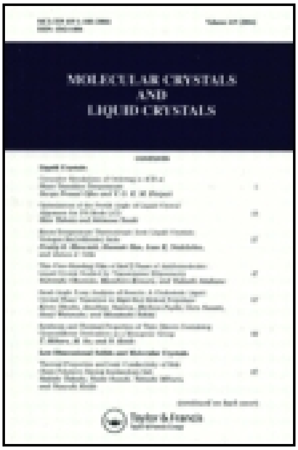

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Induction of Mesomorphism Through Supramolecular Association in Coordination Pd (Ii) Compounds of Dialkyl 2,2″-Bipyridine-4,4″-Dicarboxylates

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INDUCTION OF MESOMORPHISM THROUGH SUPRAMOLECULAR ASSOCIATION IN COORDINATION Pd (II) COMPOUNDS OF DIALKYL 2,2′-BIPYRIDINE-4,4′-DICARBOXYLATES

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A series of three 4,4′-disubstituted-2,2′-bipyridines and the corresponding mononuclear cis-dichloro palladium(II) complexes have been synthesized. None of the ligands show mesomorphism. Upon their complexation to Pd(II) the peculiar structural arrangement characterized by intermolecular associations of the new derivatives induces mesogenic properties, confirming the new and exciting role of the coordination chemistry in metal-mediated formation of liquid crystals.

Keywords: metallomesogens; palladium; dialkyl 2,2′-bipyridine-4,4′-dicarboxylates; coordination compounds

INTRODUCTION

The thermotropic metallomesogens form a new class of liquid crystalline compounds, displaying novel physical properties, whose synthesis was initially performed starting from mesogenic ligands. The high transition

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temperatures and the poor thermal stability often found for this class of materials were the principal drawback which prompted doubts about the suitability of liquid crystalline metal complexes as materials for practical applications. Within thirty years numerous strategies were developed in order to reduce the transition temperatures and improve the knowledge about new, unconventional structural features of metal-containing liquid crystals allowing the role of metallomesogens to overturn. [1,2] At the present time coordination chemistry could be also synonimous of metal-mediated formation of liquid crystals owing the ability of a metal ion to induce mesomorphism in non mesomorphic ligands. This phenomenon can be achieved via changes of molecular conformation, shape and structure induced both by complexation [3–6] and inter or intramolecular interactions of different nature giving rise supramolecular assemblies. [7–9]

In this context, the so called complementary shape approach has expecially attracted our interest. 2,2′-Bipyridine are very attractive ligands because of their extensive coordination chemistry and their versatility: the spectroscopic and chemical properties indeed can be tuned by the choice of the metal centre and the substituents. Moreover judiciously functionalized ligands can be metallated and give rise to new mesogenic structures based on specific molecular correlations. In this paper we explore the possibility to achieve this target by obtaining attractive dimeric or polymeric associations between mononuclear cis-dichloro-palladium complexes by means intense dipolar forces. Herein we describe the synthesis and characterization of a series of dialkyl 2,2′-bipyridine-4,4′-dicarboxylates, $\mathbf{L_n}$, and of their square-planar dichloro palladium derivatives $\mathbf{[L_nPdCl_2]}$ **1–3**.

EXPERIMENTAL SECTION

Measurements

The infrared spectra were recorded on a Perkin Elmer FT 2000 spectrophotometer and the ^{1}H NMR spectra were recorded on a Bruker WH-300 spectrometer in $CDCl_3$ solution, with TMS as internal standard. Elemental analyses were performed with a Perkin-Elmer 2400 analyzer. The textures of the mesophases were studied with a Zeiss Axioscope polarizing microscope equipped with a Linkam C0 600 heating stage. The transition temperatures and enthalpies were measured on a Perkin-Elmer Pyris 1 Differential Scanning Calorimeter with a heating and cooling rate of 10°C/min. The apparatus was calibrated with indium. Two or more heating/cooling cycles were performed on each sample.

The X-ray powder diffraction patterns were obtained by an INEL CPS120 powder diffractometer equipped with a position sensitive detector covering a scattering angle of 120°, with an angular revolution of 0.018°. Monochromatized CuKα radiation (λ 1.54 Å) impinged on the −1 mm thick sample, the temperature of which was controlled to ± 0.1° by a hot stage containing electrical resistors.

Synthesis

[Pd(PhCN)$_2$Cl$_2$] was synthesised as reported in the reference 10.

Synthesis of L_n Ligands

4,4′-dicarboxy-2,2′-bipyridine, ***I***. The synthesis of **I** was performed modifying slightly the reported method [11a]. 1.0 g (5.43 mmoles) of 4,4′-dimethyl-2,2′-bipyridine was added to a solution of sulfuric acid (98%, 35 mL). 6.34 g (21.56 mmoles) of potassium dichromate were then added in small portions to the resulting solution, in order to keep the temperature between 70 and 80°C. The solution was stirred until the temperature fell below 40°C. The deep green reaction mixture was poured in 160 ml of ice water and filtered. The solid was washed with water until the filtrate was colourless and allowed to dry. The resulting light yellow solid was then further purified by refluxing it in 35 ml of 65% nitric acid for 6 hours. This solution was poured over ice, diluted with 200 ml of water and cooled to 5°C. The precipitate was filtered, washed with water (5 × 10 ml), then acetone (2 × 10 ml) and allowed to dry giving 1.28 g (96%) of **I** as a fine white solid.

M. p. > 350°C; the^{1}H NMR spectrum was in accordance with that reported in the literature [11b]. The product was used without further purification in the next step.

Dioctyl 2,2′-bipyridine-4,4′-dicarboxylate, ***L_1***. A mixture of 4,4′-dicarboxy-2,2′-bipyridine, **I** (0,40 g, 1.64 mmol) and thionyl chloride (15 mL) were refluxed under nitrogen until a clear yellow solution was obtained. The excess of thionyl chloride was removed and the residue dried under vacuum for the 2 h. The acid chloride was suspended in toluene (12 mL) and treated with a slight excess of octanol (0.62 mL, 3.94 mmol). The mixture was heated at reflux until to give a weakly pink solution. Chloroform (30 mL) was added and the mixture washed with saturated sodium hydrogen carbonate solution (30 mL). The aqueous layer was then shaken with chloroform (3 × 10 mL). The organic extract was washed with water (100 mL), dried over anhydrous sodium sulphate, filtered and evaporated to dryness. Recrystallization from ethanol gave colourless crystals in a 78% yield. M.p. 64°C. Anal. Calcd. for $C_{28}H_{40}N_2O_4$: C, 71.76; H, 8.60; N, 5.98. Found: C, 70.92; H, 8.22; N, 6.46.

^{1}H NMR (300 MHz, CDCl$_3$): δ 8.95 (2 H, s, H$^{3,3'}$), 8.87 (2 H, d, $J = 5.0$ Hz, H$^{6,6'}$), 7.91 (2 H, dd, $J = 5.0$, 1.5 Hz, H$^{5,5'}$), 4.39 (4 H, t, $J = 6.7$ Hz, H$^{a,a'}$), 1.82 (4 H, q, $J = 6.7$ Hz, H$^{b,b'}$), 1.36 (20 H, m, H$^{c,c'}$), 0.88 (6 H, t, $J = 6.7$ Hz, H$^{d,d'}$). IR (KBr): $\nu_{C=O}$ 1726 cm^{-1}(s).

The homologous $\mathbf{L_n}$ ligands were synthesized following the procedure described for $\mathbf{L_1}$:colors, yields, melting points (M.p.), elemental analyses, NMR and IR data are as follows.

*Dihexadecyl 2,2′-bipyridine- 4,4′-dicarboxylate, **L₂**.* Recrystallized from chloroform/ethanol. White. Yield 91%. M.p. 81°C. Anal. Calcd. for $C_{44}H_{72}N_2O_4$: C, 76.25; H, 10.47, N 4.04. Found: C, 76.18; H, 10.65; N, 3.81.^{1}H NMR (300 MHz, CDCl$_3$): δ 8.95 (2H, s, H$^{3,3'}$), 8.87 (2H, d, $J = 5.0$ Hz, H$^{6,6'}$), 7.91 (2H, dd, $J = 5.0$, 1.5 Hz, H$^{5,5'}$), 4.39 (4H, t, $J = 6.7$ Hz, H$^{a,a'}$), 1.80 (4H, m, H$^{b,b'}$), 1.34 (52H, m, H$^{c,c'}$), 0.88 (6H, t, $J = 6.7$ Hz, H$^{d,d'}$). IR (KBr): $\nu_{C=O}$ 1715 cm^{-1} (s).

*Didocosyl 2,2′-bipyridine- 4,4′-dicarboxylate, **L₃**.* Recrystallized from chloroform/ethanol. White. Yield 90%. M.p. 92°C. Anal. Calcd. for $C_{56}H_{96}N_2O_4$: C 78.08; H 11.23; N 3.25. Found: C, 77.83; H, 11.02; N, 3.69. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.95 (2H, s, H$^{3,3'}$), 8.87 (2H, d,$J = 5.0$ Hz, H$^{6,6'}$), 7.90 (2H, dd, $J = 5.0$, 1.8 Hz, H$^{5,5'}$), 4.39 (4H, t, $J = 6.7$ Hz, H$^{a,a'}$), 1.80 (4H, m, H$^{b,b'}$), 1.30 (76H, m, H$^{c,c'}$), 0.88 (6H, t,$J = 6.7$ Hz, H$^{d,d'}$). IR (KBr): $\nu_{C=O}$ 1715 cm^{-1} (s).

Synthesis of [L$_n$PdCl$_2$] Complexes

*(2,2′-bipyridyl-4,4′-bis-octylcarboxylate)palladium(II)chloride, **[L₁PdCl₂], 1**.* A solution of [Pd(PhCN)$_2$Cl$_2$] (0.15 g, 0.39 mmol) and dioctyl 2,2′-bipyridine-4,4′-dicarboxylate, $\mathbf{L_1}$ (0.18 g, 0.39 mmol) in chloroform (10 mL) was heated at reflux for 5 h. The solvent was evaporated and the residue recrystallizated from dichloromethane/diethyl ether to give the complexes as yellow solid. Yield 87%. Thermotropic behaviour in Table I. Anal. Calcd. for $C_{28}Cl_2H_{40}N_2O_4Pd$: C 52.06; H 6.24; N 4.34. Found: C, 52.07; H, 5.86; N, 4.79.^{1}H NMR (300 MHz, CDCl$_3$): δ 9.57 (2 H, d, $J = 5.0$ Hz, H$^{6,6'}$), 8.65 (2 H, s, H$^{3,3'}$), 8.12 (2 H, d, $J = 5.0$ Hz, H$^{5,5'}$), 4.48 (4 H, t, $J = 6.6$ Hz, H$^{a,a'}$), 1.84 (4 H, m, H$^{b,b'}$), 1.30 (20 H, m, H$^{c,c'}$), 0.89 (6 H, m, H$^{d,d'}$). IR (KBr): $\nu_{C=O}$ 1729 cm^{-1} (s).

The homologous **[L$_n$PdCl$_2$]** complexes were synthesized following the procedure described for **1** starting from the suitable ligands. Colors, yields, elemental analyses, NMR and IR data are as follows.

*(2,2′-bipyridyl-4,4′-bis-hexadecylcarboxylate)palladiuml(II)chloride, **[L₂PdCl₂], 2**.* Yellow. Yield 81%. Thermotropic behaviour in Table I. Anal. Calcd. for $C_{44}Cl_2H_{72}N_2O_4Pd$: C 60.72; H 8.34; N 3.22. Found: C, 59.03; H, 8.58; N, 3.47.^{1}H NMR (300 MHz, CDCl$_3$): δ 9.52 (2 H, d, $J = 6.3$ Hz, H$^{6,6'}$), 8.65 (2 H, s, H$^{3,3'}$), 8.10 (2 H, d, $J = 6.3$ Hz, H$^{5,5'}$), 4.47 (4 H, t,

TABLE 1 Optical and Thermal Properties of the **[L_nPdCl$_2$]** Complexes **1–3**

Complex	Transition[a]	T[°C]	ΔH[KJmol^{-1}]
1	Cr- Cr′	84.4	3.0
	Cr′ - I	180.9	12.2
	I- Cr	177.8	10.7
2	Cr- Cr′	97.0	7.9
	Cr′ - SmAd	130.0	0.2
	SmAd- I	155.9	13.6
	I- SmAd	154.9	14.2
	SmAd- Cr	80.3	7.9
3	Cr- Cr′	86.9	43.0
	Cr′ - SmAd	97.8	5.3
	SmAd- I	139.6	12.2
	I- SmAd	137.8	11.9
	SmAd- Cr′	80.1	6.2
	Cr′ - Cr	68.8	54.5

[a]Cr: crystal; Sm: smectic; I: isotropic liquid.

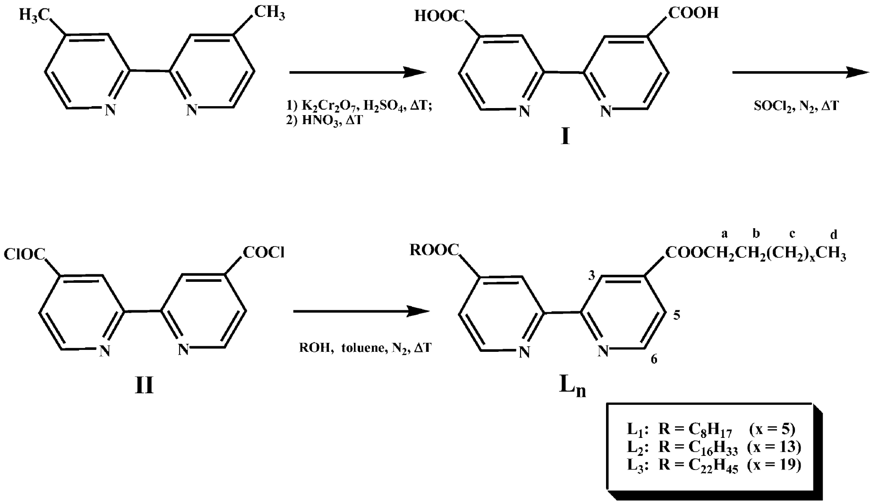
$J = 6.4$ Hz, $H^{a,a'}$), 1.86 (4 H, m, $H^{b,b'}$), 1.26 (52 H, m, $H^{c,c'}$), 0.88 (6 H, t, $J = 6.4$ Hz $H^{d,d'}$). IR (KBr): $\nu_{C=O}$ 1726 cm^{-1} (s).

(2,2′-bipyridyl-4,4′-bis-docosylcarboxylate)palladium(II)chloride, [L$_3$PdCl$_2$], 3. Yellow. Yield 85%. Thermotropic behaviour in Table I. Anal. Calcd. for $C_{56}Cl_2H_{96}N_2O_4Pd$: C 64.75; H 9.31; N 2.70. Found: C, 64.88; H, 9.15; N, 2.86.^{1}H NMR (300 MHz, CDCl$_3$): δ 9.58 (2 H, d, $J = 5.8$ Hz, $H^{6,6'}$), 8.64 (2 H, s, $H^{3,3'}$), 8.12 (2 H, d, $J =$ 5.8, 1.7 Hz, $H^{5,5'}$), 4.47 (4 H, t, $J = 6.7$ Hz, $H^{a,a'}$), 1.84 (4 H, m, $H^{b,b'}$), 1.29 (76 H, m, $H^{c,c'}$), 0.88 (6 H, t, $J = 6.7$ Hz, $H^{d,d'}$). IR (KBr): $\nu_{C=O}$ 1735 cm^{-1} (s).

RESULTS AND DISCUSSION

The preparation of the diesters **L_n** in which the number of carbon atoms in the aliphatic chains are gradually increased from 8 to 22, was carried out in a three step synthesis, as described in Scheme 1.

The oxidation of the 4,4′-dimethyl-2,2′-bipyridine using potassium dichromate gives the diacid **I**, which was reacted with thionyl chloride to affords the dichloride **II**. Finally, the esterification of **II** with the appropriate n-alkyl alcohols, in toluene under reflux, gave the ligands **L_n** as white crystalline products in very high yields. Reaction of ligands **L_n** with an equimolar amount of [Pd(PhCN)$_2$Cl$_2$] produced the square planar cis-dichloro-palladium complexes **[L_nPdCl$_2$],** according to Scheme 2. All the ligands and complexes were characterized by elemental analyses, IR and ^{1}H NMR spectroscopies, whose data are given in the experimental section.



SCHEME 1 Synthesis and proton numbering scheme for **Ln** ligands.

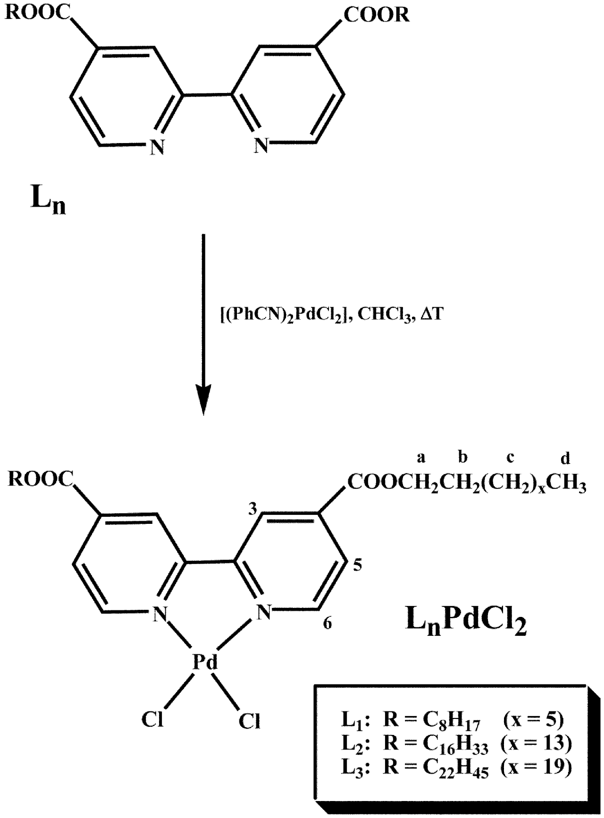
In the ^{1}H NMR spectrum, for all of the investigated complexes the resonance attributable to the $H^{6,6'}$ protons is low-field shifted of about 0.7 ppm with respect to the ligands, confirming that the metal complexation has occurred.

None of the 4-4′-diesters $\mathbf{L_n}$ are liquid crystals but most of the palladium complexes are and their thermal behaviour, investigated by polarized optical microscope and differential scanning calorimetry (DSC), is summarized in Table 1.

All the $\mathbf{[L_nPdCl_2]}$ complexes show a crystal to crystal transition followed by a smectic phase, except compound **1**, which melts directly to an isotropic liquid at 181°C. Themosaic-like textures observed for complexes **2** and **3** (Fig. 1) is not consistent with a conventional disordered Smectic phase. When cooled from their isotropic phases they retain the optical texture of the mesophase giving a glassy solid stable for long time.

As expected, the melting and clearing points decrease with the lenght of the aliphatic chains on going from 16 (**2**) to 22 carbon atoms (**3**) and, as a consequence, a larger stability of the mesophase is observed. From DSC analysis very high enthalpy values were measured for the mesophase-isotropic liquid transitions suggesting an unusual, highly correlated type of arrangement of the molecules. However, from these data we cannot make a definitive conclusion about the nature of the mesophase.

X-ray diffraction (XRD) studies on complexes **2** and **3** made possible to unequivocally assign the nature of the mesophase. The XRD pattern of sample **2** (Fig. 2) exhibits sharp inner reflections and diffuse outer halos



SCHEME 2 Synthesis and proton numbering scheme for **[L_nPdCl_2]** complexes.

and is consistent with a layered structure of the smectic type. In fact, the inner reflections consist of a set of *00n* peaks centered at $q = 2\pi n/d$ ($q = 2\pi \sin\theta/\lambda$ is the modulus of the scattering vector, 2θ is the scattering angle), where n is an integer ($n = 1$–4) and $d = 36.6$ Å is the smectic layer spacing. The wide diffuse outer halo centered about $q = 1.3$ Å^{-1} is associated with the short-range liquid-like positional ordering of the hydrocarbon chains and corresponds to the average interchain distance ≈ 4.8 Å in the smectic planes. Based on the fact that the spacing of the smectic layers in this compound are larger than the calculated molecular length in the fully extended configuration ($L \approx 28$ Å), but smaller than 2L, we can deduce that the molecules are not arranged in single molecular layers but are organized in semi bilayers partially interdigitated. Thus this smectic phase can be classified as an semi-bilayer SmA_d phase. [12]

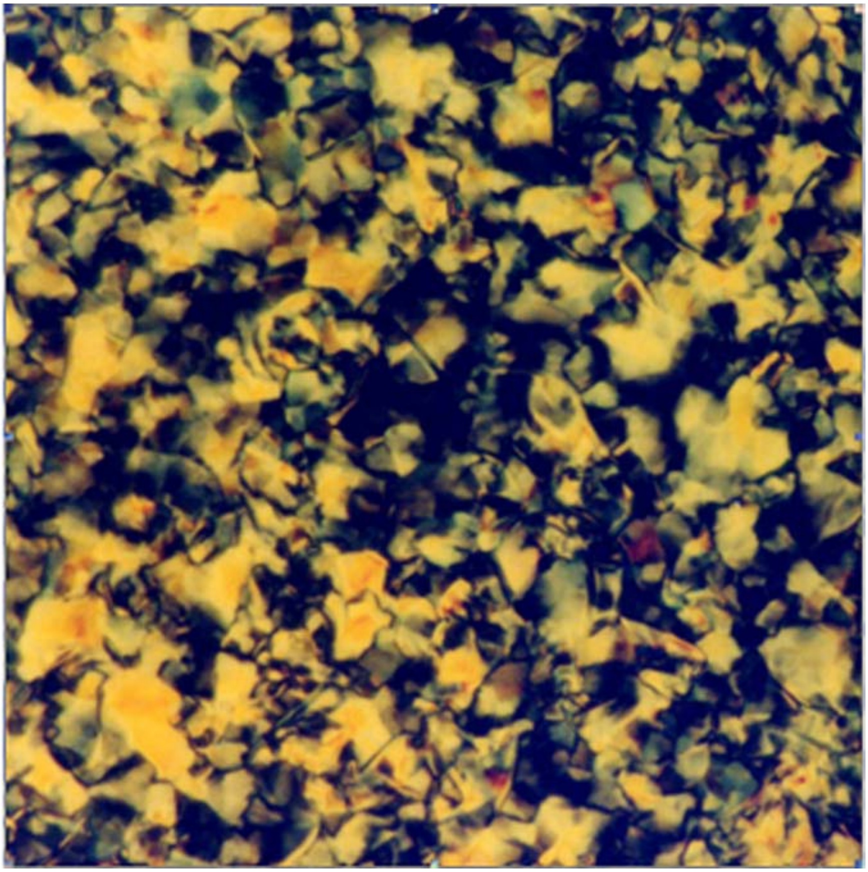


FIGURE 1 Optical texture (100x) observed for complex **[L$_3$PdCl$_2$]**. SmAd phase at 138°C on cooling from the isotropic phase.

However, differently from the typical XRD pattern of the smectic phase of conventional calamitic liquid crystals, this pattern shows two additional peaks, corresponding to spacings $d_1 = 10.5\,\text{Å}$ and $d_2 = 3.4\,\text{Å}$, which are significantly broader than those of the *00n* series. These peaks could arise from Pd-Pd in-plane correlations along mutually-orthogonal directions parallel and orthogonal, respectively, to the long side of the molecular core (i.e. the axis of the benzene rings). A similar XRD pattern was observed in the high temperature mesophase of **3**, which is consistent with the same semi-bilayer SmA$_d$ molecular arrangement of **2**, with a smectic layer spacing $d = 45.0\,\text{Å}$ (calculated molecular length ($L \approx 36\,\text{Å}$).

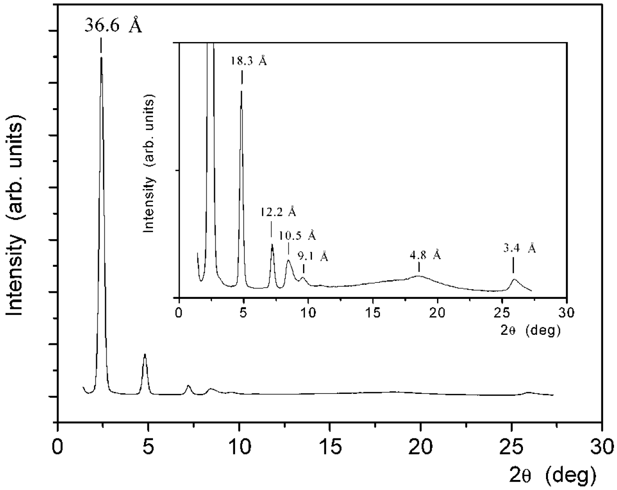


FIGURE 2 XRD pattern (λ 1.54 Å) of the high temperature smectic phase of **[L_2PdCl_2]** recorded at T = 140°C. The inset reports the same pattern expanded in the vertical axis in order to evidence the weak reflections.

The molecular geometry of a single molecule of complex **2** has been minimised using the Cerius 3.0 molecular modelling software package (UFF force field). The overall geometry is typical of a molecule with a rod-like shape, since the hydrophobic forces between the flexible chains tend to keep them parallel and at a distance of about 5 Å (Fig. 3a). On the basis of the XRD experimental data and the geometry of the minimised single

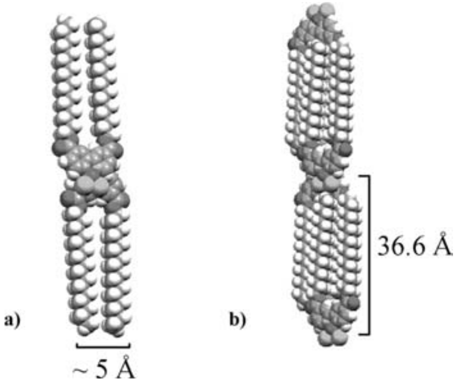


FIGURE 3 Molecular packing of two minimised molecules (a) and the formation of the smectic A arrangement (b) of **[L_2PdCl_2]** complex.

molecule (L < d < 2L), the molecular organization can be hypothesized as illustrated in Figure 3b, even in absence of crystal packing minimization.

Thus, we can assume that the large dipole moment adopted by the bipirydine ligand forced in the *cisoid* conformation by means the complexation [13], will induce favorable dipole-dipole interactions and antiparallel correlations of the nearest neighbour molecules, characterised by short intermetallic Pd—Pd distances. The flexible chains of the resulting dimers tend to align leading to a global rod-like molecular shape and a lamellar supramolecular organization of the interdigitated pairs.

CONCLUSIONS

We have prepared and characterized a new series of three bifunctionalized dialkyl 2,2′-bipyridine-4,4′-dicarboxylates and the corresponding mononuclear cis-dichloro palladium(II) complexes **[L_nPdCl_2]**. None of the ligands show mesomorphism while the coordination to a $PdCl_2$ moiety has led to metallomesogenic species confirming the role of the coordination chemistry in the metal-mediated formation of liquid crystals. All the **[L_nPdCl_2]** complexes show a crystalline polymorphism and, for the highest homologous, an enantiotropic lamellar mesophase. On the basis of XRD studies in the liquid crystalline state and from molecular modelling simulation, we have proposed a model in which the promotion of a dipolar moment upon complexation in **[L_nPdCl_2]** molecules induces self-assembling in dimers, with antiparallel disposition and short Pd—Pd intermolecular distances. Moreover, the most efficient space filling has been reached by aggregation of each pair of molecules into a bilayered structure. The lamellar spacing is 1.3 times the molecular length of a single molecule giving rise to a semi-bilayered SmAd phase.

The thermotropic phase behaviour and the supramolecular organization of **[L_nPdCl_2]** complexes make them promising candidate for design new metallomesogens with tunable properties. Future research will be planned in order to change both metal centre and substituents to use coupling of dipoles as molecular architecture tools.

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