DOI: 10.1002/ejic.200700786

Supramolecular Aggregates in Fluid Phases: Mesomorphic *ortho*-Palladated Complexes with Substituted Crown Ethers and Their Potassium Adducts

Silverio Coco,*[a] Carlos Cordovilla,[a] Pablo Espinet,*[a] Jean-Louis Gallani,[b] Daniel Guillon,[b] and Bertrand Donnio[b]

Keywords: Crown ethers / Palladium / Liquid crystals / Langmuir films

New imines (HL) containing substituted dibenzo-18-crown-6-ethers and their dinuclear *ortho*-palladated complexes, $[Pd(\mu\text{-}X)L]_2$ ($X^- = CH_3COO^-$, Cl^-), have been prepared. The free imine ligands are not liquid crystals, but the palladium complexes, including acetato-bridged derivatives, show liquid-crystal properties. The mesomorphic palladium complexes bear six or eight alkoxy chains. Although a columnar arrangement of these chains might be expected, a smectic arrangement is in fact preferred for half of the metallomesogens prepared, which show a smectic C mesophase. Complexation with potassium produces a significant increase in the mesophase range and stability. Moreover, both the free imines and the corresponding liquid-crystalline *ortho*-palladated complexes form stable Langmuir films at the air–water interface.

Introduction

Functional liquid crystals that combine specific properties with supramolecular organization and fluidity in the mesophase have attracted considerable attention in materials research because they are academically interesting and because of their potential applications in a wide variety of advanced technologies.[1,2] They can be used as functional materials for information and mass transport,[3,4] sensing,[5,6] catalysis, stimuli responsiveness and electrooptical displays.[7,8] The range of systems that can be used in this field has provided a rich diversity of functional liquid-crystalline assemblies. Among them, an interesting example consists of liquid-crystalline phthalocyanines modified with crown ether moieties that combine ion channels and electron wires in hexagonal columnar (Col_h) phases.[9] In this mesophase there is a central electron wire of stacked phthalocyanine cores surrounded by four ion channels formed from dialkoxy-substituted dibenzo-18-crown-6 groups.[4] Also well-known is the ability of crown ether groups to coordinate cations and thus promote the solubility of inorganic salts in organic solutions; this has made them attractive building blocks in supramolecular chemistry.[10–12] Moreover, the incorporation of crown ether groups into thin ordered films is a rapidly growing field because these systems can be used as models for the study of molecular recognition and interaction phenomena at interfaces.[4,13,14]

Some organic liquid crystals containing crown ethers are also known;[2,15–25] the coordination of alkaline salts to the crown ether group of mesogenic systems produces different modifications of their mesogenic properties. These modifications include increases or decreases in the mesophase stability,[15,16,20,21,23] as well as changes in the mesophase types.[2,16,19–21,25]

On the other hand, a large variety of metals and ligands have been used to prepare metal-containing liquid crystals. Among them, *ortho*-palladated complexes are one of the most studied classes of metallomesogens.[26–29] It is surprising that only a few examples of metallomesogens containing crown ethers have been reported: namely, a family of *ortho*-palladated complexes[30] and some crown ether substituted phthalocyanine complexes of copper, lutetium and lithium.[31–33]

Our group has recently reported palladium(II) metallomesogens of crown ether derivatized imines, which have allowed us to propose and support a plausible model for extraction and transport with these complexes.[34] As a continuation of these studies, we report here the synthesis of liquid-crystalline *ortho*-palladated complexes with substituted dibenzo-18-crown-6-ethers. This family of complexes has afforded examples of metallomesogens based on dinuclear imino palladium(II) complexes including complexes with acetato bridges, which generally do not display mesomorphic behaviour. Their complexation with potassium produces a significant increase in mesophase range and stability. Moreover, both the free imines and the correspond-

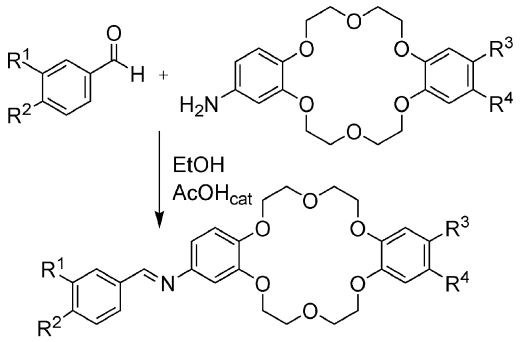
[a] Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid,
47005 Valladolid, Spain
[b] Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), UMR 7504 (CNRS-ULP),
23 rue du Loess, BP 43, 67034 Strasbourg Cedex 2, France

ing liquid-crystalline *ortho*-palladated complexes form stable Langmuir films at the air–water interface.

Results and Discussion

Synthesis and Characterization

The Schiff bases **1** were synthesized in ethanol by an acetic acid catalyzed condensation between the corresponding substituted benzaldehyde and the amines containing the dibenzo-18-crown-6 group (Scheme 1), as described for related Schiff bases.[35]



1a: $R^1 = R^3 = R^4 = H$; $R^2 = OC_2H_5$
1b: $R^1 = H$; $R^2 = R^3 = R^4 = OC_{10}H_{21}$
1c: $R^1 = R^2 = R^3 = R^4 = OC_{10}H_{21}$

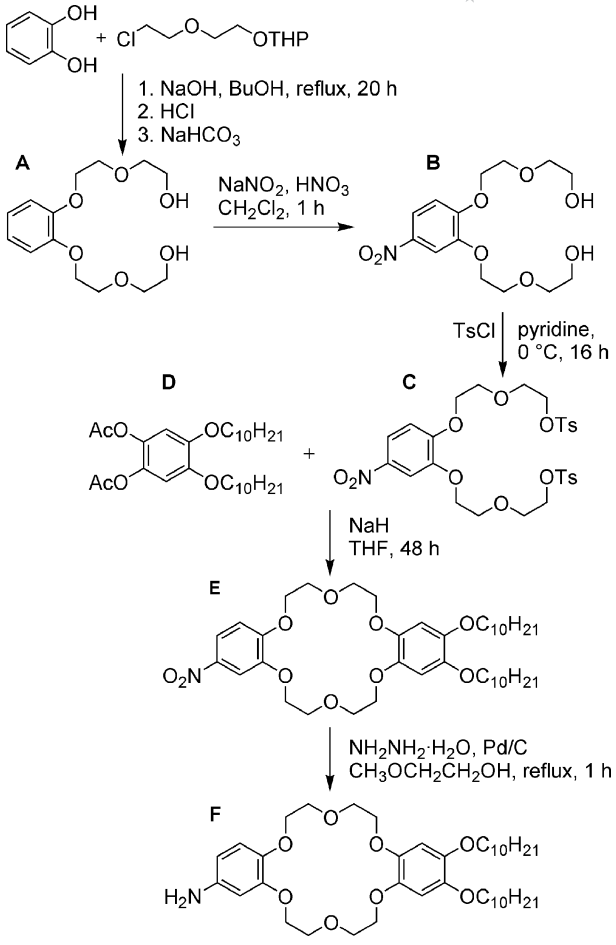
Scheme 1.

The dibenzo-18-crown-6 aniline **F** used in this work was prepared in five steps by starting from cathecol (Scheme 2).

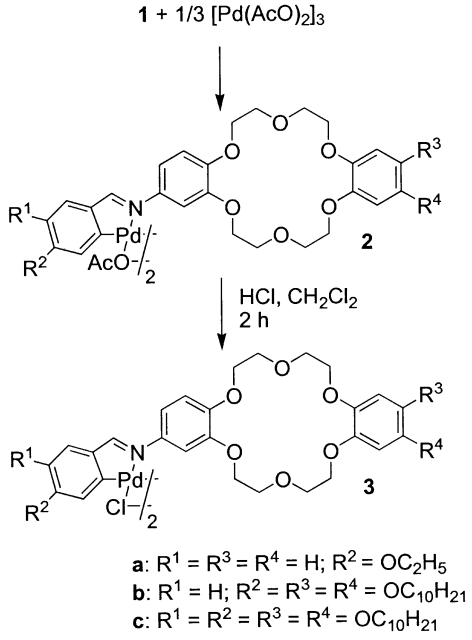
The alkylation of catechol with tetrahydropyranyl-protected diethyleneglycol chloride gave, after in situ deprotection, dialcohol **A**, which was converted into **B** by subsequent nitration. The treatment of **B** with *p*-toluenesulfonyl chloride yielded the *p*-toluenesulfonate dialcohol **C**. Coupling this with 1,2-bis(decyloxy)-4,5-bis(acetoxy)benzene (**D**) gave the nitro crown ether derivative **E**. Finally, the reduction of **E** with hydrazine monohydrate with a palladium-on-carbon catalyst produced the desired amine **F**.

The cyclopalladated complexes were synthesized as depicted in Scheme 3. The *ortho*-metallation of the imine ligand to give acetato complexes was carried out as described elsewhere.[36] The treatment of the acetato-bridged derivatives **2** in dichloromethane with a solution of HCl in diethyl ether afforded the chloro compounds **3** (Scheme 3), which were isolated as yellowish solids.

The elemental analyses, yields, relevant IR data and ^1H NMR spectra for the complexes are given in the experimental section. The main structural features for complexes analogous to **1**, **2** and **3** but without crown ether groups have been reported in detail in previous papers,[37–40] and are assumed to be similar here. The acetato-bridged complexes are butterfly-shaped, while the chloro-bridged complexes are planar. In both types of complexes only the *anti* isomer is formed in the cases reported here.



Scheme 2.



a: $R^1 = R^3 = R^4 = H$; $R^2 = OC_2H_5$
b: $R^1 = H$; $R^2 = R^3 = R^4 = OC_{10}H_{21}$
c: $R^1 = R^2 = R^3 = R^4 = OC_{10}H_{21}$

Scheme 3.

The complexation of **2b**,**c** and **3b**,**c** with $KClO_4$ was achieved by dissolving the corresponding crown ether com-

pound with the potassium salt in dichloromethane/ethanol (2:1) in a crown ether/potassium molar ratio of 1:1 at room temperature, and by subsequently removing the solvent in vacuo. All potassium perchlorate complexes were isolated as pale brown solids. Potassium was chosen according to its cation size; it forms the most stable 1:1 complexes with dibenzo-18-crown-6.[41] The perchlorate anion was chosen because of its relatively weak coordination character towards soft transition metals. The potassium-containing complexes are soluble in dichloromethane and $CDCl_3$, while $KClO_4$ is insoluble. The coordination of the perchlorate group to the potassium cation is evident from the IR spectra that show three bands at ca. 1122, 1111 and 1087 cm^{-1}.[42] The number of bands in the IR spectrum has been successfully used to derive information regarding the bonding modes of the perchlorate group. Three bands in the Cl–O stretching region indicate the presence of a perchlorate group coordinated in a bidentate fashion. Thus, two oxygen atoms of the perchlorate ligand together with the oxygen atoms of the crown ether would complete the coordination of potassium (Figure 1), as described for similar sodium and potassium perchlorate adducts.[34,43]

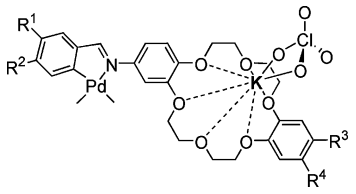


Figure 1. Chemical structure of the potassium perchlorate adducts.

The potassium adducts were characterized by ^1H NMR spectroscopy. In contrast to its *ortho*-palladated precursor, the acetato-bridged complex [**k2b**] shows, in addition to small shifts of the aromatic protons, two sets of resonances in a molar ratio close to 1:2. The signals for the methyl groups of the acetato bridges and those of the imine ligands reveal that this splitting corresponds to the presence of *syn* and *anti* isomers in the potassium perchlorate crown complexes, which shows that complexation induces *anti* to *syn* isomerization so that a slow equilibrium is reached.

Mesomorphic Behaviour

Although the free imine ligands used are not liquid crystals, all the palladium complexes show a mesomorphic behaviour except complexes of series **a**. In fact, the series **a** compounds lack flexible lateral groups and do not possess the basic requirements to be mesogenic. They were synthesized with the main purpose being to obtain suitable crystals for X-ray determination; unfortunately, this was not achieved. The optical, thermal and thermodynamic data of all the prepared compounds are gathered in Table 1.

Table 1. Optical, thermal and thermodynamic data for complexes **1**, **2** and **3**.

	Transition[a]	*T*/°C	ΔH/kJ mol^{-1}
1a	Cr → I	161.4	68.3
1b	Cr → Cr′	34.9	10.1
	Cr′ → I	124.9	91.21
1c	Cr → I	121.9	118.3
2a	Cr → dec	110[c]	–
2b	Cr → Cr′	81.0	12.1
	Cr′→ SmC	107.6	35.7
	SmC → I	121.9	3.6
	I → SmC	117.7	–5.3
	SmC → G	49.2	
	G → SmC	55.8	
	SmC → I	119.7	4.5
2c	Cr → Cr′	47.5	13.3
	Cr′→ I	96.4	73.6[b]
	I → M	77.1	–9.3
	M → G	43.8	
	G → Cr′′	66.6	–16.7[b]
	Cr′′→ I	93.1	63.7[b]
3a	Cr → dec	215[c]	–
3b	Cr + G → Cr + Cr′	80.6	–19.3
	Cr + Cr′ → SmC	109.8	235.7[b]
	SmC → I	200[c]	–
3c	Cr → Cr′	53.0	41.3
	Cr′ → Cr′′	92.5	21.4
	Cr′′ → I	141.4[d]	46.7
	I → M	139.0	–3.0
	M → Cr′′′	90.1	18.3

[a] Data refer to the second heating DSC cycle (for monotropic compounds **2c** and **3c**, first heating and cooling data were also collected); Cr = crystal, SmC = smectic C, G = glass, M = unidentified mesophase, I = isotropic liquid, dec = decomposition. [b] Combined enthalpies. [c] Optical microscopy data. [d] Peak data.

The dimeric molecules of the acetato and chloro complexes **2b** and **3b** bear six alkoxy chains altogether. Although one might expect a columnar arrangement of these chains, a smectic arrangement seems to be preferred, and the compounds show a smectic C mesophase. This mesophase was identified with optical microscopy by its texture (Figure 2) and by the fact that it was not possible to induce either hometropic regions or brownian flashes under mechanical stress. However, greyish textures are observed by mechanical displacement.[44,45]

Figure 2. Polarized optical microscopic texture (×200) observed for **2b** at 110 °C on cooling from the isotropic liquid.

In contrast, complexes **2c** and **3c**, having one more chain per Pd atom—that is eight alkoxy chains per dimer—show monotropic mesomorphic behaviour. The optical textures, when viewed with a polarizing microscope on cooling from the isotropic melt, exhibit a fan-like texture frequently observed for columnar hexagonal mesogens. However, the small sizes of the domains formed did not allow us to conclusively identify the type of mesophase.

When derivative **2b** is cooled from the mesophase, crystallization is not observed, and a glass transition appears [Figure 3, (b)]. The glass transition is reversible to give a glass–SmC transition followed by a SmC–isotropic liquid transition [Figure 3, (c)]. Similar behaviour is observed for compound **2c**.

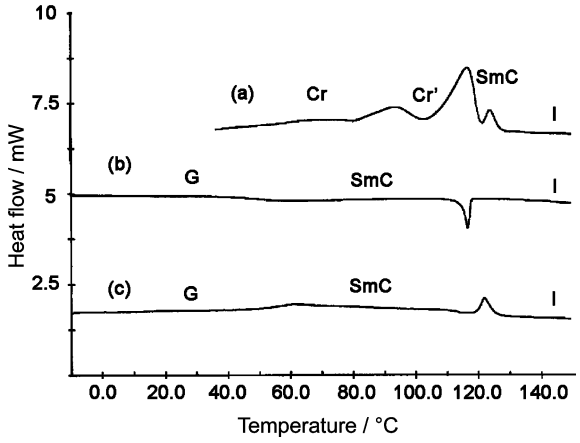


Figure 3. DSC scans of **2b**: (a) first heating, (b) first cooling and (c) second heating.

In general, butterfly-shaped *ortho*-metallated acetato-bridged complexes are not mesomorphic because of their unfavourable molecular structure.[29,40] Thus it is somewhat unexpected that the compounds reported here are mesomorphic; the positive change must be related to the presence of crown ether groups. The effect of incorporating cyclic polyether moieties in *ortho*-palladated systems is not a simple matter, but the importance of the distribution of polar and nonpolar structural units within anisotropic molecules for the formation of mesophases is well-known. In this respect, besides the effects in molecular geometry and the possible conformational effects, microsegregation is probably an important contribution to the induction of a liquid-crystalline behaviour. Microsegregation is favoured in molecules with a well-defined intramolecular contrast, i.e. in complexes with distinct polar/rigid and less polar/flexible segments.[46] Thus, the introduction of crown ether groups in a system, which is expected to enhance microsegregation, will facilitate mesophase formation, as observed.

The complexation of the crown ether derivatives with $KClO_4$ to give the corresponding adducts produces an important change in the mesomorphic properties. The optical textures observed from the first heating cycle are the same as those for the crown ether parent palladium complexes; the DSC traces, however, are complex and show several ill-defined, flattened endothermic peaks. Yet, on subsequent heat–cool cycles, the DSC traces clearly appear simpler. We suspect that during the first heating there are a number of small conformational changes that occur upon going from the crystal to the mesophase, which remain in the glass obtained upon cooling, and thus result in a simpler behaviour during the second heating (except for [**k2c**], which displays a melting point in the second heating). Compared to the parent complexes, the potassium complexes demonstrate an important increase in the clearing temperatures and the mesophase stability; as a consequence, all of the potassium complexes studied show enantiotropic liquid-crystalline behaviour (Table 2).

Table 2. Optical, thermal and thermodynamic data for potassium crown complexes.

Compound	Transition[a]	T/°C	ΔH/kJ mol^{-1}
[**k2b**]	G → SmC	81.5	
	SmC → I[b]	193.3	1.8
[**k2c**]	Cr → M	93.7	5.8
	M → I	147.0	3.2
[**k3b**]	G → SmC	85.4	
	SmC → I	178.5	0.5
[**k3c**]	G → M	110.0[c]	
	M → I	207.1	3.3

[a] Data refer to the second heating DSC cycle; Cr = crystal, Sm = smectic, G = glass, M = unidentified mesophase, I = isotropic liquid. [b] Decomposition. [c] Optical microscopy data.

The changes in intermolecular forces upon potassium complexation are manifold: the molecules become more polar, and the inclusion of potassium ions into the cavities of the macrocyclic units increases the rigidity of the crown ether group, but probably also increases the width of the molecule (Figure 1).[43] On the other hand, microsegregation probably improves upon complexation, and this is known to stabilize the mesophases. For the acetato complexes, an important change is the formation of a *syn*/*anti* isomeric mixture. In such a complex system, a simple rational explanation of the effect of potassium complexation on the mesomorphic behaviour is impossible, but at least we see that the effect is systematic.

Temperature-dependent X-ray diffraction experiments were systematically carried out in order to unequivocally identify the nature of the mesophase.

The XRD patterns of **2b** measured between 100 and 120 °C exhibit a broad scattering in the wide angle part of the diffractogram (at ca. 4.5–4.6 Å), which corresponds to the molten chains in the liquid-like order, and only one fine, sharp signal in the small angle region (39.1 Å). Thus, the mesophase was assigned on the basis of its texture only, obtained by polarized-light optical microscopy, as a smectic C phase (Figure 2). Another broad peak at 9.0–10.0 Å could be assigned to the average distance between complexes in the smectic layers. The occurrence of this mesophase is consistent with the presence of a transverse dipolar moment in the molecule.[47]

As expected from the DSC traces of **3b**, a change in the X-ray pattern, which corresponds to a modification of the

molecular packing, was detected between 115 and 125 °C. This change was characterized by the disappearance of the strong, sharp peaks of the crystalline phase and the appearance of a small-angle reflection with a periodicity of about 42 Å. At 145 °C, three sharp, intense small-angle diffraction peaks, corresponding to distances of 39.7, 19.8 and 13.1 Å in a 1:2:3 ratio, were indexed as (00*l*) = (001), (002), (003), respectively. In addition, two diffuse peaks observed around 9.0–10.0 and 4.5 Å were assigned to the average distance between molecules in the smectic layers and to the liquid-like order of the molten alkoxy chains, respectively.

For both complexes (**2b** and **3b**), although the molecular areas are rather large because of the bulky crown ether moieties, they are indeed compatible with a smectic-like mesomorphism, with the core being slightly tilted in the layers and the aliphatic chains being in a very disordered state (Table 3). A possible molecular arrangement for **3b** is sketched in Scheme 4. Since the molecules are composed of three different chemically incompatible blocks, they are likely to segregate in the bulk in order to minimize their interactions, which would form three different zones. The rigid central part forms a central sublayer, and since the complexes are preferentially in a *trans* symmetry (due to the bulky crown ether part), the outer sublayers consist of alternating aliphatic chains and crown ether parts on either side of the central inner sublayer. Moreover, the distance of ca 9.0 Å would then correspond to the lateral interactions between neighbouring crown ethers organized into a hexagonal network. In such a case, the hexagonal surface area (S_H = 1/2.9.5^2.3$^{1/2}$ = 80 Å^2) almost matches the molecular area.

As for **2c** and **3c**, their monotropic behaviour precludes any unequivocal phase assignment. The results of the polarized optical microscopy (POM) studies allow to tentatively predict the formation of a hexagonal columnar phase (the complexes have eight chains in total), although the presence of only one peak at 39.1 Å (**3c**), observable on the X-ray patterns registered on cooling, cannot confirm the phase identity. Another broad peak at 5.0 Å, which can be assigned to the molten chains, was also seen.

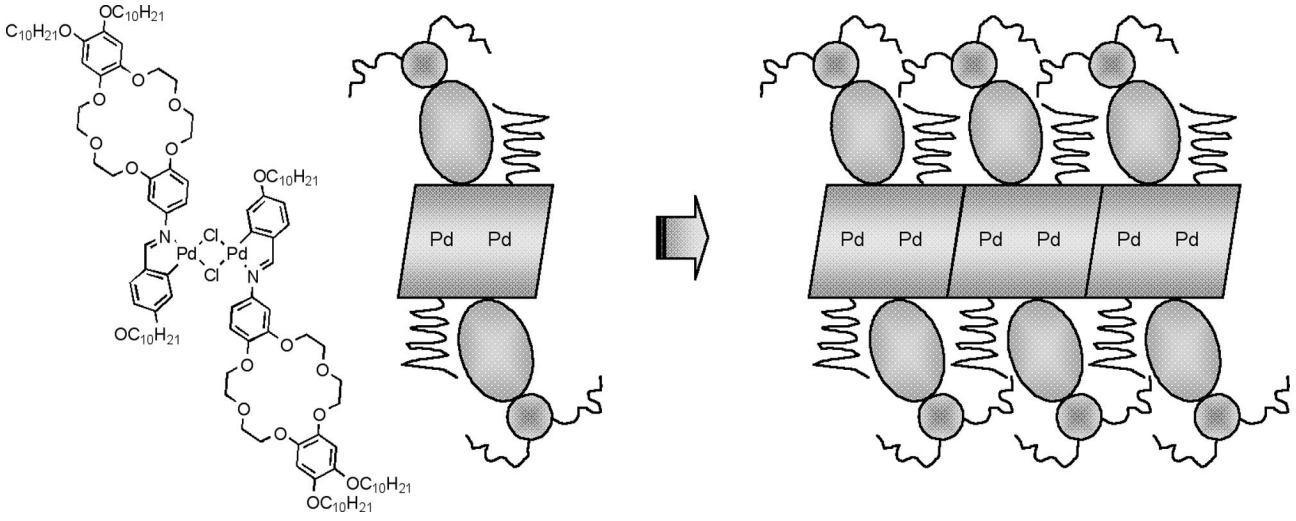
Table 3. Structural data from X-ray diffraction experiments for **2b** and **3b**.

	Transition *T*/°C	d_{mes}/Å	Indexing[a] *I*	*hkl*	d_{calc}/Å	Parameters[b]
2b	Cr 107.6 SmC 121.9 I	39.1	VS (sh)	001	39.1	V = 3890 Å^3
		9.0–10.0	VS (br)			A_M = 99.5 Å^2
		4.5	VS (br)			A_{ch} = 33.17 Å^2
3b	Cr 109.8 SmC 200 dec	39.71	VS (sh)	001	39.57	V = 3880 Å^3
		19.81	S (sh)	002	19.78	A_M = 98.0 Å^2
		13.13	S (sh)	003	13.19	A_{ch} = 32.7 Å^2
		9.0–10	VS (br)			
		4.6	VS (br)			

[a] [d_{calc} = 1/3·(d_{001} + 2·d_{002} + 3·d_{003})]. [b] V is the molecular volume, A_M the molecular area (A_M = V/d) and A_{ch} the chain area (A_{ch} = A_M/3).

In the event of a smectic phase, the molecular area (A_M = 100.75 Å^2, i.e., 25.0 Å^2 per chain for an estimated volume of 3940 Å^3) is indicative of a dense packing of the molecules into a nontilted phase. In the case of a Col$_h$ phase, the only possible columnar arrangement, about two molecules or, more precisely, two molecular equivalents, would match perfectly with the volume of a 4.5 Å thick columnar slice. Thus, columnar and smectic arrangements cannot be discriminated nor excluded here.

As for the complexes incorporating potassium perchlorate, the phases were assigned mainly on the basis of their optical textures because of the limited thermal stability of the sample under the X-ray diffraction experimental conditions. In all cases, only one diffraction peak was observed {[**2bk**] 38.6; [**2ck**] 38.0; [**3bk**] 38.0, 9.4, 4.5; [**3ck**] 36.6 Å}, and no unequivocal phase assignment can be made.



Scheme 4.

Langmuir Films

The imines **1b**,**c** and the complexes **2b**,**c** and **3b**,**c** can form Langmuir films at the air–water interface. The isotherms obtained at 25 °C and the molecular areas extrapolated to zero surface pressure are shown in Figure 4. These values are in good agreement with the areas estimated by molecular modeling, which means that the molecules spread as monomolecular layers at the air–water interface. In the case of the imines **1b**,**c**, these areas are very similar to the estimated value for the area of the molecular core (palladium-coordinated core plus crown ether), which suggests that these groups are arranged parallel to the water surface (side-on disposition) and the alkoxy substituents normal to the film surface. In contrast, the molecular areas of the palladium complexes **2b**,**c** and **3b**,**c** are slightly smaller than expected for a side-on disposition of the molecular core, but larger than expected for an edge-on orientation, which indicates that the molecules will take a tilted edge-on disposition.

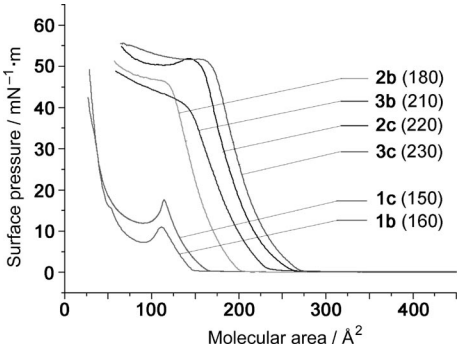


Figure 4. Surface pressure–molecular area isotherms at 25 °C. Extrapolated molecular areas are given in brackets.

Brewster angle microscopy (BAM) was used in successive compression/decompression cycles in the case of **1b** and **2b** to study the reversibility of the process and the homogeneity of the films. Compound **2b** spontaneously forms a liquid film at large molecular areas. Upon compression, the film becomes continuous and defectless. The collapse takes the appearance of linear/ramified structures. The decompression is reversible: expanding holes form in the liquid film during decompression. Compound **1b** also has an initial state in which the molecules spontaneously form liquid-like assemblies. The completed film looks homogeneous and defectless. Collapse appears at a lower surface pressure than for **2b** and seems to be cooperative in the sense that the collapse of the film keeps progressing even if the compression is stopped. This is seen with the BAM and also because the surface pressure keeps decreasing even without motion of the barriers. The molecules form aggregates of irregular shape, and hence the films are probably solid. Upon decompression there is some degree of reversibility. The solid/collapsed structures seem to melt into a liquid again. After 15 minutes the film has evolved into a 2D foam where only very few solid parts remain. Still, there must be some aggregation remaining, in particular around the Wilhelmy plate, as the surface pressure does not return to zero.

Conclusions

In summary, mesomorphic *ortho*-palladated $[Pd(\mu\text{-}X)L]_2$ ($X^- = CH_3COO^-$, Cl^-) complexes with unusual imines containing substituted dibenzo-18-crown-6-ethers have been prepared. Although the free imine ligands obtained are not liquid crystals, the palladium complexes, including the usually unfavorable acetato-bridged derivatives, show liquid-crystal properties. In spite of having six or eight alkoxy chains that might induce discotic phases, at least half of the prepared palladium complexes self-organize in what is clearly a smectic order. Complexation with potassium produces a significant increase in the mesophase range and stability. Moreover, both the free imines and the corresponding liquid-crystalline *ortho*-palladated complexes form stable Langmuir films at the air–water interface.

Experimental Section

^{1}H NMR spectra were recorded at 300 MHz with a Bruker AC 300 instrument in $CDCl_3$ and CD_2Cl_2. Chemical shifts, in ppm, are reported relative to internal TMS for ^{1}H. Combustion analyses were performed with a Perkin–Elmer 2400 microanalyzer. IR spectra were recorded on a FT 1720X Perkin–Elmer instrument (400–4000 cm^{-1}), with samples being prepared as KBr pellets, or a Perkin–Elmer 883 spectrophotometer (400–200 cm^{-1}), with samples being prepared as a Nujol emulsion supported between two polyethylene films. Microscopy studies were carried out by using a Leitz polarizing microscope equipped with a Mettler FP-82HT hot stage and a Mettler FP-90 temperature controller at a heating rate of ca. 10 °C min^{-1}. For DSC, a Perkin–Elmer DSC7 instrument was used, which was calibrated with water and indium; the scanning rate was 10 °C min^{-1}, the samples were sealed in aluminum capsules in the air and the holder atmosphere was dry nitrogen.

The XRD patterns were obtained with two different experimental setups (I, II). In all cases, a linear monochromatic Cu-$K_{\alpha 1}$ beam (λ = 1.5405 Å) was obtained using a sealed-tube generator (900 W) equipped with a bent quartz monochromator. In the first set, the transmission Guinier geometry (I) was used, whereas Debye–Scherrer-like (II) was used in the second experimental setup. In all cases, the crude powder was used to fill Lindemann capillaries of 1 mm diameter and 10 μm wall thickness. The initial set of diffraction patterns was recorded on an image plate; periodicities up to 80 Å could be measured, and the sample temperature controlled to within ±0.3 °C in the 20 to 350 °C temperature range. The second set of diffraction patterns (II) was recorded with a curved Inel CPS120 counter gas-filled detector linked to a data acquisition computer (for periodicities up to 60 Å) or these could be measured on image plates (for periodicities up to 100 Å); the sample temperature was controlled to within ±0.05 °C in the 20 to 200 °C temperature range. In each case, exposure times were varied from 1 to 24 h.

Langmuir films have been prepared on a standard TEFLON® trough filled with ultrapure water at room temperature. The compounds were dissolved in dichloromethane in 1 mg mL^{-1} concentrations to prepare the spreading solution.

Brewster angle microscopy observations were performed with an apparatus from NFT (Göttingen, Germany, www.nanofilm.de).

All solvents were dried and distilled before use. All reactions were carried out under nitrogen atmosphere. *p*-Toluenesulfonyl chloride was recrystallized[48] and K_2CO_3 was dried in an oven prior to use.

Literature methods were used to prepare $[Pd(AcO)_2]_3$,[49] 2-(2′-chloroethoxy)ethyl 2′′-tetrahydropyranyl ether[50] and 1,2-bis(decyloxy)-4,5-bis(acetoxy)benzene.[51]

Preparation of 1,2-Bis[2′-(2′′-hydroxyethoxy)ethoxy]benzene (A): 2-(2′-Chloroethoxy)ethyl 2″-tetrahydropyranyl ether (90.08 g, 0.43 mol) was added dropwise to a refluxing suspension of catechol (23.63 g, 0.21 mol) and NaOH (17.2 g, 0.43 mol) in 1-butanol (0.5 L). The suspension was heated at reflux for 20 h and, once the mixture was cooled, concentrated HCl (12 mL) was added, and the mixture was stirred for 1 h. $NaHCO_3$ (58 g, 0.82 mol) was then added, and the filtered solution was washed with 1 M NaOH and with water. Volatiles were pumped off in vacuo (130 °C, 5 Torr). Yield 33.48 g (56%) of a dark viscous oil. ^{1}H NMR ($CDCl_3$): δ = 3.63–4.13 (m, 16 H, CH_2O), 6.86–6.91 (m, 4 H, ArH) ppm.

Preparation of 1,2-Bis[2′-(2′′-hydroxyethoxy)ethoxy]-3-nitrobenzene (B): Compound **A** (33.84 g, 0.12 mol) and $NaNO_2$ were dissolved in CH_2Cl_2 (200 mL), and concentrated HNO_3 (27 mL, 68%) was added. The solution was stirred for 1 h and then washed with water until a neutral pH was obtained. The organic layer was dried with anhydrous $MgSO_4$ and filtered, and the solvent was evaporated. Yield 23.38 g (59%) of a white solid. ^{1}H NMR ($CDCl_3$): δ = 3.43 (s, 2 H, OH), 3.66–4.25 (m, 16 H, CH_2O), 6.90 (d, 1 H, ArH), 7.74 (d, 1 H, ArH), 7.85 (dd, 1 H, ArH) ppm.

Preparation of 1,2-Bis{2′-[2′′-(*p*-tolylsufonyloxy)ethoxy]}-3-nitrobenzene (C): Compound **B** (15.41 g, 46.4 mmol) was dissolved in pyridine (75 mL), and the solution was cooled down to –10 °C. A solution of *p*-toluenesufonyl chloride (21.09 g, 110.6 mmol) in pyridine was added dropwise to this and stirred for 2 h at –5 °C and overnight at 0 °C. The resulting solution was poured onto ice (100 g), acidified with 6 M HCl and extracted with CH_2Cl_2. The organic layer was dried with anhydrous $MgSO_4$ and filtered, and the solvents were evaporated. Yield 24.02 g (80%) of a dark viscous oil. ^{1}H NMR ($CDCl_3$): δ = 2.37 (s, 6 H, CH_3), 3.72–4.14 (m, 16 H, CH_2O), 6.88 (d, 1 H, ArH), 7.27 (d, 4 H, ArH), 7.67 (d, 1 H, ArH), 7.73 (d, 4 H, ArH), 7.81 (dd, 1 H, ArH) ppm.

Preparation of [4′,5′-Bis(decyloxy)-4′′-nitro]dibenzo[1′,2′-*b*:1′′,2′′-*k*]-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene (E): Compound **D** (2.62 g, 5.2 mmol) was heated at reflux with NaH (832.0 mg, 60% dispersion in mineral oil, 20.8 mmol) in THF (100 mL) for 1 h. A solution of **C** (3.31 g, 5.2 mmol) in THF (100 mL) was added dropwise to this, and the mixture was refluxed for 48 h. The suspension was cooled, and water (50 mL) and diethyl ether (100 mL) were added to it. After being stirred for 5 min, the solid that formed was collected by filtration and redissolved in dichloromethane. The solution was filtered through a hydrophilic polypropylene membrane filter (0.2 mm), and the solvents were evaporated. Yield 1.55 g (42%) of a slightly brown solid. ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, 6 H, CH_3), 1.27–1.78 (m, 32 H, CH_2), 3.90–4.25 (m, 32 H, CH_2O), 6.57 (s, 2 H, ArH), 6.88 (d, 1 H, ArH), 7.67 (d, 1 H, ArH), 7.72 (d, 1 H, ArH), 7.90 (dd, 1 H, ArH) ppm.

Preparation of [4′,5′-Bis(decyloxy)-4′′-amino]dibenzo[1′,2′-*b*:1′′,2′′-*k*]-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene (F): Compound **E** (500 mg, 0.70 mmol), Pd/C (45 mg, 5%) and hydrazine monohydrate (4.63 g, 92 mmol) were suspended in ethoxyethanol (50 mL) and heated at reflux for 1 h. The hot solution was filtered, and the solvents were evaporated. Yield 0.43 g (90%). ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, 6 H, CH_3), 1.27–1.80 (m, 32 H, CH_2), 3.90–4.12 (m, 32 H, CH_2O), 6.22 (dd, 1 H, ArH), 6.28 (d, 1 H, ArH), 6.58 (s, 2 H, ArH), 6.71 (d, 1 H, ArH) ppm.

Preparation of the Imines 1a–c: All of the imines were synthesized by condensation of their respective aldehydes and anilines in absolute ethanol with acetic acid as catalyst.[35]

1a: Yield 0.11 g (81%). IR (KBr): $\tilde{\nu}$ = 1604 [ν(C=N)] cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.45 (t, 3 H, CH_3), 4.11 (c, 2 H, $ArOCH_2$), 4.05–4.20 (m, 16 H, CH_2O), 6.77 (dd, 1 H, ArH), 6.83 (d, 1 H, ArH), 6.86 (m, 4 H, ArH), 6.87 (d, 1 H, ArH), 6.98 (d, 2 H, ArH), 7.81 (d, 2 H, ArH), 8.39 (s, 1 H, CH=N) ppm. $C_{29}H_{33}NO_7$ (507.6): calcd. C 68.6, H 6.6, N 2.8; found C 68.3, H 6.8, N 3.0.

1b: Yield 1.38 g (95%). IR (KBr): $\tilde{\nu}$ = 1605 [ν(C=N)] cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, 9 H, CH_3), 1.28–1.86 (m, 48 H, CH_2), 3.81–4.22 (m, 22 H, CH_2O), 6.60 (s, 2 H, ArH), 6.78 (dd, 1 H, ArH), 6.84 (d, 1 H, ArH), 6.89 (d, 1 H, ArH), 6.97 (d, 2 H, ArH), 7.81 (d, 2 H, ArH), 8.39 (s, 1 H, CH=N) ppm. $C_{57}H_{89}NO_9$ (932.2): calcd. C 73.4, H 9.6, N 1.5; found C 73.2, H 9.4, N 1.8.

1c: Yield 1.39 g (80%). IR (KBr): $\tilde{\nu}$ = 1598 [ν(C=N)] cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, 12 H, CH_3), 1.28–1.84 (m, 64 H, CH_2), 3,89–4.17 (m, 24 H, CH_2O), 6.56 (s, 2 H, ArH), 6.77 (dd, 1 H, ArH), 6.82 (d, 1 H, ArH), 6.88 (d, 1 H, ArH), 6.92 (d, 1 H, ArH), 7.28 (dd, 1 H, ArH), 7.53 (d, 1 H, ArH), 8.36 (s, 1 H, CH=N) ppm. $C_{67}H_{109}NO_{10}$ (1088.6): calcd. C 73.9, H 10.1, N 1.3; found C 73.8, H 10.1, N 1.5.

Preparation of the $[Pd(\mu\text{-}OAc)L]_2$ Acetate Complexes 2a–c: A mixture of palladium acetate and a stoichiometric amount of the corresponding imine in glacial acetic acid was stirred at 50 °C for 16 h. The solvent was removed and the residue was dissolved in CH_2Cl_2 and filtered through silica before the solvent was again evaporated. The resulting oil was treated with acetone and the yellow solid was collected by filtration.

2a: Yield 0.09 g (76%). IR (KBr): $\tilde{\nu}$ = 1590 [ν(C=N)], 1570 [$\nu(COO)_{as}$], 1413 [$\nu(COO)_s$] cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.31 (t, 6 H, CH_3), 1.91 (s, 6 H, CH_3CO_2), 3.59–3.61 (m, 4 H, $ArOCH_2$), 3.78–4.17 (m, 32 H, CH_2O), 5.90 (dd, 2 H, ArH), 6.00 (d, 2 H, ArH), 6.56 (m, 4 H, ArH), 6.81 (d, 2 H, ArH), 6.88 (m, 8 H, ArH), 7.11 (d, 2 H, ArH), 7.46 (s, 2 H, CH=N) ppm. $C_{62}H_{70}N_2O_{18}Pd_2$ (1344.1): calcd. C 55.4, H 5.2, N 2.1; found C 55.6, H 4.9, N 2.4.

2b: Yield 0.92 g (82%). IR (KBr): $\tilde{\nu}$ = 1592 [ν(C=N)], 1570 [$\nu(COO)_{as}$], 1414 [$\nu(COO)_s$] cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 0.88 (t, 18 H, CH_3), 1.27–1.77 (m, 96 H, CH_2), 1.87 (s, 6 H, CH_3CO_2), 3.54–4.16 (m, 44 H, OCH_2), 5.93 (dd, 2 H, ArH), 5.96 (d, 2 H, ArH), 6.52 (m, 4 H, ArH), 6.55 (s, 4 H, ArH), 6.75 (d, 2 H, ArH), 7.13 (d, 2 H, ArH), 7.50 (s, 2 H, CH=N) ppm. $C_{118}H_{182}N_2O_{22}Pd_2$ (2193.6): calcd. C 64.6, H 8.4, N 1.3; found C 64.3, H 8.2, N 1.5.

2c: Yield 0.98 g (85%). IR (KBr): $\tilde{\nu}$ = 1592 [ν(C=N)], 1570 [$\nu(COO)_{as}$], 1417 [$\nu(COO)_s$] cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 0.88 (t, 24 H, CH_3), 1.28–1.86 (m, 128 H, CH_2), 1.88 (s, 6 H, CH_3CO_2), 3.42–4.15 (m, 48 H, OCH_2), 5.88 (d, 2 H, ArH), 5.95 (dd, 2 H, ArH), 6.48 (d, 2 H, ArH), 6.55 (s, 4 H, ArH), 6.74 (s, 2 H, ArH), 6.81 (s, 2 H, ArH), 7.48 (s, 2 H, CH=N) ppm. $C_{138}H_{222}N_2O_{24}Pd_2$ (2506.1): calcd. C 66.1, H 8.9, N 1.1; found C 66.0, H 8.8, N 1.3.

Preparation of the $[Pd(\mu\text{-}Cl)L]_2$ Chloro Complexes, 3a–c: To a stirred solution of $[Pd(\mu\text{-}OAc)L]_2$ in CH_2Cl_2 was added dropwise a stoichiometric amount of a HCl solution in diethyl ether. After the solution was stirred for 1 h, the solvent was evaporated, and the resulting oil was treated with acetone in order to obtain a yellow solid, which was filtered off.

3a: Yield 0.042 g (85%). IR (Nujol): $\tilde{\nu}$ = 1578 [ν(C=N)], 247 [ν(Pd–Cl)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.35 (t, 6 H, CH_3), 3.91–4.50 (m, 36 H, CH_2O), 6.55 (dd, 2 H, ArH), 6.76–6.85 (m, 6 H, ArH), 6.90 (s, 8 H, ArH), 7.04 (d, 2 H, ArH), 7.20 (d, 2 H, ArH), 7.81 (s, 2 H, CH=N) ppm. $C_{58}H_{64}N_2Cl_2O_{14}Pd_2$ (1225.2): calcd. C 53.7, H 5.0, N 2.2; found C 54.0, H 5.3, N 2.0.

3b: Yield 0.42 g (83%). IR (Nujol): $\tilde{\nu}$ = 1578 [ν(C=N)], 248 [ν(Pd–Cl)] cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 0.88 (t, 18 H, CH_3), 1.27–1.78 (m, 96 H, CH_2), 3.90–4.26 (m, 44 H, OCH_2), 6.58 (s, 4 H, ArH), 6.60–6.80 (m, 8 H, ArH), 7.01 (d, 2 H, ArH), 7.25 (d, 2 H, ArH), 7.86 (s, 2 H, CH=N) ppm. $C_{114}H_{176}N_2Cl_2O_{18}Pd_2$ (2146.4): calcd. C 63.8, H 8.3, N, 1.3; found C, 63.6, H 8.2, N 1.6.

3c: Yield 0.11 g (59%). IR (Nujol): $\tilde{\nu}$ = 1587 [ν(C=N)], 245 [ν(Pd–Cl)] cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.88 (t, 24 H, CH_3), 1.26–1.76 (m, 128 H, CH_2), 3.89–4.12 (m, 48 H, OCH_2), 6.58 (s, 4 H, ArH), 6.82–6.97 (m, 8 H, ArH), 6.97 (d 2 H, ArH), 7.75 (s, 2 H, CH=N) ppm. $C_{134}H_{216}N_2Cl_2O_{20}Pd_2$ (2458.9): calcd. C 65.4, H 8.9, N 1.1; found C 65.1, H 8.6, N 1.3.

General Procedure for Complexation: All potassium complexes were prepared by following the same general procedure. $KClO_4$ and the corresponding crown ether compound, in a crown ether/potassium molar ratio of 1:1, were dissolved in dichloromethane/ethanol (2:1). The solvent was removed under vacuum, and all complexes were isolated as pale brown solids.

2bk [(O_2ClO_2)KCrown2b]: IR (KBr): $\tilde{\nu}$ = 1591 [ν(C=N)], 1570 [$\nu(COO)_{as}$], 1420 [$\nu(COO)_s$], 1122, 1111, 1087 [ν(Cl–O)] cm^{-1}. ^1H NMR (CD_2Cl_2): *syn* isomer: δ = 0.86 (t, 18 H, CH_3), 1.39–1.76 (m, 96 H, CH_2), 2.12 (s, 3 H, CH_3CO_2), 2.26 (s, 3 H, CH_3CO_2), 3.56–4.36 (m, 44 H, OCH_2), 6.14 (d, 2 H, ArH), 6.31 (dd, 2 H, ArH), 6.45–6.70 (m, 10 H, ArH), 6.99 (d, 2 H, ArH), 7.78 (s, 2 H, CH=N). *anti* isomer: δ = 0.86 (t, 18 H, CH_3), 1.39–1.76 (m, 96 H, CH_2), 1.90 (s, 6 H, CH_3CO_2), 3.56–4.36 (m, 44 H, OCH_2), 5.88 (d, 2 H, ArH), 6.15 (dd, 2 H, ArH), 6.45–6.70 (m, 8 H, ArH), 6.67 (d, 2 H, ArH), 7.18 (d, 2 H, ArH), 7.59 (s, 2 H, CH=N) ppm.

2ck [(O_2ClO_2)KCrown2c]: IR (KBr): $\tilde{\nu}$ = 1582 [(ν(C=N + νCOO_{as})], 1415 [$\nu(COO)_s$], 1123, 1111 (sh), 1095 [ν(Cl–O)] cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 0.88 (t, 24 H, CH_3), 1.28–1.77 (m, 128 H, CH_2), 2.05 (s, 6 H, CH_3CO_2), 3.67–4.24 (m, 48 H, OCH_2), 5.70 (d, 2 H, ArH), 6.45 (br, 2 H, ArH), 6.61 (m, 6 H, ArH), 7.07 (m, 4 H, ArH), 7.94 (s, 2 H, CH=N) ppm.

3bk [(O_2ClO_2)KCrown3b]: IR (Nujol): $\tilde{\nu}$ = 1580 [ν(C=N)], 248 [ν(Pd–Cl)], 1122, 1109, 1093 [ν(Cl–O)] cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 0.86 (t, 18 H, CH_3), 1.39–1.76 (m, 96 H, CH_2), 3.79–4.22 (m, 44 H, OCH_2), 6.56 (s, 4 H, ArH), 6.65 (dd, 2 H, ArH), 6.82 (dd, 2 H, ArH), 6.90 (m, 4 H, ArH), 7.11 (d, 2 H, ArH), 7.31 (d, 2 H, ArH), 7.92 (s, 2 H, CH=N) ppm.

3ck [(O_2ClO_2)KCrown3c]: IR (Nujol): $\tilde{\nu}$ = 1588 [ν(C=N)], 245 [ν(Pd–Cl)], 1123, 1113, 1089 [ν(Cl–O)] cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 0.88 (t, 24 H, CH_3), 1.28–1.75 (m, 128 H, CH_2), 3.92–4.11 (m, 48 H, OCH_2), 6.56 (s, 4 H, ArH), 6.82 (dd, 2 H, ArH), 6.89 (d, 2 H, ArH), 6.90 (s, 2 H, ArH), 6.94 (s, 2 H, ArH), 7.10 (d, 2 H, ArH), 7.88 (s, 2 H, CH=N) ppm.

CAUTION: Perchlorates are potentially explosive. Although we have not experienced any problems, even under heating conditions, they should be handled with care and small samples should be used.

Acknowledgments

This work was sponsored by the Ministerio de Educación y Ciencia (MEC) (Project CTQ2005-08729/BQU) and the Junta de Castilla y León (Project VA099A05). C. C. thanks the MEC for a grant.

[1] T. Kato, N. Mizoshita, K. Kishimoto, *Angew. Chem. Int. Ed.* **2006**, *45*, 38–68.
[2] J. W. Goodby, G. H. Mehl, I. M. Saez, R. P. Tuffin, G. Mackenzie, R. Auzély-Velty, T. Benvegnu, D. Plusquellec, *Chem. Commun.* **1998**, 2057–2058.
[3] M. Yoshio, T. Mukai, H. Ohno, T. Kato, *J. Am. Chem. Soc.* **2004**, *126*, 994–995.
[4] C. F. van Nostrum, S. J. Picken, A.-J. Schouten, R. J. M. Nolte, *J. Am. Chem. Soc.* **1995**, *117*, 9957–9965.
[5] K. Kimura, Y. Kawai, S. Yajima, Y. Sakurai, *Chem. Commun.* **2001**, 1302–1303.
[6] M. Stępien, B. Donnio, J. L. Sessler, *Angew. Chem. Int. Ed.* **2007**, *46*, 1431–1435.
[7] M. J. O'Callagham, M. D. Wand, C. M. Walker, M. Nakata, *Appl. Phys. Lett.* **2004**, *85*, 6344–6346.
[8] H. J. Coles, M. N. Pivnenko, *Nature* **2005**, *436*, 997–1000.
[9] C. F. van Nostrum, S. J. Picken, R. J. M. Nolte, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2173–2175.
[10] J.-M. Lehn, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 89–112.
[11] D. J. Cram, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1009–1020.
[12] C. J. Pedersen, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1021–1027.
[13] I. K. Lednev, M. C. Petty, *Adv. Mater.* **1996**, *8*, 615–630.
[14] T. I. Sergeeva, S. P. Gromov, A. I. Vedernikov, M. S. Kapichnikova, M. V. Alfimov, V.-T. Lieu, D. Möbius, M. S. Tsarkova, S. Y. Zaitsev, *Colloids Surf.* **2005**, *255*, 201–209.
[15] G.-X. He, F. Wada, K. Kikukawa, S. Shinkai, T. Matsuda, *J. Org. Chem.* **1990**, *55*, 541–548.
[16] G. Johansson, V. Percec, G. Ungar, D. Abramic, *J. Chem. Soc. Perkin Trans. 1* **1994**, 447–459.
[17] R. P. Tuffin, K. J. Toyne, J. W. Goodby, *J. Mater. Chem.* **1996**, *6*, 1271–1282.
[18] C. F. van Nostrum, *Adv. Mater.* **1996**, *8*, 1027–1030.
[19] V. Percec, G. Johansson, G. Ungar, J. P. Zhou, *J. Am. Chem. Soc.* **1996**, *118*, 9855–9866.
[20] J. A. Schröter, C. Tschierske, M. Wittenberg, J. H. Wendorff, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1119–1121.
[21] K. Leblanc, P. Berdagué, J. Rault, P.-P. Bayle, P. Judeinstein, *Chem. Commun.* **2000**, 1291–1292.
[22] A. Mourran, U. Beginn, G. Zipp, M. Möller, *Langmuir* **2004**, *20*, 673–679.
[23] A. Schultz, S. Laschat, A. Saipa, F. Gießelmann, M. Nimtz, J. L. Schulte, A. Baro, B. Miehlich, *Adv. Funct. Mater.* **2004**, *14*, 163–168.
[24] T. Hegmann, B. Neumann, R. Wolf, C. Tschierske, *J. Mater. Chem.* **2005**, *15*, 1025–1034.
[25] N. Steinke, W. Frey, A. Baro, S. Laschat, C. Drees, M. Nimtz, C. Hägele, F. Giesselmann, *Chem. Eur. J.* **2006**, *12*, 1026–1035.
[26] P. Espinet, M. A. Esteruelas, L. A. Oro, J. L. Serrano, E. Sola, *Coord. Chem. Rev.* **1992**, *117*, 215–274.
[27] *Metallomesogens* (Ed,: J. L. Serrano), VCH, Weinheim, **1996**.
[28] a) D. W. Bruce, *Inorganic Materials* (Eds.: D. W. Bruce, D. O'Hare), Wiley, Chichester, 2nd ed., **1996**, ch. 8.
[29] B. Donnio, D. Guillon, D. W. Bruce, R. Deschenaux, *Metallomesogens, Comprehensive Organometallic Chemistry III: From Fundamentals to Applications* (Eds.: R. H. Crabtree, D. M. P. Mingos), Elsevier, Oxford, UK, vol 12, **2006**: *Applications III: Functional Materials, Environmental and Biological Applications,* (Ed.: D. O'Hare), ch. 12.05, pp. 195–294.
[30] T. Hegmann, B. Neumann, J. Kain, S. Diele, C. Tschierske, *J. Mater. Chem.* **2000**, *10*, 2244–2248.
[31] C. Sirlin, L. Bosio, J. Simon, V. Ahsen, E. Yilmazer, Ö. Bekâroglu, *Chem. Phys. Lett.* **1987**, *139*, 362–364.
[32] Z. Belardi, C. Sirlin, J. Simon, J. J. Andre, *J. Phys. Chem.* **1989**, *93*, 8105–8110.
[33] J. F. Van der Pol, E. Neeleman, J. W. Zwikker, R. J. M. Nolte, W. Drenth, J. Aerts, R. Visser, S. J. Picken, *Liq. Cryst.* **1989**, *6*, 577–592.

[34] J. Arias, M. Bardají, P. Espinet, *J. Organomet. Chem.* **2006**, *691*, 4990–4999.
[35] M. B. Ros, N. Ruiz, J. L. Serrano, P. Espinet, *Liq. Cryst.* **1991**, *9*, 77–96.
[36] M. J. Baena, P. Espinet, M. B. Ros, J. L. Serrano, *J. Mater. Chem.* **1996**, *6*, 1291–1296.
[37] H. Onoue, K. Minami, K. Nakagawa, *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3480–3485.
[38] N. Nakamoto, *IR and Raman Spectra of Inorganic and Coordination Compounds*, Wiley Interscience, 3rd ed., **1978**.
[39] M. J. Baena, J. Buey, P. Espinet, H.-S. Kitzerow, G. Heppke, *Angew. Chem. Int. Ed.* **1993**, *32*, 1201–1203.
[40] M. J. Baena, J. Buey, P. Espinet, C. E. García-Prieto, *J. Organomet. Chem.* **2005**, *690*, 998–1010.
[41] C. J. Pedersen, *J. Am. Chem. Soc.* **1967**, *89*, 7017–7036.
[42] A. R. Davis, C. J. Murphy, R. A. Plane, *Inorg. Chem.* **1970**, *9*, 423–425.
[43] J. S. Kim, W. K. Lee, L.-H. Suh, J.-G. Kim, J. Yoon, J. H. Lee, *J. Org. Chem.* **2000**, *65*, 7215–7217.
[44] G. W. Gray, J. W. Goodby, *Smectic Liquid Crystals. Textures and Structures*, Hill, Glasgow, London, **1984**.
[45] I. Dierking, *Textures of Liquid Crystals*, Wiley-VCH, Weinheim, **2003**.
[46] C. Tschierske, *J. Mater. Chem.* **1998**, *8*, 1485–1508.
[47] N. L. Mc Millan, *Phys. Rev. A* **1973**, *8*, 1921–1929.
[48] D. D. Perrin, W. L. F. Armarego, *Purification of Laboratory Chemicals,* Pergamon Press, Oxford, 3rd ed., **1988**, pp. 291.
[49] T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer, G. Wilkinson, *J. Chem. Soc.* **1965**, 3632–3640.
[50] E. P. Kyba, R. C. Helgeson, K. Madan, G. W. Gokel, T. L. Tarnowski, S. S. Moore, D. J. Cram, *J. Am. Chem. Soc.* **1977**, *99*, 2564–2571.
[51] C. F. Van Nostrum, S. Picken, A. Schouten, J. M. Nolte, *J. Am. Chem. Soc.* **1995**, *117*, 9957–9965.

Received: July 24, 2007
Published Online: January 15, 2008

