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Liquid crystalline properties of bis(salicylaldiminato)copper(II) complexes: the first columnar discotics derived from salicylaldimine Schiff bases

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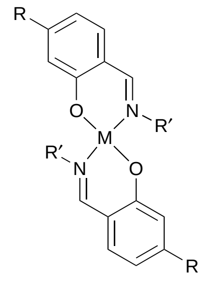
The synthesis and mesomorphic properties of a homologous series of *N*-(2-hydroxy-4-*n*-alkoxybenzylidene)-3′,4′-di-*n*-alkoxylanilines and their copper(II) complexes bis[(*N*-3′,4′-dialkoxyphenyl)-4-*n*-alkoxylsalicylaldiminato]copper(II) are reported. The disc-like copper complexes exhibited columnar hexagonal disordered mesophases, which were characterized by DSC analysis and optical polarized microscopy. The structure of the mesophases was confirmed by X-ray powder diffraction (XRD). The mesomorphic properties for these copper complexes were compared with other similar metallomesogenic bis(salicylaldiminato)copper(II) complexes in terms of molecular structural differences.

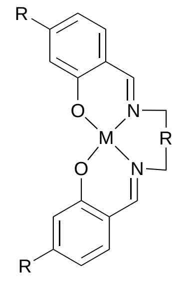
There has been extensive research on the synthesis and characterization of metallomesogens[1–5] during the past decade. Introduction of single or multiple metal centers into molecular systems has allowed the design and generation of a wide variety of geometric molecules, which were expected to exhibit interesting mesomorphic and physical properties.[3] These observed novel properties mainly arose from the combination of rich coordination chemistry and large polarizability, which are characteristic features[5] of transition metal atoms. The formation of mesophases was often facilitated by intermolecular dative interactions exhibited in such metallomesogens, since the metal complexes are generally coordinatively unsaturated. The relationship between molecular structures and physical properties still remains a challenging task for material chemists to explore and understand. In spite of the fact that they seem to be very promising for development in technology applications, the status of research using this type of metallomesogenic materials[3,5] is still in its infancy.

Metal complexes (structures **I** and **II**) of Schiff bases derived from salicylaldimine[5,6] and *β*-diketonates[7–9] (**III** and **IV**) are among the best known complexes that exhibit mesogenic properties in metallomesogenic systems. There have been numerous investigations of metal *β*-diketonates complexes, and almost all of the transition metals (particularly 3d) show mesomorphism with *β*-diketonates. A variety of transition metals (Fe, Rh, Ir, VO, Ni, Co, Cu, Pt, Pd, *etc.*) show mesomorphism with salicylaldimine derivative Schiff bases. All of these complexes derived from salicylaldimine Schiff bases were more likely of rod- or brick-like shapes with two or four extended flexible sidechains, and these complexes thus all exhibited either nematic (N) or various smectic (S) (or chiral smectic) phases predominantly, regardless of the metal center incorporated in such systems. Differences in the mesogenic properties of these Schiff base metal complexes were attributed to the various types of geometric coordination of the metal centers.

The transition of mesophases from rod-like nematic or smectic phases into disc-like discotics was possible by adjusting the ratio[2,3] of width-to-length (*d*/*l*, *i.e.*, aspect ratio) of the molecular shape. Here, we report the synthesis and mesomorphic properties of a homologous series of copper(II) complexes with the following structure; bis[(*N*-3′,4′-dialkoxyphenyl)-4-*n*-alkoxysalicylaldiminato]copper(II). To the best of our knowledge these complexes derived from salicylaldimines are the first disc-like molecules to exhibit columnar discotic phases.



I



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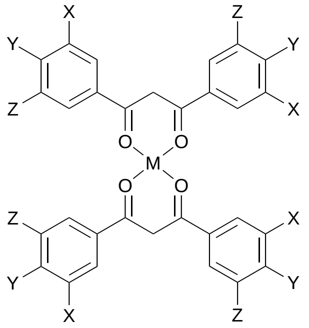

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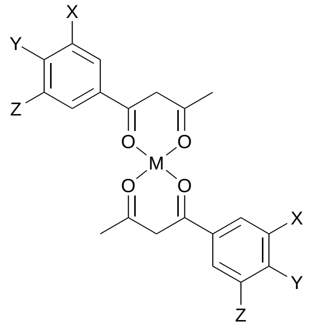

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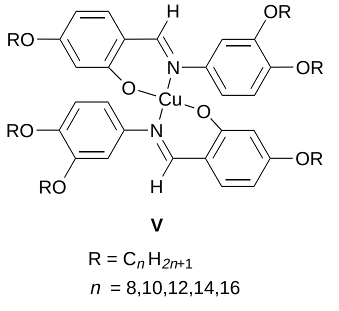


V

R = C_nH_{2n+1}
n = 8,10,12,14,16

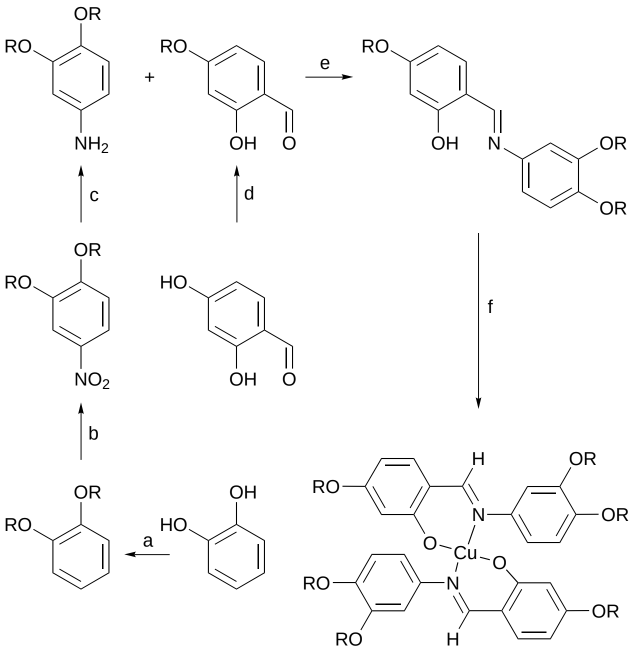
Results and Discussion

Synthesis

The preparation of copper complexes was straightforward. The condensation of 1-amino-3,4-dialkoxybenzene and 4-alkoxy-2-hydroxybenzaldehyde in refluxing CH_2Cl_2 gave light yellow *N*-(2-hydroxy-4-*n*-alkoxybenzylidene)-3′, 4′-dialkoxyanilines in high yields. These Schiff base derivatives were then reacted with copper(II) acetate to produce the green-to-brown metal complexes. These copper compounds are all paramagnetic, and their ^{1}H and ^{13}C NMR spectra display only broad alkoxy signals. All other proton signals close to the paramagnetic copper centers are unobserved. Elemental analysis also confirmed the bimetallic identity of the complexes. The typical synthetic pathways for these complexes are summarized in Scheme 1. Several attempts to prepare vanadyl complexes by refluxing or stirring the reaction mixture at room temperature were unsuccessful. Unreacted Schiff base ligands were recovered after work-up.

Mesomorphic properties

The copper complexes all exhibit liquid crystalline behavior of columnar discotics, which were characterized based on DSC analysis and polarized optical microscopy. The phase-transition temperature and enthalpies of copper complexes **V** are given in Table 1. DSC analyses of the copper complexes showed typical discotic phase transitions[10] of crystal-to-discotic-to-isotropic (Cry→Col→I). Additional crystal-to-crystal ($K_1 \rightarrow K_2$) transitions were also observed for complexes with lower carbon lengths (*i.e.* $n=8$, 10). Upon heating, the copper complexes melt to give birefringent fluid phases with columnar superstructures, as is often observed for disc-shaped molecules. At crystal-to-discotic transition the flexible side chains undergo disordering but the central core remains stacked in columns, however, the core unstacks at discotic-to-isotropic transition. A larger enthalpy for the crystal-to-liquid crystal transition at lower temperatures (136–179 °C) and a lower enthalpy for the liquid crystal-to-isotropic transition at higher temperatures (253–325 °C) was observed; this low value of the transition enthalpy indicated that the mesophases were relatively disordered. The temperature range of discotic mesophases for copper complexes was quite wide (between 120 and 150 °C) and slightly sensitive to the carbon number of sidechains. For example, the temperature range for complexes decreased with carbon length (*e.g.* $T=148$ °C for $n=8$ and $T=118$ °C for $n=16$), which is often observed for discotic[10] metallogens.



Scheme 1*Reaction conditions*: a: RBr (2.1 equiv.), K_2CO_3 (5.0 equiv.), refluxed in CH_3COCH_3, 24 h; b: HNO_3 (conc. 1.1 equiv.), refluxed in CH_2Cl_2, 16 h; c: $H_2NNH_2 \cdot H_2O$ (5.0 equiv.), Pd/C (0.1 g, 10%), refluxed in C_2H_5OH, 24 h; d: RBr (1.0 equiv.), $KHCO_3$ (1.1 equiv.), refluxed in CH_3COCH_3, 24 h; e: CH_3COOH (few drops), refluxed in CH_2Cl_2, 24 h; f: $Cu(OAc)_2$ (2.0 equiv.), KOH, refluxed in THF–C_2H_5OH, 24 h.

Table 1 Phase behavior[a] of copper complexes V

$n=8$	$K_1 \xrightarrow{163.2\ (13.5)} K_2 \underset{133.1\ (6.14)}{\overset{178.9\ (11.4)}{\rightleftharpoons}} \text{Col}_{\text{hd}} \underset{323.1}{\overset{325.5}{\rightleftharpoons}} I_d$
10	$K_1 \xrightarrow{152.4\ (10.1)} K_2 \underset{133.1\ (10.5)}{\overset{165.7\ (13.3)}{\rightleftharpoons}} \text{Col}_{\text{hd}} \underset{311.4}{\overset{313.0}{\rightleftharpoons}} I_d$
12	$K_2 \underset{114.1\ (19.2)}{\overset{142.7\ (23.4)}{\rightleftharpoons}} \text{Col}_{\text{hd}} \underset{290.5\ (4.22)}{\overset{292.6\ (4.26)}{\rightleftharpoons}} I$
14	$K_2 \underset{106.7\ (18.7)}{\overset{139.4\ (19.8)}{\rightleftharpoons}} \text{Col}_{\text{hd}} \underset{263.9\ (2.63)}{\overset{271.7\ (3.22)}{\rightleftharpoons}} I$
16	$K_2 \underset{106.2\ (19.9)}{\overset{135.7\ (20.8)}{\rightleftharpoons}} \text{Col}_{\text{hd}} \underset{244.9\ (2.55)}{\overset{252.7\ (3.22)}{\rightleftharpoons}} I$

[a] K_1, K_2 = crystal phase; Col_{hd} = columnar hexagonal disordered; I = isotropic; I_d = isotropic with decomposition. The transition temperature (°C) and enthalpies (in parentheses, kJ mol^{-1}) are determined by DSC at a scan rate of 10.0 °C min^{-1}.

These copper complexes exhibit relatively high clearing points (325–253 °C), and for a few complexes with lower carbon numbers ($n=8$, 10) this is accompanied by partial decomposition. The melting and clearing points both decrease as the sidechain length increases. When cooled from their isotropic phases, they display optical textures (Fig. 1) which are a mixture of pseudo-focal-conics and mosaic regions with linear birefringent defects, suggesting hexagonal columnar[10] structures. The possibility of rectangular phases was also readily excluded owing to the absence of mosaic textures with prominent wedge-shaped[8c] defect patterns.

For metallogens[3,5] with similar molecular structures, increasing the number of flexible sidechains results generally in a

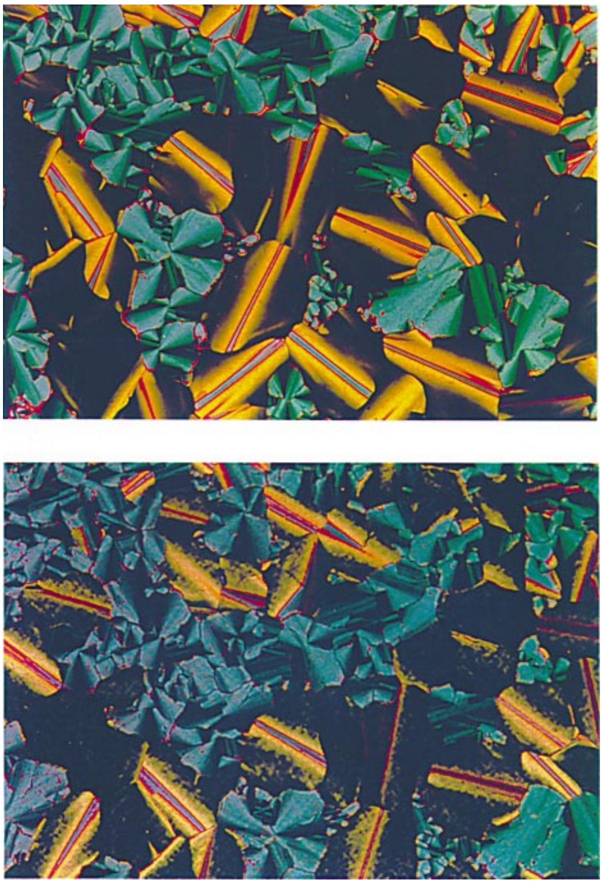


Fig. 1 Optical texture (100×) observed for copper complex V ($n=14$). Col_{hd} phase at 245 °C (top); K phase at 60 °C (bottom).

lowering of melting and clearing points, and subsequently increasing the stability of the mesophases. However, in this system of copper complexes derived from salicylideneamine derivatives, this lowering in temperatures was not observed. As a matter of fact the trend was reversed. For complexes **V** with six sidechains in total the clearing points were in the range 325–253 °C from $n=8$ to $n=16$, while those for similar copper complexes with four sidechains in total bis[*N*-(4-alkoxyphenyl)-4-alkoxysalicylaldiminato]copper(II)[6] (similar to structure **I**) were in the range 165–132 °C. This drastic increase by *ca.* 120 °C in clearing temperature suggested that the type of molecular packing which accounts for the melting and clearing point in the mesophase for these two similar series of metal complexes was substantially different. The bis[*N*-(4-alkoxyphenyl)-4-alkoxysalicylaldiminato]copper(II) complexes which were rod-like formed smectic A and smectic C phases, however, complexes **V** are disc-like and exhibit columnar discotic phases as expected.

To further confirm the structure of the mesophases, we performed powder XRD diffraction experiments. A summary of the diffraction peaks and lattice constants for the complexes is given in Table 2. For example, as shown in Fig. 2, the copper complex with $n=12$ displays a diffraction pattern of a two-dimensional hexagonal lattice with an intense peak and two weak peaks at 32.82, 18.91 and 16.88 Å, respectively, at 200 °C. These are characteristic of a discotic columnar (Col_{hd}) 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. These values correspond to an intercolumnar distance (*a* parameter of the hexagonal lattice) of 37.88 Å. Most complexes also display an interesting additional broad halo peak at mid-angle of *d*-spacing *ca.* 6.00 Å. However, liquid-like correlations between the rigid cores occur at wider angle regions of 5.11–5.19 Å. The absence of distinct peaks at high angle is consistent with DSC analysis of low enthalpies for the discotic-to-isotropic transition, indicative of a highly disordered mesophase; *i.e.* there is no long-range order along the columns. The temperature dependence of the lattice parameters in liquid crystals was also observed in these copper complexes. We find that the low-angle reflections of complexes generally shift to lower *d*-spacings with decreasing temperature (*e.g.* $d=36.78$ Å at 270 °C and $d=35.08$ Å at 240 °C for complex **V**; $n=10$). The hexagonal lattices also correlate well with increasing sidechain lengths.

Table 2 Variable-temperature XRD diffraction data for copper complexes (**V**)

complex	mesophase (temperature/°C)	lattice spacing/Å	*d*-spacing/Å obs. (calc.)	Miller indices
$n=10$	Col_{hd} (270)	36.78	31.85 (31.85)	(10)
			18.39 (18.39)	(11)
			15.97 (15.93)	(20)
			5.98 (br)	
			5.11 (br)	
	Col_{hd} (240)	35.08	30.38 (30.38)	(10)
			17.39 (17.54)	(11)
			15.70 (15.19)	(20)
			6.11 (br)	
			5.14 (br)	
$n=12$	Col_{hd} (200)	37.88	32.82 (32.82)	(10)
			18.91 (18.94)	(11)
			16.88 (16.41)	(20)
			5.11 (br)	
	Col_{hd} (170)	37.62	32.58 (32.58)	(10)
			18.73 (18.81)	(11)
			16.70 (16.29)	(20)
			5.09 (br)	
$n=14$	Col_{hd} (200)	41.76	36.17 (36.17)	(10)
			20.74 (20.88)	(11)
			18.17 (18.08)	(20)
			13.69 (13.67)	(30)
			5.19 (br)	
	Col_{hd} (170)	41.72	36.13 (36.13)	(10)
			20.73 (20.86)	(11)
			18.07 (18.07)	(20)
			13.61 (13.65)	(30)
			5.13 (br)	(30)
$n=16$	Col_{hd} (200)	42.46	36.77 (36.77)	(10)
			21.28 (21.23)	(11)
			18.89 (18.39)	(20)
			13.69 (13.89)	(30)
			11.92 (12.25)	(31)
			5.13 (br)	

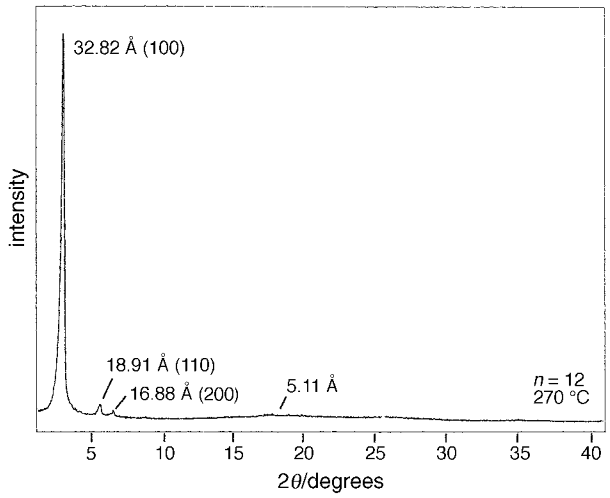


Fig. 2 X-Ray diffraction data for the columnar hexagonal disordered phases of copper complexes ($n=12$)

Summary

We have prepared and characterized a series of copper complexes derived from salicylaldimine Schiff bases. These disc-like molecules exhibited enantiotropic columnar hexagonal phases as expected. While it is still true that rod-like molecules gave nematic or smectic phases, and disc-like molecules gave discotic phases, respectively, the results in this paper demonstrated that the transition of mesophases (nematics to discotics) can be accomplished from structurally similar molecules by increasing the numbers of sidechains.

Experimental

All chemicals and solvents were reagent grade from Aldrich Chemical Co. and used without further purification. The solvents were dried by standard techniques. ^1H and ^{13}C NMR spectra were measured on a Bruker DRS-200 instrument. DSC thermograms were carried out on a Perkin-Elmer DSC-7 instrument and calibrated with a pure indium sample. All phase behaviors are determined at a scan rate of 10.0 °C min^{-1} unless otherwise noted. 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 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. The detector was calibrated using mica and silicon standards. The powder samples were charged in Lindemann capillary tubes (80 mm long and 0.01 mm thick) from Charles Supper Co. with a inner diameter of 0.10 or 0.15 mm. Samples were heated to above the isotropic temperature and kept at that temperature for 10 min. The sample then was cooled at a rate of 5.0 °C min^{-1} to the appropriate temperature and diffraction data collected.

Preparations

1,2-didodecyloxybenzene. Under a nitrogen atmosphere, catechol (5.0 g, 0.045 mol), anhydrous K_2CO_3 (25.1 g, 0.18 mol), bromododecane (23.7 g, 0.10 mol) and KI (0.5 g) were mixed in 250 ml of dried acetone. The reaction mixture was refluxed for 24 h. The reaction solution was filtered to remove any solid and the filtrate was concentrated to give the yellow solid product. White needles were obtained after recrystallization from CH_2Cl_2–CH_3OH (mp 46.8 °C, yield 86%). ^1H NMR ($CDCl_3$): δ 0.88 (t, CH_3, 6 H), 1.26–1.86 (m, CH_2, 40 H), 3.98 (t, OCH_2, 4 H), 6.88 (s, C_6H_4, 4 H). ^{13}C NMR ($CDCl_3$): δ 14.10, 22.68, 26.05, 29.36, 29.67, 31.92, 69.24, 114.1, 121.0, 149.2.

1-Nitro-3,4-didodecyloxybenzene. A solution of 1,2-didodecanoxybenzene (5.0 g, 0.011 mol) dissolved in 150 ml of CH_2Cl_2 was added a solution of concentrated nitric acid (1·10 ml) at 0 °C. Then the mixture was refluxed for 16 h. The solution was extracted three times with distilled water. The organic CH_2Cl_2 solution was dried in anhydrous $MgSO_4$ and concentrated to give a white solid. Milky cotton-like crystals were obtained after recrystallization from CH_2Cl_2–CH_3OH (mp 72.0 °C, yield, 86.4%). ^1H NMR ($CDCl_3$): δ 0.88 (t, $J = 6.4$ Hz, CH_3, 6 H), 1.24–1.89 (m, CH_2, 40 H), 4.04 (2 × d, $J = 6.4$, 6.5 Hz, OCH_2, 4 H), 6.84 (dd, $J = 3.0$, 8.9 Hz, C_6H_3, 1 H), 7.69 (d, $J = 2.5$ Hz, C_6H_3, 1 H), 7.84 (dd, $J = 2.8$, 9.0 Hz, C_6H_3, 1 H). ^{13}C NMR ($CDCl_3$): δ 14.07, 22.66, 25.89, 28.89, 29.30, 29.60, 31.89, 69.40, 108.0, 111.0, 117.6, 141.1, 148.6, 154.7.

1-Amino-3,4-didodecyloxybenzene. A mixture of 1-nitro-3,4-didodecanoxybenzene (5.0 g, 0.01 mol) and palladium (0.10 g, 10% on carbon) was added to 150 ml of absolute ethanol in a 250 ml three-necked round bottomed flask. A solution of hydrazine hydrate (5.0 ml) diluted in 20 ml of absolute ethanol was slowly added to the flask and the reaction mixture was refluxed for 24 h. Black solids were filtered off by use of Celite 545. The solution was reduced in volume to *ca.* 25 ml, and then was left in a refrigerator overnight. The product was obtained as white crystals (mp 55.0 °C, yield 86%). ^1H NMR ($CDCl_3$): δ 0.86 (t, $J = 6.4$ Hz, CH_3, 6 H), 1.24–1.84 (m, CH_2, 40 H), 3.40 (s, NH_2, 2 H), 3.89 (2 × d, $J = 6.5$, 6.5 Hz, OCH_2, 4 H), 6.19 (dd, $J = 2.6$, 8.2 Hz, C_6H_3, 1 H), 6.28 (d, $J = 2.5$ Hz, C_6H_3, 1 H), 6.71 (d, $J = 8.3$ Hz, C_6H_3, 1 H). ^{13}C NMR ($CDCl_3$): δ 14.08, 22.68, 26.04, 29.32, 29.46, 29.65, 31.90, 68.93, 70.92, 102.7, 106.9, 117.3, 140.9, 142.0, 150.6.

4-Dodecyloxy-2-hydroxybenzaldehyde. 2,4-Dihydroxybenzaldehyde (5.0 g, 0.036 mol), $KHCO_3$ (4.0 g, 0.04 mol), KI (catalytic amount) and 1-bromododecane (8.1 g, 0.035 mol) were mixed in 125 ml of dried acetone under a nitrogen atmosphere. The mixture was refluxed for 24 h. The reaction mixture was filtered while hot to remove insoluble solids. Dilute HCl (1.0 M) was added to neutralize the warm solution. The solution was extracted twice with $CHCl_3$ (100 ml). The combined $CHCl_3$ extract solution was concentrated to give a purple solid which was purified by chromatography eluting with chloroform–hexane (1 : 1, v/v). Evaporation of the solvent gave the product as a white solid. Yield 87–93%, mp 39.0 °C. ^1H NMR ($CDCl_3$): δ 0.86 (t, $J = 6.4$ Hz, CH_3, 3 H), 1.14–1.83 [m, $(CH_2)_{10}$, 20 H], 3.97 (t, $J = 6.47$ Hz, OCH_2, 2 H), 6.38 (d, $J = 2.3$ Hz, C_6H_3, 1 H), 6.50 (dd, $J = 2.4$, 5.5 Hz, C_6H_3, 1 H), 7.38 (d, $J = 8.7$ Hz, C_6H_3, 1 H), 9.67 (s, CHO, 1 H), 11.45 (s, C_6H_3OH, 1 H). ^{13}C NMR ($CDCl_3$): δ 14.08, 22.67, 25.88, 28.91, 29.29, 29.52, 29.60, 29.72, 31.90, 68.57, 101.0, 108.8, 114.9, 135.2, 164.5, 166.4, 194.3.

***N*-(2-Hydroxy-4-*n*-alkoxybenzylidene)-3′,4′-dialkoxyanilines.** 4-Dodecoxy-2-hydroxybenzaldehyde (2.0 g, 0.0065 mol), 3,4-didodecyloxyphenylamine (3.0 g, mol) and acetic acid (a few drops) were mixed in 100 ml of dried CH_2Cl_2 under a nitrogen atmosphere. The reaction mixture was refluxed for 24 h. The solution was concentrated to give a brown solid, which was purified by column chromatography using CH_2Cl_2–hexane (1/1) as eluent. The product was isolated as golden needles after recrystallization from acetone (mp 86.5 °C, yield 92%). ^1H NMR ($CDCl_3$): δ 0.86 (t, $J = 6.4$ Hz, CH_3, 9 H), 1.16–1.86 [m, $(CH_2)_{10}$, 60 H], 3.99 (t, $J = 3.2$ Hz, OCH_2, 6 H), 6.42 (dd, $J = 2.3$, 8.9 Hz, C_6H_3, 1 H), 6.47 (d, $J = 2.3$ Hz, C_6H_3, 1 H), 6.83 (m, C_6H_3, 1 H), 7.21 (d, $J = 9.0$ Hz, C_6H_3, 1 H), 8.46 (s, CHN, 1 H), 13.86 (s, C_6H_3OH, 1 H). ^{13}C NMR ($CDCl_3$): δ 14.06, 22.65, 26.01, 29.06, 29.33, 29.62, 31.90, 68.17, 69.28, 69.62, 101.5, 107.3, 107.4, 112.5, 112.9, 114.3, 133.2, 141.6, 148.0, 149.8, 159.4, 163.4, 163.8.

Bis[(*N*-3′,4′-didodecyloxyphenyl)-4-*n*-dodecyloxysalicylaldiminato]copper(II). *N*-(2-Hydroxy-4-*n*-dodecyloxybenzylidene)-3′,4′-didodecyloxyaniline (0.50 g, 0.00067 mol) dissolved in 20 ml of absolute ethanol and 10 ml of dried THF was added to a hot absolute ethanol solution (5.0 ml) of copper(II) chloride dihydrate (0.11 g, 0.00067 mol). The mixture was refluxed for 24 h. Methanol (10 ml) was added and the solution was allowed to stand in a refrigerator overnight. The green solids thus collected were redissolved in 25 ml of THF, and the solution was then filtered through Celite 545 to remove any insoluble solids. The THF solution was concentrated to dryness, and the product recrystallized from THF–methanol. The product was obtained as fine yellow–green crystals. Yield 56%. Anal. for $C_{98}H_{164}O_8N_2Cu$; calc. C, 75.36; H, 10.58. Found: C, 75.02; H, 10.34%.

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