Bent-core liquid-crystalline derivative of tetrathiafulvalene: Photoresponsivity and deracemization

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A bent-core mesogen containing a tetrathiafulvalene group is studied. The mesophase is an optically isotropic spongelike smectic phase without optical activity. The material responds to uv light in a peculiar way, showing photoconductivity and, in some circumstances, changing its mesomorphic properties. Under an electric field, large chiral domains are segregated from an initial racemic phase within a few minutes.

The incorporation of electro- and photoactive units into soft materials is an attractive method for the preparation of systems which may function in molecular electronics [1,2]. The processing of the materials can be influenced by temperature and physical fields, which provide a useful way to modify their behavior. Tetrathiafulvalene (TTF) and its derivatives may be considered among the most prominent components of these systems, providing many good organic conductors and superconductors. These systems behave as excellent electron donors, and work on the basis of the π-π overlap of the constituent molecules, which usually crystallize forming chains or stacks due to the strong interaction between sulfur atoms [3,4]. Semiconductors obtained from TTF derivatives are p type and have allowed, for example, the implementation of organic field-effect transistors (OFETs) [5,6], where the TTF derivative connects the source and drain electrodes, and an n-type Si semiconductor substrate constitutes the gate terminal. Furthermore, due to the strong photoresponsivity of the employed TTF derivative, some of these OFETs operate also as phototransistors, showing a clear increase of the drain current, for constant drain and gate voltages, when the device is illuminated with white light [6].

A further step in the investigation of new organic materials with good charge transport properties is the synthesis of liquid-crystalline derivatives of TTF. However, although this strategy seems to be rather obvious, only a few mesogenic compounds derived from TTF have been reported up to now. These are calamitic and diskotic liquid crystals with the TTF moiety at the center of their molecular cores [7–10]. The former present nematic and smectic-A (SmA) mesophases in different temperature ranges, while rectangular columnar phases have been proposed for the diskotic compounds. Some of these materials show Ohmic response under dc voltages, and very low ac conductivity, mainly dominated by ionic impurities [9]. Others, however, exhibit fast electronic conduction with mobilities as high as 1 cm^2 V^{-1} s^{-1}. Successful OFET operation has been reported in a few cases [11].

In order to improve the potentialities of TTF-based liquid crystals we have designed a bent-core molecule based on

these moieties. Bent-core liquid crystals have been the object of intensive study over recent years due to their interesting and unusual properties [12–16]. Among these, some peculiar characteristics are the good degree of polar stereocontrol, the high nonlinear optical efficiency, and chiral segregation even when the molecular constituents are achiral.

In this work we have focused on the study of a tilted lamellar mesophase with macroscopic polarization within each layer (SmCP phase). This phase presents structural chirality as a consequence of the molecular tilt with respect to the smectic plane normal. The reason for the study is twofold since, on the one hand, the good packing of the bent-core molecules within the layers can enhance the charge transfer properties of TTF groups and, on the other hand, the mesomorphic properties of this kind of material present a high sensitivity to chemical structure modifications that very often give rise to new interesting properties. In this respect, in the present work we have observed a very remarkable chirality segregation induced by the electric field. This effect is clearly detectable due to the dramatic change of the mesomorphic properties induced by uv light illumination which gives rise to an optically isotropic liquid-crystalline phase.

In this paper, we report on a structural characterization of the mesophase when the material is subjected to an electric field and/or uv light. The study is based on texture observation and x-ray diffraction measurements. Additionally we have investigated some photoconductivity properties and several characteristics of the deracemization process under an electric field.

The chemical structure and phase sequence of the studied compound on cooling appears in Fig. 1. The synthetic procedure for the compound will be described elsewhere. The phase assignment has been made on the basis of differential scanning calorimetry, small-angle x-ray diffraction, and second harmonic generation (SHG) measurements together with texture observations. The x-ray diffraction pattern of the mesophase shows two peaks, which correspond to the first and second order of a given periodicity compatible with the layer spacing implying a microscopic SmCP structure. The experimental details are reported in Ref. [17].

For texture observation, samples were prepared in commercially available cells (Linkam) with nominal thickness of
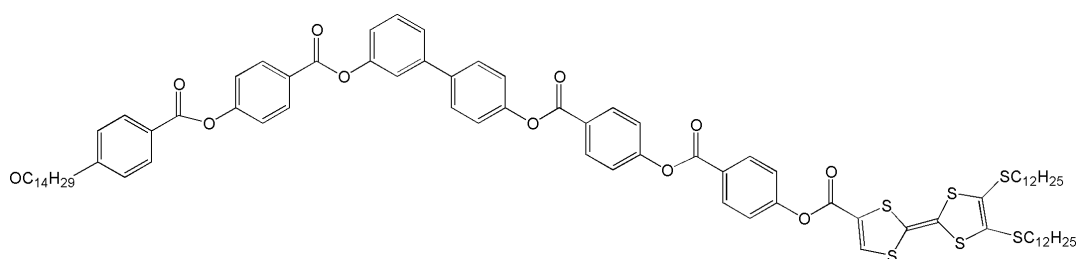
Isotropic 155.8 ºC **SmCP** (sponge like) 65 ºC **Glass**

FIG. 1. Chemical structure and phase sequence on cooling of the studied compound.

5 μm and indium tin oxide electrodes of area 0.81 cm^2. On cooling from the isotropic into the SmCP phase, the material exhibits a black texture hardly distinguishable from the isotropic liquid by simple observation on the polarizing microscope [see Fig. 2(a)]. No chiral domains are observed when uncrossing the polarizers, which indicates a racemic structure. This isotropic racemic texture is not usual though it has been reported before in some bent-core mesogens [18–21]. After applying an electric field of 10 V μm^{-1}, very small bright birefringent domains appear [see Fig. 2(b)] with high birefringence, which indicate a synclinic arrangement. On removal of the electric field, the domains present a gray color [Fig. 2(c)] with smaller birefringence corresponding to an anticlinic structure. It is important to point out that the virgin dark texture is not recovered once the electric field has been removed. Therefore, it can be concluded that the material undergoes a field-induced phase transition from a presumably spongelike dark phase, the racemic version of the dark conglomerate, to an anticlinic antiferroelectric smectic phase (SmC$_A$P$_A$) which is stabilized by surface effects. The antiferroelectric character of the field-induced ground state was confirmed by the disappearance of the SHG signal on removing the field.

We also carried out photoconductivity studies in this material by measuring the sample electrical resistance. For the experiment a 10 MΩ resistor was set in parallel to the sample and the equivalent resistance was measured by using a HP 34401A multimeter. Prior to the irradiation with uv light the resistance was measured from room temperature up to appearance of the isotropic liquid. The sample resistance values appear in Fig. 3. As expected, conductivity increases

with temperature, and in the glassy state the material presents very large resistance. After this preliminary characterization the sample was illuminated with an ELC-403 halogen lamp (Electro-lite Co.) and the irradiation on the sample in the wavelength range 340–380 nm was about 50 mW cm^{-2}. The inset of Fig. 3 shows the conductivity behavior versus time of the sample upon illumination in the mesophase (open circles, 135 °C) and the isotropic liquid (solid circles, 160 °C). As can be seen, the conductivity increases noticeably in the light-on state. This effect is especially remarkable in the SmCP phase, where the increment is larger than one order of magnitude. Photoconductivity is also observed in the low-temperature glassy state but the effect is less important (the conductivity is about twice larger for the illuminated sample). In all phases the effect is reversible and its response time is much shorter than 1 s. During the illumination process the sample texture remains unaltered. The conductivity values are similar in the virgin dark state as in the field-induced SmC$_A$P$_A$ phase. The general features of the
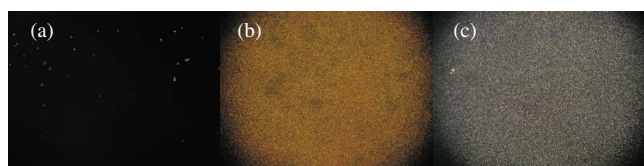

FIG. 2. (Color online) Textures exhibited by the compound on the polarizing microscope. (a) Dark texture obtained on cooling from the isotropic liquid. This texture does not present chiral domains. (b) Bright birefringent texture induced by the application of an electric field of 10 V μm^{-1}. This texture is compatible with a synclinic state. (c) Low-birefringence texture obtained on removal of the electric field (SmC$_A$P$_A$).
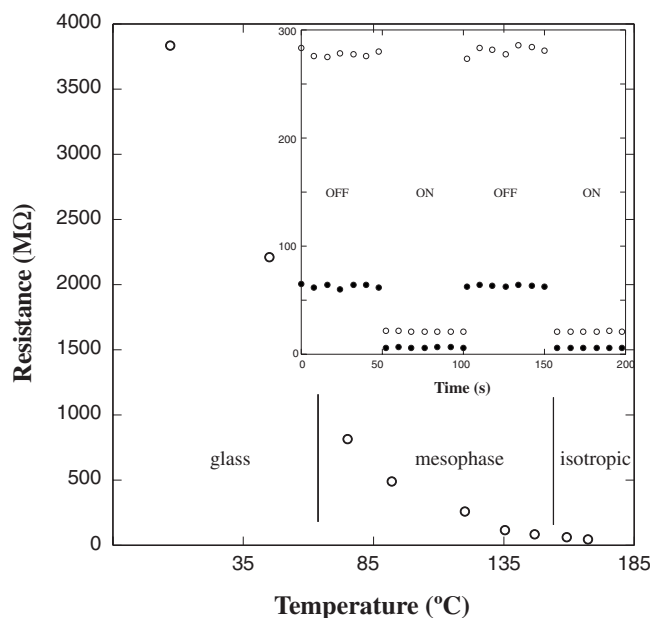

FIG. 3. Electrical resistance of the sample versus temperature. In the inset the photoconductivity effect is shown when illuminating with uv light the mesophase (open circles) and the isotropic phase (solid circles). Ordinate axis units are also MΩ. In the mesophase the effect is especially noticeable.
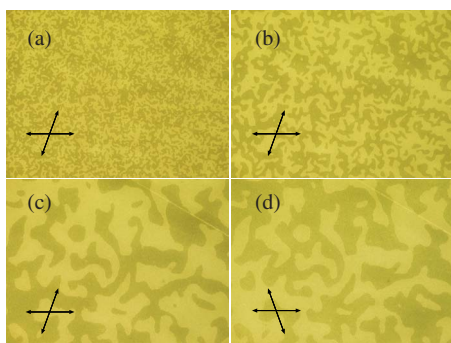
FIG. 4. (Color online) Growth of chiral domains under electric field. The texture is obtained under electric field after light irradiation in the mesophase near the clearing point. The photographs (a)–(c) were taken subsequently at time intervals of 40 s. Arrows indicate polarizer orientation. (d) The same as (c) but with the polarizers uncrossed in the opposite sense.
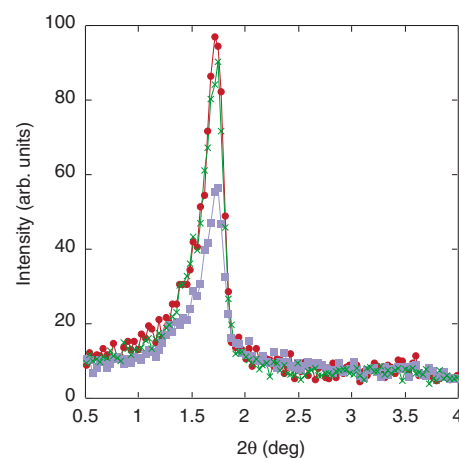

FIG. 5. (Color online) Small-angle x-ray diffraction pattern at 152 °C. Circles, squares, and crosses correspond, respectively, to data before, during, and after the illumination of the sample with uv light. The second-order smectic peak is hardly visible because of the short exposure time to the x-ray beam (about 1 min).

photoconductivity and, in particular, the ratios between dark and photocurrents in the three phases are similar to those found in liquid-crystal materials especially designed to present photoconductive properties [22].

However, an unusual behavior is observed if the illumination is carried out in the SmCP phase at a temperature close to appearance of the isotropic liquid (approximately less than 5 °C below the clearing point). Under these conditions, if the sample is irradiated in the field-induced birefringent state the texture becomes dark gradually, being perfectly isotropic after about 1 min of illumination. After light removal, the texture remains dark and no chiral domains can be observed when the polarizers are uncrossed. In contrast to the nonilluminated sample, a subsequent electric field application does not result in a change to a birefringent texture. However, under electric field, the dark texture develops chiral domains of opposite handedness whose size increases noticeably in a short period of time (see Fig. 4). This field-induced texture demonstrates the mesomorphic character of the dark texture after the light is turned off. If the sample is heated up to the clearing point and subsequently cooled down into the mesophase, the birefringent texture is no longer obtained after electric field application. A grainy yellow texture embedded in the dark one is observed instead. This yellow birefringent texture relaxes into the chiral dark state after field removal. This effect is observed whenever the sample has been illuminated near the clearing point, either in the original dark state or in the field-induced birefringent state.

In order to clarify the light-induced transformation near the clearing point, small-angle x-ray diffraction studies were carried out in a powder sample at 152 °C (Lindemann capillaries of diameter 0.5 mm). The diffraction pattern shows two sharp peaks at small angles that correspond to the first and second orders of the smectic periodicity. In the experiment the irradiation conditions are similar to those described above. After 1 min of illumination the first-order peak clearly decreases and remains steady during the rest of the irradiation period (see Fig. 5). After the light is switched off, the peak recovers its initial value. This result indicates that, on illumination, part of the sample undergoes a phase tran-

sition to the isotropic liquid. The inner portion of the sample remains in the mesomorphic state probably due to the strong light absorption of the material.

The light-induced phase transition to the isotropic liquid cannot be explained in terms of a mere heating of the sample, since the field-induced birefringent phase, which appears in the virgin sample, is no longer obtained after uv light exposure. Therefore, an irreversible molecular alteration must have happened. A consequence is the reduction of the domain size to a mesoscopic scale due to the disorder induced by the altered molecules. This idea is supported by the small size of the grainy yellow texture embedded in the dark texture that the material shows under electric field. Assuming this hypothesis, only a small portion of the domains would present macroscopic size so as to exhibit birefringence (yellow grainy domains in Fig. 4).

It is important to point out that the electric field induces a fast chiral segregation in the dark texture that has been exposed to uv light near the clearing point (see Fig. 4). Presumably this segregation takes place even in the virgin mesophase after field application; in fact the texture is homochiral. However, as the material is birefringent, rotatory power is not observed. Field-induced chiral segregation has also been reported in calamitic racemic mixtures [23,24] but with much longer time scale (months) [24]. In addition, a similar chiral segregation has been previously reported in a bent-core compound [20] when it is cooling from the isotropic phase under field.

It is interesting to remark that the disappearance of the birefringent texture and its substitution by the optically isotropic mesophase after illumination is an irreversible process. Even the procedure of heating the material up to the isotropic liquid point and cooling down again under field is insufficient to reproduce the birefringent phase. The starting point for the change of texture is likely to be the generation of charge carriers. In addition, at temperatures close enough to appearance of the isotropic liquid, a molecular modification takes place under light, which is evidenced by a transi-

tion to the isotropic liquid. Probably this modification involves a change of the molecular shape from the bent profile (adequate for promoting the mesophase) to something different. The investigation of the origin of these light-driven molecular changes will be a subject for future work. A similar isothermal transition to the isotropic liquid has also been observed upon illumination with blue light in some mesogens (including bent-core materials) whose molecules have azo or azoxy groups [25–29]. In those cases the molecular shape is changed by the passage from *trans* to *cis* conformations, and the effect is reversible. In the present case however the material "remembers" the transition to the isotropic liquid and is irreversibly transformed.

As has been mentioned above, the effect is different at lower temperatures far from the isotropic liquid. In these temperatures the light is unable to induce any transition to the isotropic phase and, as a consequence, the behavior of the material under field is normal (i.e., birefringent domains appear under field instead of a dark conglomerate phase). This indicates that the decrease of the electrical resistance upon illumination is due to the photogeneration of charge carriers that do not alter the chemical nature of the molecules.

The investigation of the character of the photocurrent (ionic or electronic) has not been treated in this work. To analyze this point it would be very interesting to carry out time-of-flight measurements on very pure samples [30,31]. We consider that the conduction can be electronic in the mesophase due to the relatively high π-π overlap in the TTF groups of the constituent molecules, because of their efficient packing in this kind of structure. This idea is supported by the fact that the resistance ratio between light-off and -on states in the isotropic phase would be expected to be equal to or larger than that in the mesophase if the conduction was exclusively ionic [22]. On the contrary, in our case this ratio is 30% higher in the mesophase. The analysis of the nature of the conductivity is our project for future work.

In summary, a bent-core mesogen containing a TTF group has been studied. The material spontaneously presents an achiral optically isotropic mesophase (spongelike SmCP phase), which can be converted into a normal SmC_AP_A phase after treatment with an electric field. In addition we have found some unusual photoinduced effects. Just below the clearing point, illumination with uv light induces a transition to the isotropic liquid, which creates a permanent memory in the material and suppresses the formation of macroscopic SmC_AP_A domains. A dark conglomerate phase appears instead, where the electric field segregates chiral domains of opposite chirality. Furthermore, in the whole temperature range we have detected the existence of photoconductivity. The effect is especially remarkable in the mesophase and isotropic phase. The possibility of electronic conduction in the mesophase has been briefly discussed.

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