Liquid Crystals

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Distorted Arene Core Allows Room-Temperature Columnar Liquid-Crystal Glass with Minimal Side Chains**

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A phenanthro[1,2,3,4,*ghi*]perylene-1,6,7,12,13,16-hexacarboxylic hexaester with only methyl and ethyl alkyl chains was obtained in a metastable, columnar, liquid-crystalline state at room temperature. By using racemic swallow-tailed side chains, an electronically complementary triimide was obtained in a thermodynamically stable room-temperature columnar liquid-crystal (ColLC) phase. The concept of mesophase stabilization by atropoisomeric nonplanar chromophores of low inversion barrier is introduced. Concomitantly, the tuning of electronic levels for donor–acceptor heterojunction devices by varying the carboxylic substitution patterns and lateral extensions of perylenic chromophores is illustrated.

Organic heterojunction solar cells are predominantly based on interdigitated bulk heterojunctions,[1] which constitute one way out of the dilemma caused by the low exciton diffusion lengths in disordered organic materials, but the random structures of most bulk heterojunctions include many inactive areas because of the nonideal bicontinuity of the "active" layer.[2] Attempts to use molecular self-assembly to obtain better controlled interdigitation may in principle enhance device performance,[2,3] but in materials in which self-assembly improves exciton diffusion length to an extent that it equals or exceeds the layer thickness, self-assembly may render interdigitation unnecessary altogether. This is the case for columnar liquid crystals (ColLCs), in which the exciton diffusion length along the columns is of the order of 50 to 70 nm,[4] which is similar to the thicknesses of the individual layers of organic bilayer solar cells.[5]

Recently, Thiebaut et al. realized a stack of two homeotropically (i.e. columns upright) aligned ColLCs by sequential spin-coating of two nonmiscible materials followed by thermal annealing.[6] Even though the materials used were not electronically complementary enough to constitute a donor–acceptor pair and even though the layers were thicker than optimal (hundreds instead of tens of nm), this proof-of-principle shows the feasibility of such types of double layers.

Another well-known method to obtain 50-nm thin films is based on slow organic vapor phase deposition (OVPD).[7] This process generally allows the formation of films with highly regular thickness, low loss of products, and enhanced processability.[8] Nevertheless, the vacuum deposition of organic molecular materials is limited to materials of moderate molecular weight to avoid harmfully high evaporation temperatures, whereas all known room temperature columnar liquid crystals bear at least four extended, in most cases racemically branched, alkyl side chains to suppress crystallization and therefore come with a considerable molecular weight.

A more exotic approach to suppress crystallization that avoids this increase of molecular weight would be the use of distorted bistable aromatic cores instead of chiral racemic side chains. [4]-Helicene fragments are known to be nonplanar owing to the overcrowding between the two hydrogen atoms located in the bay region.[9] This arrangement induces configurational multiplicity of the aromatic core, because the energy barrier to switch from one atropoisomer to the other is low enough to allow fast exchange at room temperature.

Herein, we report the use of a [4]-helicene fragment in a core extended perylene to induce enough distortion and flexibility to obtain a room-temperature ColLC with very short alkyl chains: Highly carboxy-substituted phenanthro[1,2,3,4,*ghi*]perylenes[12] were synthesized by quantitative photocyclization of a hexasubstituted 1-(α-naphtyl)perylene (Scheme 1). The new hexaester material **6** features three pairs of vicinal carboxylic groups that allow tuning of electronic properties by replacing up to three pairs of ester groups by imide groups.

Perylene-3,4,9,10-tetracarboxylic tetramethylester is of low solubility in common organic solvents, thus making the slightly longer and well-soluble tetraethylester **5** a better choice of starting material.[13] Its bromination is known to yield a separable mixture of 1,6-dibromo, 1,7-dibromo, 1-bromo, and non-brominated products,[12] from which the monobrominated can be isolated by column chromatography as the product with intermediate polarity.

An ester-functionalized counterpart for Suzuki cross-coupling, 1,8-dicarboxymethyl naphthalene-4-boronic pinacol ester (**4**), was obtained in two steps from 4-bromonaphthalic anhydride (Scheme 1). The two bricks were then cross-coupled by a slow (4 day) but efficient Suzuki reaction. Surprisingly, the resulting hexasubstituted 1-naphthylperylene contains already 15% of cyclized product. The cyclization is then completed by irradiation in the presence of oxidant to yield phenanthroperylene **6** in 78% yield over two steps.

Differential scanning calorimetry (see the Supporting Information) and X-ray diffraction studies on powder of **6** revealed an enantiotopic ColLC phase of hexagonal symmetry between 219 and 247 °C. While in alkyl-, alkoxy-,

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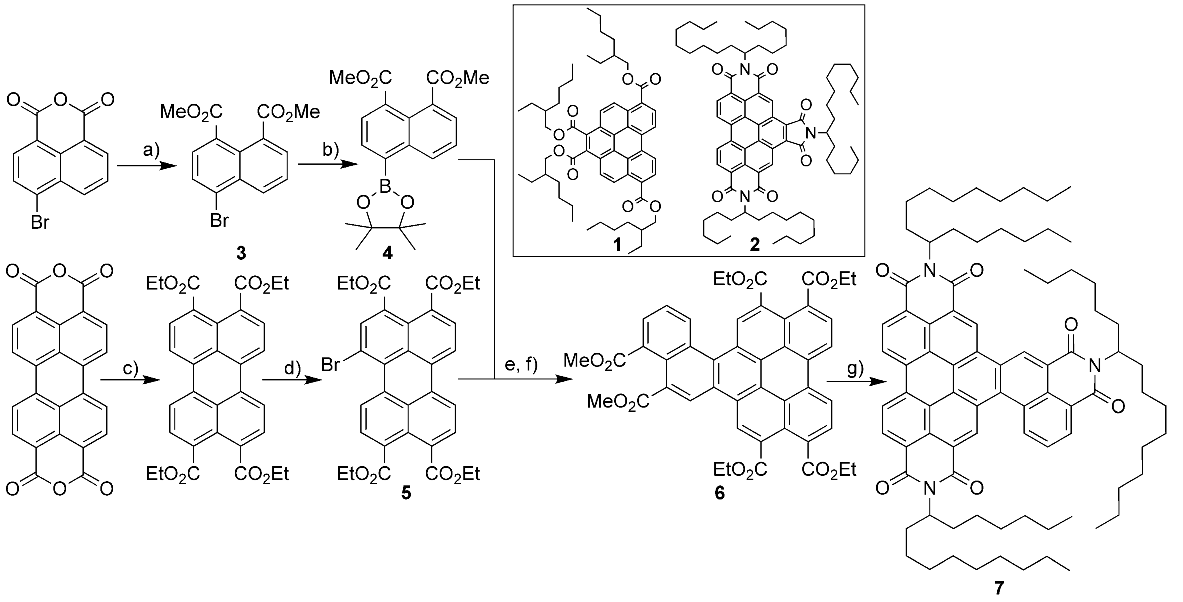

Scheme 1. Synthesis of **6** and **7**: a) MeI, MeOH, 1,8-diazabicyclo[5.4.0]undec-7-ene, 60 °C, 3 h, 75 %; b) bispinacolato-diboron, AcOK, [PdCl$_2$(dppf)], toluene, 80 °C, 16 h, 93 % (dppf = 1,1′-bis(diphenylphosphanyl)ferrocene); c) EtI, EtOH, K$_2$CO$_3$, 82 °C, 3 d, 90 %; d) Br$_2$, K$_2$CO$_3$, CH$_2$Cl$_2$, 25 °C, 7 h, 25 %; e) K$_2$CO$_3$(aq.), [Pd(PPh$_3$)$_4$], 80 °C, 4 d; f) I$_2$, light, toluene, 118 °C, 3 h, then 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, 118 °C, 3 h, 78 % over two steps; g) 7-hexadecylamine, imidazole, 180 °C, 16 h, 34 %.

alkylthio-, and alkanoyloxy-substituted disk-shaped mesogens, alkyl chains of at least five carbon atoms in length are necessary to induce columnar liquid-crystalline self-assembly,[14] we have noted previously that in many alkoxycarbonyl-substituted series, already the ethyl derivatives show a columnar mesophase, albeit always only at elevated temperatures.[15] The dimethyltetraethyl derivative **6** is no exception to that rule. However, in stark contrast to all other known short-chain ColLCs esters, its liquid-crystalline phase is maintained at room temperature after cooling, making it a room-temperature ColLC of small molecular weight. This result was asserted by the powder X-ray diffractogram of **6** (Figure 1), which remains essentially the same as in the enantiotopic columnar phase (230 °C) even 2 months after its quenching from the high-temperature enantiotropic domain to room temperature; only the broad peak at wide angles corresponding to the fluid dimension of the phase, that is, the intracolumnar stacking, shifts from 3.7 Å to 3.5 Å, reflecting the increase of density of the material when cooled by more than 200 °C; contraction-induced shifts in the parameters of the hexagonal lattice and accompanying changes in shape factors are less significant. In the near-absence of chains, the commonly observed broad signature of alkyl chain interactions at around $q = 14\ \text{nm}^{-1}$ is only weakly expressed, whereas an unusual very broad peak corresponding to about twice the disk-to-disk distance is notable at about $q = 9\ \text{nm}^{-1}$ and might tentatively be interpreted as the signature of second-next-neighbor interactions along the columns caused by roughly pairwise stacking so that the thicker, nonplanar tetrahelicenic fragments of neighboring disks are oriented towards opposite sides of the column.

At room temperature, the mesophase is frozen in a glassy state, as shearing of samples between glass slides is no longer possible. In thin films between bare or ITO-covered glass slides (ITO = indium tin oxide), homeotropic growth was observed upon cooling through the clearing temperature, and the hexagonal symmetry of the mesophase was confirmed by X-ray diffraction of a homeotropically oriented sample (Figure 2).

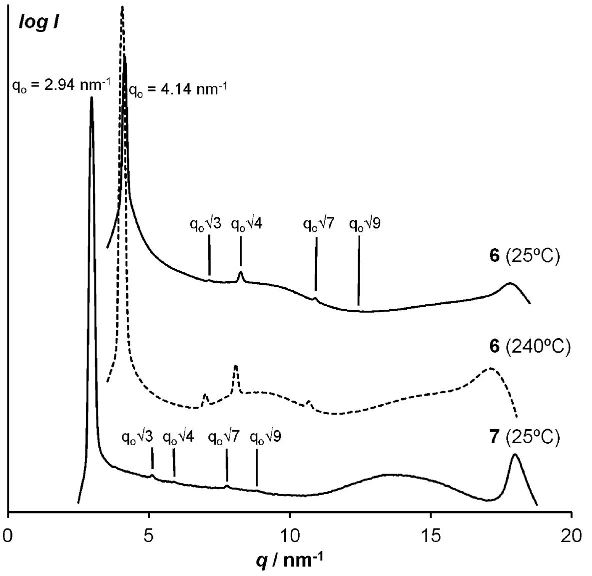

Figure 1. Powder X-ray diffractogram of **6** at room temperature 2 months after quenching from 245 °C, and at 240 °C (dashed), and of **7** at room temperature. Intercolumnar distances: **6**: 1.75 nm; **7**: 2.47 nm.

This result exemplifies that there is an alternative to extended branched side chains as an efficient way to induce enough disorder to obtain glassy ColLCs at room temperature

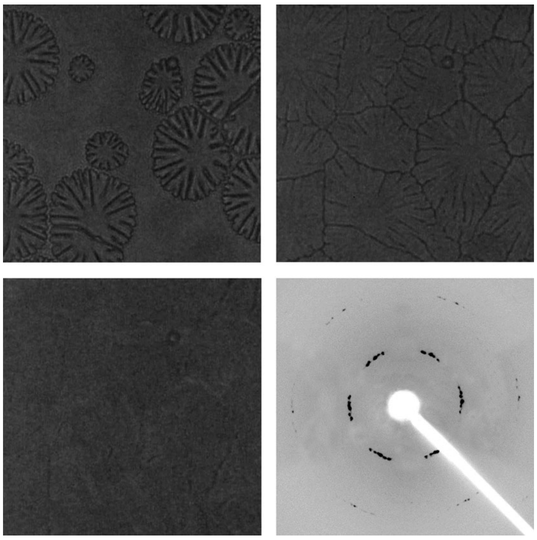

Figure 2. Homeotropic growth of **6** between ITO-coated glass slides as seen by polarized optical microscopy (slightly uncrossed polarizers, contrast enhanced, 0.2 mm×0.2 mm): upper left: at cooling through liquid-to-LC phase transition; upper right: at slightly lower temperature; lower left: at 100 °C. Lower right: X-ray diffraction pattern of a homeotropically oriented sample taken at room temperature between thin glass slides: several domains of slightly different orientations of the hexagonal column lattice in the sample plane are diffracted simultaneously, as the beam width covers more than one domain.

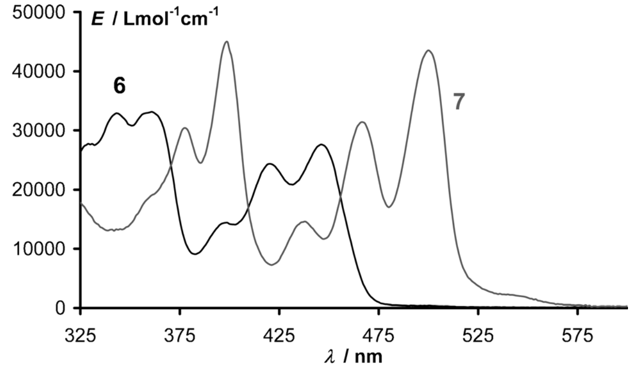

Figure 3. UV/Vis absorption spectra of **6** and **7** in dichloromethane.

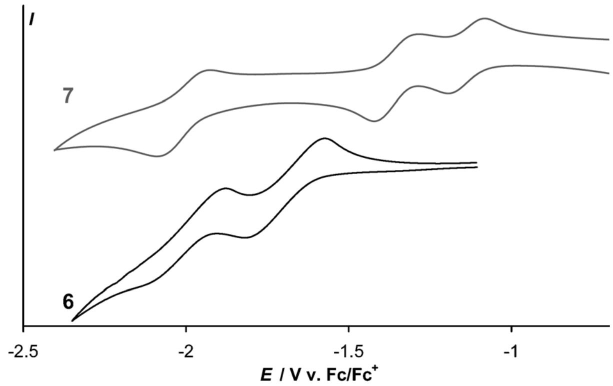

Figure 4. Cyclic voltammetry on 1 mM solutions of **6** and **7** in 0.1 M solutions of Bu_4NPF_6 in dichloromethane. Scan rate: 0.1 Vs^{-1}.

from aromatic chromophores. Compound **6** can be vaporized without decomposition already under moderately reduced pressure, as we could verify with a standard laboratory sublimation apparatus under a vacuum of 10^{-2} mbar at 280 °C, with no difference in the ^{1}H NMR spectrum before and after vacuum deposition. This result implies that under the high-vacuum conditions typically used for device fabrication (10^{-7} to 10^{-5} mbar), **6** will sublime at temperatures not higher than those needed thereafter for annealing at the liquid-to-LC phase transition. Mesogens such as **6** with bistable core conformation and low inversion barrier may thus constitute a preferred choice for low-molecular-weight vacuum deposited ColLC thin films.

To explore the variability of donor/acceptor character with different functionalizations at the carboxylic moieties, we condensed **6** with 7-aminohexadecane (Scheme 1) to obtain a corresponding triimide **7**, which shows an enantiotopic hexagonal columnar mesophase at room temperature with an accessible clarification temperature of 178 °C. Owing to the near absence of side chains in **6**, the intercolumnar distance in the hexagonal organization of **6** (1.75 nm) is about $\sqrt{2}$ times smaller than that of **7** (2.47 nm), equaling to 2 times more chromophores per surface area.

The absorption spectra of **6** and **7** show very similar peak patterns and a considerable 50 nm red-shift of the imide peaks with respect to the corresponding peaks of the ester (Figure 3). The absorption of **6** and **7** is red-shifted by 25 nm relative to those of homologous benzo[*ghi*]perylenes **1** and **2**[10] as a result of the extension of the chromophore.

We performed cyclic voltammetry on both phenanthroperylenes **6** and **7** (Figure 4) to compare their electronic properties with those of benzoperylenes **1** and **2**. As expected, **7** shows stronger electron-acceptor type behavior than **6**. The first reduction potentials of **6** (−1.66 V) and **7** (−1.12 V) are both comparable to their benzoperylene homologues (**1**: −1.73 V and **2**: −1.09 V), leading to similar LUMO energy levels (**1**: −3.44 eV, **6**: −3.51 eV; **2**: −4.08 eV, **7**: −4.05 eV). As **6** exhibits a bathochromic shift of the absorption edge ($\lambda_{\text{offset}} =$ 475 nm) of 25 nm compared to **1** ($\lambda_{\text{offset}} = 450$ nm[10]), its HOMO energy level is shifted relative to that of **1** to yield an improved HOMO energy step with respect to **2** (HOMO energy levels: **1**: −6.50 eV, **6**: −6.42 eV; **2**: −6.91 eV, **7**: −6.56 eV). A heterojunction between **6** and **2** would consequently exhibit near-ideal offsets[11] of 0.57 eV between LUMO and 0.49 eV between HOMO energy levels to enhance charge dissociation at the interface and avoid charge recombination.

In summary, illustrated by the use of a [4]helicene-containing phenanthroperylene, we have shown that the incorporation of configurationally ambidextrous elements, such as atropoisomeric moieties of low racemization barrier, in the aromatic system itself constitute a viable approach to stabilize liquid-crystalline mesomorphic self-assembly at room temperature. Large, disorder-inferring lateral substituents can thus be eliminated and low molecular weights, which are preferable for vacuum deposition into optoelectronic devices, can be obtained. We also demonstrated how the combined effects of the variation of carboxylic substitution and of the lateral extension of perylene-type chromophores can be tuned to obtain electronically tuned donor–acceptor couples for organic heterojunction devices.

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