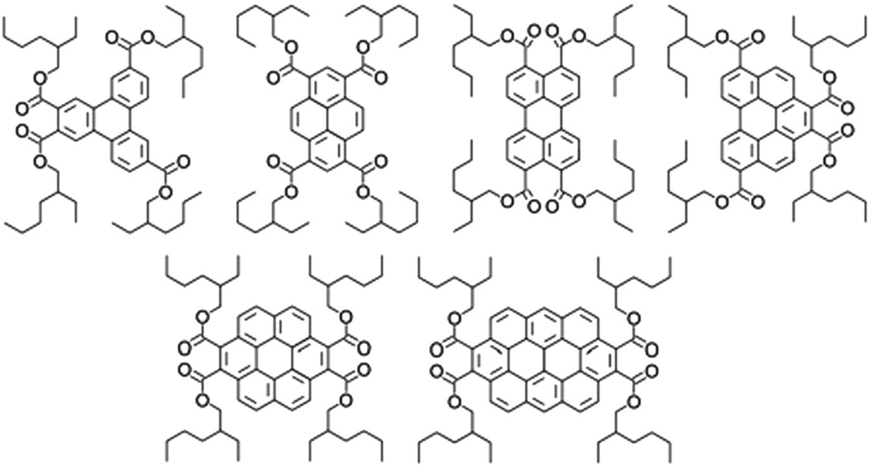

Figure 2. Aromatic esters with branched alkyl chains that show a hexagonal columnar mesophase at room temperature.

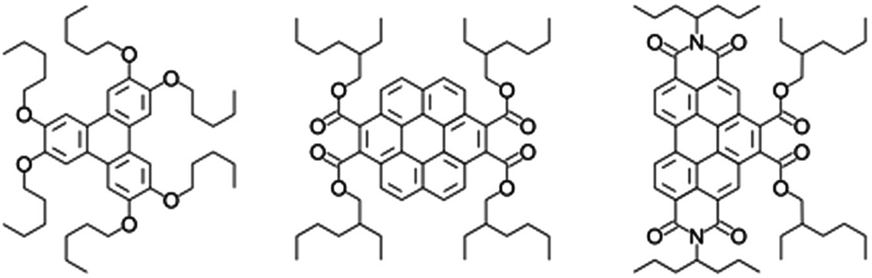

Figure 3. Columnar materials showing increasing acceptor-type behaviour with increasing electron-withdrawing substituents (from left to right).

six tetraesters depicted in Figure 2, derived from triphenylene, pyrene, perylene, benzoperylene, coronene and ovalene, respectively. If such esters are combined with more conventional, more electron-rich ethers such as hexaalkoxy-triphenylenes [10], they take the role of the electron-acceptor, whereas if they are combined with their more electron-deficient imide cousins such as benzoperylenehexacarboxylic diimido-diesters [11], they take the role of the electron-donor (Fig. 3).

4. Towards Homeotropic Self-Organizing Organic Structures

In contrast with the liquid crystal displays (LCDs) where the liquid crystal is sandwiched between two glass slides a few micrometres distant from each other and which are filled by capillarity, photovoltaic devices are usually fabricated by sequential deposition of the donor and acceptor organic layers (which are typically 100 nm thick) on the anodic substrate. The cathode is added by vacuum deposition afterwards. In order to benefit from the good uniaxial charge carrier properties of discotic materials, it is necessary to control the orientation of the active layer in the geometry of an *open* supported film with a face-on configuration of the molecules corresponding to homeotropic alignment (Fig. 4). The necessity to have a well-aligned material in homeotropic orientation has been recently emphasized by grazing incidence X-ray diffraction experiments [12]. The main result can be summarized by the fact that a pristine (as-deposited) open columnar liquid crystal films exhibit a total absence of homeotropic domains. The samples consist of small domains of hexagonal columnar liquid crystal, whose individual average column orientations arbitrarily point to all possible directions within the plane of the discotic layer [13]. This degenerate planar alignment corresponds to the worst orientation for carrying charges or excitons in organic photovoltaic devices. Indeed, the axis of good conductivity being along the columns, no path of good mobility exists for the charge to move through the organic layer.

We have demonstrated that this orientation can be overcome and totally reversed to an all-homeotropic alignment by a specific thermal annealing, by which it is possible to kinetically stabilize the homeotropic alignment [12–14]. The process implies, in a first step, to heat up the discotic material into its isotropic liquid phase, followed in a second step by a thermal quenching down to room temperature with the nucleation and the growth of columnar liquid crystal germs. The six-fold symmetry observed during the growth by optical microscopy evidences the homeotropic anchoring (Fig. 5). This thermal process associated with a surface treatment [15] of the solid substrate can induce a homeotropic orientation of hexagonal columnar mesophases with film thicknesses of the discotic layer down to 50 nm [16]. This face-on alignment of the molecules is thermodynamically metastable in the geometry of an open film, but it can be preserved until the deposition of the cathode, and becomes thermodynamically stable in the configuration between two solid interfaces. Thanks to a specific design of two *immiscible* discotic compounds, such a strategy of columnar LC alignment has been extended to the realization of an *oriented* bilayer, providing the first proof of principle of an organic heterojunction based on two aligned columnar LCs [17]. Recently, we have developed an alternative method to induce the homeotropic alignment by avoiding the first step in the isotropic liquid phase where some dewetting (destabilization of the thin film by the formation of droplets) can occur. It is based on an *anchoring transition* from planar to homeotropic alignment of the columnar liquid crystal which is performed between the two electrodes of the device by a thermal annealing at a temperature below the isotropic liquid

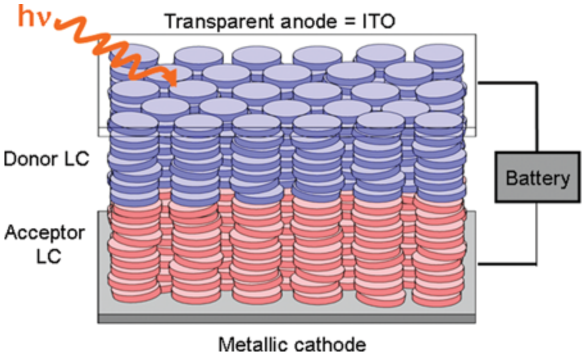

Figure 4. Schematic representation of an OPVC based on two self-organized discotic columnar liquid crystals in homeotropic (or face-on) orientation. (Figure appears in color online.)

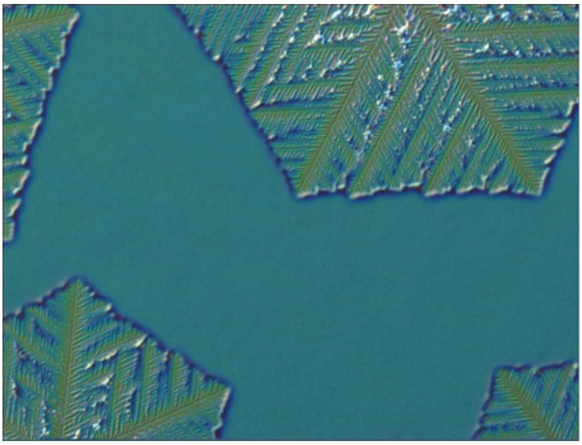

Figure 5. Dendritic growth of a columnar liquid crystal germ in homeotropic orientation observed in open supported thin film by differential interference contrast microscopy. The image size is 880 μm × 650 μm. (Figure appears in color online.)

phase, where the fluidity of the liquid crystal increases. A detailed investigation of this anchoring transition has been lately achieved [18].

5. Conclusion

Various discotic molecules with electron donor or acceptor character and room temperature liquid crystal mesophase have been synthesized in view to be used in organic solar cells. The achievement of uniform homeotropic alignment of discotic columnar liquid crystals is pursued in order to obtain a sharp increase in charge carrier mobility and exciton diffusion length [19]. Our studies have evidenced different ways to overcome the dewetting phenomenon and to control the morphology of columnar liquid crystals in thin films (thickness lower than 100 nm). The demonstration of the feasibility, via a simple process, of devices with self-assembled materials will be the next goal of our work. It may pave the way for more efficient organic solar cells.

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