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FULL PAPER

Ionic columnar metallomesogens formed by three-coordinated copper(I) complexes

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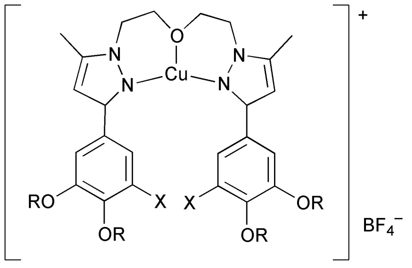
Two series of copper(I) complexes (**1**, **2**) derived from bis{2-[3′-(3″,4″-dialkoxyphenyl)-5′-methyl-1′-pyrazolyl]ethyl} ethers and from bis{2-[3′-(3″,4″,5′-trialkoxyphenyl)-5′-methyl-1′-pyrazolyl]ethyl} ethers were prepared and characterized. These ionic copper(I) complexes were obtained by reaction of the ethers with $[Cu(MeCN)_4]BF_4$ in refluxing acetonitrile. All three-coordinated copper(I) complexes isolated as off-white solids were characterized by NMR spectroscopy and elemental analysis, and their mesomorphic properties were also studied by polarized optical microscopy, differential scanning calorimetry (DSC) and powder X-ray diffraction (XRD). Results indicated that these complexes exhibited hexagonal columnar phases (Col_h). The clearing points of all compounds were relatively low (94–112 °C) and the temperature range of the mesophases was *ca.* 45–68 °C. Powder XRD diffraction patterns showed three sharp reflections in the small angle region corresponding to a ratio of their positions of $1 : (1/3)^{1/2} : (1/2)$, indicating typical hexagonal columnar phases.

Introduction

Coordination compounds are known as the largest category among metallomesogenic materials.[1] Numerous coordination compounds with a variety of novel geometric metal centers and molecular shapes have been created by incorporation of metal centers. In addition, compounds with copper ions incorporated in the core group comprise the largest group in this type of metal-containing liquid crystals because of their well-known chemistry and/or versatile structures. The properties of the central copper ion, which shows a variety of coordination geometries in both the +I and the +II oxidation states, are largely controlled *via* the imposed coordination environment. However, those exhibiting liquid crystalline properties consist mostly of Cu(II) ions with square planar structures at the metal center. Known metallomesogens[1] exhibiting various smectic, nematic as well as columnar liquid crystallinity have been prepared and studied. These metallomesogens showed interesting chemical and physical properties in part due to the paramagnetism induced by the presence of a copper(II)-d^9 (or -d^1) center, which generally can produce potential applications. Certain diimine ligands,[2] for example 2,2′-bipyridyl or 1,10-phenanthrolines, are known to enhance the stability of the Cu(I) oxidation state relative to Cu(II). In addition a tetrahedral arrangement at the copper center in most Cu(I) complexes[3] is generally preferred. Square planar coordination is mostly observed in Cu(II) complexes and such complexes[1] generally readily give rise to liquid crystallinity, whereas compounds with tetrahedral geometries are often not mesomorphic. A novel example of tetrahedral Cu(I) complexes derived from Schiff-bases exhibiting columnar mesophases[4] was recently prepared and studied. Examples of non-mesogenic copper(I) complexes with a three-coordinate geometry are known and not uncommon. However, examples exhibiting mesomorphic properties had not previously been reported.

Here we wish to report the preparation, characterization and mesomorphic studies of two series of half-disc-like copper(I) complexes derived from bis{2 [3′-(3″,4″-dialkoxy- and bis{2-[3′-(3″,4″,5″-trialkoxyphenyl)-5′-methyl-1′-pyrazolyl]ethyl} ethers that exhibit hexagonal columnar phases and in which the central copper(I) ion shows three-coordinate geometry. All prepared copper(I) complexes with four (**1**) or six (**2**) alkoxy chains were found to exhibit enantiotropic hexagonal columnar (Col_h) phases. To the best of our knowledge these are the first copper(I) complexes with three-coordinate geometry to exhibit mesomorphic properties.



R = $(CH_2)_nH$
1 X = H
2 X= OR

Results and discussion

Synthesis and characterization

The synthetic pathway to copper(I) complexes **1**, **2** is summarized in Scheme 1. The unsymmetrical β-diketones (3,4-dialkoxyphenylbutane-1,3-diones) were prepared by literature procedures.[5] 3-Methyl-5-(3′,4′-dialkoxyphenyl)pyrazoles were obtained by condensation reaction[6] of 3,4-dialkoxyphenylbutane-1,3-diones and hydrazine hydrate in refluxing etnanol with a yield of 76–82%. ^1H and ^{13}C NMR spectroscopy were used to characterize these compounds. For example, the ^1H NMR spectrum of 3-methyl-5-(3′,4′-dialkoxyphenyl)pyrazole showed two characteristic peaks at δ 2.29–2.31 and 6.26–6.27, respectively, assigned to terminal methyl ($-CH_3$) and olefinic methine-H (–C=CH). The bis{2-[3′-(3″,4″-dialkoxyphenyl)-5′-methyl-1′-pyrazolyl]ethyl ethers were readily prepared by nucleophilic substitution[7] of 3-methyl-5-(3′,4′-dialkoxyphenyl)-pyrazoles with bis(2-bromoethyl) ether in the presence of NaH powder as base in refluxing dried THF. The yields were in the range 70–76% and the products were isolated as pale yellow solids. The copper(I) complexes were prepared by reaction[7] of the pyrazolylethyl ethers with $[Cu(MeCN)_4]BF_4$[8] in refluxing

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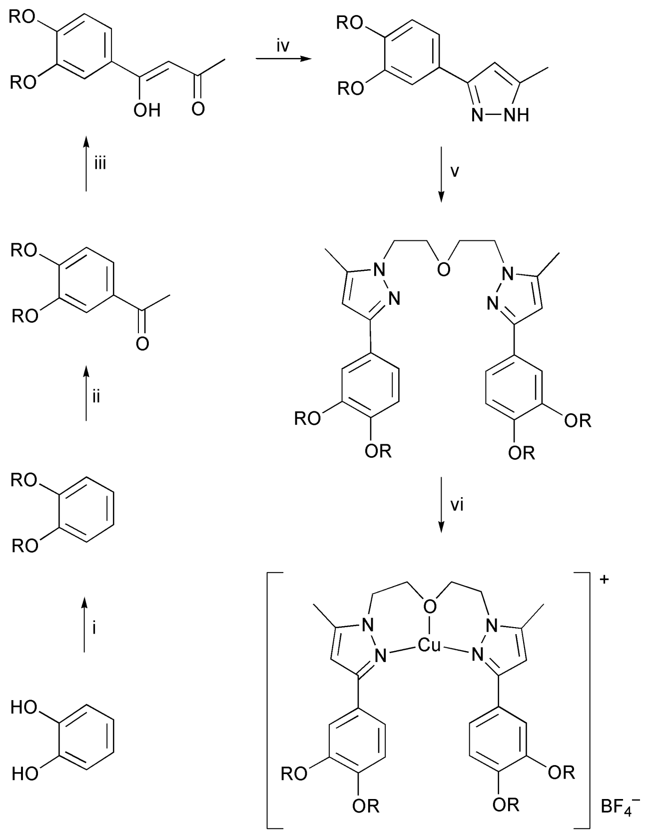

Scheme 1 *Reagents and conditions*: i, RBr (2.1 equiv.), K_2CO_3 (5.0 equiv.), KI (cat.) reflux in Me_2CO, 48 h, 78–95%; ii, MeCOCl (1.2 equiv.), $AlCl_3$ (1.5 equiv.), stirred in CH_2Cl_2 at 0 °C, then reflux for 24 h, 72–85%; iii, ethyl acetate (1.25 equiv.), NaH (2.0 equiv.), reflux in dried THF, 12 h, 76–85%; iv, $N_2H_4{\cdot}H_2O$ (2.0 equiv.), reflux in absolute ethanol, 2 h, then stirred at r.t. for 12 h, 76–82%, v, $(BrCH_2CH_2)_2O$ (0.50 equiv.), NaH (2.0 equiv.), reflux in dried THF, 60 h, 70–76%, vi, $[Cu(MeCN)_4]BF_4$ (1.1 equiv.), reflux in dried MeCN, 12 h, 76–80%.

dried acetonitrile and obtained as off-white solids. These copper(I) compounds were generally stored in a glove box, though they were relatively stable upon exposure to air without any noticeable oxidation. All the copper(I) compounds were diamagnetic species and gave distinct ^1H and ^{13}C NMR spectroscopic data.

Mesogenic properties

Although similar metal-free pyrazolate derivatives[6] which exhibit mesogenic properties have been described and studied, examples of metal-containing mesogens derived from related pyrazolates were unknown. Coinage metals are already known to form trimeric structures,[9] and these complexes were found to present novel supramolecular structures and interesting reactivities. One particular example containing a trinuclear gold ring[10] that exhibited a hexagonal columnar mesophase at room temperature has been reported by Serrano and co-workers. These trinuclear complexes were primarily prepared from non-mesogenic 3,5-bis(3′,4′-didecyloxyphenyl)pyrazole and AuCl(tht) (tht = tetrahydrothiophene).

The preparation and study of known Cu(I) complexes is relatively limited due to the spectroscopic "invisibility" of the spin-paired d^{10} cuprous ion center. In addition, this limited study of Cu(I) chemistry might be also attributed to the tendency towards disproportionation[11a] and/or facile autoxidation[11b] of Cu(I) in the presence of air. In this work pyrazolate-type derivatives, bis{2-[3-methyl-5-(3″,4″-dialkoxyphenyl)-1-pyrazolyl]ethyl} ethers were chosen as tridentate ligands to generate three-coordinate Cu(I) complexes. A few similar nonmesogenic Cu(I) complexes[7] derived from bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine, bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl] ether and bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl] sulfide have been prepared and a single crystal structure was determined for the ether. In this structure a T-shape coordination environment at the Cu(I) center due to the steric constraints of the ligand was described, and in which a distance of Cu(I) of 0.067(1) Å out of the plane defined by the three coordinating atoms was observed. The counter-cation BF_4^- was not associated with the Cu(I) center. In this work a similar coordination of Cu(I) complexes was adopted, and the possible adoption of mesogenic properties by these compounds was studied. The results obtained might extend potential metallomesogenic materials resulting from such Cu(I) complexes.

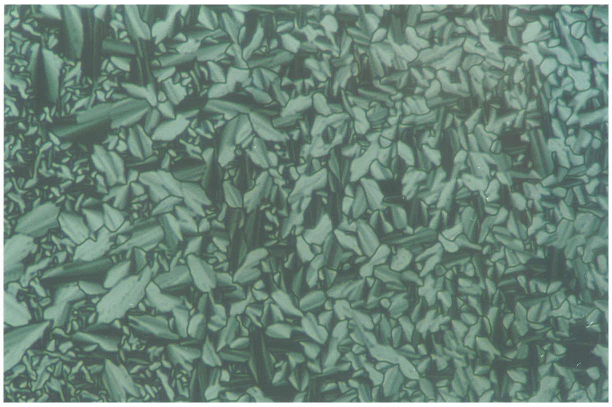

Fig. 1 Optical texture (100×) observed by copper(I) complex **1** (n = 14) (Col_{hd} phase at 90.0 °C).

The thermal behavior of compounds **1**, **2** were invistigated by polarized optical microscopy and differential scanning calorimetry and the transition temperatures of the compounds are listed in Table 1. All these copper(I) complexes with four (**1**) or six (**2**) alkoxy chains exhibited liquid crystalline behavior characteristic of columnar discotics. Two enantropic transitions, crystal–mesophase (Cr–M) and mesophase–isotropic (M–I) were also typically observed for these compounds. Results of DSC analysis indicated a higher enthalpy for the Cr–M transition at lower temperatures (*ca.* 45–59.0 °C on heating) and a relatively lower enthalpy for the M–I transition at higher temperatures (94–112.0 °C). This lower transition enthalpy suggests that the mesophases were all in a disordered state, indicating a more disordered stacking[5,12] between the molecules within a column. On the other hand, in a more ordered columnar[13b,c] phase (Col_{ho}) a larger enthalpy for the M–I transition relative to the enthalpy for the Cr–M transition is expected and observed in many columnar arrangements. The difference in these two columnar phases, disordered or ordered, can be observed and generally differentiated[13] by powder XRD diffraction. The temperature range of mesophases is in the range 49–68 °C for the cooling process, and is slightly sensitive to the carbon number of the sidechains. Higher sidechain density in compounds **2** resulted in a lowering of the clearing temperature by *ca.* 10 °C compared to compounds **1**. Both the melting and clearing temperatures decreased as the side chain length increases, as is normally observed in other compounds exhibiting similar columnar phases. Under optical polarized microscopy upon heating the compounds melt to give viscous birefringent fluid phases[12] with columnar superstructures. When cooled from their isotropic phases, they displayed an optical texture of pseudo-focal-conics with linear birefringent defects, as shown in Fig. 1. Such textures suggest hexagonal columnar structures. The formation of columnar phases in half-disc molecules is generally dependent on both the sidechain density and carbon length of the alkoxy sidechains. Elongation of the carbon length on the alkoxy sidechains and/or increase in the numbr of sidechains is found to stabilize the mesogenic core. Most half-disc molecules with lower sidechain density are proposed to form stable columnar mesophases by

Table 1 Phase behaviour[a] of copper(I) complexes **1**, **2**

1 $n=$	8	Cr	$\underset{41.5\ (25.4)}{\overset{52.7\ (26.0)}{\rightleftharpoons}}$	Col$_{hd}$	$\underset{107.0\ (1.12)}{\overset{111.8\ (1.13)}{\rightleftharpoons}}$	I
	10	Cr	$\underset{44.4\ (36.1)}{\overset{58.7\ (36.5)}{\rightleftharpoons}}$	Col$_{hd}$	$\underset{107.4\ (1.69)}{\overset{108.0\ (2.96)}{\rightleftharpoons}}$	I
	12	Cr	$\underset{30.4\ (14.0)}{\overset{45.1\ (13.9)}{\rightleftharpoons}}$	Col$_{hd}$	$\underset{98.5\ (1.05)}{\overset{101.9\ (1.10)}{\rightleftharpoons}}$	I
	14	Cr	$\underset{35.9\ (26.5)}{\overset{54.6\ (26.8)}{\rightleftharpoons}}$	Col$_{hd}$	$\underset{100.1\ (1.42)}{\overset{104.0\ (1.38)}{\rightleftharpoons}}$	I
	16	Cr	$\underset{41.8\ (33.6)}{\overset{51.8\ (33.7)}{\rightleftharpoons}}$	Col$_{hd}$	$\underset{96.2\ (2.94)}{\overset{100.0\ (3.18)}{\rightleftharpoons}}$	I
2	14	Cr	$\underset{41.0\ (29.1)}{\overset{48.5\ (28.3)}{\rightleftharpoons}}$	Col$_{hd}$	$\underset{90.4\ (1.70)}{\overset{93.9\ (1.71)}{\rightleftharpoons}}$	I

[a] n = No. of carbons in the sidechains; Cr = crystal phase; Col$_{hd}$ = disordered hexagonal columnar phase; I = isotropic. The transition temperatures (°C) and enthalpies (in parentheses, kJ mol^{-1} are determined by DSC at scan rate of 10.0 °C min^{-1}.

Table 2 Variable-temperature XRD diffraction data for compounds **1**

Complex		Mesophase	Lattice spacing/Å	*d*-Spacing/Å obs. (calc.)	Miller indices
1	$n = 8$	Col$_{hd}$ (95 °C)	35.06	30.36 (30.36)	(10)
				17.23 (17.53)	(11)
				15.35 (15.18)	(20)
				4.38 (br)	
	10	Col$_{hd}$ (95 °C)	36.92	31.98 (31.98)	(10)
				18.62 (18.46)	(11)
				16.04 (15.99)	(20)
				4.58 (br)	
	12	Col$_{hd}$ (95 °C)	38.90	33.70 (33.70)	(10)
				19.33 (19.45)	(11)
				16.46 (16.85)	(20)
				4.52 (br)	
	14	Col$_{hd}$ (95 °C)	40.96	35.47 (35.47)	(10)
				20.50 (20.48)	(11)
				17.32 (17.74)	(20)
				4.59 (br)	
	16	Col$_{hd}$ (85 °C)	43.06	37.29 (37.29)	(10)
				21.23 (21.53)	(11)
				18.42 (18.65)	(20)
				4.41 (br)	

arrangement of dimeric or trimeric units in the columnar phases.

To confirm the columnar structure of the mesophase of compounds **1**, powder X-ray diffraction experiments were performed on all the compounds. A summary of the XRD diffraction peaks and lattice constants for the complexes at mesophase temperatures are given in Table 2. For example, for **1** ($n = 14$) a diffraction pattern of a two-dimensional hexagonal lattice with one intense peak and two weaker peaks, at 35.47, 20.50 and 17.32 Å respectively, was observed at 95 °C. This is characteristic of a hexagonal columnar phase with a *d*-spacing ratio of 1, $(1/3)^{1/2}$ and $(1/4)^{1/2}$, corresponding to Miller indices; (10), (11) and (20), respectively. This reflection pattern corresponds to an intercolumnar distance (*a* parameter of the hexagonal lattice) of 40.96 Å. In addition, a quite broad diffuse band centered at 4.38–4.51 Å, which corresponds to liquid-like correlations between alkoxy chains and the mesogenic core was also detected in the wide-angle region. The lack of relatively sharp peaks at wide angles excluded a more regular periodicity along the columns, consistent with DSC analysis which showed lower enthalpies for the columnar-to-isotropic transition.

Summary

New pyrazolylethyl ether derivatives have been utilized to prepare metallomesogenic compounds. The copper(I) ion used as the core group was three-coordinate in geometry. These novel Cu(I) compounds exhibited hexagonal columnar phases and the clearing temperatures of these compounds were relatively low. This lower clearing temperature might be attributed to a smaller core size of the three-coordinate geometrical center relative to that in regular square planar Cu(II). In addition, the

Table 3 Elemental analysis[a] (%) of compounds **1**, **2**

Compound	*n*	C	H	N
1	8	64.12 (64.08)	8.64 (8.64)	4.95 (5.34)
	10	66.20 (66.16)	9.16 (9.19)	4.84 (4.82)
	12	67.80 (67.87)	9.68 (9.65)	4.38 (4.40)
	14	69.42 (69.31)	9.98 (10.03)	4.06 (4.04)
	16	70.38 (70.53)	10.38 (10.36)	3.73 (3.74)
2	14	71.61 (71.54)	10.88 (10.90)	3.09 (3.09)

[a] Calculated values in parentheses.

stability of the Cu(I) oxidation state in these compounds was enhanced by the [N, O] bonding environment provided by the pyrazolylethyl ethers.

Experimental

All chemicals and solvents were reagent grades from Aldrich Chemical Co. The solvents were dried by standard techniques. ^{1}H and ^{13}C NMR spectra were measured on a Bruker DRS-200. IR spectra were obtained on a Bio-Rad FPS155 spectrometer. DSC thermal analysis was carried out on a Mettler DSC-820 and phase transitions determined at a scan rate of 10.0 °C min^{-1}. Optical polarized microscopy was carried out on a Nikkon MICROPHOT-FXA microscope with a Mettler FP90/FP82HT hot stage system. X-Ray powder diffraction (XRD) studies were performed on an INEL MPD-diffractometer with a 2.0 kW Cu-K X-Ray source equipped with an INEL CPS-120 position sensitive detector and a variable temperature capillary furnace. Elemental analysis for carbon, hydrogen and nitrogen were conducted on a Heraeus CHN-O-Rapid elemental analyzer, and the results are listed in Table 3. The preparation procedures for 1,2-dialkoxybenzenes, 3,4-dialkoxyacetophenones, methyl-3,4,5-trialkoxybenzoates, 3,4,5-trialkoxybenzoic acids, 3,4,5-trialkoxyacetophenones, 3,4-dialkoxyphenylbutane-1,3-diones, 3,4,5-trialkoxyphenylbutane-1,3-diones, 3-methyl-5-(3,4-dialkoxyphenyl)pyrazoles and 3-methyl-5-(3,4,5-trialkoxyphenyl)pyrazoles[6] were as in the literature.[5,6]

1,2-Ditetradecyloxybenzene

White crystals, yield 76%. ^{1}H NMR (CDCl$_3$): δ 0.84 (t, CH$_3$, 6H), 1.26–1.84 (m, CH$_2$, 48H), 3.97 (t, OCH$_2$, 4H), 6.87 (s, C$_6$H$_4$, 4H). ^{13}C NMR (CDCl$_3$): δ 14.09, 22.68, 26.05, 29.36, 29.44, 29.70, 31.92, 69.25, 114.10, 120.97, 149.23.

3,4-Ditetradecanoxyacetophenone

White crystals, yield 70%. ^{1}H NMR (CDCl$_3$): δ 0.82 (t, CH$_3$, 6H), 1.23–1.81 (m, CH$_2$, 48H), 2.53 (s, COCH$_3$, 3H), 4.03 (tt, OCH$_2$, 4H), 6.85 (d, C$_6$H$_3$, 1H), 7.48 (s, C6H$_3$, 1H), 7.53 (d, C$_6$H$_3$, 1H). ^{13}C NMR (CDCl$_3$): δ 13.95, 22.53, 25.83, 26.04, 28.88, 29.00, 29.21, 29.54, 31.77, 68.86, 69.06, 111.35, 112.18, 123.00, 130.07, 148.66, 153.35, 196.74 (C=O).

Methyl-3,4,5-tritetradecanoxybenzoate

^{1}H NMR (CDCl$_3$): δ 0.86 (t, CH$_3$, 9H), 1.24–1.83 (m, CH$_2$, 72H), 3.87 (s, OCH$_3$, 3H), 3.99 (tt, OCH$_2$, 6H), 7.23 (s, C$_6$H$_2$, 2H). ^{13}C NMR (CDCl$_3$): δ 14.13, 22.70, 26.13, 29.34, 29.44, 29.63, 29.71, 29.74, 29.80, 30.35, 31.95, 52.10, 69.19, 75.49, 107.89, 124.67, 142.40, 152.79, 166.90 (CO$_2$).

3,4,5-Tritetradecanoxybenzoic acid

^{1}H NMR (CDCl$_3$): δ 0.87 (t, CH$_3$, 9H), 1.14–1.83 (m, CH$_2$, 72H), 4.02 (tt, OCH$_2$, 6H), 7.29 (s, C$_6$H$_2$, 2H). ^{13}C NMR (CDCl$_3$): δ 14.07, 22.68, 26.07, 29.37, 29.70, 30.33, 31.92, 69.24, 73.55, 108.67, 123.62, 143.27, 152.87, 171.72 (CO$_2$).

3,4,5-Tritetradecyloxyacetophenone

^{1}H NMR (CDCl$_3$): δ 0.85 (t, CH$_3$, 9H), 1.24–1.76 (m, CH$_2$, 72H), 2.54 (s, CH$_3$, 3H), 4.00 (tt, OCH$_2$, 6H), 7.15 (s, C$_6$H$_2$, 2H). ^{13}C NMR (CDCl$_3$): δ 14.12, 22.69, 26.05, 26.45, 29.37, 29.70, 30.30, 31.92, 69.25, 73.52, 107.06, 132.03, 142.80, 152.85, 197.19 (C=O).

3,4-Ditetradecoxyphenylbutane-1,3-dione

Light yellow crystals, yield 79%. ^{1}H NMR(CDCl$_3$; δ 0.82 (t, CH$_3$, 6H), 1.19–1.79 (m, CH$_2$, 48H), 2.16 (s, COCH$_3$, 3H), 4.00 (t, OCH$_2$, 4H), 6.06 (s, COCH, 1H), 6.77 (d, C$_6$H$_3$, 1H), 7.41 (s, C$_6$H$_3$, 1H), 7.45 (d, C$_6$H$_3$, 1H), 16.20 (s, OH, 1H). ^{13}C NMR (CDCl$_3$): δ 14.10, 22.67, 25.84, 25.97, 29.08, 29.24, 29.39, 29.57, 31.90, 68.94, 69.21, 96.08, 110.79, 111.77, 120.29, 128.23, 148.76, 153.46, 183.64 (COH), 192.79 (C=O).

3,4,5-Tritetradecoxyphenylbutane-1,3-dione

Light yellow solid, yield 79%. ^{1}H NMR (CDCl$_3$): δ 0.82 (t, CH$_3$, 9H), 1.15–1.77 (m, CH$_2$, 72H), 2.15 (s, COCH$_3$, 3H), 3.99 (m, OCH$_2$, 6H), 6.08 (s, COCH, 1H), 6.89 (s, C$_6$H$_2$, 2H), 16.20 (s, OH, 1H). ^{13}C NMR (CDCl$_3$): δ 13.99, 22.25, 25.89, 26.06, 29.10, 29.25, 29.34, 29.65, 31.90, 68.99, 69.22, 96.01, 111.70, 128.26, 148.74, 153.47, 183.59 (COH), 192.81 (C=O).

3-Methyl-5-(3′,4′-ditetradecanoxyphenyl)pyrazole

A solution of 3,4-tetradecoxyphenylbutane-1,3-dione (2.00 g, 3.40 mmol) dissolved in hot ethanol was added to a solution of hydrazine hydrate (80% w/w, 2.56 ml). The mixture was gently refluxed for 2 h and stirred at room temperature for another 12 h. The light yellow solid was collected after the solution had been kept in the refrigerator overnight. The solid was recrystallized from ethanol to give white crystals. Yield 80%, mp 58.0–58.30 °C. ^{1}H NMR (CDCl$_3$): δ 0.83 (t, CH$_3$, 6H), 1.24–1.84 (m, CH$_2$, 48H), 2.29 (s, CNCH$_3$, 3H), 3.98 (t, OCH$_2$, 4H), 6.27 (s, CNCH, 1H), 6.85 (d, C$_6$H$_3$, 1H), 7.16 (d, C$_6$H$_3$, 1H), 7.25 (s, C$_6$H$_3$, 1H). ^{13}C NMR (CDCl$_3$): δ 11.66, 14.01, 22.51, 25.83, 29.22, 29.54, 31.76, 69.15, 69.43, 101.78, 111.45, 113.35, 118.35, 133.28 (CNH), 143.22, 148.75, 149.23 (C=N), 152.32.

3-Methyl-5-(3′,4′,5′-tritetradecanoxyphenyl)pyrazole

White solid. Yield 78%, mp 46.0–46.4 °C. ^{1}H NMR (CDCl$_3$): δ 0.86 (t, CH$_3$, 9H), 1.25–1.81 (m, CH$_2$, 72H), 2.31 (s, CNCH$_3$, 3H), 3.98 (tt, OCH$_2$, 6H), 6.26 (s, CNCH, 1H), 6.88 (s, C$_6$H$_2$, 2H). ^{13}C NMR (CDCl$_3$): δ 11.57, 14.07, 22.66, 26.11, 29.42, 29.71, 30.32, 31.91, 69.08, 73.45, 101.86, 104.41, 127.32 (CNH), 138.21, 142.93, 149.97 (C=N), 153.33.

Bis{2-[3′-(3″,4″-ditetradecanoxyphenyl)-5′-methyl-1′-pyrazolyl]-ethyl} ether

3-(3′,4′-Ditetradecanoxyphenyl)-5-methylpyrazole (1.00 g, 1.7 mmol) dissolved in dried THF was added to a solution of powdered NaH (0.086 g, 3.4 mmol) suspended in dried THF. To this solution was slowly added bis(2-bromoethyl) ether (0.207 g, 0.85 mmol) and the mixture was refluxed for 72 h. Dilute hydrochloric acid (1.0 M) was added to neutralize the solution and the solution was extracted three times with water. The organic layers were collected and dried over anhydrous MgSO$_4$. The solution was concentrated and the resulting solid purified by chromatography eluting with methylene chloride. The product was isolated as a light yellow solid after recrystallization from methylene chloride–methanol. Yield 76%, mp 76.2–76.6 °C. ^{1}H NMR (CDCl$_3$): δ 0.86 (t, CH$_3$, 12H), 1.25–1.76 (m, CH$_2$, 96H), 2.20 (s, CNCH$_3$, 6H), 3.75 (t, NCH$_2$, 4H), 3.98 (t, OCH$_2$, 8H), 4.03 (t, OCH$_2$, 4H), 6.28 (s, CNCH, 2H), 6.39 (s, C$_6$H$_3$, 2H), 7.68 (d, C$_6$H$_3$, 4H). ^{13}C NMR (CDCl$_3$): δ 11.92, 14.02, 22.58, 25.78, 29.29, 29.58, 31.96, 49.02, 69.41 (NCH$_2$), 70.86, 101.09, 103.11, 104.98, 135.33 (CNH), 140.28, 149.89 (C=N), 160.58.

IR (thin film): 2958, 2911, 2852, 1895, 1612, 1577, 1442, 1301, 1249, 1116, 934 cm^{-1}.

Bis{2-[3′-(3″,4″,5″-tritetradecanoxyphenyl)-5′-methyl-1′-pyrazolyl]ethyl} ether

Yield 72%, mp 69.3–69.50 °C. ^{1}H NMR (CDCl$_3$): δ 0.86 (t, CH$_3$, 18H), 1.25–1.83 (m, CH$_2$, 144H), 2.21 (s, CNCH$_3$, 6H), 3.83 (t, NCH$_2$, 4H), 3.99 (tt, OCH$_2$, 12H), 4.05 (t, OCH$_2$, 4H), 6.22 (s, CNCH$_2$, 2H), 6.39 (s, C$_6$H$_2$, 2H), 7.66 (s, C$_6$H$_2$, 2H). ^{13}C NMR (CDCl$_3$): δ 12.02, 14.11, 23.62, 25.88, 29.30, 29.44, 29.68, 32.12, 48.81, 69.50 (NCH$_2$), 71.16, 100.79, 109.23, 135.33 (CNH), 140.58, 151.08 (C=N), 162.31, 167.82. IR (thin film): 2958, 2913, 2854, 1891, 1614, 1580, 1440, 1305, 1244, 1119, 938 cm^{-1}.

(Bis{2-[3′-(3″,4″-ditetradecanoxyphenyl)-5′-methyl-1′pyrazolyl]-ethyl} ether)copper(I) tetrafluoroborate

A hot ethanol solution of bis{2-[3′-(3″,4″-ditetradecanoxy-phenyl)-5′-methyl-1′-pyrazolyl]ethyl} ether (0.10 g, 0.10 mmol) was added dropwise to a solution of [Cu(MeCN)$_4$]BF$_4$ (0.025 g, 0.10 mmol) dissolved in 50 ml of dried degased acetonitrile. The mixture was refluxed for 48 h. The solution was concentrated to dryness and then recrystallized from methylene chloride–methanol. An off white solid was collected. Yield 80%. ^{1}H NMR (CDCl$_3$): δ 0.86 (t, CH$_3$, 12H), 1.24–1.75 (m, CH$_2$, 96H), 2.18 (s, CNCH$_3$, 6H), 3.78 (t, NCH$_2$, 4H), 3.96 (tt, OCH$_2$, 8H), 4.06 (t, OCH$_2$, 4H), 6.20 (s, CNCH, 2H), 6.34 (s, C$_6$H$_3$, 2H), 7.85 (d, C$_6$H$_3$, 4H). ^{13}C NMR (CDCl$_3$): δ 11.20, 14.11, 22.68, 26.10, 29.32, 29.56, 31.92, 48.77, 69.41 (NCH$_2$), 71.14, 101.12, 102.86, 104.20, 135.21 (CNH), 140.38, 150.13 (C=N), 160.46. IR (thin film): 2956, 2919, 2850, 1606, 1586, 1465, 1309, 1264, 1179, 1139, 940 cm^{-1}. Anal. for C$_{80}$H$_{138}$O$_5$N$_4$Cu, Calc. C, 69.31; H, 10.03; N, 4.04. Found: C, 69.42; H, 9.98; N, 4.06%.

(Bis{2-[3′(3″,4″,5″-tritetradecanoxyphenyl)-5′-methyl-1′-pyrazolyl]ethyl} ether) copper(I) tetrafluoroborate

Yield 70%. ^{1}H NMR (CDCl$_3$): δ 0.86 (t, CH$_3$, 18H), 1.25–1.83 (m, CH$_2$, 144H), 2.21 (s, CNCH$_3$, 6H), 3.78 (t, NCH$_2$, 4H), 3.99 (tt, OCH$_2$, 12H), 4.06 (t, och$_2$, 4H), 6.20 (s, CNCH, 2H), 6.32 (s, C$_6$H$_2$, 2H), 7.63 (s, C$_6$H$_2$, 2H). ^{13}C NMR (CDCl$_3$): δ 12.02, 14.11, 23.62, 25.88, 29.30, 29.44, 29.68, 32.12, 48.81, 69.50 (NCH$_2$), 71.16, 102.08, 109.23, 136.23 (CNH), 140.58, 151.08 (C=N), 161.89, 167.76. IR (thin film): 2957, 2921, 2848, 1608, 1582, 1466, 1311, 1266, 1175, 1136, 941 cm^{-1}. Anal. for C$_{108}$H$_{194}$O$_7$N$_4$Cu, Calc. C, 71.54; H, 10.90; N, 3.09. Found: C, 71.61; H, 10.88; N, 3.09%.

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