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Mesomorphic Dithiooxamide Complexes of Platinum(II)

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Complexation of non-mesomorphic dithiooxamide ligands to Pt(II) leads to square planar complexes which exhibit mesomorphic properties. The synthesis of these complexes was accomplished in three steps: the formation of bisamides, starting from conveniently substituted anilines, their conversion into dithiooxamides and the reaction of these sulfur derivatives with $[PtCl_2(dmso)_2]$. Four, eight and twelve-chained complexes were obtained and their behaviour as potentially mesomorphic material was studied. The eight-chained complexes **21** ($n = 12$–16) and the twelve-chained complexes **22** ($n = 8,11,13$) exhibit columnar mesophases which have been characterised by optical microscopy, X-ray scattering and related miscibility studies.

Keywords: Liquid crystals; Metallomesogens; Platinum; S ligands

INTRODUCTION

The presence of a metal centre in a mesomorphic material leads to the incorporation of the metal into an anisotropic fluid. Hence, many properties associated

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with metals, such as magnetism, electron-transfer and absorption, can be studied and perhaps utilized in such an environment. For example, some of us have obtained highly dichroic metallomesogens.[1] The rôle of the metal in metallomesogens can include connecting non-mesomorphic ligands to generate mesomorphic complexes, or allowing geometries to be realised which are simply not available through purely organic systems.[2]

The study of metal-based liquid crystals has developed enormously in the last fifteen years or so. This development has led to the realization of a great diversity of metal complexes which have been shown to exhibit thermotropic (nematic, lamellar and columnar) and lyotropic (micellar and columnar) mesophases. Recently new metal-ligand combinations are being identified as potentially mesomorphic, and known systems are also being modified in order to generate mesomorphic materials.[3]

Metallomesogens of sulfur-based ligands have been previously described by a few authors. In 1977 Giroud and Mueller-Westerhoff reported some Ni,[4] and later Pt[5] complexes **1** of non-mesomorphic dithiolene ligands (Figure 1) which were found to show nematic and smectic C phases. Then Veber[6]studied more highly substituted derivatives **2** which were shown[7] to be crystalline rather than mesomorphic by X-ray methods. These results were followed by those of Ohta[8] who reported the synthesis of octasubstituted derivatives **3** showing columnar phases. Dithiobenzoates represented a stimulating class of ligands which were studied by some of us[9] and by Ohta.[10] Square planar complexes of Ni(II) and Pd(II) **4** (Figure 2) were reported by both groups, while we obtained and studied Zn(II) and Au(III) derivatives **5** and **6**, too. An interesting feature of the Ni(II) complexes was that a ligand redistribution reaction occurred at the clearing point, leading to some decomposition and formation of a mixed dithiobenzoato-trithiobenzoato complex which was also mesomorphic. Other sulfur-containing metallomesogens include silver thiolates,[11] which exhibit a rich and complex mesomorphism, and dithiocarbamates.[12,13]

Dithiooxamides, readily prepared by the reaction of primary amines with oxalyl chloride, followed by treatment with P_4S_{10},[14] can be reacted with a variety of metal derivatives to form bi- and polynuclear metal complexes with a coordination mode depending on the electronic nature of the metal.[15] Recently some of us reported[16] the synthesis of several Pt complexes of secondary alkyl and aryl substituted dithiooxamides, focusing attention on their structures which show a rigid unsaturated core, with Pt atom lying on the same plane of the thioamide moiety S-C-N, and four groups linked to the four amide nitrogen atoms (see **19–22** in Scheme 1). These structural features suggested the possibility of synthesising metal-containing liquid crystals. Indeed, there are certain structural similarities between these complexes and glyoximato complexes of the group 10

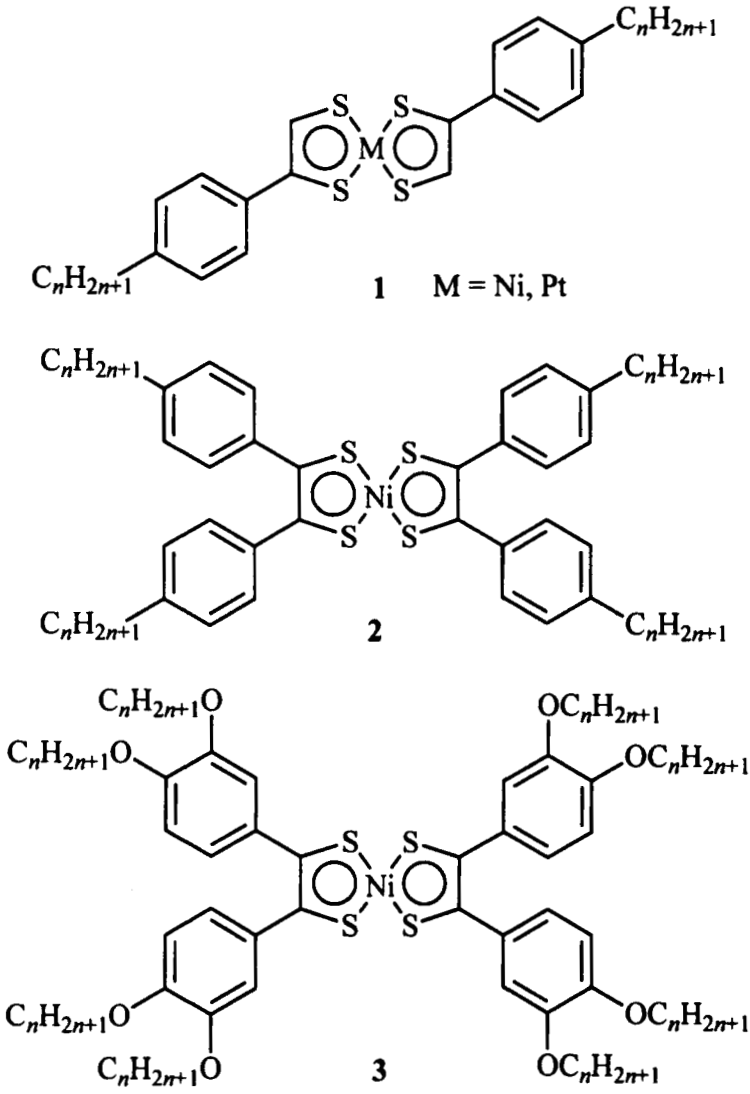


FIGURE 1 Structure of mesogenic dithiolenes **1–3**

metals published by Ohta (Figure 3), which exhibit columnar mesophases and, in some cases, thermochromism associated with the mesomorphic properties.[17] A comparison with the work on dithiolene complexes shows another stimulating side of this research: there is clearly the opportunity to modify the aryl group

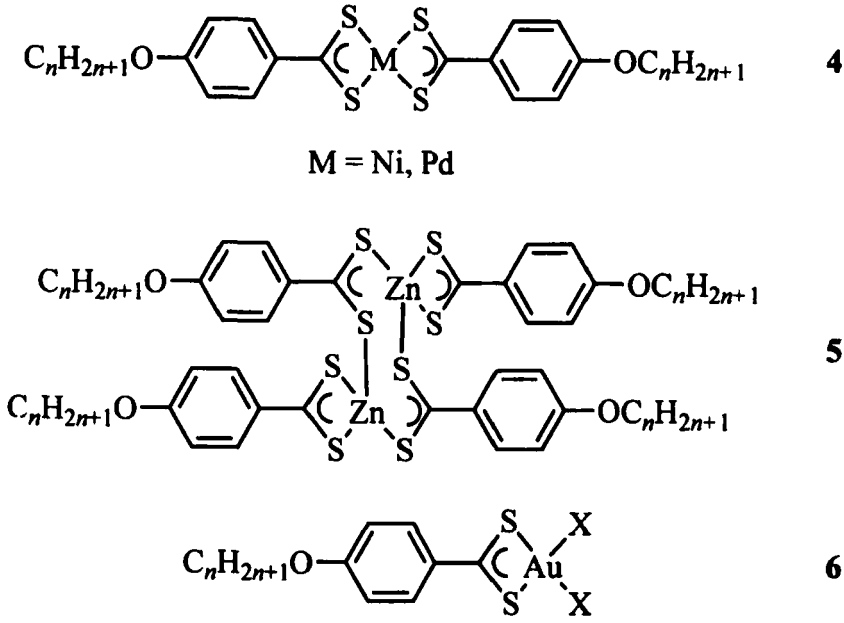


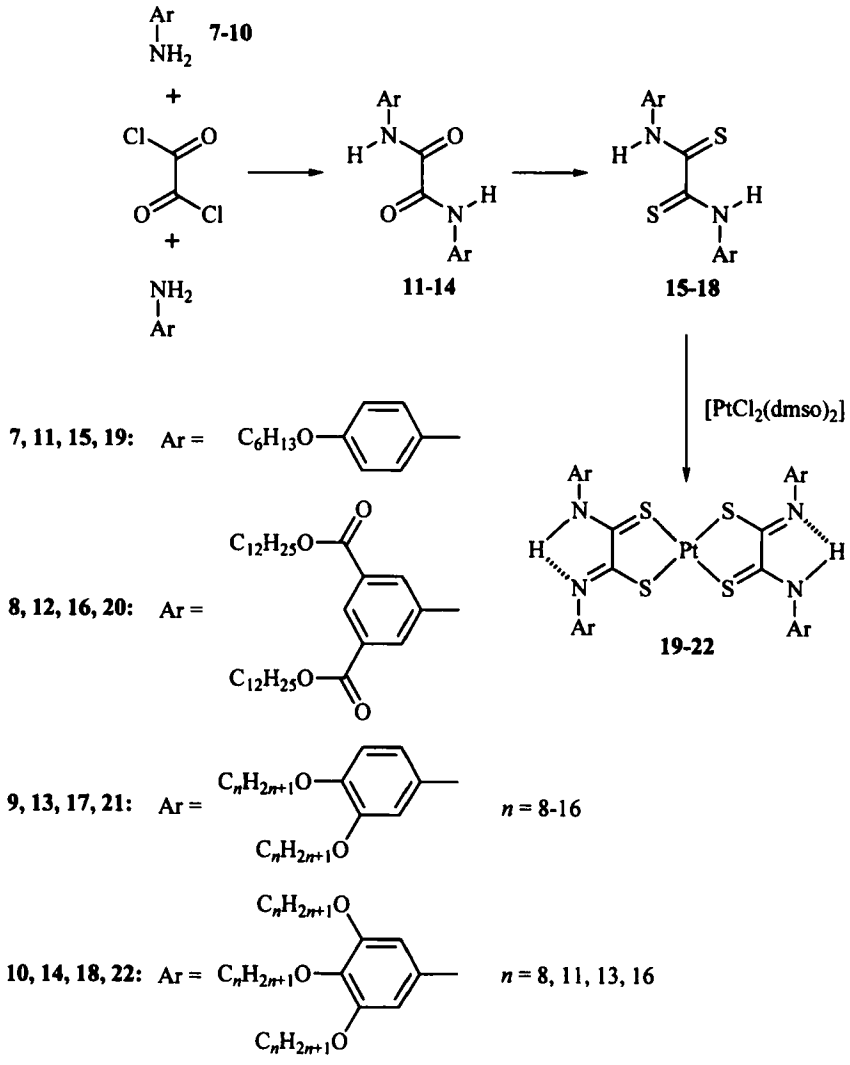
FIGURE 2 Mesomorphic dithiobenzoates **4–6**

attached to the dithiooxamide ligands to effect a number of structural changes and to examine their effect on the mesomorphism of the resulting complexes.

RESULTS AND DISCUSSION

The synthesis of complexes **19–22** (Scheme 1) was accomplished in three steps starting from conveniently substituted anilines. The first step concerned the formation of bisamides **11–14** by reaction of two equivalents of aniline with one equivalent of oxalyl chloride, then the conversion of **11–14** into dithiooxamides **15–18** was performed by treatment with P_4S_{10};[14] finally, the reaction of sulfur compounds **15–18** with $[PtCl_2(dmso)_2]$ led smoothly to the intensely purple coloured complexes **19–22**. The synthesis of complexes **19** and **20** was previously reported.[16]

3,4-Dialkoxyanilines **9** were obtained from 4-nitrocatechol which underwent a classical Williamson ether synthesis and subsequent reduction of the nitro group with $SnCl_2$.[16] 3,4,5-Trialkoxyanilines **10** were easily prepared following an already described procedure[18] which involved exhaustive alkylation of pyro-



SCHEME 1

gallol, nitration of 1,2,3-trialkoxybenzenes, and reduction of the nitro group by hydrazine monohydrate / graphite in ethanol solution. The pyrogallol alkylation mode, recommended by the literature,[18] gave, in our hands, poor yields of 1,2,3-trialkoxybenzenes. We have improved the alkylation procedure by using sodium hydroxide, instead of potassium carbonate, and by adding three equivalents of alkyl iodides in subsequent small amounts to avoid the formation of dialkyl ethers as side-products.

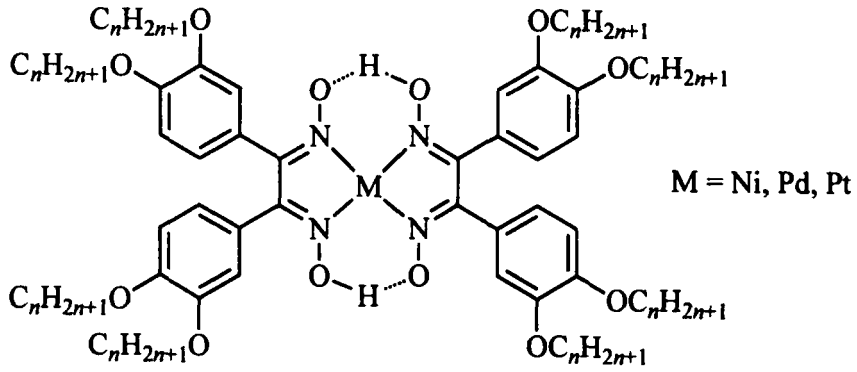


FIGURE 3 Mesomorphic glyoximate complexes

Complexes **19–22** were examined for liquid crystal behaviour using polarised optical microscopy, differential scanning calorimetry (DSC) and, in one case (complex **21** with $n = 12$), X-ray diffraction. Optical microscopy studies were made extremely difficult by the intense colour of the complexes, and the rather viscous nature of the mesophases formed by **21** and **22** led to broad DSC traces.

The four-chained complex **19** was not mesomorphic, as might have been anticipated by comparison with Veber's work on dithiolenes. It simply melted to an isotropic liquid and showed no signs of any monotropic phases on cooling. Similarly, complex **20** was non-mesomorphic, with a melting point of 105 °C, in spite of the notionally required eight peripheral chains. Studies of macrocyclic liquid crystals[19] have shown that the substitution pattern around the periphery of a disk-like molecule is rather important in the promotion or not of mesomorphism, and Ringsdorf[20] found that 3,5-disubstitution does not, in general, lead to mesogens with columnar mesophases. The reasons for this behaviour are not entirely clear but arguments concerning coverage of the molecular periphery and filling of free space have been advanced.[19]

We obtained more encouraging results with the eight-chained complexes **21** (Table I): for $n = 8$–11, the materials melted straight to the isotropic state with no sign of any monotropic phases, while the complexes **21** ($n = 12$–16) were found to be mesomorphic. Their mesophase was initially identified as columnar hexagonal from optical microscopy on account of its characteristic texture,[21] although, as already pointed out, the intense colour of the complexes made this measurement rather difficult. Final confirmation of the identity of the phase was provided by X-ray diffraction experiments on the derivative **21** ($n = 12$), at 110 °C on cooling, which showed a mesophase with a well-developed hexagonal net-

work with spacings in the ratio 1 : √3 : √4 : √7, characteristic of hexagonal symmetry with a d_{10} value of 29.1 Å, corresponding to an intercolumnar separation of 33.6 Å. The complexes were found to be co-miscible, indicating that there was no change in phase as the chain length was increased.

TABLE I Thermal data for complexes **21** and **22**

	Transition	*T [°C]*	*ΔH/kJ mol^{-1}*
Complexes 21			
$n = 8$	Crys-I	107	63.8
9	Crys-I	105	57.9
10	Crys-I	112	103.3[a]
11	Crys-I	113	92.8
12	Crys-Col_h	111	110.7
	Col_h-I	116	2.2
13	Crys-Col_h	113	125.3
	Col_h-I	119	2.4
14	Crys-Col_h	110	137.6
	Col_h-I	119	2.5
15	Crys-Col_h	115	134.8
	Col_h-I	118	2.5
16	Crys-Col_h	106	131.6
	Col_h-I	114	2.8
Complexes 22			
$n = 8$	Crys-Col_h	83	97.4
	Col_h-I	125	1.3
11	Crys-Col_h	55	105.6
	Col_h-I	103	1.0
13	Crys-Col_h	42	108.3
	Col_h-I	59	1.1
16	Crys-I	39	112.8

a. Second and subsequent heats give $\Delta H = 72$ kJ mol^{-1}.

Some of our observations during the optical microscopy studies of these complexes led us to question the long-term stability of the complexes in air since we did not always obtain reliable data for the mesomorphism of the complexes. One would normally expect a rather smooth progression of melting and clearing points for a homologous series, but our results were not always consistent with this. In the end, we found that the most reproducible results were obtained when the sample was crystallised immediately before use, sometimes after passing through a short alumina plug.

Encouraged by these results, we undertook the synthesis of the more highly substituted complexes **22**showing alkoxy chains in the 3, 4 and 5 positions of the phenyl rings (Scheme 1). Four derivatives **22** were synthesised with $n = 8$, 11, 13, and 16. The first three compounds were mesomorphic, showing a columnar hexagonal phase identified by optical microscopy by comparison with complexes **21**, while the last complex **22**($n = 16$) simply melted to an isotropic liquid with no sign of a monotropic mesophase on cooling (Table I). The melting and clearing points of these complexes are lower than those of complexes **21** due to the presence of four additional chains which destabilise both the crystal and columnar phases. The additional chains also result in the formation of a rather viscous mesophase. The observed lack of mesomorphism for complex **22**($n = 16$) is a consequence of the fact that an increase of chain length in this system determines a decrease of the clearing point faster than the melting point (melting point decreases 41 °C for 5 extra carbons in the chain, while the clearing point decreases 66 °C).

The luminescence properties of Pt dithiooxamides in solution and in a frozen matrix have recently been reported.[22] It is therefore expected a great interest in observing how these isotropic phase properties will be modified in the columnar mesophase. Furthermore, by analogy with the behaviour of disk-like mesogens of Pd and Pt carrying large numbers of peripheral chains,[23] these materials could show lyotropic phases in alkane solvents, which might make mesomorphism measurements easier.

CONCLUSION

In this paper we have reported the synthesis and mesomorphism of a new series of metallomesogens formed by complexation of non-mesomorphic dithiooxamides to Pt(II). Mesophases were observed for conveniently substituted complexes **21** and **22** having eight and twelve peripheral chains, respectively. The columnar hexagonal nature of the mesophases was confirmed by optical microscopy, X-ray diffraction and related miscibility studies.

EXPERIMENTAL SECTION

General Remarks

Complexes **19, 20, 21** ($n = 10$ and 12) were previously described.[16] Solvents were purified according to standard procedures. All reactions were monitored by

TLC on commercially available precoated plates (Aldrich silica gel 60 F 254) and the products were visualized with vanillin [vanillin (1 g) dissolved in MeOH (60 ml) and H_2SO_4 conc. (0.6 ml)]. Silica gel used for column chromatography was Aldrich 60. All complexes **21** and **22** were obtained in quantitative yields, except the recovery loss. The study of their thermal behaviour was achieved by DSC analysis, carried out by a Perkin-Elmer DSC7 instrument using various heating rates (2, 5 and 10 K min^{-1}). The mesomorphism was studied by hot-stage polarising microscopy using an Olympus BH50 microscope equipped with a Linkam TH600 hot-stage and PR600 temperature controller. All new compounds were characterised by satisfactory elemental analyses. IR spectra were taken with a Perkin Elmer 1600 FT spectrophotometer in $CHCl_3$ solutions. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer at 300 and 75 MHz respectively in $CDCl_3$solutions with $SiMe_4$ as internal standard; J values are given in Hz. The homologous series of complexes **21, 22**, ligands **17, 18**, diamides **13, 14** and their synthetic precursors show very similar ^1H and ^{13}C NMR absorptions, therefore only the characterization of some typical compounds is reported herein.

Synthesis of complexes 21, 22, dithiooxamides 17, 18 and dioxamides 13, 14

These compounds were obtained by standard procedures already described.[16]

Complex 21 (n = 14). – ^1H NMR: δ 7.31 (dd, J_{ortho} 8.6, J_{meta} 2.4, H-6), 7.22 (d, H-2), 6.94 (d, H-5), 4.04 and 4.03 (two t, J_{vic} 6.7, OCH_2), 1.8–1.1 [m, $(CH_2)_{12}Me$], 0.9–0.8 (m, Me). – ^{13}C NMR: δ 177.20 (CS), 149.15 (C-3), 148.42 (C-4), 132.30 (C-1), 115.89 (C-6), 113.12 (C-5), 109.45 (C-2), 69.45 and 69.38 (OCH_2), 31.95–22.71 [$(CH_2)_{12}Me$], 14.80 (Me).

N,N′-Di-[3,4-di(tetradecyloxy)phenyl]ethanedithiooxamide (17, n = 14). – 62% Yield. – Mp 130–132 °C. – ^1H NMR: δ 12.38 (s, NH), 7.82 (d, J_{meta} 2.2, H-2), 7.52 (dd, J_{ortho} 8.8, H-6), 6.94 (d, H-5), 4.06 and 4.04 (two t, J_{vic} 6.6, OCH_2), 1.8–1.1 [m, $(CH_2)_{12}Me$], 0.89 (t, J_{vic} 6.6, Me).

N,N′-Di-[3,4-di(tetradecyloxy)phenyl]ethanedioxamide (13, n= 14). – 80% Yield. - Mp 158–160 °C. – ^1H NMR: δ 9.24 (s, NH), 7.37 (d, J_{meta} 2.6, H-2), 7.08 (dd, J_{ortho} 8.7, H-6), 6.88 (d, H-5), 4.02 and 3.99 (two t, J_{vic} 7.3, OCH_2), 1.8–1.2 [m, $(CH_2)_{12}Me$], 0.88 (t, J_{vic} 6.7, Me).

Complex 22 (n = 13). – ^1H NMR: δ 6.84 (s, H-2,6), 3.98 (t, J_{vic} 6.2, OCH_2), 1.9–1.1 [m, $(CH_2)_{11}Me$], 0.9–0.8 (m, Me). – ^{13}C NMR: δ 177.80 (CS), 153.34 (C-3,5), 137.16 (C-4), 136.47 (C-1), 101.86 (C-2,6), 73.59 and 69.26 (OCH_2), 31.92–22.68 [$(CH_2)_{11}Me$], 14.10 (Me).

N,N′-Di-[3,4,5-tri(tridecyloxy)phenyl]ethanedithiooxamide (18, *n* = 13). – 95% Yield. – Mp 85–87 °C. – ^{1}H NMR: δ 12.34 (s, NH), 7.38 (s, H-2,6), 4.02 and 3.98 (two t, J_{vic} 6.4, OCH_2), 1.9–1.2 [m, $(CH_2)_{11}Me$], 0.88 (t, J_{vic} 6.5, Me). – ^{13}C NMR: δ 179.39 (CS), 153.09 (C-3,5), 137.31 (C-4), 133.55 (C-1), 100.79 (C-2,6), 73.59 (4-OCH_2), 69.28 (3,5-OCH_2), 32.81–22.69 [$(CH_2)_{11}$Me], 14.11 (Me). – IR: ν_{max} 3424 (NH), 2926, 2854, 1600, 1503, 1467, 1118, 1046 (CS) cm^{-1}.

N,N′-Di-[3,4,5-tri(tridecyloxy)phenyl]ethanedioxamide (14, *n*= 13). – 70% Yield. - Mp 75–77 °C. – ^{1}H NMR: δ 9.20 (s, NH), 6.91 (s, H-2,6), 3.98 and 3.93 (two t, J_{vic} 6.4, OCH_2), 1.9–1.1 [m, $(CH_2)_{11}Me$], 0.88 (t, J_{vic} 6.5, Me). – ^{13}C NMR: δ 157.22 (CO), 153.36 (C-3,5), 131.69 (C-1,4), 98.65 (C-2,6), 73.54 (4-OCH_2), 69.12 (3,5-OCH_2), 31.91–22.68 [$(CH_2)_{11}$Me], 14.10 (Me). – IR: ν_{max} 3375 (NH), 2926, 2854, 2359, 2341, 1685 (CO), 1117 cm^{-1}.

Synthesis of 3,4-dialkoxyanilines 9 and related 1,2-dialkoxy-4-nitrobenzenes

These compounds were obtained by standard procedures already described.[16,24]

3,4-Di(tetradecyloxy)aniline (9, *n* = 14). – 70% Yield. – Mp 44–46 °C. – ^{1}H NMR: δ 6.73 (d, J_{ortho}8.7, H-5), 6.30 (d, J_{meta} 2.9, H-2), 6.20 (dd, H-6), 3.93 and 3.89 (two t, J_{vic} 6.7, OCH_2), 1.8–1.2 [m, $(CH_2)_{12}$Me], 0.89 (t, J_{vic} 6.6, Me).

1,2-Di(tetradecyloxy)-4-nitrobenzene. – 60% Yield. – Mp 70–71 °C. – ^{1}H NMR: δ 7.87 (dd, J_{ortho} 8.6, J_{meta} 2.5, H-5), 7.72 (d, H-3), 6.87 (d, H-6), 4.08 and 4.06 (two t, J_{vic}6.9, OCH_2), 1.8–1.2 [m, $(CH_2)_{12}$Me], 0.88 (t, J_{vic} 6.7, Me).

Synthesis of 3,4,5-trialkoxyanilines 10 and related 5-nitro-1,2,3-trialkoxybenzenes

These compounds were obtained by standard procedures already described.[18]

3,4,5-Tri(tridecyloxy)aniline (10, *n* = 13). – 70% Yield. – M.p. 80–81 °C. – ^{1}H NMR: δ 5.90 (s, H-2,6), 3.9–3.8 (m, OCH_2), 1.8–1.2 [m, $(CH_2)_{11}$Me], 0.88 (t, J_{vic} 6.5, Me). – ^{13}C NMR: δ 153.70 (C-3,5), 141.66 (C-1), 131.31 (C-4), 94.69 (C-2,6), 73.57 (4-OCH_2), 68.96 (3,5-OCH_2), 32.80–22.68 [$(CH_2)_{11}$Me], 14.11 (Me). – IR: ν_{max} 3444 and 3376 (NH_2), 2926, 2854, 1605, 1466, 1120 cm^{-1}.

5-Nitro-1,2,3-tri(tridecyloxy)benzene. – 85% Yield. – Mp 63–65 °C. – ^{1}H NMR: δ 7.49 (s, H-4,6), 4.06 and 4.03 (t, J_{vic} 6.4, OCH_2), 1.84 (five lines, J_{vic}6.6) and 1.75 (five lines, J_{vic} 6.4) (OCH_2CH_2), 1.5–1.2 [m, $(CH_2)_{10}$Me], 0.88 (t, J_{vic} 6.5, Me). – ^{13}C NMR: δ 152.67 (C-1,3), 143.78 (C-5), 143.12 (C-2), 102.09 (C-4,6), 73.80 (2-OCH_2), 69.42 (1,3-OCH_2), 31.91–22.68 [$(CH_2)_{11}$Me],

14.10 (Me). – IR: ν_{max} 2926, 2854, 1522 (NO_2), 1464, 1339 (NO_2), 1220, 1117 cm^{-1}.

General procedure for the synthesis of 1,2,3-trialkoxybenzenes

To a solution of pyrogallol (12.6 g, 0.1 mol) in dimethylformamide (20 ml), NaOH (4 g, 0.1 mol) and alkyl iodide (0.1 mol) were added. The mixture was heated at 100 °C under stirring. Subsequent additions in small amounts of base (8 g, 0.2 mol) and alkyl iodide (0.2 mol) were performed when the reaction mixture reached neutral pH. When the conversion of pyrogallol into the fully alkylated compound was complete (from 4 to 10 days) as verified by TLC monitoring (petrol/Et_2O 80:20 as eluant) the reaction mixture was cooled to room temperature and portioned out between H_2O and $CHCl_3$. The organic phase was washed with H_2O, dried (Na_2SO_4) and the solvent removed *in vacuo*. The crude reaction mixture was purified by column chromatography eluting first with petrol and then with petrol/Et_2O 98:2. The yields in 1,2,3-trialkoxybenzenes were between 65% and 75%.

1,2,3-Tri(tridecyloxy)benzene. – 65% Yield. – Mp 65–67 °C. – ^1H NMR: δ 6.90 (t, J_{ortho} 8.3, H-5), 6.53 (d, H-4,6), 3.96 and 3.94 (two t, J_{vic} 6.4, OCH_2), 1.77 (five lines, J_{vic} 6.6) and 1.65 (five lines, J_{vic}6.4) (OCH_2CH_2) 1.5–1.2 [m, $(CH_2)_{10}Me$], 0.88 (t, J_{vic} 6.7, Me). – ^{13}C NMR: δ 153.39 (C-1,3), 138.37 (C-2), 123.09 (C-5), 106.74 (C-4,6), 73.36 (2-OCH_2), 69.07 (1,3-OCH_2), 32.79–22.67 [$(CH_2)_{11}$ Me], 14.10 (Me). – IR: ν_{max} 2926, 2854, 1595, 1464, 1379, 1299, 1253, 1214, 1101 cm^{-1}.

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