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Preparation of discotic metallomesogens based on phenacylpyridines showing room temperature columnar phases

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Discotic metallomesogens were prepared by complexation of phenacylpyridine ligands with copper(II) and palladium(II) ions. Picoline derivatives with an alkoxy chain were prepared by the reaction of 5-hydroxy-2-methylpyridine with alkyl bromides. In a similar manner, methyl 3,4,5-trialkoxybenzoates were obtained from methyl 3,4,5-trihydroxybenzoates and alkyl bromides. 5-Alkoxy-2-methylpyridines were metallated with lithium diisopropylamine and reacted with methyl benzoates to give ligand compounds **1–3**. Metal complexes **Cu1–3** and **Pd1–3** were prepared by complexation of the ligands with copper(II) acetate and palladium(II) acetate in tetrahydrofuran, respectively. The ligands did not form liquid crystals, but their metal complexes showed enantiotropic columnar hexagonal mesophases at room temperature.
The metal complexes of phenacylpyridines showed a superior ability to self-assemble into ordered phases compared to their structural analogues, the salicylaldiminato complexes.

Keywords: metallomesogen; phenacylpyridine; salicylaldimine; discotic liquid crystal

1. Introduction

Metallomesogens, liquid crystalline compounds with metal ion cores, have attracted great attention because they have anisotropic optical, mechanical, magnetic and electric properties, as do organic liquid crystals, and also unique properties of d- or f-block metals (e.g., optical and magnetic properties, and redox activity) [1–15]. Mesophase formation depends mainly on the intermolecular interactions between ligand groups and their arrangements around metal ions. A coordination of metal ions can even induce the formation of mesophases from non-mesomorphic ligands. The metal ions which can coordinate with a linear or a square planar bond are generally used for metallomesogens. Silver(I), rhodium(I), iridium(I), nickel(II), copper(II), palladium(II) and platinum(II) can satisfy these conditions.

The ligands generally have two or more electron donating atoms, such as oxygen or nitrogen, capable of coordinating with the metal cation. Salicylaldimines have been extensively studied as ligands in metal coordination [16–21]. Phenacylpyridines closely resemble salicylaldimines, but there have only been a few reports on their mesogenic complexes. For example, the Šunjić group [22] reported copper(II) complexes of 4-alkoxyphenacyl-5-alkoxypyridines, which showed smectic A phases.

In this work, we synthesised room temperature columnar liquid crystalline metallomesogens based on phenacylpyridines. The copper(II) and palladium(II) ions which can form a square planar coordinate were used for the complexation. Notably, the metallomesogen with phenacylpyridine ligands formed much more stable mesophases than did the salicylaldiminato one. Scheme 1 shows the structures of the discotic metallomesogens with salicylaldimine ligands and phenacylpyridine ligands. Compound **I** obtained from salicylaldimine ligands formed columnar hexagonal mesophases with very high melting (165.7°C) and clearing (313.0°C) points [18]. When two more alkoxy tails were attached in an effort to reduce the melting point, compound **II** did not show mesophases [20]. On the contrary, its structural analogue, compound **Cu2**, which was prepared in this study showed a hexagonal columnar mesophase even at room temperature.

2. Experimental details

2.1 Measurements

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance DPX-300 (300 MHz) and an Avance 500 (125 MHz) spectrometer, respectively. Fourier transform infrared (FT-IR) spectra were obtained with a Perkin Elmer Spectrum GX I using a KBr pellet. Elemental analysis was performed using a CE instrument EA 1110 analyser. The differential scanning calorimetry (DSC) measurements were performed with a TA-modulated DSC Q10 at a scanning rate of 10°C/min. The optical microscopy study was performed using a Leica DM LP equipped with a Mettler Toledo FP 82HT heating stage and a Mettler Toledo FP 90 central process controller. X-ray diffraction (XRD) patterns were recorded by a Bruker

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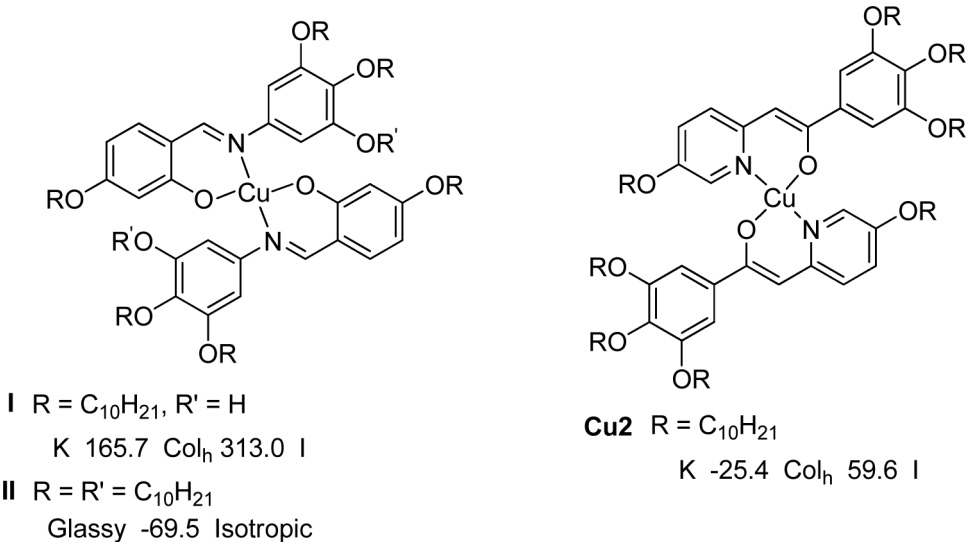


Scheme 1. Discotic metal complexes of salicylaldimines and phenacylpyridines.

NANOSTAR (Cu Kα radiation, $\lambda = 1.54$ Å). Ultraviolet–visible (UV-Vis) spectra were obtained with the use of a Sinco 3150 spectrophotometer.

2.2 Materials

5-Hydroxy-2-methylpyridine (99%), methyl 3,4,5-trihydroxybenzoate (98%), 1-bromooctane, 1-bromodecane, 1-bromododecane, lithium diisopropylamide (2 M solution in heptane/tetrahydrofuran (THF)/ethylbenzene), copper(II) acetate and palladium(II) acetate were purchased from Aldrich and used without further purification. THF was dried over sodium metal and distilled. N,N-dimethylformamide (DMF) was dried over BaO and distilled.

2.3 Synthesis

2.3.1 5-Octyloxy-2-methylpyridine

To a mixture of 5-hydroxy-2-methylpyridine (0.88 g, 8 mmol) and potassium carbonate (1.1 g, 8 mmol) in DMF (20 mL) was added a solution of 1-bromoocatne (1.4 mL, 8.5 mmol) in DMF (15 mL) dropwise. After stirring at 70°C for 4 h, 20 mL of chloroform was added. The solid in the reaction mixture was removed by filtration. After evaporation, the product was isolated by column chromatography on silica gel using a mixture of ethyl acetate and *n*-hexane (1:6, v/v) as eluent. Yield: 72.8%. ^{1}H NMR ($CDCl_3$): δ 8.17 (s, Ar–H, 1H), 7.03–7.11 (m, Ar–H, 2H), 3.98 (t, $J = 6.5$ Hz, ArO–CH_2–, 2H), 2.48 (s, ArCH_3, 3H), 1.80–1.75 (m, OCH_2–CH_2–, 2H), 1.46–1.28 (m, –CH_2–, 10H), 0.88 (t, $J = 6.3$ Hz, –CH_3, 3H).

2.3.2 5-Decyloxy-2-methylpyridine

This compound was synthesised by the same procedure described for the synthesis of 5-octyloxy-2-methylpyridine from 5-hydroxy-2-methylpyridine (0.88 g, 8 mmol), potassium carbonate (1.1 g, 8 mmol) and 1-bromodecane (1.7 mL, 8.5 mmol). Yield: 74.5%. ^{1}H NMR ($CDCl_3$): δ 8.17 (s, Ar–H, 1H), 7.03–7.11 (m, Ar–H, 2H), 3.98 (t, $J = 6.5$ Hz, ArO–CH_2–, 2H), 2.47 (s, ArCH_3, 3H), 1.80–1.75 (m, OCH_2–CH_2–, 2H), 1.46–1.28 (m, –CH_2–, 14H), 0.88 (t, $J = 6.3$ Hz, –CH_3, 3H).

2.3.3 5-Dodecyloxy-2-methylpyridine

This compound was synthesised by the same procedure described for the synthesis of 5-octyloxy-2-methylpyridine from 5-hydroxy-2-methylpyridine (0.88 g, 8 mmol), potassium carbonate (1.1 g, 8 mmol) and 1-bromododecane (2.0 mL, 8.5 mmol). Yield: 71.6%. ^{1}H NMR ($CDCl_3$): δ 8.17 (s, Ar–H, 1H), 7.03–7.11 (m, Ar–H, 2H), 3.97 (t, $J = 6.5$ Hz, ArO–CH_2–, 2H), 2.47 (s, ArCH_3, 3H), 1.80–1.75 (m, OCH_2–CH_2–, 2H), 1.46–1.28 (m, –CH_2–, 18H), 0.88 (t, $J = 6.3$ Hz, –CH_3, 3H).

2.3.4 Methyl 3,4,5-trioctyloxybenzoate

To a mixture of potassium carbonate (16.6 g, 120 mmol) and methyl 3,4,5-trihydroxybenzoate (3.6 g, 20 mmol) in DMF (100 mL) was added 1-bromooctane (11.6 g, 60 mmol) dropwise. The reaction mixture was stirred at 60°C for 8 h, cooled to room temperature and poured into ice/water (1 L). The product was isolated by filtration and recrystallised from acetone. Yield: 63%.

^{1}H NMR ($CDCl_3$): δ 7.24 (s, Ar–H, 2H), 4.0 (tt, overlap, O–CH_2–, 6H), 3.88 (s, –OCH_3, 3H), 1.83–1.73 (m, OCH_2–CH_2–, 6H), 1.53–1.26 (m, –CH_2–, 30H), 0.9 (t, $J = 6.5$ Hz, –CH_3, 9H).

2.3.5 *Methyl 3,4,5-tridecyloxybenzoate*

This compound was synthesised by the same procedure described for the synthesis of methyl 3,4,5-trioctyloxybenzoate from methyl 3,4,5-trihydroxybenzoate (5.52 g, 30 mmol), potassium carbonate (24.9 g, 180 mmol) and 1-bromodecane (19.9 g, 90 mmol). Yield: 69%. ^{1}H NMR ($CDCl_3$): δ 7.24 (s, Ar–H, 2H), 4.0 (tt, overlap, O–CH_2–, 6H), 3.88 (s, O–CH_3, 3H), 1.83–1.73 (m, OCH_2–CH_2–, 6H), 1.53–1.26 (m, –CH_2–, 42H), 0.9 (t, $J = 6.5$ Hz, –CH_3, 9H).

2.3.6 *Methyl 3,4,5-tridodecyloxybenzoate*

This compound was synthesised by the same procedure described for the synthesis of methyl 3,4,5-trioctyloxybenzoate from methyl 3,4,5-trihydroxybenzoate (5.52 g, 30 mmol), potassium carbonate (24.9 g, 180 mmol) and 1-bromododecane (22.43 g, 90 mmol). Yield: 67%. ^{1}H NMR ($CDCl_3$): δ 7.24 (s, Ar–H, 2H), 4.0 (tt, overlap, O–CH_2–, 6H), 3.88 (s, O–CH_3, 3H), 1.83–1.73 (m, OCH_2–CH_2–, 6H), 1.53–1.26 (m, –CH_2–, 54H), 0.9 (t, $J = 6.5$ Hz, –CH_3, 9H).

2.3.7 *3,4,5-Trioctyloxyphenacyl-5-octyloxypyridine (**1**)*

To a stirring solution of 5-octyloxy-2-methylpyridine (0.66 g, 3 mmol) in THF (10 mL) was added lithium diisopropylamide (1 mL, 2 M solution, 2 mmol) dropwise through a syringe at –78°C. The solution was stirred for 30 min at the same temperature and then allowed to warm to room temperature. After stirring for 2 h at room temperature, the solution was cooled to 0°C and a solution of methyl 3,4,5-trioctyloxybenzoate (1.04 g, 2 mmol) in THF (5 mL) was added dropwise through a syringe. The solution was stirred for 18 h at room temperature and then saturated aqueous ammonium chloride (10 mL) was added. The organic phase was separated and the aqueous phase was shaken with chloroform (60 mL). The combined organic layers were dried over anhydrous $MgSO_4$. After filtration and evaporation, the product was isolated by column chromatography on silica gel [ethyl acetate/*n*-hexane (1:6, v/v)] as a viscous liquid. Yield: 53.4%. ^{1}H NMR ($CDCl_3$): δ 14.62 (br, enolic OH, 1H), 8.25 (s, pyridine-6H of keto, 1H), 8.03 (s, pyridine-6H of enol, 1H), 7.33–7.02 (m, ArH, 4H), 5.91 (s, vinylic proton of enol, 1H), 4.39 (s, –CH_2–C=O–, 2H), 4.06–3.96 (m, O–CH_2–, 8H), 1.83–1.73 (m, OCH_2–CH_2–, 8H), 1.53–1.26 (m, –CH_2–, 40H), 0.9 (t, $J = 6.5$ Hz, –CH_3, 12H). ^{13}C NMR ($CDCl_3$, 125 MHz): 196.4, 154.3, 153.0, 147.4, 143.1, 137.6, 131.5, 124.3, 122.1, 108.0, 73.7, 69.4, 68.7, 48.0, 32.1, 30.5, 29.5, 26.3, 22.9, 14.3. IR (KBr, cm^{-1}): 3617, 2920, 1672, 1583, 1468, 1388, 1338, 1244, 1118. Anal. Calcd for $C_{45}H_{75}NO_5$: C, 76.12; H, 10.65; N, 1.97. Found: C, 76.27; H, 10.84; N, 1.96.

2.3.8 *3,4,5-Tridecyloxyphenacyl-5-decyloxypyridine (**2**)*

This compound was synthesised by the same procedure described for the synthesis of 3,4,5-trioctyloxyphenacyl-5-octyloxypyridine from 5-decyloxy-2-methylpyridine (0.75 g, 3 mmol) and methyl 3,4,5-tridecyloxy benzoate (1.21 g, 2 mmol). Yield: 46.2%. ^{1}H NMR ($CDCl_3$): δ 8.23 (s, pyridine-6H of keto, 1H), 8.03 (s, pyridine-6H of enol, 1H), 7.31–7.01 (m, ArH, 4H), 5.91 (s, vinylic proton of enol, 1H), 4.37 (s, –CH_2–C=O–, 2H), 4.06–3.96 (m, O–CH_2–, 8H), 1.83–1.73 (m, OCH_2–CH_2–, 8H), 1.53–1.26 (m, –CH_2–, 56H), 0.9 (t, $J = 6.5$ Hz, –CH_3, 12H). ^{13}C NMR ($CDCl_3$, 125 MHz): 196.4, 154.3, 153.0, 147.4, 143.1, 137.6, 131.5, 124.3, 122.1, 108.0, 73.7, 69.4, 68.7, 48.0, 32.1, 30.5, 29.5, 26.3, 22.9, 14.3. IR (KBr, cm^{-1}): 3617, 2915, 1673, 1582, 1460, 1388, 1338, 1287, 1240, 1114. Anal. Calcd for $C_{53}H_{91}NO_5$: C, 77.41; H, 11.15; N, 1.70. Found: C, 77.18; H, 11.49; N, 1.80.

2.3.9 *3,4,5-Tridodecyloxyphenacyl-5-dodecyloxypyridine (**3**)*

This compound was synthesised by the same procedure described for the synthesis of 3,4,5-trioctyloxyphenacyl-5-octyloxypyridine from 5-dodecyloxy-2-methylpyridine (0.83 g, 3 mmol) and methyl 3,4,5-tridodecyloxybenzoate (1.38 g, 2 mmol). Yield: 40.1%. ^{1}H NMR ($CDCl_3$): δ 8.23 (s, pyridine-2H of keto, 1H), 8.03 (s, pyridine-2H of enol, 1H), 7.31–7.01 (m, ArH, 4H), 5.91 (s, vinylic proton of enol, 1H), 4.37 (s, –CH_2–C=O–, 2H), 4.06–3.96 (m, O–CH_2–, 8H), 1.83–1.73 (m, OCH_2–CH_2–, 8H), 1.53–1.26 (m, –CH_2–, 72H), 0.9 (t, $J = 6.5$ Hz, –CH_3, 12H). ^{13}C NMR ($CDCl_3$, 125 MHz): 196.4, 154.3, 153.0, 147.4, 143.1, 137.6, 131.5, 124.3, 122.1, 108.0, 73.7, 69.4, 68.7, 48.0, 32.1, 30.5, 29.5, 26.3, 22.9, 14.3. IR (KBr, cm^{-1}): 3587, 2907, 1672, 1582, 1468, 1388, 1338, 1274, 1244, 1117. Anal. Calcd for $C_{61}H_{107}NO_5$: C, 78.40; H, 11.54; N, 1.50. Found: C, 78.14; H, 11.67; N, 1.63.

2.3.10 *General procedures of metal complexation*

Copper(II) acetate or palladium(II) acetate (0.15 mmol) was added to a solution of a ligand compound (0.3 mmol) in THF (10 mL) and the solution was stirred for 2 h at room temperature. After evaporation of the

solvent, the product was isolated by column chromatography on silica gel using ethyl acetate/*n*-hexane (1:20, v/v) as eluent.

*2.3.11 Copper(II) complex of 3,4,5-trioctyloxyphenacyl-5-octyloxypyridine (***Cu1***)*

Yield: 76.3%. ^{1}H NMR ($CDCl_3$): δ 3.95 (br, O–CH_2–, 16H), 1.75 (br, OCH_2–CH_2–, 16H), 1.53–0.98 (br, –CH_2–, 80H), 0.88 (br, –CH_3, 24H). ^{13}C NMR ($CDCl_3$, 125 MHz): 73.8, 69.4, 32.1, 30.6, 29.6, 26.3, 22.9, 14.3. IR (KBr, cm^{-1}): 3550, 2924, 1652, 1577, 1468, 1429, 1370, 1338, 1262, 1113. Anal. Calcd for $C_{90}H_{148}CuN_2O_{10}$: C, 72.95; H, 10.07; N, 1.89. Found: C, 73.21; H, 10.31; N, 1.88.

*2.3.12 Copper(II) complex of 3,4,5-tridecyloxyphenacyl-5-decyloxypyridine (***Cu2***)*

Yield: 81.5%. ^{1}H NMR ($CDCl_3$): δ 3.95 (br, O–CH_2–, 16H), 1.75 (br, OCH_2–CH_2–, 16H), 1.53–0.98 (br, –CH_2–, 112H), 0.88 (br, –CH_3, 24H). ^{13}C NMR ($CDCl_3$, 125 MHz): 73.8, 69.4, 32.1, 30.6, 29.6, 26.3, 22.9, 14.3. IR (KBr, cm^{-1}): 3492, 2924, 1652, 1578, 1468, 1429, 1373, 1338, 1271, 1113. Anal. Calcd for $C_{106}H_{180}CuN_2O_{10}$: C, 74.62; H, 10.63; N, 1.64. Found: C, 74.40; H, 10.76; N, 1.56.

*2.3.13 Copper(II) complex of 3,4,5-tridodecyloxyphenacyl-5-dodecyloxypyridine (***Cu3***)*

Yield: 78.1%. ^{1}H NMR ($CDCl_3$): δ 3.95 (br, O–CH_2–, 16H), 1.75 (br, OCH_2–CH_2–, 16H), 1.53–0.98 (br, –CH_2–, 144H), 0.88 (br, –CH_3, 24H). ^{13}C NMR ($CDCl_3$, 125 MHz): 73.8, 69.4, 32.1, 30.6, 29.6, 26.3, 22.9, 14.3. IR (KBr, cm^{-1}): 3531, 2922, 1650, 1577, 1467, 1429, 1370, 1341, 1262, 1113. Anal. Calcd for $C_{122}H_{212}CuN_2O_{10}$: C, 75.90; H, 11.07; N, 1.45. Found: C, 76.02; H, 11.23; N, 1.40.

*2.3.14 Palladium(II) complex of 3,4,5-trioctyloxyphenacyl-5-octyloxypyridine (***Pd1***)*

Yield: 95.1%. ^{1}H NMR ($CDCl_3$): δ 8.68 (s, Ar–H, 2H), 7.20 (d, $J = 8.8$ Hz, Ar–H, 2H), 6.99 (d, $J = 8.9$ Hz, Ar–H, 2H), 6.94 (s, Ar–H, 4H), 5.71 (s, vinylic proton, 2H), 4.0 (tt, overlap, O–CH_2–, 12H), 3.88 (t, $J = 6.4$ Hz, O–CH_2–, 4H), 1.81–1.64 (m, OCH_2–CH_2–, 16H), 1.55–1.21 (m, –CH_2–, 80H), 0.91 (t, $J = 6.5$ Hz, –CH_3, 24H). ^{13}C NMR ($CDCl_3$, 125 MHz): 164.8, 152.9, 150.4, 148.1, 139.3, 135.0, 132.5, 126.5, 122.8, 105.7, 96.1, 73.7, 69.5, 32.1, 30.6, 29.8, 26.3, 22.9, 14.3. IR (KBr, cm^{-1}): 3449, 2922, 1619, 1578, 1493, 1429, 1378, 1331, 1257, 1182, 1114. Anal. Calcd for $C_{90}H_{148}N_2O_{10}Pd$: C, 70.90; H, 9.78; N, 1.84. Found: C, 71.13; H, 9.98; N, 1.79.

*2.3.15 Palladium(II) complex of 3,4,5-tridecyloxyphenacyl-5-decyloxypyridine (***Pd2***)*

Yield: 97.4%. ^{1}H NMR ($CDCl_3$): δ 8.68 (s, Ar–H, 2H), 7.20 (d, $J = 8.8$ Hz, Ar–H, 2H), 6.99 (d, $J = 8.9$ Hz, Ar–H, 2H), 6.94 (s, Ar–H, 4H), 5.71 (s, vinylic proton, 2H), 4.0 (tt, overlap, O–CH_2–, 12H), 3.88 (t, $J = 6.4$ Hz, O–CH_2–, 4H), 1.81–1.64 (m, OCH_2–CH_2–, 16H), 1.55–1.21 (m, –CH_2–, 112H), 0.91 (t, $J = 6.5$ Hz, –CH_3, 24H). ^{13}C NMR ($CDCl_3$, 125 MHz): 164.8, 152,9, 150.4, 148.1, 139.3, 135.0, 132.5, 126.5, 122.8, 105.7, 96.1, 73.7, 69.5, 32.1, 30.6, 29.8, 26.3, 22.9, 14.3. IR (KBr, cm^{-1}): 3487, 2920, 1620, 1578, 1493, 1431, 1378, 1325, 1257, 1182, 1114. Anal. Calcd for $C_{106}H_{180}N_2O_{10}Pd$: C, 72.79; H, 10.37; N, 1.60. Found: 72.50; H, 10.51; N, 1.58.

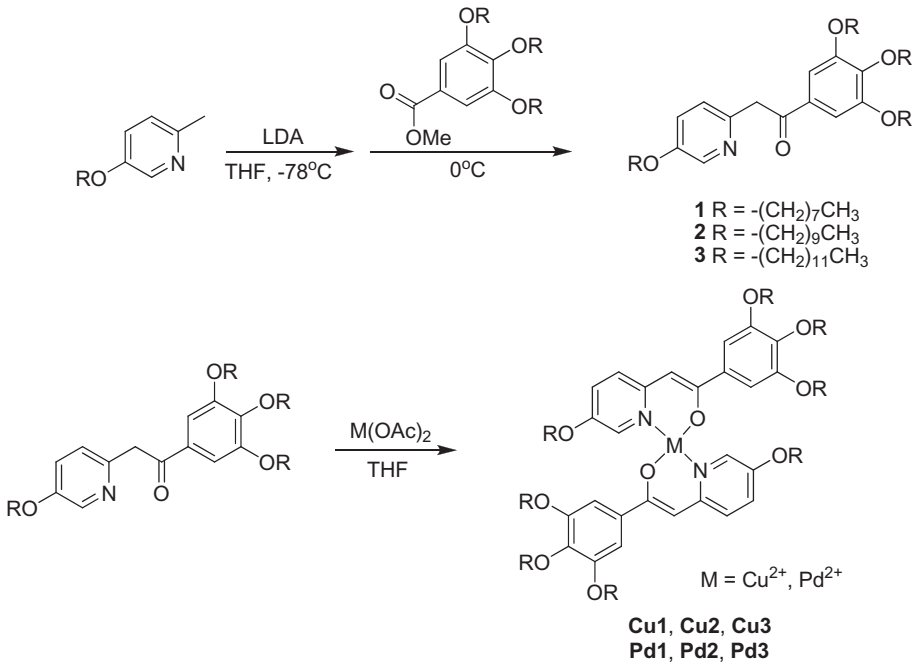
*2.3.16 Palladium (II) complex of 3,4,5-tridodecyloxyphenacyl-5-dodecyloxypyridine (***Pd3***)*

Yield: 93.1%. ^{1}H NMR ($CDCl_3$): δ 8.68 (s, Ar–H, 2H), 7.20 (d, $J = 8.8$ Hz, Ar–H, 2H), 6.99 (d, $J = 8.9$ Hz, Ar–H, 2H), 6.94 (s, Ar–H, 4H), 5.71 (s, vinylic proton, 2H), 4.0 (tt, overlap, O–CH_2–, 12H), 3.88 (t, $J = 6.4$ Hz, O–CH_2–, 4H), 1.81–1.64 (m, OCH_2–CH_2–, 16H), 1.55–1.21 (m, –CH_2–, 144H), 0.91 (t, $J = 6.5$ Hz, –CH_3, 24H). ^{13}C NMR ($CDCl_3$, 125 MHz): 164.8, 152,9, 150.4, 148.1, 139.3, 135.0, 132.5, 126.5, 122.8, 105.7, 96.1, 73.7, 69.5, 32.1, 30.6, 29.8, 26.3, 22.9, 14.3. IR (KBr, cm^{-1}): 3473, 2922, 1617, 1578, 1488, 1429, 1378, 1331, 1249, 1182, 1116. Anal. Calcd for $C_{122}H_{212}N_2O_{10}Pd$: C, 74.25; H, 10.83; N, 1.42. Found: C, 74.43; H, 11.06; N, 1.42.

3. Results and discussion

Phenacylpyridine ligands and their metal complexes were prepared according to Scheme 2. Picoline derivatives with an alkoxy chain were prepared by the reaction of 5-hydroxy-2-methylpyridine with alkyl bromides in *N*,*N*-dimethylformamide using potassium carbonate as a base [22, 23]. In a similar manner, methyl 3,4,5-trialkoxybenzoates were obtained from methyl 3,4,5-trihydroxybenzoates and alkyl bromides [24]. 5-Alkoxy-2-methylpyridines were metallated with lithium diisopropylamine and reacted with methyl benzoates to give ligand compounds **1**–**3**. Metal complexes **Cu1**–**3** and **Pd1**–**3** were prepared by complexation of the ligands with copper(II) acetate and palladium(II) acetate in tetrahydrofuran, respectively.

The ligands and their metal complexes were characterised by ^{1}H NMR, ^{13}C NMR, FT-IR, UV-Vis spectroscopy and elemental analysis. The ^{1}H NMR spectra of the ligands in $CDCl_3$ showed that enol and keto forms coexisted at room temperature. The peaks of the vinyl



Scheme 2. Synthesis of phenacylpyridine ligands and their metal complexes.

proton of the enol form and the protons of the keto form appeared at around 5.9 and 4.4 ppm, respectively. From the area ratio of these two peaks, the compositions of the keto forms were determined to be 80% for **1**, 92% for **2** and 88% for **3**. After coordination with palladium(II), only the vinyl proton peak appeared at 5.7 ppm indicating that the keto tautomers had been converted to enols during complexation. The phenacylpyridine coordinated with metal ions in a similar manner to the salicylaldimine. In the enol form of the phenacylpyridine, the nitrogen of the heterocyclic ring and the oxygen of the enol would match the nitrogen of the imino group and the oxygen of the phenol group of the salicylaldimine, respectively. In the ^{1}H NMR spectra of the copper(II) complexes, the peaks of the aromatic parts near to copper(II) did not appear due to the antiferromagnetic nature of copper(II), while the peaks of the alkyl tails, which were distant from the centre, still appeared.

In the IR spectra of the ligands, C=C stretching vibration peaks were observed around 1672 cm^{-1}, suggesting the existence of enol forms in the solid state. After the complexation with copper and palladium, the peaks were shifted by 20 and 53 cm^{-1}, respectively, to lower wavelengths (1652 and 1619 cm^{-1}). Figure 1 shows the UV-Vis spectra of ligand **2** and its metal complexes in tetrahydrofuran. Two broad absorption bands that appeared at 290 and 348 nm were shifted to 308 and 380 nm and to 322 and 389 nm after complexation with copper and palladium, respectively.

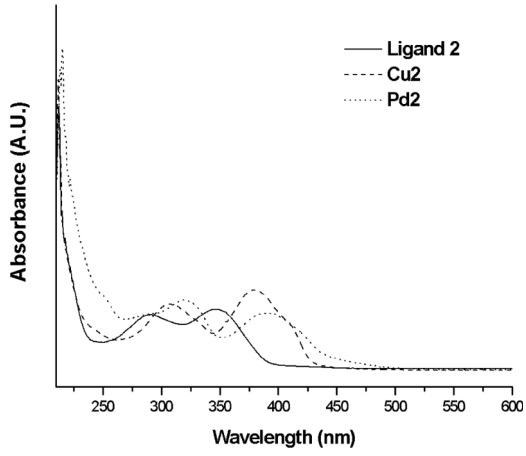


Figure 1. UV-Vis spectra of ligand **2**, **Cu2** and **Pd2**.

The thermotropic properties of the complexes were investigated by polarising optical microscopy (POM) and differential scanning calorimetry (DSC). Ligands **1**–**3** did not form liquid crystals, but their metal complexes showed enantiotropic mesophases, except **Pd1**. In the DSC analysis, for example, **Cu2** showed a melt transition at 59.6°C with an enthalpy of 5.5 kJ/mol on heating. In the subsequent cooling cycle, an isotropic to liquid crystal transition occurred at 51.7°C with an enthalpy of 6.1 kJ/mol and a liquid crystal to crystal transition occurred at –37.8°C with an enthalpy of 4.1

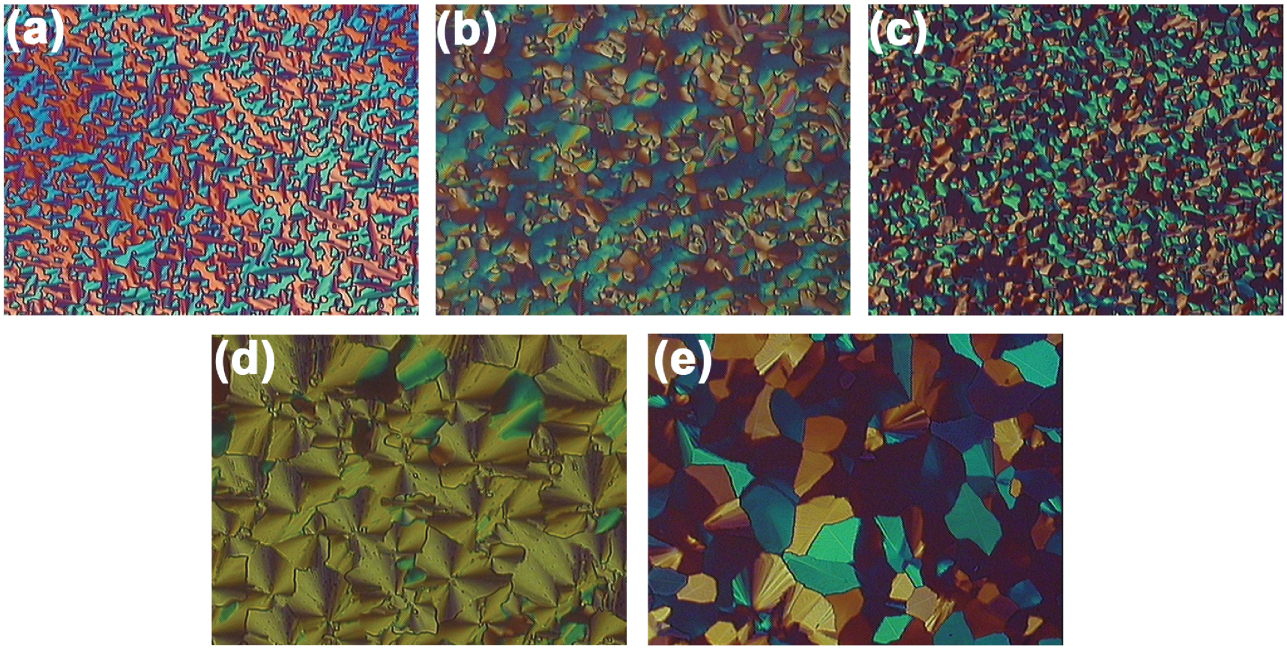


Figure 2. POM images of (a) **Cu1**, (b) **Cu2**, (c) **Cu3**, (d) **Pd2** and (e) **Pd3**.

kJ/mol. In the POM analysis, a birefringent phase with a mosaic texture was observed on heating and cooling (Figure 2). **Cu1**, **Cu3**, **Pd2** and **Pd3** complexes also showed enantiotropic transitions similar to those of **Cu2**. These mesophases were all stable even at room temperature. The phase transition temperatures and corresponding enthalpy values for the complexes are given in Table 1.

The liquid crystalline structures of the complexes were investigated by using an XRD technique. In the small angle X-ray diffractogram of **Cu1** obtained at room temperature on cooling, three reflection peaks corresponding to the d spacings of 2.40, 1.38 and 1.20 nm appeared (Figure 3). These reflections were indexed in sequence as (100), (110) and (200) of a hexagonal columnar lattice with the lattice parameter of $a = 2.77$ nm. **Cu2** and **Cu3** showed two reflection peaks corresponding to the d spacings of 2.53 and 1.45 and 2.67 and 1.53 nm, respectively. These reflections were indexed in sequence as (100) and (110) of a hexagonal columnar lattice with the lattice parameters of $a = 2.92$ and 3.08 nm, respectively. The length of **Cu1** calculated using the MM2 method (inset of Figure 3) was about 0.7 nm longer than the lattice constant. We presumed that interdigitation of alkoxy chains occurred between the columns. The interdigitation length of the alkoxy chains increased as the length of the alkoxy chains increased. **Pd2** and **Pd3** also showed two peaks for (100) and (110) reflections. The XRD data of the complexes are summarised in Table 2.

4. Conclusions

We prepared metallomesogens based on phenacylpyridine ligands. The ligands were isolated as a mixture of two tautomer forms, keto and enol. The enols were suitable for coordination with Cu(II) and Pd(II) to form stable metal complexes. The metal complexes of phenacylpyridines showed a superior ability to self-assemble into ordered phases on heating and cooling compared to their structural analogues, the salicylaldiminato complexes. They formed columnar hexagonal mesophases even at room temperature.

Table 1. DSC data of the complexes (scan rate: 10°C min^{-1}).

Compound	T/°C (ΔH/kJ mol^{-1}) on heating	T/°C (ΔH/kJ mol^{-1}) on cooling
Cu1	Col_h 51.4 (3.0) I	I 44.2 (3.9) Col_h
Cu2	Cr –25.4 (5.5) Col_h 59.6 (5.5) I	I 51.7 (6.1) Col_h –37.8 (4.1) Cr
Cu3	Cr 12.8 (58) Col_h 54.2 (5.6) I	I 45.7 (5.8) Col_h –0.4 (58) Cr
Pd1	Glassy 35.6 (1.2) I	
Pd2	Cr –10.8 (5.6) Col_h 42.0 (2.4) I	I 28.1 (1.0) Col_h –22.8 (4.5) Cr
Pd3	Cr 10.7 (50) Col_h 51.3 (6.1) I	I 46.4 (5.7) Col_h –3.2 (49) Cr

Cr = crystal; Col_h = hexagonal columnar; I = isotropic.

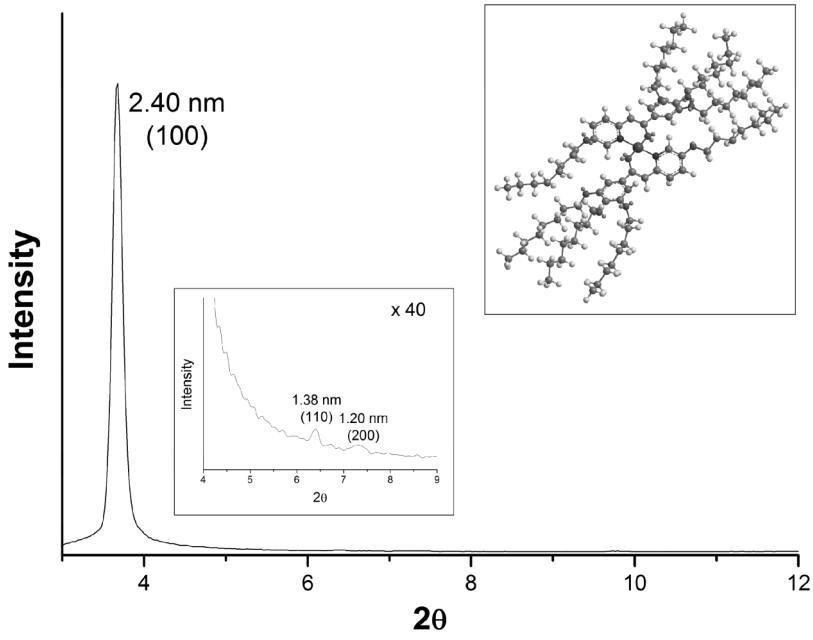


Figure 3. X-ray diffractogram of **Cu1**. The inset shows the molecular model of **Cu1**.

Table 2. XRD data of liquid crystalline phases.

Compound	Phase	*d* spacing/nm (index)	*a*/nm	l_{calc}/nm
Cu1	Col_h	2.40 (100), 1.38 (110), 1.20 (200)	2.77	3.48
Cu2	Col_h	2.53 (100), 1.45 (110)	2.92	4.00
Cu3	Col_h	2.67 (100), 1.53 (110)	3.08	4.49
Pd2	Col_h	2.66 (100), 1.58 (110)	3.07	4.00
Pd3	Col_h	2.78 (100), 1.61 (110)	3.21	4.49

Col_h = hexagonal columnar; a = lattice constant; l_{calc} = calculated extended length of the compound.

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