Synthesis and Mesomorphic Properties of Palladium(II) Complexes Based on 3,4,5-Trialkoxy Benzonitrile Ligands

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The synthesis and characterization of the nitrile ligands 3,4,5-tridodecyloxy benzonitrile (**7**) and 3,4,5-trioctadecyloxy bezonitrile (**8**), and their corresponding palladium(II) complexes are described. The nitrile ligands display only a crystalline phase and do not show liquid crystalline behavior, while their corresponding palladium(II) complexes display an enantiotropic columnar mesophase. The induction of the columnar mesophase is mainly due to dimerization through the palladium complexation of the half disk-like nitrile ligands giving rise to a trans square planar geometry.

Introduction

In recent years there has been growing interest in liquid crystals containing transition metals (metallomesogens) because of their special combination of liquid crystalline and metallic properties which can give rise to special electro-optic and magnetic characteristics. Such an application potential is related to the molecular structures which result in different liquid crystalline phases.[1-3]

So far, it is well documented that the tendency for a given molecule to display a particular liquid crystalline phase is related to its shape, aspect ratio, and dipolar properties.[4] Rod-like molecules generally assemble into nematic or smectic phases, while disc-like molecules tend to display columnar phases. Although a number of systematic studies on the influence of the molecular structure on the mesomorphic properties have been reported on conventional organic liquid crystals, this kind of study is rare in liquid crystals based on molecules containing transition metal coordination complexes.[3] Therefore, it is important to understand the influence of molecular structure on the mesophase for metallomesogens to create novel liquid crystalline materials.

In general, the thermotropic columnar mesophases are formed by flat, disc-like structures, comprising a rigid core such as polycyclic aromatic structure with four to eight aliphatic side chains.[5] Also, half disc-like molecules such as phananthridinone derivatives induce columnar mesophases as a result of dimeric association of two half discs through intermolecular hydrogen bonding. Such a dimeric association can be attributed to metal complexation of appropriate ligands which gives rise to the formation of a liquid crystalline phase.[6]

The goal of this paper is to present the synthesis of nitrile ligands based on half disc-shaped 3,4,5-trialkoxyphenyl and their corresponding palladium complexes with a trans square planar geometry.[7] The mesomorphic properties of the resulting palladium complexes characterized by differential scanning calorimetry (DSC) and thermal optical polarized microscopy are also discussed.

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Experimental

Materials

Propyl gallate (97%), 1-bromododecane (97%), 1-bromooctadecane (99 %), dichloropalladium(II) (99%) (all from Aldrich) and the other conventional reagents were used as received. Bis(benzonitrile)dichloropalladium(II) was prepared according to the procedure described previously.[8]

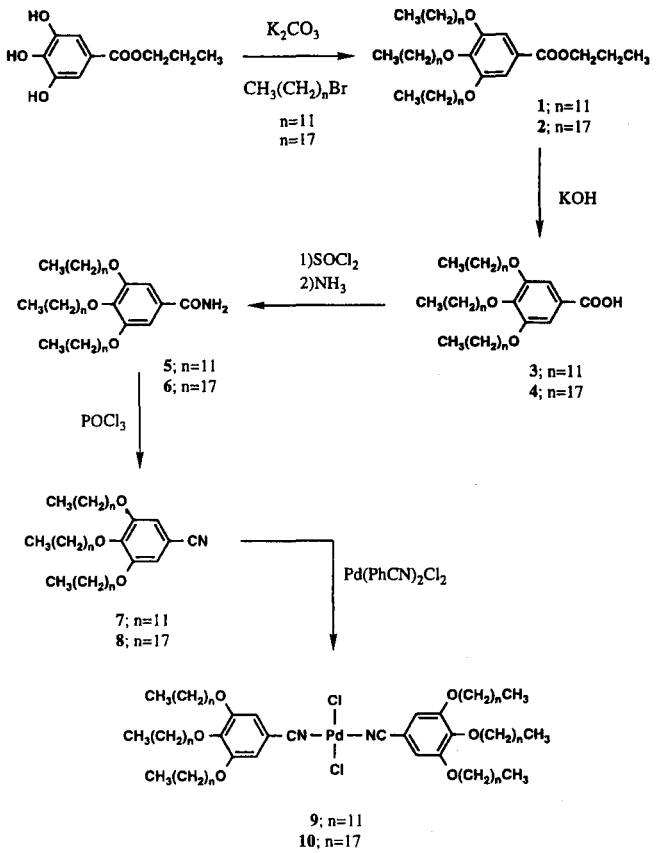
Techniques

^{1}H NMR spectra were recorded from $CDCl_3$ solution on a Bruker AM 300 spectrometer operating at 300 MHz proton frequency or a Bruker AM 500 spectrometer. TMS was used as internal standard. Infrared (IR) spectra were recorded on a Nicolet Impact 400 FT IR spectrophotometer using KBr pellet. A Perkin Elmer DSC-7 differential scanning calorimeter, equipped with a 1020 thermal analysis controller was used to determine the thermal transitions which were reported as the maxima and minima of their endothermic or exothermic peaks, respectively. In all cases, heating and cooling rates were 10 °C/min unless otherwise specified. A Nikon Optiphot 2-pol optical polarized microscope (magnification: 100x) equipped with a Mettler FP 82 hot stage and a Mettler FP 90 central processor was used to observe the thermal transitions and to analyze the anisotropic textures.[9,10] The Pd(II) complexes were purified by repeated recrystallization from a mixture of CH_2Cl_2 and *n*-hexane until transition temperatures remain constant. Their purity was checked by the absence of the melting endotherm of the free nitrile ligand in the DSC scan of the complex and the absence of the CN stretching band corresponding to the free ligand in IR spectrum.

Synthesis

The synthsis of nitrile ligands and their corresponding palladium complexes is outlined in Scheme 1. The complexation reactions and reaction workups were carried out under an atmosphere of prepurified N_2 at room temperature by using standard Schlenk techniques.[11]

Propyl-3,4,5-tridodecyloxy benzoate (1) and propyl-3,4,5-trioctadecyloxy benzoate (2). **1** and **2** were synthesized according to the procedure reported in a previous publication.[12]



Scheme 1. Synthesis of the nitrile ligands **7**, **8** and the complexes **9**, **10**.

3,4,5-Tridodecyloxy benzoic acid (3) and 3,4,5-trioctadecyloxy benzoic acid (4). **3** and **4** were synthesized according to the procedure reported in a previous publication.[12]

3,4,5-Tridodecyloxy benzamide (5). A solution of **3** (2.5 g, 3.7 mmol), $SOCl_2$ (2.1 mL, 10.8 mmol) and 50 mL of $CHCl_3$ was refluxed for 3 h. The solvent and excess $SOCl_2$ were then removed in a reduced pressure. $CHCl_3$ (30 mL) was added and NH_3 gas then bubbled into the reaction mixture for 20 min. The resulting solution was poured into water and extracted with $CHCl_3$. The $CHCl_3$ solution was dried over magnesium sulfate and the solvent was then removed in a rotary evaporator. The obtained solid was recrystallized from *n*-hexane to yield 2.2 g (87%) of white crystals.

T_m; 52.1 °C, T_i; 78.6 °C (DSC). ^{1}H NMR ($CDCl_3$, TMS, δ, ppm); 0.88 (m, 3H, CH_3-), 1.24-1.47 (m, 54H, $CH_3(CH_2)_9$-), 1.68-1.86 (m, 6H, OCH_2CH_2), 4.00 (m, 6H, OCH_2), 5.82 (s, 2H, NH_2), 7.00 (s, 2 Ar-H). IR (KBr) cm^{-1}; 1650 ($\gamma_{C=O}$), 3184, 3362 (γ_{N-H}).

3,4,5-Trioctadecyloxy benzamide (6). **6** was synthesized according to the procedure for **5**.

Yield; 80%. T_m; 93.0 °C (DSC). ^{1}H NMR ($CDCl_3$, TMS, δ, ppm); 0.88 (m, 3H, CH_3-), 1.26-1.47 (m, 90H, $CH_3(CH_2)_{15}$-), 1.68-1.86 (m, 6H, OCH_2CH_2), 4.00 (m, 6H, OCH_2), 5.82 (s, 2H, NH_2), 7.00 (s, 2 Ar-H). IR (KBr) cm^{-1}; 1657 ($\gamma_{C=O}$), 3184, 3363 (γ_{N-H}).

3,4,5-Tridodecyloxy benzonitrile (7). A solution of **5** (2 g, 2.96 mmol) and $POCl_3$ (1.5 mL, 15.9 mmol) in 30 mL of $CHCl_3$ was refluxed for 8 h. After cooled to room temperature, the solution was neutralized with dilute aqueous NaOH solution. The solution was extracted with CH_2Cl_2 and the CH_2Cl_2 solution was dried over magnesium sulfate. The solvent was then removed in a rotary evaporator. The obtained solid was purified by column chromatography (silica gel, CH_2Cl_2 eluent) to yield 1.6 g (80%) of white crystals.

mp 61.3 °C. ^{1}H NMR ($CDCl_3$, TMS, δ, ppm); 0.88 (m, 3H, CH_3-), 1.24-1.43 (m, 54H, $CH_3(CH_2)_9$-), 1.73-1.83 (m, 6H, OCH_2CH_2), 3.98 (m, 6H, OCH_2), 6.81 (s, 2 Ar-H). IR (KBr) cm^{-1}; 2230 (γ_{CN}).

3,4,5-Trioctadecyloxy benzonitrile (8). **8** was synthesized according to the procedure for **7**.

Yield; 62%. mp 82.1 °C. ^{1}H NMR ($CDCl_3$, TMS, δ, ppm); 0.88 (m, 3H, CH_3-), 1.26-1.46 (m, 90H, $CH_3(CH_2)_{15}$-), 1.76-1.87 (m, 6H, OCH_2CH_2), 3.98 (m, 6H, OCH_2), 6.80 (s, 2 Ar-H). IR (KBr) cm^{-1}; 2229 (γ_{CN}).

Dichlorobis(3,4,5-tridodecyloxy benzonitrile)palladium(II) (9). A solution of **7** (51 mg, 0.078 mmol) and $Pd(PhCN)_2Cl_2$ (15 mg, 0.039 mmol) in 10 mL of CH_2Cl_2 was stirred at room temperature for 8 h under nitrogen. The solvent was removed under vacuum to yield yellow residue which was recrystallized from a mixture of CH_2Cl_2 and *n*-hexane to yield 12 mg (37%) of yellow crystals. The absence of free ligand was verified by DSC (absence of the melting point of the free ligand in the heating and cooling scans), optical polarized microscopy and IR (the absence of the CN stretching band corresponding to the free ligand).

^{1}H NMR ($CDCl_3$, TMS, δ, ppm); 0.88 (m, 3H, CH_3-), 1.24-1.43 (m, 54H, $CH_3(CH_2)_9$-), 1.73-1.83 (m, 6H, OCH_2CH_2), 3.98 (m, 6H, OCH_2), 6.84 (s, 2 Ar-H). IR (KBr) cm^{-1}; 2297 (γ_{CN}).

Dichlorobis(3,4,5-trioctadecyloxy benzonitrile) palladium(II) (10). **10** was synthesized according to the procedure for **9**.

Yield; 29%. ^{1}H NMR ($CDCl_3$, TMS, δ, ppm); 0.88 (m, 3H, CH_3-), 1.26-1.46 (m, 90H, $CH_3(CH_2)_{15}$-), 1.76-1.87 (m, 6H, OCH_2CH_2), 3.98 (m, 6H, OCH_2), 6.88 (s, 2 Ar-H). IR (KBr) cm^{-1}; 2292 (γ_{CN}).

Results and Discussion

The nitrile ligands based on 3,4,5-alkoxyphenyl were prepared from the corresponding acid compounds in two steps, involving amidation with thionyl chloride and then ammonia to the amide and dehydration with phosphoryl chloride to the nitrile as outlined in Scheme 1. The synthesized nitrile ligands were characterized to have the expected structure by spectral analyses. The palladium-nitrile complexes were prepared by a ligand exchange reaction with [$PdCl_2(PhCN)_2$] and the corresponding nitrile ligands. The resulting complexes were characterized by IR spectra. Figure 1 shows selective absorption regions of IR spectra corresponding to CN streching of free ligand **7** and the corresponding complex. As can be seen in this figure, compared with free ligand, an absorption due to the streching frequency of a CN group of the complex was observed at higher frequency (*ca.* 70 cm^{-1}) than that of the free ligand. This shift is due to the σ donation of the antibonding nitrogen lone pair to palladium and consistent with the results

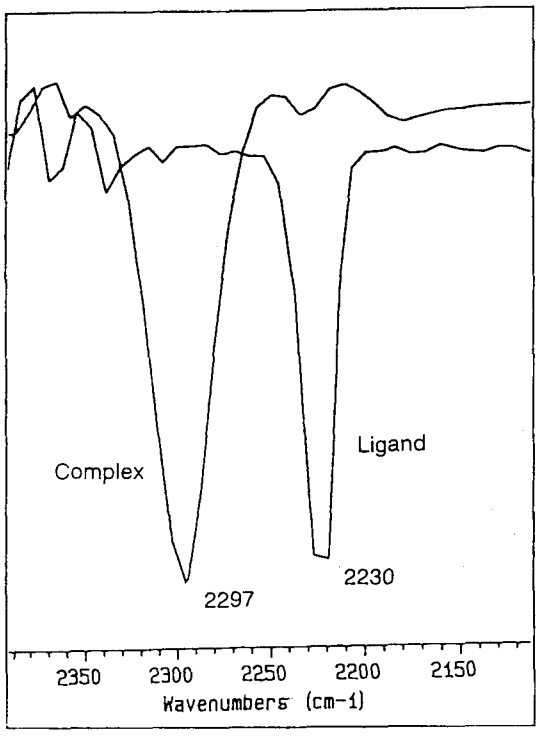


Figure 1. IR spectra corresponding to CN absorptions of the nitrile ligand **7** and the complex **9**.

described previously.[13,14]

The mesomorphic phase behavior of the amide derivatives **5, 6** and the complexes **9, 10** was investigated by differential scanning calorimetry (DSC) and thermal optical polarized microscopy. Representative DSC traces of amide derivatives and the complexes are presented in Figure 2. The phase transition temperatures and the corresponding thermodynamic parameters of these derivatives are summarized in Table 1. The amide derivative **5** based on dodecyloxy side chains exhibits an enantiotropic columnar mesophase which undergoes isotropization at 78.6 °C on heating, while **6** based on octadecyloxy side chains displays a monotropic columnar mesophase. The columnar mesophase shows a pseudo-focal conic texture on the optical polarized microscope as shown in Figure 3a, which is common feature for columnar phase.[9,10,19] The columnar mesophase of amide derivatives is formed through dimerization through the hydrogen bonding of their amide groups. According to the crystal structure of benzamide dimer exhibiting coplanar structure,[15] it seems evident that the mesogenic units are formed by dimerization through hydrogen bonding. The existence of interdimeric hydrogen bonding is supported by the IR experimental results. The absorption of the C=O stretching vibrations appears near 1650 cm^{-1} for the amide derivatives **5, 6**, which is lower frequency (*ca.* 40 cm^{-1}) than that of the free amides. This is due to the decreased double bond character of carbonyl group caused by hydrogen bonding and consistent with the results described previously.[6,16-18] However, the nitrile derivatives **7, 8**, which are not possible to form dimeric association through the hydrogen bonding, exhibit only a crystalline phase and do not display liquid crystalline behavior (see Exp. section). This result also supports that the dimeric association of half disc-

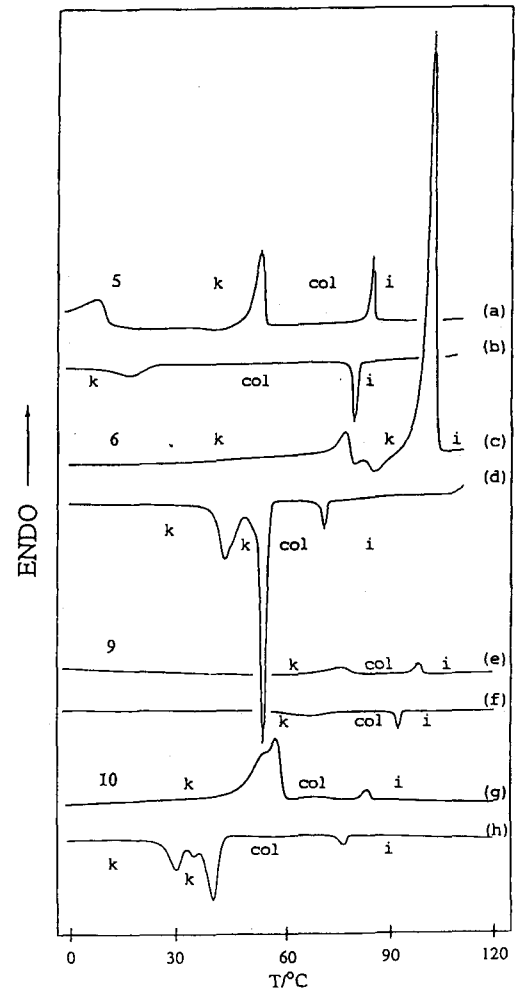


Figure 2. DSC traces (10 °C/min) recorded during the heating scan (a), the cooling scan (b) of **5**, the heating scan (c), the cooling scan (d) of **6**, the heating scan (e), the cooling scan (f) of **9**, the heating scan (g) and the cooling scan (h) of **10**.

like molecules plays a key role in the formation of columnar mesophase.

In this context, dimerization through palladium complexation of nitrile ligands is expected to induce columnar

Table 1. Thermal transitions and the corresponding enthalpy changes of the amide derivatives **5, 6** and the Palladium(II) complexes **9, 10** (k: crystalline phase, col: columnar phase, i: isotropic phase)

Compound	Phase transition (°C) and corresponding enthalpy changes (kJ/mol)	
	heating	cooling
5	k 52.1 (14.5) col 78.6 (5.4) i	i 75.0 (5.4) col 21.3 (4.7) k
6	k 93.0 (90.4) i	i 67.7 (3.7) col 53.4 (67.4) k
9	k 73.3 (5.8) col 91.2 (3.0) i	i 87.0 (3.2) col 66.8 (4.9) k
10	k 58.4 (75.8) col 80.4 (3.7) i	i 74.8 (4.2) col 43.9 (73.8) k

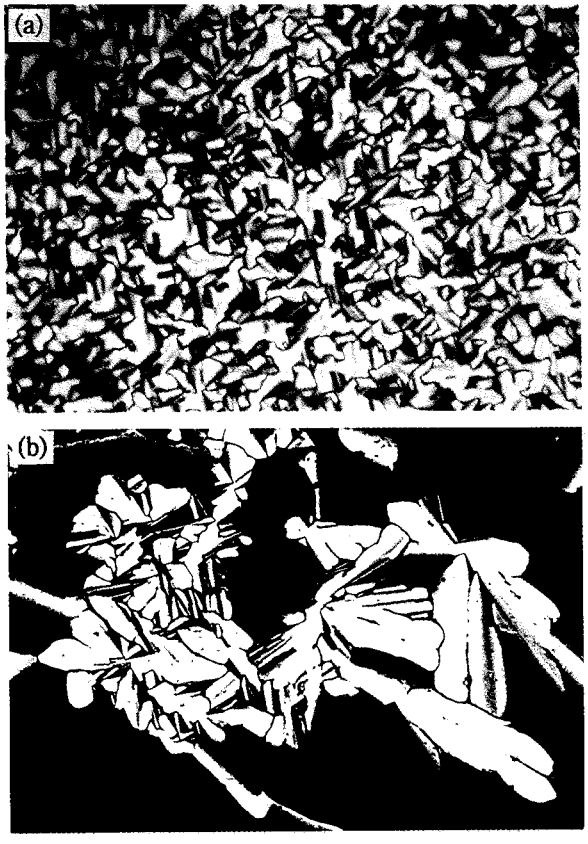


Figure 3. Representative optical polarized micrographs (100X) of the texture exhibited by the columnar mesophase of (a) **6** at 67 °C on the cooling scan and (b) **10** at 74 °C on the cooling scan.

mesophase because it gives rise to a trans square planar geometry with coplanar structure of aromatic core.[7] Therefore, we have proceeded to synthesized the palladium complexes based on half disc-like nitrile ligand. In contrast to the nitrile ligands, the palladium complex with dodecyloxy side chains (**9**) display a crystal melting at 73.3 °C followed by a columnar mesophase which undergoes isotropization at 91.2 °C on the heating scan as shown in Figure 2 and Table 1. On cooling from isotropic phase, the complex shows a columnar phase followed by a crystalline phase. The complex with octadecyloxy side chains (**10**) also shows a similar phase behavior which exhibits an enantiotropic columnar mesophase except that thermal transitions corresponding to T_m and T_i are lower compared to those of **9**. Examination by thermal optical polarized microscopy confirmed that the complexes form an enantiotropic mesophases. Cooling from the isotropic liquid, the complexes form the platelet-like texture growth as shown in Figure 3b, that is common characteristic of columnar mesophase formation.[19] The X-ray experiments to obtain the detailed structural information on the columnar phase are in progress.

In conclusion, the nitrile ligands based on half disc-shaped 3,4,5-trialkoxyphenyl and their corresponding palladium complexes were synthesized. In contrast to the nitrile ligands which do not show liquid crystalline phase behavior, the palladium complexes display an enantiotropic columnar mesophase. This result demonstrates that non mesomorphic nitriles based on half disc-like trialkoxyphenyl can induce an enantiotropic columnar liquid crystalline phase through dimerization caused by palladium complexation giving rise to a square planar geometry with coplanar structure of aromatic core.

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