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Novel chiral dimesogenic bidentate ligands and their Cu(II) and Pd(II) metal complexes

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The synthesis and characterization of cholesterol-based dimesogenic bidentate ligands and their Cu(II) and Pd(II) metallomesogens are reported in detail. To understand structure–property relationships in these materials the terminal alkoxy chains and the central metal atom have been varied. Our studies reveal that chiral dimesogenic bidentate ligands with *n*-butyloxy chains exhibit smectic A (SmA), twist grain boundary and chiral nematic (N*) mesophases while substitution with either *n*-decyloxy or 3,7-dimethyloctyloxy chains also show a ferroelectrically switchable chiral smectic C (SmC*) mesophase. The metal complexes with *n*-butyloxy chains show only the SmA phase whereas higher chain length derivatives exhibit N* phase irrespective of the metal atom present. The ligands are thermally stable whereas their metal complexes, especially Pd(II) systems, seem to be heat sensitive. Spontaneous polarization, response time and tilt angle measurements have been carried out in the smectic C* phase of the two ligands.

1. Introduction

Cholesterol is a well known natural product and frequently appears as an important building block in liquid crystals, organic gels and many other molecular assemblies [1]. Its versatility originates from its rigid molecular structure that possesses eight chiral centres giving rise to 256 stereoisomers. Interestingly, only one isomer is produced in nature and it is commercially available as an inexpensive natural product [2]. The first reported example of a thermotropic liquid crystal was in fact derived from cholesterol, namely cholesteryl benzoate [3] and since its discovery many conventional (over 3000) low molar mass liquid crystals consisting of a cholesteryl ester unit as the chiral part of the molecule have been reported [1(*a*), 4]. Recently, there have been reports describing chiral non-symmetrical dimers of dimesogens consisting of a cholesteryl ester unit as a chiral segment attached to a non-chiral aromatic segment containing Schiffs base, azobenzene, stilbene, tolan or biphenyl units [5–7]. A polymethylene chain serves as a spacer between the two segments. These investigations reveal that such compounds exhibit a variety of interesting mesophases. It is interesting to note, however, that cholesterol-based bidentate dimesogenic ligands and the corresponding metallomesogens had not been reported till recently. As part of our continuing work on the molecular design, synthesis and evaluation of the thermal behaviour of cholesterol-based oligomeric liquid crystals, we initiated synthetic work to introduce a metal atom into these materials in order to evaluate structure–property relationships. More importantly, it was reasoned that owing to the presence of a chiral (cholesteryl ester) unit in these new systems they may exhibit ferroelectric properties. We have reported recently the first examples of cholesterol-based dimesogenic bidentate ligands and their metal-organic systems (figure 1) in the form of a short paper [8]. Here we report detailed synthetic procedures, characterization and electro-optical measurements of those ligands and their metal complexes.

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2. Experimental

2.1. *General information*

Chemicals were obtained from either Aldrich, Lancaster or a local source and used without further purification,

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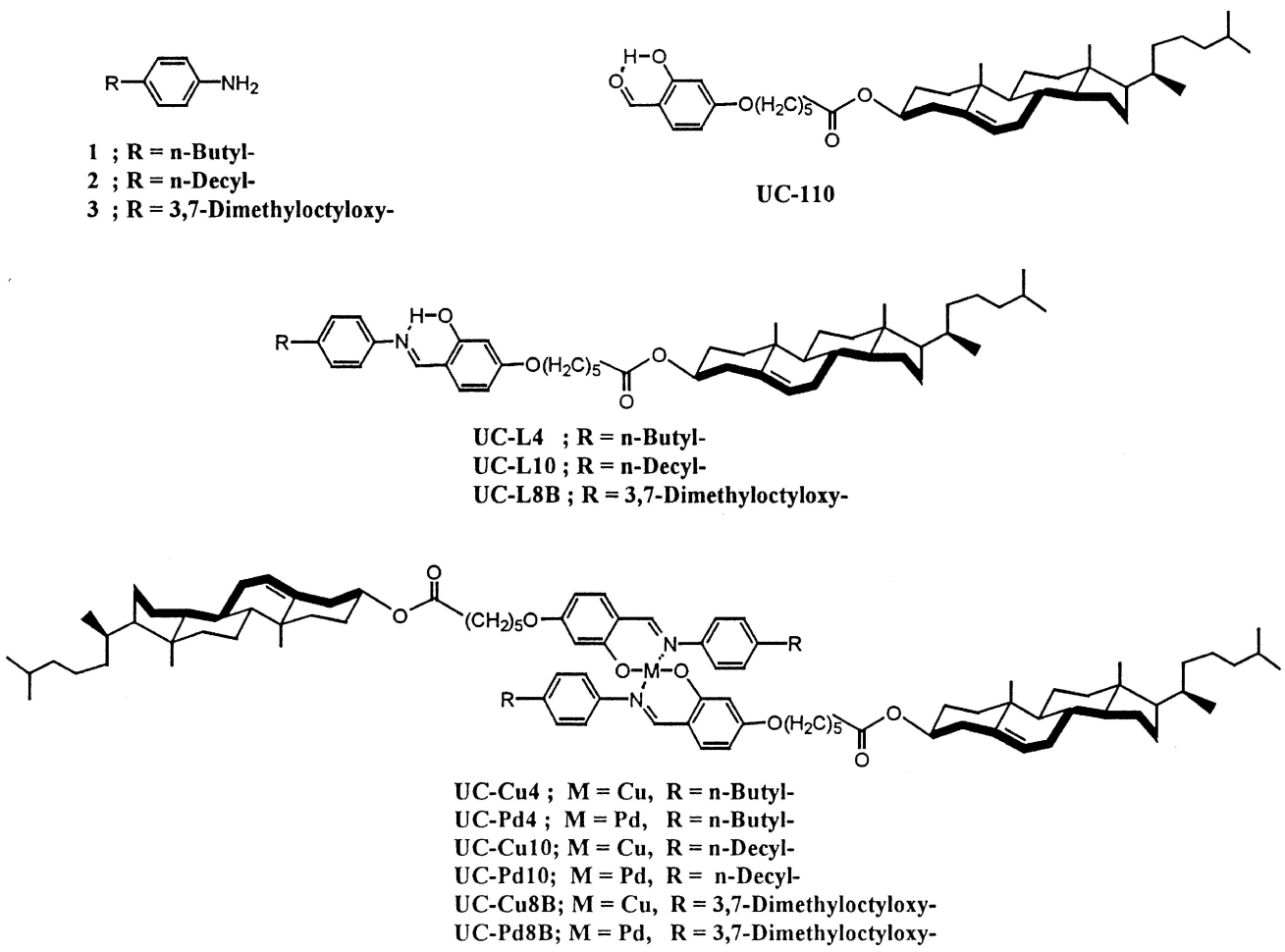


Figure 1. Molecular structure of the intermediates, dimesogenic bidentate ligands and their metal complexes.

while solvents were purified and dried following standard procedures. The compounds synthesized were purified following column chromatographic separation techniques using either silica gel or neutral or basic aluminium oxide as a stationary phase. Thin layer chromatography (TLC) was performed on aluminium sheets pre-coated with silica gel (Merck, Kieselge10, F254). IR spectra were recorded using a Perkin Elmer Spectrum 1000 FTIR spectrometer. NMR spectra were recorded using either Bruker DRX-500 (500 MHz), DPX-200 (200 MHz) or Jeol-90Q (90 MHz) spectrometers. For ^{1}H NMR spectra, the chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS) as an internal standard. Mass spectra were recorded on a Jeol JMS-600H spectrometer in FAB$^+$ mode using 3-nitrobenzylalcohol as a liquid matrix. Elemental analysis was performed using Sumigraph NCH-21 (Sumica Chemical Analysis Service Co. Ltd., Japan). The metal content (%) was estimated by ICP after decomposition of the samples using a mixture of conc. HCl and HNO_3. The ICP instrument used was an HVR-1700 (Seiko Instrument Inc.). The wavelength used for copper was 324.8 nm and for Pd 340.5 nm. The materials were investigated for their liquid crystalline behaviour using an optical polarizing microscope (Leitz DMRXP) in conjunction with a programmable hot stage (Mettler FP90) and by differential scanning calorimetry (Perkin Elmer DSC7). Samples for optical observation were made using clean untreated glass plates.

2.2. *Synthetic procedures*

2.2.1. *3,7-Dimethyloctyl p-toluenesulphonate (**5**)*

To a magnetically stirred, cooled (5–10°C) solution of 3,7-dimethyl-1-octanol (3 g, 19 mmol, 1.0 equiv.) in pyridine (5.5 ml) was added, portionwise, *p*-toluenesulphonyl chloride (4 g, 20.8 mmol, 1.1 equiv.) over a period of 30 min. The reaction mixture was allowed to warm to room temperature with continued stirring for 24 h. The

mixture was then poured into ice-cold 3M HCl (aq.) solution and extracted with ether. The organic layer was washed with water and brine. Evaporation of the solvent yielded a pale yellow oil, which was purified by column chromatography using silica gel (60–120 mesh). Elution with a 1/1 mixture of CH_2Cl_2/hexane gave a colourless oil. $R_f = 0.39$ (10% EtOAc/hexane); yield 3.1 g (61%). IR (neat): ν_{max}/cm^{-1} 2955, 2869, 1364 and 1188. ^1H NMR ($CDCl_3$, 90 MHz): δ 7.82 (d, $J = 8.5$ Hz, 2H, Ar), 7.3 (d, $J = 8.5$, 2H, Ar), 4.05 (t, $J = 8.1$, 2H, $-OCH_2-$), 2.42 (s, 3H, $1 \times -CH_3$), 1.92–1 (m, 10H, $2 \times -CH-$, $4 \times -CH_2-$), 0.92 (d, $J = 5.5$, 3H, $1 \times -CH_3$) and 0.87 (d, $J = 6.1$, 6H, $2 \times -CH_3$).

2.2.2. *4-(3,7-Dimethyloctyloxy)acetanilide (**4**)*

To a magnetically stirred suspension of sodium hydride (previously washed with hexanes and dried) (0.4 g, 9 mmol, 1.05 equiv.) in dry DMF (HPLC grade, 10 ml) was added a solution of 4-acetamidophenol (1.3 g, 8.6 mmol, 1 equiv.) in DMF (10 ml) over a period of 10 min at room temperature under an argon atmosphere. After stirring the resulting suspension vigorously at room temperature for 2 h, a solution of compound **5** (2.7 g, 8.6 mmol, 1 equiv.) in DMF (5 ml) was added and stirring was continued at 85–100°C for a period of 24 h. The mixture was then poured into ice-cold water and extracted with ether. The organic layer was washed with water and brine. Evaporation of the solvent yielded an off-white solid that was purified by column chromatography using silica gel (230–400 mesh). Elution with 30% EtOAc/hexanes furnished a white solid. $R_f = 0.38$ (30% EtOACc/hexane); yield quantative, m.p. 73–74°C. IR (KBr pellet): ν_{max}/cm^{-1} 2926, 1659 and 1510. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.37 (d, $J = 8.9$ Hz, 2H, Ar), 6.84 (d, $J = 9.0$, 2H, Ar), 3.96 (t, $J = 7.4$, 2H, $-OCH_2-$), 2.1 (s, 3H, $1 \times -CH_3$), 1.96–1 (m, 10H, $2 \times -CH-$, $4 \times -CH_2-$), 0.93 (d, $J = 6.3$, 3H, $1 \times -CH_3$) and 0.87 (d, $J = 6.56$, 6H, $2 \times -CH_3$). MS: m/z 292.1 $[M + 1]^+$ (calculated for $C_{18}H_{29}NO_2$).

2.2.3. *4-(3,7-Dimethyloctyloxy)aniline (**3**)*

A mixture of compound **4** (1.2 g, 4.1 mmol), ethanol (20 ml) and conc. HCl (2.5 ml) was heated at reflux until the oily suspension disappeared. The reaction mixture was evaporated *in vacuo* and the solid residue poured onto cold water and neutralized by adding 10% NaOH (aq) solution. The mixture was extracted with ether and the organic layer washed with water and brine. Evaporation of the solvent yielded a brown oil that was purified by column chromatography using basic alumina. Elution with 10% EtOAc/hexane furnished a pale brown oil. $R_f = 0.4$ (30% EtOAc/hexane); yield 0.6 g (55%). IR (KBr pellet): ν_{max}/cm^{-1} 3432, 3359, 3218, 2926, 2869, 1625 and 1512. ^1H NMR ($CDCl_3$, 200 MHz): δ 6.74 (m, 2H, Ar), 6.64 (m, 2H, Ar), 3.88 (m, 2H, $-OCH_2-$), 3.4 (br s, 2H, $-NH_2$), 1.96–1 (m, 10H, $2 \times -CH-$, $4 \times -CH_2-$), 0.92 (d, $J = 6.4$, 3H, $1 \times -CH_3$) and 0.87 (d, $J = 6.6$, 6H, $2 \times -CH_3$). MS m/z 249.5 $[M]^+$ (calculated for $C_{16}H_{27}NO$).

2.2.4. *Cholesteryl 6-(3-hydroxy-4-formylphenoxy)-hexanoate (**UC-110**)*

A mixture of cholesteryl 6-bromohexanoate (4 g, 7.11 mmol, 1.0 equiv.), 2,4-dihydroxybenzaldehyde (0.98 g, 7.11 mmol, 1.0 equiv.), potassium hydrogen carbonate (3.56 g, 35.6 mmol, 5 equiv.) in dry acetone (50 ml) was heated at reflux for 48 h under an argon atmosphere. The reaction mixture was evaporated *in vacuo* to give a solid residue that was poured into cold water. The off-white separated solid was collected by filtration and purified by column chromatography using silica gel (230–400 mesh). Elution with 10% EtOAc/hexane furnished a white solid that was further purified by repeated recrystallization from a mixture of CH_2Cl_2/ethanol (1/10). $R_f = 0.26$ (20% EtOAc/hexane); yield 2.1 g (48%). IR Thermal behaviour (°C): Cr 85.2 N* 117.7 I. IR (KBr pellet): ν_{max}/cm^{-1} 3135, 2867, 1731 and 1584. ^1H NMR ($CDCl_3$, 200 MHz): δ 11.47 (s, 1H, $-OH$), 9.71 (s, 1H, $-CHO$), 7.41 (d, $J = 8.7$ Hz, 1H, Ar), 6.52 (dd, $J = 8.7$, $J = 2.32$, 1H, Ar), 6.40 (d, $J = 2.3$, 1H, Ar), 5.37 (brd, $J = 4.0$, 1H, olefinic), 4.60 (m, 1H, $-CH-OCO-$), 4.01 (t, $J = 6.3$, 2H, $-OCH_2-$), 2.32 (m, 4H, $2 \times$ allylic methylene), 2.02–0.9 (m, 32H, $6 \times -CH-$, $13 \times -CH_2-$), 1.01 (s, 3H, $-CH_3$), 0.91 (d, $J = 6.4$, 3H, $-CH_3$), 0.86 (d, $J = 6.1$, 6H, $2 \times -CH_3$) and 0.67 (s, 3H, $-CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): 194.30, 172.93, 166.30, 164.51, 139.62, 135.21, 122.65, 115.06, 108.70, 101.07, 73.85, 68.21, 56.66, 56.11, 50.00, 42.29, 39.71, 39.5, 38.14, 36.96, 36.57, 36.16, 35.77, 34.48, 31.85, 28.61, 28.20, 27.99, 27.80, 25.47, 24.68, 24.26, 23.81, 22.80, 22.50, 21.00, 19.29, 18.70 and 11.83. MS: m/z 644.1 $[M + 1 + Na]^+$ (calculated for $C_{40}H_{60}O_5$).

2.2.5. *General synthetic procedure for the preparation of dimesogenic bidentate ligands (**UC-L4, UC-L10** and **UC-L8B**)*

A mixture of compound **UC-110** (1 g, 1.6 mmol, 1.0 equiv.), 4-(*n*-alkyl/alkoxy)aniline (1.68 mmol, 1.05 equiv.) and glacial acetic acid (a drop) in absolute ethanol (50 ml) was heated at reflux for 2 h. The yellow solid obtained upon cooling was collected by filtration, washed with hot ethanol and dried. The crude product was purified by repeated recrystallization from a $CHCl_3$/ethanol (1 : 10) mixture.

2.2.5.1. *N-[2-Hydroxy-4-(6-cholesteryloxycarbonyl)pentyloxybenzylidene]-4-n-butylaniline (**UC-L4**)*. A yellow solid, $R_f = 0.31$ (10% EtOAc/hexane), yield 1.1 g (quantitative). Thermal behaviour (°C): Cr 130.1 SmA 174.9 N* 203.0 I

(a transient TGB phase was observed between SmA and N*). IR (KBr pellet): ν_{max}/cm^{-1} 2950, 2867, 1726, 1624, 1599 and 1566. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.51 (s, 1H, CH=N), 7.25 (d, $J = 4.3$ Hz, 1H, Ar), 7.21 and 7.18 (AA′BB′ pattern, 4H, $\Delta\nu = 10.3$ Hz, $J = 8.6$ Hz, Ar), 6.47 (m, 1H, Ar), 6.44 (d, $J = 2.4$, 1H, Ar), 5.37 (br d, $J = 4.8$, 1H, olefinic), 4.62 (m, 1H, CHOCH), 4.0 (t, $J = 6.4$, 2H, OCH_2), 2.62 (t, $J = 7.6$, 2H, $ArCH_2$), 2.32 (m, 4H, $2 \times$ allylic methylene), 2.02–0.91 (m, 39H, $6 \times$ CH $15 \times CH_2$ $1 \times CH_3$), 1.01 (s, 3H, CH_3), 0.91 (d, $J = 6.1$, 3H, CH_3), 0.87 (d, $J = 1.9$, 3H, CH_3), 0.86 (d, $J = 1.8$, 3H, CH_3) and 0.67 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, spin echo FT): δ 173.02 (CO), 164.11 (C), 163.38 (C), 160.6 (CH), 145.95 (C), 141.38 (C), 139.72 (C), 133.38 (CH), 129.36 (CH), 122.67 (CH), 120.83 (CH), 113.15 (C), 107.46 (CH), 101.68 (CH), 73.80 (CH), 67.88 (CH_2), 56.75 (CH), 56.21 (CH), 50.09 (CH), 42.37 (C), 39.80 (CH_2), 39.58 (CH_2), 38.22 (CH_2), 37.05 (CH_2), 36.65 (C), 36.26 (CH_2), 35.86 (CH), 35.24 (CH_2), 34.62 (CH_2), 33.71 (CH_2), 31.97 (CH_2), 31.92 (CH), 28.84 (CH_2), 28.29 (CH_2), 28.07 (CH), 27.89 (CH_2), 25.63 (CH_2), 24.83 (CH_2), 24.35 (CH_2), 23.91 (CH_2), 22.89 (CH_3), 22.64 (CH_3), 22.39 (CH_2), 21.0 (CH_2), 19.28 (CH_3), 18.79 (CH_3), 14.01 (CH_3) and 11.91 (CH_3). MS: m/z 752.7 $[M + H]^+$. Elemental analysis for $C_{50}H_{73}NO_4$: calcd C 79.85, H 9.78, N 1.86; found C 79.50, H 9.50, N 1.8%.

2.2.5.2. *N-[2-Hydroxy-4-(6-cholesteryloxycarbonyl)pentyloxybenzylidene]-4-n-decylaniline (**UC-L10**)*. A yellow solid, $R_f = 0.31$ (10% EtOAc/hexane), yield 1.1 g (quantitative). Thermal behaviour (°C): Cr 120.3 SmC* 153.6 SmA 185.6 N* 187.2 I (a transient TGB phase was observed between SmA and N*). For IR, ^1H, ^{13}C (spin echo FT) NMR details see earlier publication [8]. Elemental analysis for $C_{56}H_{85}NO_4$: calcd C 80.43, H 10.24, N 1.67; found C 80.20, H 10.30, N 1.50%.

2.2.5.3. *N-[2-Hydroxy-4-(6-cholesteryloxycarbonyl)pentyloxybenzylidene]-4-(3,7-dimethyloctyloxy)aniline (**UC-L8B**)*. A yellow solid, $R_f = 0.31$ (10% EtOAc/hexane), yield 1.3 g (quantitative). Thermal behaviour (°C): Cr 116.7 SmC* 146.4 SmA 176.5 N* 179.6 I (a transient TGB phase was observed between SmA and N*). IR (KBr pellet): ν_{max}/cm^{-1} 2951, 2867, 1730, 1623, 1595 and 1569. ^1H NMR (500 MHz, $CDCl_3$): δ 8.51 (s, 1H, CH=N), 7.23 (m, 3H, Ar), 6.94 (d, $J = 8.9$, 2H, Ar), 6.47 (m, 2H, Ar), 5.39 (br d, $J = 4.8$, 1H, olefinic), 4.63 (m, 1H, CHOCH), 4.03 (t, 4H, $2 \times OCH_2$), 2.33 (m, 4H, $2 \times$ allylic methylene), 2.02–0.90 (m, 42H, $8 \times$ CH, $17 \times CH_2$), 1.03 (s, 3H, CH_3), 0.96 (d, $J = 6.6$, 6H, $2 \times CH_3$), 0.93 (d, $J = 6.5$, 3H, CH_3), 0.88 (m, 9H, $3 \times CH_3$) and 0.68 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, spin echo FT): δ 172.86, 165.35, 163.66, 163.0, 159.3, 157.90, 141.1, 139.6, 133.02, 126.16, 122.51, 121.84, 116.15, 113.08, 107.2, 101.53, 73.72, 67.71, 66.58, 56.6, 56.06, 49.95, 42.22, 39.65, 39.42, 39.15, 38.06, 37.20, 36.90, 36.50, 36.11, 35.7, 34.50, 31.78, 29.78, 28.68, 28.12, 27.90, 27.73, 25.47, 24.66, 24.55, 24.17, 23.74, 22.71, 22.59, 22.46, 20.94, 19.57, 19.20, 18.62 and 11.75. MS: m/z 852.28. $[M]^+$. Elemental analysis for $C_{56}H_{85}NO_4$: calcd C 78.92, H 10.05, N 1.64: found C 78.40, H 9.80, N 1.50%.

2.2.6. *General synthetic procedure for the preparation of copper complexes **UC-Cu4, UC-Cu10** and **UC-Cu8B***

A flask equipped with a magnetic stirrer, reflux condenser and argon inlet was charged with dimesogenic bidentate ligand (0.45 mmol, 1 equiv.), methanol (10 ml) and benzene (10 ml). The yellow solution obtained was heated at reflux and then a solution of copper(II) acetate monohydrate (0.05 g, 0.25 mmol, 0.55 equiv.) in methanol (5 ml) was added. The dark-brown coloured suspension obtained was heated at 60°C for 2 h. The reaction mixture was cooled to room temperature and stirring continued for 12 h. The brown coloured solid obtained was collected by filtration and was purified by repeated recrystallization from a mixture of $CHCl_3$/ethanol (1/10).

2.2.6.1. *Bis[N-(n-butylphenyl)-4-(6-cholesteryloxycarbonyl)pentyloxysalicylaldiminato]copper(II) (**UC-Cu4**)*. A dark-brown solid, yield 0.41 g (75%). Thermal behaviour (°C): Cr 153.9 SmA 231.3 I. IR (KBr pellet): ν_{max}/cm^{-1} 2937, 2868, 1733, 1610, 1521 and 1506. MS: m/z 1587.6 $[M + Na]^+$. Elemental analysis for $C_{100}H_{144}CuN_2O_8$: calcd C 76.71, H 9.23, N 1.79; found C 76.30, H 9.0, N 1.60%. Metal content: calcd Cu 4.06; found Cu 4.20%.

2.2.6.2. *Bis[N-(n-decylphenyl)-4-(6-cholesteryloxycarbonyl)pentyloxysalicylaldiminato]copper(II) (**UC-Cu10**)*. A brown solid, yield 0.47 g (80%). Thermal behaviour (°C): Cr 182.1 N* 189.5 I. For IR results see our earlier publication [8]. Elemental analysis for $C_{112}H_{168}CuN_2O_8$: calcd C 77.57, H 9.76, N 1.62; found C 77.40, H 9.50, N 1.50%. Metal content analysis: calcd Cu 3.66; found Cu 4.0%.

2.2.6.3. *Bis[N-(3,7-dimethyloctyloxyphenyl)-4-(6-cholesteryloxycarbonyl)pentyloxysalicylaldiminato]copper(II) (**UC-Cu8B**)*. A brown solid, yield 0.53 g (88%). Thermal behaviour (°C): Cr 180.7 (N* 173.8) I. IR (KBr pellet): ν_{max}/cm^{-1} 2933, 2867, 1732, 1611, 1590 and 1523. MS: m/z 1787.2 $[M + Na]^+$. Elemental analysis for $C_{112}H_{168}CuN_2O_{10}$: calcd C 76.16, H 9.59, N 1.59; found C 75.80, H 9.30, N 1.50%. Metal content: calcd. Cu 3.59; found Cu 3.70%.

2.2.7. *General synthetic procedure employed for the preparation of palladium complexes* ***UC-CPd4, UC-Pd10*** *and* ***UC-Pd8B***

A flask equipped with a magnetic stirrer, reflux condenser and argon inlet was charged with dimesogenic bidentate ligand (0.6 mmol, 1 equiv.), palladium(II) chloride (0.053 g, 0.3 mmol, 0.5 equiv.), potassium carbonate (0.14 g, 1 mmol, 1.7 equiv.) and acetonitrile (15 ml). The yellow suspension obtained was heated at reflux for 24 h. The dull yellow solid that separated was collected by filtration and dissolved in $CHCl_3$; the solution was filtered and to the filtrate was added a large excess of abs. ethanol to give a thick yellow precipitate that was collected by filtration. The crude compound was purified by repeated recrystallization from a mixture of $CHCl_3$/ethanol (1/10).

2.2.7.1. *Bis[N-(n-butylphenyl)-4-(6-cholesteryloxycarbonyl)pentyloxysalicylaldiminato]palladium(II) (**UC-Pd4**)*. A yellow solid, yield 0.4 g (70%). Thermal behaviour (°C): Cr 219.2 SmA 252.2 I. IR (KBr pellet): ν_{max}/cm^{-1} 2934, 2867, 1733 and 1609 and 1599. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.5 (s, 2H, CH=N), 7.22 and 7.19 (AA′BB′ pattern, 8H, $\Delta\nu = 10.1$ Hz, $J = 8.5$ Hz, Ar), 7.01 (d, $J =$ 8.9, 2H, Ar), 6.12 (dd, $J = 8.8$, $J = 2.4$, 2H, Ar), 5.54 (d, $J = 2.3$, 2H, Ar), 5.37 (br d, $J = 4.7$, 2H, olefinic), 4.60 (m, 2H, CHOCH), 3.76 (t, $J = 6.2$, 4H, $2 \times OCH_2$), 2.65 (t, $J = 7.6$, 4H, $2 \times ArCH_2$), 2.30 (m, 8H, $2 \times$ allylic methylene), 2.05–0.90 (m, 78H, $12 \times CH$ $30 \times CH_2$ $2 \times CH_3$), 1.01 (s, 6H, $2 \times {}^{-}CH_3$), 0.91 (d, $J = 6.5$, 6H, $2 \times {}^{-}CH_3$), 0.87 (d, $J = 1.8$, 6H, $2 \times {}^{-}CH_3$), 0.85 (d, $J =$ 1.7, 6H, $2 \times {}^{-}CH_3$) and 0.67 (s, 6H, $2 \times {}^{-}CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$, spin echo FT): δ 173.01 (CO), 166.96 (C), 164.91 (C), 161.0 (CH), 147.54 (C), 140.66 (C), 139.74 (C), 135.45 (CH), 127.94 (CH), 124.74 (CH), 122.69 (CH), 114.71 (C), 106.52 (CH), 102.04 (CH), 73.88 (CH), 67.24 (CH_2), 56.75 (CH), 56.21 (CH), 50.10 (CH), 42.37 (C), 39.80 (CH_2), 39.58 (CH_2), 38.22 (CH_2), 37.07 (CH_2), 36.66 (C), 36.25 (CH_2), 35.85 (CH), 35.31 (CH_2), 34.61 (CH_2), 34.06 (CH_2), 31.98 (CH_2), 31.92 (CH), 28.84 (CH_2), 28.07 (CH), 27.89 (CH_2), 25.67 (CH_2), 24.85 (CH_2), 24.35 (CH_2), 23.90 (CH_2), 22.89 (CH_3), 22.62 (CH_3), 22.42 (CH_2), 21.11 (CH_2), 19.40 (CH_3), 18.79 (CH_3), 14.07 (CH_3) and 11.92 (CH_3). MS: m/z 1607.1 $[M]^+$. Elemental analysis for $C_{100}H_{144}N_2O_4Pd$: cald C 74.66, H 9.02, N 1.74; found C 74.40, H 8.80, N 1.50%. Metal content: calcd Pd 6.62; found Pd 6.0%.

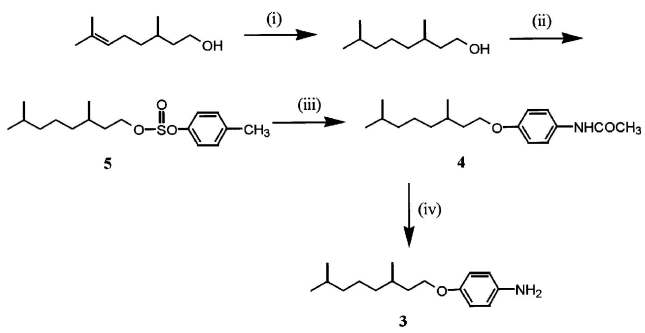
2.2.7.2. *Bis[N-(n-decylphenyl)-4-(6-cholesteryloxycarbonyl)pentyloxysalicylaldiminato]palladium(II) (**UC-Pd10**)*. A yellow solid, yield 0.4 g (64%). Thermal behaviour (°C): Cr 215.3 N* 218.9 I. For IR, ^{1}H and ^{13}C (spin echo FT) NMR details see our earlier publication [8]. Elemental analysis for $C_{112}H_{168}N_2O_8Pd$: calcd C 75.70, H 9.53, N 1.58; found C 75.40, H 9.30, N 1.40%. Metal content: calcd. Pd 5.98; found Pd 5.8%.

2.2.7.3. *Bis[N-(3,7-dimethyloctyloxyphenyl)-4-(6-cholesteryloxycarbonyl)pentyloxysalicylaldiminato]palladium-(II) (**UC-Pd8B**)*. A yellow solid, yield 0.28 g (45%). Thermal behaviour (°C): Cr 214.7 (N* 201.8) I. IR (pellet): ν_{max}/cm^{-1} 2949, 2866, 1726, 1610, 1590 and 1504. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55 (s, 2H, CH=N), 7.22 (d, $J = 8.7$, 4H, Ar), 7.02 (d, $J = 8.8$, 2H, Ar), 6.90 (d, $J = 8.8$, 4H, Ar), 6.12 (dd, $J = 11$, $J = 8.72$, 2H, Ar), 5.64 (d, $J = 2.3$, 2H, Ar), 5.34 (br d, $J = 4.7$, 2H, olefinic), 4.60 (m, 2H, $2 \times$ CHOCO), 4.02 (m, 4H, $2 \times OCH_2$), 3.80 (t, $J = 6.2$, 4H, $2 \times OCH_2$), 2.3 (m, 8H, $2 \times$ allylic methylene), 2.05–0.90 (m, 84H, $16 \times CH$, $34 \times CH_2$), 1.01 (s, 6H, $2 \times CH_3$), 0.96 (d, $J = 6.5$, 12H, $4 \times {}^{-}CH_3$), 0.91 (d, $J = 6.5$, 6H, $2 \times {}^{-}CH_3$), 0.87 (m, 18H, $6 \times CH_3$), and 0.66 (s, 6H, $2 \times CH_3$). MS: m/z 1807.2 $[M]^+$. Elemental analysis for $C_{112}H_{168}N_2O_8Pd$: calcd C 74.36, H 9.36, N 1.55; found C 74.10, H 9.20, N 1.40%. Metal content: calcd Pd 5.88; found Pd 5.80%.

3. Results and discussion

3.1. *Synthesis and characterization*

In our present studies the molecular design incorporates a salicylaldimine segment covalently connected to a cholesteryl ester entity via an *n*-pentyl spacer to form a mesogenic bidentate ligand which chelates to Cu(II) and Pd(II) to furnish the novel metal-organic systems. The dimesogenic ligands (**UC-L4**, **UC-L10**, **UC-L8B**) and their Cu(II) (**UC-Cu4**, **UC-Cu10**, **UC-Cu8B**) and Pd(II) (**UC-Pd4**, **UC-Pd10**, **UC-Pd8B**) complexes were obtained as reported. 4-*n*-Butylaniline (**1**) and 4-*n*-decylaniline (**2**) were synthesized starting from 4-nitrobenzaldenyde [6*b*] while 4-(3,7-dimethyloctyloxy)-aniline (**3**) was prepared as shown in the scheme. The molecular structures of all the intermediates, ligands and their metal



Scheme. Reagents and Conditions: (i) H_2/Pd-C (10%), abs.EtOH, 1 atm, rt, 2 h; (ii) tosyl chloride, Py, rt, 24 h; (iii) $NaH/HOC_6H_4NHCOCH_3$, DMF, 85–100°C, 24 h; (iv) conc. HCl, EtOH, reflux, 2 h.

complexes were determined with the help of spectral data (IR, ^{1}H, ^{13}C (SEFT) and FAB MS) and elemental analyses. The analytical results were found to be consistent with the proposed structures. All the ligands exhibit C=O and C=N stretching vibration bands in the regions 1722–1730 and 1622–1624 cm^{-1}, respectively. The metal complexes show stretching vibrations in the 1726–1734 and 1609–1611 cm^{-1} regions due to the C=O and C=N groups, respectively. The noticeable shift of the ligand C=N stretching band to lower frequencies in the complexes indicates the coordination of the N atom.

The ligands and Pd(II) complexes show very similar ^{1}H and ^{13}C SEFT (spin echo Fourier transform) spectra except for changes in chemical shift positions as well as the pattern of the protons resonating in the higher frequency regions (above 5 ppm). As a representative example the ^{1}H and ^{13}C spectra for the ligand **UC-L4** and the complex **UC-Pd4** are shown in figures 2 (*a*, *b*) and 3 (*a*, *b*), respectively. Comparison of the ^{1}H NMR spectra of the ligand, 2 (*a*) and the complex 3 (*a*), reveals a significant chemical shift as well as a change in the splitting pattern of the peaks for the protons C, D, E and F (see molecular structure shown in figures 2 and 3). Specifically, the protons C, D, E and F of the ligand **UC-L4**, resonate at *c.* δ 6.44 [as a doublet (d)], 6.47 [as a multiplet (m)], 7.25 [as a doublet (d)] and 8.51 ppm [as a singlet (s)] respectively; figure 2 (*a*). Upon chelation with Pd(II), the resonances for protons C, D, E and F move upfield appearing at *c.* δ 5.54 (d), 6.12 [as a doublet of doublet (dd)], 7.01 (d) and 7.50 ppm (s) respectively; figure 3 (*a*). This means that these protons are shielded by the presence of the metal atom. Similar chemical shift changes are also found in the ^{13}C spectra; compare figures 2 (*b*) and 3 (*b*). Thus NMR spectroscopic analysis unambiguously proves the formation of the metal complex.

3.2. *Thermal behaviour*

The mesophase sequence and transition temperatures of all the ligands and their metal complexes have been given in the experimental section (some of these data were reported earlier [8]). For the purpose of discussion, here we briefly review the thermal behaviour of these compounds. The presence of SmA and N* mesophases has been confirmed, based on the observation of characteristic focal-conic and oily-streak textures, respectively. The TGB phase showed the usual filament texture and coexists along with the SmA and N* mesophases. In other words, it was a transient phase, as evident from the observation of textures corresponding to these three mesophases appearing almost simultaneously. The ligand **UC-L4** exhibits enantiotropic SmA, TGB and N* mesophases with transition temperatures being highly reproducible, indicating the chemical stability of the material. In contrast, the corresponding copper complex **UC-Cu4** and palladium complex **UC-Pd4** show a SmA mesophase only.

The ligand **UC-L10** shows SmC*, SmA, TGB and N* phases. The existence of the SmC* phase was confirmed by the observation of dechiralization lines running over the focal-conic texture and also by electro-optical switching characteristics which are discussed in detail in the following sections. The corresponding metal complexes **UC-Cu10** and **UC-Pd10** of the ligand **UC-L10** show only the N* mesophase. The ligand **UC-L8B** also shows SmC*, SmA, TGB and N* mesophases, while its metal complexes **UC-Cu8B** and **UC-Pd8B** show a narrow temperature range monotropic N* mesophase only. Our study reveals that the copper complexes are more thermally stable than the palladium complexes.

3.3. *Electro-optical measurements*

The dimesogenic bidentate ligands **UC-L8B** and **UC-L10** stabilize the SmC* phase. As reported earlier, preliminary electro-optic studies for these two compounds show a very clear ferroelectric switching [8]. Now we report detailed spontaneous polarization ($\mathbf{P}_s$), response time (τ) and tilt angle (θ) measurements carried out in the SmC* phase of these two ligands. Polarization values were evaluated by measuring the voltage drop across a standard resistance on application of a triangular voltage to the sample. Response time was determined by applying a square wave field and considering the time required for the sample response to increase from 10% to 90% of its maximum value as reported earlier. Electro-optic tilt angle in the smectic C* phase was measured from the angular difference between the two minimum intensity positions for opposite signs of the field.

Figures 4 (*a*) and 4 (*b*) show the variation of $\mathbf{P}_s$ with reduced temperature, $T_c - T$, (T_c is the SmA to SmC* transition temperature) for **UC-L8B** and **UC-L10**, respectively. The observed value of polarization is small for both samples. It increases with increasing $T_c - T$, and the saturated values are $\sim$30 and $\sim$20 nC cm^{-2} [$(T_c - T) = 30^\circ$C] for **UC-L8B** and **UC-L10**, respectively. A low value of $\mathbf{P}_s$ in both samples may be attributed to the absence of strong lateral dipolates at the chiral centre leading to moderate steric hindrance.

Figures 5 (*a*) and 5 (*b*) show the dependence of response time on inverse temperature, $1/T$, for the ligands **UC-L8B** and **UC-L10**, respectively. τ is of the order $\sim$40 µs close to the transition and increases with increasing $T_c - T$, reaching $\sim$350 µs away from the transition for both **UC-L8B** and **UC-L10**. The thermal variation shows an Arrhenius behaviour away from the transition, i.e. 10°C below the transition. The activation energy w, is calculated from the expression $\tau = \tau_0 \exp(-w/kT)$, has a value of

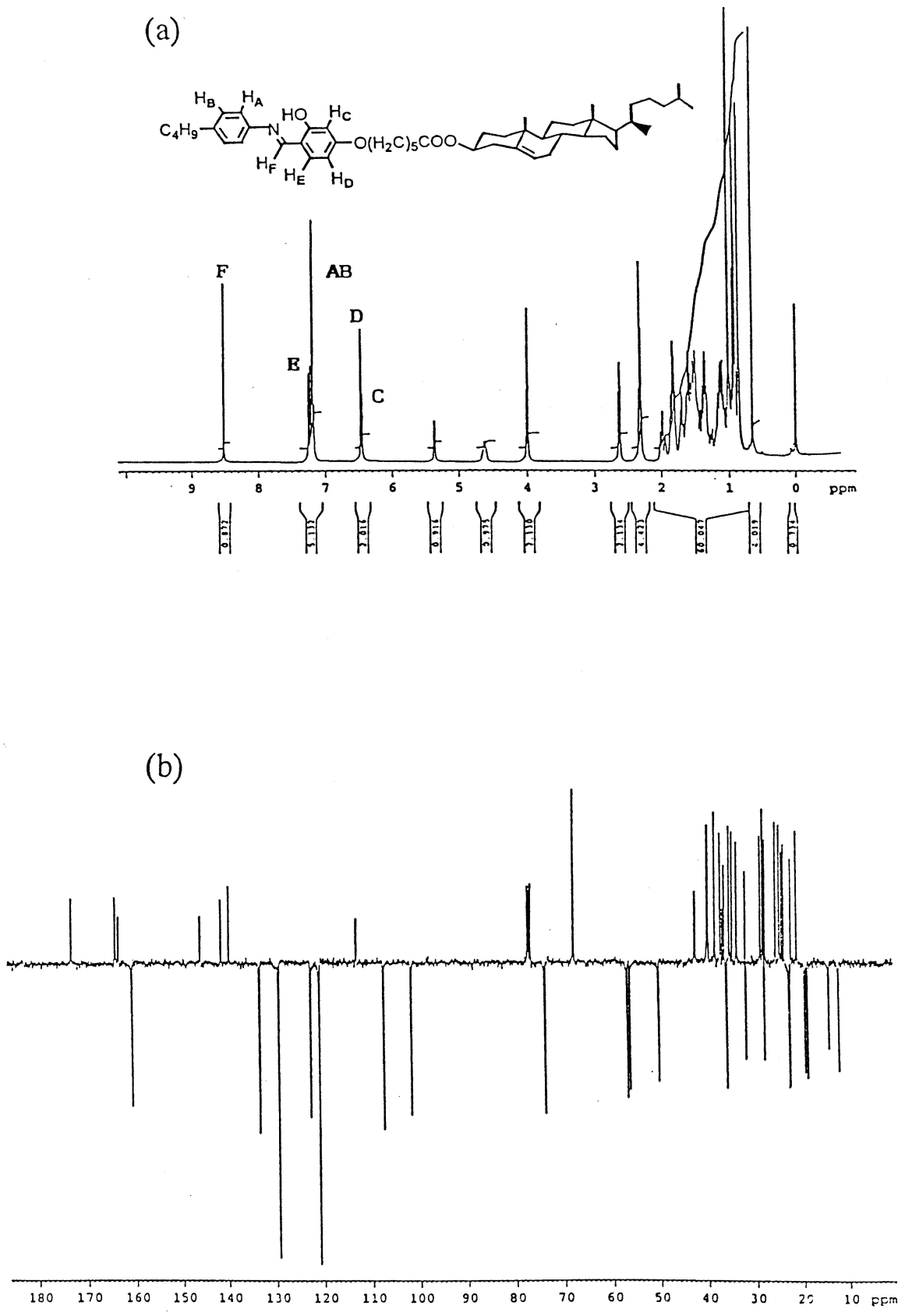


Figure 2. (*a*) ^{1}H and (*b*) ^{13}C NMR spectra of the ligand **UC-L4**.

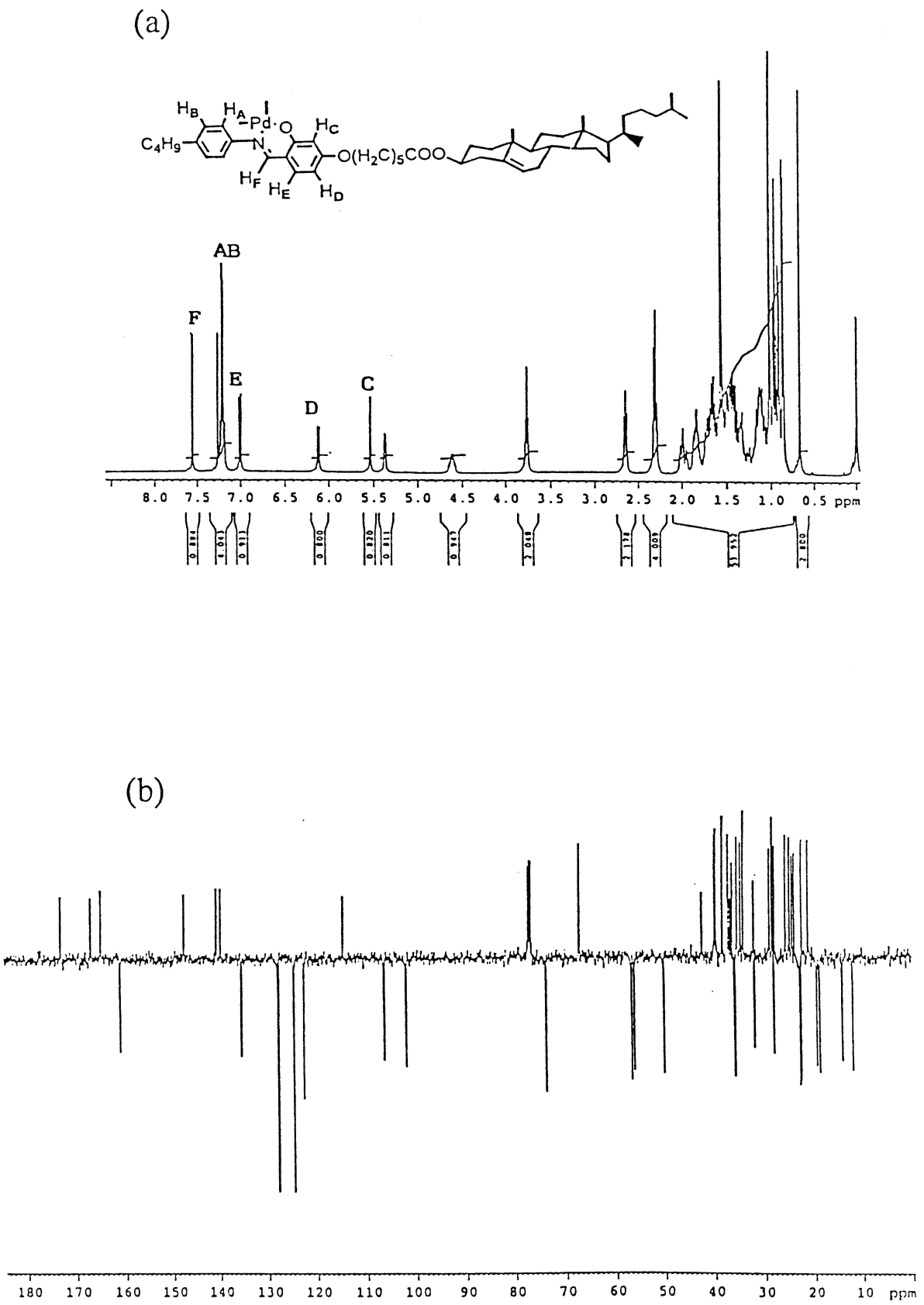
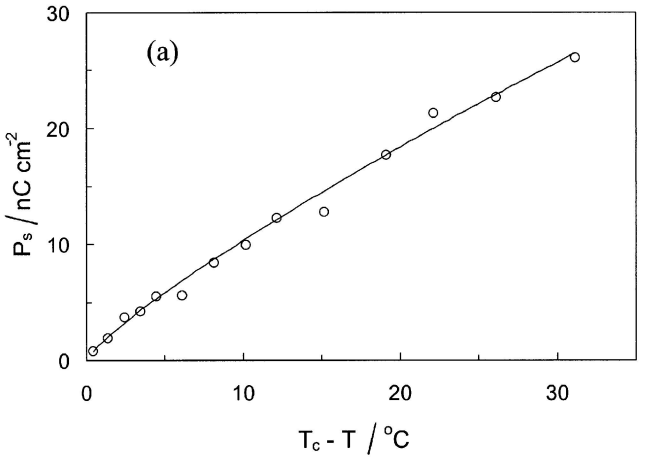


Figure 3. (*a*) ^{1}H and (*b*) ^{13}C NMR spectrum of the metal complex **UC-Pd4**.



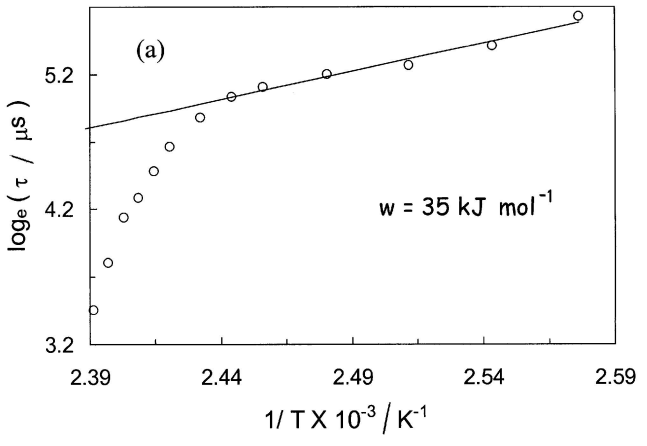
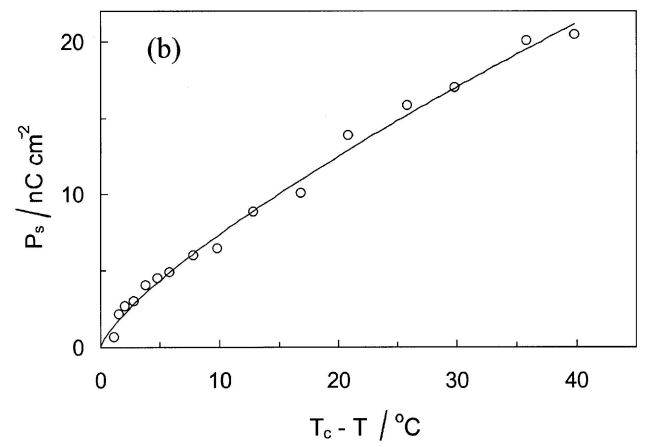


Figure 4. Plots of $\mathbf{P}_s$ variation with reduced temperature, $T_c - T$, (T_c is the SmA to the SmC* transition temperature) for (*a*) **UC-L8B** and (*b*) **UC-L10**.



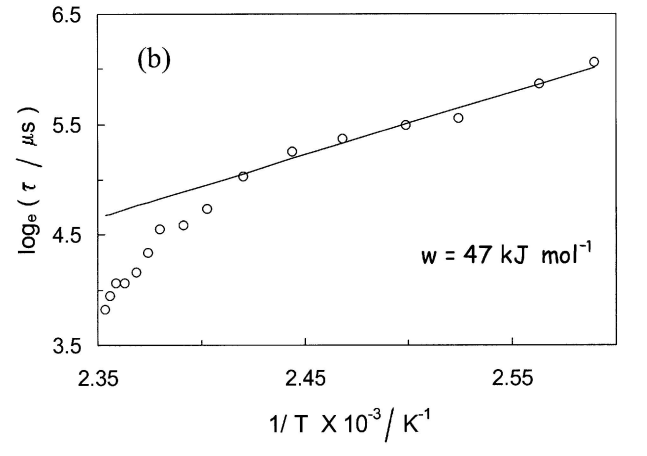


Figure 5. Response time (τ) versus inverse temperature, ($1/T$) for ligands (*a*) **UC-L8B** and (*b*) **UC-L10**.

34.7 kJ mol^{-1} for **UC-L8B** and 47 kJ mol^{-1} for **UC-L10**. Figures 6(*a*) and 6(*b*) show plots of the electro-optic tilt angle versus reduced temperature for the ligands **UC-L8B** and **UC-L10**, respectively. As expected, the tilt angle is small near the transition, increasing with increasing $T_c - T$ and saturating at $\sim 30^\circ$. The tilt angle θ is the primary order parameter for the smectic C phase. Thus, it is conventional to express its temperature dependence using a power law expression, viz. $\theta = \theta_0[(T_c - T)/T_c]^\beta$. A least-square fit to this expression is shown as a solid line in figures 6(*a*) and 6(*b*) and is seen to describe the data quite well. The exponent value of $\beta = 0.5$ suggests that in both cases the transition is truly meanfield-like.

4. Conclusion

We have presented the detailed synthesis and characterization of the first examples of cholesterol-based dimesogenic bidentate ligands and their Cu(II) and Pd(II) metal complexes (metallomesogens). Our studies reveal that the dimesogenic bidentate ligands exhibit a number of mesophases whereas their metal complexes shows just one. The mesomorphic behaviour of the ligands, as well as of their metal complexes, seems to depend on the length of the terminal alkoxy tail. These cholesterol-based ligands appear to be interesting materials as two of them show ferroelectrical switching in the SmC* mesophase. A systematic investigation involving the variation of both the length of the alkylene spacer as well as the terminal alkoxy chains of such ligands now needs to be undertaken in order to improve our understanding of structure–property relationships in this class of materials.

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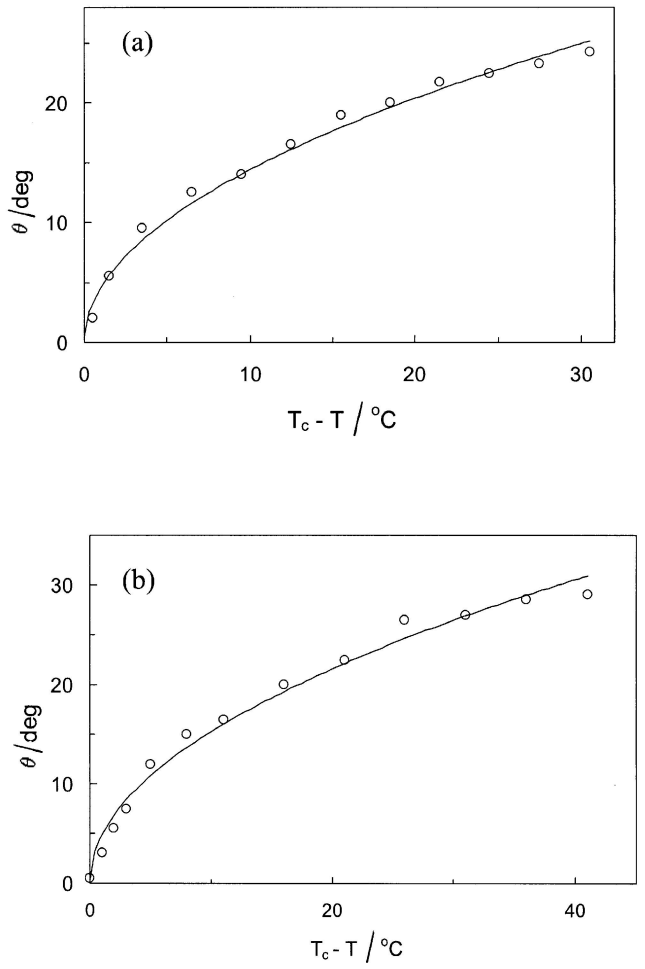

Figure 6. Electro-optic tilt angle versus reduced temperature for the ligands (*a*) **UC-L8B** and (*b*) **UC-L10**.

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