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Formation of disordered hexagonal arrangements in bis(β,δ-triketonato)copper(II) complexes

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Two homologous series of 1-(4-alkoxy-2-hydroxyphenyl)-3-(3,4,5-trialkoxyphenyl)propane-1,3-diones and 1-(2-hydroxyphenyl)-3-(3,4,5-trialkoxyphenyl)propane-1,3-diones were prepared by base-catalysed rearrangement of 4-alkoxy-2-(3,4,5-trialkoxybenzoyloxy)acetophenones and 2-(3,4,5-trialkoxybenzoyloxy)acetophenones, respectively. The reaction of these β,δ-triketones with copper(II) acetate gave liquid-crystalline dicopper complexes, bis[1-(4-alkoxy-2-hydroxyphenyl)-3-(3,4,5-trialkoxyphenyl)propane-1,3-dionato]- and bis[1-(2-hydroxyphenyl)-3-(3,4,5-trialkoxyphenyl)propane-1,3-dionato]-copper(II). These copper complexes exhibit disordered hexagonal columnar (D_{hd}) mesophases which were identified by DSC analysis and polarized optical microscopy, and were also confirmed by X-ray powder diffraction. The variable-temperature EPR spectra were also studied.

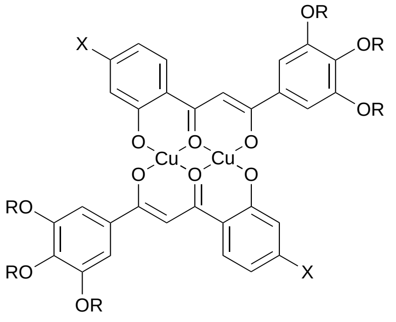
Metal co-ordination complexes constitute a large group of metallomesogenic materials[1] because of their well known rich and versatile chemistry. New types of such materials with novel physical properties due to incorporation of metal centers arise mainly from changes in the geometrical and electronic structures. In these systems liquid crystals containing multinuclear centers represent another fast-growing subgroup. These polymetallic systems[2] can not only produce more complicated structures leading to possible formation of molecular superstructures, but also facilitate attempts to understand the inter- as well as intra-molecular interaction between the metal centers in such systems. The formation of new materials from these metallic complexes may lead to many magneto- and electro-optical applications. For example, heterobinuclear complexes with two co-ordination sites capable of binding two different paramagnetic metal ions may generate magnetic materials if they are properly aligned.

We have been investigating bimetallomesogenic structures in which two metal centers were incorporated either in closer proximity[3] or more remote[4] from each other. Similar bimetallic liquid crystals[2a–d,3a,4,5] have been prepared in a variety of molecular structures, and most were found to form a columnar discotic mesophase. These bimetallomesogenic complexes exhibited not only various mesophases, but also interesting novel physical properties. Among them the heterobinuclear complexes in particular are worthy of special attention, since they are very promising in the development of a new field of metallomesogens, ferromagnetic liquid crystals.

In this paper we report our results on the preparation and mesomorphic studies of a series of dicopper liquid crystalline complexes.

Results and Discussion

Synthesis



R = $(CH_2)_{n-1}CH_3$

1 X = H

2 X = OR

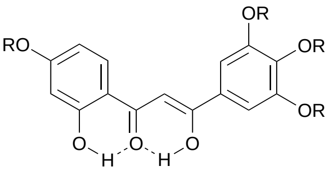
We have synthesized and characterized a number of dicopper complexes of β,δ-triketones, bis[1-(2-hydroxy-4-alkoxyphenyl)-3-(3,4,5-trialkoxyphenyl)propane-1,3-dionato]copper(II) **2** and bis[1-(2-hydroxyphenyl)-3-(3,4,5-trialkoxyphenyl)propane-1,3-dionato]copper(II) **1**. Literature procedures[6] involving Claisen condensation in the presence of sodium hydride or sodium ethoxide, starting either from methyl 4-alkoxy-2-hydroxybenzoate and 3,4,5-trialkoxyacetophenone, or from 4-alkoxy-2-hydroxyacetophenone and methyl 3,4,5-trialkoxybenzoate, gave no or low yields of the desired β,δ-triketones with separation difficulties. Another unsuccessful synthetic pathway involved first protection of the phenolic hydroxy group, then Claisen condensation reaction by NaH base, and finally deprotection of the hydroxy group to give the β,δ-triketones. Instead, for example, 2-(3,4,5-trialkoxybenzoyloxy)-4-alkoxyacetophenones, prepared by reactions of 3,4,5-trialkoxybenzoic acid chlorides and alkoxy-2-hydroxyacetophenones in dried pyridine with high yields, were then converted into 1-(4-alkoxy-2-hydroxyphenyl)-3-(3,4,5-trialkoxyphenyl)propane-1,3-diones by base-catalysed[7] rearrangement. The base used in this reaction was preheated powder potassium hydroxide. The neutralization temperature during this rearrangement reaction must be kept at 0 °C in order to avoid the further flavone-related side reactions under acidic conditions. The yields of the products were fairly high, 71–83%. Another series of 1-(2-hydroxyphenyl)-3-(3,4,5-trialkoxyphenyl)propane-1,3-diones was obtained by the same procedures. The NMR spectroscopic data showed that these β,δ-triketones exist in different keto–enol tautomeric forms. In $CDCl_3$ three characteristic ^1H NMR peaks at δ 6.68, 12.55 and 15.59 assigned to olefinic methine H, phenol H and enol H are indicative of the dominance of structures **A** and **B**. The ratio of the different tautomers was mainly dependent on the solvent. The structures **A** and **B** were also preferred by solid samples according to the absence of an absorption band at 1730 cm^{-1} which was observed for samples in $CHCl_3$ solution.

The β,δ-triketones reacted with copper acetate or copper chloride to give dicopper complexes. Yellow-to-green microneedle crystals were obtained by recrystallization from tetrahydrofuran (thf)–methanol. The dicopper compounds are

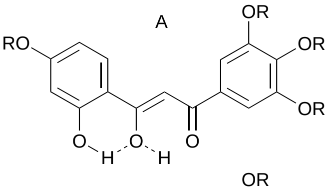
Table 1 Phase behaviors* of dicopper complexes **1** and **2**

Complex **1** $n = 5$	$K_1 \xrightleftharpoons[103.6\,(1.34)]{142.1\,(0.63)} K_2 \xrightleftharpoons[132.8\,(21.9)]{237.2\,(27.8)} Col_{hd} \xrightleftharpoons[230.8]{242.3} I_d$
6	$K \xrightleftharpoons[132.3\,(16.8)]{180.3\,(18.2)} Col_{hd} \xrightleftharpoons[226.2\,(0.16)]{233.2\,(0.17)} I$
7	$K_1 \xrightleftharpoons[43.4\,(0.79)]{55.7\,(0.75)} K_2 \xrightleftharpoons[108.4\,(3.47)]{141.8\,(3.22)} Col_{hd} \xrightleftharpoons[221.4\,(0.03)]{228.4\,(0.02)} I$
8	$K \xrightleftharpoons[83.8\,(1.63)]{129.2\,(1.59)} Col_{hd} \xrightleftharpoons[219.4\,(0.01)]{223.5\,(0.01)} I$
10	$K \xrightleftharpoons[69.3\,(1.92)]{101.3\,(2.68)} Col_{hd} \xrightleftharpoons[214.7\,(0.13)]{218.8\,(0.08)} I$
12	$K \xrightleftharpoons[55.8\,(0.42)]{83.4\,(0.54)} Col_{hd} \xrightleftharpoons[197.6\,(0.13)]{202.4\,(0.06)} I$
14	$K_1 \xrightleftharpoons[14.8\,(42.2)]{36.3\,(48.9)} K_2 \xrightleftharpoons[43.0\,(9.70)]{75.7\,(13.3)} Col_{hd} \xrightleftharpoons[187.0\,(0.13)]{190.5\,(0.13)} I$
2 $n = 6$	$K_1 \xrightarrow{74.2\,(19.5)} K_2 \xrightleftharpoons[43.5\,(10.5)]{112.3\,(63.1)} Col_{hd} \xrightleftharpoons[221.5\,(4.10)]{229.7\,(4.26)} I$
7	$K \xrightarrow{92.0\,(24.0)} Col_{hd} \xrightleftharpoons[224.0\,(6.27)]{231.1\,(6.52)} I$
8	$K \xrightarrow{89.8\,(78.6)} Col_{hd} \xrightleftharpoons[215.3\,(7.44)]{227.5\,(8.03)} I$
10	$K_1 \xrightarrow{54.6\,(17.5)} K_2 \xrightarrow{86.2\,(162)} Col_{hd} \xrightleftharpoons[202.4\,(7.48)]{214.7\,(6.65)} I$

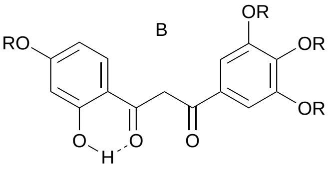
* K_1, K_2 = Crystal phase; Col_{hd} = columnar hexagonal disordered; I = isotropic; I_d = isotropic with decomposition. The transition temperature (°C) and enthalpies (in parentheses, kJ mol^{-1}) were determined by DSC at a scan rate of 10.0 °C min^{-1}.



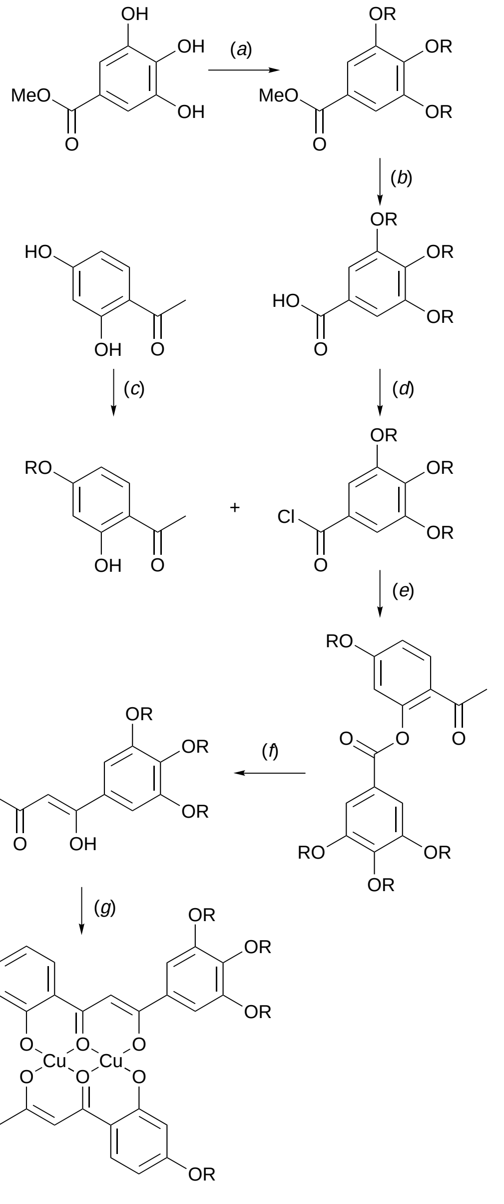
A



B



C



Scheme 1 (*a*) RBr (3.0 equivalents), K_2CO_3 (7.0 equivalents), KI (catalyst), refluxing in MeCOMe, 72 h, yield 73–94%; (*b*) KOH (2.0 equivalents), reflux in thf–water (5 : 1), 12 h, 92–98%; (*c*) RBr (1.0 equivalent), K_2CO_3 (1.0 equivalent), KI, refluxing in MeCOMe, 24 h, 79–88%; (*d*) $SOCl_2$ (2.0 equivalents), reflux in dried thf, 4 h; (*e*) stirring in thf at 0 °C, then warming and stirring at room temperature, 16 h, 77–79%; (*f*) KOH (1.5 equivalents), stirring in dried pyridine at 50 °C, 30 min, 71–83%; (*g*) $Cu(O_2CMe)_2$ (1.1 equivalents), KOH (a pellet), reflux in CH_2Cl_2–MeOH, 2 h, 73–81%

all paramagnetic, and their ^1H and ^{13}C NMR spectra display only broad alkoxy signals. All other protons close to the paramagnetic copper centers are not observed. Elemental analysis also confirmed the bimetallic identity of the complexes. The typical synthetic pathways for these bimetallic complexes **2** are summarized in Scheme 1.

Mesomorphic properties

The formation of mesophases in metallomesogens is substantially affected by weak intermolecular co-ordination forces between the metal complexes. In these systems the attractive co-ordination force, weak dipole–dipole and dispersion forces between metal centers or metal interactions with co-ordinating atoms (such as O, S or N) in neighbouring molecules, is often influential. In many metallomesogen systems co-operation of different metal centers often results in the formation and structures of mesophases. For bimetallic centers as an extended core group in such polymetallic systems the delicate balance of the two molecular features appeared to be particularly important. In discotic columnar mesophases[8] the disc-like molecules stack into columns in hexagonal (Col_h) or rectangular (Col_r) arrangement. Within a column the molecules can be either periodically or aperiodically stacked. Moreover, certain molecules which are themselves not disc-shaped[2a,5c,9] may also exhibit similar columnar phases.

The copper complexes **1** and **2** all exhibit the liquid-crystalline behavior of columnar discotics, according to DSC analysis and polarized optical microscopy. The phase behavior of the complexes is summarized in Table 1. Upon heating the complexes melt to give birefrigent fluid phases with columnar superstructures as is often observed for disc-shaped molecules. The DSC analysis showed typical discotic phase transitions, crystal-to-discotic-to-isotropic (Cry ⟶ Col ⟶ I). At the crystal-to-discotic transition the flexible side chains undergo disorder but the central core remains stacked in columns, however, the core unstacks at the discotic-to-isotropic transition. A typical large enthalpy for the crystal-to-liquid crystal transition at lower temperature (76–237 °C) and a low enthalpy for the liquid crystal-to-isotropic transition at higher temperature (191–242 °C) were observed, and the latter value indicated that

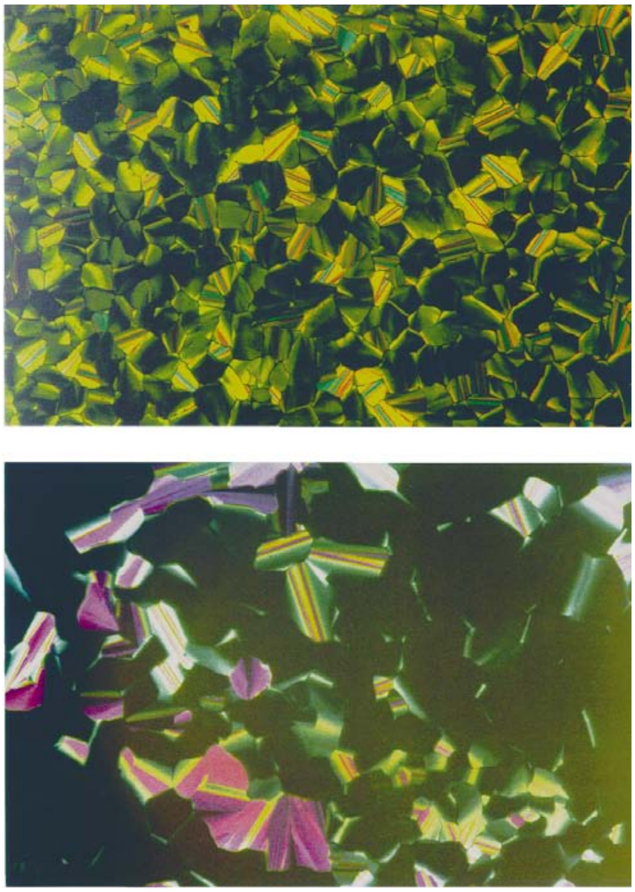


Fig. 1 Texture shown by complex **1** (R = $C_{10}H_{21}$) at 122 °C (top) and by **2** (R = C_8H_{17}) at 162 °C (bottom)

the mesophases were highly disordered. The temperature range of discotic mesophases for copper complexes is sensitive to the number of side chains. For example, the temperature range for complexes **1** increased with carbon chain length (*i.e.* $T = 53$ °C for $n = 6$ and 115 °C for $n = 14$), however the temperature for **2** remained approximately in the same range (*i.e.* $T = 117$–140 °C for $n = 6$ to 10).

Complexes **1** are more likely to be rod shaped, however two molecules stacking perpendicularly can still display a disc-like shape similar to that of **2**. Besides, the formation of liquid crystallinity in these bimetallic systems is very sensitive to the density of the flexible side chains. For example, liquid crystallinity is totally suppressed in derivatives substituted by 4-alkoxyphenyl or 3,4-dialkoxyphenyl groups instead of 3,4,5-trialkoxyphenyls. Highly ordered crystalline mesophases were observed in these complexes with four or six alkoxy side chains.

Complexes **1** exhibit relatively high clearing points (224–242 °C), and a few undergo partial decomposition ($n = 4$ or 5). The melting and clearing points both decreased as the side-chain length increased. When cooled from their isotropic phases, they display optical textures (see Fig. 1) which are a mixture of pseudo-focal conics and mosaic regions with linear birefrigent defects, suggesting hexagonal columnar structures.

Powder X-ray diffraction was used to confirm the structures of the mesophases. A summary of the diffraction peaks and lattice constants for complexes **1** and **2** is given in Table 2. For example, complex **1** ($n = 14$) displays a diffraction pattern corresponding to a two-dimensional hexagonal lattice with a strong and two weak peaks at 38.02, 21.77 and 19.07 Å. These are characteristic of a discotic columnar $\mathrm{Col_{hd}}$ phase with *d*-spacing ratios of 1, $(1/3)^{\frac{1}{2}}$, $(1/4)^{\frac{1}{2}}$ and $(1/7)^{\frac{1}{2}}$, corresponding to Miller indices (100), (110), (200) and (300), respectively. However, liquid-like correlations between the rigid cores occur at wider angle regions of 5.20–5.27 Å. Most complexes also display an interesting additional broad halo peak at mid-angle of core–core correlation *d* spacing ≈ 6.08 Å. The common temperature dependence of the lattice parameters in liquid crystals was also observed for these copper complexes. The low-angle reflections of complexes generally shift to a larger *d* spacing with decreasing temperature [*i.e.* $d = 32.54$ Å at 100 °C and 31.82 Å at 120 °C for complex **1** ($n = 10$)], which indicates a lattice expansion in the mesophase. The absence of distinct peaks at wide angle is consistent with the DSC analysis which yields low enthalpies for the discotic-to-isotropic transition, indicative of a highly disordered mesophase. The hexagonal lattices are correlated well with increasing side-chain lengths.

Table 2 Variable-temperature XRD data for copper complexes **1** and **2**

Complex	Mesophase	Lattice spacing *a*/Å	*d* spacing/Å obs. (calc.)	Miller indices
1 $n = 14$	$\mathrm{Col_{hd}}$ at 130 °C	43.90	38.02 (38.02)	(100)
			21.77 (21.95)	(110)
			19.07 (19.01)	(200)
			6.03 (br)	
			5.22 (br)	
10	$\mathrm{Col_{hd}}$ at 120 °C	36.74	31.82 (31.82)	(100)
			18.35 (18.37)	(110)
			15.91 (15.91)	(200)
			5.24 (br)	
	$\mathrm{Col_{hd}}$ at 100 °C	37.57	32.54 (32.54)	(100)
			18.71 (18.79)	(110)
			16.39 (15.27)	(200)
			5.20 (br)	
8	$\mathrm{Col_{hd}}$ at 160 °C	33.72	29.20 (29.20)	(100)
			16.91 (16.86)	(110)
			14.58 (14.60)	(200)
			6.09 (br)	
			5.27 (br)	
7	$\mathrm{Col_{hd}}$ at 140 °C	32.09	27.79 (27.79)	(100)
			16.02 (16.04)	(110)
			13.93 (13.89)	(200)
			5.24 (br)	
6	$\mathrm{Col_{hd}}$ at 70 °C	31.00	26.85 (26.85)	(100)
			15.55 (15.50)	(110)
			13.43 (13.42)	(200)
			5.25 (br)	
2 $n = 10$	$\mathrm{Col_{hd}}$ at 170 °C	37.38	32.37 (32.37)	(100)
			18.52 (18.69)	(110)
			16.06 (16.19)	(200)
			6.09 (br)	
			5.27 (br)	
6	$\mathrm{Col_{hd}}$ at 160 °C	31.41	27.21 (27.21)	(100)
			15.79 (15.71)	(110)
			13.62 (13.60)	(200)
			5.27 (br)	

EPR studies

Electron paramagnetic resonance spectroscopy has proved to be a valuable technique[10] for investigating the mesomorphic behavior of paramagnetic metallomesogenic materials. The inter- or intra-molecular exchange, molecular ordering and dynamic molecular motion in different mesophases can be determined. Fig. 2 shows the X-band EPR spectra of dicopper complex **1** ($n = 12$) measured at different temperatures. The spectra consist of broad lines, and the hyperfine structure, if any, is hardly resolved. The top spectrum (*a*), corresponds to the as-received sample taken at room temperature, consists of two features, one shoulder barely observed in the low-field region and the other in the high-field region. When the sample was warmed to the clearing point at 210 °C the signal width [Fig. 2(*b*)] became narrower and the intensity reduced. However, spectra (*c*) and (*d*) showed similar, but broader signals when measured at the mesophase temperatures of 160 and 90 °C. Spectrum (*e*) showed that the hyperfine structure is somehow better resolved when cooling back to room

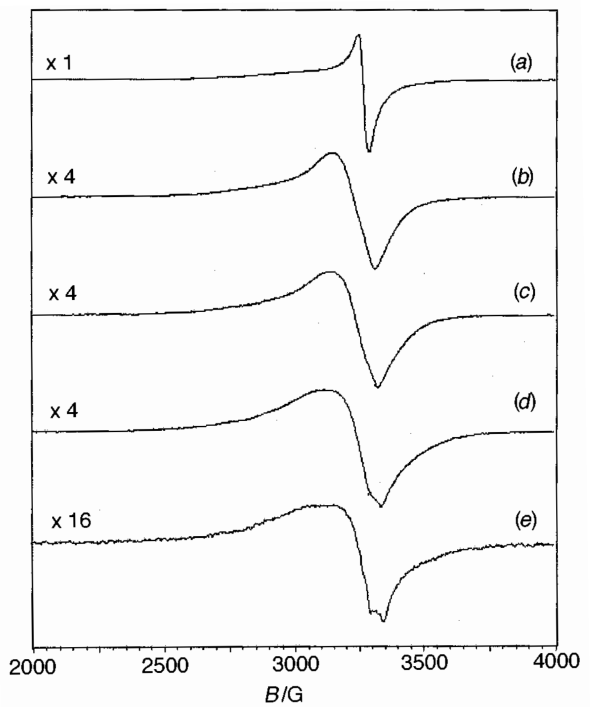


Fig. 2 The EPR spectra of copper complex **1** ($n = 12$) measured at (*a*) room temperature of as-received samples, (*b*) 483 K (isotropic phase), (*c*) 433 K (discotic phase), (*d*) 363 K (discotic phase) and (*e*) on cooling back to room temperature; G = 10^{-4} T

temperature. The EPR data also indicated that the spectra were independent of the aliphatic chain length.

Future research will focus on attempts to prepare heterobimetallic complexes, and also study the related physical properties of these bimetallic complexes, particularly to understand the effects of two remote metal centers on liquid crystallinity.

Experimental

All chemicals and solvents were reagent grade from Aldrich Chemical Co. and used without further purification. Tetrahydrofuran and 1,2-dimethoxyethane (dme) were dried over sodium–benzophenone; pyridine was predried over KOH pellets for prolonged periods, followed by distillation fresh from BaO before use. Proton and ^{13}C NMR spectra were measured on a Bruker DRS-200 spectrometer, infrared spectra on a Bio-Rad FTS-155 using polystyrene as a standard. The DSC thermographs 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° min^{-1} unless otherwise noted. Polarized optical microscopy was carried out on a Nikkon MICROPHOT-FXA 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 a mica and silicon standard. The powder samples were charged in Lindemann capillary tubes (80 mm long and 1/100 mm thick; Charles Supper Co.) having an inner diameter of 0.1 or 0.2 mm. The sample was heated above the isotropic temperature and allowed to remain at that temperature for 10 min. It was then cooled at a rate of 5.0 °C min^{-1} to the desired temperature and then the diffraction data were collected. The EPR measurements were made with an EMX Bruker spectrometer at X-band. Powder samples were placed in quartz tubes of 2.0 mm diameter.

The methyl 3,4,5-trialkoxybenzoate ester was prepared by literature procedures.[3,4] The elemental analyses of the copper complexes are given in Table 3.

Table 3 Elemental analysis of dicopper complexes **1** and **2** with calculated values in parentheses

		Analysis (%)	
Complex	R	C	H
1	C_5H_{11}	72.73 (72.60)	8.04 (8.12)
	C_6H_{13}	73.65 (73.62)	8.53 (8.61)
	C_7H_{15}	74.75 (74.49)	9.13 (9.03)
	C_8H_{17}	75.38 (75.25)	9.43 (9.39)
	$C_{10}H_{21}$	76.56 (76.49)	9.85 (9.98)
	$C_{12}H_{25}$	77.65 (77.47)	10.48 (10.45)
	$C_{14}H_{29}$	78.11 (78.26)	10.71 (10.83)
2	C_6H_{13}	73.65 (73.36)	8.83 (9.16)
	C_7H_{15}	74.75 (74.36)	9.33 (9.58)
	C_8H_{17}	75.38 (75.21)	9.73 (9.94)
	$C_{10}H_{21}$	76.56 (76.57)	10.32 (10.51)

General preparative procedures

For 4-alkoxy-2-hydroxyacetophenone. 2,4-Dihydroxyacetophenone (5.00 g, 0.033 mmol), 1-bromodecane (7.27 g, 0.0033 mmol), K_2CO_3 (4.54 g, 0.0033 mmol) and KI (catalytic amount) were mixed, and then refluxed in dried acetone (250 cm^3) for 24 h under a nitrogen atmosphere. The reaction mixture was filtered and concentrated. To the solution was added an aqueous solution of KOH (0.2 M, 100 cm^3), and then extracted twice with CH_2Cl_2 (100 cm^3). The combined CH_2Cl_2 solution was dried over $MgSO_4$ and reduced to give a pink solid. White needle crystals were obtained after recrystallization from EtOH. Yield 88%. ^{1}H NMR ($CDCl_3$): δ 0.86 (t, CH_3, 3 H), 1.25–1.77 (m, CH_2, 16 H), 2.53 (s, $COCH_3$, 3 H), 3.96 (t, OCH_2, 8 H), 6.37 (d, C_6H_3, 1 H), 6.44 (s, C_6H_3, 1 H), 7.58 (d, C_6H_3, 1 H) and 12.73 (s, OH, 1 H). ^{13}C NMR ($CDCl_3$): δ 13.92, 22.55, 25.79, 25.83, 28.77, 29.14, 29.40, 31.74, 68.18, 101.1, 107.7, 113.6, 132.0, 165.1, 165.6 and 202.1.

For 3,4,5-trialkoxybenzoic acid. Methyl 3,4,5-tridecyloxybenzoate (10.0 g, 0.02 mol) was refluxed in thf–water (60 cm^3:40 cm^3) in the presence of KOH (1.12 g, 0.02 mol) for 24 h. The solution was twice extracted with CH_2Cl_2. 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. Yield 94%. ^{1}H NMR ($CDCl_3$): δ 0.92 (t, 9 H, CH_3), 1.31 (m, 42 H, CH_2), 1.83 (m, 6 H, CH_2), 4.07 (t, 6 H, OCH_2) and 7.36 (s, 2 H, C_6H_2). ^{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, 108.4, 123.6, 143.0, 152.7 and 172.0.

For 3,4,5-tridecyloxybenzoyl chloride. 3,4,5-Tridecyloxybenzoic acid (5.0 g, 0.0085 mol) dissolved in dried thf (100 cm^3) was added dropwise to a thf solution of $SOCl_2$ (1.24 cm^3, 0.017 mol) at ice-bath temperature under a nitrogen atmosphere. The mixture was slowly warmed to room temperature and then refluxed for 4 h. The solution was concentrated to remove thf and excess of $SOCl_2$. This process was repeated several times to remove any residual $SOCl_2$ which would affect the following reaction. The white solid thus obtained was directly used for the next reaction without any purification or recrystallization.

For 4-alkoxy-2-(3,4,5-trialkoxybenzoyloxy)acetophenone. 3,4,5-Tridecyloxybenzoyl chloride prepared above was dissolved in dried pyridine (100 cm^3) at 0 °C and mixed with 4-decyloxy-2-hydroxyacetophenone (2.49 g, 0.0085 mol). The ice-bath was then removed after 1 h, and the reaction mixture was stirred at room temperature for 16 h. The solution was neutralized with HCl(aq), and then extracted twice with CH_2Cl_2 (50 cm^3). The solution was concentrated to give a light yellow solid. A white solid was obtained after recrystallization from CH_2Cl_2–MeOH. Yield 74%. ^{1}H NMR ($CDCl_3$): δ 0.86 (t, CH_3, 12 H), 1.26 (m, CH_2, 56 H), 1.82 (m, CH_2, 8 H), 2.49 (s, $COCH_3$, 3 H), 4.07 (t, OCH_2, 8 H), 6.70 (s, C_6H_2, 2 H), 6.86 (d, C_6H_3, 1 H), 7.43 (s, C_6H_3, 1 H) and 7.91 (d, C_6H_3, 1 H). ^{13}C NMR ($CDCl_3$): δ 14.04, 22.64, 26.05, 29.27, 29.32, 29.34, 29.53, 29.59, 29.62, 29.66, 29.70, 29.74, 30.33, 31.89, 69.20, 73.52, 108.7, 123.5, 123.8, 126.0, 130.1, 131.4, 133.2, 143.3, 149.5, 153.0, 164.8 and 197.5.

For 1-(4-alkoxy-2-hydroxyphenyl)-3-(3,4,5-trialkoxyphenyl)- and 1-(2-hydroxyphenyl)-3-(3,4,5-trialkoxyphenyl)-propane-1,3-diones. 4-Decyloxy-2-(3,4,5-tridecyloxybenzoyloxy)acetophenone (2.0 g, 0.0020 mol) dissolved in dried pyridine (50 cm^3) was warmed to 50 °C, and KOH powder (0.1722 g, 0.0030 mol) was slowly added. The mixture was stirred at 50 °C for 30 min then neutralized with HCl(aq) and extracted with CH_2Cl_2 (100 cm^3). The solution was concentrated to give a yellow solid. A light yellow solid was obtained after recrystallization from $CHCl_3$–MeOH. Yield 80%. ^{1}H NMR ($CDCl_3$): δ 0.88 (t, CH_3, 12 H), 1.27 (m, CH_2, 56 H), 1.87 (m, CH_2, 8 H), 4.06 (t, OCH_2, 8 H), 6.58 (s, CHCO, 1 H), 6.60 (s, C_6H_3, 1 H), 6.64 (d, C_6H_3, 1 H), 7.11 (s, C_6H_2, 2 H), 7.72 (d, C_6H_3, 1 H), 12.57 (s, OH, 1 H) and 15.57 (s, *H*OCH=C, 1 H). ^{13}C NMR ($CDCl_3$): δ 14.07, 22.66, 25.94, 26.07, 26.10, 28.98, 29.29, 29.34, 29.37, 29.41, 29.53, 29.58, 29.63, 29.65, 29.71, 30.35, 31.87, 31.91, 31.92, 68.38, 69.49, 73.61, 91.41, 101.8, 105.7, 108.2, 112.4, 128.6, 129.9, 142.2, 153.2, 165.2, 165.4, 176.3 and 193.9.

1-(2-Hydroxyphenyl)-3-(3,4,5-tridecyloxyphenyl)propane-1,3-dione: yield 79%, light yellow solid. ^{1}H NMR ($CDCl_3$): δ 0.88 (t, CH_3, 9 H), 1.27 (m, CH_2, 54 H), 1.78 (m, CH_2, 6 H), 4.05 (t, OCH_2, 6 H), 6.65 (s, CHCO, 1 H), 6.73 (s, C_6H_3, 1 H), 6.87 (d, C_6H_3, 1 H), 7.54 (s, C_6H_2, 2 H), 7.76 (d, C_6H_3, 1 H), 12.01 (s, OH, 1 H) and 15.81 (s, *H*OCH=C, 1 H). ^{13}C NMR ($CDCl_3$): δ 14.72, 23.30, 23.32, 26.69, 26.73, 29.97, 30.01, 30.04, 30.19, 30.21, 30.26, 30.29, 30.35, 30.97, 32.54, 32.56, 70.12, 92.44, 106.5, 119.4, 119.6, 128.9, 129.0, 136.3, 143.2, 153.9, 163.0, 178.6 and 195.6.

For bis[1-(4-alkoxy-2-hydroxyphenyl)-3-(3,4,5-trialkoxyphenyl)propane-1,3-dionato]- and bis[1-(2-hydroxyphenyl)-3-(3,4,5-trialkoxyphenyl)propane-1,3-dionato]-copper(II). *Bis*[1-(4-*decyloxy*-2-*hydroxyphenyl*)-3-(3,4,5-*tridecyloxyphenyl*)*propane*-1,3-*dionate*]*copper*(II). 1-(4-Decyloxy-2-hydroxyphenyl)-3-(3,4,5-tridecyloxyphenyl)propane-1,3-dione (0.30 g, 0.0004 mol) dissolved in CH_2Cl_2 (2 cm^3) was added dropwise to a hot MeOH (10 cm^3) solution of $Cu(O_2CMe)_2 \cdot H_2O$ (0.0845 g, 0.0004 mol). A KOH pellet (0.0449 g, 0.0008 mol) was added and the solution was refluxed for 2 h. It was filtered and concentrated to give a brownish solid. A light green solid was obtained after recrystallization from ethyl acetate–methanol. Yield 72%. IR (thin film): 2919, 2850, 1623, 1588, 1530, 1518, 1496, 1469, 1451, 1397, 1368, 1335, 1309, 1250, 1191, 1145, 1131, 1128, 1031, 987, 972, 860, 831, 811, 792, 774, 732 and 671 cm^{-1}.

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