

TTF-based bent-core liquid crystals†

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The synthesis and characterization of bent-core liquid crystals which incorporate TTF groups is reported; different bent-core mesophases are induced depending on the molecular structure and properties derived from their compact packing have been studied.

Of the many π -functional units that are employed in molecular materials, tetrathiafulvalene (TTF) and its derivatives are heterocyclic systems which are particularly interesting from a number of viewpoints, especially because they can be oxidized to produce conducting materials through their π -stacked columnar arrangement. Intensive studies have focused on TTF for the preparation of conductive materials in bulk and thin film states.¹ Furthermore, TTFs are also very useful for sensors, molecular switches, NLO responses, OFETs^{1c,2a} or in the nanoscience area,^{2b} especially with regard to molecular electronics. It has been stated that TTF-based materials offer widespread potential and versatility through incorporation of the π -rich redox-active building block into materials.^{1c} The control of the supramolecular arrangement in shape and size is the key to success in this area. Thus different self-assembling approaches, using non-covalent interactions, gelification or liquid crystal phases, have been used to organize this moiety.^{1,2}

Liquid crystals are of great interest not only for their well-known applications in devices but also, because they are drawing the attention of fields such as biology, medicine, physics, chemistry and materials science. Mesophases offer soft phases with lamellar, columnar or cubic arrangements³ and a current goal is to use the fourth state of matter to achieve ordered functional systems.

In 1996, a new type of mesogenic material appeared, the so-called bent-core liquid crystals.⁴ Bent-core molecules are of prime interest in liquid crystal research because of their special properties, which arise from their unique molecular structure and their compact packing that restricts rotational freedom. Features such as the occurrence of polar order within layers or columns, as well as the appearance of some supramolecular chiral structures from non-chiral molecules are of fundamental scientific interest. Sometimes the chirality can be switched under external electric fields. Furthermore, these mesomorphic materials give rise to antiferroelectric, ferroelectric⁴ or non-linear responses,⁵ often with exceptional values for the relevant parameters. Mesomorphic properties result from a suitable combination of the shape of a molecule and the magnitude and direction of the molecular interactions. The few examples reported show that the high tendency of TTF moieties to stack allows classical mesophases, through a proper molecular structure.^{1c,6} Here, we report the synthesis and characterization of three bent-core liquid crystals which incorporate TTF (Fig. 1). Additionally, these new compounds add to the scarce polycatenar bent-core materials reported⁷ which interestingly induce axially polar columnar mesophases. We have found that different bent-core mesophases are induced depending on the molecular structure and that they show properties resulting from their compact packing.

These compounds were prepared following synthetic routes reported⁸ or adapted from the literature (see ESI†). The phase sequences of the compounds were determined by polarizing optical microscopy and differential scanning calorimetry. The different mesophases of **I**, **II** and **III** were assigned on the basis of the textures observed by optical microscopy (Fig. 2), as well

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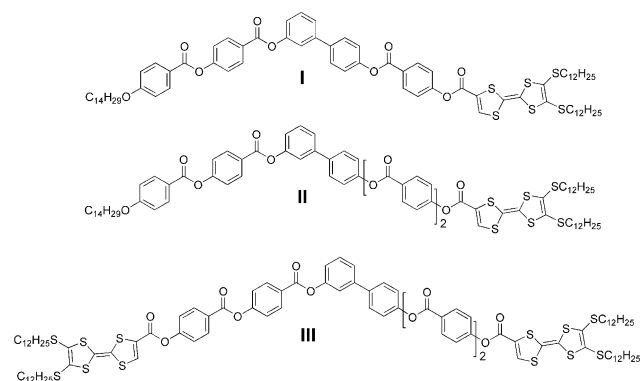


Fig. 1 Chemical structure of the compounds **I**, **II** and **III**.

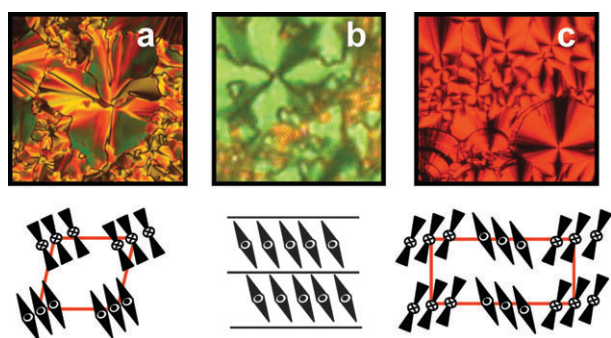


Fig. 2 Textures (top) and possible molecular packing within the mesophases (bottom) for: (a) **I**, Col_{ob}; (b) **II**, SmCP under electric field and (c) **III**, USmCP.

Table 1 Phase sequences for compounds **I**, **II** and **III**

Compound	Phase transition ^{ab} /°C [kJ mol ⁻¹]
I	C 101.0 [25.5] Col _{ob} 117.6 [17.9] Is
II	C 96.5 [26.7] SmCP 158.1 [23.4] Is
III	USmCP (g) ~ 90 USmCP 172.6 [4.3] Is

^a Data determined by DSC from first scans at scanning rate of 10 °C min⁻¹ on heating. ^b C: crystalline solid, Col_{ob}: oblique columnar mesophase, SmCP: SmC polar mesophase, USmCP: undulated SmCP mesophase, g: glassy mesophase, Is: isotropic liquid phase.

as from X-ray patterns taken in the mesophase. The results of these studies are collected in Tables 1 and 2.

These compounds exhibit bent-core liquid crystalline phases within a significant temperature range. X-Ray diffraction patterns showing a diffuse peak at wide angles were obtained for the three compounds, suggesting the mesophase order. Small-angle X-ray diffraction diagrams from **I** revealed an oblique lattice consistent with a Col_{ob} arrangement, where layer fragments form the columns (Fig. 2). For **II**, diffraction patterns show two peaks, which correspond to the 1st and 2nd orders of a given periodicity; the difference between the measured layer thickness (51 Å) and the estimated molecular length (70 Å) indicates molecular tilting in the layers, thus a SmCP phase is proposed. Small-angle X-ray diffraction experiments for **III** show peaks that were indexed on the basis of a rectangular lattice. The existence of a strong (01) reflection indicates a clear smectic character. An anharmonic undulated smectic phase is proposed. Fig. 2c shows one of the possible structures compatible with Fourier analysis of the intensities.⁹ Other possibilities for the molecular packing of **I** and **III** can be obtained by changing the distribution of the polarization directions of the blocks, being compatible with an antiferroelectric ordering (see below). The precise polarization

Table 2 X-Ray data for compounds **I**, **II** and **III**

Compound	Measured spacing/Å	Parameters
I	(01) 46.81, (10) 37.76, (11) 32.99, (11) 26.75, (02) 23.40	$a = 39 \text{ \AA}$, $c = 48 \text{ \AA}$ $\beta = 78$
II	(01) 51.80, (02) 25.26	$c = 51 \text{ \AA}$
III	(20) 72.72, (01) 52.45, (11) 49.35, (31) 35.51, (02) 26.15	$a = 141 \text{ \AA}$, $c = 52 \text{ \AA}$

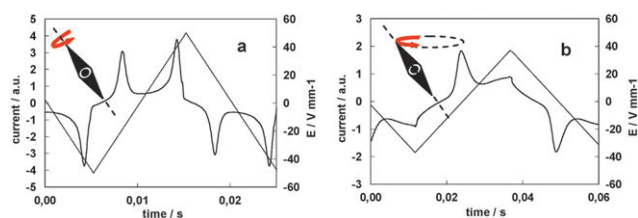


Fig. 3 Polarization switching current under a triangular-wave electric field and mechanisms proposed for the polar switching of **I** (a) and **II** (b).

directions of the columns cannot be determined with non-resonant X-ray diffraction. Compounds **II** and **III** are no longer fluid below some temperature but the diffuse peaks remain. This fact confirms the vitrification of the mesophases.

An attractive feature of some bent-core liquid crystalline phases is their switching response under electric field. This behavior was investigated for **I**, **II** and **III** within 5 μm ITO-coated cells. Upon application of a triangular-wave field an antiferroelectric-like switching current response (Fig. 3a), but without texture changes, was detected for **I**. This implies that the switching occurs around the long molecular axis. A ferroelectric-like switching current response was observed for **II** (Fig. 3b), but second harmonic generation (SHG) activity disappears when the field was off, suggesting an antiferroelectric ground state. Spontaneous polarizations around 400 nC cm⁻² were measured for **I** and **II**. No appreciable switching was observed for **III**.

SHG signals in unaligned cells of **I** and **II** under electric fields of 30 V μm⁻¹ were about 5 times larger than SHG intensities in classical bent-core liquid crystals in the same conditions.¹⁰ This corresponds to second-order dielectric susceptibility coefficients $d \approx 20 \text{ pm V}^{-1}$. Compound **III** was SHG inactive, at least under electric fields below 20 V μm⁻¹ (damage threshold).

The 1st and 2nd one-electron oxidation potentials of these TTF derivatives in solution are at approximately 0.66 and 1.06 V, respectively (see ESI†).¹¹ Both redox processes are reversible. The presence of carboxy groups reduces the donor ability of the TTF core of the molecules in comparison with others of the TTF family.^{8b,12}

The conductivity of one of the compounds (**II**) has been studied (Fig. S5†). The material shows a clear photoconductivity upon illumination with UV light. In the mesophase the ratio between photo and dark currents is larger than in the other phases (Fig. S6†), suggesting electronic conduction.^{9a}

In summary, we have succeeded in the preparation of innovative polycatenar π-functional bent-core liquid crystals. Depending on the molecular structure, close-packed lamellar and columnar arrangements can be induced, which could provide a significant orbital overlap of the π-rich redox-active building blocks within these structures. Furthermore, the dielectric and optical response of these materials, as well as the redox properties of these compounds, confirm this new type of TTF-based liquid crystals as a potential strategy for new functional materials.

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