

## Switchable Columnar Metallomesogens. New Helical Self-Assembling Systems

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**Abstract:** Chiral oxovanadium(IV), copper(II), and palladium(II)  $\beta$ -diketonates show a room-temperature columnar mesophase which undergoes ferroelectric switching. All the compounds were obtained as liquid crystals at room temperature, and crystallization or melting processes were not detected by differential scanning calorimetry carried out to  $-20$  °C. The mesophase was investigated by optical microscopy, DSC and X-ray diffraction, and identified as a rectangular columnar ( $P2_1$ ). The flowerlike texture observed for all the compounds led us to deduce a high tilt angle (ca.  $40^\circ$ ) of the molecules with respect to the column axis. Circular dichroism has confirmed the existence of a helical arrangement within the column. This result is in accordance with the so-called columnar mode found at low frequencies (ca.  $10^{-3}$  Hz) in dielectric spectroscopy studies. The electrooptical response of these materials has been examined by means of a photomultiplier. The results obtained can be explained by considering a strong influence of the high tilt angle found in the mesophase.

### Introduction

Molecular design by means of metal complexation of organic ligands has recently been developed as a useful tool to obtain mesogenic structures capable of organizing into supramolecular organizations which display specific properties such as ferroelectricity and nonlinear optical phenomena.<sup>1</sup>

Our interest in metal-containing liquid crystals led us to develop several studies on chiral mesogenic dimers consisting of two organic ligands bridged through transition metal centers. As a result, molecular structures which differ from the classical rodlike FLCs arrange into the required supramolecular organization (i.e. SmC\*) to show ferroelectricity.<sup>2</sup>

To develop this area further, we have focused our attention on recently described columnar FLCs. Indeed, as theoretically predicted<sup>3</sup> and experimentally proved,<sup>4</sup> a columnar mesophase

consisting of chiral molecules tilted with respect to the column axis can be ferroelectrically switched. The possibility of achieving ferroelectric switching in a columnar liquid crystal comes from the appearance of a macroscopic polarization perpendicular to the column axis. The origin of this polarization lies in the tilt-induced molecular dipole moment within the columnar phase. However, many questions regarding the molecular organization within the mesophase and the switching mechanism remain unanswered.

On the basis of these studies, we planned the design of ferroelectric columnar metallomesogens by taking advantage of the possibility of obtaining disklike molecules by means of metal complexation. A survey of the literature on this subject led us to envisage great potential for metal bis(1,3-diphenyl-1,3-propanedionates) bearing 10 peripheral tails. Several studies have demonstrated the tendency of this structure to promote columnar mesomorphic arrangements.<sup>5</sup> X-ray diffraction studies carried out in our laboratory on copper(II) bis[1-(2,3-didecylloxyphenyl)-3-(2,3,4-tridecylloxyphenyl)-1,3-propanedionate] showed the existence of a hexagonal columnar mesophase which is stable at room temperature and last til about 140 °C.

Taking this copper(II)  $\beta$ -diketonate as a model, it was necessary to modify its structure in order to increase repulsion between tails and promote the approach of the cores in order to induce tilting.<sup>6</sup> Since tilting is known to break the hexagonal

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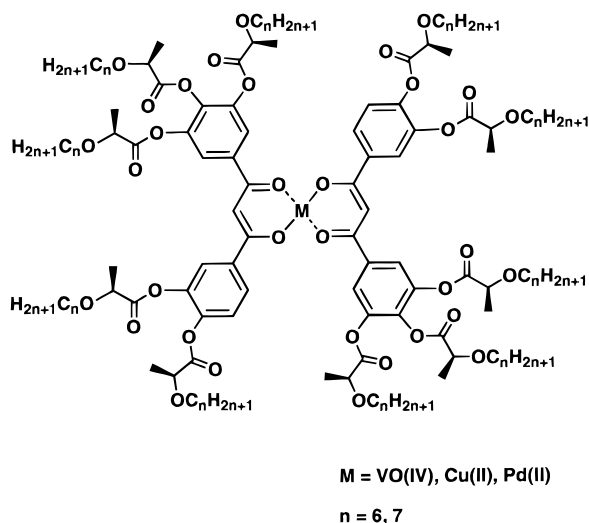
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Chart 1



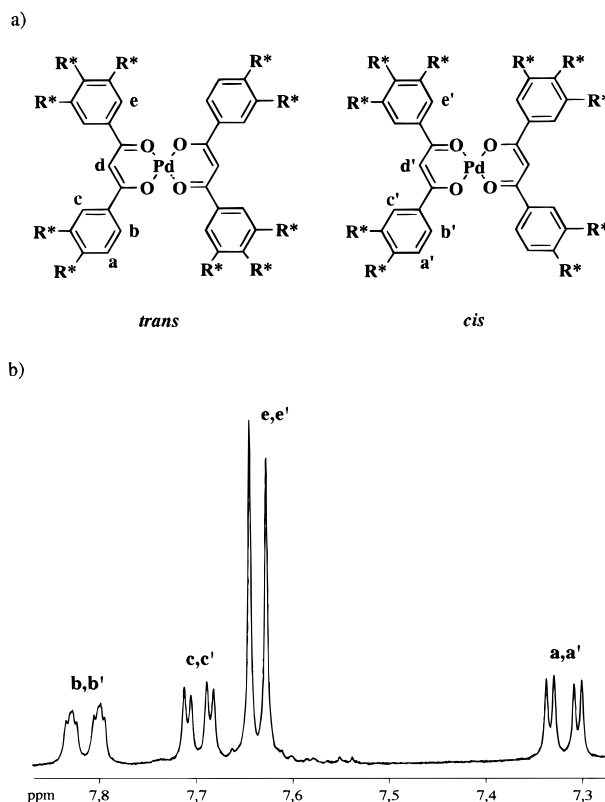
symmetry,<sup>7</sup> it was envisaged that this should result in the appearance of a rectangular columnar arrangement. Moreover, there are two types of rectangular lattice,  $P2_1$  and  $C2$ , which can both be ferroelectric. Incorporation of stereogenic centers in the peripheral tails would simultaneously induce the above effect and give the molecule the necessary chiral character. Experiments developed on organic disklike molecules show that *O*-alkoxyacetic acid derivatives are effective as chiral tails for columnar FLCs.<sup>4a</sup> Moreover, this group carries a strong dipole moment associated with the stereogenic center which has proved to favor high Ps values in calamitic FLCs.<sup>8</sup>

Bearing in mind all these factors we have designed new chiral metal  $\beta$ -diketonates whose structure is represented in Chart 1. The target molecules consist of two pentasubstituted 1,3-diphenylpropanedione ligands complexed to either vanadium(IV), copper(II), or palladium(II), thus giving rise to a disklike core surrounded by 10 chiral tails derived from L-(–)-lactic acid.

The mesomorphic behavior of these materials has been investigated by several different techniques which have given clear indications about the structure of the chiral mesophase. Thus, X-ray diffraction, circular dichroism, and dielectric spectroscopy have provided decisive data in the elucidation of the molecular arrangement within the ferroelectric mesophase. In addition, the ferroelectric behavior of these complexes has been studied in terms of their optical response to an alternating electric field applied to the aligned sample. In fact, columns lying parallel to the conducting glass surfaces give rise to the existence of two possible switching ground states on the application of positive or negative voltages. The clear similarity between these switching states and those of a tilted smectic layer will be employed as a means to interpret the electrooptical behavior of our disklike complexes by comparison with the electrooptical behavior of a well-studied calamitic FLC.

## Results and Discussion

**Synthesis and Molecular Structure Characterization.** The synthetic pathway to the target compounds is depicted in Scheme 1. The chiral tails, “6” and “7”, derived from L-(–)-lactic acid, were prepared by *O*-alkylation of (–)-ethyl L-lactate ester with the corresponding alkyl iodide using  $\text{Ag}_2\text{O}$  as a base.<sup>9</sup>



**Figure 1.** (a) Structure of the two possible isomers of the palladium complex  $\text{dK}''7''\text{Pd}$ . (b) Aromatic region of the  $^1\text{H}$  NMR spectrum corresponding to the complex  $\text{dK}''7''\text{Pd}$ .

In the preparation of the  $\beta$ -diketone ligands it was first necessary to obtain the penta-*O*-benzyl protected  $\beta$ -diketone ( $\text{pBdK}$ ) since ester groups (acting as linkages between the chiral tails and the mesogenic nucleus) were not compatible with the basic reaction conditions used to couple the methyl ester ( $\text{MtBB}$ ) and the acetophenone ( $\text{dBA}$ ). The coupling reaction was performed according to a literature method,<sup>10</sup> and a subsequent deprotection step with palladium hydroxide on carbon<sup>11</sup> was carried out to give the pentahydroxy- $\beta$ -diketone ( $\text{pHdK}$ ). This pentahydroxylated intermediate reacts with 5 mol of the chiral acid “6” or “7” in the presence of DCC/DMAP<sup>12</sup> to give the  $\beta$ -diketone ligands  $\text{dK}''6''$  and  $\text{dK}''7''$ .

Coordination of the  $\beta$ -diketone ligands ( $\text{dK}''6''$  and  $\text{dK}''7''$ ) with the appropriate metal was carried out by reaction of the equivalent amount of ligand and the appropriate salt, i.e.,  $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{Cu}(\text{AcO})_2 \cdot \text{H}_2\text{O}$ , and  $\text{Pd}(\text{AcO})_2$ .

**Structural Characterization of the Complexes.** The  $\beta$ -diketone ligands used in these complexes bear two different substituted aromatic rings, and therefore, the coordination of two ligands to the metal can give rise to either *cis* or *trans* isomers, or a mixture of both (Figure 1a). Nuclear magnetic resonance is a useful tool to elucidate the presence or absence of these two possible isomers. In the cases of the palladium complexes, it is possible to fully characterize their molecular structures by nuclear magnetic resonance. In contrast, the paramagnetic nature of vanadium(IV) and copper(II) makes it impossible to investigate these derivatives using this technique. However, it seems reasonable that the results obtained on the palladium systems can be extrapolated to the vanadyl and copper

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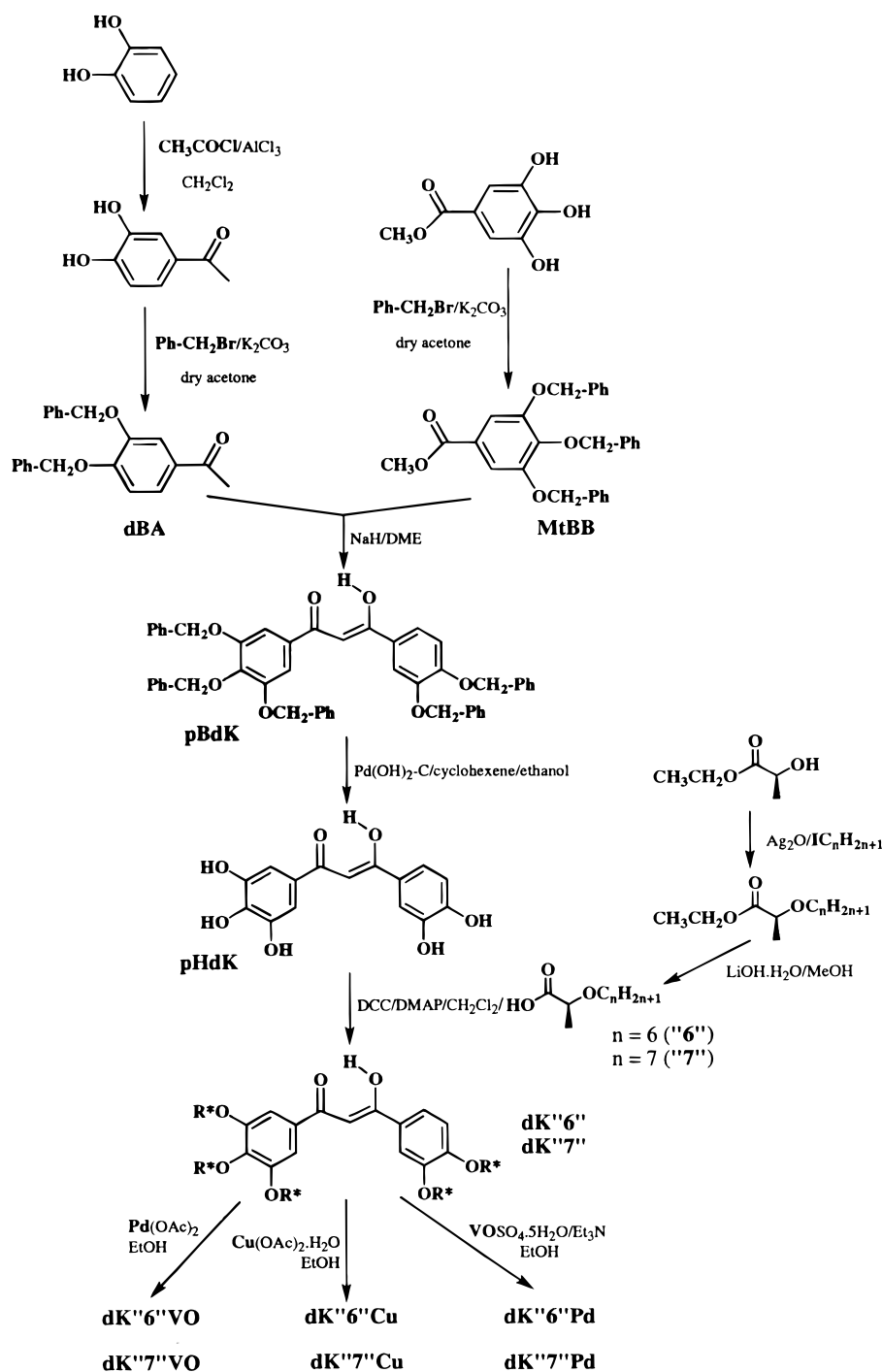
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Scheme 1



compounds, given that their synthetic processes are very similar.

Both palladium complexes have spectra that are more complicated than those expected for a single compound. The aromatic region of the spectrum of compound **dK''7''Pd** is represented in Figure 1b. It can be seen that two signals appear for each aromatic hydrogen, and that these signals have similar intensities. The signal corresponding to proton *d* (6.51 ppm) appears as a single peak, but it is broader than that corresponding to the free ligand. The spectrum is consistent with the existence of two different geometrical isomers (cis and trans) in the ratio 1:1.

**Mesomorphic Properties.** All six complexes show enantiotropic liquid crystalline behavior. Only one type of mesophase has been detected in each compound, and it is already

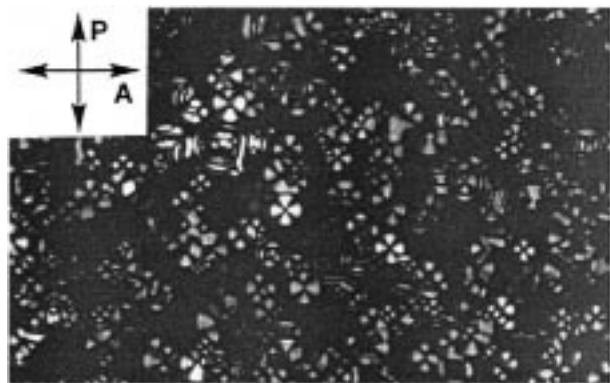
present in the sample obtained from the synthetic procedure. The clearing points of all compounds are gathered in Table 1. Melting or crystallization peaks were not observed in the DSC scans, even in the first heating. As the temperature is decreased the material becomes very viscous. It is possible that, at a certain temperature, the material turns into an amorphous solid, although no glass transition was observed in any of the complexes in the cooling process, even down to  $-20^\circ\text{C}$ .

**Structural Characterization of the Mesophase. Optical Microscopy.** All the complexes are obtained as liquid crystalline materials after the synthetic and purification processes. At room temperature, the mesophase is very viscous in all cases. As the temperature is increased the materials become progressively more fluid. Transition to the isotropic liquid is very slow

**Table 1.** Transition Temperatures (°C) Obtained by Differential Scanning Calorimetry<sup>a</sup>

compd	K		col <sub>i</sub> <sup>*</sup>	I	
<b>dK“6”VO</b>	—	<−20	•	125	•
<b>dK“6”Cu</b>	—	<−20	•	130	•
<b>dK“6”Pd</b>	—	<−20	•	149	•
<b>dK“7”VO</b>	—	<−20	•	122	•
<b>dK“7”Cu</b>	—	<−20	•	132	•
<b>dK“7”Pd</b>	—	<−20	•	147	•

<sup>a</sup> Scan rate: 10 °C/min. (—): the crystalline phase has not been detected by either DSC or optical microscopy cooling down until −20 °C.



**Figure 2.** Photomicrograph of the texture of compound **dK“7”VO** showing Maltese crosses. The picture was taken at room temperature after annealing the sample at 100 °C for 20 h.

in all cases and occurs over a broad temperature range (ca. 20 °C).

The textures observed are different and 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 mesophase forms very slowly in all cases, and, when completely formed, its texture does not change even on cooling to −20 °C. In contrast, palladium complexes (**dK“6”Pd** and **dK“7”Pd**) develop the liquid crystalline state very quickly on cooling the isotropic liquid. The texture is quite different to that observed for copper and vanadium complexes and appears more crystalline, and the material is more viscous. This characteristic is probably due to a more ordered molecular arrangement as deduced from X-ray diffraction studies (see below). In a similar way to the vanadium and copper complexes, this texture does not change 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 texture with Maltese crosses often appears. The extinction brushes are inclined with respect to the direction of the crossed polarizers, indicating the presence of molecular tilt (Figure 2). Sometimes this inclination is not observed in a freshly formed mesophase. The inclination will then appear on cooling or on annealing the sample. However, at other times the inclination is very small (10–15°) 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 time or when the temperature increases.

**Infrared Spectroscopy.** The strong dipole associated with the V=O bond perpendicular to the molecular plane led us to

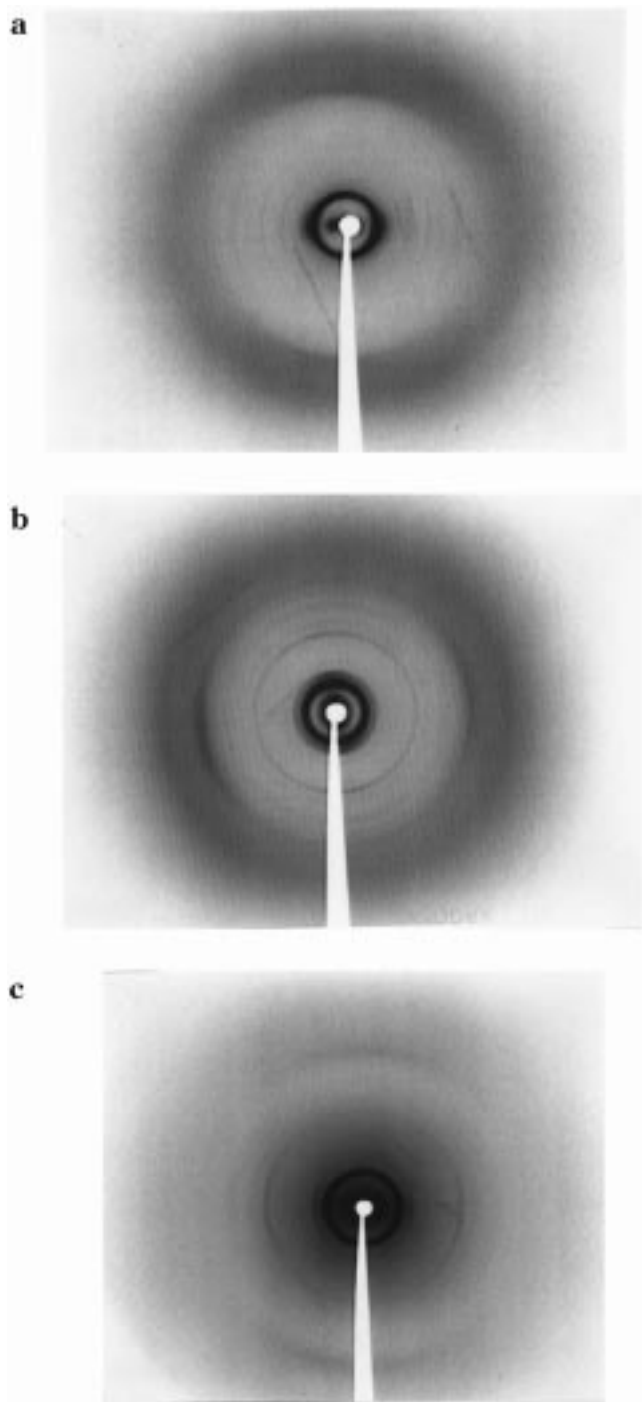
investigate the existence of intermolecular V=O–V=O interactions along the column, as proposed by other authors.<sup>13</sup> This phenomenon should give rise to a linear polar order along the columnar axis. The presence of associated V=O bonds is manifested as a band at 900 cm<sup>−1</sup> in the infrared spectra. The IR spectra recorded for both vanadium complexes showed a band at 985 cm<sup>−1</sup>, corresponding to the stretching of isolated V=O bonds. It is likely that the molecular tilt accounts for the absence of V=O–V=O interactions as the vanadyl groups are in a disposition away from the columnar axis.

**X-ray Diffraction.** The structures of the compounds were investigated by X-ray diffraction at room temperature as well as at high temperature (75 °C). The aim of this study was to characterize the type of mesophase as well as to determine the structural parameters. The results obtained are gathered in Table 2, and several representative photographs are shown in Figure 3.

From the patterns it can be deduced that some of the samples (**dK“6”Cu** and **dK“6”VO**) spontaneously adopt a preferential orientation on being introduced into the Lindemann glass capillary. This is revealed by the fact that diffraction arcs are obtained instead of the rings that would have been obtained if the sample was completely disoriented (Figure 3a). This phenomenon is due to the tendency of columnar mesophases to align themselves as a consequence of mechanical stress, such as that produced when the sample is pushed to the bottom of the capillary tube with a metal or glass rod. It is interesting to note that in these two compounds the column axes align themselves perpendicular to the capillary wall. This phenomenon was not observed in any of the other samples (**dK“6”Pd**, **dK“7”Cu**, **dK“7”VO** and **dK“7”Pd**). However, **dK“6”Pd** and **dK“7”Cu** did give aligned patterns after being sheared with a glass rod in the direction of the capillary axis at a temperature close to the transition to the isotropic liquid (Figure 3b). This behavior is due to the fact that the highly viscous mesophases at room-temperature become more fluid as the temperature increases, thus making their alignment easier. Compound **dK“7”VO** spontaneously adopted a particular orientation at 75 °C as a consequence of its higher fluidity, which enabled the sample to slide down the capillary wall. Alignment, although partial, makes the interpretation of the X-ray patterns easier as it facilitates the distinction between the interferences produced in the direction of the column axes and the interferences produced in the plane perpendicular to that direction.

The X-ray patterns confirm that all the compounds in the series exhibit a columnar mesophase between room temperature and the temperature of transition to the isotropic liquid. At room temperature all the patterns show several sharp reflections in the equatorial region, i.e., the plane perpendicular to the column axes (vertical direction in Figure 3a and horizontal direction in Figure 3b) that can be assigned, in all cases, to a two-dimensional rectangular lattice. The proposed indexing, the lattice constants, and the observed and calculated spacings are gathered in Table 2. In the meridian, i.e., the direction of the column axes (horizontal in Figure 3a and vertical in Figure 3b), the pattern is more simple: two broad maxima are observed, of which the one at lower scattering angles (higher distances) is stronger and narrower for the palladium derivatives (**dK“6”Pd** and **dK“7”Pd**) than for the other compounds. This suggests that this maximum, corresponding to distances between 5.3 and 5.7 Å depending on the particular compound (Table 2), arises from intracolumnar metal–metal interferences. At the same

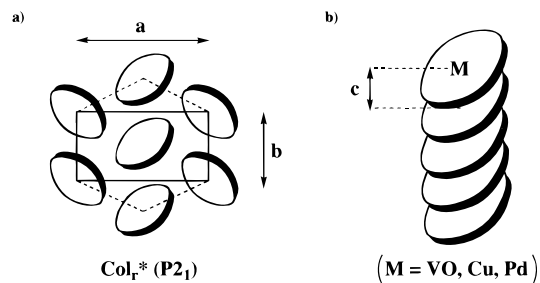
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**Figure 3.** X-ray patterns: (a) **dK'6''VO** at room temperature, (b) **dK'6''Pd** at room temperature, and (c) **dK'6''Pd** at 75 °C. The capillary axis lies horizontal in (a) and (b), and vertical in (c).

time, it can be deduced that the stacking order within the columns extends over longer distances in the palladium derivatives. This is consistent with the higher viscosity observed in **dK'6''Pd** and **dK'7''Pd**, and thus it can be concluded that their mesophases are more *ordered* than those of the other compounds. It is interesting to note that the stacking distance is longer for the oxovanadium derivatives (**dK'6''VO** and **dK'7''VO**), as expected from the presence of the oxygen atom axially coordinated to the vanadium atom, and this must force the molecules further away from each other.

All of the features discussed above are unambiguously characteristic of a rectangular columnar mesophase in which the molecules stack one on top of another and the columns



**Figure 4.** Schematic representation of the columnar rectangular mesophase showing (a) view along the  $c$  axis and (b) view perpendicular to the  $c$  axis.

generated adopt a rectangular packing. 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. It is interesting to note that for all the compounds the lattice constants  $a$  and  $b$  of the rectangular lattice (Table 2) are in the ratio  $\sqrt{3}$ , which in principle should correspond to a hexagonal structure. However, the  $(2\ 1\ 0)$  reflection that is observed in all the patterns, is not consistent with a hexagonal symmetry. A hexagonal cell is equivalent to a  $C$ -centered orthorhombic cell with lattice constants  $a$  and  $b$ , where  $b$  is the lattice constant of the hexagonal cell and  $a$  is equal to  $b\sqrt{3}$ . A  $C$ -centered orthorhombic symmetry implies that the molecule located at  $(1/2, 1/2, 0)$  has the same orientation as the molecule located at  $(0, 0, 0)$ , and thus all the  $(h\ k\ 0)$  reflections with an odd value for  $h + k$  should be systematically absent. This is not the case in the compounds in question, as revealed by the presence of an extra reflection, and so it can be concluded that, although the column axes are located at the nodes of a hexagonal network, there is an alternation in the tilt direction in such a way that a rectangular symmetry arises from a herringbone arrangement of the elliptical sections of the columns. The resulting space group is  $P2_1$ . The same kind of *pseudohexagonal* arrangement has been found in the columnar mesophase of a number of nonchiral metal-free phthalocyanines.<sup>14</sup> A schematical representation of this structure is shown in Figure 4.

The outermost maximum observed in the equatorial region corresponds to distances between 4.2 and 4.4 Å, and this deserves special attention. This maximum is superimposed over an almost isotropic diffuse ring extending from 4.5 to 4.7 Å, which is typically observed in columnar mesophases and assigned to interferences between the molten aliphatic chains. However, the reinforced scattering in the meridian region points to some kind of additional order. Two possible explanations can be proposed:

(i) This maximum could arise from intermolecular interferences along the direction perpendicular to the molecular planes. Under this assumption, the different value measured for this distance compared to the metal–metal distance along the column axis would confirm the existence of a tilt angle that could be estimated as  $\theta = \cos^{-1}(d_{D-D}/d_{M-M})$ , where  $d_{D-D}$  is the perpendicular disk-disk distance and  $d_{M-M}$  the metal–metal distance. From this formula a tilt angle  $\theta$  of about 36–40° would be deduced for our compounds. However, this theory seems to us rather improbable, as interferences between the stacked disks must give rise to maxima in the direction perpendicular to the molecular planes. If the molecules are tilted, the scattered intensity should be split to both sides of the meridian, a situation which has not been observed in our

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**Table 2.** X-ray Diffraction Data for the col<sub>i</sub>\* Mesophase: Lattice Constants, Measured and Calculated Lattice Spacings, Proposed Indexing, and Calculated Density

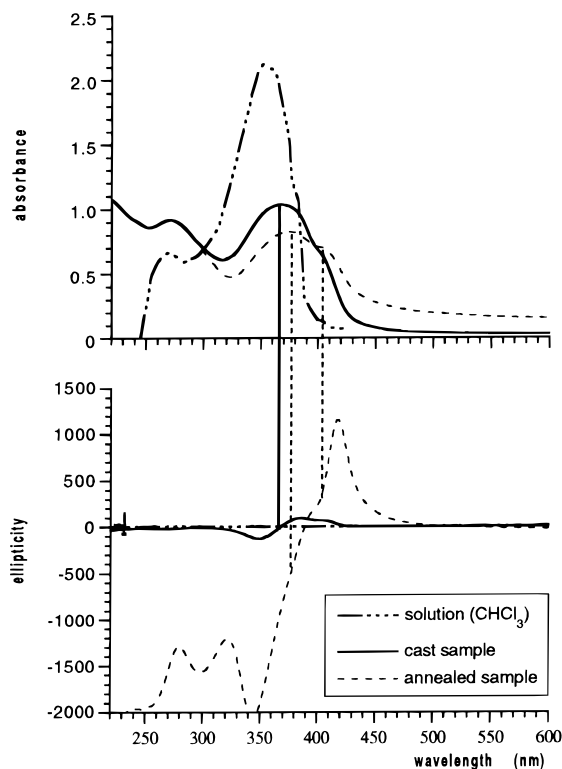
compd	lattice constants (Å)	$d_{\text{obs}}$ (Å)	$d_{\text{calc}}$ (Å)	$hkl$	calcd density (g cm <sup>-3</sup> )
<b>dK“6”VO</b>	$a = 46.1$ $b = 26.6$ $c = 5.7$	23.18	23.05	110, 200	1.06
		17.24	17.42	210	
		13.39	13.30	020, 310	
		11.56	11.52	220, 400	
		8.77	8.71	130, 420, 510	
		7.51	7.68	330, 600	
		5.7 (br)		001	
		4.4 (br)			
<b>dK“6”Cu</b>	$a = 48.5$ $b = 28.0$ $c = 5.4$	24.14	24.25	110, 200	1.01
		18.30	18.33	210	
		9.09	9.17	130, 420, 510	
		8.11	8.08	330, 600	
		6.77	6.72	240, 530, 710	
		6.20	6.06, 6.10	440, 800	
		5.4 (br)		001	
		4.2 (br)			
<b>dK“6”Pd</b>	$a = 46.9$ $b = 27.1$ $c = 5.4$	23.44	23.45	110, 200	1.10
		17.61	17.73	210	
		13.66	13.55	020, 310	
		8.83	8.87	130, 420, 510	
		7.82	7.82	330, 600	
		6.51	6.51	240, 530, 710	
		5.4 (br)		001	
		4.3 (br)			
<b>dK“7”VO</b>	$a = 48.3$ $b = 27.9$ $c = 5.7$	24.25	24.15	110, 200	1.03
		18.08	18.26	210	
		12.19	12.08	220, 400	
		9.03	9.13	130, 420, 510	
		6.97	6.97	040, 620	
		6.73	6.70	240, 530, 710	
		5.7 (br)		001	
		4.4 (br)			
<b>dK“7”Cu</b>	$a = 49.7$ $b = 28.7$ $c = 5.3$	24.87	24.85	110, 200	1.04
		18.78	18.78	210	
		9.38	9.39	130, 420, 510	
		8.30	8.28	330, 600	
		7.10	7.17	040, 620	
		6.87	6.89	240, 530, 710	
		6.22	6.21	440, 800	
		5.3 (br)		001	
<b>dK“7”Pd</b>	$a = 49.5$ $b = 28.6$ $c = 5.4$	24.54	24.75	110, 200	1.05
		18.72	18.72	210	
		14.50	14.30	020, 310	
		12.44	12.38	220, 400	
		9.33	9.36	130, 420, 510	
		8.26	8.25	330, 600	
		6.90	6.87	240, 530, 710	
		6.14	6.19	440, 800	
		5.4 (br)		001	
		4.3 (br)			

patterns. However, in the absence of well-aligned samples, it is difficult to establish a definitive conclusion.

(ii) A more plausible explanation is that this scattering is due to intra- and intermolecular interferences between the ordered parts of the side chains. Indeed, the side groups of these disklike mesogens are unconventional in that they contain an ester linkage and a branch, both of which impart an unusual degree of rigidity on the chain from the point of attachment to the phenyl ring to the oxygen atom bonded to the stereogenic carbon. Thus, nearly half of the mass of the side groups is contained in the rigid part, which on average will extend radially from the inner part of the column. Thus the main contribution of the chains to the X-ray scattering will take place in the direction of the column axis. On the other hand, the terminal hexyl or heptyl groups will be in a state of conformational disorder and will contribute mainly to the isotropic halo.

The X-ray patterns obtained at high temperatures (75 °C, Figure 3c) indicate that the symmetry of the mesophase is the same as at room temperature. Although the rectangular lattice parameters vary slightly, this change is irrelevant. However, the two scattering maxima corresponding to the intracolumnar order become broader and diffuse, so they spread and, in some cases, even end up overlapping each other. This suggests that the coherence length of the stacking diminishes, so the columns become more *disordered*, and, at the same time, the conformational freedom of the side chains increases.

In addition to the diffraction maxima discussed above (collected in Table 2), one additional peak is observed in the small-angle X-ray patterns at a diffraction angle of  $\theta$  about 0.5° which cannot be assigned to the rectangular lattice. Although this maximum is very weak, it can clearly be seen in the powder patterns obtained from nonoriented samples at room temperature.



**Figure 5.** UV and CD spectra recorded for the complex **dK'7VO** under different conditions: solution in THF (0.1 g/L) and thin film deposited on a quartz substrate by spin coating (cast sample and annealed sample, 100 °C for 20 h).

However, this peak almost disappears in the oriented patterns and in the high-temperature patterns. As the chiral columns are most probably twisted in the columnar structure, this small-angle maximum, which corresponds to a spacing of about  $84 \pm 2 \text{ \AA}$ , may well arise from the intracolumnar periodic modulation resulting from the column twisting. The helical pitch in chiral columnar mesophases has been measured by other authors using X-ray diffraction in powder<sup>15</sup> as well as in oriented samples.<sup>16</sup> However, we believe that alignment should unwind the helix, which is consistent with the fact that in our oriented samples the corresponding diffraction maximum disappears. The fact that this peak is also not observed in the high temperature patterns is probably due to its shifting to smaller angles because of the increase in the helical pitch upon heating, so it falls beyond the angular range of measurement of our apparatus.

**Circular Dichroism.** The UV and CD spectra of complex **dK'7VO** are represented in Figure 5. Three types of spectrum were recorded for the complex: (i) from a solution of the compounds in THF (0.1 g/L), (ii) from the neat compound deposited on a quartz substrate, and (iii) a freshly prepared thin film and also after annealing the thin film (100 °C for 20 h).

The first point to be highlighted is the fact that no CD signal was detected for the solution, whereas strong CD signals were recorded for both thin film samples (treated and untreated). This first observation leads us to believe that the optical activity of these complexes does not come from the presence of 10 stereogenic centers in each molecule but from the columnar structures present in the mesophase.

The CD spectrum of a freshly prepared thin film (ca.  $1.04 \mu\text{m}^{17}$ ) shows a positive exciton splitting centered at the wavelength of the  $\pi-\pi^*$  transition (365 nm). The exciton coupling phenomenon is a consequence of through-space interaction between two chromophores having an electric dipole moment allowed transition.<sup>18</sup> These dipoles must not be parallel since the exciton effect is the result of a vectorial product. In the particular case under discussion here and given that the molecules are planar and stacked in columns, the exciton splitting can only be due to intermolecular interaction of the electric dipole moment of the  $\pi-\pi^*$  transition being tilted with respect to the columnar axis and description of a helix along the column. From these results we can confirm the existence of a helical arrangement within the column. Moreover, the positive sign of the exciton splitting corresponds to a right-handed helical arrangement of the electric transitions, and this leads to a "minus" helix.

The CD spectra of the annealed thin films show much higher optical activity in both materials. Moreover, the Cotton effect (corresponding to a shoulder in the UV spectra) of the CD spectrum of the cast sample becomes a new exciton coupling centered at the wavelength of the UV shoulder (406 nm). On careful examination of this spectrum we can see that its shape corresponds to the appearance of the aforementioned second exciton splitting (406 nm) whose negative Cotton effect cancels out the positive Cotton effect of the former exciton coupling (376 nm). It is possible that some sort of chiral rearrangement of the structure of the mesophase during the annealing process might account for this CD spectrum. The resulting organization might consist of a helical superstructure, which has already been postulated by some authors.<sup>4c</sup> However, appropriate interpretation of the experimental evidence relies on the calculation of the CD spectra.

**Broadband Dielectric Spectroscopy.** The study of the dependence of the dielectric permittivity on the frequency of the applied electric field and the temperature enables information to be gained about the molecular structure and the motions of the molecules within the material (modes). A complete dielectric study of the complexes will be published elsewhere.<sup>19</sup>

Three modes have been found for these materials, and the dependence of each relaxation frequency upon temperature is represented in Figure 6.

The two modes appearing at high frequencies ( $10^6$  and  $10^9$  Hz) are related to motions of either the whole or a part of the molecule. Molecular modes are a consequence of rotations or fluctuations of molecular dipole moments. Since the molecules are tilted and chiral, a tilt induced dipole is contained in the plane of the molecule. Hence, the low-frequency process (mode l,  $10^6$  Hz) can be assigned to the rotation of the whole disklike molecule around the axis perpendicular to the molecular plane. The origin of the relaxation at  $10^9$  Hz (mode h) should be related to motions of the side groups of the disks. They contain an ester linkage and a branch which provide an important degree of rigidity to the chain from the point of attachment to the phenyl ring to the oxygen atom in the stereogenic center. A third mode at lower frequency appears below the clearing point and corresponds to a collective mode. This process does not appear in achiral compounds. Its dielectric strength<sup>19</sup> and frequency

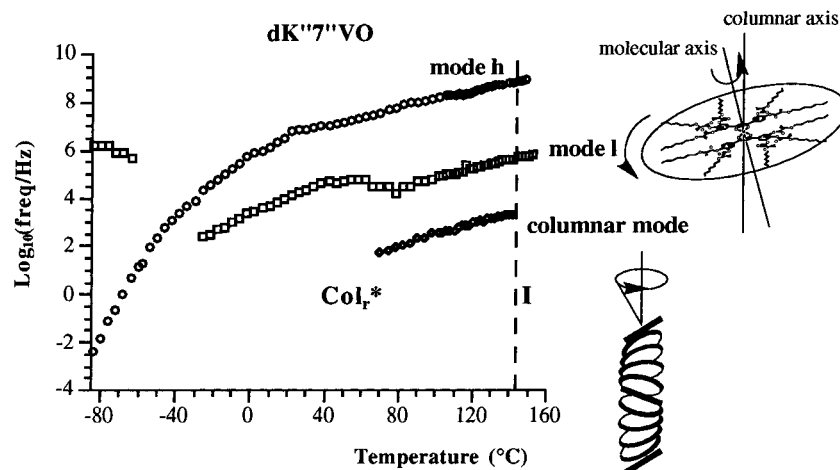
(15) Van Nostrum, C. F.; Bosman, A. W.; Gelink, G. H.; Schouten, P. G.; Warman, J. M.; Kentgens, A. P. M.; Devillers, M. A. C.; Mieijerink, A.; Picken, S. J.; Sohlhing, U.; Schouten, A. J.; Nolte, R. J. M. *Chem. Eur. J.* **1995**, *1*, 171–182.

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(19) de la Fuente, M. R.; Palacios, B.; Pérez-Jubindo, M. A.; Iglesias, R.; Serrano, J. L.; Sierra, T. Submitted for publication.



**Figure 6.** Temperature dependence of the different modes: (a) and (b) molecular modes and (c) columnar mode, corresponding to compound **dK''7''VO**. Representation of the motions corresponding to the low-frequency molecular model and to the columnar mode.

make it closely related to the Goldstone mode of the  $\text{SmC}^*$  phase, which is due to azimuthal fluctuations of the molecular director. On the basis of these experimental results it does not seem unreasonable to think in terms of a helical structure within the mesophase consisting of tilted molecules whose tilt direction rotates along the columnar axis. Indeed, this explanation is in complete agreement with the results obtained from circular dichroism.

**Ferroelectric Behavior.** The results discussed above, which confirm a tilted columnar arrangement for these mesogenic complexes, prompted us to investigate their ferroelectric behavior. We focused our experiments on the compounds with the heptyloxy group in the stereogenic center (**dK''7''VO**, **dK''7''Cu**, and **dK''7''Pd**).

Initially the compounds were studied in  $4\ \mu\text{m}$  cells with a polyimide coating. The texture was always dendritic when the mesophase formed at a cooling rate of  $10\ ^\circ\text{C}/\text{min}$ . In every case an electrooptic response was observed with alternating fields stronger than  $50\ \text{Vpp}$  from the clearing temperature down to  $70\text{--}90\ ^\circ\text{C}$ . The mesophase does not display any texture change below this temperature, but the viscosity increases dramatically on cooling, thus preventing the commutation phenomenon. As already explained in the section describing optical microscopy studies, when the mesophase was allowed to develop at very slow rate ( $0.1\ ^\circ\text{C}/\text{min}$ ) or when it was annealed at  $100\ ^\circ\text{C}$ , a flowerlike texture (tilted Maltese crosses) appears. When an alternating electric field is applied to this texture, the extinction brushes of the crosses rotate back and forth.

The samples were also studied between two ITO-coated glass surfaces with no alignment treatment. The cell thicknesses were estimated to be between  $25$  and  $30\ \mu\text{m}$ . On cooling the material down from the isotropic liquid the textures were similar to those observed in commercial cells. In these cells, the material could be aligned (with the columns parallel to the glass plates) by the shearing technique carried out at ca.  $110\ ^\circ\text{C}$ , a temperature at which the materials have some fluidity. After several minutes under the influence of the electric field the alignment was partially destroyed.

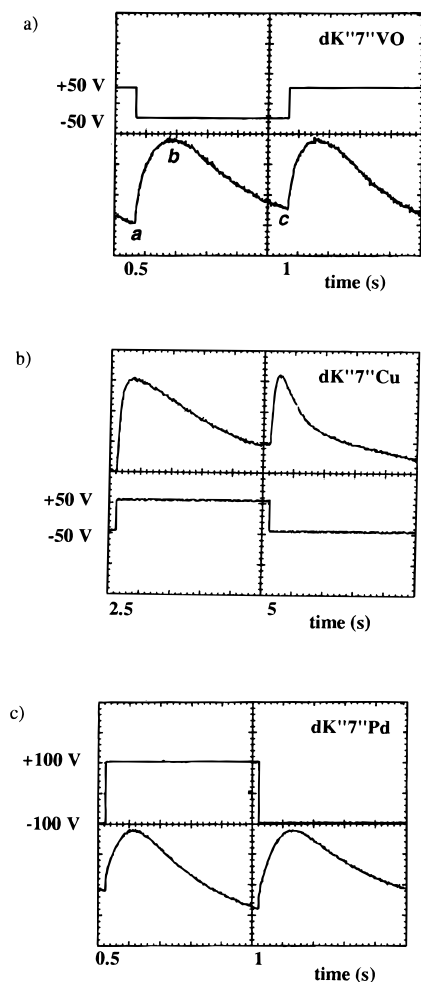
It was impossible to evaluate the spontaneous polarization values, probably due to the high conductivity of the materials which masks the current caused by the inversion of the polarization.

**Electrooptic Effect.** The electrooptical response of sheared samples (as mentioned above) could be recorded by means of

a photomultiplier connected to the polarizing microscope. The photocurrent was registered on an oscilloscope. All three materials were investigated by varying the intensity and the frequency of the square wave. Figure 7a–c represent the oscilloscope signal of the photocurrent generated by the three complexes at different voltages and frequencies. The experiments had to be carried out at very low frequencies and with intense electric fields due to the high viscosity of the materials. Indeed, the long response times of these materials enabled us to follow the switching process by observing the sample through the polarizing microscope. All the experiments were carried out at around  $100\ ^\circ\text{C}$ , a temperature at which the fluidity was sufficient to allow the switching process. Using a frequency of  $1\ \text{Hz}$  (Figure 7a) and a voltage of  $100\ \text{Vpp}$ , a two-step switching consisting first of a quick change to a transmission state and then a second slower change to a dark state was observed for the oxovanadium complex. The signal on the oscilloscope has a shape corresponding to a transition between two states with a similar contrast (*a* and *c*) through an intermediate state showing the maximum light transmission (*b*) of the process. Similar responses were obtained for copper (Figure 7b) and palladium (Figure 7c) complexes using slightly modified measurement conditions which must be related to the different viscosities of the materials. Under an electric field of  $100\ \text{Vpp}$  at a frequency of  $0.2\ \text{Hz}$  for the copper complex and a field of  $200\ \text{Vpp}$  at a frequency of  $1\ \text{Hz}$  for palladium complex, three different contrast states (*a*, *b*, and *c*) appeared in the oscilloscope signal.

Interpretation of these experimental results was initially based on two possibilities. We first thought in terms of a process consisting of the helix winding and unwinding, as some authors have already proposed.<sup>4c</sup> However, the fields at which the materials have been studied seem to be strong enough to keep the columnar helix unwound and, besides, shearing giving rise to a birefringent texture also seems to destroy the helical arrangement (see the X-ray diffraction studies). A second possibility arises by considering that the high tilt of the extinction brushes of the Maltese cross texture is related with this response. The support for this idea comes from the study of a calamitic ferroelectric liquid crystal with a high tilt angle. Indeed, smectic layers with the molecular long axis tilted with respect to their normal can be considered equivalent to the columns with the disklike molecules tilted with respect to the column axis. On the basis of this analogy, the electrooptic effect in calamitic ferroelectric liquid crystals can be related to the electrooptic





**Figure 7.** Optical response of the three complexes **dK''7''VO**, **dK''7''Cu**, and **dK''7''Pd** under a rectangular voltage.

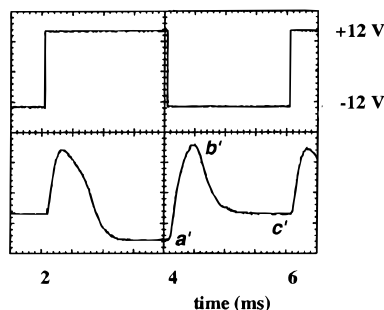
effect in columnar liquid crystals. Experiments were performed with a calamitic liquid crystal, **III(OH)a**,<sup>20</sup> with a high tilt angle (37°). Results from this compound show that molecules switch between two ferroelectric states (separated by an angle of 74°) through an intermediate state of maximum transmission. This last state would correspond to a transition state in which rodlike molecules are oriented at an angle of 45° with respect to the polarizer. In an attempt to emulate the response of a material with a long response time which cannot easily follow the reversal of the field, even at very low frequencies, we studied this calamitic compound at a very high frequency. The signal registered on the oscilloscope (Figure 8) was very similar to that recorded for the disklike complexes.

Figure 9 depicts, in a simplified way, the determinant effect of the tilt angle in the optical response of the materials by comparing them with the response of the calamitic compound studied.

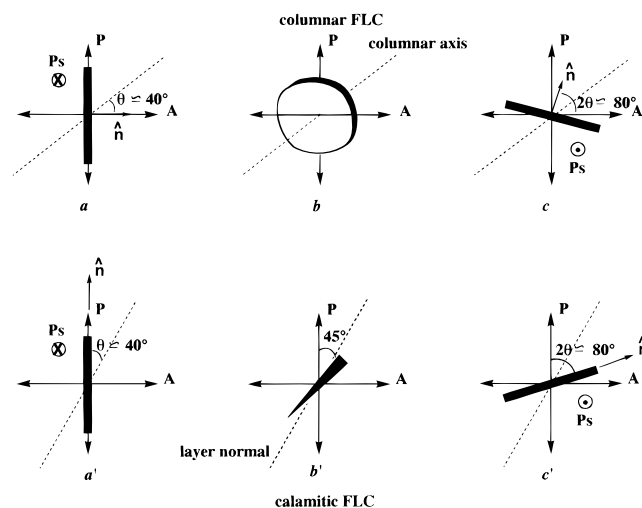
## Conclusions

Coordination of two  $\beta$ -diketone ligands bearing five chiral tails with oxovanadium(IV), copper(II) and palladium(II) has led to the first switchable columnar metallomesogens.

The appropriate combination of different characterization techniques—optical microscopy (in conjunction with a photomultiplier), differential scanning calorimetry, X-ray diffraction,



**Figure 8.** Optical response of the calamitic compound **III(OH)a**<sup>20</sup> with a high tilt angle (37°).



**Figure 9.** Schematic representation of the three contrast situations proposed to explain the optical response of the columnar complexes by comparison with a calamitic SmC\* FLC with a high tilt angle. The maximum transmission corresponds to states b and b' in which both types of molecules are oriented 45° with respect to the crossed polarizers. Initial switching states, a and a', correspond to complete extinction situations (0° from the polarizer), and final switching states, c and c', correspond to situations close to extinction (ca. 10° from the analyzer).

circular dichroism, and dielectric spectroscopy—has allowed a rigorous analysis of the mesophase structure and the switching process of these compounds.

All the complexes show only a single mesophase which is stable at room temperature. The mesophase has been identified as rectangular columnar by X-ray diffraction. Circular dichroism has demonstrated the existence of helical order within the column. Only a nonparallel arrangement of the planar molecules within the column, together with the rotation of the molecular director along the column axis describing a minus helix, can account for the appearance of a positive exciton coupling corresponding to the  $\pi$ – $\pi^*$  transition. The presence of this helix can explain the appearance of a Goldstone-like mode (the so-called columnar mode) when the material is studied by dielectric spectroscopy. This mode would be related to azimuthal fluctuations of the molecular director. By application of an alternating electric field, an electrooptic effect can be observed for all the complexes. The response of the material to the field is in accordance with a strong tilting of the molecules with respect to the column axis.

## Experimental Section

**General Procedure for the Preparation of the (2S)-2-Alkoxypropionic Acids "6" and "7".** To a solution of 4.96 g (0.042 mol) of ethyl lactate and 0.099 mol of the corresponding iodoalkane was added

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16.94 (0.073 mol) of silver(I) oxide. The mixture was refluxed for 24 h in the dark. The mixture was filtered through Celite, which was washed with diethyl ether, and the solvent was removed under vacuum. To the resulting mixture, which contained the ester (ca. 4 g as estimated from  $^1\text{H}$  NMR spectroscopy) and byproducts such as starting material, iododalkane, alkanol, and alkyl ether, was added 150 mL of methanol, 70 mL of water, and 6 g of LiOH, and the mixture was stirred overnight at room temperature. After this time, 150 mL of 3.5% NaOH was added. The organic products were extracted with diethyl ether. The aqueous phase, which contains the salt of the chiral acid, was acidified by the addition of HCl. The acid was extracted with diethyl ether and dried over  $\text{MgSO}_4$ , and the solvent evaporated. The colorless product was purified by flash chromatography using a hexane/ethyl acetate [9:1] mixture as eluent.

**(2S)-2-Hexyloxypropanoic Acid ("6").** Yield: 42%.  $[\alpha]_{\text{D}}^{25}$ :  $-22^\circ$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.86 (t, 3H), 1.20–1.40 (m, 6H), 1.42 (d,  $J = 6.9$  Hz, 3H), 1.50–1.60 (m, 2H), 3.42 (dt,  $J = 9.0, 6.6$  Hz, 1H), 3.55 (dt,  $J = 9.0, 6.6$  Hz, 1H), 3.96 (c,  $J = 6.9$  Hz, 1H), 10.00 (s, 1H).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.0, 18.2, 22.5, 25.6, 29.6, 31.6, 70.6, 74.5, 178.2. IR (neat): 3700–2500, 1719, 1458, 1127  $\text{cm}^{-1}$ . MS (FAB $^+$ )  $m/z$  (%): 175 [M + H] $^+$ .

**(2S)-2-Heptyloxypropanoic Acid ("7").** Yield: 55%.  $[\alpha]_{\text{D}}^{25}$ :  $-20^\circ$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.86 (t,  $J = 6.5$  Hz, 3H), 1.20–1.35 (m, 8H), 1.43 (d,  $J = 6.9$  Hz, 3H), 1.59 (t,  $J = 6.9$  Hz, 2H), 3.42 (dt,  $J = 9.0, 6.7$  Hz, 1H), 3.55 (dt,  $J = 9.0, 6.7$  Hz, 1H), 3.97 (c,  $J = 6.9$  Hz, 1H), 7.5 (s, 1H).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.0, 18.1, 22.6, 25.9, 29.0, 29.6, 31.7, 70.6, 74.5, 177.3. IR (neat): 3700–2500, 1723, 1458, 1241, 1127  $\text{cm}^{-1}$ . MS (FAB $^+$ )  $m/z$  (%): 189 [M + H] $^+$ .

**Preparation of Methyl 3,4,5-Tribenzyloxybenzoate (MtBB).** A mixture of 4 g (0.022 mol) of methyl 3,4,5-trihydroxybenzoate, 9 g (0.065 mol) of anhydrous potassium carbonate, and 11.1 g (0.065 mol) of benzyl bromide in 200 mL of dry acetone was refluxed for 6 h. The mixture was poured into water, the white precipitate was extracted with diethyl ether and dried over  $\text{MgSO}_4$ , and the solvent removed under vacuum. The product obtained was recrystallized from hexane. The ester was obtained as a white solid in a 76% yield. mp: 98  $^\circ\text{C}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.87 (s, 3H), 5.10 (s, 2H), 5.12 (s, 4H), 7.20–7.50 (m, 17H).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  52.2, 71.2, 75.1, 109.0, 125.2, 127.6, 128.0, 128.2, 128.6, 136.7, 137.5, 142.4, 152.6, 166.6. IR (Nujol): 1716, 1587, 1427, 1336, 1215, 1111  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{29}\text{H}_{26}\text{O}_5$ : C, 76.63; H, 5.77. Found: C, 76.22; H, 5.34.

**Preparation of 3,4-Dihydroxyacetophenone (dHA).** A suspension of 5 g (0.045 mol) of catechol in  $\text{CH}_2\text{Cl}_2$  was slowly added to a stirred suspension of 18.2 g (0.136 mol) of aluminum trichloride in dry  $\text{CH}_2\text{Cl}_2$  under an inert atmosphere. Acetyl chloride (3.3 mL, 0.046 mol) was then added by syringe. After stirring at room temperature overnight, the mixture was poured into dilute HCl, extracted with diethyl ether, and dried over  $\text{MgSO}_4$ . The product obtained after removing the solvent was purified by flash chromatography using hexane/ethyl acetate [3:1] as eluent and recrystallized from hexane. Yield: 51%.  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  2.49 (s, 3H), 6.85 (d,  $J = 8.6$  Hz, 1H), 7.38–7.42 (m, 2H), 9.38 (s, 1H), 9.88 (s, 1H).  $^{13}\text{C}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  26.3, 115.0, 115.1, 121.8, 129.1, 145.2, 150.7, 196.3. IR (Nujol): 3450–3000, 1663, 1591, 1524, 1456, 1375  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_8\text{H}_8\text{O}_3$ : C, 63.15; H, 5.30. Found: C, 62.98; H, 5.05.

**Preparation of 3,4-Dibenzyloxyacetophenone (dBA).** To a solution of 2 g (0.013 mol) of 3,4-dihydroxyacetophenone and 4.5 g (0.026 mol) of benzyl bromide in dry acetone was added 3.63 g (0.026 mol) of anhydrous  $\text{K}_2\text{CO}_3$ . After refluxing for 20 h the reaction mixture was allowed to cool, and the salts were filtered off. The solvent was removed under vacuum, and a solid was obtained which was purified by two recrystallizations from ethanol and hexane, respectively. Yield: 78%. mp: 84  $^\circ\text{C}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.49 (s, 3H), 5.19 (s, 2H), 5.22 (s, 2H), 6.91 (d,  $J = 8.2$  Hz, 1H), 7.3–7.5 (m, 10H), 7.50 (dd,  $J = 8.4, 1.6$  Hz, 1H), 7.58 (d,  $J = 1.6$  Hz, 1H).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  26.2, 70.8, 71.1, 112.9, 113.7, 123.5, 127.1, 127.4, 128.0, 128.0, 128.5, 128.6, 130.8, 136.5, 136.8, 148.6, 153.2, 196.7. IR (Nujol): 1668, 1588, 1514, 1425, 1146  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{22}\text{H}_{20}\text{O}_3$ : C, 79.50; H, 6.06. Found: C, 79.37; H, 6.87.

**Preparation of 1-(3,4-dibenzyloxyphenyl)-3-(3,4,5-tribenzyloxyphenyl)-1,3-propanedione (pBdK).** To a solution of 4.5 g (0.01 mol) of methyl 3,4,5-tribenzyloxybenzoate and 3.3 g (0.01 mol) of 3,4-dibenzyloxyacetophenone in dry dimethoxyethane, under an inert atmosphere, was added 0.476 g (0.02 mol) of sodium hydride. The reaction mixture was refluxed for 14 h, and then cooled, poured into water. The solution was acidified with dilute HCl and the precipitate obtained was collected by filtration. The solid was dissolved in dichloromethane and filtered to eliminate solid impurities. The solvent was removed under vacuum, the solid was stirred in hot ethanol to remove any starting materials, and the yellow pure product was filtered off. Yield: 72%. mp: 128  $^\circ\text{C}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.13 (s, 2H), 5.15 (s, 4H), 5.22 (s, 2H), 5.24 (s, 2H), 6.49 (s, 1H), 6.97 (d,  $J = 8.5$  Hz, 1H), 7.20–7.50 (m, 28H), 7.59 (d,  $J = 2.0$  Hz, 1H), 16.95 (s, 1H).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  70.9, 71.5, 71.5, 75.2, 92.3, 107.1, 113.4, 113.5, 121.7, 127.2, 127.5, 127.6, 128.0, 128.1, 128.2, 128.6, 128.6, 130.9, 136.5, 136.7, 136.8, 137.4, 142.2, 148.7, 152.8, 184.1, 185.0. IR (Nujol): 1664, 1594, 1454, 1273  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{50}\text{H}_{42}\text{O}_7$ : C, 79.56; H, 5.61. Found: C, 79.31; H, 5.57.

**Preparation of 1-(3,4-Dihydroxyphenyl)-3-(3,4,5-trihydroxyphenyl)-1,3-propanedione (pHdK).** A suspension of 3.5 g (4.6 mmol) of the protected  $\beta$ -diketone and 1.75 g of 10% palladium hydroxide on carbon in 35 mL of cyclohexene and 90 mL of absolute ethanol was refluxed for 2 h. The mixture was cooled and filtered through Celite to remove the catalyst. The ethanol was removed, and dichloromethane and hexane were added. A brown precipitate formed and was collected by filtration. Yield 91%.  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  6.78 (s, 1H), 6.83 (d,  $J = 8.1$  Hz, 1H), 7.05 (s, 2H), 7.44–7.49 (m, 2H), 9.11 (s, 1H), 9.26 (s, 2H), 9.35 (s, 1H), 9.89 (s, 1H), 17.40 (s, 1H).  $^{13}\text{C}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  90.9, 106.7, 114.3, 115.6, 120.2, 125.1, 126.3, 138.5, 145.5, 145.7, 146.0, 150.4, 184.3. IR (Nujol): 1653, 1592, 1522, 1458, 1294  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{15}\text{H}_{12}\text{O}_7$ : C, 59.22; H, 3.98. Found: C, 59.13; H, 3.88.

**General Procedure for the Preparation of the Ligands dK"6" and dK"7".** To a solution of 0.5 g (1.64 mmol) of the pentahydroxy  $\beta$ -diketone in dry dichloromethane was added 8.62 mmol of the chiral acid with stirring under an inert atmosphere. A solution of 1.8 g (9.02 mmol) of dicyclohexylcarbodiimide in dichloromethane was added by syringe. Finally, 180 mg (1.48 mmol) of (dimethylamino)pyridine in dichloromethane was added. The mixture was stirred at room temperature for 2 days. The precipitated dicyclohexylurea was filtered off. The solvent was removed, and the product purified by flash chromatography using hexane/ethyl acetate [9:1] as eluent to give the pure product as a red liquid.

**1-{3,4-Bis[(2S)-2-hexyloxypropanoyloxy]phenyl}-3-{3,4,5-tris-[(2S)-2-hexyloxypropanoyloxy]phenyl}-1,3-propanedione (dK"6").** Yield: 36%.  $[\alpha]_{\text{D}}^{25}$ :  $-65^\circ$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.86 (t,  $J = 6.9$  Hz, 15H), 1.20–1.40 (m, 30H), 1.50–1.70 (m, 25H), 3.40–3.50 (m, 5H), 3.60–3.70 (m, 5H), 4.10–4.20 (m, 5H), 6.68 (s, 1H), 7.38 (d,  $J = 8.7$  Hz, 1H), 7.76 (s, 2H), 7.82 (d,  $J = 2.1$  Hz, 1H), 7.86 (dd,  $J = 8.4, 2.1$  Hz, 1H), 16.63 (s, 1H).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.0, 18.7, 22.6, 25.7, 29.7, 31.6, 71.0, 74.7, 93.3, 119.5, 122.6, 123.7, 125.7, 133.7, 143.5, 168.9, 170.3, 170.6, 183.2, 184.0, 202.5, 206.1. IR (neat): 1783, 1608, 1576, 1467, 1260, 1116  $\text{cm}^{-1}$ . MS (FAB $^+$ )  $m/z$  (%): 1086 [M + H] $^+$ .

**1-{3,4-Bis[(2S)-2-heptyloxypropanoyloxy]phenyl}-3-{3,4,5-tris-[(2S)-2-heptyloxypropanoyloxy]phenyl}-1,3-propanedione (dK"7").** Yield: 22%.  $[\alpha]_{\text{D}}^{25}$ :  $-64^\circ$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.85 (t,  $J = 6.6$  Hz, 15H), 1.20–1.35 (m, 40H), 1.54 (d,  $J = 6.7$  Hz, 15H), 1.50–1.65 (m, 10H), 3.35–3.50 (m, 5H), 3.60–3.75 (m, 5H), 4.05–4.20 (m, 5H), 7.38 (d,  $J = 8.4$  Hz, 1H), 7.75 (s, 2H), 7.82 (d,  $J = 2.0$  Hz, 1H), 7.87 (dd,  $J = 8.6, 2.1$  Hz, 1H), 16.63 (s, 1H).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.0, 18.7, 22.6, 26.0, 29.1, 29.8, 31.8, 70.9, 74.7, 93.3, 119.5, 122.6, 123.7, 125.7, 133.6, 137.5, 142.1, 143.5, 145.4, 168.9, 170.3, 170.6, 183.2, 184.0. IR (neat): 1782, 1608, 1576, 1466, 1260, 1116  $\text{cm}^{-1}$ . MS (FAB $^+$ )  $m/z$  (%): 1156 [M + H] $^+$ .

**Preparation of Bis{1-[3,4-bis[(2S)-2-hexyloxypropanoyloxy]phenyl]-3-[3,4,5-tris[(2S)-2-hexyloxypropanoyloxy]phenyl]-1,3-propanedionato}oxovanadium(IV) (dK"6"VO).** To a solution of 206.15 mg (0.19 mmol) of the chiral  $\beta$ -diketone dK"6" in 8 mL of ethanol was added 19.2 mg (0.19 mmol) of triethylamine in ethanol.

A solution of 23 mg (0.091 mmol) of  $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$  in 5 mL of ethanol/water was added dropwise to the above solution. In few seconds a greenish precipitate appeared, and the mixture was stirred at room temperature for an hour. The precipitate was then filtered off and washed with water. The waxy material obtained was dissolved in chloroform and filtered through Celite. After the solvent had evaporated, the complex was obtained as a green solid. Yield: 72%. IR (Nujol): 1778, 1538, 1484, 1119, 985  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{120}\text{H}_{182}\text{O}_{35}\text{V}$ : C, 64.49; H, 8.15. Found: C, 64.89; H, 8.55. MS ( $\text{FAB}^+$ )  $m/z$  (%): 2235 [ $\text{M}$ ] $^+$ .

**Preparation of Bis{1-[3,4-bis(2S)-2-heptyloxypropanoyloxy]phenyl}-3-[3,4,5-tris(2S)-2-heptyloxypropanoyloxy]phenyl}-1,3-propanedionato}oxovanadium(IV) (dK<sup>6</sup>VO).** To a solution of 196.35 mg (0.17 mmol) of the chiral  $\beta$ -diketone dK<sup>6</sup> in 3 mL of diethyl ether was added 19.4 mg (0.19 mmol) of triethylamine. A solution of 22 mg (0.087 mmol) of  $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$  in 5 mL of methanol/water was then added dropwise to the above solution. The reaction mixture was stirred at room temperature for 2 h. After evaporating the solvent a waxy product was obtained which was dissolved in diethyl ether. After filtering through Celite, the solution was concentrated, and the complex precipitated with cold ethanol and filtered off as a green waxy material. Yield: 68%. IR (Nujol): 1779, 1541, 1483, 1118, 983  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{130}\text{H}_{202}\text{O}_{35}\text{V}$ : C, 65.74; H, 8.51. Found: C, 65.35; H, 7.61. MS ( $\text{FAB}^+$ )  $m/z$  (%): 2375 [ $\text{M}$ ] $^+$ .

**General Procedure for the Preparation of dK<sup>6</sup>Cu and dK<sup>7</sup>Cu.** To a solution of 0.092 mmol of the corresponding chiral  $\beta$ -diketone (dK<sup>6</sup> or dK<sup>7</sup>) in 4 mL of absolute ethanol was added dropwise a solution of 9.2 mg (0.046 mmol) of  $\text{Cu}(\text{AcO})_2 \cdot \text{H}_2\text{O}$  in ethanol/water. The reaction mixture was stirred at room temperature for 1 h. The precipitate was then filtered off and washed with water. The compound obtained was dissolved in chloroform and filtered through Celite. The pure complex was obtained after evaporating the solvent.

**Bis{1-[3,4-bis(2S)-2-hexyloxypropanoyloxy]phenyl}-3-[3,4,5-tris(2S)-2-hexyloxypropanoyloxy]phenyl}-1,3-propanedionato}copper(II) (dK<sup>6</sup>Cu).** Yield: 79%. IR (Nujol): 1778, 1549, 1483, 1120  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{120}\text{H}_{182}\text{O}_{34}\text{Cu}$ : C, 64.59; H, 8.17. Found: C, 64.31; H, 8.16. MS ( $\text{FAB}^+$ )  $m/z$  (%): 2361 [ $\text{M} + 2\text{Cu} + 2\text{H}$ ] $^+$ .

**Bis{1-[3,4-bis(2S)-2-heptyloxypropanoyloxy]phenyl}-3-[3,4,5-tris(2S)-2-heptyloxypropanoyloxy]phenyl}-1,3-propanedionato}copper(II) (dK<sup>7</sup>Cu).** Yield: 72%. IR (Nujol): 1778, 1538, 1485, 1378, 1122  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{130}\text{H}_{202}\text{O}_{34}\text{Cu}$ : C, 65.84; H, 8.53. Found: C, 65.56; H, 7.92. MS ( $\text{FAB}^+$ )  $m/z$  (%): 2436 [ $\text{M} + \text{Cu}$ ] $^+$ .

**General Procedure for the Preparation of dK<sup>6</sup>Pd and dK<sup>7</sup>Pd.** To a solution of 0.185 mmol of the corresponding chiral  $\beta$ -diketone (dK<sup>6</sup> and dK<sup>7</sup>) in 8 mL of ethanol was added dropwise a solution of 21.1 mg (0.094 mmol) of  $\text{PdAcO}_2$  in ethanol. The reaction mixture was stirred at room temperature. After half an hour a green-brown precipitate appeared. The reaction mixture was stirred a further 5 h, and the precipitate was collected by filtration. The product was dissolved in chloroform, filtered through Celite, and reprecipitated with cold ethanol. A yellow-orange waxy material was obtained.

**Bis{1-[3,4-bis(2S)-2-hexyloxypropanoyloxy]phenyl}-3-[3,4,5-tris(2S)-2-hexyloxypropanoyloxy]phenyl}-1,3-propanedionato}palladium(II) (dK<sup>6</sup>Pd).** Yield: 48%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.80–0.90 (m, 30H), 1.2–1.4 (m, 60H), 1.45–1.65 (m, 50H), 3.30–3.50 (m, 10H), 3.60–3.70 (m, 10H), 4.00–4.20 (m, 10H), 6.49 (s, 2H), 7.30 (d,  $J = 8.4$  Hz, 1H), 7.32 (d,  $J = 8.7$  Hz, 1H), 7.62 (s, 2H), 7.63 (s, 2H), 7.67 (d,  $J = 1.8$  Hz, 1H), 7.70 (d,  $J = 1.8$  Hz, 1H), 7.78–7.84 (m, 2H).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.0, 16.4, 18.7, 18.8, 22.6, 25.7, 29.7, 31.6, 70.9, 74.5, 74.6, 74.7, 96.6, 119.9, 122.8, 123.4, 126.2, 134.8, 136.8, 141.6, 143.1, 144.7, 168.9, 170.2, 170.6, 179.7, 180.7, 180.8, 190.1, 192.7. IR (Nujol): 1778, 1538, 1482, 1121  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{120}\text{H}_{182}\text{O}_{34}\text{Pd}$ : C, 63.37; H, 8.01. Found: C, 63.09; H, 7.44. MS ( $\text{FAB}^+$ )  $m/z$  (%): 2376 [ $\text{M} + \text{Pd} - 3\text{H}$ ] $^+$ .

**Bis{1-[3,4-bis(2S)-2-heptyloxypropanoyloxy]phenyl}-3-[3,4,5-tris(2S)-2-heptyloxypropanoyloxy]phenyl}-1,3-propanedionato}palladium(II) (dK<sup>7</sup>Pd).** Yield: 46%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.80–0.90 (m, 30H), 1.20–1.40 (m, 80H), 1.50–1.60 (m, 50H), 3.35–3.50 (m, 10H), 3.60–3.75 (m, 10H), 4.00–4.20 (m, 10H), 6.51 (s, 2H), 7.31 (d,  $J = 8.6$  Hz, 1H), 7.32 (d,  $J = 8.6$  Hz, 1H), 7.63 (s, 2H), 7.65 (s, 2H), 7.69 (d,  $J = 2.0$  Hz, 1H), 7.71 (d,  $J = 2.0$  Hz, 1H), 7.81 (dd,  $J = 8.6, 2.0$  Hz, 1H), 7.82 (dd,  $J = 8.6, 2.0$  Hz, 1H).  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.1, 18.8, 22.6, 26.0, 29.1, 29.8, 31.8, 70.9, 74.6, 96.6, 119.9, 122.8, 123.4, 126.1, 134.8, 136.8, 141.6, 143.1, 144.7, 168.9, 170.2, 170.6, 179.7, 179.8, 180.7, 180.8. IR (Nujol): 1779, 1537, 1462, 1374, 1122  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{130}\text{H}_{202}\text{O}_{34}\text{Pd}$ : C, 64.64; H, 8.37. Found: C, 64.28; H, 8.17. MS ( $\text{FAB}^+$ )  $m/z$  (%): 2518 [ $\text{M} + \text{Pd} - 3\text{H}$ ] $^+$ .

**Techniques.** Infrared spectra for all the complexes were obtained by using a Perkin-Elmer 1600 (FTIR) spectrophotometer in the 400–4000  $\text{cm}^{-1}$  spectral range.  $^1\text{H}$  NMR spectra were recorded on a Varian Unity 300-MHz spectrometer in deuteriochloroform solutions. Specific rotations were measured in a polarimeter Perkin-Elmer 241-AC using either neat samples or solutions in dichloromethane. Microanalysis was performed with a Perkin-Elmer 240 B microanalyzer.

The textures of the mesophases were studied with an optical microscope (Nikon) with crossed polarizers and connected to a Mettler FP82 hot stage and a Mettler FP80 central processor. Measurements of the transition temperatures were made using a TA2910 differential scanning calorimeter with a heating or cooling rate of 10  $^\circ\text{C}/\text{min}$ . The apparatus was calibrated with indium (156.6  $^\circ\text{C}$ , 28.44 J/g) and tin (232.1  $^\circ\text{C}$ , 60.5 J/g).

X-ray diffraction studies were carried out at room temperature and at 75  $^\circ\text{C}$  using a Pinhole camera (Anton-Paar) operating with a point-focused Ni-filtered Cu K $\alpha$  beam. The sample was held in Lindemann glass capillaries (1 mm diameter) and heated, when necessary, with a variable-temperature attachment. The diffraction patterns were collected on flat photographic film.

CD spectra were recorded in a Jasco J-710 at room temperature and a speed scan of 50 nm/min. Quartz deposited samples were obtained by spin-coating a solution of the corresponding complex in THF. The concentration of the solutions were  $10^{-2}$  mol/L. Solvent evaporation was carried out in a spin-coater KarlSuss CT60.

The complex dielectric permittivity was measured over 11 decades of frequency ( $10^{-2}$ – $10^9$  Hz) using three different measuring systems: a Schulmberger 1260 frequency response analyzer accomplished with a high-impedance preamplifier of a variable gain ( $10^{-2}$ – $10^6$  Hz), and two impedance analyzers, the HP 4191A ( $10^2$ – $10^7$  Hz) and the HP 4192A ( $10^6$ – $10^9$  Hz). The cell consisted of two gold plated brass electrodes (diameter 5 mm) separated by 50  $\mu\text{m}$  thick silica spacers. The details of the experimental setup have been described elsewhere.<sup>21</sup>

The electrooptic effect of the complexes was studied by means of a photomultiplier hooked-up to the microscope. The signal was registered in an oscilloscope Tektronix TDS 310. The square wave voltage was supplied by a HP3245A Function Generator. The samples were sandwiched between two glasses with indium tin oxide (ITO) electrodes. Good alignment was achieved by shearing the sample at a temperature at which the mesophase was enough fluid (ca. 100  $^\circ\text{C}$ ).

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