JOURNAL OF Materials CHEMISTRY

Formation of columnar arrangements in copper(II) complexes of 2-phenylazomethinopyridine derivatives

Chung K. Lai,* Kuo-Wen Wang and Raymond Lin

Department of Chemistry, National Central University, Chung-Li, Taiwan, ROC

Received 7th August 1998, Accepted 20th August 1998

The synthesis and mesomorphic properties of a homologous series of 2-(3′,4′,5′-trialkoxyphenyl)-azomethinopyridines and their copper(II) complexes are reported. Liquid crystalline properties of the copper(II) complexes were studied by DSC analysis and polarized optical microscopy. The results indicated that copper complexes with six sidechains (**3**) exhibited columnar phases, whereas copper(II) complexes with two or four sidechains (**1** and **2**) formed only crystalline phases. The structures of the mesophases for copper(II) complexes **3** were characterized and confirmed as disordered hexagonal columnar phases (Col_{hd}) by powder X-ray diffraction. Relatively high clearing points and the short range of mesophase temperature for the copper complexes were attributed to a relatively strong interaction of pyridyl core–core groups within the columns. The EPR spectra measured at various temperatures were also examined.

Introduction

Generation of various geometries and molecular shapes by incorporation of metal centers into organic moieties has been widely applied to produce metallomesogenic structures.[1,2] Transition metal coordination compounds are the largest category among this type of metallomesogenic materials owing to their well known chemistry and rich structural diversity. Columnar arrangements[3–5] can be generated by use of complementary shapes of various molecules; disc-like,[3,4] half disc-like[5] or tapered molecules, and of those, disc-like molecular structures are often formed by symmetric bonds with coordination metal centers. Ligands used in this group were mostly of various derivatives;[1a] such as β-diketones, salicylaldehydes, salicylaldimines, enaminoketones, aroylhydrazine and pyrroles. Metal complexes thus prepared often produced disc-like shaped molecules, and usually exhibited hexagonal or/and rectangular columnar phases. These so-called metal-containing liquid crystals are highly promising potential candidates in electro-magnetic applications. In addition, the metal centers incorporated are also found to play an important role in the resulting mesomorphic properties and physical properties. Selective incorporation of different metal centers with a specific ligand often results in completely opposite mesomorphic properties. While a detailed explanation based on the structural and electronic configuration of metal centers on the mesomorphic properties has been extensively discussed, a precise prediction of phase behavior has not yet been feasible. Here, we report the preparation, characterization and mesomorphic properties of a new series of copper complexes derived from 2-(3,4,5-trialkoxyphenyl)azomethinopyridine structures, which exhibit disordered hexagonal columnar phases.

Results and discussion

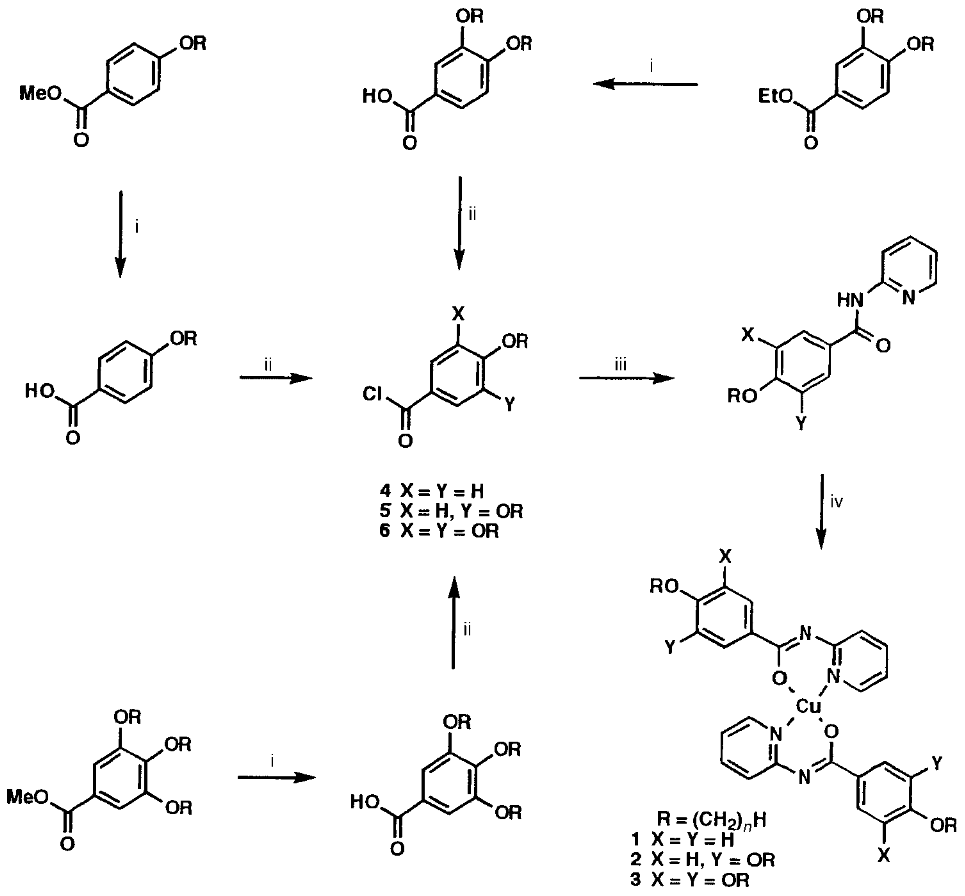
Synthesis

The synthetic route used to prepare substituted 2-phenylazomethinopyridine derivatives and their copper(II) complexes is shown in Scheme 1. Methyl 3,4,5-trialkoxybenzoates and 3,4,5-trialkoxybenzoic acids were synthesized by literature procedures,[4] and 3,4,5-trialkoxybenzoic acid chlorides were obtained from the reaction of 3,4,5-trialkoxybenzoic acids and thionyl chloride in dried tetrahydrofuran. The 2-(3,4,5-trialkoxyphenyl)azomethinopyridine derivatives were synthesized by a condensation reaction of 2-aminopyridine with freshly prepared 3,4,5-trialkoxybenzoic acid chlorides in dried pyridine. These pyridine-based ligands obtained were white and obtained in a yield of 86–90%, and are highly soluble in organic solvents. The ligands were characterized by ^1H and ^{13}C NMR spectroscopy. Three characteristic peaks at δ 5.64, 6.75 and 10.19 were assigned to olefinic methine-H (–CH=C–), aldehyde-H (–CH=N–) and imine-H (–C=N–H), and correct structures were also supported by characteristic ^{13}C NMR peaks at *ca.* 189.63 and 153.73 assigned to keto C–O and C–N groups. Copper(II) complexes were obtained by the reaction of 2-phenylazomethinopyridines with copper(II) perchlorate hexahydrate in refluxing THF–methanol. Reactions with copper(II) acetate or copper(II) chloride with or without a base (for example KOH) resulted in recovery of intact ligands. Recrystallization twice from THF–methanol gave pure yellow–greenish solids. Copper (d^9) compounds which are paramagnetic display only broad alkoxy signals in ^1H and ^{13}C NMR spectra. Elemental analysis data in Table 1 also confirmed the purity and identity of the complexes.

Mesomorphic properties

Liquid crystalline behavior for these copper(II) complexes was studied and characterized by DSC analysis and polarized optical microscopy. The formation of mesophases was found to be sensitive to the numbers of sidechains and the carbon length of the sidechains, as often observed in columnar phases. Copper complexes with six sidechains (**3**) exhibited columnar phases, whereas copper(II) complexes with two (**1**) or four sidechains (**2**) formed only crystalline phases. The phase-transition temperatures and enthalpies of all copper complexes **1**–**3** are given in Table 2. For complexes **3**, only when the carbon chain lengths (n) were $\geqslant 16$, (*i.e.* $n=16$ and $n=18$) was liquid crystallinity observed. The DSC analysis of copper complexes **3** showed typical columnar phase transitions of crystal-to-columnar-to-isotropic ($K \rightarrow Col \rightarrow I$). Additional crystal-to-crystal ($K_1 \rightarrow K_2$) transitions were also observed for complexes with lower carbon chain lengths (*i.e.* $n=10$, 12, 14).

Upon heating, copper complexes melt into liquid crystalline phases with an optical texture of columnar superstructures as is often observed for disc-shaped molecules, and the textures observed showed highly characteristic birefrigence.[4] A typical larger enthalpy (10.6–20.7 kJ mol^{-1}) for the crystal-to-liquid crystal transition at lower temperatures (161–177 °C) and a relatively lower enthalpy (0.84–1.60 kJ mol^{-1}) for the liquid crystal-to-isotropic transition at higher temperatures



Scheme 1 *Reagents and conditions*: i, KOH (2.0 equiv.), refluxing in THF–H_2O (10:1), 12–24 h, 92–96%; ii, $SOCl_2$ (2.0 equiv.), refluxing in dried THF, 4 h; iii, 1-aminopyridine (1.0 equiv.), refluxing in dried pyridine at 0 °C, then warming up and stirring at room temp., 16 h, 86–90%; iv, $Cu(ClO_4)_2 \cdot H_2O$, refluxing in THF–EtOH, 2 h, 76–82%.

Table 1 Elemental analysis data (%) of copper(II) complexes **1**–**3**[a]

Compound		C	H	N
3	$n = 12$	74.01 (73.73)	10.53 (10.44)	3.54 (3.58)
	14	75.02 (74.89)	10.93 (10.82)	3.24 (3.23)
	16	75.99 (75.84)	11.36 (11.14)	3.02 (2.95)
	18	76.71 (76.63)	11.45 (11.40)	2.75 (2.71)
2	18	75.55 (75.27)	10.68 (10.66)	3.72 (3.66)
1	18	72.64 (72.43)	9.22 (9.12)	5.67 (5.63)

[a]Required values in parentheses.

(179–180 °C) were observed. This relatively low value of the transition enthalpy indicated that the mesophases were highly disordered. The temperature range of columnar mesophases for the copper complexes is slightly sensitive to the carbon number of sidechains. At the crystal-to-columnar transition the flexible side chains undergo disordering but the central core remains stacked in columns, however, the core unstacked at the columnar-to-isotropic transition.

When cooled from their isotropic phases, the liquid crystalline complexes displayed optical textures, shown in Fig. 1, which were a mixture of pseudo focal-conics and mosaic regions with linear birefrigent defects, suggesting hexagonal columnar structures. The possibility of rectangular phases was also easily excluded owing to the absence of mosaic textures with prominent wedge-shaped defect patterns. To further confirm the structure of the mesophases, we performed a powder XRD diffraction experiment. The copper complex **3** ($n = 18$) displayed a diffraction pattern of a two-dimensional hexagonal lattice with an intense peak at $2\theta = 43.61°$ at 175 °C. This diffraction corresponded to an intercolumnar distance (*a* parameter of the hexagonal lattice) of 50.34 Å. However, liquid-like correlations between the rigid cores occurred at wider angle regions of 5.21 Å. Two other weaker characteristic diffractions[4] corresponding to Miller indices (110) and (200), respectively, with a *d*-spacing ratio of $(1/3)^{1/2}$ and $(1/4)^{1/2}$ were however not observed. The absence of distinct peaks at higher angle was consistent with DSC analysis of a relatively lower enthalpy for the columnar-to-isotropic transition, indicative of a highly disordered mesophase; *i.e.* there is no long-range order along the columns.

In most metallomesogens reported, the formation of liquid crystals is found to be controlled or determined by the magnitude of the intermolecular interaction forces[1a] which hold the metallomesogenic structures together. When they are either too weak or too strong, a liquid crystalline phase is not observed. Compared with other similar copper(II) complexes with six sidechains, one feature noted for copper complexes **3** is that only derivatives with longer chains ($n = 16$ and 18) exhibited columnar phases and derivatives with shorter chains ($n = 10$, 12, 14) formed crystalline phases. Meanwhile they have a relatively short range (4.0–18 °C) of mesophase temperatures. An increased electron density due to the presence of lone pair electrons on the nitrogen atoms appears to increase the intermolecular interaction between the stacking molecules, and this increasing force causes an increase in molecular packing or regularity within the columns. Therefore, longer chains or/and more chains were critically needed to induce the mesophase, and only a short temperature range of the mesophase was observed.

EPR studies

X-Band EPR spectra of the copper complex **3** ($n = 16$) measured at different temperatures are shown in Fig. 2. The

Table 2 Phase behavior[a] of copper(II) complexes **1**–**3**

3	$n=12$	K_1	78.7 (17.4) ⇌ 71.5 (16.5)	K_2	196.7 (19.4) ⇌ 176.2 (15.8)	I		
	14	K_1	88.3 (25.8) ⇌ 82.4 (30.1)	K2	185.0 (22.3) ⇌ 172.7 (19.4)	I		
	16	K_1	87.7 (29.1) ⇌ 83.3 (26.8)	K_2	176.8 (19.4) ⇌ 159.8 (20.7)	Col_{hd}	179.1 (1.22) ⇌ 173.4 (1.60)	I
	18	K_1	94.3 (21.6) ⇌ 88.3 (27.2)	K_2	161.2 (10.6) ⇌ 137.9 (12.0)	Col_{hd}	179.6 (0.90) ⇌ 172.4 (0.84)	I
2	18	K_1	84.3 (30.8) ⇌ 77.7 (33.0)	K_2	240.2 ⇌ 216.2	I_d		
1	18	K_1	94.3 (21.6) ⇌ 88.3 (27.2)	K_2	294.5 ⇌ 269.2	I_d		

[a] n is the number of carbons in the alkoxy chain. K_1,K_2=crystal phases; Col_{hd}=columnar hexagonal disordered phase; I=isotropic; I_d= isotropic with decomposition. The transition temperatures (°C) and enthalpies (in parentheses, kJ mol) were determined by DSC at a scan rate of 5.0 °C min^{-1}.

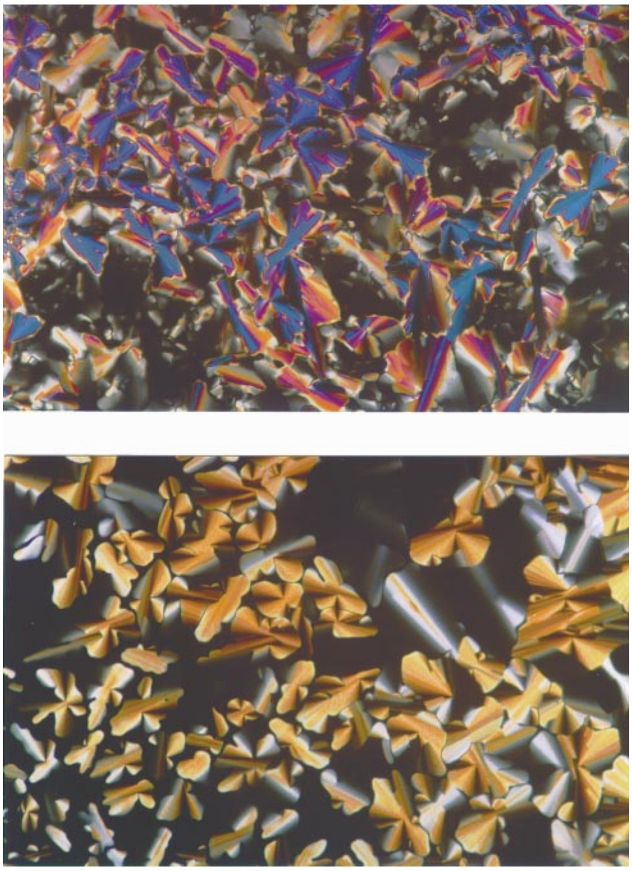


Fig. 1 Optica l textures (100 ×) exhibited by complex **3** (n=16). Col_{hd} phase at 170 °C (top: thick sample) and at 165 °C (bottom: thin sample).

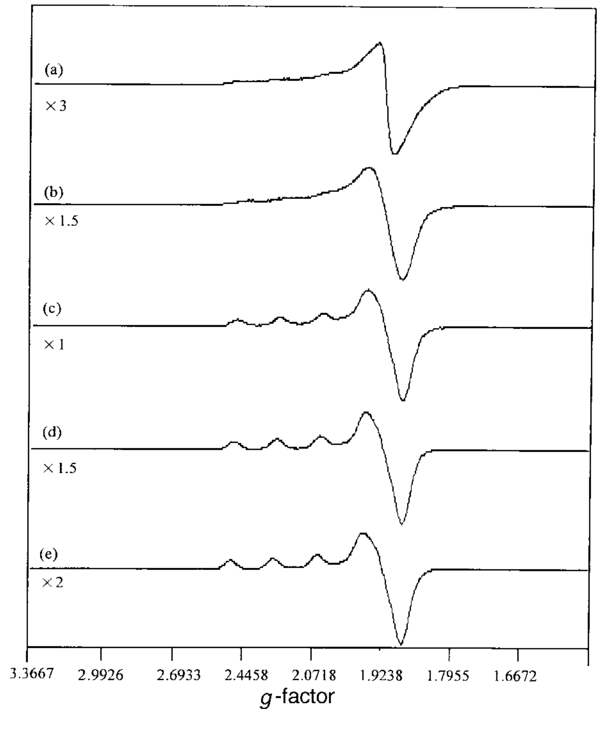


Fig. 2 EPR spectra of copper complex **3** (n=16) measured at: (a) room temperature of as-prepared sample, (b) 459 K; isotropic phase, (c) 438 K; columnar phase, (d) 370 K; crystalline phase, (e) cooling back to room temperature.

top spectrum in Fig. 2(a) was for the as-prepared sample measured at room temperature, and consisted of two features, one barely observable shoulder at low field and a high-field signal. When the sample was heated to the clearing point at 186 °C the signal width [Fig. 2(b)] became broader and unsymmetric with increased intensity. However, the spectrum on cooling to 165 °C [Fig. 2(c)] corresponding to the mesophase, showed signals with clear hyperfine lines in the low-field region, with three signals being observable and resolved. As the temperature was further reduced to 97 °C [Fig. 2(d)] and 25 °C [Fig. 2(e)], similar signals were observed. The slight change of these signals with temperature was probably due to a preferred molecular orientation or arrangement at different temperatures. Mesogenic copper complexes of bidentate Schiff bases have been extensively[6] studied by EPR spectroscopy. In most derivatives broad and unsymmetric signals at different temperatures were observed, and the absence of the hyperfine structures was generally attributed to the strong exchange interaction among the paramagnetic copper centers.

Conclusion

Systematic studies on a homologous series of compounds have allowed for a better understanding of the relationship between the molecular structures and mesomorphic properties. Mesomorphic data obtained in this work suggested that the mesophases might be thermodynamically destabilized due to the presence of nitrogen electron lone pairs. Strong molecular interactions in the mesophase could be partially overcome with surrounding by more or/and longer flexible chains.

Experimental

All chemicals were reagent grade from Aldrich and used without further purification. THF was dried over sodium benzophenone ketyl, and pyridine was predried over KOH pellets for prolonged periods and followed by fresh distillation from BaO before use. ^{1}H and ^{13}C NMR spectra were measured on a Bruker DRS-200 spectrometer in $CDCl_3$ using TMS as an internal standard. IR spectra were recorded on a Bio-Rad FTS-155 instrument using polystyrene as a standard. DSC thermograms were obtained on a Perkin-Elmer DSC-7 instrument and calibrated with a pure indium sample. All phase behaviors were determined at a scan rate of 10.0 °C min^{-1} unless otherwise noted. Optical polarized microscopy was carried out on Nikkon MICROPHOT-FXA instrument with a Mettler FP90/FP82HT hot stage system. X-Ray powder diffraction (XRD) studies were conducted on an INEL MPD-diffractometer with a 2.0 kW Cu-Kα X-ray source equipped with an INEL CPS-120 position sensitive detector and a variable temperature capillary furnace with an accuracy of ±0.10 °C in the vicinity of the capillary tube (80 mm long × 0.01 mm thick from Charles Supper Co). The detector was calibrated using mica and silicon standards. EPR measurements were taken with a EMX Bruker spectrometer in X-band and powder samples were placed into quartz tubes of 2.0 mm diameter. Methyl 3,4,5-trialkoxybenzoate esters, methyl 4-alkoxybenzoate esters and ethyl 3,4-dialkoxybenzoate esters were prepared by literature procedures.

Methyl 3,4,5-tridodecyloxybenzoate

White solid, yield 90%. ^{1}H NMR ($CDCl_3$): δ 0.86(t, CH_3, 9H), 1.26–1.84(m, CH_2, 60H), 3.88(s, OCH_3, 3H), 4.03(t, OCH_2, 6H), 7.25(s, C_6H_2, 2H). ^{13}C NMR ($CDCl_3$): δ 14.18, 22.75, 26.14, 29.36, 29.45, 29.62, 29.71, 29.75, 29.39, 30.39, 32.00, 52.13, 69.22, 75.53, 105.02($C^{2,6}$), 124.69(C^1), 142.01($C^{3,5}$), 152.83(C^4), 166.89(C=O).

Ethyl 3,4-ditetradecyloxybenzoate

White solid, yield 87%. ^{1}H NMR ($CDCl_3$): δ 0.87(t, CH_3, 6H), 1.24–1.83(m, CH_2, 51H), 3.97(t, $J = 8.19$ Hz, OCH_2, 4H), 4.28(q, OCH_2, 2H), 6.80(d, $J = 8.44$ Hz, C_6H_3, 1H), 7.47(s, C_6H_3, 1H), 7.57(d, $J = 6.42$ Hz, C_6H_3, 1H). ^{13}C NMR ($CDCl_3$): δ 13.91, 14.21, 22.51, 25.84, 28.93, 29.21, 31.74, 60.48, 68.84, 69.13, 111.7(C^6), 114.2(C^2), 122.6(C^5), 123.2(C^1), 148.3(C^4), 152.9(C^3), 166.3(C=O).

Methyl 4-octadecanoxybenzoate

White solid, yield 95%. ^{1}H NMR ($CDCl_3$): δ 0.82(t, $J = 6.73$ Hz, CH_3, 3H), 1.24–1.84 (m, CH_2, 32H), 3.82(s, OCH_3, 3H), 3.93(t, $J = 7.31$ Hz, OCH_2, 2H), 6.84(d, $J = 8.82$ Hz, C_6H_4, 2H), 7.97(d, $J = 8.82$ Hz, C_6H_4, 2H). ^{13}C NMR($CDCl_3$): δ 14.04, 22.57, 25.93, 29.00, 29.14, 31.74, 51.43, 67.95, 113.83($C^{2,6}$), 122.16(C^1), 131.32($C^{3,5}$), 162.77(C^4), 166.53(C=O).

3,4,5-Tridodecyloxybenzoic acid (general procedure for 3,4,5-trialkoxylbenzoic acids)

A mixture of methyl 3,4,5-tridodecyloxy benzoate (5.0 g, 0.07 mol) and KOH (0.56 g, 0.10 mol) was refluxed in 100 ml of THF–H_2O (6:4, v/v) for 24 h and the solution extracted twice with dichloromethane (100 ml). The CH_2Cl_2 layer was collected and dried over $MgSO_4$. The solution was concentrated to give a white solid, which was recrystallized from THF–MeOH or acetone. Yield 92%. ^{1}H NMR ($CDCl_3$): δ 0.86(t, CH_3, 9H), 1.14–1.83(m, CH_2, 60H), 4.00(t, OCH_2, 6H), 7.26(s, C_6H_2, 2H). ^{13}C NMR ($CDCl_3$): δ 14.00, 22.70, 26.22, 29.43, 29.77, 30.04, 31.95, 68.88, 73.36, 107.97, 126.00, 141.96, 152.57, 172.02.

3,4-Ditetradecyloxybenzoic acid

Yield 94%. ^{1}H NMR ($CDCl_3$): δ 0.92 (t, CH_3, 6H), 1.31(m, CH_2, 44H), 1.83(m, CH_2, 2H), 4.07(t, 4H, OCH_2, 4H), 6.89(d, C_6H_3, 1H), 7.53(s, C_6H_3, 1H), 7.58(d, C_6H_3, 1H). ^{13}C NMR ($CDCl_3$): δ 13.91, 22.53, 25.90, 25.73, 29.14, 29.21, 29.25, 29.41, 29.44, 29.49, 29.52, 29.58, 30.19, 31.77, 31.79, 69.00, 73.35, 116.4, 121.2, 148.0, 152.7, 172.0.

4-Octadecanoxybenzoic acid

White solid, yield 85%. ^{1}H NMR ($CDCl_3$): δ 0.86(t, 3H, CH_3), 1.23–1.83(m, CH_2, 32H), 3.93(t, 2H, OCH_2), 6.98(d, 2H, C_6H_4), 8.02(d, 2H, C_6H_4). ^{13}C NMR ($CDCl_3$): δ 14.03, 22.61, 25.91, 29.04, 29.29, 29.61, 31.85, 68.71, 114.09, 126.03, 129.69, 162.33, 171.82.

3,4,5-Tridecyloxybenzoic acid chloride (general procedure for the synthesis of 3,4,5-trialkoxybenzoic acid chlorides)

3,4,5-Tridecyloxybenzoic acid (5.0 g, 0.0085 mol) dissolved in dried THF (100 ml) was added dropwise to a THF solution of fresh $SOCl_2$ (1.24 ml, 0.017 mol) at ice-bath temperature under N_2 atmosphere. The mixture was stirred, and gently warmed to room temperature. The mixture was allowed to reflux for 4 h. The solution was concentrated to remove THF and excess $SOCl_2$. The milky paste was redissolved in 100 ml of dried THF, and then the solution concentrated. This process was repeated several times to remove any residual $SOCl_2$ which would affect the following reactions. The white solid thus obtained was directly used for the next reaction without any further purification or recrystallization.

3,4,5-Trioctadecanoxy-*N*-pyridin-2-ylbenzamide (general procedure for the synthesis of *N*-pyridin-2-ylbenzamide derivatives)

Freshly prepared 3,4,5-trioctadecanoxybenzoic acid chloride (5.0 g, 5.29 mmol) was dissolved in dried pyridine (50 ml) under nitrogen atmosphere, and to this solution 2-aminopyridine (0.50 g, 5.29 mmol) in pyridine (20 ml) was added slowly at room temperature. The mixture was stirred for 8 h, and then gently refluxed for 3 h. The solution was concentrated to half its volume, and left in a freezer overnight. The resulting white solid was filtered off, and recrystallized from THF–methanol. Yield 65%. ^{1}H NMR ($CDCl_3$): δ 0.85(t, CH_3, 9H), 1.14–1.83(m, CH_2, 96H), 4.01(t, OCH_2, 6H), 7.06(dd, C_5H_4N, 1H), 7.12(s, C_6H_2, 2H), 7.75(dd, C_5H_4N, 1H), 8.26(d, C_5H_4N, 1H), 8.38(d, C_5H_4N, 1H), 8.81(s, NH, 1H). ^{13}C NMR ($CDCl_3$): δ 14.10, 22.06, 22.68, 29.36, 29.71, 30.32, 31.92, 69.35, 73.54, 105.77, 114.13, 119.83, 128.89, 138.53, 141.77, 147.77, 151.65, 153.23, 165.48. IR (thin film): 3488, 3413, 2929, 2842, 1655, 1636, 1619, 1578, 1566, 1538, 1504, 1470, 1431, 1383, 1343, 1309, 1219, 1125, 987, 776 cm^{-1}.

3,4-Dioctadecanoxy-*N*-pyridin-2-yl-benzamide

White solid, yield 65.5%. ^{1}H NMR ($CDCl_3$): δ 0.85(t, CH_3, 6H), 1.23–1.81(m, CH_2, 64H), 4.01(t, OCH_2, 4H), 6.87(d, C_6H_3, 1H), 7.08(dd, C_5H_4N, 1H), 7.43(s, C_6H_3, 1H), 7.47(d, C_6H_3, 1H), 7.74(dd, C_5H_4N, 1H), 8.27(d, C_5H_4N, 1H), 8.39(d, C_5H_4N, 1H), 8.81 (s, NH, 1H). ^{13}C NMR ($CDCl_3$): δ 13.93, 22.52, 25.84, 29.03, 29.23, 29.55, 31.76, 69.14, 102.02, 112.54, 114.09, 119.04, 120.15, 126.25, 138.30, 147.43, 148.91, 151.75, 152.47, 165.28.

4-Octadecanoxy-*N*-pyridin-2-ylbenzamide

White solid, yield 62%. ^{1}H NMR ($CDCl_3$): δ 0.80(t, CH_3, 3H), 0.94–1.79(m, CH_2, 32H), 3.91(t, OCH_2, 2H), 6.91(d, C_6H_4, 2H), 7.07(dd, C_5H_4N, 1H), 7.75(dd, C_5H_4N, 1H), 7.74(d, C_6H_4, 2H), 8.28(d, C_5H_4N, 1H), 8.39(d, C_5H_4N, 1H), 8.81(s, NH, 1H). ^{13}C NMR ($CDCl_3$): δ 14.03, 22.61, 25.91, 29.04, 29.29, 29.61, 31.85, 68.17, 114.32, 112.08, 119.44, 126.03, 129.21, 138.44, 147.36, 151.87, 162.34, 165.35.

Bis[3,4,5-trioctadecanoxy-*N*-pyridin-2-ylbenzamide]copper(II) (general procedure for the synthesis of copper complexes of *N*-pyridin-2-ylbenzamide derivatives)

3,4,5-Trioctadecanoxy-*N*-pyridin-2-ylbenzamide (0.20 g, 0.023 mmol) dissolved in THF (5.0 ml) was added to a solution of copper(II) perchlorate hexahydrate (0.042 g, 0.0115 mmol) in methanol (10 ml). Upon addition a light green solid started to suspend in solution, and the solution was gently refluxed for 2 h. The green solid was filtered off, collected and recrystallized from CH_2Cl_2–MeOH. Yield 82%. IR (thin film): 2929, 2848, 1624, 1577, 1529, 1503, 1469, 1429, 1341, 1240, 1119, 1051, 783, 729, 628 cm^{-1}. Anal. Calc. for $C_{132}H_{234}N_4O_8Cu$: C, 76.63; H, 11.40; N, 2.71. Found: C, 76.71; H, 11.45; N, 2.75%.

Bis[3,4-dioctadecanoxy-*N*-pyridin-2-ylbenzamide]copper(II)

Green solid, yield 87%. IR (thin film): 2929, 2862, 1664, 1637, 1570, 1516, 1483, 1119, 1055, 781, 728, 631 cm^{-1}. Anal. Calc. for $C_{96}H_{162}N_4O_6Cu$: C, 75.27; H, 10.66; N, 3.66. Found: C, 75.55; H, 10.68; N, 3.72%.

Bis[4-octadecanoxy-*N*-pyridin-2-ylbenzamide]copper(II)

Green solid, yield 78%. IR (thin film): 2922, 2862, 1617, 1604, 1516, 1475, 1355, 1268, 1240, 1180, 1093, 1066, 783, 622 cm^{-1}. Anal. Calc. for $C_{60}H_{90}N_4O_4Cu$: C, 72.43; H, 9.12; N, 5.63. Found: C, 72.64; H, 9.22; N, 5.67%.

Acknowledgments

We thank the National Science Council of Taiwan, ROC for funding (NSC-88-2113-M-008-009) in generous support of this work.

References

1 (*a*) J. L. Serrano, in *Metallomesogens; Synthesis, Properties, and Applications*, VCH, New York, 1996; (*b*) D. W. Bruce and D. O'Hare, *Inorganic Materials*, John Wiley & Sons, 1992, pp. 407–490.

2 S. A. Hudson and P. M. Maitlis, *Chem. Rev.*, 1993, **93**, 861; P. Espinet, M. A. Esteruelas, L. A. Oro, J. L. Serrano and E. Sola, *Coord. Chem. Rev.*, 1992, **117**, 215; P. Maitlis and A. M. Giroud-Godquin, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 375.

3 (*a*) C. Destrade, P. Foucher, H. Gasparoux, H. T. Nguyen, A. M. Levelut and J. Malthete, *Mol. Cryst. Liq. Cryst.*, 1984, **106**, 121; (*b*) S. Chandrasekhar and G. S. Ranganath, *Rep. Prog. Phys.*, 1990, **53**, 57.

4 (*a*) C. K. Lai, C. H. Tsai and Y. S. Pang, *J. Mater. Chem.*, 1998, **8**, 1355; (*b*) C. K. Lai, C. H. Chang and C. H. Tsai, *J. Mater. Chem.*, 1998, **8**, 599; (*c*) C. K. Lai, F. G. Chen, Y. J. Ku, C. H. Tsai and R. Lin, *J. Chem. Soc., Dalton Trans.*, 1997, 4683; (*d*) C. K. Lai and F. J. Lin, *J. Chem. Soc., Dalton Trans.*, 1997, 17; (*e*) C. K. Lai, M. Y. Lu and F. J. Lin, *Liq. Cryst.*, 1997, **23**, 313; (*f*) H. Zheng, C. K. Lai and T. M. Swager, *Chem. Mater.*, 1995, **7**, 2067; (*g*) C. K. Lai, A. G. Serrete and T. M. Swager, *J. Am. Chem. Soc.*, 1992, **114**, 7948.

5 (*a*) S. T. Trzaska and T. M. Swager, *Chem. Mater.*, 1998, **10**, 438; (*b*) H. Zheng, C. K. Lai and T. M. Swager, *Chem. Mater.*, 1994, **6**, 101; (*c*) J. Barberá, C. Cativiela, J. L. Serrano and M. M. Zurbano, *Adv. Mater.*, 1991, **3**, 602; (*d*) H. Zheng, C. K. Lai and T. M. Swager, *Chem. Mater.*, 1994, **6**, 101; (*e*) A. G. Serrette, C. K. Lai and T. M. Swager, *Chem. Mater.*, 1994, **6**, 2252.

6 (*a*) P. J. Alonso, M. Marcos, J. I. Martínez, V. M. Orera, M. L. Sanjuán and J. L. Serrano, *Liq. Cryst.*, 1993, **13**, 585; (*b*) M. P. Eastman, M. Horng, B. Freiha and K. W. Shew, *Liq. Cryst.*, 1987, **2**, 223; (*c*) M. Ghedini, S. Morrone, D. Gatteschi and C. Zanchini, *Chem. Mater.*, 1991, **3**, 752; (*d*) N. Hoshino, A. Kodama, T. Shibuya, Y. Matsunaga and S. Miyajima, *Inorg. Chem.*, 1991, **30**, 3091; (*e*) E. Campillos, M. Marcos, J. L. Serrano, J. Barberá, P. L. Alonso and J. I. Martínez, *Chem. Mater.*, 1993, **5**, 1518.

Paper 8/06268D