Switchable Columnar Metallomesogens

José Luis Serrano* and Teresa Sierra[a]

Abstract: Chiral columnar liquid crystals have recently appeared as a promising new type of ferroelectric materials. To date, all the columnar liquid crystals that have been reported to show ferroelectric switching consist of organic compounds. However, metal-containing liquid crystals open this field to a significant number of new structures and offer the possibility of adding to the ferroelectric behavior other properties inherent to the presence of metals in the structure, such as magnetism, as well as the use of new methods of characterization (EPR, synchrotron radiation, etc.). The potential of columnar metal-containing liquid crystals as ferroelectric materials has been demonstrated even though only a few organic columnar ferroelectric liquid crystals have been described. As a first approach to this type of material, this concepts article describes the results obtained with chiral metal β-diketonates that show ferroelectric switching in the columnar mesophase. It has been shown that these materials have a helical columnar arrangement in the mesomorphic state, and a chiral superstructure has been proposed from circular dichroism studies. This type of supramolecular structure plays a fundamental role in the ferroelectric properties of these compounds. The discussion is mainly focused on the strategy employed for the molecular design, and on the interpretation of the mesophase structure and the electrooptic effect. The use of a diverse range of techniques, both those commonly used in the field of liquid crystals and those that are more specific will be highlighted, and the principles of these specific techniques are summarized together with a justification of their applicability to this study.

Keywords: circular dichroism · ferroelectricity · helical structures · liquid crystals · structure elucidation

Introduction

To date, columnar metallomesogens have been mainly proposed for potential applications derived from their properties based on photon, electron, and ion transport.[1] These effects require the existence of special electronic and structural features of the disklike molecules, but no molecular motions are required. Similar to organic columnar liquid crystals, columnar metallomesogens may be designed to show ferroelectric switching under an alternating electric field. However, in this case it is necessary to consider the dynamic properties of the mesophase since the electrooptic effect involves not only movement of charge but also molecular motion.

Considering the evolution of the field of ferroelectric liquid crystals, we can outline a chronological order for the incorporation of the different types of mesogenic compounds. In 1975[2] the first organic calamitic ferroelectric liquid crystal was described after the theoretical prediction by R. Meyer in 1974[3] that, by symmetry conditions, the SmC* could display a polar order of molecular dipoles, and hence be ferroelectric. In 1989[4] metallomesogens were shown for the first time to organize into supramolecular polar systems, and consequently to display properties that require macroscopic C_2 symmetry. Indeed, the ferroelectric behavior of chiral complexes showing the polar SmC* phase has been studied and, in a similar way to organic ferroelectric liquid crystals, ferroelectric metallomesogens have even demonstrated second-order nonlinear optical properties.[1] Most of these compounds have been obtained by coordination of two organic ligands through a metallic bridge, with the organic ligands bearing stereogenic centers in their terminal alkyl tails. In this way, molecular shapes differed considerably from the classical rodlike shape. For example, ferroelectric behavior has been found in open-book dinuclear palladium complexes,[4] H-shaped chloro-bridged dinuclear palladium complexes,[5] and K-shaped benzylideneamine β-diketone palladium complexes.[6]

In 1982[7] a theoretical prediction stated that a columnar rectangular mesophase could be ferroelectric if it consisted of chiral molecules. Further X-ray studies concluded that steric hindrance between columns would prevent ferroelectric switching in this case.[8] However, in 1992 Bock and Helfrich[9] reported the ferroelectric behavior of a chiral discotic mesogen designed to have a large dipole moment induced by molecular tilting. Subsequently several columnar liquid

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crystals have been described that show ferroelectric switching under an electric field.[10]

Metallomesogens should also play an important role in this field. Metal complexation of organic ligands has been shown to be a useful route to disklike molecules capable of stacking in columns that organize to give columnar mesophases.[11] Furthermore, if the disklike molecules are chiral, for example bearing stereogenic centers in the peripheral tails of the organic ligands, a ferroelectric columnar phase should be obtained similar to those discovered in columnar organic liquid crystals. Moreover, metal-containing liquid crystals can display other properties inherent to metals,[12] and could even allow new structures with the stereogenic centers in the core of the discotic molecule.

Other attempts to achieve ferroelectric columnar organizations have been based on bowl-shaped molecules that can stack to give polarization along the column axis.[13] The existence of such a ferroelectric polarization has been demonstrated in organic materials.[13a] However, no evidence of it has been reported for similar metal-containing systems so far.[13b,c]

Herein we describe work that has been carried out on columnar metallomesogens specifically designed to show a ferroelectric polarization perpendicular to the column axis. Concepts established to understand the origins of the spontaneous polarization in columnar mesophases are summarized. Emphasis is placed on the structural elucidation, achieved by the use of a diverse range of techniques, of the ferroelectric mesophase. The principles of the most relevant techniques, such as circular dichroism and broadband dielectric spectroscopy, are briefly presented to explain their applicability to this particular field. In addition, a strategy used to explain the observed electrooptic effect is described.

Abstract in Spanish: *Los cristales líquidos columnares quirales han demostrado recientemente su potencial como materiales ferroeléctricos. Todos los cristales líquidos columnares descritos hasta la fecha como ferroeléctricos son de naturaleza orgánica. Sin embargo, los compuestos metalomesógenos abren este campo a un amplio número de estructuras y ofrecen la posibilidad de, junto con el comportamiento ferroeléctrico, obtener otras propiedades inherentes a la presencia de metales, tales como magnetismo, color, etc., así como el uso de nuevos métodos de caracterización (EPR, sincrotrón, etc.). El potencial de los metalomesógenos columnares como materiales ferroeléctricos se ha demostrado cuando sólo se ha descrito un pequeño número de estructuras orgánicas que muestran ferroelectricidad en la fase columnar. Como primera aproximación a este tipo de materiales, este artículo describe los resultados obtenidos con β-dicetonatos metálicos quirales que muestran conmutación ferroeléctrica en la mesofase columnar. Se demuestra que estos materiales poseen una organización helicoidal en el estado mesomorfo, y se propone la existencia de una superstructura quiral a partir de los resultados de dicroísmo circular. Este tipo de estructura supramolecular juega un papel fundamental en el comportamiento ferroeléctrico. La discusión se enfoca principalmente hacia la estrategia utilizada en el diseño de las moléculas, así como en la interpretación de la estructura de la mesofase y del efecto electroóptico. Se hace especial énfasis en el uso de diversas técnicas, tanto aquellas comunes al estudio de compuestos mesógenos, como otras más específicas. Se resumen los principios fundamentales de éstas así como una justificación de su empleo en este estudio particular.*

Concepts

Structure of the ferroelectric columnar phase: The appearance of spontaneous polarization in a columnar phase is possible when chiral molecules are tilted with regard to the column axis. The tilt induces the appearance of a dipole moment within the plane of the molecule. Tilt, promoted by repulsion between tails and attraction between rigid cores,[14] mainly affects the cores, whereas the peripheral tails maintain an orientation almost perpendicular to the column axis. In this conformation a deflection point appears in the molecule. If the stereogenic center is located at the position where the tails and core deflect, dipole moments contained at these sites tend to align along a preferred direction, and hence a net polarization perpendicular to the column axis appears (Figure 1). Only when tilting is directed either in the same direction in all the columns or alternates in such a way that columnar polarizations do not cancel out can a macroscopic polarization be obtained that can be switched by an electric field. These conditions are fulfilled by rectangular columnar phases with C_2 and $P2_1$ symmetries, respectively.

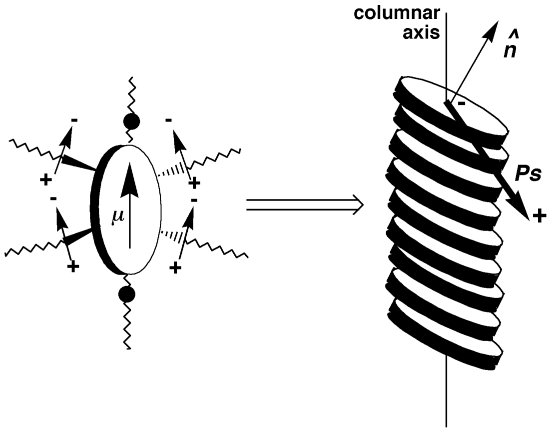


Figure 1. Schematic representation of the tilt induced dipole moment of a chiral discotic molecule (left) as the origin of a net polarization (ferroelectricity) in tilted columnar phases (right). The chemical nomenclature for the molecular dipoles has been adopted. Adapted from reference [10c].

If a sample is placed in a cell with the column axes parallel with respect to the conducting glasses (this can be achieved by rubbing), the polarization will be perpendicular to the glass surfaces. An electric field applied across the material will bring about rotation of the molecules so that polarization aligns parallel to the external field. In this geometry two possible switching ground states, compatible with the rectangular lattice, can be defined which are related by a 180° angle around the column axis. If the sample is placed between crossed polarizers, bright and dark situations can be obtained in a similar way to those occurring in ferroelectric smectic liquid crystals[15] (Figure 2).

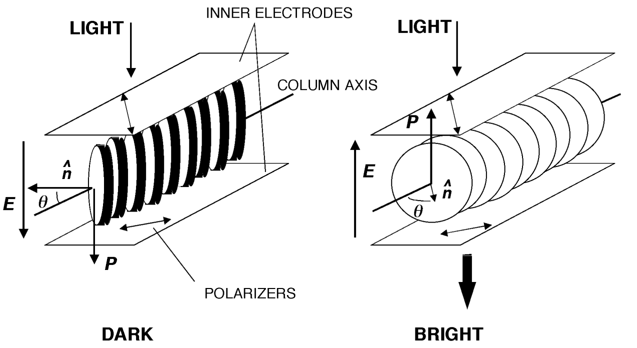


Figure 2. Proposed ferroelectric switching of a tilted columnar mesophase. Adapted from reference [10e].

When a columnar mesophase is allowed to form within a cell without treatment (i.e. without surface coating or mechanical stress), a flowerlike texture showing Maltese crosses appears. This texture arises when columns align in concentric circles around defects.[16] Since molecules are tilted with regard to the column axis in rectangular columnar mesophases, the black brushes of the cross are rotated from polarizer directions by an angle equal to the tilt angle. When an alternating electric field is applied, the brushes rotate back and forth with a displacement twice the tilt angle.

Switching mechanism: Although the phenomenon of switching in discotic systems has been experimentally proven, the mechanism is not yet completely understood. Three mechanisms have been proposed[10d] to explain how molecules rotate between both ground states when the electric field is reversed (Figure 3a–c): a) Switching through an untilted state and rotation of the chains, describing a cone, to change the direction of the associated dipole. b) Director precession, in which the chains move up or down parallel to the column axis. c) Director precession and column rotation as a whole around the column axis, with the chains remaining unchanged.

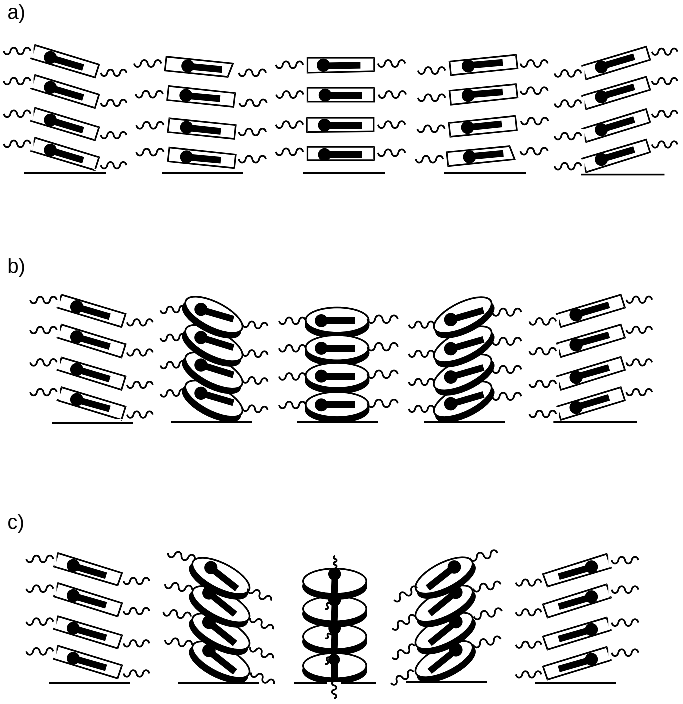
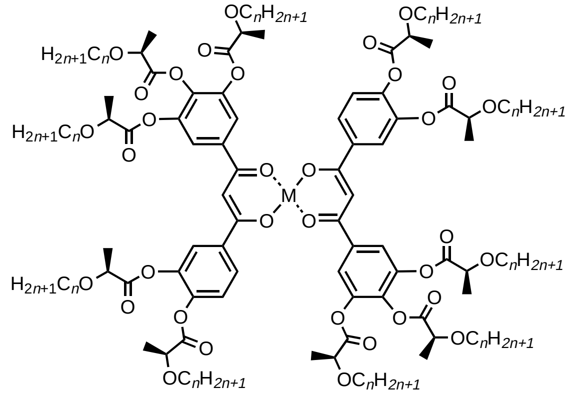


Figure 3. Three possible mechanisms to explain the switching in tilted columnar phases as proposed by Scherowsky and Chen.[10d] Adapted from reference [10d].

Objective and Strategy

The possibility of employing metallomesogens as ferroelectric columnar materials was first considered in connection with the possibility of obtaining disklike molecules by means of metal complexation of organic ligands.



$M = VO^{IV}, Cu^{II}, Pd^{II}$ $n = 6, 7$

Scheme 1. Structure of the decasubstituted metal β-diketonates designed as switchable columnar metallomesogens.

In order to develop this idea, target molecules were designed (Scheme 1) on the basis of previous studies on β-diketone-based metallomesogens.[17] Bis-(1,3-diphenyl-1,3-propanedione) copper(II), bearing 10 peripheral tails, produces mesophases with columnar stacking and a hexagonal two-dimensional arrangement of the columns.[18] Moreover, this hexagonal columnar mesophase is stable from room temperature up to about 140 °C. Incorporation of stereogenic centers in the peripheral tails gives the molecule the necessary chiral character and, simultaneously, promotes repulsion between the tails and approach between the cores, thus inducing tilting within the columns. Tilting is known to break the hexagonal symmetry,[19] and it was envisaged that this should result in the appearance of a rectangular columnar arrangement that would potentially be ferroelectric. Previous studies on organic disklike molecules show that *O*-alkoxylactic acid derivatives are effective as chiral tails for columnar FLCs.[9] Moreover, this group carries a strong dipole moment associated with the stereogenic center, which has proved to favor high spontaneous polarization (Ps) values in calamitic FLCs.[20]

Characterization techniques: One of the aspects of this study that deserves particular attention is the elucidation of the supramolecular organization within the mesophase and the nature of its ferroelectric behavior. For this reason, it is of interest to describe the most important features of the techniques used and the specific aspects that make them useful tools for the study of ferroelectric columnar liquid crystals.

Mesophase identification: Identification of the mesophase can be carried out by means of the techniques commonly used for liquid crystals, that is polarized light microscopy, differential scanning calorimetry, and X-ray diffraction. However, to confirm the existence of a helical superstructure, as claimed by some authors,[10b,d] more specific techniques, such as circular dichroism and dielectric spectroscopy, have been employed.

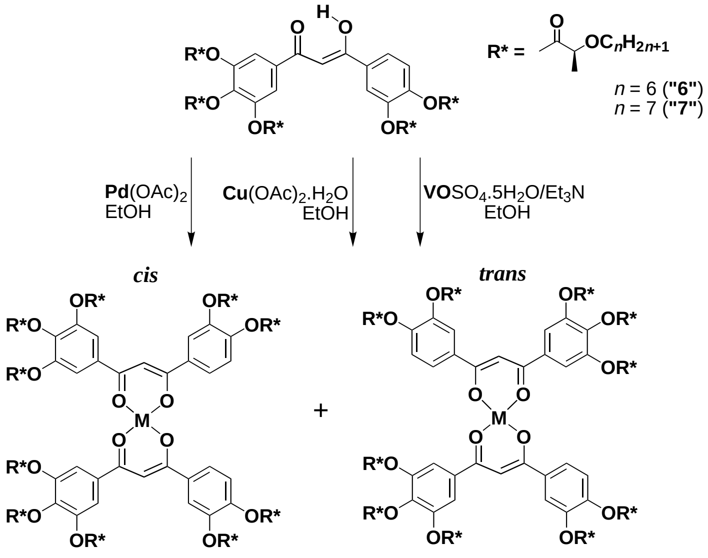
Helical structure characterization: Circular dichroism in the mesophase might allow the identification of helical ordering within the column by the observation of an exciton-split effect in the corresponding CD spectrum.[21] The appearance of exciton splitting is related to a through-space interaction between two or more chromophores exhibiting allowed $\pi-\pi^*$ absorption bands. Such an interaction splits the excited state into two energy levels. For the exciton splitting to occur, interacting electric transition moments must not be parallel since it is the result of a vectorial product. In the case of β-diketonate complexes, the $\pi-\pi^*$ transition of planar cores stacked in columns obeys the conditions for exciton splitting in the CD spectrum of the mesophase if the molecules are tilted with respect to the column axis, and the tilt direction describes a helix around the column axis (i.e. through-space interaction of nonparallel electric transition moments). Circular dichroism experiments on the mesophase require thin samples. Spin-coating can be used given the high viscosity of the mesophase at room temperature, and this technique allows thin films to be obtained on a quartz substrate.

Broadband dielectric spectroscopy gives information about the molecular structure and molecular motions within the material (modes) through the study of the dependence of the dielectric permittivity on the frequency of the applied electric field and the temperature.[22] Two types of mode can be found in liquid crystals, molecular and collective modes. The first type of mode corresponds to independent motions of the molecule. Collective modes are related to the supramolecular organization of the material, and hence are of crucial importance to elucidate the structure of the mesophase. This technique has been mainly used in the study of helical organizations in chiral mesophases in calamitic ferroelectric liquid crystals. The so-called Goldstone mode appears in chiral smectic phases and is related to azimuthal fluctuations of the molecular director, that is winding and unwinding of the SmC* helix. However, few studies have been performed of the dynamic properties of columnar mesophases,[23] and none of these studies were based on metal-containing materials.

Characterization of the electrooptic effect: The electrooptic effect arising from the above compounds was investigated by means of a photomultiplier linked to the polarizing microscope and connected to an oscilloscope. The special nature of the ferroelectric behavior of the columnar phase was demonstrated by comparison with the corresponding behavior of a calamitic liquid crystal. Indeed, smectic layers with the molecular axis tilted with respect to the layer normal can be considered equivalent to columns in which the disklike molecules are tilted with respect to the column axis. On the basis of this analogy, the electrooptical response in calamitic ferroelectric liquid crystals can be related to the electrooptical response in columnar liquid crystals as far as their effect on polarized light is concerned. The main difference between both types of mesophase is the viscosity, and hence the frequency of the applied electric field used for their study. In order to emulate the response of the columnar materials with long response times, which cannot easily follow the reversal of the field, the calamitic compound was studied at a very high frequency (250 Hz).

Results and Discussion

Synthesis and characterization: The synthetic pathway to the target compounds has been described elsewhere.[24] Given the different substitution of the two aromatic rings of the β-diketone ligands, it was possible that a mixture of both *cis* and *trans* geometric isomers would be obtained (Scheme 2). Indeed, NMR spectroscopy proved useful to identify the presence of these isomers in a 1:1 ratio in the palladium complexes. Two signals of equal intensity were obtained for each aromatic proton. The paramagnetic character of vanadium(IV) and copper(II) made it impossible to determine the structure of these complexes by NMR spectroscopy. However, given the similarity of the synthetic processes it appears reasonable that the results for the palladium complexes are also applicable to the vanadyl and copper analogues.



dK"6"VO dK"6"Cu dK"6"Pd

dK"7"VO dK"7"Cu dK"7"Pd

Scheme 2. Synthesis of the complexes and structure of the two possible geometric isomers (*cis* and *trans*).

Mesomorphic behavior: All six complexes obtained were found to be mesomorphic materials. The clearing points, which are given in Table 1, were determined by differential scanning calorimetry. Melting or crystallization peaks were not observed in any of the cases studied. As the temperature was decreased, the materials became very viscous. It is possible that, at a certain temperature, the material becomes an amorphous solid, although no glass transition was observed in any of the complexes in the cooling process, even down to −20 °C.

Table 1. Transition temperatures [°C] obtained by differential scanning calorimetry. Scan rate: 10 K min^{-1}. (–): the crystalline phase has not been detected by either DSC or optical microscopy cooling down to −20 °C.

Compound	K		Col$_r$*		I
dK"6"VO	–	< −20	•	125	•
dK"6"Cu	–	< −20	•	130	•
dK"6"Pd	–	< −20	•	149	•
dK"7"VO	–	< −20	•	122	•
dK"7"Cu	–	< −20	•	132	•
dK"7"Pd	–	< −20	•	147	•

Optical microscopy studies were carried out to identify the mesophase of each compound. The textures observed depend on the nature of the metal coordinated to the ligands. On cooling from the isotropic liquid, the mesophases of oxovanadium (**dK"6"VO** and **dK"7"VO**) and copper (**dK"6"Cu** and **dK"7"Cu**) complexes display dendritic textures. The texture of the palladium complexes (**dK"6"Pd** and **dK"7"Pd**) is quite different to that observed for the copper and vanadium complexes and is suggestive of a more crystalline phase. In all cases, the texture does not change even on cooling to −20 °C.

When the mesophase is either allowed to form at a very slow rate or annealed at 100 °C for several hours, a flowerlike texture with Maltese crosses often appears, which suggests the existence of a columnar mesophase. The extinction brushes are inclined with respect to the direction of the crossed polarizers, indicating the presence of molecular tilt (Figure 4). Sometimes this inclination is not observed in a freshly formed mesophase. The inclination will subsequently appear on cooling or on annealing the sample. However, at other times the inclination is very small (10 to 15°) and increases to nearly 40° after the sample is maintained at 100 °C for several hours.

It is also worth mentioning that all the materials can be aligned to give a birefringent texture when they are sheared at around 100 °C. However, the alignment of the sheared material tends to be destroyed after a prolonged period or when the temperature is increased.

Structure of the mesophase: Infrared spectroscopy was carried out on neat samples of oxovanadium(IV) complexes to investigate the tilt of the molecules within the column. Stretching of polymeric V=O bonds is manifested as a band at 900 cm^{-1} in the IR spectra, whereas free V=O bonds give rise to a band at 985 cm^{-1}. In columnar liquid crystals consisting of oxovanadium(IV) β-diketonate complexes, with the V=O bond perpendicular to the molecular plane, V=O···V=O interactions appear if these bonds are aligned along the column axis.[25] By applying this simple concept to our materials, the chiral β-diketone units must be tilted with respect to the column axis since the only band observed in the IR spectra corresponded to the isolated V=O bond. This fact suggests that the V=O bonds point away from the column axis.

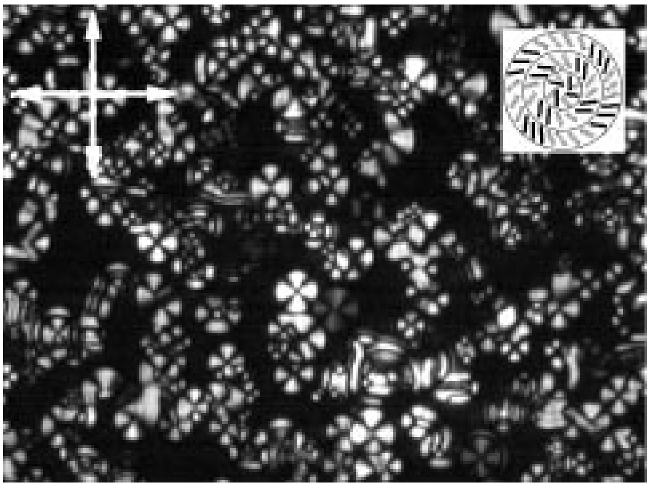


Figure 4. Photomicrograph of the texture of the annealed (100 °C for 20 h) columnar mesophase of compound **dK"7"VO**. The texture shows Maltese crosses inclined with respect to the crossed polarizers indicating the presence of molecular tilt as represented in the figure at the top righthand corner of the picture.

To characterize the type of columnar mesophase and to determine the structural parameters, the materials were investigated by X-ray diffraction at room temperature as well as at a higher temperature (75 °C) (Figure 5).

The X-ray patterns confirm that all the compounds in the series exhibit a columnar mesophase between room temperature and the temperature where they transform to an isotropic liquid (Figure 5a represents the pattern of **dK"6"Pd** at room temperature as an example). At room temperature all the patterns show several sharp reflections in the equatorial region, that is the plane perpendicular to the axes of the columns, that can be assigned, in all cases, to a two-dimensional rectangular lattice. In the meridian, that is the direction of the column axes, the pattern is simpler: two broad maxima are observed, of which the one at lower scattering angles (higher distances), corresponding to distances between 5.3 and 5.7 Å, arises from intracolumnar metal–metal interferences. From density considerations, it can be deduced that the unit cell contains two molecules, which are located at the corner and at the center of the cell. The symmetry of the mesophase has been assigned to the space group $P2_1$,[24] which is characterized by a herringbone arrangement of the elliptical sections of the columns, as represented in Figure 5b.

Identification of a helical organization: In addition to the diffraction maxima described above, one additional peak is observed in the small-angle X-ray patterns at a diffraction angle θ of about 0.5°. This peak cannot be assigned to the rectangular lattice. The peak can clearly be seen in the powder pattern obtained from non-oriented samples at room temperature, but it almost disappears in the oriented patterns and in

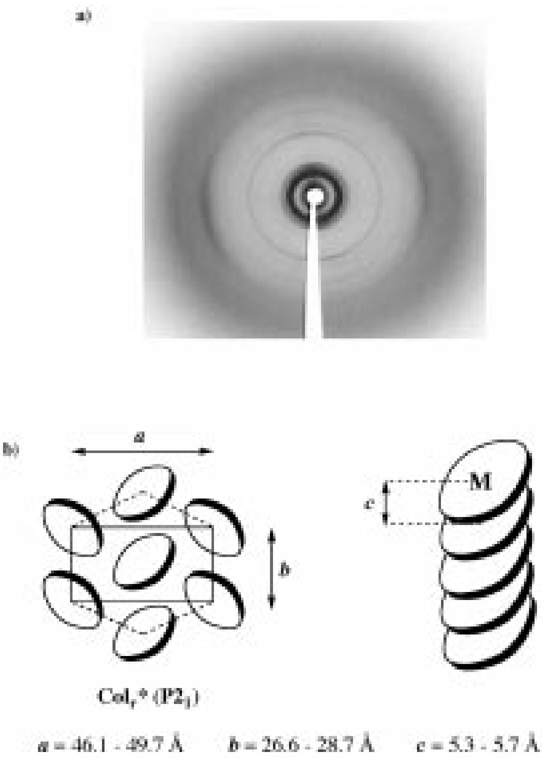


Figure 5. a) X-ray pattern of compound **dK"6"Pd** at room temperature. b) Schematic representation of the columnar rectangular mesophase showing a view along the *c* axis and a view perpendicular to the *c* axis. Lattice parameter ranges are also included.

the high-temperature patterns, and could correspond to an intracolumnar periodic modulation resulting from a helical structure.

However, the most suitable technique to determine the existence of this chiral superstructure is circular dichroism. As far as we can tell using the above techniques, the compounds in question possess several features that make it possible the exciton splitting phenomenon to occur: i) The molecules exhibit an allowed transition ($\pi-\pi^*$) associated with the β-diketone group. ii) The molecules are planar and stack to form columns. iii) The molecules are tilted with regard to the column axis. Given the possibility of a helical arrangement within the column, it would be expected that an exciton splitting would appear at the wavelength of the $\pi-\pi^*$ absorption band.

The CD spectra were recorded for three types of sample. An initial spectrum was obtained from solutions of the complexes in THF in order to investigate the influence of the stereogenic centers on the optical activity. As can be observed for the complex **dK"7"VO** (Figure 6a) no CD signal was detected in this situation. However, the CD spectrum of a freshly prepared thin-film of the complex showed a strong signal, indicating the existence of some sort of formal optical activity in the mesophase. Moreover, a positive exciton splitting centered at the wavelength of the $\pi-\pi^*$ transition (365 nm) appeared. This signal represents the experimental confirmation of the existence of a helix within the column (Figure 6b), taking into account the requirements for the appearance of exciton splitting.

More surprising was the CD spectrum of the sample after annealing at 100 °C for 20 h. First, the optical activity is increased by a factor of ten. Second, a second exciton splitting appears at the wavelength of the Cotton effect in the CD of the untreated sample (406 nm), a wavelength that corresponds to a shoulder in the UV spectrum. A tempting explanation might be the formation of a double helix (Figure 6c) during annealing, as has been proposed by some authors[10b], but this ought to be confirmed by calculation of the CD spectra by means of molecular orbital methods.

The presence of the helical arrangement within the column, as observed by circular dichroism, should also be detectable by broadband dielectric spectroscopy in a similar way to azimuthal fluctuations of the director of the SmC* phase (i.e. winding and unwinding of the helix) in ferroelectric calamitic

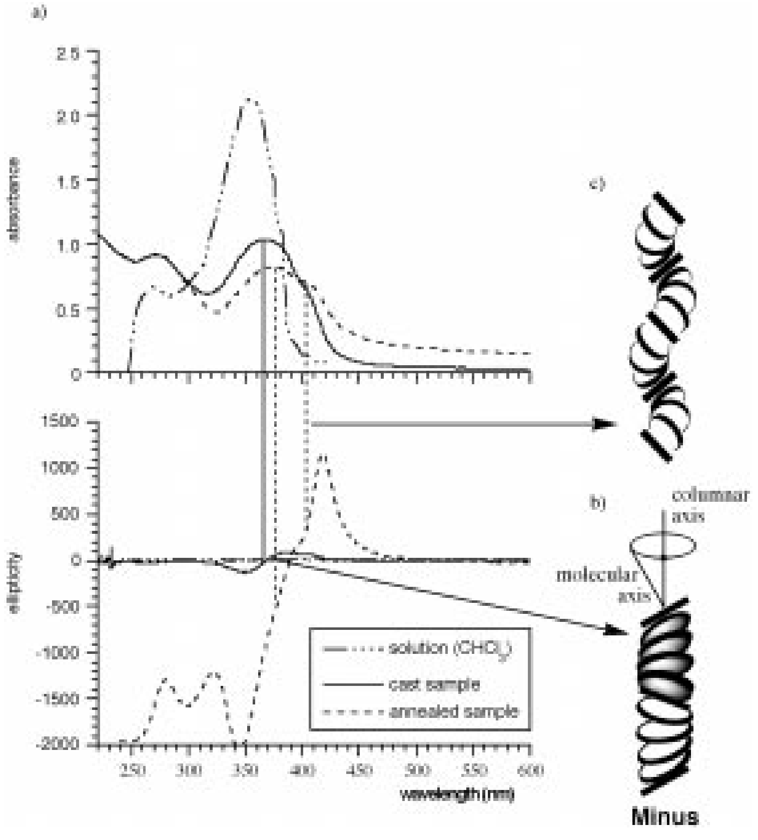


Figure 6. a) UV and CD spectra recorded for complex **dK"7"VO** under three different conditions: solution in THF (0.1 g L^{-1}) and thin film deposited on a quartz substrate by spin coating (cast sample and annealed sample, 100 °C for 20 h). b, c) The structures of the proposed helical arrangements are represented related with the appearance of exciton-splitting signals.

liquid crystals. In the $\mathrm{Col_r}^*$ phase, there is a tilt-induced dipole moment within the plane of the molecule, and consequently azimuthal fluctuations of the molecular director around the axis of the helix would allow a collective contribution (collective mode) of these dipoles to the dielectric permittivity. Indeed, three modes have been found for these materials and a complete dielectric study of them is reported elsewhere.[26] The mode observed at the lowest frequency is particularly noteworthy. It appears below the clearing point, thus corresponding to a collective mode of the supramolecular organization in the mesophase, and does not appear in achiral compounds. The dielectric strength and frequency of this mode make it closely related to the Goldstone mode of the SmC* phase, which is due to azimuthal fluctuations of the molecular director. On the basis of these experimental results it is reasonable to assign the origin of this mode to the existence of a helical structure within the mesophase consisting of tilted molecules whose tilt direction rotates along the columnar axis (Figure 6b). In fact, this explanation is in complete agreement with the results obtained from circular dichroism.

Ferroelectric behavior: From the studies described above, it can be confirmed that these materials fulfill the structural requirements to show ferroelectric switching. The spontaneous polarization has been impossible to evaluate, probably due to the high conductivity of the materials masking the current caused by the inversion of the polarization. However, the electrooptic response of sheared samples could be recorded by means of a photomultiplier connected to the polarizing microscope, and registered on an oscilloscope. The best way to align columnar liquid crystals is by means of the shearing technique so that the columnar axes lie parallel to the glass surfaces. By following this method, cells were prepared with a thickness of around 25–30 μm. In this alignment the macroscopic polarization is perpendicular to the conducting glass surfaces. Given the high viscosity of the materials the frequencies used were very low (0.2–1.0 Hz), and the strength of the applied electric field was in the range 100–200 Vpp. In all three cases a special type of electrooptical behavior was observed (Figure 7a shows the optical response of the complex **dK“7”VO** as an example). During a pulse, the cell contrast changes between two dark states, ***a*** and ***c***, through an intermediate transmission step, ***b***. In an attempt to explain this behavior the possibility of the influence of winding and unwinding processes of the helix was first considered. However, the shearing technique and the strong fields would destroy the helical arrangement. A second possibility considered was based on the large tilt angle of the molecules within the column. As explained at the end of the strategy section, it seemed reasonable to compare this result with the electrooptic behavior of a calamitic ferroelectric liquid crystal with a high tilt angle, about 45°.[27] As can be seen in Figure 7, a strong similarity exists between the electrooptic responses of both

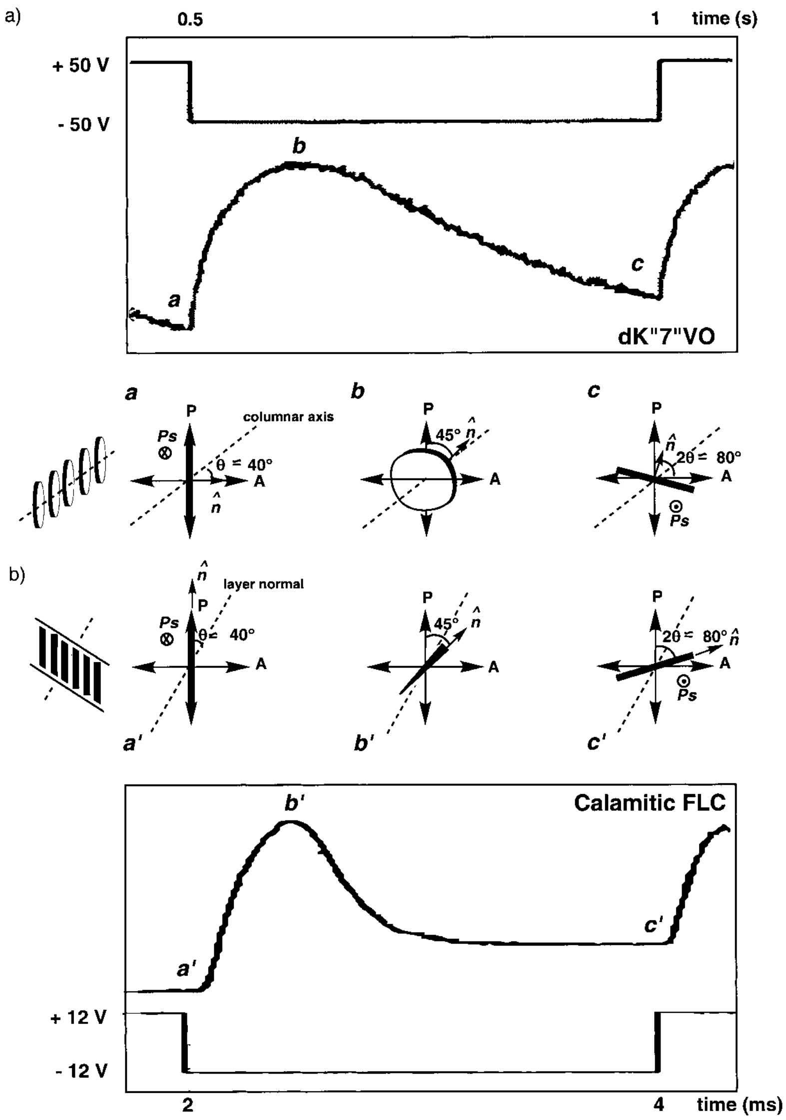


Figure 7. Electrooptic response of the columnar compound **dK“7”VO** (a) and comparison with the electrooptic response of a high tilt angle calamitic FLC (b). The scheme represents the three contrasting situations proposed to explain the similar response of both compounds. The intermediate states with the maximum transmission (*b* and *b*′) correspond to situations in which the molecular directors are oriented 45° with respect to the crossed polarizers. Extinction states, *a* and *a*′, correspond to an orientation of the directors along one of the polarizers. Final states, *c* and *c*′, close to extinction, are represented by molecular directors oriented almost parallel (ca. 10°) to one of the polarizers.

the discotic and the calamitic molecules, when working at frequencies at which the material cannot easily follow the reversal of the field (1 Hz and 250 Hz, respectively). Such frequencies were chosen on the basis of the viscosity of the compounds. In both cases the final switching state corresponds to a rotation of the director by very close to 90° and hence the molecule is located almost parallel to the second polarizer. This situation gives rise to a low light transmission, ***c***. The intermediate state of maximum transmission, ***b***, would correspond to a 45° orientation of the director with respect to both polarizers.

Conclusion

In the design of new molecular structures to show known properties of liquid crystals, such as ferroelectricity, metallomesogens have already appeared as a promising alternative to organic mesogens. In the specific case of columnar ferroelectric liquid crystals, metal complexation of organic ligands has been shown to be an attractive possibility through the example of chiral metal β-diketonates, which have demonstrated their capability to switch under an alternating electric field. This response is only possible because a polar organization can be achieved because of the nature of stacking of these disklike complexes. Moreover, these materials have also allowed a complete elucidation of the structure of the ferroelectric columnar mesophase. For example, the helical arrangement within the column, which had already been proposed to exist, has now been experimentally confirmed by circular dichroism and broadband dielectric spectroscopy. The results presented here are not only significant in themselves, but also because they represent a step forward towards understanding the ferroelectric switching mechanism of columnar liquid crystals by providing a deeper knowledge of the supramolecular organization of the ferroelectric mesophase.

At this point, the authors would like to emphasize the potential of these materials on the basis of the intrinsic characteristics of metal-containing liquid crystals. In addition to broadening the possibilities for molecular design, we can also take advantage of features such as their high viscosity, which allows them, more likely, to undergo freezing of the mesophase order. This property could appear to be a drawback for electrooptic applications, but can also be considered an advantage when the polar organization of the mesophase is to be used to achieve nonlinear optical phenomena, in which ferroelectric liquid crystals, in general, are playing an important role.

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