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Discotic salicylaldimato metal complexes exhibiting columnar mesophases and their mixtures with rod-like salicylaldimato complexes

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The synthesis and mesomorphism of a series of discotic metal complexes of salicylaldimine ligands is reported. None of the ligands was mesomorphic, but the longer chain length complexes showed a $\mathrm{Col_h}$ phase as evidenced by optical microscopy. Phase diagrams were constructed using rod- and disk-like salicylaldimato complexes, where one was designed to have Lewis acid characteristics and the other Lewis base properties. It was hoped that an associative Lewis acid/base interaction would prevent phase separation of the two components, which may point a way to the realization of a mixture with a biaxial nematic phase. The form of the phase diagrams is discussed.

1. Introduction

Since 1984 when the first liquid crystalline salicylaldimato metal complexes were reported by Galyametdinov and co-workers [1], an extensive characterization of this family of metallomesogens has been carried out [2]. The basic metal/salicylaldimato combination is attractive for the construction of metallomesogens for, as indicated in figure 1, there are several substitutional possibilities and a wide variety of metals which may be incorporated including both d- and f-block elements [3].

Almost exclusively, the investigated salicylaldimato metallomesogens have possessed a calamitic (rod-like) mesogenic group to which terminal flexible alkyl chains are attached, resulting in mesogens which exhibit either nematic or smectic phases. However, by the attachment of additional alkyl chain substituents, a molecular shape with a reduced length-to-breadth ratio is formed, and polycatenar and even disk-like mesogens can result. Such structures will have a reduced tendency to form lamellar mesophases and be more favourable for the formation of columnar mesophases. For example, Courtieu and co-workers have investigated some polycatenar derivatives as illustrated in Figure 2 [4]. The chlorinated derivatives (*a*) showed induction of a nematic phase when the chlorine was *para* to the coordinated oxygen, but suppression of mesomorphism when introduced *ortho* to the coordinated oxygen. However, in the extended systems (*b*), the more classically polycatenar materials showed a $\mathrm{Col_0}$ phase.

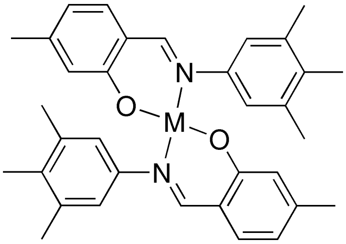

Figure 1. The basic metal/salicylaldimato combination.

Columnar phases have also been seen in lanthanide derivatives of the ligand shown in figure 3 where the complexes had the stoichiometry $[\mathrm{Ln(L)_2(L{-}H)}][\mathrm{CF_3SO_3}]_2$, i.e. the lanthanide was bound by two neutral and one deprotonated ligand [5].

In rather simpler systems, however, Lai *et al.* reported the copper(II) complexes (figure 4) to form columnar hexagonal mesophases [6]. However these tetracatenar mesogens were reported to have high melting points, in the range 135 to 180°C, and the clearing points in the range 250 to 325°C.

Systems with reduced melting points were reported more recently by Barberá *et al.* using more highly substituted systems, and complexes of $\mathrm{Cu^{II}}$ and $\mathrm{Pd^{II}}$ were made with the ligands shown in figure 5 [7]. It was found that ligands (*b*) and (*c*) were mesomorphic,

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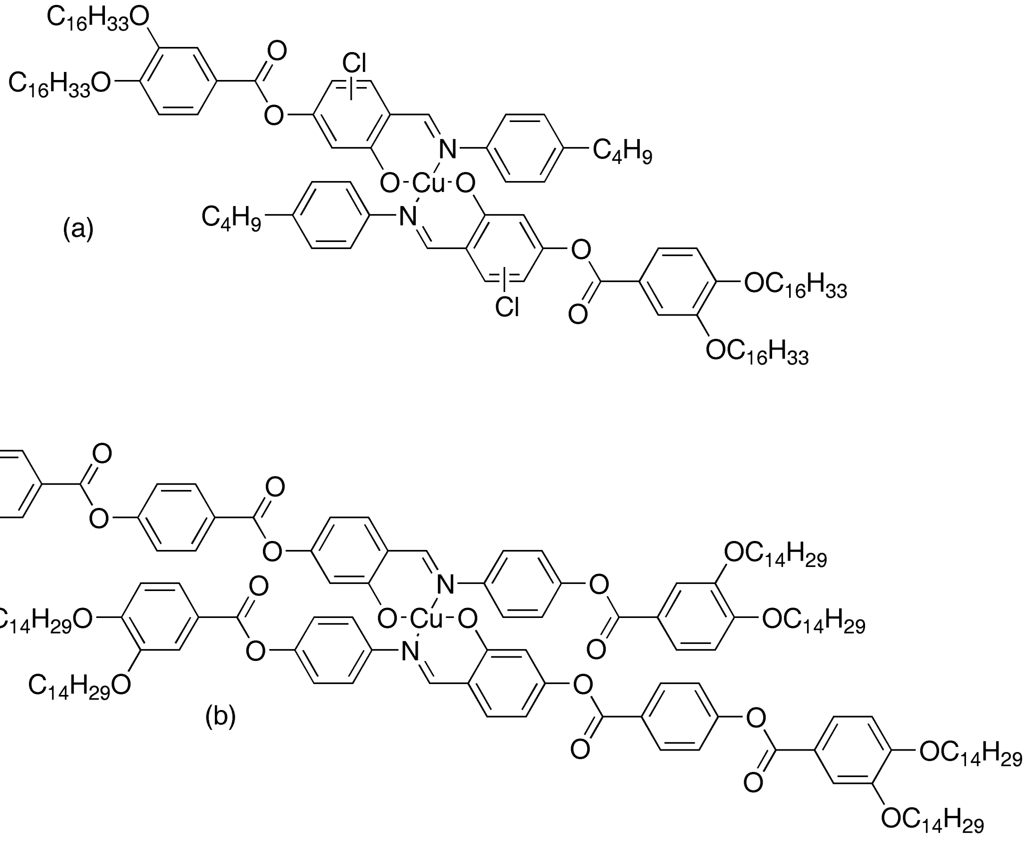


Figure 2. Polycatenar salicylaldimato complexes reported by Courtieu and co-workers.

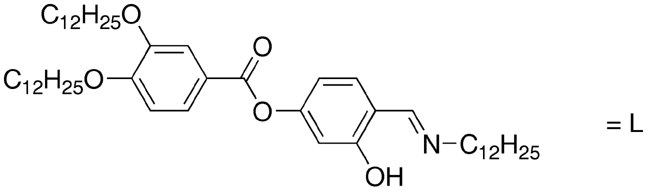


Figure 3. Salicylaldimine ligand used to generate columnar phases with lanthanide triflates.

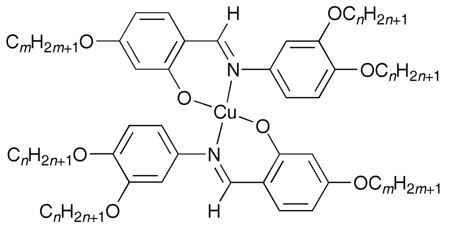


Figure 4. Lai's disk-like metal salicylaldimates.

although strongly monotropically so, whereas for Cu^{II}, only (*c*) gave a mesophase while both (*c*) and (*d*) gave mesophases for Pd^{II}. Other examples of related complexes may be found in reference [8]. We were similarly interested in the possibilities of forming columnar phases with the preparation of more highly substituted salicylaldimato complexes, as the greater degree of conformational flexibility might result in lower melting and clearing temperatures. The results of these studies are now reported [9].

2. Synthesis

The synthesis of the complexes is set out in figure 6. The amine side of the ligand was constructed by reacting a 4-alkyloxybenzoic acid with 3,4-dihydroxynitrobenzene to give 3,4-bis(4-alkyloxybenzoyloxy)nitrobenzene; this was then reduced with $SnCl_2$ in 2-propanol under reflux. The salicylaldehyde fragment was prepared by esterification of 3,4,5-trialkyloxybenzoic acid with 2,4-dihydroxybenzaldehyde to give 2-hydroxy-4-(3′,4′,5′-trialkyloxybenzoyloxy)benzaldehyde. The salicylaldimine was then synthesized by reaction of the aldehyde and amine in ethanol under acid catalysis. Finally, the complexes were prepared by reaction of the salicylaldimine with an appropriate metal salt in ethanol. The new materials were characterized by ^{1}H NMR spectroscopy (except for the paramagnetic metal complexes) and elemental microanalysis; details are given in § 5. Four chain lengths were synthesized,

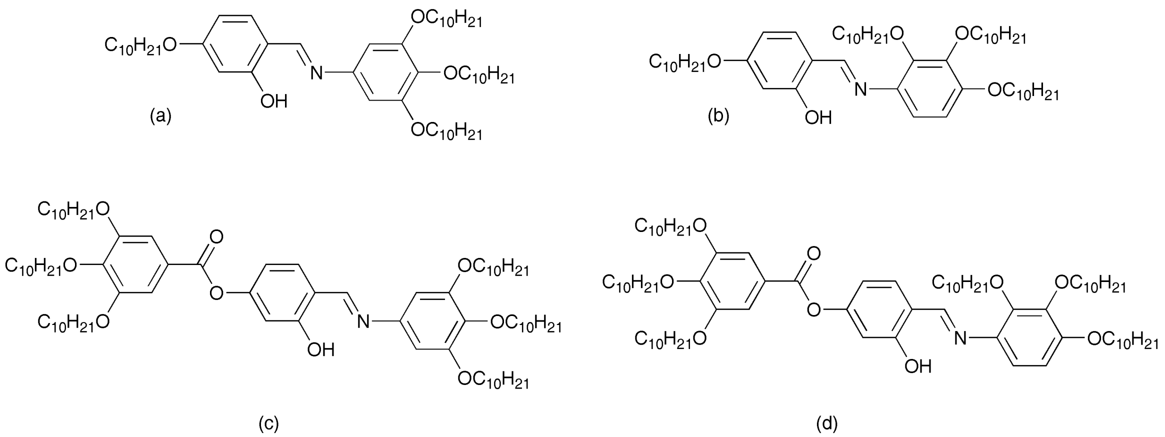


Figure 5. Polycatenar salicylaldimines employed by Barberá *et al.* in the synthesis of mesogenic complexes of Cu^{II} and Pd^{II}.

ranging from methoxy to hexadecyloxy to give an overview of how chain length affects mesomorphism.

3. Mesomorphism

The thermal properties of the ligands and their complexes are collected in table 1, where it can be seen that none of the ligands was mesomorphic, although the melting point dropped off dramatically with increasing chain length. On looking at the complexes, it is found that none of the complexes with $n=1$ and 4 was mesomorphic, with the shortest chain materials melting with decomposition above 200°C. Perhaps surprisingly, none of the nickel complexes was mesomorphic and all melted directly to the isotropic state, with no sign of a monotropic mesophase appearing on cooling.

However, for $n=10$, the complexes of Pd and Fe–Cl did show liquid crystalline behaviour, as did the complexes of Pd, Cu and Fe–Cl for $n=16$. All formed a single, columnar mesophase which was characterized as having hexagonal symmetry on the basis of its optical texture (figure 7). It was found to be impossible to measure the melting entropies of several of the complexes by DSC, due to the tendency to form a glassy phase rather than for crystallization to occur, on cooling the columnar mesophase after the initial heating of a virgin sample.

Liquid crystalline phases were not observed for any complexes with methyl and butyl chains, due partly the their high melting points but also to the alkyl chains being of insufficient volume fill the voids between the columns of self-assembled disc-shaped molecules. The clearing temperatures of the liquid crystalline phases of chloroiron(III) complexes were observed to be markedly higher than the corresponding palladium(II) and copper(II) complexes. It is suggested that this arises from electron donation from the chloride atoms attached to one given discotic molecule to the iron(III) atom of the neighbouring molecule, thus enhancing the stability of the columnar mesophase.

4. Binary phase diagram studies with rod-like salicylaldimines

As well as constituting an investigation of the mesomorphism of these disk-like salicylaldimines, one purpose in their synthesis related to a possible avenue for realizing the biaxial nematic phase [10]. Thus, it is know that, in principle at least, a N_B phase can be formed from mixtures of rod- and disk-like materials as the resulting system will have two directors. This is because the optimum packing arrangement for such a system will align the director of the calamitic material perpendicular to that of the disk. However, various lattice model approaches have shown that mixtures of rods and disks separate into two, uniaxial phases, one rich in rods, the other in disks; this is borne out by experiment [11]. This issue has been addressed recently via the synthesis of covalently linked rods and disks [12, 13], and, interestingly, it has been shown that such covalent rod–disk dimers can act as shape amphiphiles to co-solubilize rod/disk mixtures [14].

It has been established by simulation that while mixtures of rod- and disk-like compounds will phase separate, such mixtures can be stabilized by allowing the rod and disk to interact via some attractive potential whose strength is of the order of a hydrogen bond [15]. This idea interested us, but rather than use hydrogen bonding we elected to use Lewis acid/base interactions employing square-planar metal complexes as the Lewis acid and the non-bonded pair of electrons on a ligated atom, belonging to a second complex, as the Lewis base (figure 8). Thus, in selecting salicylaldimine complexes, we chose a readily variable ligand system which could be used to generate both calamitic

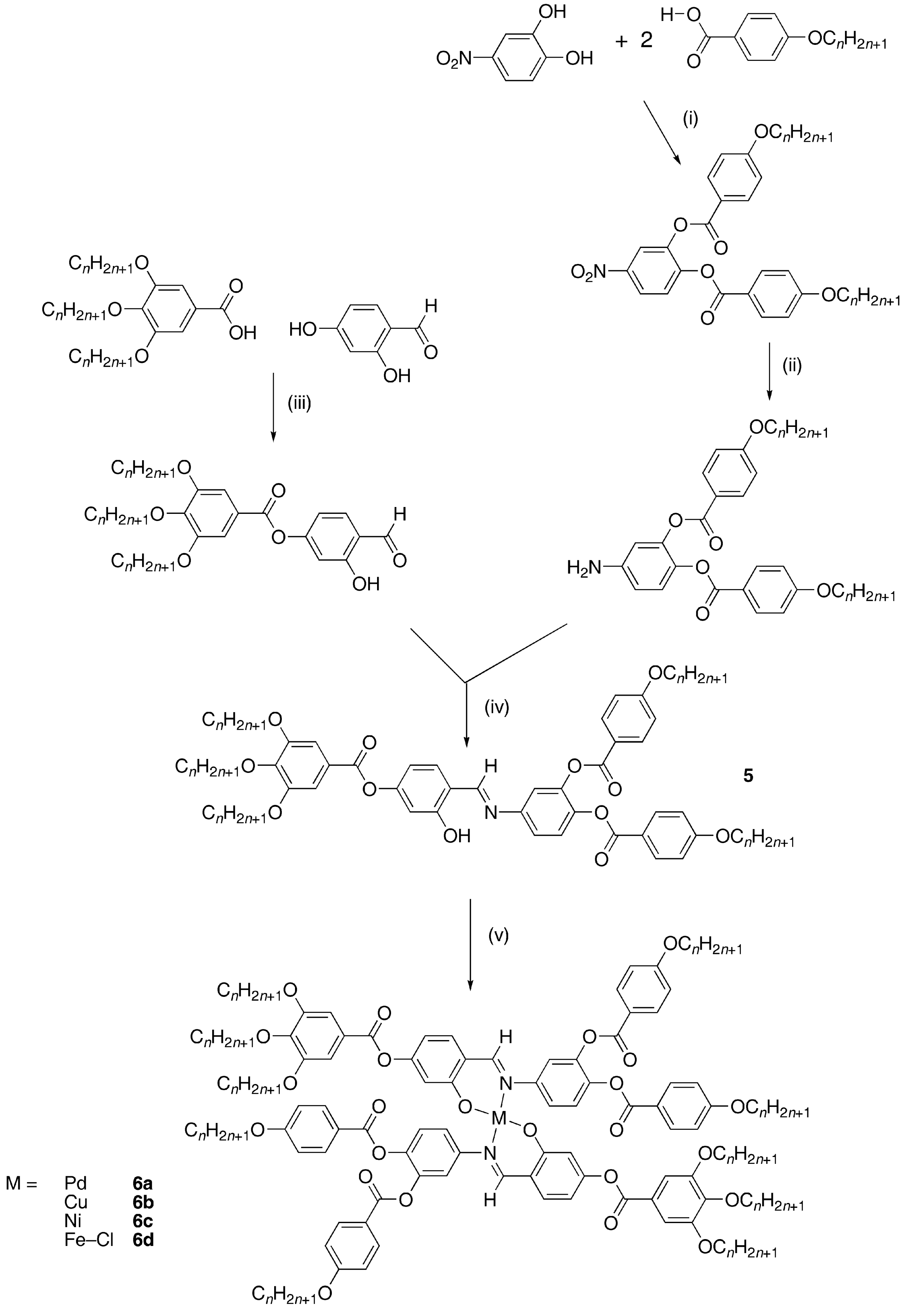


Figure 6. Synthesis of the new complexes. Reagents and conditions: (i) DCCI, DMAP, 4A molecular sieves, dry THF; (ii) $SnCl_2$/propan-2-ol; (iii) DCCI, DMAP, 4A molecular sieves, dry THF; (iv) acetic acid, ethanol; (v) appropriate metal salt, ethanol.

Table 1. Thermal behaviour of the new compounds.

Compound	n	Transition	T/°C	ΔH/kJ mol^{-1}	ΔS/R
5	1	Cr–I	168	59	16
5	4	Cr–I	95	27	9
5	10	Cr–I	68	16	6
5	16	Cr–I	58	84	31
6a	1	Cr–I	288	[a]	[a]
6a	4	Cr–I	182	65	17
6a	10	Cr–Col$_h$	99	128	41
		Col$_h$–I	104	6	2
6a	16	Cr–Col	52	134	50
		Col–I	111	4	1
6b	1	Cr–I	250	[a]	[a]
6b	4	Cr–I	160	38	11
6b	10	Cr–I	93	[b]	[b]
6b	16	Cr–Col	57	134	49
		Col–I	102	5	1
6c	1	Cr–I	280	[a]	[a]
6c	4	Cr–I	198	12	3
6c	10	Cr–I	77	[b]	[b]
6c	16	Cr–I	90	[b]	[b]
6d	10	Cr–Col	68	134	49
		Col–I	172	5	1
6d	16	Cr–Col	[b]	[b]	[b]
		Col–I	160	16	5

[a] Due to sample decomposition, measurement was not possible.

[b] Crystallization was in complete, so no meaningful enthalpy change could be recorded.

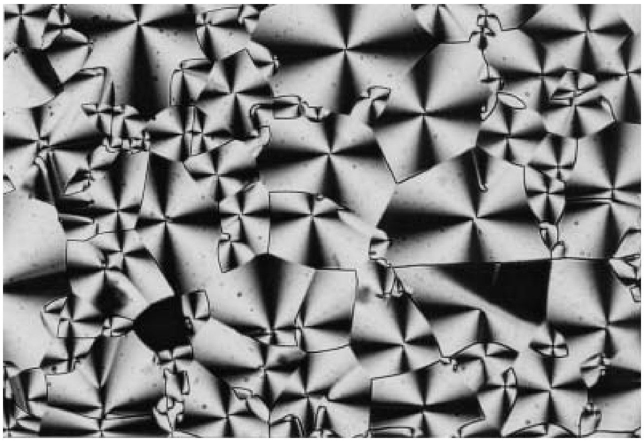


Figure 7. Optical micrograph of the Col$_h$ phase of **6a**–10 at 100°C on cooling from the isotropic phase (reproduced from ref. [8] by permission of the Royal Society of Chemistry).

and discotic mesogens, and one which will bind a wide variety of metals, allowing the desired Lewis acid/base combination to be realized.

In the simulations reported by Vanakaras *et al.*, both the calamitic and discotic component possessed a nematic phase [15], but in the present study, we were unable to synthesize a discotic salicylaldimine complex with this phase and so were forced to employ disks showing columnar phases. Therefore, we chose to use **6d**–10 as the disk, expecting to employ a non-bonded pair of electrons on the chlorine atom bound to iron as the Lewis base, and the nematic Ni^{II} complex (**7**) shown in figure 9 and first reported by Marcos *et al.* [16].

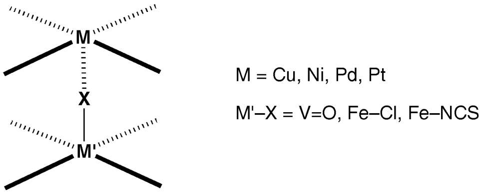
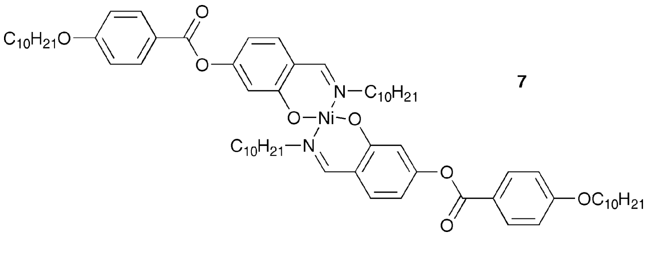


Figure 8. Schematic of the proposed Lewis acid/Lewis base interaction.

The binary phase diagram of the two components (figure 10) shows that when the calamitic nickel complex is added to the discotic chloroiron(III) material, the Col$_h$ phase of the latter is strongly destabilized, and by 40 mol% of rod, the columnar phase has disappeared. Similarly, when the disk is added to the rod, the nematic phase is strongly destabilized and has disappeared by 30 mol% disk. Very evidently, there is a pronounced miscibility gap between the two components and no evidence for any associative interaction.

One possible reason for the lack of miscibility in the phase diagram shown in figure 10 is that the chloride ligand does not extend far enough above the central plane containing the iron to allow it to interact with any neighbouring complexes. If this is an issue, then it may be that the use of a longer anionic ligand on iron could solve this problem, a suitable candidate being thiocyanate. However, before undertaking the synthesis of potentially mesomorphic derivatives, we undertook model studies.

Thus, the model compound bis(κ^2-dithiocarbamato)(N-thiocyanato)iron(III) was prepared [17]. This compound



7

Cr • 131 • N • 160 • I

Figure 9. Structure and mesomorphism of the calamitic nickel(II) salicylaldimine complexes used in the first mixture study.

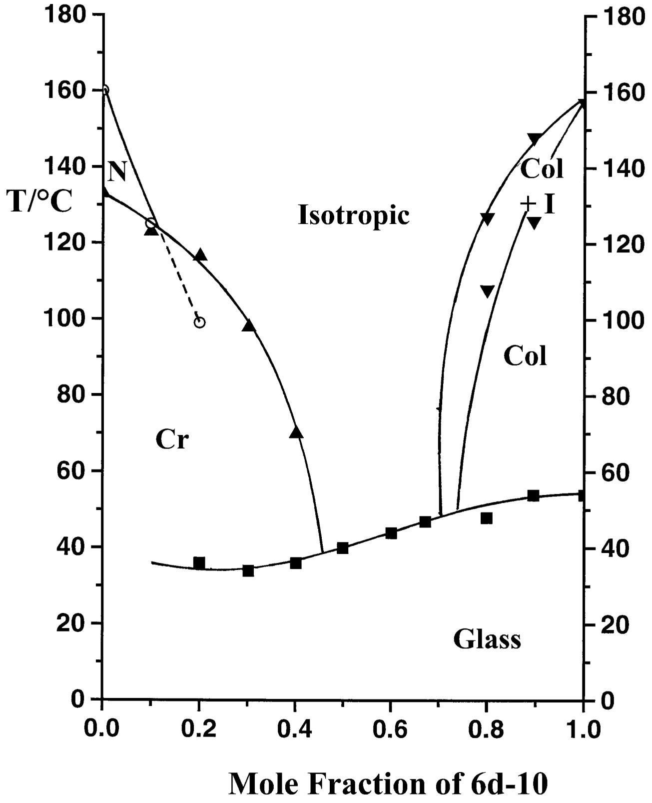
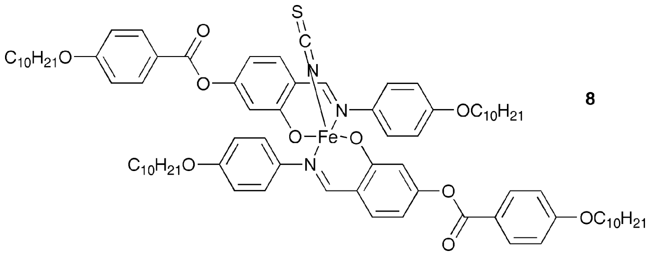


Figure 10. Binary phase diagram of **6d**–10 and a calamitic Ni^{II} complex.

is not liquid crystalline, but was used to probe interactions in mixtures by infrared spectroscopy using a variable temperature cell. This iron complex has a strong N=C absorption band at 2052 cm^{-1}, and when mixed with the copper analogue of **7** (Cr•117•N•136•I) in four-fold excess and at 120°C in the N phase [18], the absorption shifted to 2022 cm^{-1}, indicative of binding to the copper centre. Similarly, in mixtures with the nickel(II) complex shown in figure 9, the same shift is observed. Encouraged by these observations, we then synthesized the thiocyanate complex (**8**) shown in figure 11 which is, to the best of our knowledge, the first mesomorphic iron(III) thiocyanate complex reported. We then constructed a second binary phase diagram using this iron complex and the palladium complex **6a**–10. For this phase diagram, we chose the palladium complex as we reasoned that the softer sulphur would bind more readily to the soft Pd^{II} centre.



8

Cr • 97 • SmC • 183 • N • 202 • I

Figure 11. New thiocyanatoiron(III) complex synthesized in this study.

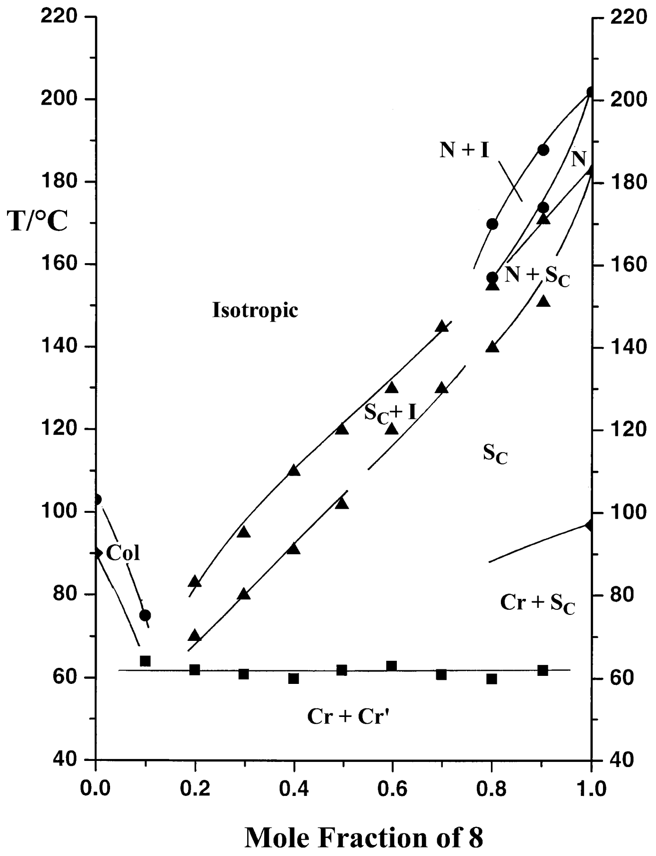


Figure 12. Binary phase diagram between **6a**–10 and **8**.

The resulting phase diagram (figure 12) has a very different form. Thus, addition of the discotic palladium species to **8** destabilizes the nematic phase completely by 20 mol%, but the SmC phase persists to 80 mol% disk, showing a remarkable degree of miscibility between a rod- and disk-like mesogen. Beyond 80 mol% disk, the phase observed is columnar and so, once more, there is a miscibility gap. It is interesting to speculate on whether the increased solubility of the iron disk in the palladium rod reflects some complex formation mediated by the thiocyanate ligand. However, formation of a new, discrete species would mean that at this composition, there should be no biphasic behaviour evident in the phase diagram (cf. behaviour in hydrogen–bonded mesogens [19]) and so we must conclude that any such associations are somewhat transient, if indeed they are present at all.

Table 2. Analytical data for mesomorphic complexes.

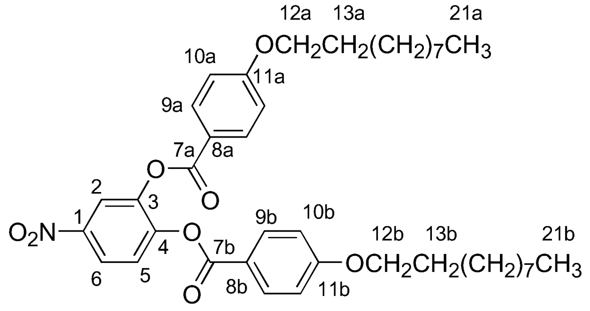
Compound	Yield/%	Calculated (found)/% C	H	N
6a–10	85	72.5 (72.4)	8.9 (8.9)	1.0 (1.0)
6a–16	79	75.6 (75.8)	10.1 (9.8)	0.8 (1.0)
6b–10	78	73.7 (72.8)	9.0 (9.1)	1.0 (0.8)
6b–16	75	76.5 (76.9)	10.3 (10.8)	0.8 (1.0)
6c–10	64	73.8 (73.7)	9.4 (9.0)	1.0 (0.9)
6c–16	59	76.6 (76.4)	10.3 (10.7)	0.8 (0.8)
6d–10	72	72.9 (72.7)	8.9 (9.1)	1.0 (0.8)
6d–16	76	75.9 (75.3)	10.2 (10.6)	0.8 (0.6)

5. Experimental

All solvents were dried before use and reagents were used as received. Instrumentation used for characterization and analysis is as described elsewhere [20]. Complex **7** was prepared as described in the literature [16]. Details of the synthesis of the discotic complexes are given, according to the route in figure 6, for the ligand and metal complexes with decyl alkyl chains; other homologues were prepared using the same procedure. Elemental analyses were obtained for those complexes that were mesomorphic, and are summarized in table 2.

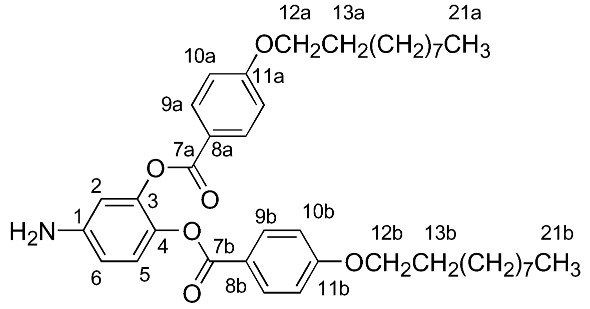
5.1. *3,4-Di(4-decyloxybenzoyloxy)nitrobenzene* **1**–*10*

4-Decyloxybenzoic acid (33.78 g, 0.121 mol) and nitrocatechol (8.96 g, 0.059 mol) were dissolved in dry THF (500 cm^3) in a flask flushed with dry nitrogen. 4A Molecular sieves (20 g), dicyclohexylcarbodiimide (DCCI) (31.31 g, 0.151 mol) and 4-(*N,N*-dimethylamino)pyridine (DMAP) (1.49 g, 0.017 mol) were added and the reaction mixture stirred at room temperature for 48 h. The cyclohexylurea by-product was filtered off and discarded, the solvent was removed from the filtrate on a rotary evaporator and the residue dissolved in dichloromethane (300 cm^3). The organic layer was extracted with acetic acid (5% v/v) then water, and dried over magnesium sulphate. The solvent was removed from the filtrate on a rotary evaporator and the product crystallized from ethanol and vacuum dried (yield 24.50 g, 61.5%). ^{1}H NMR (300.13 MHz, CDCl$_3$): δ_H 8.30 (1H, d, H^2, $J=2.6$ Hz) 8.24 (1H, dd, H^6, $J=8.9$ Hz, $J=2.7$ Hz), 8.00 (4H, dd, H^{9a,b}, $J=9.0$ Hz, $J=5.9$ Hz), 7.58 (2H, d, H^5, $J=8.9$ Hz), 6.86 (4H, dd, H^{10a,b}, $J=9.0$ Hz, $J=4.5$ Hz), 3.99, 4.00 (4H, t, H^{12a,b}, $J=6.5$ Hz), 1.79 (4H, qt, H^{13a,b}, $J=6.8$ Hz), 1.20–1.65 (28H, m, H^{14a,b}), 0.89 (6H, t, H^{21a,b}, $J=6.7$ Hz). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ_C 164.0 (C^{11a,b}), 163.4, 163.1 (C^{7a,b}), 145.1 (C^4), 143.1 (C^3), 148.3 (C^1), 132.5 (C^{9a,b}), 124.1 (C^5), 121.8 (C^{8a,b}), 114.2 (C^{10a,b}), 112.8 (C^6), 119.8 (C^2), 68.4 (C^{12a,b}), 31.9 (C^{19a,b}), 29.6–29.1 (C$^{14a–18a}$ and C$^{14b–18b}$), 26.0 (C^{13a,b}), 22.7 (C^{20a,b}), 14.1 (C^{21a,b}).



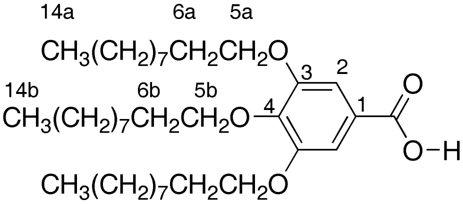
5.2. *3,4-Di[4-(decyloxy)benzoyl]aniline* **2**–*10*

3,4-Di(4′-decyloxybenzoyl)nitrobenzene (24.30 g, 0.0422 mol) and tin(II) chloride dihydrate (47.37 g, 0.210 mol) were added to propan-2-ol (350 cm^3) in a 1 dm^3 conical flask fitted with a reflux condenser. After refluxing gently for 6 h the reaction mixture was cooled to room temperature and poured into ice (~100 g). Sodium hydroxide solution (2 mol dm^{-3}) was added until the solution had a pH = 8. The mixture was then extracted twice with ethyl acetate (300 cm^3); the organic layer was washed with a sodium chloride solution (300 cm^3 of 10% w/v) followed by water (300 cm^3) and dried over anhydrous magnesium sulphate. The drying agent was filtered off and the solvent removed from the filtrate, the product crystallized from an ethanol/ethyl acetate mixture (4/1 v/v) and vacuum dried (yield 16.40 g 71.2%). ^{1}H NMR (300.13 MHz, CDCl$_3$): δ_H 7.98 (4H, AA′XX′, H^{9a,b}, $J_{AA'XX'}=8.9$ Hz), 7.10 (1H, d, H^5, $J=8.6$ Hz), 6.82 (4H, AA′XX′, H^{10a,b}, $J_{AA'XX'}=8.9$ Hz), 6.67 (1H, d, H^2, $J=2.6$ Hz), 6.59 (1H, dd, H^6, $J=8.6$ Hz, $J=2.7$ Hz), 3.99 (4H, t, H^{12a,b}, $J=6.5$ Hz), 3.45 (2H, s, NH$_2$), 1.79 (4H, qt, H^{13a,b}, $J=6.8$ Hz), 1.20–1.55 (28H, m, H^{14a,b}), 0.89 (6H, t, H^{21a,b}, $J=6.7$ Hz). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ_C 164.7, 164.1 (C^{7a,b}), 163.4, 163.3 (C^{11a,b}), 145.4 (C^4), 143.1 (C^3), 134.3 (C^1), 132.3, 132.2 (C^{9a,b}), 123.8 (C^5), 121.2 121.0 (C^{8a,b}), 114.2 (C^{10a,b}), 112.7 (C^6), 110.0 (C^2), 68.2 (C^{12a,b}), 31.9 (C^{19a,b}), 29.6–29.1 (C$^{14a–18a}$, C$^{14b–18b}$), 26.0 (C^{13a,b}), 22.7 (C^{20a,b}), 14.1 (C^{21a,b}).



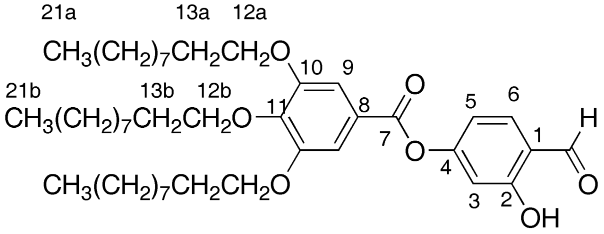
5.3. *3,4,5-Tridecyloxybenzoic acid, **3–10***

1-Bromodecane (172.93 g, 0.244 mol) and ethyl 3,4,5-trihydroxybenzoate (45.00 g, 0.244 mol) were added to potassium carbonate (151.88 g, 1.099 mol) in DMF (300 cm^3). The reaction mixture was heated under reflux for 6 h then cooled to room temperature. Water (300 cm^3) was added and the mixture extracted with dichloromethane (3 × 150 cm^3). The combined organic layer extracts were dried over anhydrous magnesium sulphate, the drying agent was filtered off and the solvent evaporated to leave a brown oil. Potassium hydroxide (24.68 g, 0.440 mol) in ethanol (95%, 500 cm^3) was added and the reaction heated under reflux for 3 h. Water (100 cm^3) was added and the solution acidified with conc. hydrochloric acid. The crude product was filtered off and twice crystallized from an ethanol/ethyl acetate mixture (4/1 v/v), and vacuum dried (yield 20.62 g, 14.3%). ^{1}H NMR (300.13 MHz, CDCl$_3$): δ_H 7.30 (2H, s, H^2), 3.99, 4.00 (6H, t, H^{5a,b}, $J = 6.5$ Hz), 1.80–1.90 (6H, m, H^{6a,b}), 1.20–1.60 (42H, m, H$^{7a–13a}$, H$^{7b–13b}$), 0.89 (9H, t, H^{14a,b}, $J = 6.7$ Hz). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ_C 172.0 (CO$_2$H), 152.8 (C^3), 143.1 (C^4), 123.7 (C^1), 110.0 (C^2), 73.5 (C^{5b}), 69.2 (C^{5a}), 31.9 (C^{12a,b}), 29.6–29.1 (C$^{7a–11a}$ C$^{7b–11b}$), 26.0 (C^{6a,b}), 22.7 (C^{13a,b}), 14.1 (C^{14a,b}).



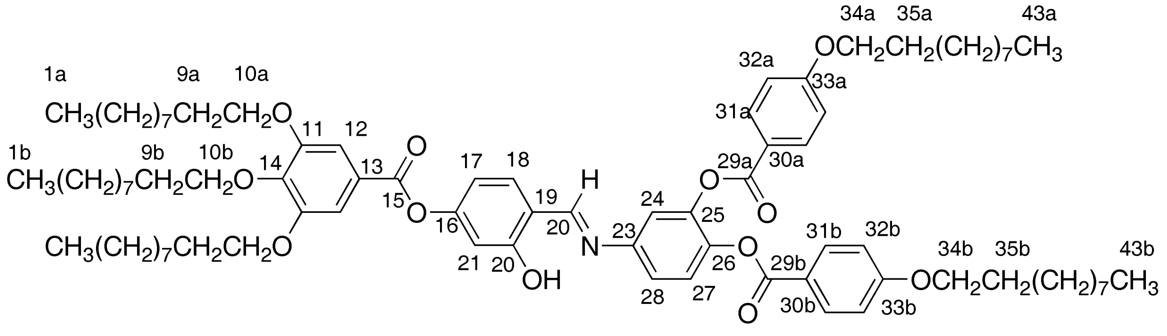
5.4. *4-(3,4,5-Tridecyloxybenzoyloxy)salicylaldehyde **4–10***

3,4,5-Tridecyloxybenzoic acid (25.61 g, 0.0433 mol) and 2,4-dihydroxybenzaldehyde (5.98 g, 0.0438 mol) were dissolved in dry THF (500 cm^3) in a flask flushed with dry nitrogen. 4A Molecular sieves (20 g), DCCI (9.39 g, 0.0455 mol) and DMAP (0.529 g, 0.0044 mol) were added and the reaction mixture stirred at room temperature for 48 h. The cyclohexylurea by-product was filtered off and discarded, the solvent was removed from the filtrate on a rotary evaporator and the residue dissolved in dichloromethane (300 cm^3). The organic layer was extracted with acetic acid (5% v/v) then water and dried over magnesium sulphate. The solvent was removed from the filtrate on a rotary evaporator and the product purified on a silica column whilst eluting with dichloromethane, then crystallized from an ethanol/ethyl acetate mixture (4/1 v/v) and vacuum dried (yield 10.01 g, 32.5%). ^{1}H NMR (300.13 MHz, CDCl$_3$): δ_H 11.30 (1H, s, OH), 9.85 (1H, s, CHO), 7.62 (1H, d, H^6, $J = 8.4$ Hz), 7.38 (2H, s, H^9), 6.90 (1H, dd, H^5, $J = 8.4$ Hz, $J = 2.0$ Hz), 6.87 (1H, d, H^3, $J = 2.0$ Hz), 4.07, 4.04 (6H, t, H^{12a,b}, $J = 6.5$ Hz), 1.80–1.90 (6H, m, H^{13a,b}), 1.20–1.65 (42H, m, H$^{14a–20a}$, H$^{14b–20b}$), 0.89 (9H, t, H^{21a,b}, $J = 6.7$ Hz). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ_C 195.5 (CHO), 164.0 (C^7), 163.2 (C^4), 157.8 (C^2), 153.0 (C^{10}), 143.0 (C^{11}), 135.0 (C^6), 123.1 (C^8), 118.7 (C^1), 114.2 (C^5), 111.0 (C^3), 108.7 (C^9), 73.6 (C^{12b}), 69.3 (C^{12a}), 31.9 (C^{19a,b}), 29.6–29.1 (C$^{14a–18a}$, C$^{14b–18b}$), 26.0 (C^{13a,b}), 22.7 (C^{20a,b}), 14.1 (C^{21a,b}).



5.5. *2-Hydroxy-4-(3,4,5-tridecyloxybenzoyloxy)-N-3,4-di(4-decyloxybenzoyloxy)salicylaldimine **5–10***

3,4-Di(4-decyloxybenzoyloxy)aniline (9.88 g, 0.0139 mol) and 4-(3,4,5-tridecyloxybenzoyloxy)salicylaldehyde (7.59 g, 0.0139 mol) were dissolved in hot absolute ethanol (200 cm^3) and 3 drops of glacial acetic acid added. The reaction mixture was refluxed gently for 3 h, cooled to room temperature and the crude product filtered. The product was then purified on a silica column using dichloromethane as eluant and crystallized from an ethanol/ethyl acetate mixture (4/1 v/v) and vacuum dried to yield 12.35 g (71.7%) of product. MS (FAB): $m/z = 1338$ [M]$^+$, C$_{84}$H$_{123}$NO$_{12}$ requires 1338. ^{1}H NMR (400.13 MHz, CDCl$_3$): δ_H 10.85 (1H, s, OH), 8.66 (1H, s, H^{22}), 8.02 (4H, AA′XX′, H$^{31a\text{ and }b}$, $J_{AA'XX'} = 8.9$ Hz), 7.43–7.41 (2H, m, H^{18}, H^{27}), 7.42 (1H, s, H^{12}), 7.35 (1H, d, H^{24}, $J = 2.4$ Hz), 7.24 (1H, dd, H^{28}, $J = 8.8$ Hz, $J = 2.2$ Hz), 6.90 (1H, d, H^{21}, $J = 2.1$ Hz), 6.85 (4H, AA′XX′, H^{32a,b}, $J_{AA'XX'} = 8.9$ Hz), 6.84–6.82 (1H, m, H^{17}), 4.25–4.05 (6H, m, H^{10a,b}), 3.98 (4H, t, H^{34a,b}, $J = 6.5$ Hz), 1.79–1.90 (10H, m, H$^{9a\text{ and }b}$, H^{35a,b},), 1.20–1.55 (70H, m, H$^{2a–7a}$, H$^{2b–7b}$, H$^{36a–42a}$, H$^{36b–42b}$), 0.89 (15H, t, H^{1a,b}, H^{43a,b}, $J = 6.6$ Hz). ^{13}C NMR (100.6 MHz, CDCl$_3$): δ_C 164.4–163.6 (C^{15} & C$^{29a\text{ and }b}$, C$^{33a\text{ and }b}$), 162.6, 162.5 (C^{16}, C^{22}), 155.1 (C^{20}), 153.0 (C^{11}), 146.5 (C^{23}), 143.4 & 143.3 (C^{14}, C^{26}), 141.6 (C^{25}), 133.4 (C^{18}), 132.3 (C$^{31a\text{ and }b}$), 124.2 (C^{27}), 123.6 (C^{13}), 120.7, 120.6 (C$^{30a\text{ and }b}$), 119.4 (C^{28}), 117.1 (C^{19}), 116.2 (C^{24}), 114.3, 114.2 (C^{32a,b}), 113.2 (C^{17}), 110.7 (C^{21}), 108.7 (C^{12}), 73.6 (C^{10b}), 69.3 (C^{10a}), 68.3 (C^{34a,b}), 31.9 (C^{3a,b}, C^{41a,b}), 29.7–26.0 (C$^{4a–9a}$, C$^{4b–9b}$, C$^{35a–40a}$, C$^{35b–40b}$), 22.7–22.6 (C^{2a,b}, C^{42a,b}), 14.1 (C^{1a,b}, C^{43a,b}).



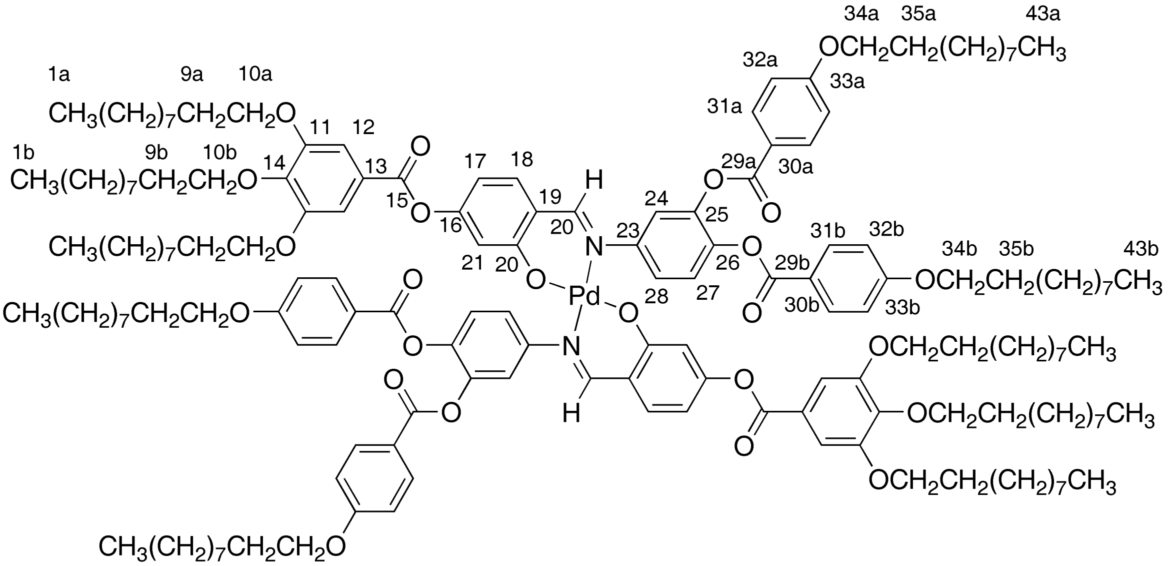
5.6. *Palladium(II) complex* ***6a****–10*

Compound **5a**–10 (2.099 g, 0.00169 mol) was dissolved in dry toluene (40 cm^3) and a solution of palladium(II) acetate (0.1904 g, 0.00085 mol) in ethanol (absolute, 10 cm^3) was added; the reaction mixture was heated to 60°C for 4 h. After cooling to room temperature, the crude product was filtered off and rinsed with cold absolute ethanol, then crystallized from a mixture of absolute ethanol/toluene (4/1 v/v) and vacuum dried (yield 3.71 g, 85.0%). MS (FAB): $m/z = 2782$ $[MH]^+$, $C_{168}H_{244}N_2O_{24}Pd$ requires 2780. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 8.00 (4H, AA′XX′, H^{31a}, $J_{AA'XX'} = 8.9$ Hz), 7.88 (2H, s, H^{22}), 7.68 (4H, AA′XX′, H^{31b}, $J_{AA'XX'} = 8.9$ Hz), 7.42 (4H, s, H^{12}), 7.38–7.36 (4H, m, H^{24}, H^{27}), 7.27–7.25 (4H, m, H^{18}, H^{28}), 6.78, 6.71 (8H, AA′XX′, $H^{32a,b}$, $J_{AA'XX'} = 8.9$ Hz), 6.58 (2H, d, H^{21}, $J = 2.0$ Hz), 6.46 (2H, dd, H^{17} $J = 8.7$ Hz), 4.10 (4H, t, H^{10b}, $J = 6.5$ Hz), 3.98–3.91 (16H, m, H^{10a}, H^{34a}, H^{34b}), 1.79–1.90 (20H, m, $H^{9a,b}$, $H^{35a,b}$), 1.20–1.55 (156H, m, $H^{2a–7a}$, $H^{2b–7b}$, $H^{36a–42a}$, $H^{36b–42b}$), 0.89 (30H, t, $H^{1a,b}$, $H^{43a,b}$, $J = 6.6$ Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 166.3–163.4s (C^{15}, C^{16}, $C^{29a,b}$, $C^{33a,b}$), 162.3 (C^{22}), 157.2 (C^{20}), 152.9 (C^{11}), 147.1 (C^{23}), 142.6, 142.5 (C^{14}, C^{26}), 141.4 (C^{25}), 133.5 (C^{18}), 132.5, 132.1 ($C^{31a,b}$), 124.4 (C^{13}), 123.3 (C^{28}), 122.4 (C^{27}), 120.8 & 120.6 ($C^{30a,b}$), 120.4 (C^{24}), 118.3 (C^{19}), 114.1 & 114.0 ($C^{32a,b}$), 113.9 (C^{17}), 110.5 (C^{21}), 108.6 (C^{12}), 73.5 (C^{10b}), 69.1 (C^{10a}), 68.2 ($C^{34a,b}$), 31.9 ($C^{3a,b}$, $C^{41a,b}$), 29.7–26.0 ($C^{4a–9a}$, $C^{4b–9b}$, $C^{35a–40a}$, $C^{35b–40b}$), 22.7–22.6 ($C^{2a,b}$, $C^{42a,b}$), 14.1 ($C^{1a,b}$, $C^{43a,b}$).

Metal complexes were similarly prepared using copper(II) acetate, nickel(II) acetate and iron(III) chloride. These complexes were paramagnetic, and because of line broadening, their characterization by NMR spectroscopy could not be carried out. The preparation of the vanadyl derivative was also attempted using vanadyl(IV) sulphate pentahydrate but was unsuccessful, with only unreacted ligand being recovered from the reaction.

5.7. *Chloro(2-hydroxy-4-decyloxy-4′-benzoyloxy)*-N-*(4-decyloxysalicylaldimato)iron(III)*

2-Hydroxy-4-(decyloxy-4′-benzoyloxy)-*N*-(4-decyloxysalicylaldimine (0.7418 g, 1.178 mmol) was dissolved in



dry toluene ($20\,\mathrm{cm}^3$) and stirred under dry nitrogen. To this solution anhydrous iron(III) chloride (0.09554 g, 0.589 mmol) dissolved in anhydrous ethanol ($10\,\mathrm{cm}^3$) was added dropwise whilst stirring at room temperature. After stirring for 18 h the solvent was removed by rotary evaporation and the recovered solid crystallized from an absolute ethanol/toluene mixture (4/1 v/v). After drying in vacuo 0.536 g, (67.5%) of brown crystalline product was collected. Calculated for $C_{80}H_{108}N_2O_{10}FeCl$ C 71.2, H 8.1, N, 2.1; found C 71.4, H 8.4, N 2.1%.

5.8. *2-Hydroxy-4-(decyloxy-4′-benzoyloxy)*-N-*(4-decyloxysalicylaldimato)thiocyanatoiron(III)*

Chloro(2-hydroxy-4-decyloxy-4′-benzoyloxy)-*N*-(4-decyloxysalicylaldimato)iron(III) (0.2500 g, 0.1853 mmol) and silver thiocyanate (0.06137 g, 0.1853 mmol) were added to dry toluene ($20\,\mathrm{cm}^3$) and heated under reflux for 48 h. The reaction mixture was filtered through celite and the solvent removed from the filtrate on a rotary evaporator; the crude product crystallized from ethanol. After drying in vacuo 0.197 g (77.5%) of brown crystalline product was collected. Calculated for $C_{81}H_{108}N_3SO_{10}Fe$ C 70.9, H, 7.9, N 3.1; found C 71.3, H 8.3, N 2.8%.

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