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Dinuclear *ortho*-metallated palladium(II) azobenzene complexes with acetato and chloro bridges: Influence of polar substituents on the mesomorphic properties

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ABSTRACT

The synthesis, characterization and mesomorphic properties of a new series of acetate and chloro-bridged dinuclear orthopalladated complexes derived from azobenzene with terminal groups of hexadecyloxy moiety at one end and different polar groups (Me, Cl, F, NO_2, CN) at the other end are described. The mesomorphic properties of both the ligands and complexes were investigated by polarizing optical microscopy and X-ray studies to understand the effect of polar group in the nature of mesophase produced. Among the complexes, all chloro-bridged complexes predominantly exhibited SmA phase. However the rare phenomenon of observing mesomorphism in acetato-bridged palladium (II) complexes due its typical open book shape had been realized in substituted acetato-bridged complexes with fluoro and cyano substituents in the ligands. Nitro and cyano substituted ligands only exhibited monotropic Smectic A phase. Model molecular arrangement based on X-ray studies is presented.

1. Introduction

One of the potential applications of cyclopalladated complexes is ligand transformation using the reactions of Pd–C bond [1–5]. The importance of orthopalladated dinuclear complexes derived from salicylaldimine ligands exhibiting very good catalytic activity, dependent upon the substituent, towards the hydrogenation of nitrobenzene and cyclohexene has been demonstrated recently [5]. Mesogenic behaviour is realised in usually unfavourable acetato/carboxylato bridged ortho-metallated dinuclear Pd(II) complexes of salicylaldiimine ligands with increased peripheral chains/crown ethers, in spite of destabilization due to the non-planarity in such complexes [6–12]. Hence functional properties along with their potential applications due to the perceived advantage of combining properties of transition metal with the coordinating molecules of liquid crystalline compounds promoted basic as well as applied research activity in this area. This research area has been well reviewed recently, with the excellent work appearing regularly [13–20]. The coordination of a metal ion to the mesogenic/non-mesogenic coordinating organic ligands with an increased contribution of aromatic core resulted to yield linear [21–27] and square planar [28–35] complexes exhibiting liquid crystalline behaviour with enhanced thermal stability. One of the predominant class of metallomesogens is the organometallic complexes of "(C, N)Pd" metallacycle viz., orthocyclopalladated imines [36–39], azines [40], and azobenzenes [41–44].

Cyclopalladated compounds have proved to be an active area of research with different examples by several groups [45–55] out of which orthopalladated imine and azobenzene compounds exhibiting large thermal range of mesomorphism have been extensively studied due to their ease of synthesis and thermal stability. Further the nature of the bridging group as well as polarity of the substituent played an important role in the mesomorphic characteristics and photo-physical properties. Hence it not only changes the geometry of the system but also alter the liquid crystalline properties. A comparative study on the azo-based cyclopalladated dimers with various bridging systems (X = Cl, Br, I, N_3, SCN) revealed that all the complexes are planar [52–55] and exist in trans conformation. However the acetato (OAc) bridged complexes exists in a typical "roof-shape" or "open-book shape" and exists in cis:trans mixture. The mesomorphism was observed for chloro, bromo, azido, and oxalato complexes but not for the iodo, thiocyanato, or acetate derivatives [18,47,56]. Further the effect of polar substituent such as H, F, Cl, NO_2, CN, OMe etc. either in para

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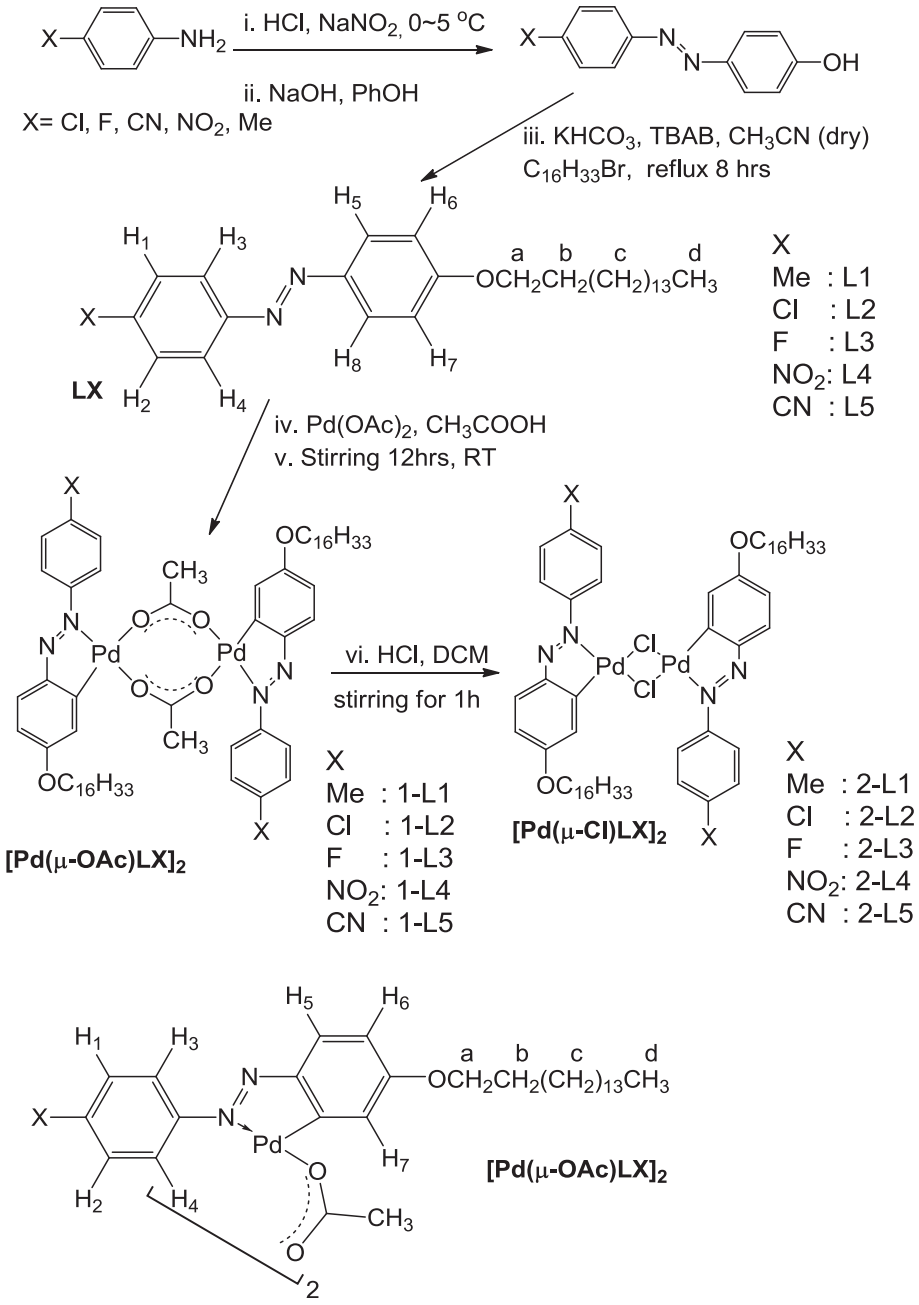
position of the aldehyde ring [57] or aniline ring [58] of chloro-and acetato-bridged complexes, derived from benzylidene imine ligand, had been studied extensively. However no such study was reported on azo cyclopalladated complexes. One of the important reasons is that the azo-based system need sufficiently long chain on both ends to fulfil the structural requirement for liquid crystalline behaviour. Most of the azo-based systems with small aliphatic chain length are non-mesogenic, whereas complexes show mesomorphic behaviour above 200 °C and decomposed on clearing point. However greater mobility of the ring having the polar substituent in *para* position together with the longer distance from the central core may allow a more important participation of the different polar groups in the molecular interactions. As a result, changes in mesogenic behaviour such as nature of mesomorphic phase, mesomorphic phase range, etc., can be expected [59], and except the few contributions from Ghedini et al. [1,40,51,55] on dinuclear cyclopalladated azo compounds with alkyl end chains at both ends of the ligand, there are no other report available in literature with a polar group in the molecule till date to our knowledge. In this article we report the synthesis and liquid crystalline properties of azo compounds with a polar group at one end and long n-hexadecyloxy chain at the other end followed by complexation with palladium acetate to infer the influence of polar end group on mesomorphism of both chloro-and acetate bridged dinuclear azo- palladium complexes.

2. Results and discussion

The chloro, fluoro, cyano, nitro and methyl substituted azo compounds were synthesized as presented in Scheme 1, following



Scheme 1. Synthesis of the dinuclear Pd(II) *ortho*-metallated compounds.

the known procedures as described in experimental section. The acetato-bridged palladium (II) complexes were prepared by the reaction of the ligand with palladium acetate by stirring at room temperature for 24 h instead of stirring at 50 °C as reported earlier. The stirring at 50 °C lead to the formation of a black paste and part of it was found in decomposed form. The acetato bridged complexes were then converted into the chloro-bridged complexes by stirring for 1 h with hydrochloric acid in dichloromethane. Synthesized compounds were characterized by elemental analysis, UV–visible spectroscopy, FTIR and NMR. Elemental analysis of ligands and complexes are consistent with the proposed structures, confirming the binuclear composition of the complexes. The materials are characterized for liquid crystalline properties by polarizing optical microscopy (POM) and phase transition temperatures are confirmed by differential scanning calorimetry (DSC).

2.1. UV-study

The optical properties of azobenzene moiety had been under scrutiny for a long time. The electronic absorption spectra of the ligand and the corresponding acetate and chloro-bridged complexes were studied in chloroform solution of same concentration ($c = 1\times10^{-4}$–10^{-5} mol L^{-1}) as shown in Fig. 1. (All the spectral data are summarized in ESI, Table S1) The free ligand shows two low energy absorption peaks (Fig. 1a) around (350 ~ 380) nm and (425 ~ 455) nm. The more intense high-energy band (ϵ_{max} = 10,000–20,000 mol L^{-1} cm^{-1}) is associated with π–π^* transition; the lower intensity band (ϵ_{max} = 700–3000 mol L^{-1} cm^{-1}) corresponds to a transition involving non-bonding orbital localized on the nitrogen atom, and leads to direct population of n–π^*excited states [55]. It was observed that λ_{max} of ligands gradually shift towards lower energy (red shift) region as the degree of polarity in the lateral substituent group increases. Polarity of the group decreases the energy of the excited state hence absorption occurs at lower wave length. Maximum red shift was observed for nitro and cyano substituted ligand due to presence of extended conjugation in these groups.

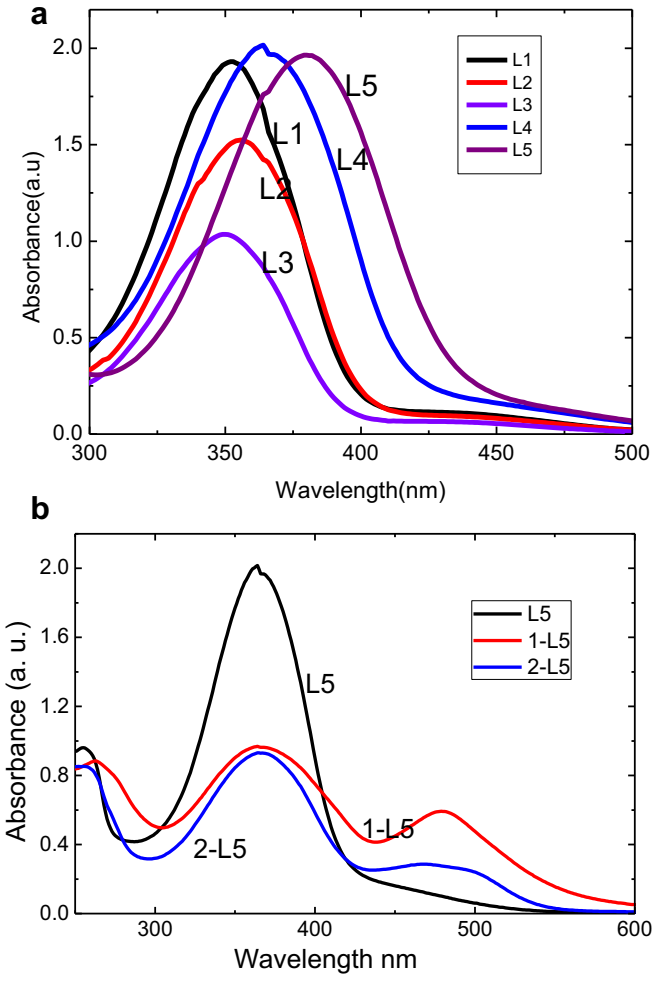


Fig. 1. UV–visible spectra of (a) ligands, (b) cyano ligand L5, acetate bridged complex 1-L5 and chloro-bridged complex, 2-L5.

The electronic absorption spectra of both the acetate and chloro-bridged orthopalladated complex also exhibit two low energy bands (Fig. 1b). The high-energy band peaks around 350–380 nm compared well with the high intense band for free ligand. On this basis, this band (ϵ_{max} = 700–3000 mol L^{-1} cm^{-1}) in the complex can be assigned to an intraligand π–π^* origin. But the band around 400–480 nm imparts colour of the complex cannot be compared n–π^* transition of the free ligand. Because this band has much higher intensity (ϵ_{max} = 4000–10,000 mol L^{-1} cm^{-1}) than the corresponding n–π^* transition of the free ligand. Thus this band finds its origin in electronic transition involving five-membered ring, i.e. the cyclopalladated ring and correspond to metal ligand charge transfer. The only difference observed in the UV-spectrum of the acetate and chloro-bridged complexes was a long tail which appeared in acetate bridged complexes due to conjugation of –COO bridging group.

2.2. FTIR-study

The FTIR-data cannot distinguish in well defined way between the ligand and the complexes. Because the –N]N- and –C=C- of phenyl ring absorption peaks appeared very close to each other and did not change much before or after complexation. One characteristic difference appeared as peak in case of acetate complex for bridging C]O bond around 1475 cm^{-1}. The additional peaks from the stretching vibration of Pd–O, Pd–C and Pd–N bonds appeared in the region 510–760 cm^{-1} in all of the complexes. The characteristic frequency for cyano group appeared around 2222 cm^{-1} for both the ligand and complexes.

2.3. NMR-study

Chemical shift (δ-value) values of the eight aromatic protons of both phenyl rings of the ligands in ^{1}H NMR spectra appeared in the range of 6–8 ppm and the signals appeared as doublet. The protons of the terminal CH_3 group of alkoxy chain appeared as triplet at ~0.88 ppm. The appearance of only one set of signals for the aromatic protons revealed that a single isomer is present in the acetate–bridge complexes [55]. The singlet at 2.15 ppm for acetate bridged palladium complex indicates that both the bridged methyl groups are chemically equivalent, which further confirm the formation of a single trans-isomer. However as previously reported for similar compounds three different triplets (δ = 3.98, 3.72, 3.47 ppm respectively) [46,55,57] which result from the diastereotropic methylene protons of alkoxy chain are observed in methyl substituted acetato-bridge complex, **1-L1** (Scheme 1). When the acetate bridge complex is converted into the chloro-bridged analogue **2-L1** (Scheme 1), through reaction with HCl, the signal at 2.15 disappeared due to the loss of bridging methyl group. In particular attention had been paid related to the proton H_7 of the orthopalladated phenyl ring. Furthermore the ^{1}H NMR signal correspond to the proton H_7 (Scheme 1) of acetate bridged complex (δ ~ 5.8) shows a strong up-field shift (~1.0 ppm) with respect to chloro-bridged complex (δ ~ 6.8). This shift could result from the

enantiotropic magnetic field created by orthopalladated ring of other ligand [46,55,57]. The ortho-metallation occurs preferentially with the alkoxy substituted phenyl ring rather than the phenyl ring with electron withdrawing Cl or CN or F or NO_2 or Me groups because of higher electron density in this ring due to electron donating ability of 4-n-hexadecyloxy group.

2.4. Mesomorphic properties

The phase behaviour of the ligand and the complexes are characterized by a combination of differential scanning calorimetry (DSC), polarizing optical microscopy (POM) attached with a hot stage and powder x-ray scattering experiment on two compounds. The phase transition temperatures and the associated thermal parameters viz., enthalpies and entropies for both ligand and complexes, were determined by differential scanning calorimetry (representative DSC of **L4** is presented Figure S1 in ESI) and are summarized in Table 1. (The value reported in this table corresponds to first heating scan). The azo-based ligands: with methyl (L1), chloro (L2) and fluoro (L3) substituents are non-mesogenic, whereas the ligands with nitro (L4) and cyano (L5) substituents are mesogenic and exhibit enantiotropic smectic A (SmA) phase which was identified by the characteristic focal conic fan textures shown in Fig. 2. All the ligands transformed into the isotropic phase below 120 °C.

The acetate bridged palladium complexes were reported as non-mesogenic [55] because of its typical "open-book" shaped geometry (Fig. 3) which restricts the orientation of the molecule

Table 1
Mesomorphic phase transition temperatures T °C, associated enthalpies (Δ*H* kJ/mol) and entropies (Δ*S* J/K/mol) of the phase transitions of all ligands (Lx), acetate 1-Lx] and chloro bridge2-Lx palladium complex. *X* = Me, Cl, F, NO_2, CN.

No	Compound	Phase Transition	Temperature °C	Δ*H* kJ/mol	Δ*S* J/mol/K
1.	L1	Cr–I	81.9	33.1	93.3
		I–Cr	69.0	48.3	141.2
2.	1-L1	Cr1–Cr2	49.7	7.3	22.6
		Cr2–I	104.0	38.7	102.6
		I–Cr	44.5	3.9	12.2
3.	2-L1	Cr → SmB	69.9	67.1	195.6
		SmB–SmA	97.6	26.3	70.9
		SmA → N	120.8	9.8	25.1
		N → I	140.2.	0.8.	1.9
		I → N	140.2[tm]		
		N → SmA	131.9[tm]		
		SmA–SmB	97.7[tm]		
		SmB– Cr	62.5[tm]		
4.	L2	Cr–I	90.6	47.1	129.5
		I–Cr	80.7	51.4	145.3
5.	1-L2	Cr–I	92.3	117.8	322.4
		I–Cr	79.2	104.6	296.9
6.	2-L2	Cr1 → Cr2	73.6	4.3	12.4
		Cr2–SmA	92.1	68.1	186.5
		SmA → I	160.0	1.5	3.5
		I → SmA	135.6	5.3	12.9
		SmA–Cr	75.8	58.5	167.7
7.	L3	Cr–I	88.7	60.9	168.3
		I–Cr	78.0	69.6	198.2
8.	1-L3	Cr → LC1	66.8	10.7	31.3
		LC1–LC2	83.4	50.6	141.9
		LC2 → I	94.3	5.5	15.0
		I → LC2	75.5[tm]	–	–
		LC2–LC1	65.5[tm]	–	–
		LC1–Cr	52.2	16.3	50.1
9.	2-L3	Cr → I	178.6	10.9	24.1
		I → SmA	144.9	8.7	21.1
		SmA–Cr	68.6	26.8	78.4
10.	L4	Cr → SmA	89.4	53.7	148.1
		SmA → I	96.5	2.3	6.3
		I → SmA	95.5	2.4	6.6
		SmA–Cr	81.1	58.5	165.2
11.	1-L4	Cr1 → Cr2	116.6	56.1	143.9
		Cr2 → I	143.6	15.0	36.0
		I–Cr	102.8	15.8	42.1
12.	2-L4	Cr → SmE	107.0	7.2	18.9
		SmE → I	182.4	16.3	35.7
		I → SmA	169.0	2.7	6.1
		SmA–SmE	53.4	6.8	20.8
13.	L5	Cr → SmA	106.0	40.1	105.8
		SmA → I	120.0[tm]	–	–
		I → SmA	110.5[tm]	–	–
		SmA–Cr	75.4	47.8	137.2
14.	1-L5	Cr → I	108.9	169.9	445.0
		I → SmA	105.7	13.3	35.1
		SmA–Cr	81.2	142.5	402.3
15.	2-L5	Cr → SmA	97.3[tm]	–	–
		SmA → I	180.7[tm]	–	–
		I → SmA	174.2[tm]	–	–
		SmA–Cr	85.6[tm]	–	–

[tm]microscopic observed temperature.

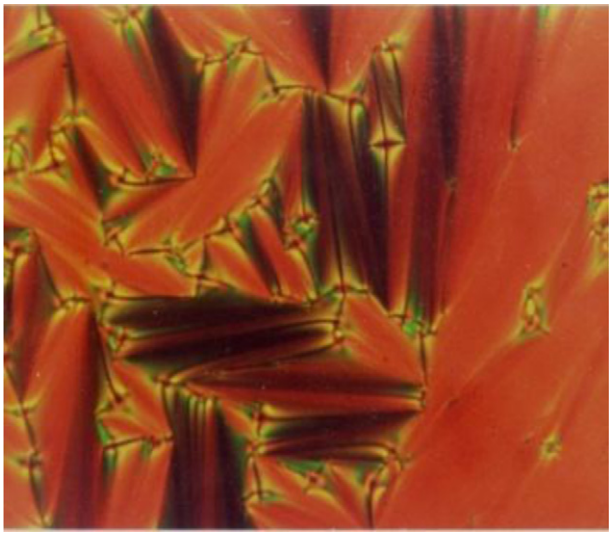


Fig. 2. Focal conic fan textures of SmA phase observed in nitro compound (L4) at 94.3 °C.

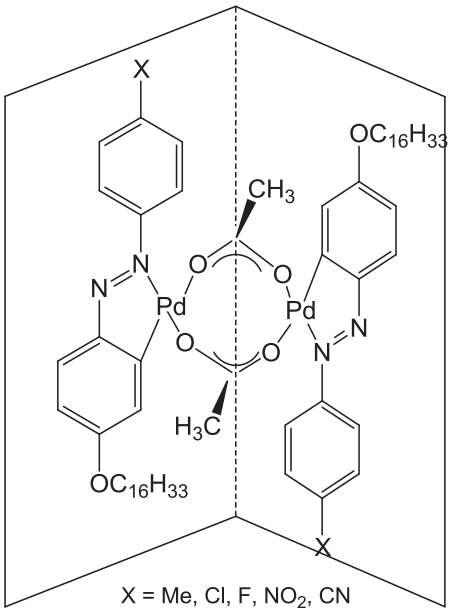


Fig. 3. Open book like structure of acetate bridged orthopalladated complexes.

within the layer structure needed for liquid crystalline behaviour. However the newly synthesized acetate bridged complexes **1-L3** and **1-L5** (fluoro and cyano substituents respectively) exhibit mesomorphism. POM studies revealed that the complex **1-L3** exhibits an unusual phase sequence of highly ordered monotropic phase variant LC1–LC2 in cooling cycle as shown in Fig. S2 (ESI). These two transitions were also observed in heating cycle of DSC at 66.8 °C and 83.4 °C with an enthalpy change of 10.7 kJ/mol and 50.6 kJ/mol respectively and finally become isotropic at 94.3 °C with small enthalpy change of 5.5 kJ/mol. The fluidity of these two phases was established by tapping on glass plate. Even though such anomalous behaviour was reported earlier in Cl bridged cyclopalladated symmetrically substituted azo compound which is related to intermolecular forces coupled with structural modifications of the mesogenic species, but no such phenomena was reported for acetate bridged complexes. Further **1-L5** exhibit monotropic Smectic A phase (Figure S3a in ESI) at 105.9 °C on cooling, which appeared as a sharp peak in DSC at 105.7 °C with an enthalpy change of 13.3 kJ/mol (Figure S3b in ESI).

The complex **2-L1**, with methyl substituent exhibited enantiotropic SmB, SmA and nematic phases (Figure S4). In DSC thermograph phase transitions were observed at 69.9 °C, 97.6 °C, 120.8 °C and 140.2 °C corresponding to crystal to SmB, SmB–SmA, SmA-nematic and nematic-isotropic phase transitions respectively in the heating cycle only. We could not observe the phase transformations in the cooling cycle in DSC. However, all the phase transitions were observed enantiotropically by POM.

The chloro (**2-L2**) and fluoro (**2-L3**) substituted chloro-bridged orthopalladated complexes exhibit SmA phase (Figure S5 in ESI) similar to those exhibited by **2-L1**. Chloro substituted dinuclear complex **2-L2**, exhibit batonnets with large homeotropic areas resembling SmA phase appeared on cooling from isotropic melt, which grows as focal conic fan like texture on lowering the temperature (Figure S5 in ESI). This transition was detected in DSC as a small peak at 135.6 °C with an enthalpy change of 5.3 kJ/mol. On further cooling, crystallization of the sample occurred which appeared as a sharp peak in DSC at 75.8 °C with a large enthalpy change of 58.5 kJ/mol. Fluoro substituted complex **2-L3**, exhibited monotropic SmA phase (Figure S5 in ESI) in cooling and the transition was detected in DSC at 144.9 °C with an enthalpy change of 8.7 kJ/mol. On further cooling SmA phase transformed to crystalline phase with a large enthalpy change of 26.8 kJ/mol at 68.6 °C. Partial decomposition was observed for chloro-bridged complexes of nitro and cyano (**2-L4 and 2-L5**) compounds on heating to isotropic liquid, which may be due to highly polar nature of NO_2 and CN groups. Compound **2-L4** exhibits SmA and SmE phases. All the chloro-bridged dinuclear cyclopalladated complexes exhibit mesomorphism while the acetate bridged complexes did not show mesomorphism except the cyano (SmA) and fluoro substituted complexes.

2.5. X-ray studies

The reported X-ray structure determination of the single crystal of di-μ-chloro-bis[(4-hydroxy-4′–methylazobenzenato-C^2, N^2) palladium (II) [54,60] revealed overall "roof-shaped" or 2D H-shaped molecular structure, in which the "(C, N)Pd" chelate rings are essentially coplanar and the two azo ligands are joined through central bridging Cl atoms with Pd_2Cl_2 unit. Interestingly the mesophase behaviour, molecular ordering transition temperatures and thermal range of mesophases are found to depend on the bridging moiety [50,55].

Temperature dependent X-ray diffraction experiments were systematically performed in the mesophases of the 4-cyano substituted acetato-bridged complex di-μ-acetato-bis[(4-cyano-4′-*n*-hexadecyloxyazobenzenato-C^2, N^2)palladium (II), **1-L5**

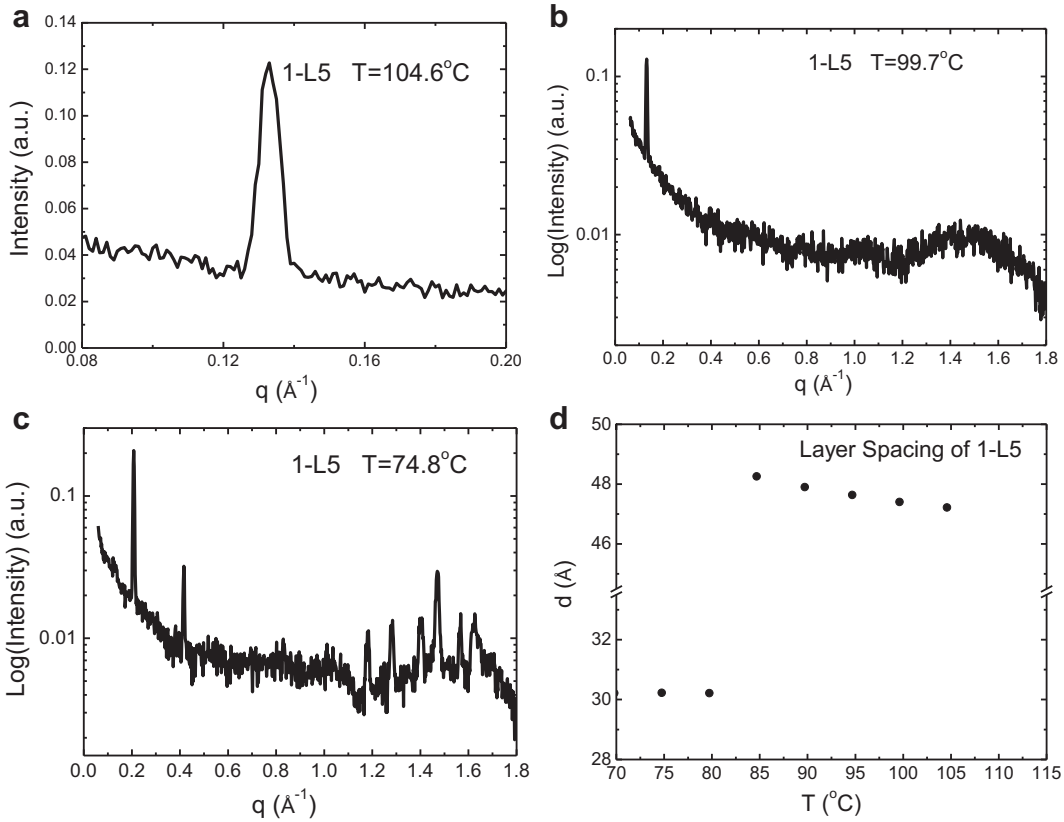


Fig. 4. X-ray diffractograms of a) 1-L5 at109.5 °C, b) 1-L5 at 99.7 °C , c) 1-L5 at 74 °C and d) Temperature variation of layer thickness of 1-L5.

(Fig. 4) in order to unequivocally identify the nature of the mesophase and to obtain additional information about the molecular packing.

The XRD patterns of **1**-**L5** measured between 81 and 105 °C exhibit a broad scattering in the wide angle part of the diffractogram (at ca. 4.2–4.4 Å) Fig. 4a, which corresponds to the molten chains in the liquid-like order. In the small angle region only one fine sharp signal at ~48.0 Å (Fig. 4a–c) was observed corresponding to layer thickness. Thus, the mesophase was assigned on the basis of its texture obtained by polarized-light optical microscopy and XRD patterns, as smectic A phase (Figure S3a ESI).

The layer spacing (48.0 Å) is significantly smaller than the calculated molecular length for a fully extended conformation of the molecule (minimized energy) as shown in Fig. 5a (53.8 Å). To explain the difference (~5.8 Å) between the theoretical molecular length of **1**-**L5** and the layer thickness, a space filling model of an antiparallel arrangement of strongly polar molecules with interdigitation of aliphatic chains as depicted in Fig. 5b–c with strong molecular axial fluctuations is proposed.

The variation in the layer spacing (1.0 Å) with temperature (Fig. 4d) does not show any significant change in SmA phase but as the phase transition took place a sudden drop in the layer thickness from 48.2 Å in SmA phase to 30.2 Å upon cooling into the solid phase was observed in complex **1**-**L5**. Such a large jump in layer thickness indicates formation of highly ordered crystal phase. The X-ray data obtained on cooling shows a pattern (Fig. 4c) confirm the formation of a crystalline species. Hence the reduction in observed layer thickness in principle suggests to a quasi-crystalline state, wherein, at temperatures comparatively lower, strong and localized (because of the low temperature) intermolecular interactions, exerted by the polar CN end groups, which can afford to a very tight crystal packing, cannot be discarded.

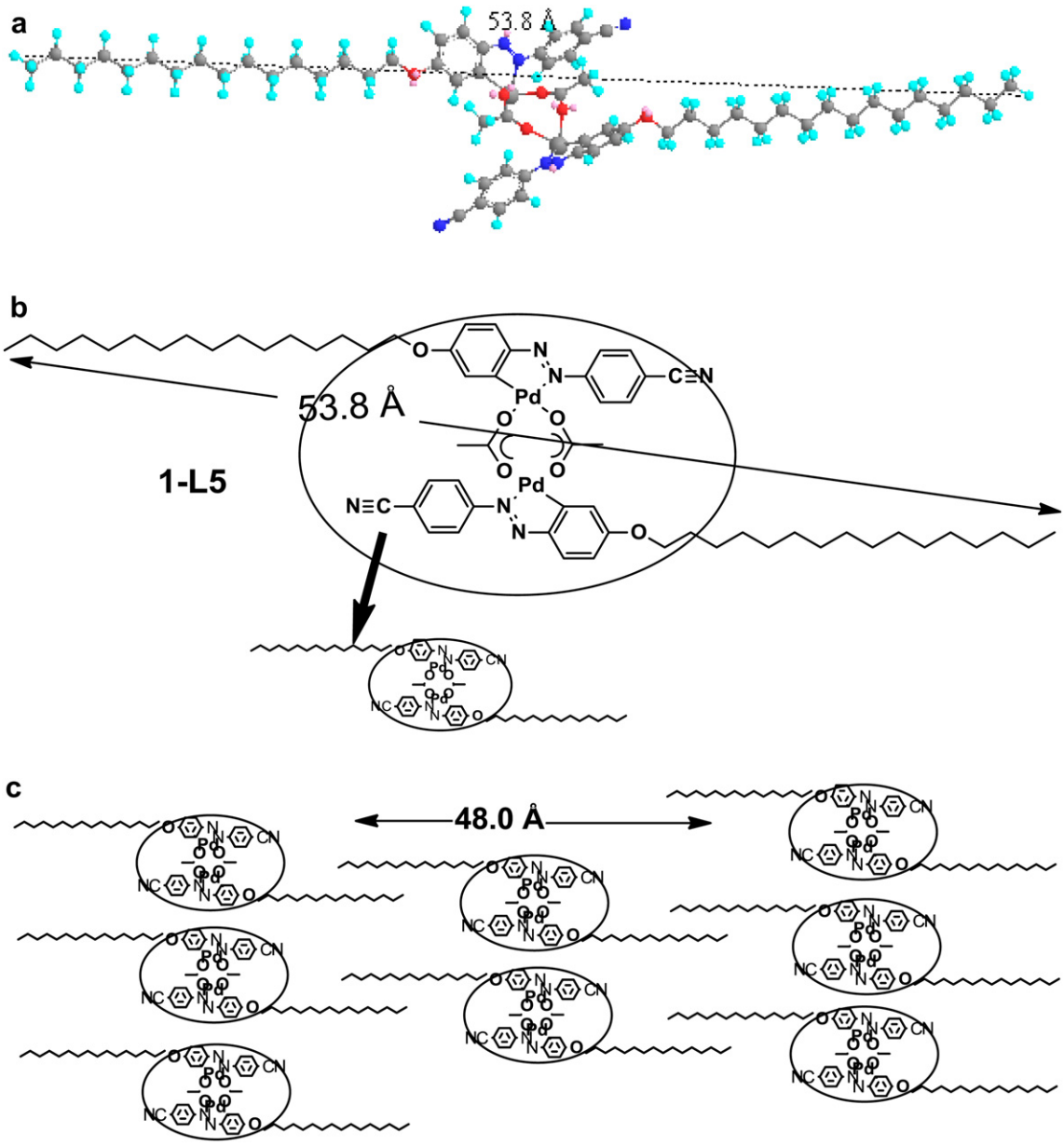


Fig. 5. a) Minimized molecular structure 1-L5, di-μ-acetato-bis[(4-cyano-4′-n-hexadecyloxybenzenato-C^2,N^2)palladium (II), (b) Model molecule and (c) proposed model of interdigitated structure in SmA phase.

3. Conclusion

A comparative study of the properties of azo-based ligand and their acetato-bridged and chloro-bridged cyclopalladated complex revealed a separate phase sequence of polar groups for the melting point of each series. For azo-based ligand the order of melting point is $-NO_2 > -CN > -F > -Cl > -CH_3$, for acetate bridge complex $-NO_2 > -CN > -CH_3 > -Cl > -F$ and for chloro bridge complex $-F > -NO_2 > -Cl > -CH_3 > -CN$. This indicates that the influence of the polar groups on the stabilization of the solid state depends on the central core of the molecule. It was noteworthy that strong electron withdrawing groups give rise to higher melting point and also liquid crystalline property. This was reflected in the ligands where only $-NO_2$ and $-CN$ substituted ligand show the mesogenic behaviour because of high electron withdrawing nature. The open book-shaped acetate bridged complexes are generally considered as non-liquid crystalline but in present case $-CN$ and $-F$ substituted acetate bridged complexes exhibit mesomorphism. Further all the planar chloro-bridged complexes show mesogenic behaviour. From the experimental results in the orthopalladated azo complexes presented here, the nature of the central core is mainly responsible for the liquid crystalline properties. The polar nature of the substituent in the aniline ring has strong influence on the mesomorphism exhibited by free ligand. The melting point of the ligand increases with the polarity of the substituent and the mesomorphism was observed in compounds with a strong electron withdrawing group ($-NO_2$, $-CN$). However no such correlation was observed in case of both the acetate and chloro-bridged complexes. Most of chloro-bridged complexes exhibited SmA phase with a characteristic focal conic fan texture with large homeotropic areas in cooling. Nematic phase was observed only in ligands with a methyl substituent and a high order phase observed in chloro substituent compounds. Mesophase textures in these highly viscous orthopalladated complexes are paramorphotic and are retained till the room temperature in solid phase.

4. Experimental

All of the chemicals were procured and used as received from M/S Tokyo Kasei Kogyo Co. Ltd., or Avocado Chemicals or E-Merck. Silica gel (60–120 mesh, Acme synthetic chemicals) was used for chromatographic separation. Silica gel G [E-Merck] was used for thin layer chromatography (TLC). The solvents and reagents are of AR grade and were distilled and dried before use following standard procedures. TLC was performed on glass slides pre-coated with silica gel. The intermediate compounds were purified by column chromatography using silica gel. UV visible absorption spectra of the compounds in $CHCl_3$ at different concentrations were recorded on a Shimadzu UV-1601PC spectrophotometer (λ_{max}in nm). All of the compounds were characterized by elemental analysis, infrared (IR) spectra (Perkin–Elmer L120-000A spectrometer), and by ^{1}H nuclear magnetic resonance (NMR) spectroscopy (JEOL AL 300 FT NMR) in $CDCl_3$ solution, chemical shifts are reported in parts per million (δ) relative to tetramethylsilane (TMS) as an internal standard. The liquid-crystal cells were placed in a computer controlled heating stage (hot and cold stage HCS302, with STC200 temperature controller configured for HCS302 from INSTEC) and the optical textures inferring the phase sequences were investigated by polarizing microscopy (Nikon polarizing microscope OPTIPHOT-POL2). The phase transition temperatures and associated enthalpies of transition were determined by differential scanning calorimetry (DSC; Perkin–Elmer DSC Pyris1 system that was calibrated previously using pure indium as a standard). The heating and cooling rates were 5 or 10 °C per minute. The X-ray diffraction analyses were carried out using unoriented sample contained in 1 mm diameter borosilicate glass capillary tubes and data were collected using a point detector mounted on a Huber four-circle goniometer at Cu–K(α) radiation from a Rigaku UltraX-18 rotating anode generator.

4.1. Synthesis of 4-chloro-4′-n-hexadecyloxyazobenzene (*L2*)

Preparation of 4-hydroxy-4′-chloroazobenzene: The ligand L2 was synthesized by the diazocoupling reaction of 4-chloro-aniline with phenol followed by the alkylation of the hydroxyl group. To 4-chloro-aniline (1.27 g, 10 mmol) were added 10 ml of distilled water containing hydrochloric acid (12 M, 2.5 ml, 30 mmol) and the mixture was heated to dissolve the contents. The solution was then cooled to 0 °C. To the resulting stirred mixture cooled at 0 °C was added, dropwise, a solution of sodium nitrite (0.69 mg, 10 mmol) in 10 mL of water. The resulting diazonium chloride was consecutively coupled with an alkaline solution of phenol (0.94 g, 10 mmol) in 10 ml of water containing 0.80 g (20 mmol) of sodium hydroxide with constant starring. The azo-dye which formed immediately as yellow precipitate was filtered, washed several times with water and dissolved in methanol or diethyl ether and the resulting organic solution dried over anhydrous sodium sulphate. The crude product obtained after removal of the solvent under reduced pressure was purified by recrystallization from cold hexane, precipitate was filtered and washed with water and methanol and dried in vacuum. Yield 1.74 g (75%).

To a suspension of 4-hydroxy-4′-chloroazobenzene (1.16 g, 5 mmol) in 100 ml of dry acetonitrile were added dried potassium carbonate (0.69 g, 5 mmol) and a catalytic amount of tetrabutylammoniumbromide (TBAB). The mixture was stirred for 1 h followed by the addition of 1-bromohexadecane (1.5 ml, 5 mmol) dropwise with constant stirring. The resulting mixture was stirred under reflux for 16 h, and progress of the reaction was monitored by TLC. After completion of the reaction, the solid residues were filtered off, excess of acetonitrile was distilled off and the solution cooled. To this solution ice cold water was added and the mixture was acidified with HCl up to pH = 2. The precipitate appeared was filtered and solid was washed with sodium bicarbonate solution, dried and finally purified by chromatography on a silica gel column eluted with a mixture of hexane-chloroform (70:30, v/v). Yield = 78%. Analytical data: ^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.88 (d, 2H, 8.7 Hz, $H_{1,2}$), 7.47(d, 2H, 8.7 Hz, $H_{3,4}$), 7.05 (d, 2H, 8.7 Hz, $H_{5,8}$), 6.98 (d, 2H, 8.7 Hz, $H_{6,7}$), 4.04 (t, 2H, 6.6), 1.82(q, 2H, 7.5), 1.25 (m, 26H), 0.88 (t, 3H, 6.3). Experimental (Calculated) data for $C_{28}H_{41}ClN_2O$: C, 73.7 (73.5%); H, 8.98 (9.04%); N, 6.12 (6.13%). IR (ν cm^{-1}), 2916, 1604, 1583, 1498, 1259.

All analogous compounds were prepared as described for 4-chloro-4′-n-hexadecyloxyazobenzene. Yields and analytical data are as follows:

4.1.1. 4-Methyl-4′-n-hexadecyloxyazobenzene (*L1*)

Yield 67%. Analytical data: ^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.86 (d, 2H, 9.0 Hz), 7.79 (d, 2H, 8.1 Hz), 7.30 (d, 2H, 8.4 Hz), 7.00 (d, 2H, 9.0 Hz), 4.03 (t, 2H, 6.3), 2.42 (m, 3H), 1.79 (d, 2H), 1.26 (m, 26H), 0.88 (t, 3H, 6.9). Experimental (Calculated) data for $C_{29}H_{44}N_2O$: C, 80.0 (79.7); H, 10.1 (10.1); N, 6.4 (6.4). IR (ν cm^{-1}), 2916, 1602, 1583, 1253.

4.1.2. 4-Fluoro-4′-n-hexadecyloxyazobenzene (*L3*)

Yield 62%. Analytical data: ^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.86 (d, 2H, 8.7 Hz, $H_{1,2}$), 7.47 (d, 2H, 8.4 Hz, $H_{3,4}$), 7.05 (d, 2H, 8.7 Hz, $H_{5,8}$), 6.98 (d, 2H, 8.7 Hz, $H_{6,7}$), 4.03 (t, 2H, 6.6), 1.82(q, 2H, 7.5), 1.26 (m, 26H), 0.88 (t, 3H, 6.3). Experimental (Calculated) data for $C_{28}H_{41}FN_2O$, C, 76.4 (76.3); H, 9.42 (9.38); N, 6.88 (6.36). IR (ν cm^{-1}), 2916, 1602, 1583, 1251.

*4.1.3. 4-Nitro-4′-n-hexadecyloxyazobenzene (**L4**)*

Yield 48%. Analytical data: ^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.34 (d, 2H, 8.7 Hz, $H_{1,2}$), 7.96(m, 4H, $H_{3,4,5,8}$), 7.00 (d, 2H, 9.0 Hz, $H_{6,7}$), 4.06 (t, 2H, 6.3), 1.83(q, 2H, 7.5), 1.26 (m, 26H), 0.88 (t, 3H, 6.3). Experimental (Calculated) data for $C_{28}H_{41}N_3O_3$: C, 72.2 (71.9); H, 9.01 (8.84); N, 9.18 (8.99). IR (ν cm^{-1}), 2916, 1602, 1581, 1519, 1342, 1249.

*4.1.4. 4-Cyano-4′-n-hexadecyloxyazobenzene (**L5**)*

Experimental (Calculated) data for $C_{29}H_{41}N_3O$: C, 77.9 (77.8); H, 9.21 (9.23); N, 9.41 (9.39). IR (ν cm^{-1}), 2920, 2220, 1598, 1581, 1500, 1269.

*4.2. Synthesis of acetate bridged complexes **1**-**L2***

To a suspension of 0.76 g (3 mmol) of palladium acetate in15 ml of acetic acid, 1.37 g, (3 mmol) of L2 was added and the mixture was stirred for 12 h at 50 °C and then allowed to cool the dark brown precipitate of acetate bridged complex was filtered off,washed with cold acetone and air dried. No trace of metallic palladium was observed. Yield = 70%. Analytical data: ^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.43 (d, 2H, 9.0 Hz, H_5), 7.80 (d, 4H, $H_{3,4}$), 7.87 (d, 4H, 6.9 Hz, $H_{1,2}$), 6.97 (d, 2H, 9.0 Hz, H_6), 5.88 (d, 2H, 6.0 Hz, H_7), 4.03 (t, 4H, 6.3), 2.09 (s, 6H), 1.80 (m, 4H), 1.26 (m, 52H), 0.88 (t, 6H, 6.9). Experimental (Calculated) data for $C_{60}H_{86}Cl_2N_4O_6Pd_2$: C, 58.3 (57.9%); H, 7.05 (6.97%); N, 4.35 (4.51%). IR (ν cm^{-1}), 2918, 1585, 1570, 1500, 1471, 1238.

All analogous acetate bridged complexes were prepared as described for palladium complex of 4-chloro-4′-n-hexadecyloxyazobenzene **1**-**L2**. Yields and analytical data are as follows:

*4.2.1. **1**-**L1***

Yield = 62%. Analytical data:, ^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.56 (d, 2H, 7.8 Hz, H_5), 7.34 (d, 4H, 7.2 Hz, $H_{3,4}$), 6.67 (d, 4H, 6.9 Hz, $H_{1,2}$), 6.59 (d, 2H, 6.9 Hz, H_6), 5.88 (d, 2H, 6.0 Hz, H_7), 4.03 (t, 4H, 6.3), 2.05–2.37 (m, 12H), 1.80 (m, 4H), 1.26 (m, 52H), 0.88 (t, 6H, 6.9). Experimental (Calculated) data for $C_{62}H_{92}N_4O_6Pd_2$: C, 62.0 (61.9); H, 7.99 (7.71); N, 4.80 (4.66). IR (ν cm^{-1}), 2918, 1636, 1602, 1500, 1259.

*4.2.2. **1**-**L3***

Yield = 58%. Analytical data ^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.89 (d, 4H, 6.9 Hz, $H_{1,2}$), 7.88 (d, 4H, $H_{3,4}$), 7.86 (d, 2H, 9.0 Hz, H_5), 6.97 (d, 2H, 9.0 Hz, H_6), 5.88 (d, 2H, 6.0 Hz, H_7), 4.03 (t, 4H, 6.3), 2.09 (s, 6H), 1.79 (m, 4H), 1.26 (m, 52H), 0.88 (t, 6H, 6.6). Experimental (Calculated) data for $C_{60}H_{86}F_2N_4O_6Pd_2$, C, 59.3 (59.5); H, 7.07 (7.16); N, 4.60 (4.63). IR (ν cm^{-1}), 2918, 1602, 1585, 1474, 1256.

*4.2.3. **1**-**L4***

Yield = 44%. Analytical data: ^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.03 (d, 4H, 9.0 Hz, $H_{1,2}$), 7.70 (d, 2H, 8.7 Hz, H_5), 7.47 (d, 4H, 9.0 Hz, $H_{3,4}$), 6.63 (d, 2H, 6.6 Hz, H_6), 5.83 (d, 2H, 2.4 Hz, H_7), 4.03 (t, 4H, 6.3), 2.15 (s, 6H), 1.79 (m, 4H), 1.26 (m, 52H), 0.88 (t, 6H, 6.6). Experimental (Calculated) data for $C_{60}H_{86}N_6O_{10}Pd_2$: C, 57.3 (57.0); H, 6.95 (6.86); N, 6.50 (6.65). IR (ν cm^{-1}), 2920, 1637, 1581, 1406, 1319, 1263.

*4.2.4. **1**-**L5***

Yield = 64%. analytical data: ^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.89 (d, 4H, 6.9 Hz, $H_{1,2}$), 7.88 (d, 4H, $H_{3,4}$), 7.86 (d, 2H, 9.0 Hz, H_5), 6.97 (d, 2H, 9.0 Hz, H_6), 5.88 (d, 2H, 6.0 Hz, H_7)), 4.03 (t, 4H, 6.3), 2.05–2.37 (m, 12H), 1.80 (m, 4H), 1.26 (m, 52H), 0.88 (t, 6H, 6.9). Experimental (calculated) data for $C_{62}H_{92}N_4O_6Pd_2$: C, 60.9 (60.8); H, 7.03 (7.08); N, 6.80 (6.86). IR (ν cm^{-1}), 2914, 2222, 1608, 1587, 1502, 1474, 1249

*4.3. Synthesis of chloro-bridged complexes **2**-**L2***

A solution of hydrochloric acid in methanol (Pd: HCl, 1:1) was cautiously added to a stirred solution of 0.5 g (0.3 mmol) of acetate bridge complex in 30 ml of dichloromethane. As the reaction proceeded, the initially dark red colour solution turns to orange. After 1 h the solution was evaporated to dryness, and the residue was recrystallized from methanol and dichloromethane mixture to give orange colour product. Yield = 48%. Analytical data: ^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.91 (d, 4H, 9.0 Hz, $H_{1,2}$),7.83 (d, 4H, 8.7 Hz, $H_{3,4}$), 7.47 (d, 2H, 9.0 Hz, H_5), 6.98 (d, 2H, 8.7 Hz, H_6), 6.87 (d, 2H, 8.7 Hz, H_7), 4.04 (t, 4H, 6.3), 1.82 (m, 4H), 1.26 (m, 52H), 0.88 (t, 6H, 6.6). Experimental (calculated) data for $C_{56}H_{80}Cl_4N_4O_2Pd_2$; C, 56.3 (56.2%); H, 6.67 (6.74%); N, 4.55 (4.68%). IR (ν cm^{-1}), 2918, 1598, 1583, 1502, 1469, 1257.

All analogous chloro-bridged complexes were prepared as described for palladium complex of 4-chloro-4′-n-hexadecyloxyazobenzene **2**-**L2**. Yields and analytical data are as follows:

*4.3.1. **2**-**L1***

Yield = 44%, Analytical data: ^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.81 (d, 4H, 7.8 Hz, $H_{3,4}$), 7.74 (d, 2H, 7.8 Hz, H_5), 7.00 (d, 4H, 6.9 Hz, $H_{1,2}$), 6.72 (d, 2H, 8.7 Hz, H_6), 6.85 (d, 2H, 6.0 Hz, H_7), 4.05 (t, 4H, 6.3), 2.43 (m, 6H), 1.81 (m, 4H), 1.26 (m, 52H), 0.88 (t, 6H, 6.9). Experimental (Calculated) data for $C_{58}H_{86}Cl_2N_4O_2Pd_2$: C, 60.2 (60.3); H, 7.61 (7.50); N, 4.99 (4.85). IR (ν cm^{-1}), 2916, 1602, 1581, 1500, 1471, 1253.

*4.3.2. **2**-**L3***

Yield = 38%, Analytical data: ^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.79 (d, 4H, 9.0 Hz, $H_{1,2}$), 7.76 (d, 4H, 8.1 Hz, $H_{3,4}$), 6.91 (d, 2H, 8.4 Hz, H_5), 6.81 (d, 2H, 8.7 Hz, H_7), 6.73 (d, 2H, 8.7 Hz, H_6), 4.04 (t, 4H, 6.3), 1.80 (m, 4H), 1.26 (m, 52H), 0.88 (t, 6H, 6.6). Experimental (Calculated) data for $C_{56}H_{80}Cl_2F_2N_4O_2Pd_2$, C, 57.8 (57.8); H, 7.00 (6.93); N, 4.90 (4.82). IR (ν cm^{-1}), 2916, 1577, 1259.

*4.3.3. **2**-**L4***

Yield = 32%, Analytical data: ^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.30 (d, 4H, 7.2 Hz, $H_{1,2}$), 7.91 (d, 2H, 7.5 Hz, H_5), 7.84 (d, 4H, 8.4 Hz, $H_{3,4}$), 6.77 (m, 4H, $H_{6,7}$), 4.07 (t, 4H, 6.3), 1.81 (m, 4H), 1.26 (m, 52H), 0.88 (t, 6H, 6.6). Experimental (Calculated) data for $C_{56}H_{80}Cl_2N_6O_6Pd_2$: C, 55.1 (55.2); H, 6.60 (6.63); N, 7.10 (6.91). IR (ν cm^{-1}), 2916, 1581, 1529, 1402, 1315, 1273.

*4.3.4. **2**-**L5***

Yield = 32%, Analytical data: ^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.30 (d, 4H, 7.2 Hz, $H_{1,2}$), 7.91 (d, 2H, 7.5 Hz, H_5), 7.84 (d, 4H, 8.4 Hz, $H_{3,4}$), 6.77 (m, 4H, $H_{6,7}$), 4.04 (t, 4H, 6.3), 1.80 (m, 4H), 1.26 (m, 52H), 0.88 (t, 6H, 6.6). Experimental (Calculated) data for $C_{58}H_{86}Cl_2N_4O_2Pd_2$: C, 58.9 (59.1); H, 6.83 (6.85); 7.11 (7.14). IR (ν cm^{-1}), 2916, 2220, 1598, 1581, 1500, 1465, 1249.

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Appendix A. Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2012.04.001.

References

[1] M. Ghedini, I. Aiello, A. Crispini, A. Golemme, M. Deda, D. Pucci, Coord. Chem. Rev. 250 (2006) 1373–1390.

[2] J.M. Vila, M.Y. Pereira, in: J. Dupont, M. Pfeffer (Eds.), Palladacycles: Synthesis, Characterization and Applications, Wiley-VCH Verlag GmbH & Co, KGaA, Weinheim, 2008, pp. 87–108.
[3] J. Dupont, C.S. Consorti, J. Spencer, Chem. Rev 105 (2005) 2527–2571.
[4] A. Kilic, D. Kilinc, E. Tas, I. Yilmaz, M. Durgun, I. Ozdemir, S. Yaser, J. Organomett. Chem. 695 (2010) 697–706.
[5] B. Donnio, D.W. Bruce, in: J. Dupont, M. Pfeffer (Eds.), Palladacycles: Synthesis, Characterization and Applications, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2008, pp. 239–283.
[6] V. Circu, C.M. Simonescu, Cryst. Res. Technol. 45 (2010) 512–516.
[7] V. Circu, F. Dumitrascu, Cryst. 534 (2011) 41–49.
[8] S. Coco, C. Cordovilla, P. Espinet, J.L. Gallani, D. Guillon, B. Donnio, Eur. J. Inorg. Chem (2008) 1210–1218.
[9] A.S. Mocanu, M. Ilis, F. Dumitrascu, M. Ilie, V. Circu, Inorg. Chim. Acta 363 (2010) 729–736.
[10] J.L. Serrano, Metallomesogens, Synthesis, Properties and Applications, VCH Publishers, Weinheim, Germany, 1996.
[11] D.W. Bruce, in: D.W. Bruce, D. O'Hare (Eds.), Inorganic Materials, second ed. Wiley, Chichester, 1996, pp. 429–520.
[12] D.W. Bruce, J. Chem. Soc. Dalton Trans. (1993) 2983–2989.
[13] J.P. Rourke, D.W. Bruce, T.B. Marder, J. Chem. Soc. DaltonTrans (1995) 317–318.
[14] H. Zheng, B. Xu, T.M. Swager, Chem. Mater. 9 (1996) 907–911.
[15] M.J. Baena, P. Espinet, M.B. Ros, J.L. Serrano, J. Mater. Chem. 6 (1996) 1291–1296.
[16] F. Neve, M. Ghedini, A. Crispini, Chem. Commun. (1996) 2463–2464.
[17] M. Ghedini, D. Pucci, F. Neve, Chem. Commun. (1996) 137–138.
[18] J.S. Seo, Y.S. Yoo, M.G. Choi, J. Mater. Chem. 11 (2001) 1332–1338.
[19] R. Deschenaux, M. Schweissguth, M.T. Vilches, A.M. Levelut, D. Hautot, G.J. Long, D. Luneau, Organometallics 18 (1999) 5553–5559.
[20] R. Deschenaux, F. Monnet, E. Serrano, F. Turpin, A.M. Levelut, Helv. Chim. Acta 81 (1998) 2072–2077.
[21] T. Kaharu, R. Ishii, T. Aadachi, T. Yoshida, S. Takahashi, J. Mater. Chem. 5 (1995) 687–692.
[22] T. Kaharu, T. Tanaka, M. Sawada, S. Takahashi, J. Mater. Chem. 4 (1994) 859–865.
[23] H. Adams, N.A. Bailey, D.W. Bruce, S.C. Davis, D.A. Dunmur, P.D. Hempstead, S.A. Hudson, S. Thorpe, J. Mater. Chem. 2 (1992) 395–400.
[24] M. Marcos, M.B. Ros, J.L. Serrano, M.A. Esteruelas, E. Sola, L.A. Oro, J. Barbera, Chem. Mater. 2 (1990) 748–758.
[25] T. Hegmann, J. Kain, S. Diele, G. Pelzl, C. Tschierske, Angew. Chem. Int. Ed. 40 (2001) 887–890.
[26] M. Ghedini, S. Morrone, O. Francescangeli, R. Bartolino, Chem. Mater. 6 (1994) 1971–1977.
[27] K. Ohta, H. Akimoto, T. Fujimoto, I. Yamamoto, J. Mater. Chem. 4 (1994) 61–69.
[28] W. Pyzuk, E. Gorecka, A. Krowczynski, J. Przedmojski, Liq. Cryst. 14 (1993) 773–784.
[29] M.N. Abser, M. Bellwood, M.C. Holmes, R.W. McCabe, J. Chem. Soc. Chem. Commun. (1993) 1062–1063.
[30] K. Ohta, O. Takenaka, H. Hasebe, Y. Morizumi, T. Fujimoto, I. Yamamoto, Cryst. 195 (1991) 135–148.
[31] A.B. Blake, J.R. Chipperfield, S. Clark, P.G. Nelson, J. Chem. Soc. Dalton Trans. (1991) 1159–1160.
[32] I. Wu, P. Chaing, W. Chang, H. Sheu, G. Lee, C.K. Lai, Tetrahedron 67 (2011) 7358–7369.
[33] D.P. Lydon, J.P. Rourke, Chem. Commun. (1997) 1741–1742.
[34] B. Heinrich, K. Praefcke, D. Guillon, J. Mater. Chem. 7 (1997) 1363–1372.
[35] M.J. Baena, J. Barbera, P. Espinet, A. Ezcurra, M.B. Ros, J.L. Serrano, J. Am. Chem. Soc. 116 (1994) 1899–1906.
[36] J. Barbera, P. Espinet, E. Lalinde, M. Marcos, J.L. Serrano, Liq. Cryst. 2 (1987) 833–842.
[37] P. Espinet, E. Lalinde, M. Marcos, J. Perez, J.L. Serrano, Organometallics 9 (1990) 555–560.
[38] N. Hoshino, H. Hasegawa, Y. Matsunaga, Liq. Cryst. 9 (1991) 267–276.
[39] M. Ghedini, S. Armentano, F. Neve, S. Licoccia, J. Chem. Soc. Dalton Trans. (1988) 1565–1567.
[40] M. Ghedini, M. Longeri, R. Bartolino, Mol. Cryst. Liq. Cryst. 84 (1982) 207–211.
[41] L. Zhang, D. Huang, N. Xiong, J. Yang, G. Li, N. Shu, Cryst 237 (1993) 285–297.
[42] M. Marcos, J.L. Serrano, T. Sierra, M.J. Gimenez, Chem. Mater. 5 (1993) 1332–1337.
[43] K. Praefcke, S. Diele, J. Pickardt, B. Gundogan, U. Nutz, D. Singer, Liq. Cryst 18 (1995) 857–865.
[44] N.J. Thompson, R. Iglesias, J.L. Serrano, M.J. Baena, P. Espinet, J. Mater. Chem. 6 (1996) 1741–1744.
[45] D.P. Lydon, G.W.V. Cave, J.P. Rourke, J. Mater. Chem. 7 (1997) 403–406.
[46] M.A. Ciriano, P. Espinet, E. Lalinde, M.B. Ros, J.L. Serrano, J. Mol. Struct. 196 (1989) 327–341.
[47] J. Buey, L. Diez, P. Espinet, H.S. Kitzerow, J.A. Miguel, Chem. Mater. 8 (1996) 2375–2381.
[48] M. Ghedini, S. Licoccia, S. Armentano, R. Bartolino, Cryst 108 (1984) 269–275.
[49] A.M.M. Lanfredi, F. Ugozzoli, M. Ghedini, S. Licoccia, Inorg. Chim. Acta 86 (1984) 165–168.
[50] M. Ghedini, S. Licoccia, S. Armentano, F. Neve, Inorg. Chim. Acta 134 (1987) 23–24.
[51] M. Ghedini, A. Crispini, Comments Inorg. Chem. 21 (1999) 53–68.
[52] M. Marcos, M.B. Ros, J.L. Serrano, Cryst. 3 (1988) 1129–1136.
[53] M. Ghedini, S. Armentano, G. Munno, A. Crispini, F. Neve, Liq. Cryst 8 (1990) 739–744.
[54] M.B. Ros, N. Ruiz, J.L. Serrano, P. Espinet, Liq. Cryst. 9 (1991) 77–86.
[55] M. Ghedini, D. Pucci, A. Crispini, I. Aiello, F. Barigelletti, A. Gessi, O. Francescangeli, Appl. Organometal. Chem. 13 (1999) 565–581.
[56] and references there inH. Durr, H. Bouas-Larent (Eds.), Photochromism, Elsevier, Amsterdam, 1990, p. 16.
[57] J. Buey, P. Espinet, J. Organomet. Chem. 507 (1996) 137–145.
[58] M. Ghedini, D. Pucci, G. de Munno, D. Viterbo, F. Neve, S. Armentano, Chem.Mater. 3 (1991) 65–72.
[59] A.M. Levelut, M. Veber, O. Francescangeli, S. Melone, M. Ghedini, F. Neve, F.P. Nicoletta, R. Bartolino, Liq. Cryst. 19 (1995) 241–249.
[60] A. Crispini, M. Ghedini, S. Morrone, D. Pucci, O. Francescangeli, Liq. Cryst. 20 (1996) 67–76.