A liquid-crystalline fullerene–oligophenylenevinylene dyad which displays columnar mesomorphism†

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The design, synthesis and liquid-crystalline properties of a family of hybrid compounds which are built from rod-like (oligophenylenevinylene) and disc-like [poly(benzyl ether)] units are reported. All compounds form columnar phases within broad temperature ranges; the mesophases are stable even below room temperature. Weak photovoltaic effect was observed for the C$_{60}$–OPV dyad. For the molecule having a terminal OH group, frustration of the hexagonal packing was observed and gave rise to a rare phase sequence. For this material, a columnar phase with trigonal symmetry and doubling of the crystallographic lattice was found below the hexagonal columnar phase.

Introduction

The design of functional materials for the development of the nanotechnology by the bottom-up approach has attracted growing interest in the scientific community. Liquid crystals are important materials in this area as their properties can be tuned and controlled at the molecular level up to a high degree of sophistication. As a consequence, liquid crystals have made possible the development of devices with tailor-made properties. Obviously, a detailed understanding of the characteristics and performances of the devices requires that the supramolecular organization of the liquid-crystalline components be known. For complex molecules, the molecular structure-supramolecular organization relationship is often difficult to establish.

Molecular shape is one of the key factors which determines the type and structure of liquid-crystalline phases: rod-like mesogens preferably form lamellar phases, whereas disc-like molecules have the tendency to form columnar phases. The hexagonal columnar phase, the most common columnar phase, is also found for molecules that do not have a well-defined disc-like shape, such as polycatenars and dendrimers. To generate more complex columnar phases, self-segregation at the sub-molecular level has to be considered. In this context, strong activity is devoted to the synthesis and study of hybrid materials which carry geometrically and/or chemically incompatible units and which are able to display unusual organizations such as laminated smectics, lamello-columnar phases, kagome columnar phases, trigonal columnar structures or hexagonal super-lattices. Unusual phase sequences can also be obtained.

The fluidity of the mesophases makes them sensitive to external stimuli and allows the construction of mechanically/electrically/magnetically tuneable systems showing electron transport, fluorescence and lasing. For example, there are attempts to design liquid crystals for application in photovoltaics by introducing strong electron donors and electron acceptors within a single mesogenic molecule in order to benefit from spontaneous nano-segregation which leads to large heterojunction surfaces.

[60] Fullerene (C$_{60}$) is an effective electron acceptor unit and was successfully used for photovoltaic applications as an n-type semiconductor in combination with a p-type π-conjugated polymers or oligomers. The performances of this type of devices depend on the morphology of the film because of the phase separation which could lead to ineffective charge mobility. Interestingly, for fullerene-containing thermotropic liquid crystals, electron transport within layered mesophases has been observed. This result indicates that C$_{60}$ can be an effective component in photovoltaics based on liquid crystal technology. However, higher charge mobility can be expected within columnar phases. Thus, the design of fullerene-containing liquid crystals, which show columnar mesomorphism, in which C$_{60}$ is covalently linked to an electron donor unit is a conceptual challenge in synthetic chemistry. Indeed, to the best of our knowledge, such materials have not yet been reported.

Functionalization of C$_{60}$ with liquid-crystalline dendritic addends allowed the control of the mesomorphic properties as the bulky, hard C$_{60}$ core is hidden in the dendritic matrix. On the other hand, liquid-crystalline poly(benzyl ether) dendrons are ideal mesomorphic promoters for the design of C$_{60}$ derivatives which display columnar mesomorphism.

We describe, herein, the synthesis, liquid-crystalline properties and supramolecular organization of a family of materials
Results and discussion

Synthesis

The synthesis of 1–4 required the preparation of the OPV derivative 5 (Scheme 1). Reduction of compound 6 gave bis- alcohol 7 which was reacted with carboxylic acid derivative 8 to give alcohol 9. Esterification of the latter with benzoic acid derivative 10 provided monoprotected OPV 5. The assembly of the basic building blocks is shown in Scheme 2. Condensation of 5 with monoacid 11 gave protected intermediate 1. Deprotection of the latter with Zn(BF4)2 led to phenol derivative 2 which reacted with third-generation dendrimer 12 to give malonate-based dendrimer 3. Finally, addition of 3 with C60 under Bingel reaction conditions gave C60–OPV dyad 4. The liquid-crystalline properties and X-ray structural studies

The liquid-crystalline properties and X-ray (XRD) data of compounds 1–4 are reported in Table 1. No crystallization or glass transition was detected when the samples were supercooled below room temperature. They all show hexagonal columnar phases (Col6) of p6mm symmetry (Fig. 1) with similar lattice parameters: a ≈ 45 to 47 Å (Table 1). The lattice size is only weakly temperature dependent with a negative thermal expansion coefficient lower than 0.1 Å K⁻¹. There is no difference in lattice parameters for compounds having one or two dendrons in their structure. In both cases, the column diameter corresponds roughly to the size of the disc-like molecular fragment. Apparently, for compounds 1–4, the columnar cross-section is made of a single dendritic unit while the rod-like building blocks are randomly distributed between the columns (Fig. 1c). In the case of compounds 3 and 4 which have two dendrons per molecule, the unit cell contains half of the molecule, and the structure can be considered as intercalated molecular. Such intercalation is characteristic for molecules bearing more than one discotic unit.²⁹ To further study the supramolecular organization, polarized IR experiments were performed on samples which were aligned by shearing. The anisotropy of the phenyl stretching signal (D, defined as the ratio of signal intensity for light polarized along and perpendicular to the column axis) is rather weak, i.e. D ≈ 0.6, despite a nearly perfect alignment of the samples (Fig. 2). This result suggests that the molecules have a high degree of internal molecular motion. The columns should be pictured as regions where the dendritic parts of the molecules are collected rather than a stacking of flat objects, and the whole structure as a result of nano-segregation of incompatible molecular fragments. Even a lower anisotropy, i.e. D ≈ 1.1, was obtained for the signals related to CH2 symmetric and asymmetric stretching modes, showing molten state of terminal alkyl chains.

While compounds 1, 3 and 4 display only one mesophase, compound 2, bearing an OH group, shows a richer mesomorphism. Indeed, on cooling the sample from the highest-temperature Col6 phase, the latter transforms into another columnar phase with doubled lattice parameter (Col6D6, D6 stands for doubled). However, there is no noticeable

Scheme 1 (i) LiAlH4, THF, rt, 2 h, 76%; (ii) N-(3-dimethylaminopropyl)-N-ethylcarbodiimide (EDC), 4-(dimethylamino)pyridinium p-toluenesulfonate (DPTS), CH2Cl2, 0 °C and then rt, overnight; yield: for 9, 40%; for 5, 55%. 

![Scheme 1](image-url)

[Diagram of chemical reactions and structures]
Scheme 2  (i) N,N'-Dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridinium p-toluenesulfonate (DPTS), CH₂Cl₂, 0 °C and then rt, overnight, 96%; (ii) Zn(BF₄)₂·6–7H₂O, THF/H₂O, 50 °C, 24 h, 73%; (iii) DCC, DPTS, CH₂Cl₂, 0 °C and then rt, overnight, 92%; (iv) 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), I₂, toluene, rt, overnight, 69%. 
Table 1  Phase-transition temperatures (in °C, heating runs), enthalpy changes (between parentheses in kJ mol⁻¹) and X-ray data

<table>
<thead>
<tr>
<th>Phase sequence</th>
<th>Unit cell</th>
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<tbody>
<tr>
<td>1 Col₉ 69 (8.3) I</td>
<td>$\alpha = 46.8$ Å at 50 °C</td>
</tr>
<tr>
<td>2 Col₁₂₈ 48° Col₁₆₈.₆ 66° Col₁₈₈ 80 (10.1) I</td>
<td>Col₁₂₈, $\alpha = 46.0$ Å at 70 °C; Col₁₆₈.₆, $\alpha = 94.7$ Å at 50 °C; Col₁₈₈, $\alpha = 99.4$ Å, $b = 164.5$ Å at 30 °C</td>
</tr>
<tr>
<td>3 Col₁₈₄ 104 (21.8) I</td>
<td>$\alpha = 47.1$ Å at 30 °C</td>
</tr>
<tr>
<td>4 Col₁₉₄ 94 (19.4) I</td>
<td>$\alpha = 45.8$ Å at 70 °C</td>
</tr>
</tbody>
</table>

*From X-ray studies (not detected by DSC).*

![X-Ray diffraction pattern for compounds 1 (a) and 3 (b) having one or two dendron units per molecule; the signals coming from hexagonal lattices for both materials are nearly at the same position. The corresponding lattice parameter is 46.8 Å and 47.1 Å for 1 and 3, respectively. (c) Electron density map for compound 3 in the Col₉ phase reconstructed from X-ray data by reverse Fourier transform taking positive square root of signal intensity as structure factor; the regions of higher electron density (columns) are made of dendrons, the regions of lower electron density are filled by rod-like fragments and aliphatic terminal chains. The size of the map is 25 × 25 nm².](image-url)

**Fig. 1**

![Absorption of polarized IR light (arbitrary units) for aligned sample of compound 1. Observed absorption bands at 1514 cm⁻¹ and 2852 cm⁻¹ are due to phenyl stretching and CH₂ symmetric stretching modes, respectively. Lines are guides for eye.](image-url)

Fig. 2 Absorption of polarized IR light (arbitrary units) for aligned sample of compound 1. Observed absorption bands at 1514 cm⁻¹ and 2852 cm⁻¹ are due to phenyl stretching and CH₂ symmetric stretching modes, respectively. Lines are guides for eye. Modification of the texture at the Col₉-Col₁₂₈₆ phase transition (Polarized Optical Microscopy) is not measurable enthalpy change ($\Delta H < 0.01$ J g⁻¹). Doubling of the crystallographic unit cell is signified by the appearance of a few additional signals in the X-ray pattern (Fig. 3). In the Col₁₂₈₆ phase, the most intense signal [indexed as (20)] remains at the same position as the (10) signal of the Col₉ phase. The intensity of the (10) signal of the Col₁₂₈₆ superlattice is below 10% of the main (20) signal intensity, evidencing that doubling of the crystallographic lattice parameter is caused by additional, weak electron density modulation superimposed on the basic hexagonal structure. Possibly, as the temperature decreases, the rod-like molecular fragments become long-range positionally ordered in the lattice. The phase transition occurs by a stepwise increase of their correlation length. In the Col₉ phase, some short range order of rod-like units is already present (correlation length ~100 Å is comparable to the lattice parameter) as indicated by the weak diffused lowest-angle signal in the X-ray pattern (Fig. 3b). In the postulated structure of the Col₁₂₈₆ phase, the rod-like units of three neighbouring molecules are collected together. However, this requires that every fourth molecule is frustrated and the...
position of its rod-like unit is randomized around discs (Fig. 3d). The electron density map, reconstructed from the X-ray data (Fig. 3c), is consistent with the postulated molecular packing. In order to obtain the electron density distribution, reverse Fourier transform of the X-ray pattern was performed, taking the square root of signal intensities as structure factor amplitudes. Unfortunately, for soft matter there is no unambiguous algorithm to find structure factor phases due to a limited number of signals in the X-ray patterns. In the reverse Fourier transformation performed here, the phases of structure factors related to signals coming from the basic hexagonal lattice were taken as 0 (as in the case of the map for CoL, phase shown in Fig. 1c), while the phases of structure factors related to additional signals coming from the superlattice were taken as ±π/2. This choice allowed the differentiation of electron density in regions between columns. Among several simulated electron density distributions the one matching the proposed structure model was chosen, the other maps had non-realistic electron density that do not agree with the molecular structures. It should be noticed that although the structure of the CoL3DB phase has trigonal p3m1 symmetry, its X-ray pattern shows p6mnm symmetry, as the non-resonant X-ray diffraction cannot distinguish between trigonal and hexagonal symmetries. On further cooling the sample, the hexagonal lattice of the CoL3DB phase deforms continuously into a rectangular one (CoL3DB), in which the double lattice periodicity is preserved. Distortion from the hexagonal structure measured as ratio of unit cell parameters is small: \( bla = 1.66 \) was found in the CoL3DB phase, while for the hexagonal lattice, \( bla = \sqrt{3} \) is expected. It should be mentioned that all liquid-crystalline phases observed for compound 2 are fluid with liquid-like order inside the columns. Due to steric reasons, the molecules freeze their rotation, preserving short range positional order along the columns.

Compound 2 behaves differently than the other materials, most likely, because of hydrogen bonds between the OH groups which help to collect rod-like fragments in the inter-columnar space and allow for their long-range 2D order. The molecules terminated with the silane group, i.e., 1, or a second dendron, i.e., 3 and 4, have more freedom to distribute their rod-like units randomly around the columns. Thus, non-long-range structure of rods is formed in the hexagonal lattice made of columns.

**Photovoltaic studies**

Square wave voltammetry performed for dyad 4 in TBAHFP/THF solution shows that the electrochemical gap, that is, the energy difference between the first reduction step of C60 and the oxidation of OPV unit, is comparable to the energy of photon of visible light (Fig. 4). The relatively small electrochemical gap (1.7 eV) gives a strong hint that the photoexcited state of compound 4 might relax by a non-radiative mechanism to the charge separated state with electrons on C60 and holes on OPV. Indeed, large decrease of fluorescence intensity (by a factor of 7) and shortening of fluorescence lifetime were observed for compound 4 in comparison to the C60-free precursor 3 (Fig. 5).

The formation of a charge-separated state was confirmed by a small but clear photovoltaic effect in the liquid-crystalline state (Fig. 4). In the experiment, the sample was deposited onto an ITO electrode as a thin film and covered with conductive solution; the system was exposed to increasing voltage and periodically illuminated. The low value of photocurrent might be explained by poor space separation of the OPV and C60 units, causing fast charge recombination.

**Conclusions**

We have shown that rod-disc hybrid mesogens easily form columnar phases, even if they contain a bulky C60 cage in the molecular structure. Competition between steric interactions and hydrogen bonding might cause frustration in hexagonal lattice. In order to reduce the frustration, the system develops additional order of rods superimposed on the hexagonal columnar structure of discs. Fullerene derivative 4 shows photovoltaic effect in the columnar phase. The effect is small since there are not well-defined ‘channels’ in the structure transporting electrons and holes.

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