Invited Paper

Novel columnar LCs for a new generation of organic solar cells

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ABSTRACT

High exciton diffusion lengths and charge carrier mobilities along the columns and the capability to align make columnar LCs promising materials for solar cells. Given the lack of columnar LCs based on acceptor-type aromatic systems needed for donor-acceptor heterojunction devices, we have developed novel carboxylic-functionalized arene chromophores. We found large columnar temperature ranges and widely tunable electronic properties. First device results are very encouraging, including very high open circuit voltages. This illustrates that the combination of both donor-type and acceptor-type columnar LCs can lead to solar cells with pronounced donor-acceptor junctions. The perspective of using the good transport properties of such columnar materials throughout the active layers offers thus a novel approach to highly structured plastic photovoltaic devices.

Keywords: columnar liquid crystals – discotic liquid crystals – organic solar cells – self-assembly – charge transport – exciton diffusion

THE QUEST FOR EFFICIENT ORGANIC SOLAR CELLS

Silicon solar cells are an established technology that converts solar energy into electric energy with reasonable yield (>17%), and which is reliable (current modules come with a guaranteed lifetime of 25 years). Their best efficiencies so far obtained with organic (also called plastic) solar cells are around 5%,[1] and their stability will certainly never beat the robustness of inorganic devices. So what is the point of going plastic?

The thickness of the silicon layer in common silicon solar cells is typically around 200µm. Silicon cells absorb essentially all visible and near IR light below 1100nm. To be efficient, the silicon used has to be extremely pure, as its conductivity is controlled by a band mechanism which relies on the large range periodicity of the silicon atoms. Any impurity that affects this periodicity strongly affects the conductivity. This means that highly zone refined silicon is needed for solar cells, and this pushes the energetic costs of the fabrication of silicon solar cells. Silicon modules therefore need to run a few years before they have paid back the energy needed for their production. Which is not a problem if the cell is used for continuous energy supply during its guaranteed lifetime of tens of years, but which may be a problem for applications where a cheap but not decade-lasting off-grid energy supply is needed.

Organic dyes and pigments have in general less broad absorption spectra than silicon, covering typically a range of 200nm, e.g. 550nm-750nm for phthalocyanines, and they are much better absorbers than silicon, so a layer thickness of 50 to 100nm is in general enough to absorb most of the incoming light of appropriate wavelength. This means that a solar cell made of organic dyes needs about three orders of magnitude less active material than a silicon cell, which can

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make organic cells far cheaper, and that one can adapt the absorption to a desired wavelength range, e.g. to make semitransparent see-through cells. The smaller layer thickness also means that the organic materials have to meet less stringent purity criteria – an exciton or a charge has to hop over only about 100 molecules without meeting a trapping impurity to survive on its path through the organic layer. And no long range periodicity is needed, because in contrast to the band transport mechanism in silicon, charge transport in organics relies on discrete charge hopping from molecule to molecule.

Given these lesser purity needs and given they are solution-processable, they may be produced by cheap roll-to-roll printing techniques. A further advantage for organic cells is their potential mechanical flexibility – if all elements are plastic, including the electrodes (which remains a challenge), then rollable, foldable and on-cloth photovoltaic power supplies become feasible. So whilst organic photovoltaic cells will not replace silicon cells on rooftops, they may beat silicon for a place on windows or on handbags that can recharge mobile phones.

Current organic solar cells suffer from low efficiencies because only a small fraction of the absorbed photons are successfully converted into electrons in the external circuit. As most organic materials used in solar cells are disordered amorphous or glassy molecular solids or polymers, their exciton diffusion lengths (the average hopping range during the lifetime of an excited state that has been created by absorption of a photon) are about one order of magnitude smaller than the layer thickness. Similarly, if an exciton manages to survive until it reaches an interface where it can split into electrical charges, the charges created have difficulties reaching the electrodes due to the low charge mobilities of organic disordered solids. This means that by increasing the exciton diffusion lengths and the charge mobilities one should be able to increase significantly the efficiencies of organic solar cells.

COLUMNAR LIQUID CRYSTALS AS CHARGE AND EXCITON TRANSPORT MATERIALS

Aromatic single crystals have charge carrier mobilities that are several orders of magnitude better than those of disordered layers : e.g. a mobility of 35 $cm^2V^{-1}s^{-1}$ is measured in pentacene single crystals,[2] whereas polycrystalline pentacene films[3] have mobilities of around 10^{-7} to 10^{-5} $cm^2V^{-1}s^{-1}$. Exciton diffusion lengths are likewise higher in highly ordered crystalline films than in polycrystalline films, varying from a few nm to about 90 nm depending on the material and its structure.[4] Using thin continuous crystalline layers with no or few grain boundaries inside would thus be an excellent way to increase efficiency, if such layers would be easy to make. But the fabrication of such layers is cumbersome and incompatible with solution processing or high-throughput evaporation techniques.

Liquid crystals (LCs) offer an alternative approach to well-organized continuous layers. In contrast to liquid-to-crystal phase transitions, which are characterized by supercooling and spontaneous crystal nucleation that is hard to control, liquid-to-LC phase transitions show no or little such hysteretic behavior. LC germs can thus be grown in a controlled way close to the phase transition temperature, and their ability to orient their axes preferentially with respect to the substrate may allow the growth of large domains in an optimized orientation for through-layer charge and exciton transport.

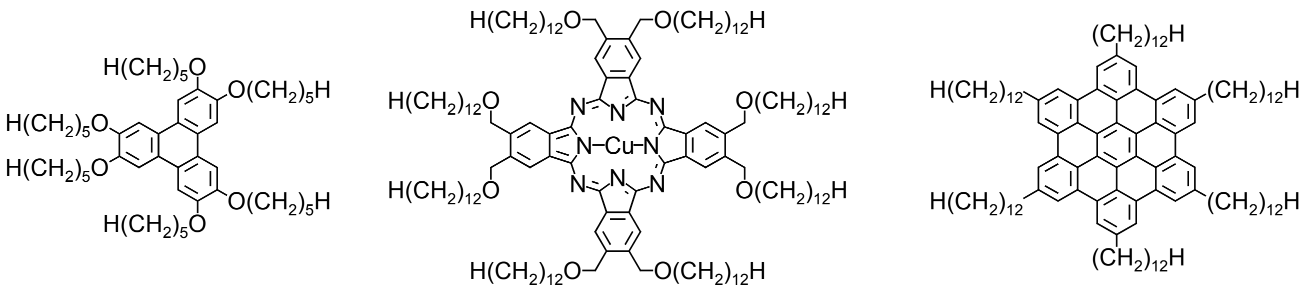
There are three fundamental classes of LCs:

Nematic LCs such as used in most liquid crystal displays (LCDs) are oriented fluids of roughly parallel objects (rod-shaped semi-flexible molecules in most cases) with no long range positional molecular order.

Smectic LCs are made of 2D layers of parallel objects, with long range positional order in one direction (the one perpendicular to the layers) and two fluid-like dimensions (each layer is a 2D fluid).

Columnar LCs[5] are made of stacks of parallel objects, where the stacks or columns form a 2D crystal lattice, and where only one fluid dimension without long-range positional order remains (the stacking direction within the column).

In contrast to smectics and most nematics, most columnar LCs are made of semi-flexible disk-shaped molecules: extended conjugated aromatic planes surrounded by flexible alkyl chains. The two most common classes of columnar LCs are hexasubstituted triphenylenes[6] such as **1**, and octasubstituted phthalocyanines[7] such as **2**. A type of particularly large column-forming hydrocarbon disks are hexabenzocoronenes[8] such as **3**.



1 **2** **3**

Examples for three of the most common types of columnar liquid crystals : triphenylenes, phthalocyanines and hexabenzocoronenes

Whilst nematic LCs are fluid and, given their lack of positional order, do not offer better charge or exciton transport properties than amorphous glasses, some smectic and most columnar LCs are highly viscous materials in which the close vicinity of the aromatic cores of neighboring molecules can give rise to good charge mobilities and exciton diffusion lengths. The value of the charge mobility of typical moderate size columnar materials[9] such as **1** is of the order of 10^{-3} $cm^2V^{-1}s^{-1}$, about four orders of magnitude smaller than pentacene single crystals and around three orders of magnitude higher than polycrystalline pentacene. Larger materials such as **3** show mobilities in excess of 10^{-1} $cm^2V^{-1}s^{-1}$, as measured by a microwave absorption method.[10] But the charge mobilities of columnar liquid crystals depend not only on the size of the aromatic system, but also on the degree of intracolumnar order: Increasingly regular stacking of the disks within a column makes the mobility rise from 10^{-3} $cm^2V^{-1}s^{-1}$ in hexa(pentoxy)triphenylene **1** via 10^{-2} $cm^2V^{-1}s^{-1}$ in hexa(butoxy)triphenylene to 10^{-1} $cm^2V^{-1}s^{-1}$ in hexa(hexylthio)triphenylene, as measured by the time-of-flight technique.[11]

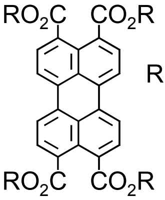
The exciton diffusion lengths along the columns in triphenylene columnar LCs have been found to span about 200 molecules,[12] or 70 nm, similar to the average thickness of an absorptive layer in an organic solar cell.

COLUMNAR LIQUID CRYSTALS WITH DONOR- AND ACCEPTOR-TYPE BEHAVIOR

In contrast to silicon, where absorption-caused excitation of an electron from the valence to the conduction band creates a negative charge that is essentially free to move away from its positive counterpart, excitation of an electron in an organic dye from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) does not create separated charges immediately. The created exciton, or excited electron-hole pair, may hop from the molecule of initial excitation to neighboring molecules, but the two charges remain strongly bound until they reach an appropriate donor-acceptor interface after a number of discrete hops. At this interface, if the steps in HOMO energy level and in LUMO energy level between the donor molecule and the acceptor molecule are bigger than the binding energy of the exciton of around 0.3 eV,[13] the two opposite charges can finally separate and start their journey from the interface to the receiving electrode.

So organic solar cells can only be efficient if they include at least two electronically contrasting organic transport materials, one donor and the other acceptor. This means that if good exciton and charge transport is to be induced by columnar LC organization, both columnar donor-type materials and columnar acceptor-type materials are needed. It has to be noted that donor and acceptor are relative terms: a material of intermediate HOMO and LUMO energy levels may act as donor when combined with a stronger acceptor, and act as an acceptor when combined with a stronger donor.

Most of the established columnar mesogens such as **1**, **2** or **3** are alkoxy-, alkanoyloxy-, or alkyl-substituted arenes with a relatively high electron density in the aromatic core, and electron-deficient columnar systems were virtually non-existent at the end of the last millenium. We set out to synthesize new classes of columnogens with marked acceptor-type structures. One electron-withdrawing type of substituent seemed to have been particularly neglected in the earlier works on columnar LCs: Whereas $Ar(OC(=O)R)_n$-type esters obtained by esterification of oligophenols had yielded a large number of columnar LC families, the reverse structure $Ar(C(=O)OR)_n$ where the electron-withdrawing carbonyl groups are conjugated to the arene π system, had not been explored for columnar mesophases. To our surprise, already the commercially available, and not very disk-shaped, perylene-tetracarboxylic dianhydride (PTCDA), a well-known and widely used deep red acceptor dye, yielded hexagonal columnar LC esters **4** with large temperature ranges.[14] When combined with a hexaalkoxy-triphenylene as donor material, such esters yield bilayer solar cells with open circuit voltages in excess of 1V, reflecting the considerable energy differences between the respective HOMO energies and the respective LUMO energies of the two materials. This confirms that esters such as **4** are electronically quite complementary to conventional donor-type materials.



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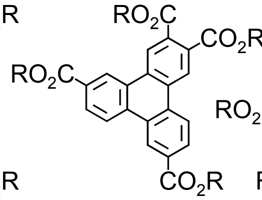

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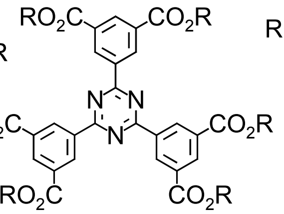

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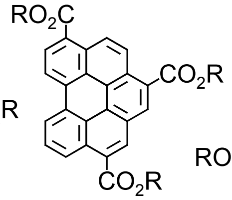

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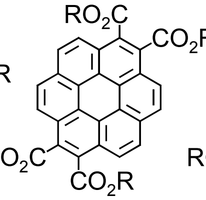

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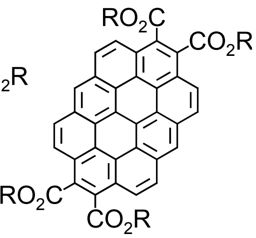

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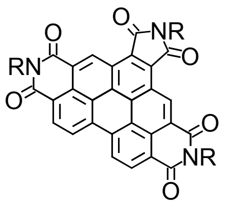
We then explored other such ester systems with other arene cores, and found columnar phases with a broad variety of systems, such as triphenylenes **5**,[15] triphenyltriazines **6**,[16] benzoperylenes **7**,[17] coronenes **8**[18] and ovalenes **9**.[19] To further increase the acceptor-type character of these columnar LCs, we also tried to include N-alkyl dicarboximide groups, known for their even stronger electron-withdrawing effect compared to alkoxycarbonyl substituents, and obtained columnar benzoperylene triimides **10**, benzoperylene diimido-diesters **11** and coronene imido-diesters **12**, whilst others reported that perylene *n*-alkyl diimides **13**[20] and quaterrylene diimides **14**[21] with α-branched alkyl substituents also exhibit columnar phases at elevated temperatures.



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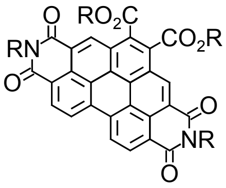

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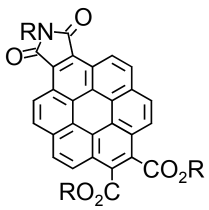

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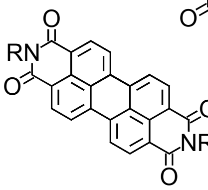

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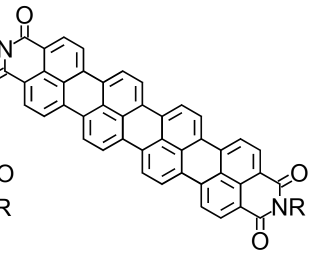

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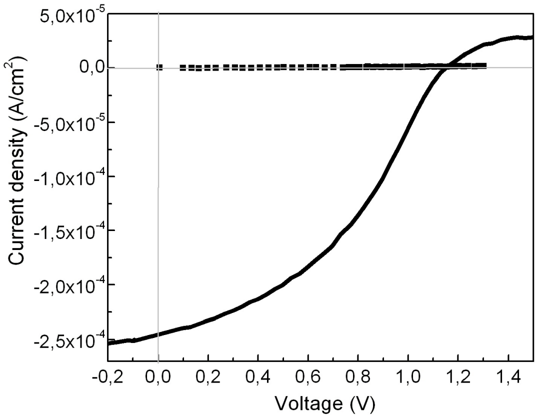
That such imides are much stronger acceptors than the aforementioned esters becomes evident when examples of both classes are combined in bilayer solar cells: When we combined a benzoperylene triimide **10** (with R=3-pentyl) as acceptor with a benzoperylene triester **7** (with R=ethyl), we could obtain a high open circuit voltage (V_{oc}) of 1.16 V, illustrating that when combined with **10**, the triester **7** behaves as donor. Even though these simple solar cells based on a planar donor-acceptor heterojunction were fabricated by conventional thermal vacuum evaporation yet without any attempt to obtain uniformly aligned films of the two materials, they already yielded a short circuit current (I_{cc}) of 0.24 mA/cm^2 and a reasonable fill factor (maximum power divided by $I_{cc} \times V_{oc}$) of 40%, and thus an external quantum efficiency (electrons per photons) of 13% at 400 nm monochromatic irradiation, corresponding to a power efficiency of 2.0% at a light intensity of 5.8 mW/cm^2.[22] Considerably higher currents, better fill factors and thus better efficiencies should be attainable once uniformly aligned layers will be realized in which all column axes and thus the paths of good electron and exciton mobility are perpendicular to the substrate.



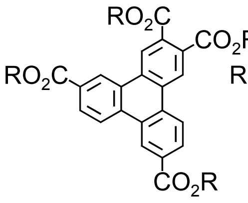
Current-voltage characteristics of an ITO/**7**/**10**/Al cell in the dark (dots) and under λ=400 nm monochromatic illumination (solid line)

COLUMNAR LIQUID CRYSTALS THAT ABSORB VISIBLE LIGHT

The organic layers in a plastic solar cell have not only to be good acceptors and donors with good charge and exciton transport properties, they also have to be efficient absorbers for at least part of the solar spectrum. To absorb a large part of the energetically useful part of the spectrum (c. 400-1000 nm), materials of different absorption wavelength ranges should be combined. Whilst triphenylenes **1** and **5** or triphenyltriazines **6** only absorb at ultraviolet wavelengths, and compounds such as coronenes **8** and **12** or ovalenes **9** suffer from small extinction coefficients, yellow benzoperylenes **7**, **10** and **11**, orange-red perylenes **4** and **13**, blue-green phthalocyanines **2** and near-IR absorbing quaterrylenes **14** show intense absorption bands at useful wavelengths. Combining for example green donor-type phthalocyanines **2** with red acceptor-type perylenes **13** would yield devices that absorb still not all, but a large part of the visible solar spectrum.

COLUMNAR LIQUID CRYSTALS AT ROOM TEMPERATURE

Most materials with a mesophase exhibit their liquid crystalline state at elevated temperatures. Triphenylene **1** for example shows its columnar mesophase between 69 and 122°C, whilst phthalocyanine **2** and hexabenzocoronene **3** are LCs above 53 and 106°C, respectively. If the columnar LC state is to be used in solar cells – in uniformly aligned layers without transport-disrupting crystal grain boundaries – then the liquid crystalline phase should be thermodynamically stable at room temperature. As most known liquid crystalline materials are crystalline at room temperature, the LCD industry systematically relies on mixing multiple components in order to suppress crystallization far below room temperature. This mixture approach is feasible for display applications where only the average optical and elastic properties of the mixture governs the device performance. But as transport properties are intimately linked to the molecule-to-molecule concordance of energy levels, homogeneous mixing is a feasible approach for solar cells only where compounds of sufficiently similar energy levels are combined. This means that mixing of compounds with different alkyl chain lengths or mixing of different electronically similar isomers is promising, but mixing of species with different chromophores or different donating or accepting functional groups is problematic. The probably most secure approach, where mixing is used to suppress crystallization entropically, but where the material remains a single product with regard to analytical spectra, solvent solubility, molecular weight, vacuum sublimation temperature etc, is the use of chiral racemic side chains: A material such as perylene **4** with four racemic side chains is a mixture of 7 stereoisomers which all have quasi-identical physical properties, and less symmetric triphenylene **5** is a mixture of 16 stereoisomers. A lower intrinsic symmetry of the core contributes to lower crystallization temperatures and wider mesophase ranges already with nonchiral chains. This is illustrated by the comparison of four- and three-chain triphenylenes **5** and **15** and coronenes **8** and **16**:



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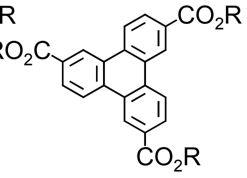

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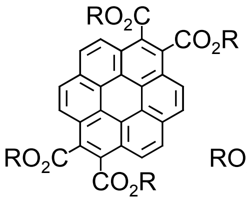

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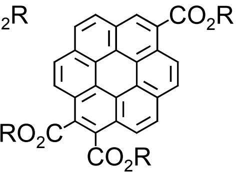

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From **5** to **15** the number of flexible chains decreases and the symmetry increases, and as a consequence, with e.g. R = butyl the columnar mesophase is stable between 49 and 147°C for **5**, whereas for **15**, no columnar mesophase exists at all (only a short-lived monotropic nematic phase is observed). On the other hand, from **8** to **16**, the decrease in chain number is counterbalanced by a decrease in symmetry, and thus the mesophase range of **16** (from 71 to 215°C with R = butyl) is essentially as large as for **8** (88 to 233°C).

The influence of core symmetry on the crystallization temperature is less apparent if the melting points are already suppressed below room temperature by racemic chains: With R = *rac*-2-ethylhexyl, **8** is crystalline up to +12°C, but no crystallization is observed down to –60°C not only with **5**, but also with more symmetric **4** and **9**.

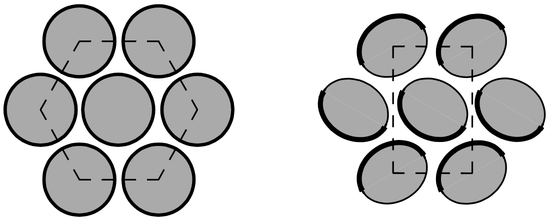
Use of branched racemic side chains thus emerges as an efficient and general approach to columnar mesophases that are stable at room temperature and below. But room temperature liquid crystallinity is not the sole requirement with respect to mesophase range that is crucial for the elaboration of well-arranged columnar films: To be able to uniformly align the liquid crystalline state with respect to the substrate, it is also of great benefit if the material has an accessible LC-to-liquid transition temperature, in order to allow the controlled growth of well-oriented columnar domains during the liquid-to-LC transition. Especially with large cores such as phthalocyanines **2,** hexabenzocoronenes **3** and ovalenes **9** and with cores like **10**, **13** and **14** that only bear imide substituents (whose rigidly fixed in-plane dipoles tend to enforce strong aggregation even at very high temperatures), inaccessibly high clearing temperatures above 300°C are often observed. In such cases, the number or length of the alkyl side chains has to be increased considerably to bring this transition temperature down to acceptable values. Increasing the chromophore size for longer-wavelength absorption or introducing strongly electron-accepting imide groups comes therefore with the additional challenge of introducing more and longer flexible substituents.

PHASE SYMMETRY AND ALIGNMENT

Columnar mesophases can be classified by the symmetry of their column lattice.

The simplest and most common symmetry is hexagonal: As the rotational positions of the disks within their planes are in general disordered, the average disk can be considered to be circular even if the molecular shape is anything but round. As long as the disks are on average perpendicular to the column axis, the columns then will have circular cross sections, and such circular columns pack most efficiently on a hexagonal lattice. Hence most columnar LCs have hexagonal symmetry. In particular, most ethers $Ar(OR)_n$ and arenecarboxylic esters $Ar(C(=O)OR)_n$ tend to form hexagonal phases.

Other symmetries appear if the disks are staggered, i. e. tilted with respect to the plane perpendicular to the column axis. The column cross section then is not circular anymore, and rectangular or oblique column lattices are the result. Such staggered phases are in particular encountered with alkanoyloxyarenes $Ar(OC(=O)R)_n$ and with metallomesogens with a central metal atom, such as phthalocyanines like **2**. In the latter case, staggering is preferred as it avoids direct contact between metal atoms, which prefer to approach a nitrogen atom in each neighboring disk. In most non-hexagonal phases, the tilt directions of the disks alter between adjacent columns, and thus the disks of adjacent columns are not parallel.[23]



Left: hexagonal column lattice, seen along the column axes. Right: example of a hexagonal columnar phase with two groups of columns whose disks tilt into different directions.

The phase symmetry of a given columnar LC has consequences for its alignment on polar surfaces such as electrodes. As the electronically active aromatic part of the molecule is inclined to interact with the polar surface, the disks close to the surface have a tendency to align parallel (face-on) to the surface, which favors the upright (homeotropic) growth of the columns on the surface. Such face-on alignment is mostly observed with hexagonal phases. In rectangular and oblique phases with different tilt directions in different columns, a face-on alignment of all disks is no longer possible, and thus most often an edge-on alignment of the disks, with the columns lying flat on the surface, is observed. The axis of good charge and exciton transport is thus more easily aligned favorably in hexagonal phases than in rectangular ones, and the latter have to be avoided in order to favor homeotropic film growth.

Whilst samples that are heated between two flat substrates (in the simplest case two glass slides) to the isotropic liquid phase and then cooled down again easily align homeotropically if the mesophase is hexagonal, this favored alignment is more difficult to achieve in thin open films on a single solid substrate: Albeit the solid substrate favors the preferred face-on alignment, the LC-air interface strongly favors the unfavorable edge-on alignment, because the aromatic molecular cores prefer to interact with each other and tend to avoid being exposed to air or vacuum. It is nevertheless possible at least with some materials, e. g. with arene carboxylates such as **5**, to achieve homogeneously homeotropically aligned films by adjusting the cooling speed from the isotropic liquid.[24]

CONCLUSIONS AND OUTLOOK

In summary, the recent development by us and others of a variety of acceptor-type columnar liquid crystals, the access to room temperature mesophases with the help of chiral racemic side chains, and the homeotropic alignment of such materials in thin films together provide a basic set of ingredients on the way to a new kind of organic solar cells based on anisotropically self-assembled, efficiently charge and exciton transporting, donor and acceptor layers.

Much more work remains to be done: A greater variety of well-aligning columnar chromophores is needed to be able to efficiently harvest the solar energy at all wavelengths of interest, and especially near-infrared absorbing columnar LCs with low clearing temperatures and subambient melting points still have to be developed. A deeper understanding of the factors that lead to high open circuit voltages is needed, and bi- and multilayer devices with homeotropic alignment in all layers have to be elaborated.

If the efficiency of organic solar cells should one day pass the 10% mark, excellent exciton and charge transport has to be combined with efficient absorption throughout the visible and near infrared spectral range, whilst relying on electronically highly contrasted donor and acceptor materials. The approach presented here is one of the possible answers to this quest.

ACKNOWLEDGEMENTS

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