

Preparation, characterization and mesomorphic properties of nickel and copper complexes derived from *N,N'*-bis[3-(3',4'-dialkoxyphenyl)-3-oxopropenyl]ethylenediamine

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The preparation, characterization and mesomorphic properties of copper and nickel complexes derived from *N,N'*-bis[3-(3',4'-dialkoxyphenyl)-3-oxopropenyl]ethylenediamine are reported. Liquid crystalline behavior for these structurally similar complexes was found to be strongly dependent both on the number of sidechains and metal centers incorporated. Nickel complexes with four or six alkoxy sidechains exhibited columnar phases. However, nickel complexes with two alkoxy sidechains and all copper complexes regardless the numbers of the sidechains were not liquid crystalline. The structure of the mesophases was confirmed as columnar hexagonal (Col_h) by powder XRD diffraction. The data that the copper complexes have slightly lower isotropic temperatures than the analogous nickel complexes suggested that the lack of liquid crystallinity for the copper complexes may be attributed to weaker molecular interactions. The results also indicated that nickel complexes with four sidechains showed a wider range of mesophase temperature than complexes with six sidechains.

Introduction

Numerous metallomesogenic compounds with unique geometries and molecular shapes have been generated by incorporation¹ of a metal center or metal centers into organic moieties. In general the geometry of the complex is often determined by the metal center incorporated and the organic chelating ligand, and it can vary from square-planar to tetrahedral structures for complexes² with coordination numbers of four. Square-planar (*i.e.* Cu²⁺, Ni²⁺, Pd²⁺, Pt²⁺, Zn²⁺) and square-pyramidal geometries (FeCl₂⁺, VO²⁺) generally give rise to liquid crystals, whereas tetrahedral geometries are often not mesomorphic. Some of these materials have been extensively studied as potential candidates in terms of applications and all the related physical properties may originate from the rich electronic configuration of the metal centers.

Incorporation of a metal center can often induce the formation of mesophases by a non-mesogenic organic ligand, and this differentiation in mesomorphic properties is generally attributed to the change of molecular shape and/or intermolecular interaction. On the other hand the mesomorphic properties may be totally lost upon incorporation of a metal ion.

In previous studies³ we demonstrated the formation of mesophases by use of a β-enaminoketonate framework as the core group in which the better planar core based on β-enaminoketonato instead of β-diketonato structures was applied to induce the mesophases. The separation between

molecular layers is extremely critical in the formation of columnar phases since the induction of the mesophase is mainly controlled by a delicate balance of intermolecular interactions.

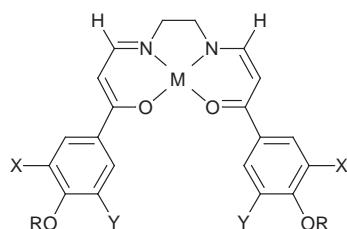
Herein we report the preparation, characterization and mesomorphic properties of three series of copper and nickel complex analogues derived from *N,N'*-bis[3-(3',4'-dialkoxyphenyl)-3-oxopropenyl]ethylenediamine. Of these, nickel complexes **2** and **3** exhibited columnar hexagonal phases, and copper complexes were not liquid crystalline.

Results and discussion

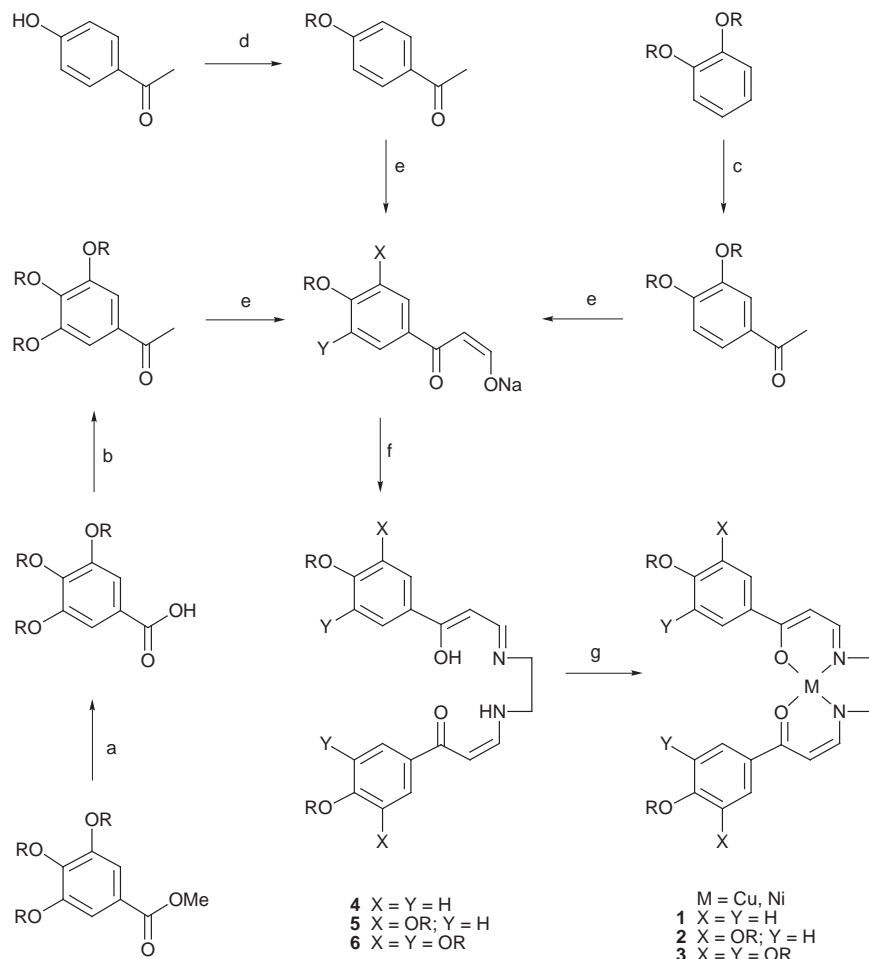
Synthesis

The synthetic pathways to copper and nickel complexes **1**, **2** and **3** are summarized in Scheme 1. The preparation of 4-alkoxyacetophenones, 3,4-dialkoxyacetophenones and 3,4,5-trialkoxyacetophenones were *via* literature procedures.⁴ The sodium salts of alkoxyphenyl-3-oxo-3-phenylpropionaldehyde derivatives were obtained by the Claisen formylation⁵ reaction of the appropriate acetophenone, ethyl formate and sodium metal dispersed in diethyl ether. The isolation of the neutral forms of alkoxyphenyl-3-oxo-3-phenylpropionaldehydes was not attempted owing to their relatively low thermal stability. The ethylenediamine Schiff bases; *N,N'*-bis[3-(3',4'-dialkoxyphenyl)-3-oxopropenyl]ethylenediamines were obtained as light yellow solids by reaction of the freshly prepared sodium salts with ethylenediamine in refluxing dried dichloromethane in high yields. The reaction⁹ of Schiff bases with copper(II) acetate monohydrate or nickel(II) acetate tetrahydrate in refluxing THF-methanol produced the complexes. Recrystallization twice from ethyl acetate or THF-methanol gave yellow solids for the nickel complexes and green-gray solids for copper complexes.

These Schiff base derivatives were characterized by ¹H and ¹³C NMR spectroscopy. Schiff bases can potentially exist possibly in three different keto-enol tautomeric⁶ forms; A, B and C (Fig. 1). The ¹H NMR data in CDCl₃, *e.g.*, for **5** (*n* = 16) showed three characteristic peaks at δ 5.64, 6.75 and 10.19, assigned to olefinic methine H (-CH=C-), aldehyde H (-CH=N-) and imine H (-C=NH-). In addition, the preference for the tautomeric A structure was also indicated by two



M = Cu, Ni; R = (CH₂)_nH
1 X = Y = H
2 X = OR; Y = H
3 X = Y = OR



Scheme 1 Reagents and conditions: a, KOH (2.0 equiv.), refluxing in THF–H₂O (9/1), 12 h; b, CH₃Li (1.1 equiv.), stirred in dried THF at 0 °C; then at RT, 12 h. c, CH₃COCl (1.1 equiv.), AlCl₃ (3.0 equiv.), stirred in CH₂Cl₂ at 0 °C, then at RT, 8 h; d, RBr (1.1 equiv.), K₂CO₃ (3.0 equiv.), refluxing in Me₂CO, 18 h; e, ethyl formate (4.5 equiv.), Na (3.0 equiv.), stirred in Et₂O at RT, 8 h; f, NH₂(CH₂)₂NH₂ (0.55 equiv.), CH₃CO₂H (3 drops), refluxing in CH₂Cl₂, 12 h; g, M(OAc)₂ (1.1 equiv.); M=Cu, Ni, refluxing in THF–CH₃OH, 12 h.

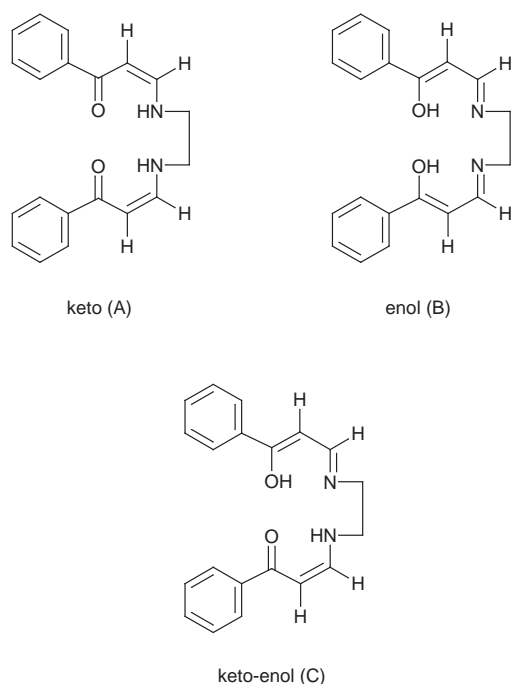


Fig. 1 Three structures of keto-enol tautomeric forms for enamminoketone derivatives.

characteristic peaks at δ 189.63 and 153.73 in the ¹³C NMR spectrum. Copper (d⁹) compounds, which are paramagnetic, displayed only broad alkoxy signals in the ¹H and ¹³C NMR spectra. However, the nickel complexes showed sharp signals, also indicating the diamagnetic configuration. Elemental analysis confirmed the purity of the complexes.

Mesomorphic properties

The liquid crystalline behavior for the metal complexes was studied by thermal analysis (DSC) and polarized optical microscopy. Nickel complexes exhibited columnar phases while copper complexes formed crystalline phases. Phase transitions and thermodynamic data for these metal complexes were summarized in Table 1. The nickel complexes **2** and **3** with four and six alkoxy sidechains exhibited enantiotropic liquid crystalline behavior, whereas complexes **1** with two sidechains were not liquid crystalline.

This dependence of sidechain density has been commonly observed in other columnar phases.^{4a-c,7c} Two transitions of crystal-to-columnar (K→Col) and columnar-to-isotropic (Col→I) were typically observed in all nickel derivatives. The molecular shapes of these metal complex are roughly half-disc, and the correlated columnar mesophases are formed by shape effects and dative interaction between neighboring complexes. Two molecules rotated by 180° are stacked in an antiparallel organization⁷ within columns.

DSC data showed that the crystal-to-mesophase transitions, for example, for nickel complexes **2**, were observed in the

Table 1 Phase behavior^a of metal complexes, **1**, **2** and **3**

1	Ni	8		K		108.6 (40.0)	I
						65.3 (41.3)	
	16		K		113.5 (85.8)	I	
					98.0 (85.3)		
	Cu	8		K		105.3 (30.4)	I
						54.1 (31.4)	
16		K		100.1 (73.9)	I		
				85.6 (88.1)			
2	Ni	10		K		110.0 (20.4)	I
						105.7 (20.9)	
	12	K	57.7 (2.84)	Col _h		108.5 (13.4)	I
						54.4 (2.64)	
	14	K	62.9 (6.00)	Col _h		105.6 (12.0)	I
						58.8 (6.03)	
	16	K	66.8 (5.90)	Col _h		100.5 (5.83)	I
						59.3 (6.50)	
	18	K	73.4 (14.9)	Col _h		102.1 (7.49)	I
						88.9 (6.40)	
Cu	10		K		93.1 (7.60)	I	
					93.9 (40.0)		
12		K			60.1 (45.6)	I	
					89.6 (36.9)		
16		K			75.7 (57.2)	I	
					88.9 (34.1)		
3	Ni	14	K	70.1 (3.55)	Col _h	75.7 (5.45)	I
						66.7 (5.16)	
	16	K	64.5 (1.60)	Col _h		70.6 (2.13)	I
						62.5 (2.90)	
	Cu	14		K		71.0 (16.5)	I
						61.3 (16.5)	
16		K			44.8 (14.5)	I	
					<20.0		

^a*n* Represents the number of carbons in the alkoxy chain. K = crystal phase; Col_h = columnar hexagonal phase; I = isotropic. The transition temperatures (°C) and enthalpies (in parenthesis, kJ mol⁻¹) are determined by DSC at a scan rate of 10.0 °C min⁻¹.

temperature range 58.0–73.0 °C on heating with the magnitude of transition enthalpies ranging from 2.84 to 14.9 kJ mol⁻¹, and isotropic points were all in the range 109.0–101.0 °C with a relatively large enthalpy (5.83–13.4 kJ mol⁻¹). The relatively large enthalpies indicated that the mesophases were in a highly ordered state.⁸ Similar thermal data were observed for nickel complexes **3**. Increasing the carbon length in the alkoxy sidechains decreased the clearing temperature, mainly due to the greater dispersive forces associated with the longer alkoxy chains. The dependence of mesophase formation on the sidechain density was also studied. Increasing the sidechain numbers of the nickel complexes from four (**2**) to six (**3**) increased the melting temperatures and decreased the clearing temperatures. On the other hand the temperature range of the mesophase was decreased from 28.7–51.0 °C for **2** to 5.6–6.1 °C for **3**, as shown in Fig. 2. These complexes have clearing temperatures relatively lower than most metallomesogenic complexes. Under a polarized optical microscope on very slow cooling from the isotropic point a mosaic texture was observed for a thin layer of samples between two glass plates, whereas, textures more like focal-conic with a large area of uniform homeotropic alignment was observed with thicker samples.

Surprisingly, none of the copper complexes displayed any mesomorphic properties regardless of the numbers of the

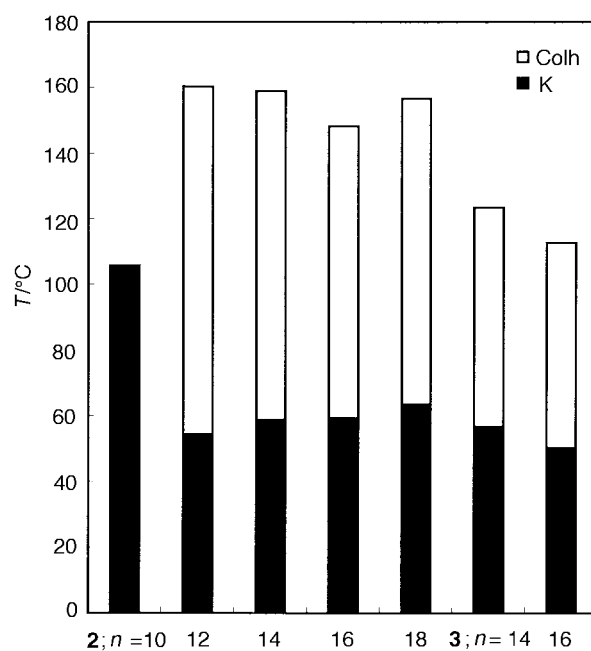


Fig. 2 Bar graph showing the phase behavior of the nickel complexes (**2** and **3**); *n* is the carbon number of the sidechains.

sidechains, and only a crystal-to-isotropic (K→I) transition was observed. Such drastic change in mesomorphic properties due to incorporation of different metals has also been observed in other systems,^{1a} and can be due to many factors. The lack of liquid crystallinity is generally believed to be attributed to weaker interaction between the copper complexes, and this suggestion was indicated by the fact that the clearing temperatures of the copper complexes were slightly lower than their nickel analogues. However, *ca.* 2–3 times larger enthalpies were observed for the crystal-to-isotropic transitions in the copper relative to the nickel complexes.

Copper and nickel complexes of similar structures derived from imineketone derivatives with six alkoxy sidechains reported by Swager's group^{7b} were found to form hexagonal disordered columnar phases. Detailed comparison of DSC data for these two types of metal complexes showed that all imineketone-derived complexes had higher isotropic points and much larger enthalpies (2–4 times) of the crystal-to-isotropic transitions than iminealdehyde-derived homologues. These observations were rationalized in that the molecular interactions in columnar arrangements for imineketone-derived complexes should be much better or/and stronger owing to the presence of terminal methyl groups. On the other hand molecular interactions in iminealdehyde-derived complexes are much weaker than in imineketone-derived complexes,⁹ and only little energy was needed to overcome such a small energy barrier as to pass into the liquid phase upon heating. These results also indicated that complexes without terminal tetrahedral methyl groups in iminealdehyde-derived materials preferred to form ordered hexagonal phases (Col_{ho}) over hexagonal disordered phases (Col_{hd}) in imineketone-derived complexes. The core–core distance was 3.68 Å (**2**, M = Cu, *n* = 12), which is close to stacking distance in imineketone-derived complexes (3.60 Å).^{7b}

The assignment of a columnar hexagonal phase was confirmed by X-ray powder diffraction data. A summary of the diffraction peaks and lattice constants for the nickel complexes **2** and **3** is given in Table 2. For example, as shown in Fig. 3, nickel complex **2** (*n* = 12) displays a diffraction pattern of a two-dimensional hexagonal lattice with one intense peak and two weak peaks at 35.09, 20.34 and 17.49 Å at 80 °C. This type of diffraction pattern is characteristic of a hexagonal

Table 2 Variable-temperature XRD diffraction data for nickel(*n*) complexes **2** and **3**

Complex	Mesophase		Lattice spacing/ Å	<i>d</i> -Spacing/ Å obs. (calc.)	Miller indices	
2	Col _h	80 °C	40.51	35.09 (35.09)	(100)	
				20.34 (20.26)	(110)	
				17.49 (17.54)	(200)	
					4.47 (br)	
					3.68	
	Col _h	104 °C	41.01	35.52 (35.52)	(100)	
				20.55 (20.51)	(110)	
				17.97 (17.76)	(200)	
					4.53 (br)	
					3.54	
	Col _h	90 °C	42.78	37.05 (37.05)	(100)	
				21.83 (21.39)	(110)	
18.64 (18.52)				(200)		
				4.78 (br)		
Col _h	80 °C	49.32	42.71 (42.71)	(100)		
			24.57 (24.66)	(110)		
			21.23 (21.35)	(200)		
				4.63 (br)		
				3.89		
Col _h	57 °C	49.16	42.57 (42.57)	(100)		
			24.80 (24.58)	(110)		
			21.39 (21.29)	(200)		
				17.53		
				4.27 (br)		
				3.96		
3	Col _h	60 °C	44.14	38.25 (38.25)	(100)	
				19.16 (19.13)	(200)	
				16.40		
					4.59 (br)	
					3.32	
	Col _h	57 °C	46.57	40.33 (40.33)	(100)	
23.30 (23.28)				(110)		
20.25 (20.16)				(200)		
				4.45 (br)		
				3.70		

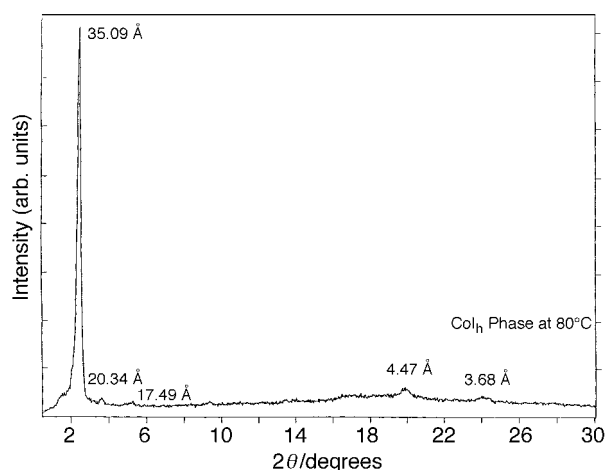


Fig. 3 Powder X-ray diffraction pattern of the columnar hexagonal phase (Col_h) at 80 °C for nickel complexes **2** (*n* = 12).

columnar (Col_h) phase with a *d*-spacing ratio of 1, (1/3)^{1/2} and (1/4)^{1/2}, corresponding to Miller indices (100), (110) and (200), respectively. This corresponds to an intercolumnar distance (*a* parameter of the hexagonal lattice) of 40.51 Å. An additional weak halo peak at medium angle (*d*-spacing ≈ 4.47 Å) was observed for most complexes. The presence of a distinct peak at *ca.* 3.68 Å indicated a relatively ordered mesophase which is consistent with DSC analysis of large enthalpies for the columnar-to-isotropic transition. This peak reflects a more regular period within the columns than

for many disordered Col_h systems. The temperature dependence of the lattice parameters in liquid crystals was also studied. We found that the low-angle reflection generally shifted to lower *d*-spacing at lower temperatures (*i.e.* *d* = 40.51 Å at 80 °C and *d* = 41.01 Å at 104 °C for complex **2**; *n* = 12). The hexagonal lattices are also well correlated with increasing side chain lengths.

Conclusion

We have prepared three series of copper and nickel complexes derived from *N,N'*-bis[3-(3',4'-dialkoxyphenyl)-3-oxoprop-1-enyl]ethylenediamine. Liquid crystalline behavior was found to be controlled by sidechain density and/or metal centres incorporated. Nickel complexes with four or six sidechains exhibited columnar hexagonal phases, and complexes with four sidechains showed a much wider range of mesophase than complexes with six sidechains. However, nickel complexes with two sidechains and all copper complexes, regardless of the number of sidechains, were non-mesomorphic. This difference might be attributed to the greater degree of molecular interaction in nickel than in copper complexes.

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 ¹³C NMR spectra were measured on a Bruker DRS-200. DSC thermographs were carried out on a Perkin-Elmer DSC-7 and calibrated with a pure indium sample. All phase behaviors are determined at a scan rate of 10.0 °C min⁻¹. Optical polarized microscopy was carried out on Nikon MICROPHOT-FXA 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-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 thickness) from Charles Supper Co. with an inner diameter of 0.10 or 0.15 mm. The sample was heated above the isotropic temperature and allowed to stay at that temperature for 10 min. The sample was then cooled at a rate of 5.0 °C min⁻¹ to the appropriate temperature and the diffraction data collected. Elemental analyses for carbon, hydrogen, and nitrogen were conducted on a Heraeus CHN-O-Rapid elemental analyzer, and the results are listed in Table 3. The compounds of 1,2-dialkoxybenzenes, 4-alkoxyacetophenones, 3,4-dialkoxyacetophenones, methyl 3,4,5-trialkoxybenzoate esters, 3,4,5-trialkoxybenzoic acids and 3,4,5-trialkoxyacetophenones were prepared according to literature procedures.^{5,7}

4-Hexadecyloxyacetophenone

White crystals, yield 85%. ¹H NMR (CDCl₃): δ 0.83(t, CH₃, 3H), 1.24–1.81(m, CH₂, 28H), 2.45(s, COCH₃, 3H), 3.93(t, OCH₂, 2H), 6.84(d, C₆H₄, 2H), 7.84(d, C₆H₄, 2H). ¹³C NMR (CDCl₃): δ 13.97, 22.56, 25.87, 26.07, 29.00, 29.25, 29.45, 31.76, 68.10(OCH₂), 113.98(C³, C⁵), 129.99(C², C⁶), 130.39(C¹), 163.01(C⁴), 196.37(C=O).

1,2-Dihexadecyloxybenzene

White crystals, yield 92%. ¹H NMR (CDCl₃): δ 0.83(t, CH₃, 6H), 1.24–1.86(m, CH₂, 56H), 3.94(t, OCH₂, 4H), 6.86(s, C₆H₄, 4H). ¹³C NMR (CDCl₃): δ 14.10, 22.68, 26.05, 29.36, 29.44, 29.70, 30.89, 31.92, 69.28, 114.13(C³, C⁶), 120.98(C⁴, C⁵), 149.24(C¹, C²).

Table 3 Elemental analysis^a of metal complexes

Complex	<i>n</i>	C (%)	H (%)	
1 Cu	8	67.66 (67.74)	7.93 (7.89)	
	16	72.10 (72.39)	9.42 (9.58)	
	8	68.28 (68.26)	8.00 (7.76)	
2 Cu	16	72.58 (72.80)	9.65 (9.63)	
	10	71.72 (71.57)	9.87 (9.81)	
	12	72.92 (72.98)	9.93 (10.27)	
3 Cu	14	74.08 (74.13)	10.76 (10.64)	
	16	75.18 (75.09)	10.92 (10.95)	
	18	76.17 (75.90)	11.24 (11.22)	
	Ni	10	71.72 (71.91)	9.87 (9.86)
		12	73.38 (73.29)	10.17 (10.31)
		14	74.57 (74.42)	10.78 (10.68)
		16	75.15 (75.36)	10.96 (10.99)
	3 Ni	18	76.24 (76.16)	11.30 (11.25)
		14	75.57 (75.42)	11.54 (11.32)
		16	76.27 (76.36)	11.58 (11.60)
14		75.86 (75.65)	11.69 (11.35)	
16	76.66 (76.57)	11.69 (11.63)		

^aCalculated values in parenthesis.

3,4-Dihexadecyloxyacetophenone

White crystals, yield 85%. ¹H NMR (CDCl₃): δ 0.83(t, CH₃, 6H), 1.24–1.84(m, CH₂, 56H), 2.52(s, CH₃, 3H), 3.99(t, OCH₂, 4H), 6.82(d, C₆H₃, 1H), 7.68(d, C₆H₃, 1H), 7.54(s, C₆H₃, 1H). ¹³C NMR (CDCl₃): δ 13.97, 22.56, 25.87, 26.07, 29.00, 29.25, 29.45, 31.76, 68.10(OCH₂), 111.49(C⁵), 112.32(C²), 123.14(C⁶), 130.40(C¹), 148.78(C³), 153.48(C⁴), 197.73(C=O).

Methyl 3,4,5-trihexadecyloxybenzoate ester

White solid, yield 92%. ¹H NMR (CDCl₃): δ 0.84(t, CH₃, 9H), 1.26–1.80(m, CH₂, 84H), 3.86(s, OCH₃, 3H), 3.97(t, OCH₂, 6H), 7.25(s, C₆H₂, 2H). ¹³C NMR (CDCl₃): δ 14.16, 22.77, 26.14, 29.35, 29.45, 29.62, 29.72, 29.75, 29.81, 30.41, 32.01, 52.11, 69.22(OCH₂), 75.50(OCH₂), 108.03(C², C⁶), 124.68(C¹), 142.43(C⁴), 152.80(C³, C⁵), 166.91(COO).

3,4,5-Trihexadecyloxybenzoic acid

White solid, yield 83%. ¹H NMR (CDCl₃): δ 0.83(t, CH₃, 9H), 1.24–1.84(m, CH₂, 84H), 3.97(t, OCH₂, 6H), 7.29(s, C₆H₂, 2H). ¹³C NMR (CDCl₃): δ 14.10, 22.69, 26.09, 29.38, 29.72, 30.34, 31.93, 69.17(OCH₂), 73.54(OCH₂), 108.54(C², C⁶), 123.66(C¹), 143.08(C⁴), 152.83(C³, C⁵), 171.87(COO).

3,4,5-Trihexadecyloxyacetophenone

White solid, yield 82%. ¹H NMR (CDCl₃): δ 0.82(t, CH₃, 9H), 1.24–1.86(m, CH₂, 84H), 2.52(s, COCH₃, 3H), 3.96(t, OCH₂, 6H), 7.15(t, C₆H₂, 2H). ¹³C NMR (CDCl₃): δ 14.05, 22.65, 26.1, 26.05, 26.30, 29.35, 29.69, 30.31, 31.68, 31.90, 69.29(OCH₂), 73.47(OCH₂), 107.11(C², C⁶), 132.06(C¹), 142.94(C⁴), 152.87(C³, C⁵), 196.92(C=O).

General procedures for the synthesis of Schiff bases

***N,N'*-Bis[3-(3',4'-dihexadecanoxyphenyl)-3-oxopropenyl]-ethylenediamine.** A mixture of freshly cut sodium (0.34 g, 0.015 mol) suspended in dry diethyl ether (25.0 ml) and 3,4-dihexadecyloxyacetophenone (3.0 g, 0.005 mol) was stirred for 0.5 h. Ethyl formate (1.85 g, 0.025 mol) was slowly added to the solution at room temperature and the mixture allowed to stir at room temperature under an N₂ atmosphere for 18 h. The pale orange cloudy solution was carefully quenched with methanol to remove any excess sodium. The solution was concentrated to give a yellow solid, which was redissolved in dichloromethane (*ca.* 20.0 ml). Then acetic acid was added slowly to neutralize the solution, and at this point the cloudy

mixture turned clear and slightly acidic (pH paper). Ethylenediamine (0.15 g, 0.0025 mol) was added and the mixture was gently refluxed for 24 h. The solution was concentrated to give the crude product as a brown solid. Yellow needles were obtained after recrystallization from dichloromethane–methanol (2:3). Yield 78.0%, mp 98.0 °C. ¹H NMR (CDCl₃): δ 0.85(t, CH₃, 12H), 1.13–1.42(m, CH₂, 104H), 1.80(t, CH₂, 8H), 3.37(m, CNCH₂, 4H), 3.98(t, OCH₂, 4H), 4.00(t, OCH₂, 4H), 5.64(d, COCH, 2H), 6.75(m, CHN, 2H), 6.83(d, C₆H₃, 2H), 7.36(d, C₆H₃, 2H), 7.45(s, C₆H₃, 2H), 10.19(m, CNH, 2H). ¹³C NMR (CDCl₃): δ 14.09, 22.67, 26.00, 29.14, 29.35, 29.69, 31.91, 50.21(NCH₂), 69.03(OCH₂), 69.16(OCH₂), 90.84(CH=), 112.03(C^{5'}), 112.17(C^{2'}), 120.78(C^{6'}), 132.25(C^{1'}), 148.72(C^{3'}), 151.91(C^{4'}), 153.73(C=N), 189.63(C=O). IR (thin film): 1636, 1590, 1545, 1516, 1464, 1374, 1335, 1269, 1219 cm⁻¹.

***N,N'*-Bis[3-(4'-hexadecanoxyphenyl)-3-oxopropenyl]ethylenediamine.** Light yellow solid, yield 84%, mp 172.0 °C. ¹H NMR (CDCl₃): δ 0.85(t, CH₃, 6H), 1.13–1.40(m, CH₂, 52H), 1.75(t, CH₂, 8H), 3.34(m, CNCH₂, 4H), 3.94(t, OCH₂, 4H), 5.61(d, COCH, 2H), 6.72(m, CHN, 2H), 6.83(d, C₆H₄, 4H), 7.77(d, C₆H₄, 4H), 10.23(m, CNH, 2H). ¹³C NMR (CDCl₃): δ 14.05, 22.59, 25.94, 29.16, 29.27, 31.74, 50.12(NCH₂), 68.03(OCH₂), 90.71(CH=), 113.89(C^{3'}), 129.00(C^{2'}), 131.89(C^{1'}), 153.76(C^{4'}), 161.63(C=N), 189.53(C=O).

***N,N'*-Bis[3-(3',4',5'-trihexadecyloxyphenyl)-3-oxopropenyl]-ethylenediamine.** Light yellow solid, yield 80%, mp 49.0 °C. ¹H NMR (CDCl₃): δ 0.85(t, CH₃, 18H), 1.12–1.42(m, CH₂, 156H), 1.74(t, CH₂, 12H), 3.39(m, CNCH₂, 4H), 3.96(t, OCH₂, 12H), 5.61(d, COCH, 2H), 6.77(m, CHN, 2H), 7.06(s, C₆H₄, 4H), 10.25(m, CNH, 2H). ¹³C NMR (CDCl₃): δ 14.10, 22.68, 26.09, 29.37, 29.71, 30.32, 31.91, 50.18(NCH₂), 69.15(OCH₂), 73.46(OCH₂), 91.02(=CH), 105.80(C^{2'}, C^{6'}), 134.37(C^{1'}), 141.15(C^{4'}), 152.82(C^{3'}, C^{5'}), 154.04(C=N), 189.80(C=O).

Copper complexes of *N,N'*-bis[3-(3',4'-dihexadecanoxyphenyl)-3-oxopropenyl]ethylenediamine (general procedures for the copper complexes)

N,N'-Bis[3-(3',4'-dihexadecanoxyphenyl)-3-oxopropenyl]-ethylenediamine (0.50 g, 0.40 mmol) dissolved in dichloromethane (5.0 ml) was added to a hot methanol solution of copper(II) acetate monohydrate (0.038 g, 0.20 mmol). Upon addition a light brown solid began to appear, and the solution was gently refluxed for 6 h. The light brown solid was filtered off, and recrystallized from dichloromethane–methanol to give a grey–green solid. Yield 72%. IR (thin film): 1621, 1599, 1578, 1495, 1466, 1437, 1401, 1383, 1327, 1271, 1231, 1202 cm⁻¹. Anal. Calc. for C₈₄H₁₄₆O₆N₂Cu: C, 75.09; H, 10.95. Found: C, 75.18; H, 10.92%.

Nickel complexes of *N,N'*-bis[3-(3',4'-dihexadecanoxyphenyl)-3-oxopropenyl]ethylenediamine (general procedures for the nickel complexes)

N,N'-Bis[3-(3',4'-dihexadecanoxyphenyl)-3-oxopropenyl]-ethylenediamine (0.50 g, 0.40 mmol) dissolved in dichloromethane (5.0 ml) was added to a hot methanol solution of nickel(II) acetate tetrahydrate (0.049 g, 0.20 mmol), and the solution gently refluxed for 4 h. The solution was concentrated to dryness to give a brown solids. A yellow solid was obtained after recrystallization from ethyl acetate. Yield 73%. ¹H NMR (CDCl₃): δ 0.88(t, CH₃, 12H), 1.27–1.49(m, CH₂, 104H), 1.84(m, CH₂, 8H), 3.18(m, CNCH₂, 4H), 4.00(t, OCH₂, 4H), 5.63(d, COCH, 2H), 6.83(m, CHN, C₆H₃, 4H), 7.39(m, C₆H₃, 4H). ¹³C NMR (CDCl₃): δ 14.07, 22.66, 26.03, 26.10, 29.25, 29.34, 29.35, 29.43, 29.51, 29.62, 29.65, 29.68, 29.71, 31.90, 57.92, 69.03, 69.31, 92.02, 112.48, 112.62, 119.88, 130.33,

148.42, 150.82, 156.14, 172.29. IR (thin film): 1603, 1580, 1536, 1511, 1493, 1443, 1381, 1362, 1329, 1273, 1241, 1206, 1164, 1136 cm^{-1} . Anal. Calc. for $\text{C}_{84}\text{H}_{146}\text{O}_6\text{N}_2\text{Ni}$: C, 75.36; H, 10.99. Found: C, 75.15; H, 10.96%.

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