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Novel amides and Schiff's bases derived from 1,3,4-oxadiazole derivatives: synthesis and mesomorphic behaviour

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The synthesis and liquid crystalline properties of novel achiral amides (**Ia–g**, **IIa–g** and **IVa,b**), achiral Schiff's bases (**IIIa–g** and **Va–g**), chiral amides (**VI, VII**) and chiral Schiff's bases (**VIII–XI**) incorporating a 1,3,4-oxadiazole ring are reported. All amides of the series **I** and **II** display an enantiotropic smectic A phase. The amide **IVa,b** did not show mesomorphic properties. Amides of the series **Ia–g** and **IIa–g** contain a flexible *n*-tetradecylthio chain, the other terminal substituent is an *n*-alkoxy chain and *n*-alkyl chain, respectively (n = 4–10) and the 1,3,4-oxadiazole is in the terminal rigid core. Amides **Ia–g** have broader mesomorphic range and higher thermal stability than the corresponding amides **IIa–g**. Amides **IVa,d** contain the 1,3,4-oxadiazole ring in the centre of the rigid core and two flexible alkoxy chains as flexible terminal substituents. Thus, the mesomorphic properties are favoured if 1,3,4-oxadiazole is shifted to a terminal position of the rigid core. Schiff's bases **IIIa–g** display an enantiotropic dimorphism smectic C–smectic A. Schiff's bases **IIIa–g** have a broader mesomorphic range than the analogous amides **Ia–g**. Schiff's bases **Va–g** exhibit a dimorphism smectic A–nematic, and in contrast to this the analogous amide **IVa,b** did not show mesomorphism. The chiral amides **VI** and **VII** and chiral Schiff's bases **X** and **XI** did not show mesomorphic properties and only the chiral Schiff's bases **VIII** and **IX** display a chiral smectic C phase in a short mesomorphic range. A density functional theory theoretical study at the B3LYP/6–311++G(d,p) level was performed in order to analyse the structural features that must be related with the mesomorphic behaviour of the reported compounds.

Keywords: 1,3,4-oxadiazoles; mesomorphic behaviour; amides; Schiff's bases

1. Introduction

Thermotropic calamitic mesomorphism can be related with several molecular features, such as lath shape and molecular linearity, which in turn can be attained by joined aromatic, aliphatic or heteroaromatic rings in the mesogenic core. In addition, the use of heterocyclic mesogenic units, such as 1,3,4-oxadiazole, might have an influence on the mesomorphic behaviour of calamitic molecules owing to the presence of lateral dipoles that arise from the asymmetric charge distribution in the heterocyclic core (*1–4*).

The 1,3,4-oxadiazoles are interesting systems for the design and synthesis of liquid crystalline compounds with a classical rod-like structure. The 1,3,4-oxadiazole derivatives are well known for their high thermal and hydrolytic stability, resistance to oxidative degradation and electron-accepting properties (*5*).

1,3,4-oxadiazole liquid crystal derivatives, having an asymmetric structures within oxadiazole ring into the central position of the mesogenic rigid core, were first reported by Dimitrowa *et al.* (*6*). Also, a series of asymmetric calamitic 1,3,4-oxadiazole-base liquid crystals containing different terminal polar units have been synthesised by Sung and Lin (*4*).

In investigations of liquid crystalline esters of 2,5-bis (4-hydroxyphenyl)-1,3,4-oxadiazoles and 2-alkylthio-5-(4-hydroxyphenyl)-1,3,4-oxadiazoles (*1, 2*), it was established that the esters of 2-alkylthio-5-(4-hydroxyphenyl)-1,3,4-oxadiazoles showed the widest mesomorphic ranges and these compounds exhibited smectic A (SmA) and nematic (N) phases. Compounds bearing a 1,3,4-oxadiazole and a pyridinium group were reported by Haristoy and Tsiourvas (*7*) in which one of the terminal group is an alkylthio chain, these materials displayed a SmA phase.

Previously, we reported symmetric esters derived from 2-alkylthio-5-(4-hydroxyphenyl)-1,3,4-oxadiazole and trans-1,4-cyclohexane dicarboxylic acid (*8*), terephthalic acid and 2,5-thiophene dicarboxylic acid (*9*). These compounds displayed SmC and SmA phases in a broad mesomorphic ranges.

On the other hand, some functional central bridging groups have shown to be very useful to promote mesomorphic properties. For example, the ester and imine groups are some of the most commonly used (*1, 10–18*). The amide group is rarely found in liquid crystals because, in general, it gives rise to strong intermolecular interactions that often preclude mesomorphic behaviour. For example, Baeyens-Volant *et al.* previously reported a number of calamitic benzamide derivatives, but only one of these compounds showed mesomorphic behaviour (*19*). Nevertheless, a

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number of mesomorphic compounds having two central linkages, one of which is an ester group and the other is an amide group, have been reported recently (*20*). Amides containing the benzothiazole (*21*) or 1,3,4-thiadiazole heterocycle have been reported by us (*22, 23*), which exhibit enantiotropic liquid crystalline properties. SmC, SmA and N phases with wider mesomorphic ranges were observed. More recently, we reported chiral amide-thiadiazole derivatives displaying chiral SmC (ferroelectric) and chiral N (cholesteric) phases with reasonable temperature ranges (*24*).

Continuing our work on the liquid crystal possibilities of the oxadiazole systems, in this paper we report the design, synthesis and phase behaviour of novel achiral amides (**Ia–g**, **IIa–g**, **IVa,b**) and achiral Schiff's bases (**IIIa–g**, **Va–g**), chiral amides (**VI, VII**) and chiral Schiff's bases (**VIII–XI**) incorporating the 1,3,4-oxadiazole moiety (see Figure 1).

The main aim of this work is to study the effect on the mesomorphic properties of: (1) the presence of alkoxy or alkyl chains present in amides of the series **I** and **II**; (2) the position of the 1,3,4-oxadiazole unit in amides **I, II** and **IV**; (3) the effect of the central linkage (the amide group present in compounds **Ia–g** and **IVa,b** was replaced by an imine group in compounds **IIIa–g** and **Va–g**, respectively); (4) the effect of the replacement of the achiral alkoxy and/or alkyl chain present both in amides (series **I**, series **II** and compounds **IV**) and in Schiff's bases of series **III** and series **V** by a chiral alkoxy chain derived from (*R*)-2-octanol and/or (*S*)-ethyl lactate.

To the best of the authors' knowledge, the prepared compounds are the first calamitic amides and Schiff's bases derived from 1,3,4-oxadiazole exhibiting mesomorphic properties.

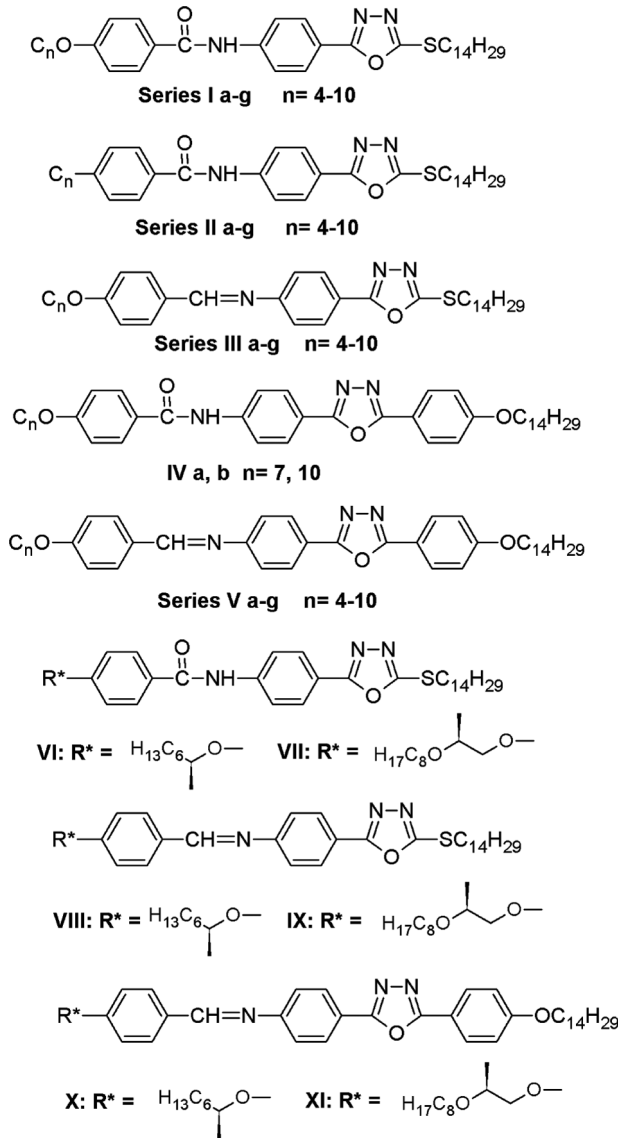


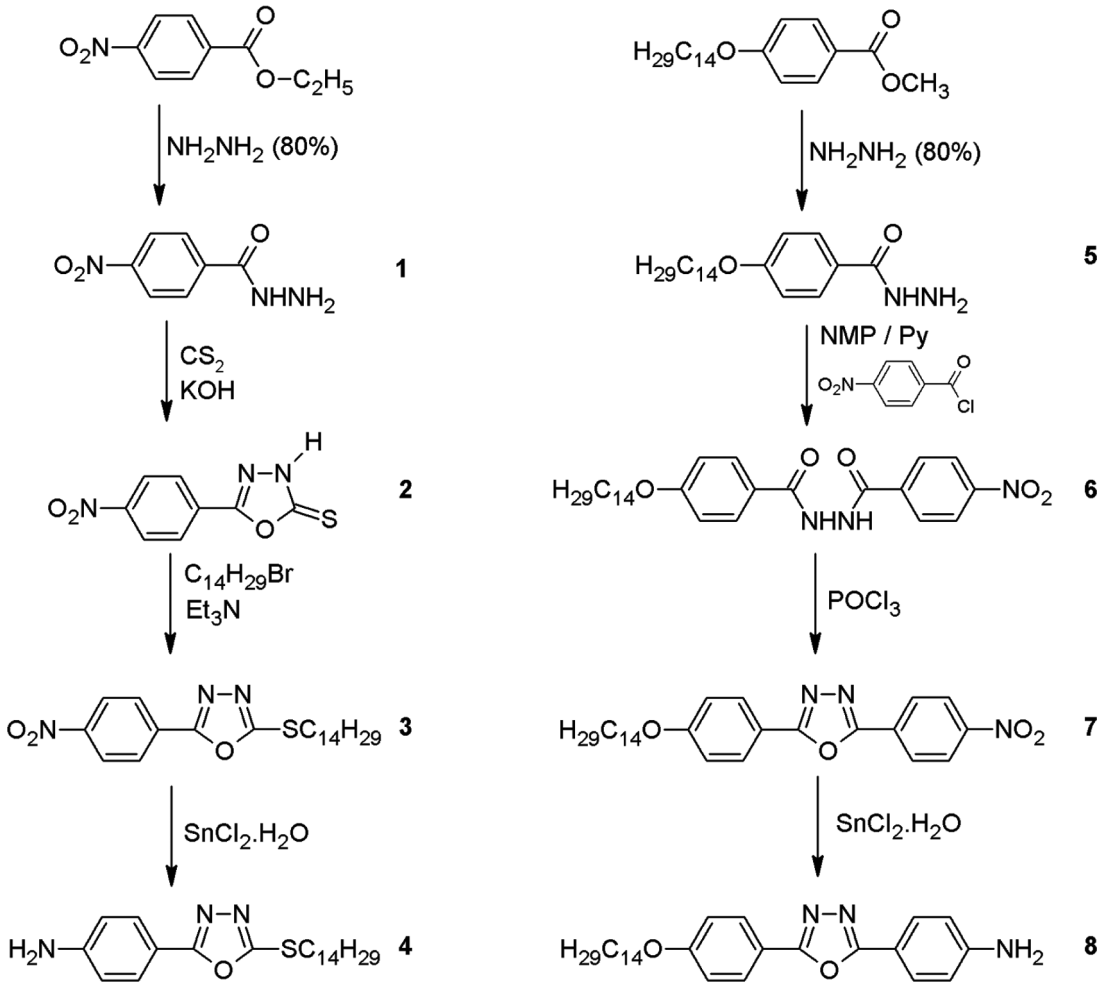
Figure 1. Structures of achiral amides **Ia–g, IIa–g** and **IVa,b**; achiral Schiff's bases **IIIa–g** and **Va–g**; chiral amides **VI** and **VII**; and chiral Schiff's bases **VIII–XI**.

2. Synthesis

The synthesis of all compounds is outlined in Schemes 1, 2 and 3. Compound **4** was synthesised by condensation of ethyl 4-nitrobenzoate with 80% hydrazine hydrate, yielding 4-nitrophenylhydrazide **1** (see (*14*)); this was reacted with carbon disulfide in basic medium leading to the formation the thione **2**. In the following sequence, the alkylation of **2** leads to the 1,3,4-oxadiazole **3** (see (*2*)). The nitro group in compound **3** was reduced to the corresponding amino 1,3,4-oxadiazole derivative **4** with $SnCl_2$ (see (*25*)).

Compound **8** was synthesised starting with the alkylation of methyl 4-hydroxybenzoate and proceeding with condensation with 80% hydrazine hydrate, yielding 4-*n*-tetradecyloxyphenylhydrazide **5** (see (*9*)). Condensation of **5** with 4-nitrobenzoyl chloride leads to the formation of the diacylhydrazine **6** (see (*4*)). Reaction of the compound **6** with $POCl_3$ leads to the 1,3,4-oxadiazole **7** (see (*4*)). The amino-1,3,4-oxadiazole derivative **8** was obtained by reduction of the nitro group of **7** with $SnCl_2$, according to the procedure described in (*25*).

The synthetic route to the amides (**Ia–g, IIa–g, IVa,b**) and Schiff's bases (**IIIa–g, Va–g**) is shown in Scheme 2. The amides **Ia-g** and **IIa-g** were obtained by reaction of compound **4** with the corresponding 4-*n*-alkoxy- and/or 4-*n*-alkylbenzoyl chloride, respectively, and amides **IVa,b** were synthesised by condensation of compound **8** with 4-*n*-heptyloxybenzoyl chloride and/or 4-*n*-decyloxybenzoylchloride, yielding amide **IVa** and **IVb**, respectively, according to the procedure described previously (*24*).

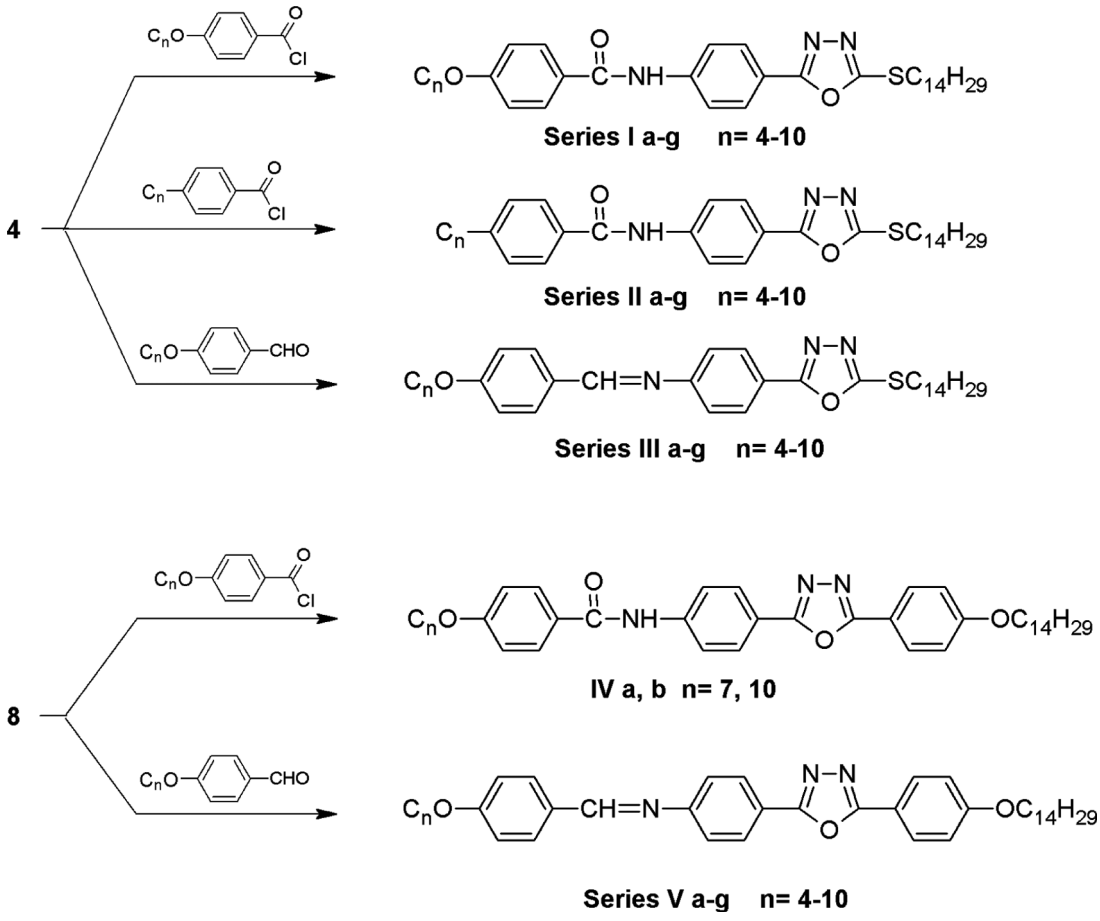


Scheme 1. Synthetic route for amino-oxadiazole derivatives **4** and **8**.

The Schiff's bases **IIIa–g** and **Va–g** were prepared by condensation of **4** or **8** with an excess of 4-*n*-alkoxybenzaldehyde, using the procedure described elsewhere (*14*, *26*).

Scheme 3 illustrates the synthesis of the chiral amides (**VI** and **VII**) and the chiral Schiff's bases (**VIII-XI**).

(*R*)-2-octanol and (*S*)-2-*n*-octyloxypropanol were chosen to prepare the chiral 4-alkoxybenzoyl chlorides and the chiral 4-alkoxybenzaldehydes. The former was purchased from Merck while the latter were prepare using (*S*)-ethyl lactate as chiral precursor, according to the method described elsewhere (*27*). The synthesis of the chiral 4-alkoxybenzoyl chlorides was achieved by a Mitsunobu reaction (*28*) starting from methyl 4-hydroxybenzoate and the corresponding chiral alcohols. The resulting esters were saponified leading to the formation of the corresponding chiral acids, followed by reaction with oxalyl chloride (*29*). The chiral 4-alkoxybenzaldehydes were synthesised by a Mitsunobu reaction (*28*) starting from 4-hydroxybenzaldehyde and the corresponding chiral alcohols (*17, 18*). The chiral amides **VI** and **VII** were obtained by reaction of compound **4** with the corresponding chiral 4-alkoxybenzoyl chlorides and the chiral Schiff's bases **VIII–XI** were prepared by condensation of **4** or **8** with the corresponding chiral 4-alkoxybenzaldehydes, as well as the procedure used in the synthesis of the corresponding achiral amides and achiral Schiff's bases. It is known that the reaction of a phenol with primary or secondary alcohols in the presence of DIAD/Triphenylphosphine (Mitsunobu reaction) produces an alkyl aryl ether. For reaction of secondary alcohols, there is inversion at the hydroxycarbon indicating that the reaction occurs by activation of the alcohol followed by SN^2 displacement by the phenol. Therefore, the Mitsunobu reaction between the methyl 4-hydroxybenzoate and/or 4-hydroxybenzaldehyde with (*R*)-2-octanol proceeded with inversion of the configuration at the chiral centre, so the stereochemistry of the corresponding chiral products is *S*. On the other



Scheme 2. Synthetic route for achiral amides **Ia–g**, **IIa–g** and **IVa,b** and achiral Schiff's bases **IIIa–g** and **Va–g**.

hand, (*S*)-2-*n*-octyloxypropanol is a primary alcohol, and the configuration at the chiral centre is not affected in the Mitsunobu reaction, therefore the stereochemistry of the compounds containing a chiral alkoxy chain derived from this alcohol is *S*.

3. Results and discussion

3.1 Mesomorphic properties

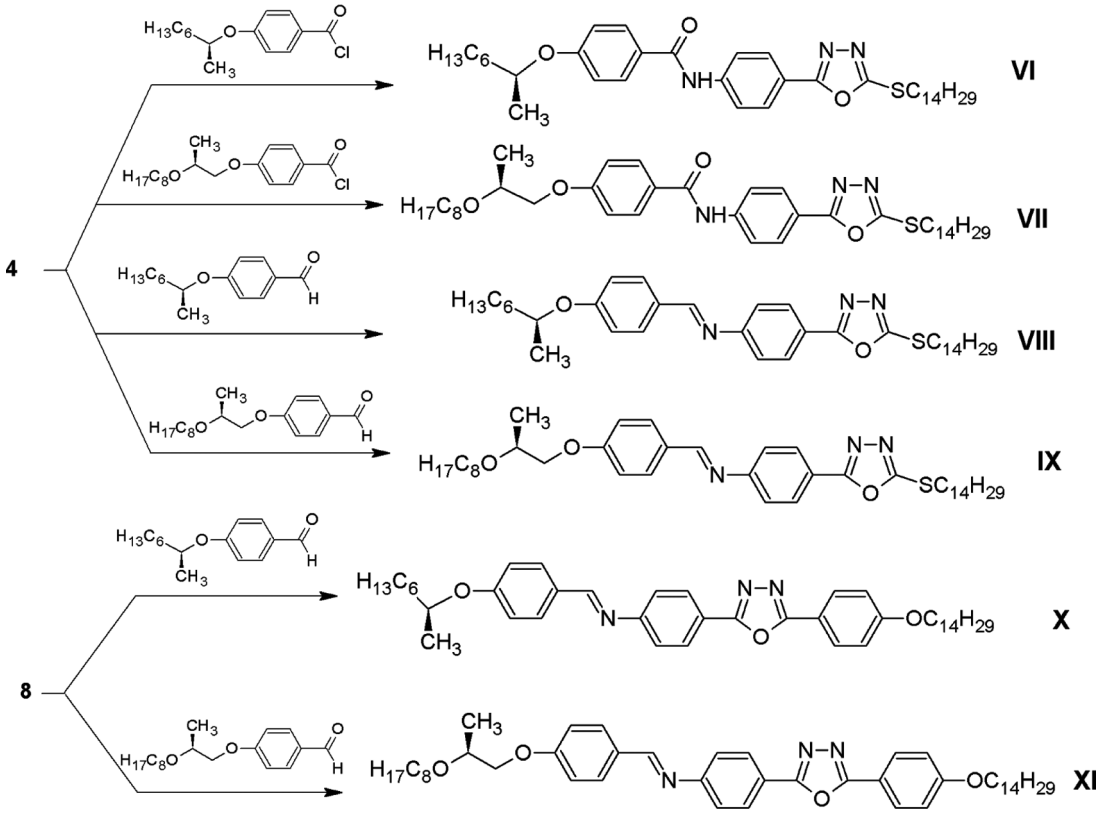
The transition temperatures and phase behaviour of the new materials are given in Tables 1–3.

As can be seen from Table 1, all compounds in series **Ia–g** and **IIa–g** exhibit mesomorphic behaviour. In each case and enantiotropic SmA mesophase is observed.

All melting temperatures of the amides **Ia–g** are in the range 114–126°C which decrease with increasing *n*-alkoxy chain length, corresponding to an average value of around 2°C for each methylene group. The clearing temperatures of these amides remained practically constant at 160°C, thus the mesomorphic temperature ranges increase in the order **Ia** (34.5°C), **Ib** (36.3°C), **Ic** (38.4°C), **Id** (41.5°C), **Ie** (42.6°C), **If** (44.7°C), **Ig** (47.0°C).

The amides of series **IIa–g** have similar melting temperatures to the corresponding amides of series **Ia–g**. In the case of amides **IIa–g**, the homologues with even number of carbon atoms in the *n*-alkyl chain have lower melting points (**IIa** 121.7°C, **IIc** 121.6°C, **IIe** 122.8°C, **IIg** 122.3°C) than those with an odd number of carbon atoms in the *n*-alkyl chain (**IIb** 126.6°C, **IId** 127.2°C, **IIf** 128.1°C). In addition, the clearing temperatures in this series increase with increase in *n*-alkyl chain length, and the mesomorphic temperature ranges increase in the order **IIa** (2.4°C), **IIb** (3.5°C), **IIc** (9.7°C), **IId** (11.4°C), **IIe** (16.3°C), **IIf** (17.9°C), **IIg** (26.4°C).

Clearly, the amides of series **Ia–g** have higher thermal stabilities and broader mesomorphic ranges than those of the amides of series **IIa–g**. These series have the same rigid core and the same alkylthio chain. The unique difference is that in series **Ia–g** the other lateral chains are alkoxy chains whereas in series **IIa–g** they are alkyl chains. This could explain the higher thermal stability and broader mesomorphic ranges of the amides of series **Ia–g**. Probably, a lateral interaction giving rise to a layered smectic order is more



Scheme 3. Synthetic route for chiral amides **VI** and **VII** and chiral Schiff's bases **VIII–XI**.

favourable for the compounds of the series **Ia–g** as compared with their analogues in series **IIa–g**, owing to a major volume occupied by the flexible melted alkoxy chains and a higher polarisability owing to the presence of the oxygen atom. These results are in accordance with the previous findings on analogous esters reported by Girdziunaite *et al*. (*2*).

The amides **IVa,b** do not show mesomorphism, exhibiting only a Cr–I transition. Thus, the mesomorphic behaviour is much more significant for amides of the series **Ia–g** and **IIa–g**. This fact can be explained if it is assumed that the bend in the molecular shape is reduced to a certain degree if the oxadiazole ring is shifted to the terminal position of the rigid aromatic core. In this position the flexible alkylthio chain allows the partial compensation of the molecular bend (*2*). In addition, from previous studies reported by Torgova *et al*. (*30*), it is known that 1,3,4-oxadiazole derivatives produce a deviation of the molecular shape from linearity which is especially strong if the oxadiazole ring occupies a central position of the rigid aromatic core. This deviation from the typical rod-like mesogen shape, could explain the lack of the mesomorphic properties of the amides **IVa,b**.

For comparative purposes, we synthesised analogous Schiff's bases, series **IIIa–g** and series **Va–g** (Scheme 2). The Schiff's bases **IIIa-g** have the same central core and the same terminal tails as amides **Ia–g**. However, some significant differences between their central linkages can be noted. Compounds in series **IIIa–g** display enantiotropic SmC and SmA mesomorphism in the whole range of *n* studied. The thermal mesomorphic ranges are similar for all derivatives (~52°C). In addition, as the length of *n*-alkoxy chain increases, the thermal mesomorphic range of the SmC phase increases and the thermal mesomorphic range of the SmA phase decreases (see Table 2).

The Schiff's bases **Va–g** display enantiotropic SmA and N mesomorphism. The homologues with $n = 4$–7 show enantiotropic N and SmA mesophases. For members with $n \geq 8$ the nematic phase is not observed. The thermal mesomorphic range is similar for all derivatives (~48°C) and, with the exception of derivatives with $n = 4$–7 which have a short N range, the members with longer chains ($n \geq 8$) display only SmA phase (see Table 2).

We now compare the mesogenic properties of the series **Ia–g** amides with analogous Schiff's bases **IIIa–g**. The amides **Ia–g** have the same central core

Table 1. Transition temperatures and enthalpies of amides **Ia–g, IIa–g** and **IVa,b**. Cr = crystal, SmA = smectic A, I = isotropic.

Compound	Transition	T (°C)	ΔH (J g^{-1})
Ia (n = 4)	Cr – SmA	126.0	71.4
	SmA – I	160.5	6.7
Ib (n = 5)	Cr – SmA	124.4	69.4
	SmA – I	160.7	6.6
Ic (n = 6)	Cr – SmA	122.5	56.5
	SmA – I	160.9	6.8
Id (n = 7)	Cr – SmA	120.0	40.7
	SmA – I	161.5	6.4
Ie (n = 8)	Cr – SmA	118.2	40.5
	SmA – I	160.8	6.5
If (n = 9)	Cr – SmA	116.5	40.4
	SmA – I	161.2	6.3
Ig (n = 10)	Cr – SmA	114.0	40.2
	SmA – I	161.0	6.1
IIa (n = 4)	Cr – SmA	121.7	65.8
	SmA – I	124.1	5.2
IIb (n = 5)	Cr – SmA	126.6	57.6
	SmA – I	130.1	5.8
IIc (n = 6)	Cr – SmA	121.6	55.4
	SmA – I	131.3	5.5
IId (n = 7)	Cr – SmA	127.2	52.1
	SmA – I	138.6	5.6
IIe (n = 8)	Cr – SmA	122.8	52.9
	SmA – I	139.1	5.4
IIf (n = 9)	Cr – SmA	128.1	51.8
	SmA – I	146.0	5.7
IIg (n = 10)	Cr – SmA	122.3	50.7
	SmA – I	148.7	5.3
IVa (n = 7)	Cr – I	220.5	85.8
IVb (n = 10)	Cr – I	215.8	80.1

Table 2. Transition temperatures and enthalpies of Schiff's bases **IIIa–g** and **Va–g**. Cr = crystal, SmC = smectic C, SmA = smectic A, N = nematic, I = isotropic.

Compound	Transition	T (°C)	ΔH (J g^{-1})
IIIa (n = 4)	Cr – SmC	88.7	66.4
	SmC – SmA	117.0[a]	–
	SmA – I	140.7	9.9
IIIb (n = 5)	Cr – SmC	88.9	66.6
	SmC – SmA	120.0[a]	–
	SmA – I	140.5	9.1
IIIc (n = 6)	Cr – SmC	89.1	66.1
	SmC – SmA	122.0[a]	–
	SmA – I	140.3	9.8
IIId (n = 7)	Cr – SmC	89.3	65.33
	SmC – SmA	124 [a]	–
	SmA – I	141.7	9.7
IIIe (n = 8)	Cr – SmC	89.9	65.1
	SmC – SmA	125.0[a]	–
	SmA – I	141.6	9.4
IIIf (n = 9)	Cr – SmC	89.1	65.9
	SmC – SmA	127.0[a]	–
	SmA – I	141.1	9.5
IIIg (n = 10)	Cr – SmC	89.4	66.0
	SmC – SmA	130.0[a]	–
	SmA – I	141.8	9.1
Va (n = 4)	Cr – SmA	114.9	44.9
	SmA – N	150.5	5.5
	N – I	162.8	0.8
Vb (n = 5)	Cr – SmA	114.5	43.4
	SmA – N	154.8	6.9
	N – I	162.5	0.9
Vc (n = 6)	Cr – SmA	115.3	46.1
	SmA – N	158.0[a]	–
	N – I	163.4	0.6
Vd (n = 7)	Cr – SmA	115.1	45.6
	SmA – N	161.0 [a]	–
	N – I	163.1	0.7
Ve (n = 8)	Cr – SmA	115.9	43.8
	SmA – I	163.6	7.5
Vf (n = 9)	Cr – SmA	115.4	44.1
	SmA – I	164.1	8.1
Vg (n = 10)	Cr – SmA	115.1	45.6
	SmA – I	163.9	8.6

[a] Optical microscopy data.

and the same terminal tails as the Schiff's bases **IIIa–g**. However, some significant differences between their central linkages can be noted. As mentioned above, the Schiff's bases **IIIa–g** display enantiotropic smectic phases, whereas the amides **Ia–g** are purely SmA in character. On the other hand, it is interesting to compare the Schiff's bases **Va–g**, in particular the homologues **Vd,g**, with the analogous amides **IVa,b**. The Schiff's bases of the series **Va–g** show enantiotropic SmA and enantiotropic N phases, whereas the amides **IVa,b** do not show mesomorphic behaviour.

When the amide group in compounds **Ia–g** and in compounds **IVa,b** is replaced by an imine group to give the Schiff's bases **IIIa–g** and **Vd,g**, respectively, the melting point is substantially lowered (~30°C and ~100°C, respectively) as seen when we compare them with the corresponding amides **Ia–g** and **IVa,b**. In addition, Schiff's bases **IIIa–g** have broader mesomorphic ranges than amides **Ia–g**. The mesomorphic behaviour was even more pronounced when the amide group present in **IVa,b** was substituted by an imine group to give the Schiff's bases **Va–g**, in particular to

Table 3. Transition temperatures and enthalpies of chiral amides **VI**, **VII** and chiral Schiff's bases **VIII–XI**. Cr = crystal, SmC* = chiral smectic C, I = isotropic.

Compound	Transition	T (°C)	ΔH (J g^{-1})
VI	Cr – I	94.1	60.1
VII	Cr – I	121.3	70.9
VIII	Cr – SmC*	57.4	65.9
	SmC* – I	63.3	7.0
IX	Cr – SmC*	78.9	53.0
	SmC* – I	84.6	6.8
X	Cr – I	99.4	68.3
XI	Cr – I	130.8	71.2

give its analogous Schiff's bases **Vd,g**. In this situation, enantiotropic SmA and N phases were observed in Schiff's base **Vd** and an enantiotropic SmA phase was observed in Schiff's base **Vg** with a mesomorphic range of 48.0 and 48.8°C, respectively; in contrast to this, the analogous amides **IVa,b** are ordinary solids that melt to the isotropic liquid at 220.5 and 215.8°C, respectively.

In order to obtain chiral mesophases (cholesteric, tilted smectic), we have also synthesised chiral amides (**VI** and **VII**) and chiral Schiff's bases (**VIII–XI**) (see Scheme 3). The achiral *n*-alkoxy and/or achiral *n*-alkyl chain in amides **I** and **II** and the achiral *n*-alkoxy chain in Schiff's bases **III** and **V** were replaced by a chiral alkoxy chain derived from (*R*)-2-octanol and/or by a chiral alkoxy chain derived from (*S*)-ethyl lactate to give the chiral amides **VI** and **VII**, and chiral Schiff's bases **VIII–XI**, respectively. The results show that the chiral alkoxy chain has a profound influence on the mesomorphic properties. While compounds of the achiral amides (series **I** and series **II**) exhibit SmA mesomorphism the chiral amides (**VI** and **VII**) do not show liquid crystalline properties, and only a crystalline phase was observed (see Table 3). Similar behaviour was observed for Schiff's bases **X** and **XI**, which do not show mesomorphic properties and only a Cr–I transition was observed in these compounds. In contrast to this, the analogous achiral Schiff's bases **Va–g** display enantiotropic SmA and N mesophases.

The Schiff's bases **VIII** and **IX** were the unique chiral compounds showing mesomorphic behaviour. These compounds display an enantiotropic chiral smectic C (SmC*) phase. The thermal mesomorphic range is substantially lower (5.9°C for compound **VIII**, 5.7°C for compound **IX**) than the analogous Schiff's bases **III** (~52°C) that display enantiotropic SmA and SmC phases.

Clearly, the replacement of the achiral alkoxy chain in amides (**I**, **II**) and in Schiff's bases (**III**, **V**) by a chiral alkoxy chain derived from chiral 2-octanol and/or chiral ethyl lactate results in the disappearance of the mesomorphic properties in amides **VI** and **VII** and in Schiff's bases **X** and **XI**. In addition, the chiral alkoxy tails cause the disappearance of the SmA phase in Schiff's bases **VIII** and **IX** and only the enantiotropic SmC phase, present in their analogous achiral Schiff's bases **III,** was maintained in compounds **VIII** and **IX**, but the thermal mesomorphic range of the SmC phase was drastically diminished from ~52°C for compounds **III** to ~5.7°C and ~5.9°C for compounds **VIII** and **IX**, respectively. Presumably, the methyl branch present in the chiral chains produces a deviation from linearity of the molecules and disturbs the formation of stable mesophases.

In summary, the mesomorphic properties of all of the compounds were found to be highly dependent on the molecular shape, on the type of terminal tail (alkoxy or alkyl, achiral or chiral alkoxy tails) and on the type of the central linkage (amide or imine).

In addition, to the best of the authors' knowledge, we have prepared the first mesomorphic Schiff's bases and amides derived from 1,3,4-oxadiazole.

3.2 Textures observed by polarising optical microscopy

The mesophases exhibited by amides (**I, II**) and Schiff's bases (**III, V**) were identified according to their optical textures, which were observed by optical microscopy, using the classification systems reported by Sackmann and Demus (*31*) and Gray and Goodby (*32*).

The mesophases were determined from textural observations using a thermal polarising microscope under heating and cooling conditions. Phase transition temperatures observed through thermal microscopy were found to be in reasonable agreement with the corresponding differential scanning calorimetry (DSC) thermograms.

The SmA phase was characterised by the formation of the typical focal-conic fan texture and homeotropic alignment coexisting with spherulitic regions. The SmC phase exhibited by Schiff's bases **III** was identified by the appearance of a fine four-brush schlieren texture. The nematic phase, present in Schiff's bases **V**, showed the characteristic schlieren texture with two- and four-brush singularities.

The SmC* phase exhibited by Schiff's bases **VIII** and **IX** was identified by its characteristic fan-shaped and pseudohomeotropic textures.

3.3 Computational study

With the aim of gaining insight into the role of shape and other molecular properties on the mesomorphic behaviour of the reported species, we have performed a density functional theory (DFT) theoretical study at B3LYP/6–311++G(d,p) level on five model compounds derived from series **I–-V** by replacing alkyl chains with methyl groups, in order to minimise the computational cost of quantum-chemical methods. All computational calculations were performed with Gaussian 03 package of programs (*33*).

Rotation around the amide and imine C–N bonds (ϕ1) and rotation of the oxadiazole moiety (ϕ2) have been investigated in order to determine the most stable conformations of model compounds **I-V** (Table 4).

Table 4. Energy barriers (kcal mol^{-1}) for the rotation of C–N bonds in amide and imine compounds (ϕ_1) and for the rotation of the oxadiazole ring (ϕ_2) calculated at B3LYP/6–311++G(d,p) level of theory for model compounds **I**–**V**.

	Energy barriers (kcal mol^{-1})	
Model compound	ϕ1	ϕ2
I	16.1	6.5
II	15.6	6.4
III	15.6	6.6
IV	17.7	6.7
V	17.8	6.9

Potential energy barriers for the rotation around amido and imine groups are predicted to be higher than 17 kcal mol^{-1}, which suggests a quite rigid conformation for these functional groups. On the other hand, the rotation of the oxadiazole moiety is expected to occur with low-energy barriers (<7 kcal mol^{-1}), indicating a high degree of conformational freedom for this motion.

Conformational analysis leads us to identify two minimum energy structures for each model compound, which differ in the relative orientation of the oxadiazole moiety with respect to the amido and imino groups, as shown in Figure 2. Geometries were subjected to vibrational analysis in order to verify that the structures correspond to true energy minima. As can be seen in Figure 2, conformers **1** and **2** are quite similar in shape, but they differ in the direction and magnitude of the molecular dipole moment as a consequence of the rotation of the oxadiazole ring. On the other hand, isotropic molecular polarisability appears to be less sensitive to conformation and remains essentially unaltered when comparing conformers of type **1** and **2**. In addition, the computational modelling indicates that the type of the central linkage, amide or imine, does not induce any significant shape difference between model compounds.

Calculated relative free energies indicate that conformers of type **1** and **2** are almost equally stable, since free energy differences between them lay within the margins of error for energy calculations at the B3LYP level of theory. Therefore, both conformations must be taken into consideration as suitable structures for model compounds for further analysis of the molecular shape and properties that must be governing the mesomorphic behaviour of the molecules under study. Herein, three main structural features have been considered in the analysis of the mesomorphic properties of compounds **I**–**V**: (a) intermolecular H-bond formation; (b) extension of the ring coplanarity in the mesogenic core; and (c) isotropic molecular polarisability of model compounds.

3.3.1 *Intermolecular H-bond capacity*

Amides are well known for their ability to participate in strong intermolecular H-bonds as proton donors (N–H) or proton acceptors (C=O). These interactions should contribute to stabilise the crystalline state on amide compounds leading to higher transition and melting temperatures than the analogous imine species. This hypothesis accounts for the mesogenic behaviour of amides of type **I** and **II**, which possess higher transition temperatures and melting points than the corresponding type **III** imines.

3.3.2 *Extension of the ring coplanarity*

Coplanarity of contiguous rings can be related to strong π–π intermolecular interactions that should favour the crystalline state over mesogenic phases. Figure 2 shows the coplanar fragments found in the minimum energy conformers of model compounds of type **I**–**V**.

As can be seen from Figure 2, compound **IV** has the largest extension of ring coplanarity among amide species (**I**, **II** and **IV**). This factor, along with its strong capacity to form intermolecular H-bonds, acts against the manifestation of mesomorphic properties and might explain why amides of type **IV** do not behave as liquid crystals.

In the case of imine species, compound **V** has a larger extension of ring coplanarity, suggesting a higher stabilisation of the crystalline state for this compound compared with compound **III**. This conclusion is supported by our experimental data which show higher transition and melting temperatures for imines of type **V** compared with imines of type **III**.

3.3.3 *Molecular isotropic polarisability (α)*

Here α can be related to the establishment of weak intermolecular interactions, such as van der Waals forces, that should be of importance in the liquid crystalline phase. In this sense, higher α values might be related with broader mesomorphic ranges for molecules of similar shape and size.

In the case of compounds **I** and **II**, higher α values are predicted for compounds containing alkoxy instead of alkyl chains. This result is in agreement with our experimental data, which indicate that compounds of type **I** have broader mesomorphic ranges than compounds of type **II**. In additionally, analogous imines of type **III** are predicted to have larger α values

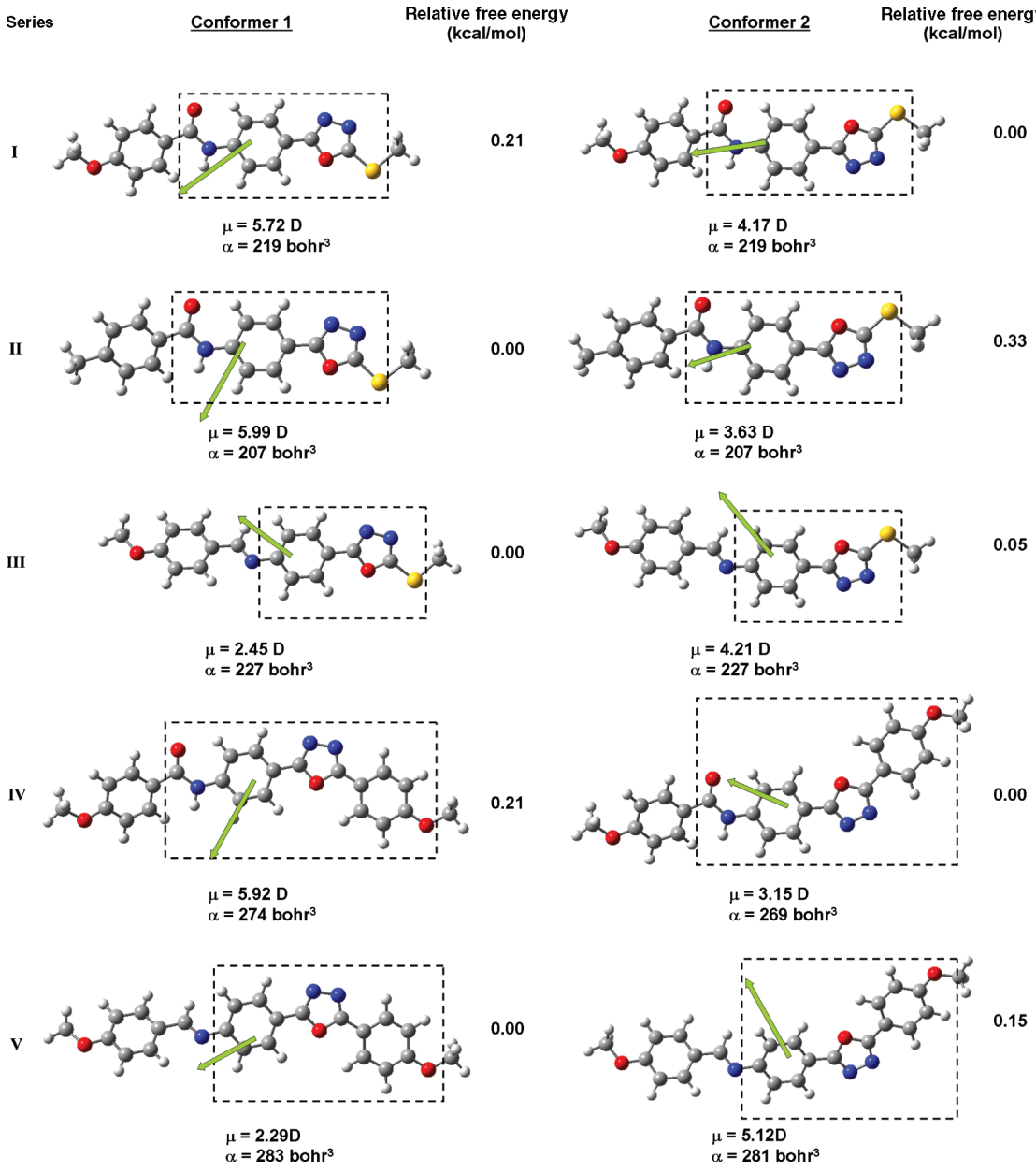


Figure 2. Minimum energy conformers for model compounds of type **I–V** obtained from DFT computational calculations at the B3LYP/6–311++G(d,p) level. Relative free energies calculated at the same level of theory are reported in kcal mol^{-1}. Molecular dipole moments μ(D) are displayed as vectors with origin in the centre of mass of the corresponding structures. Isotropic molecular polarisability $\alpha(bohr^3)$ are also reported. Ring coplanarity segments are framed in dotted lines.

than the corresponding amide compounds **I** and **II**, which can explain the fact that imines possess broader mesomorphic ranges than amide species.

4. Conclusion

New series of heterocyclic mesomorphic amides and Schiff's bases containing a 1,3,4-oxadiazole ring have been synthesised and characterised. The mesomorphic behaviour of the amides and Schiff's bases herein reported can be accounted by three main structural features: (a) intermolecular H-bond formation; (b) extension of the ring coplanarity in the mesogenic core; and (c) isotropic molecular polarisability. According to our results, strong intermolecular H-bonds preclude mesomorphic behaviour favouring

the crystalline state. On the other hand, ring coplanarity appears as a key factor that promotes liquid crystalline behaviour, which is in agreement with the hypothesis that supports this work. Finally, molecular polarisability appears to be of main importance in accounting for the mesomorphic ranges of the liquid crystalline state, since it can be related with the establishment of weak interactions (inductive and dispersive forces) that are of importance in the mesophase. These results allow us to direct our future work towards new liquid crystals with wider mesomorphic ranges and lower transition temperatures than the previous analysis of their molecular structure.

5. Experimental details

5.1 Characterisation

The structures of the compounds were confirmed by ^{1}H and ^{13}C nuclear magnetic resonance (NMR; Bruker AC-250P) spectra and Fourier transform infrared (FTIR; Nicolet 550) spectra; the purity of the final products was evaluated by thin layer chromatography (TLC).

Transition temperatures and textures of mesophases were determined by optical microscopy using an Ortholux Pol BK-11 polarising microscope equipped with a Mettler FP 800 hot stage.

The transition temperatures and enthalpies were investigated by DSC using a Rheometric DSC-V calorimeter. Samples were encapsulated in aluminium pans and studied at scanning rate of 5°C min^{-1} during heating and cooling. The instrument was calibrated using an indium standard (156.6°C, 28.44 J g^{-1}).

5.2 Synthesis of intermediates and products

4-*n*-alkoxybenzoyl chlorides, 4-*n*-alkylbenzoyl chlorides, 4-nitrobenzoyl chloride, (*S*)-ethyl lactate and (*R*)-2-octanol were purchased from Merck. The organic solvents were of analytical grade quality and were dried by traditional methods. Analytical TLC was conducted on Merck aluminium plates with 0.2 mm of silica gel 60 F-254.

The 4-*n*-alkoxybenzaldehydes were synthesised by the conventional etherification of 4-hydroxybenzaldehyde (*34*).

The chiral 4-alkoxybenzoyl chlorides and chiral 4-alkoxybenzaldehydes were synthesised by a Mitsunobu reaction starting from methyl 4-hydroxybenzoate and 4-hydroxybenzaldehyde, respectively, and the corresponding chiral alcohols (chiral 2-octanol or chiral 2-octyloxypropanol) according to the procedure describe in (*17*, *18*, *29*).

The hydrazides **1** and **5** were synthesised starting with ethyl 4-nitrobenzoate and methyl 4-*n*-tetradecyloxybenzoate, respectively, which were condensated with hydrazine hydrate (80%) according to the procedure described in (*14*).

*5.2.1 5-(4-nitro)phenyl-3H-1,3,4-oxadiazoline-2-thione (**2**)*

This compound was synthesised using the procedure described in (*2*). A solution of KOH (1.6 g) in water (10 ml) was added dropwise to a stirred suspension of hydrazide **1** (28 mmol, 5.13 g) in ethanol (80 ml) at 25°C. After all of the hydrazide has dissolved, carbon disulphide (35 mmol, 2.7 g, 2.1 ml) was added at the same temperature. The solution was evaporated in vacuum using a rotatory evaporator. The residue was poured into a mixture of 400 g ice and 100 ml concentrated hydrochloride acid. The precipitate formed was filtered off, and recrystallised from ethanol/water (4/1) yielding the thione **2**. Yield 50%, melting point 202°C.

Spectroscopic characterisation of compound **2**: ^{1}H NMR ($DMSOd_6$, TMS, 250 MHz): δppm = 8.21 (d, J = 6.9 Hz, 2H, arom. H); 8.48 (d, J = 6.9 Hz, 2H, arom. H); 12.4–16.8 (s broad, 1H, NH). ^{13}C NMR ($DMSOd_6$, TMS, 62.9 MHz): δppm = 124.6, 127.4 (arom. C); 128.0, 149.1, 158.9, 177.8 (quaternary arom. C). IR (KBr disc): cm^{-1} = 3092 (Csp^2–H); 1579 (C=C); 1514 (C=N); 1341 (C=S).

*5.2.2 5-(4-nitro)phenyl-2-n-tetradecylthio-1,3,4-oxadiazole (**3**)*

This compound was synthesised using the procedure described in (*2*). Triethylamine (3.67 mmol, 0.37 g) and *n*-tetradecylbromide (3.67 mmol, 1.02 g) were successively added dropwise to a stirred solution of **2** (3.67 mmol, 0.80 g) in absolute ethanol (10 ml). After heating the mixture for 6 h under reflux, the solvent was evaporated on a rotatory evaporator. The residue was poured into 100 ml of water, the resulting precipitate was collected and recrystallised from ethanol/water (1/1) yielding the compound **3**. Yield 67%, melting point 75–76°C.

Spectroscopic characterisation of compound **3**: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.84 (t, J = 6.8 Hz, 3H, CH_3); 1.22 (m, 22H, $11CH_2$); 1.83 (m, 2H, SCH_2–$C\underline{H}_2$); 3.31 (t, J = 7.4 Hz, 2H, SCH_2); 8.17 (d, J = 7.0 Hz, 2H, arom. H); 8.33 (d, J = 7.0 Hz, 2H, arom. H). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm 14.4, 15.1, 15.3, 15.5, 16.7, 17.0, 17.7, 18.5 (aliph. C); 110.2, 113.3 (arom. C); 115.0, 135.2, 150.0, 155.7 (quaternary arom. C). IR (KBr disc): cm^{-1} = 3092 (Csp^2–H); 2919 (Csp^3–H); 1605 (C=C); 1523 (C=N).

*5.2.3 5-(4-aminophenyl)-2-n-tetradecylthio-1,3,4-oxadiazole (**4**)*

Compound **4** was obtained using the method described in (*25*). A mixture of **3** (2.5 mmol), stannous chloride (14.9 mmol) and absolute ethanol (10 ml) was heated gently at reflux for 4 h. The resulting solution was allowed to cool to room temperature and neutralised with 10% aqueous sodium hydroxyde to pH 7. The precipitate formed was filtered and dried in a vacuum oven for 12 h. The dried solid was stirred with chloroform for 2 h and insoluble solid was filtered off. The solid obtained after evaporation of the chloroform was recrystallised from ethanol. Yield 65%, melting point 96°C.

Spectroscopic characterisation of compound **4**: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.87 (t, J = 6.7 Hz, 3H, CH_3); 1.25 (m, 22H, $11CH_2$); 1.81 (m, 2H, SCH_2–C$\underline{H}_2$); 3.25 (t, J = 7.2 Hz, 2H, SCH_2); 4.04 (s broad, 2H, NH_2); 6.71 (d, J = 6.7 Hz, 2H, arom. H); 7.79 (d, J = 6.7 Hz, 2H, arom. H). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 14.0, 22.6, 23.1, 23.5, 23.9, 24.7, 25.6, 30.8, 31.8, 32.6 (aliph. C); 113.4, 149.5 (arom. C); 114.5, 128.3, 163.0, 166.0 (quaternary arom. C). IR (KBr disc): cm^{-1} = 3414, 3328 (NH_2); 3217 (Csp^2–H); 2919 (Csp^3–H); 1603 (C=C).

*5.2.4 4-n-tetradecyloxybenzoic acid N'-(4-nitrophenyl-2-carbonyl)hydrazide (**6**)*

This compound was synthesised according to the procedure described in (*4*). 4-nitrobenzoyl chloride (18 mmol, 3.3 g) was added to a solution containing compound **5** (5.49, 18 mmol) and pyridine (18 mmol) in dried N-methyl-2-pyrrolidone (NMP) (60 ml). The reaction mixture was stirred for 12 h at room temperature and then poured into ice/water mixture. The solid product was filtered off and recrystallised from ethanol. Yield 85%, melting point 158–159°C

$$\text{IR(Kbr disc):}\,\text{cm}^{-1} = 3202\,(\text{N}-\text{H}), 2921(\text{Csp}^3-\text{H}), 1598\,(\text{C}=\text{O}).$$

This compound is insoluble in common organic solvents, so it is not possible to obtain ^{1}H NMR and ^{13}C NMR spectra.

*5.2.5. 5-(4-n-tetradecyloxy)phenyl-2-(4-nitro)phenyl-1,3,4-oxadiazole (**7**)*

This compound was synthesised according to the procedure described in (*4*). Dihydrazide **6** (4.54 mmol, 2.0 g) was dissolved in $POCl_3$ (21 ml); the solution was refluxed for 24 h, and then cooled to room temperature. Excess $POCl_3$ was removed at reduced pressure and the residue was poured into an ice/water mixture. The product was filtered off and recrystallised from ethanol to give compound **7**. Yield 90%, melting point 164–165°C.

Spectroscopic characterisation of compound **7**: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.81 (t, J = 6.8 Hz, 3H, CH_3); 1.20 (m, 22H, $11CH_2$); 1.75 (q, 2H, $OCH_2C\underline{H}_2$); 3.97 (t, J = 6.5 Hz, 2H, OCH_2); 6.97 (d, J = 8.8 Hz, 2H, arom. H); 8.01 (d, J = 8.8 Hz, 2H, arom. H); 8.25 (d, J = 8.9 Hz, 2H, arom. H); 8.34 (d, J = 8.9 Hz, 2H, arom. H). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 14.0, 22.6, 25.9, 29.0, 29.2, 29.3, 29.4, 29.5, 31.8 (aliph. C); 68.3 (OCH_2); 115.0, 124.3; 127.5, 128.8 (arom. C); 115.3, 129.5, 149.3, 162.4, 165.2, 166.9 (quaternary arom. C). IR (KBr disc): cm^{-1} = 3099 (Csp^2–H); 2921 (Csp^3–H); 1612 (C=C).

*5.2.6 5-(4-n-tetradecyloxy)phenyl-2-(4-amino)phenyl-1,3,4-oxadiazole (**8**)*

This compound was obtained using the same procedure as given for compound **4**.

Yield 80%, melting point 125°C.

Spectroscopic characterisation of compound **8**: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.91 (t, J = 6.7 Hz, 3H, CH_3); 1.30 (m, 22H, $11CH_2$); 1.83 (q, 2H, $OCH_2C\underline{H}_2$); 3.55 (s broad, 2H, $-NH_2$); 4.03 (t, J = 6.5 Hz, 2H, OCH_2); 6.79 (d, J = 8.6 Hz, 2H, arom. H); 7.03 (d, J = 8.8 Hz, 2H, arom. H); 7.93 (d, J = 8.6 Hz, 2H, arom. H); 8.06 (d, J = 8.8 Hz, 2H, arom. H). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 14.0, 22.6, 25.9, 29.0, 29.2, 29.3, 29.4, 31.8 (aliph. chain); 68.1 (OCH_2); 114.6, 114.7; 128.3, 128.4 (arom. C); 113.5, 116.3, 149.6, 161.6, 163.6, 164.4 (quaternary arom C). IR (KBr disc): cm^{-1} = 3416, 3212 (NH_2); 3099 (Csp^2–H); 2920 (Csp^3–H); 1612 (C=C).

*5.2.7 Achiral amides **Ia-g, IIa-g, IVa,b** and chiral amides **VI, VII***

Amides **Ia–g** and **IIa–g** were synthesised by condensation of the amino-oxadiazole **4** with 4-*n*-alkoxybenzoyl chloride and 4-*n*-alkylbenzoyl chloride, respectively; amides **IVa,b** were obtained by condensation of amino-oxadiazole **8** with 4-*n*-heptyloxybenzoyl chloride and 4-*n*-decyloxybenzoyl chloride, respectively, and chiral amides **VI** and **VII** were prepared by condensation of the amino-oxadiazole **4** with the corresponding chiral alkoxybenzoyl chlorides (derived from (*R*)-2-octanol for **VI** and derived from (*S*)-ethyl lactate for **VII**), using the procedure described previously (*24*).

The products were purified by crystallisation on ethanol/water (2/1). The following yields were obtained: **Ia** (91%), **Ib** (82%), **Ic** (87%), **Id** (91%), **Ie** (83%), **If** (80%), **Ig** (85%), **IIa** (84%), **IIb** (83%), **IIc**

(84%), **IId** (74%), **IIe** (76%), **IIf** (71%), **IIg** (73%), **IVa** (75%), **IVb** (68%), **VI** (65%), **VII** (61%).

Spectroscopic characterisation of amides **Ia–g**:

Ia: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.80 (t, 3H, CH_3); 0.90 (t, 3H, CH_3); 1.17–1.43 (m, 24H, $12CH_2$); 1.71 (m, 4H, OCH_2–C$\underline{H}_2$ and SCH_2–C$\underline{H}_2$); 3.19 (t, J = 7.1 Hz, 2H, SCH_2); 3.92 (t, J = 6.4 Hz, 2H, OCH_2); 6.87 (d, J = 8.3 Hz, 2H, arom. H); 7.75 (m, 4H, arom. H); 7.86 (d, J = 8.2 Hz, 2H, arom. H); 8.16 (s, 1H, NH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 13.7, 14.0, 19.1, 22.6, 28.5, 28.9, 29.1, 29.3, 29.4, 29.6, 31.1, 31.8 (aliph. C); 32.5 (SCH_2); 67.8 (OCH_2); 114.3, 120.0, 127.5, 129.0 (arom. C); 118.9, 126.1, 128.3, 141.3, 162.2, 164.5 (quaternary arom. C); 165.5 (C=O). IR (KBr disc): cm^{-1} = 3309 (NH); 2920 (Csp^3–H); 1650 (C=O); 1605 (C=C).

Ib: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.82 (t, 3H, CH_3); 0.94 (t, 3H, CH_3); 1.18–1.45 (m, 26H, $13CH_2$); 1.73 (m, 4H, OCH_2–C$\underline{H}_2$ and SCH_2–C$\underline{H}_2$); 3.20 (t, J = 7.2 Hz, 2H, SCH_2); 3.93 (t, J = 6.4 Hz, 2H, OCH_2); 6.89 (d, J = 8.2 Hz, 2H, arom. H); 7.79 (m, 4H, arom. H); 7.88 (d, J = 8.2 Hz, 2H, arom. H); 8.17 (s, 1H, NH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 13.8, 14.2, 19.1, 22.6, 28.6, 28.9, 29.1, 29.3, 29.5, 29.6, 31.1, 31.9 (aliph. C); 32.5 (SCH_2); 67.8 (OCH_2); 114.5, 120.2, 127.7, 129.2 (arom. C); 118.9, 126.2, 128.3, 141.4, 162.2, 164.6 (quaternary arom. C); 165.6 (C=O). IR (KBr disc): cm^{-1} = 3312 (NH); 2921 (Csp^3–H); 1650 (C=O); 1605 (C=C).

Ic: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.86 (t, 3H, CH_3); 0.90 (t, 3H, CH_3); 1.24–1.45 (m, 28H, $14CH_2$); 1.79 (m, 4H, OCH_2–C$\underline{H}_2$ and SCH_2–C$\underline{H}_2$); 3.26 (t, J = 7.3 Hz, 2H, SCH_2); 3.99 (t, J = 6.5 Hz, 2H, OCH_2); 6.95 (d, J = 8.2 Hz, 2H, arom. H); 7.81 (m, 4H, arom. H); 7.98 (d, J = 7.9 Hz, 2H, arom. H); 8.12 (s, 1H, NH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 14.0, 14.1, 22.5, 22.7, 25.6, 28.6, 29.0, 29.2, 29.3, 29.4, 29.6, 31.5, 31.9 (aliph. C); 32.6 (SCH_2); 68.2 (OCH_2); 114.4, 119.9, 127.6, 129.0 (arom. C); 119.0, 126.1, 128.4, 141.2, 162.3, 164.8 (quaternary arom. C); 165.3 (C=O). IR (KBr disc): cm^{-1} = 3324 (NH); 2922 (Csp^3–H); 1651 (C=O); 1605 (C=C).

Id: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.87 (t, 6H, $2CH_3$); 1.25–1.83 (m, 34H, $17CH_2$); 3.28 (t, J = 7.3 Hz, 2H, SCH_2); 4.01 (t, J = 6.5 Hz, 2H, OCH_2); 6.98 (d, J = 8.7 Hz, 2H, arom. H); 7.81 (d, J = 8.8 Hz, 2H, arom. H); 7.86 (d, J = 8.8 Hz, 2H, arom. H); 8.00 (d, J = 8.5 Hz, 2H, arom. H); 8.05 (s, 1H, NH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 14.1, 22.6, 22.7, 25.9, 28.6, 29.0, 29.2, 29.3, 29.4, 29.5, 29.6, 31.7, 31.9 (aliph. C); 32.6 (SCH_2); 68.3 (OCH_2); 114.5, 119.8, 127.6, 128.9 (arom. C); 119.1, 126.2, 128.3, 141.2, 162.3, 164.2 (quaternary arom. C); 165.2 (C=O). IR (KBr disc): cm^{-1} = 3315 (NH); 2921 (Csp^3–H); 1648 (C=O); 1604 (C=C).

Ie: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.89 (t, 6H, $2CH_3$); 1.23–1.80 (m, 36H, $18CH_2$); 3.25 (t, J = 7.2 Hz, 2H, SCH_2); 4.05 (t, J = 6.7 Hz, 2H, OCH_2); 6.99 (d, J = 8.8 Hz, 2H, arom. H); 7.80 (d, J = 8.8 Hz, 2H, arom. H); 7.87 (d, J = 8.6 Hz, 2H, arom. H); 7.99 (d, J = 8.7 Hz, 2H, arom. H); 8.1 (s, 1H, NH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 14.0, 22.5, 22.7, 26.0, 28.8, 29.0, 29.1, 29.3, 29.4, 29.5, 29.6, 31.5, 31.8 (aliph. C); 32.8 (SCH_2); 68.2 (OCH_2); 114.5, 120.0, 127.5, 128.7 (arom. C); 119.0, 126.1, 128.2, 141.5, 162.1, 164.3 (quaternary arom. C); 165.1 (C=O). IR (KBr disc): cm^{-1} = 3314 (NH); 2920 (Csp^3–H); 1649 (C=O); 1602 (C=C).

If: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.88 (t, 6H, $2CH_3$); 1.21–1.89 (m, 38H, $19CH_2$); 3.24 (t, J = 7.1 Hz, 2H, SCH_2); 4.00 (t, J = 6.3 Hz, 2H, OCH_2); 6.98 (d, J = 8.7 Hz, 2H, arom. H); 7.83 (d, J = 8.8 Hz, 2H, arom. H); 7.88 (d, J = 8.8 Hz, 2H, arom. H); 8.01 (d, J = 8.5 Hz, 2H, arom. H); 8.05 (s, 1H, NH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 14.1, 22.6, 22.7, 25.9, 28.6, 29.0, 29.2, 29.3, 29.4, 29.5, 29.6, 31.7, 31.9 (aliph. C); 32.6 (SCH_2); 68.3 (OCH_2); 114.5, 119.8, 127.6, 128.9 (arom. C); 119.1, 126.2, 128.3, 141.2, 162.3, 164.2 (quaternary arom. C); 165.2 (C=O). IR (KBr disc): cm^{-1} = 3315 (NH); 2921 (Csp^3–H); 1648 (C=O); 1604 (C=C).

Ig: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.90 (t, 6H, $2CH_3$); 1.25–1.80 (m, 40H, $20CH_2$); 3.26 (t, J = 7.5 Hz, 2H, SCH_2); 4.04 (t, J = 6.6 Hz, 2H, OCH_2); 7.00 (d, J = 8.7 Hz, 2H, arom. H); 7.82 (d, J = 8.6 Hz, 2H, arom. H); 7.88 (d, J = 8.8 Hz, 2H, arom. H); 8.10 (d, J = 8.6 Hz, 2H, arom. H); 8.06 (s, 1H, NH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 14.0, 22.4, 22.6, 26.1, 28.6, 29.0, 29.1, 29.2, 29.4, 29.6, 29.8, 31.7, 32.0 (aliph. C); 32.7 (SCH_2); 68.5 (OCH_2); 114.4, 120.0, 127.8, 128.9 (arom. C); 119.0, 126.1, 128.3, 141.1, 162.1, 164.2 (quaternary arom. C); 165.4 (C=O). IR (KBr disc): cm^{-1} = 3316 (NH); 2920 (Csp^3–H); 1650 (C=O); 1606 (C=C).

Spectroscopic characterisation of amides **IIa–g**:

IIa: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.83 (t, 6H, $2CH_3$); 1.18–1.76 (m, 28H, $14CH_2$); 2.60 (t, J = 7.5 Hz, 2H, Bz–C$\underline{H}_2$); 3.20 (t, J = 7.3 Hz, 2H, SCH_2); 7.20 (d, J = 8.1 Hz, 2H, arom. H); 7.71 (d, J = 8.1 Hz, 2H, arom. H); 7.75 (d, J = 8.6 Hz, 2H, arom. H); 7.92 (d, J = 8.5 Hz, 2H, arom. H); 8.05 (s, 1H, NH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 13.8, 14.1, 22.2, 22.6, 28.5, 28.9, 29.3, 29.5, 31.8, 32.6, 33.2, 35.5 (aliph. C); 120.0, 127.1, 127.6, 128.8 (arom. C); 119.4, 131.8, 141.2, 147.7, 163.0, 165.4 (quaternary arom. C); 165.9 (C=O). IR (KBr disc): cm^{-1} = 3309 (NH); 2921 (Csp^3–H); 1657 (C=O); 1609 (C=C).

IIb: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.80 (t, 6H, $2CH_3$); 1.17–1.77 (m, 30H, $15CH_2$);

2.58 (t, J = 7.4 Hz, 2H, Bz–C<u>H</u>$_2$); 3.19 (t, J = 7.3 Hz, 2H, SCH$_2$); 7.21 (d, J = 8.0 Hz, 2H, arom. H); 7.72 (m, 4H, arom. H); 7.90 (d, J = 8.5 Hz, 2H, arom. H); 8.18 (s, 1H, NH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 13.9, 14.0; 22.4, 22.6, 28.5, 28.9, 29.2, 29.3, 29.4, 29.6, 30.7, 31.3, 31.8, 32.6, 35.7 (aliph. C); 120.1, 127.2, 127.4, 128.6 (arom. C); 119.0, 131.7, 141.3, 147.6, 164.4, 165.6 (quaternary arom. C); 166.0 (C=O). IR (KBr disc): cm^{-1} = 3385 (NH); 2922 (Csp^3–H); 1662 (C=O); 1604 (C=C).

IIc: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.87 (t, 6H, 2CH$_3$); 1.25–1.88 (m, 32H, 16CH$_2$); 2.65 (t, J = 7.4 Hz, 2H, Bz–C<u>H</u>$_2$); 3.27 (t, J = 7.3 Hz, 2H, SCH$_2$); 7.25 (d, J = 7.1 Hz, 2H, arom. H); 7.78 (m, 4H, arom. H); 7.95 (d, J = 8.4 Hz, 2H, arom. H); 8.17 (s, 1H, NH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 13.9, 14.0, 22.4, 22.6, 28.5, 28.8, 29.3, 29.6, 31.0, 31.6, 31.8, 32.6, 35.8 (aliph. C); 120.0, 127.1, 127.5, 128.6 (arom. C); 119.4, 131.9, 141.3, 148.0, 164.3, 165.4 (quaternary arom. C); 166.0 (C=O). IR (KBr disc): cm^{-1} = 3384 (NH); 2921 (Csp^3–H); 1662 (C=O); 1604 (C=C).

For IId: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.87 (t, 6H, 2CH$_3$); 1.24–1.83 (m, 34H, 17 CH$_2$); 2.66 (t, J = 7.4 Hz, 2H, Bz–C<u>H</u>$_2$); 3.27 (t, J = 7.3 Hz, 2H, SCH$_2$); 7.27 (d, J = 8.2 Hz, 2H, arom. H); 7.77 (d, J = 8.8 Hz, 2H, arom. H); 7.81 (d, J = 8.8 Hz, 2H, arom. H); 8.00 (d, J = 8.6 Hz, 2H, arom. H); 8.08 (s, 1H, NH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 14.0, 14.1, 22.4, 22.6, 28.6, 29.1, 29.3, 29.6, 31.1, 31.7, 31.9, 32.6, 35.8 (aliph. C); 119.9, 127.0, 127.6, 128.8 (arom. C); 119.2, 131.7, 141.0, 147.8, 164.2, 165.3 (quaternary arom. C); 165.7 (C=O). IR (KBr disc): cm^{-1} = 3359 (NH); 2919 (Csp^3–H); 1659 (C=O); 1603 (C=C).

IIe: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.89 (t, 6H, 2CH$_3$); 1.26–1.85 (m, 36H, 18 CH$_2$); 2.70 (t, J = 7.3 Hz, 2H, Bz–C<u>H</u>$_2$); 3.26 (t, J = 7.3 Hz, 2H, SCH$_2$); 7.29 (d, J = 8.4 Hz, 2H, arom. H); 7.80 (d, J = 8.8 Hz, 2H, arom. H); 7.83 (d, J = 8.8 Hz, 2H, arom. H); 8.02 (d, J = 8.6 Hz, 2H, arom. H); 8.10 (s, 1H, NH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 14.1, 14.4, 22.5, 28.9, 29.1, 29.4, 29.6, 31.3, 31.8, 32.3, 32.6, 36.0 (aliph. C); 120.0, 127.1, 127.6, 128.5 (arom. C); 119.1, 131.6, 141.0, 147.9, 164.1, 165.2 (quaternary arom. C); 165.8 (C=O). IR (KBr disc): cm^{-1} = 3360 (NH); 2920 (Csp^3–H); 1660 (C=O); 1601 (C=C).

IIf: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.88 (t, 6H, 2CH$_3$); 1.21–1.80 (m, 38H, 19 CH$_2$); 2.70 (t, J = 7.5 Hz, 2H, Bz–C<u>H</u>$_2$); 3.30 (t, J = 7.4 Hz, 2H, SCH$_2$); 7.29 (d, J = 8.4 Hz, 2H, arom. H); 7.79 (d, J = 8.7 Hz, 2H, arom. H); 7.80 (d, J = 8.8 Hz, 2H, arom. H); 8.02 (d, J = 8.5 Hz, 2H, arom. H); 8.10 (s, 1H, NH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 14.1, 14.3, 22.7, 28.5, 29.1, 29.2, 29.5, 31.0, 31.4, 31.8, 32.4, 35.9 (aliph. C); 119.8, 127.1, 127.6, 128.9 (arom. C); 119.1, 131.6, 141.1, 147.8, 164.0, 165.2 (quaternary arom. C); 165.9 (C=O). IR (KBr disc): cm^{-1} = 3358 (NH); 2919 (Csp^3–H); 1658 (C=O); 1604 (C=C).

IIg: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.90 (t, 6H, 2CH$_3$); 1.26–1.85 (m, 40H, 20 CH$_2$); 2.70 (t, J = 7.4 Hz, 2H, Bz–C<u>H</u>$_2$); 3.28 (t, J = 7.4 Hz, 2H, SCH$_2$); 7.28 (d, J = 8.2 Hz, 2H, arom. H); 7.76 (d, J = 8.7 Hz, 2H, arom. H); 7.80 (d, J = 8.8 Hz, 2H, arom. H); 7.99 (d, J = 8.7 Hz, 2H, arom. H); 8.10 (s, 1H, NH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 13.90, 14.0, 22.2, 22.4, 28.5, 29.0, 29.3, 29.7, 31.1, 31.6, 31.9, 32.6, 35.9 (aliph. C); 119.8, 127.1, 127.6, 128.8 (arom. C); 119.3, 131.8, 141.1, 148.0, 164.3, 165.4 (quaternary arom. C); 165.9 (C=O). IR (KBr disc): cm^{-1} = 3360 (NH); 2920 (Csp^3–H); 1660 (C=O); 1605 (C=C).

Spectroscopic characterisation of amides **IVa,b**:

IVa: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.82 (t, 6H, 2CH$_3$); 1.20–1.73 (m, 34H, 17CH$_2$); 3.95 (m, 4H, 2 OCH$_2$); 6.89 (d, J = 8.7 Hz, 2H, arom. H); 6.95 (d, J = 8.8 Hz, 2H, arom. H); 7.76 (d, J = 8.6 Hz, 2H, arom. H); 7.79 (d, J = 8.6 Hz, 2H, arom. H); 7.98 (d, J = 8.7 Hz, 2H, arom. H); 8.02 (m, 3H, arom. H and NH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 14.0, 14.1, 22.5, 22.6, 25.9, 29.0, 29.1, 29.2, 29.3, 29.5, 31.7 (aliph. C); 68.2, 68.3 (OCH$_2$); 114.4, 114.9, 119.9, 127.8, 128.6, 128.9 (arom. C); 116.1, 119.4, 126.2, 141.1, 161.8, 162.3, 163.5, 164.9 (quaternary arom. C); 165.3 (C=O). IR (KBr disc): cm^{-1} = 3372 (NH); 3062 (Csp^2–H); 2925 (Csp^3–H); 1660 (C=O); 1608 (C=C).

IVb: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.85 (t, 6H, 2CH$_3$); 1.22–1.70 (m, 40H, 20CH$_2$); 4.05 (m, 4H, 2 OCH$_2$); 6.90 (d, J = 8.8 Hz, 2H, arom. H); 6.98 (d, J = 8.8 Hz, 2H, arom. H); 7.75 (d, J = 8.6 Hz, 2H, arom. H); 7.80 (d, J = 8.6 Hz, 2H, arom. H); 8.00 (d, J = 8.7 Hz, 2H, arom. H); 8.01 (m, 3H, arom. H and NH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 13.9, 14.1, 22.6, 22.8, 25.9, 28.9, 29.1, 29.3, 29.4, 29.5, 31.8 (aliph. C); 68.1, 68.4 (OCH$_2$); 114.6, 114.9, 120.0, 127.8, 128.5, 128.8 (arom. C); 116.0, 119.3, 126.2, 141.2, 161.9, 162.3, 163.6, 164.9 (quaternary arom. C); 165.2 (C=O). IR (KBr disc): cm^{-1} = 3370 (NH); 3061 (Csp^2–H); 2928 (Csp^3–H); 1659 (C=O); 1607 (C=C).

Spectroscopic characterisation of chiral amides **VI and VII**:

VI: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.86 (t, J = 6.4 Hz, 6H, 2CH$_3$); 1.28 (m, 35H, 16CH$_2$ and 3H of the methyl branch); 1.80 (m, 2H, SCH$_2$–C<u>H</u>$_2$–); 3.25 (t, J = 7.0 Hz, 2H, SCH$_2$); 4.42 (m, 1H, CH of the chiral tail); 6.91 (d, J = 7.8 Hz, 2H,

arom. H); 7.81 (m, 4H, arom. H); 7.95 (d, J = 7.5 Hz, 2H, arom. H); 8.30 (s, 1H, NH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 13.9, 14.0, 19.3, 22.4, 22.5, 25.2, 28.4, 28.8, 29.0, 29.1, 29.2, 29.3, 29.4, 29.5, 31.5, 31.7, 32.4, 36.0 (aliph. C); 73.8 (CH of the chiral tail); 115.20, 119.8, 127.4; 128.9 (arom. C); 118.8, 125.7, 126.2, 141.2, 161.3, 164.3 (quaternary arom. C); 165.3 (C=O). IR (KBr disc): cm^{-1} = 3296 (NH); 2920, 2852 (Csp^3–H); 1646 (C=O); 1603 (C=C); 1247 (C–O).

VII: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.80 (t, 6H, $2CH_3$); 1.17–1.96 (m, 39H, $18CH_2$ and 3H of the methyl branch); 3.21 (t, J = 7.0 Hz, 2H, SCH_2); 3.56 (t, J = 6.6 Hz, 2H, OCH_2); 3.66 (m, 1H, CH of the chiral tail); 3.92 (m, 1H, O<u>C</u>H$_2$–CH); 3.96 (m, 1H, O<u>C</u>H$_2$–CH); 7.26 (d, J = 8.8 Hz, 2H, arom H); 7.64 (d, J = 8.9 Hz, 2H, arom H); 7.90 (d, J = 8.8 Hz, 2H, arom. H); 8.37 (d, J = 8.8 Hz, 2H, arom. H); 8.95 (s, 1H, NH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 14.0, 14.1, 17.2, 22.6, 28.5, 28.9, 29.0, 29.1, 29.3, 29.4, 29.6, 29.9, 31.8 (aliph. C); 32.6 (methyl branch); 69.6, 71.6 (OCH_2); 73.55 (CH of the chiral tail); 118.1, 119.8, 127.6, 128.3 (arom. C); 121.0, 128.8, 140.0, 159.2, 161.8, 164.5 (quaternary arom. C); 165.1 (C=O). IR (KBr disc): cm^{-1} = 3347 (NH); 2919, 2849 (Csp^3–H); 1699 (C=O); 1607 (C=C); 1298 (C–O).

*5.2.8. Achiral Schiff's bases **IIIa-g, Va-g** and chiral Schiff's bases **VIII–XI***

Schiff's bases **IIIa–g** and **Va–g** were synthesised by condensation of the amino oxadiazole **4** and of the amino-oxadiazole **8**, respectively, with 4-*n*-alkoxybenzaldehyde; and chiral Schiff's bases **VIII** and **IX** were obtained by condensation of the amino-oxadiazole **4** with the corresponding chiral alkoxybenzaldehyde (derived from chiral 2-octanol for Schiff's base **VIII** and derived from chiral ethyl lactate for Schiff's base **IX**), and chiral Schiff's bases **X** and **XI** were synthesised by condensation of the amino-oxadiazole **8** with the corresponding chiral alkoxybenzaldehyde (derived from chiral 2-octanol for Schiff's base **X** and derived from chiral ethyl lactate for Schiff's base **XI**), using the procedure described elsewhere (*14*, *26*).

The products were purified by crystallisation on ethanol and by recrystallisation on petroleum ether. The following yields were obtained: **IIIa** (80%), **IIIb** (82%), **IIIc** (79%), **IIId** (82%), **IIIe** (75%), **IIIf** (73%), **IIIg** (70%), **Va** (55%), **Vb** (53%), **Vc** (54%), **Vd** (49%), **Ve** (47%), **Vf** (46%), **Vg** (44%), **VIII** (77%), **IX** (76%), **X** (40%), **XI** (33%).

Spectroscopic characterisation of Schiff's bases **IIIa–g**:

IIIa: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.50 (t, 6H, $2CH_3$); 0.71 (m, 24H, $12CH_2$); 1.30 (m, 4H, SCH_2–C<u>H</u>$_2$ and OCH_2–C<u>H</u>$_2$); 2.91 (t, 2H, SCH_2); 3.54 (t, 2H, OCH_2); 6.40 (d, J = 8.5 Hz, 2H, arom. H); 6.76 (d, J = 8.3 Hz, 2H, arom. H); 7.30 (d, J = 8.3 Hz, 2H, arom. H); 7.50 (d, J = 8.5 Hz, 2H, arom. H); 7.90 (s, 1H, N=CH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 14.0, 14.2, 22.4, 22.6, 25.7, 28.5, 28.9, 29.4, 29.2, 29.4, 31.6, 31.9 32.6 (aliph. C); 68.3 (OCH_2); 115.1, 121.4, 127.8, 131.0 (arom. C); 120.5, 128.6, 131.9, 155.2, 162.1, 164.3 (quaternary arom. C); 160.8 (CH=N). IR (KBr disc): cm^{-1} = 2920 (Csp^3–H); 1568 (C=C); 1240 (C–O).

IIIb: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.490 (t, 6H, $2CH_3$); 0.75 (m, 26H, $13CH_2$); 1.30 (m, 4H, SCH_2–C<u>H</u>$_2$ and OCH_2–C<u>H</u>$_2$); 2.80 (t, 2H, SCH_2); 3.49 (t, 2H, OCH_2); 6.41 (d, J = 8.6 Hz, 2H, arom. H); 6.73 (d, J = 8.3 Hz, 2H, arom. H); 7.28 (d, J = 8.3 Hz, 2H, arom. H); 7.48 (d, J = 8.3 Hz, 2H, arom. H); 7.81 (s, 1H, N=CH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 13.9, 14.0, 22.5, 22.7, 26.2, 28.9, 29.0, 29.3, 30.6, 31.8, 32.9 (aliph. C); 68.5 (OCH_2); 114.6, 121.3, 128.0, 130.9 (arom. C); 121.0, 128.4, 132.1, 155.2, 162.1, 164.2 (quaternary arom. C); 161.0 (CH=N). IR (KBr disc): cm^{-1} = 2921 (Csp^3–H); 1568 (C=C); 1239 (C–O).

IIIc: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.45 (t, 6H, $2CH_3$); 0.70 (m, 28H, $14CH_2$); 1.30 (m, 4H, SCH_2–C<u>H</u>$_2$ and OCH_2–C<u>H</u>$_2$); 2.75 (t, 2H, SCH_2); 3.49 (t, 2H, OCH_2); 6.45 (d, J = 8.5 Hz, 2H, arom. H); 6.73 (d, J = 8.4 Hz, 2H, arom. H); 7.31 (d, J = 8.5 Hz, 2H, arom. H); 7.51 (d, J = 8.4 Hz, 2H, arom. H); 7.81 (s, 1H, N=CH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 14.0, 14.2, 22.5, 22.7, 25.9, 28.7, 28.9, 29.2, 29.4, 29.5, 31.6, 31.9 32.6 (aliph. C); 68.0 (OCH_2); 115.0, 121.4, 127.8, 130.8 (arom. C); 120.7, 128.5, 132.1, 155.2, 162.3, 164.2 (quaternary arom. C); 160.7 (CH=N). IR (KBr disc): cm^{-1} = 2920 (Csp^3–H); 1570 (C=C); 1242 (C–O).

IIId: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.30 (t, 6H, $2CH_3$); 0.68 (m, 30H, $15CH_2$); 1.26 (m, 4H, SCH_2–C<u>H</u>$_2$ and OCH_2–C<u>H</u>$_2$); 2.71 (t, 2H, SCH_2); 3.44 (t, 2H, OCH_2); 6.42 (d, J = 8.5 Hz, 2H, arom. H); 6.71 (d, J = 8.3 Hz, 2H, arom. H); 7.29 (d, J = 8.3 Hz, 2H, arom. H); 7.45 (d, J = 8.3 Hz, 2H, arom. H); 7.80 (s, 1H, N=CH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 14.0, 14.1, 22.5, 22.6, 25.8, 28.5, 28.9, 29.2, 29.3, 29.5, 31.6, 31.8, 32.5 (aliph. C); 68.1 (OCH_2); 114.6, 121.4, 127.6, 130.8 (arom. C); 120.5, 128.4, 131.8, 155.0, 162.2, 164.2 (quaternary arom. C); 160.6 (CH=N). IR (KBr disc): cm^{-1} = 2920 (Csp^3–H); 1565 (C=C); 1240 (C–O).

IIIe: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.35 (t, 6H, $2CH_3$); 0.72 (m, 32H, $16CH_2$); 1.29 (m, 4H, SCH_2–C<u>H</u>$_2$ and OCH_2–C<u>H</u>$_2$); 2.75 (t, 2H, SCH_2); 3.46 (t, 2H, OCH_2); 6.50 (d, J = 8.6 Hz, 2H, arom. H); 6.76 (d, J = 8.6 Hz, 2H, arom. H); 7.31 (d, J = 8.3 Hz,

2H, arom. H); 7.50 (d, J = 8.3 Hz, 2H, arom. H); 7.81 (s, 1H, N=CH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 14.1, 14.3, 22.5, 22.7, 25.8, 28.0, 28.9, 29.1, 29.2, 29.4, 31.7, 31.9 32.6 (aliph. C); 68.0 (OCH_2); 114.7, 121.5, 127.6, 131.0 (arom. C); 120.4, 128.4, 131.8, 155.2, 162.1, 164.0 (quaternary arom. C); 161.0 (CH=N). IR (KBr disc): cm^{-1} = 2923 (Csp^3–H); 1570 (C=C); 1238 (C–O).

IIIf: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.39 (t, 6H, $2CH_3$); 0.75 (m, 34H, $17CH_2$); 1.31 (m, 4H, SCH_2–C<u>H</u>$_2$ and OCH_2–C<u>H</u>$_2$); 2.74 (t, 2H, SCH_2); 3.51 (t, 2H, OCH_2); 6.40 (d, J = 8.3 Hz, 2H, arom. H); 6.70 (d, J = 8.4 Hz, 2H, arom. H); 7.31 (d, J = 8.4 Hz, 2H, arom. H); 7.46 (d, J = 8.3 Hz, 2H, arom. H); 7.79 (s, 1H, N=CH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 14.0, 14.1, 21.9, 22.6, 26.0, 28.5, 29.0, 29.2, 29.3, 29.5, 31.6, 31.8, 32.4 (aliph. C); 68.0 (OCH_2); 114.7, 121.6, 127.4, 130.9 (arom. C); 120.5, 128.3, 132.0, 154.9, 162.2, 164.1 (quaternary arom. C); 160.5 (CH=N). IR (KBr disc): cm^{-1} = 2923 (Csp^3–H); 1568 (C=C); 1238 (C–O).

IIIg: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.40 (t, 6H, $2CH_3$); 0.69 (m, 36H, $18CH_2$); 1.28 (m, 4H, SCH_2–C<u>H</u>$_2$ and OCH_2–C<u>H</u>$_2$); 2.74 (t, 2H, SCH_2); 3.48 (t, 2H, OCH_2); 6.44 (d, J = 8.5 Hz, 2H, arom. H); 6.74 (d, J = 8.3 Hz, 2H, arom. H); 7.31 (d, J = 8.3 Hz, 2H, arom. H); 7.45 (d, J = 8.5 Hz, 2H, arom. H); 7.80 (s, 1H, N=CH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 14.1, 14.2, 22.4, 22.6, 25.9, 28.5, 28.8, 29.2, 29.4, 29.5, 31.5, 31.7, 32.5 (aliph. C); 68.2 (OCH_2); 115.0, 121.5, 127.6, 130.9 (arom. C); 120.6, 128.4, 131.8, 155.1, 162.3, 164.4 (quaternary arom. C); 160.5 (CH=N). IR (KBr disc): cm^{-1} = 2928 (Csp^3–H); 1568 (C=C); 1238 (C–O).

Spectroscopic characterisation of Schiff's bases **Va–g**:

Va: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.90 (t, 6H, $2CH_3$); 1.30 (m, 24H, $12CH_2$); 1.83 (m, 4H, 2 OCH_2–C<u>H</u>$_2$); 4.00 (t, 4H, 2 OCH_2); 7.00 (m, 4H, arom. H); 7.32 (d, J = 8.4 Hz, 2H, arom. H); 7.86 (d, J = 8.8 Hz, 2H, arom. H); 8.10 (d, J = 8.8 Hz, 2H, arom. H); 8.12 (d, J = 8.4 Hz, 2H, arom. H); 8.41 (s, 1H, N=CH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 14.1, 14.2, 22.4, 22.6, 26.0, 28.9, 29.0, 29.1, 29.3, 29.9, 31.6, 31.8, 31.9 (aliph. C); 68.0 (OCH_2); 114.7, 114.8, 121.5, 127.9, 128.5, 131.0 (arom. C); 116.2, 120.9, 127.5, 155.1, 161.8, 162.3, 163.6, 164.8 (quaternary arom. C); 160.8 (CH=N). IR (KBr disc): cm^{-1} = 2920 (Csp^3–H); 1604 (C=C); 1249 (C–O).

Vb: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.89 (t, 6H, $2CH_3$); 1.28 (m, 26H, $13CH_2$); 1.82 (m, 4H, 2 OCH_2–C<u>H</u>$_2$); 4.01 (t, 4H, 2 OCH_2); 6.98 (m, 4H, arom. H); 7.33 (d, J = 8.2 Hz, 2H, arom. H); 7.85 (d, J = 7.7 Hz, 2H, arom. H); 8.08 (d, J = 8.8 Hz, 2H, arom. H); 8.12 (d, J = 8.2 Hz, 2H, arom. H); 8.41 (s, 1H, N=CH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 14.0, 14.1, 22.6, 26.0, 28.9, 29.1, 29.2, 29.3, 29.4, 29.5, 31.7, 31.8, 31.9 (aliph. C); 68.0 (OCH_2); 114.9, 115.0, 121.5, 128.1, 128.5, 131.0 (arom. C); 116.0, 121.0, 127.6, 155.1, 162.0, 162.2, 163.7, 164.4 (quaternary arom. C); 160.5 (CH=N). IR (KBr disc): cm^{-1} = 2920 (Csp^3–H); 1600 (C=C); 1250 (C–O).

Vc: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.87 (t, 6H, $2CH_3$); 1.29 (m, 28H, $14CH_2$); 1.80 (m, 4H, 2 OCH_2–C<u>H</u>$_2$); 4.00 (t, 4H, 2 OCH_2); 6.97 (m, 4H, arom. H); 7.31 (d, J = 8.4 Hz, 2H, arom. H); 7.86 (d, J = 8.7 Hz, 2H, arom. H); 8.10 (d, J = 8.8 Hz, 2H, arom. H); 8.12 (d, J = 8.4 Hz, 2H, arom. H); 8.41 (s, 1H, N=CH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 13.8, 14.0, 22.4, 22.5, 26.0, 29.0, 29.2, 29.3, 29.4, 29.5, 32.0, 32.7, 32.8 (aliph. C); 68.0 (OCH_2); 114.7, 114.8, 121.6, 127.7, 128.6, 130.9 (arom. C); 116.2, 121.0, 127.7, 154.9, 162.1, 162.2, 163.7, 164.6 (quaternary arom. C); 160.9 (CH=N). IR (KBr disc): cm^{-1} = 2922 (Csp^3–H); 1604 (C=C); 1251 (C–O).

Vd: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.89 (t, 6H, $2CH_3$); 1.27 (m, 30H, $15CH_2$); 1.81 (m, 4H, 2 OCH_2–C<u>H</u>$_2$); 4.02 (t, 4H, 2 OCH_2); 6.99 (m, 4H, arom. H); 7.33 (d, J = 8.2 Hz, 2H, arom. H); 7.85 (d, J = 7.7 Hz, 2H, arom. H); 8.07 (d, J = 8.8 Hz, 2H, arom. H); 8.14 (d, J = 8.2 Hz, 2H, arom. H); 8.40 (s, 1H, N=CH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 14.0, 14.1, 22.5, 22.6, 25.9, 28.9, 29.0, 29.2, 29.3, 29.4, 29.5, 31.6, 31.7, 31.8 (aliph. C); 68.1 (OCH_2); 114.6, 114.8, 121.4, 127.7, 128.5, 130.8 (arom. C); 116.1, 120.9, 127.6, 155.0, 161.8, 162.2, 163.6, 164.4 (quaternary arom. C); 160.6 (CH=N). IR (KBr disc): cm^{-1} = 2921 (Csp^3–H); 1605 (C=C); 1252 (C–O).

Ve: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.91 (t, 6H, $2CH_3$); 1.30 (m, 32H, $16CH_2$); 1.82 (m, 4H, 2 OCH_2–C<u>H</u>$_2$); 4.00 (t, 4H, 2 OCH_2); 7.00 (m, 4H, arom. H); 7.32 (d, J = 8.3 Hz, 2H, arom. H); 7.84 (d, J = 7.9 Hz, 2H, arom. H); 8.10 (d, J = 8.2 Hz, 2H, arom. H); 8.16 (d, J = 8.3 Hz, 2H, arom. H); 8.41 (s, 1H, N=CH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 14.0, 14.2, 22.6, 22.7, 25.9, 29.0, 29.1, 29.3, 29.4, 29.5, 29.6, 31.6, 31.8, 31.9 (aliph. C); 68.1 (OCH_2); 114.7, 114.8, 121.5, 127.7, 128.6, 130.9 (arom. C); 116.1, 120.8, 127.6, 155.2, 161.9, 162.3, 163.6, 164.5 (quaternary arom. C); 160.8 (CH=N). IR (KBr disc): cm^{-1} = 2922 (Csp^3–H); 1600 (C=C); 1248 (C–O).

Vf: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.91 (t, 6H, $2CH_3$); 1.30 (m, 34H, $17CH_2$); 1.84 (m, 4H, 2 OCH_2–C<u>H</u>$_2$); 4.01 (t, 4H, 2 OCH_2); 6.98 (m, 4H, arom. H); 7.30 (d, J = 8.2 Hz, 2H, arom. H); 7.90 (d, J = 7.8 Hz, 2H, arom. H); 8.09 (d, J = 8.8 Hz, 2H, arom. H); 8.16 (d, J = 8.2 Hz, 2H, arom. H); 8.41 (s, 1H, N=CH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz):

δppm = 14.0, 14.1, 22.4, 22.7, 26.0, 28.9, 29.0, 29.1, 29.2, 29.3, 29.5, 31.5, 31.6, 31.8 (aliph. C); 68.2 (OCH_2); 114.9, 115.0, 121.4, 128.0, 128.5, 130.8 (arom. C); 116.2, 121.0, 127.6, 155.1, 162.0, 162.2, 163.5, 164.3 (quaternary arom. C); 160.7 (CH=N). IR (KBr disc): cm^{-1} = 2920 (Csp^3–H); 1604 (C=C); 1248 (C–O).

Vg: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.88 (t, 6H, $2CH_3$); 1.28 (m, 36H, $18CH_2$); 1.83 (m, 4H, 2 OCH_2–C<u>H</u>$_2$); 4.01 (t, 4H, 2 OCH_2); 6.99 (m, 4H, arom. H); 7.30 (d, *J* = 8.2 Hz, 2H, arom. H); 7.84 (d, *J* = 7.9 Hz, 2H, arom. H); 8.10 (d, *J* = 8.7 Hz, 2H, arom. H); 8.15 (d, *J* = 8.2 Hz, 2H, arom. H); 8.39 (s, 1H, N=CH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 14.0, 14.2, 22.5, 22.7, 25.9, 28.8, 29.0, 29.2, 29.3, 29.5, 29.6, 31.6, 31.7, 31.8 (aliph. C); 68.0 (OCH_2); 114.7, 114.8, 121.5, 127.9, 128.6, 130.8 (arom. C); 116.0, 120.7, 127.6, 155.2, 161.9, 162.1, 163.6, 164.5 (quaternary arom. C); 160.5 (CH=N). IR (KBr disc): cm^{-1} = 2922 (Csp^3–H); 1604 (C=C); 1250 (C–O).

Spectroscopic characterisation of chiral Schiff's bases **VIII–XI**:

VIII: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.37 (t, *J* = 5.9 Hz, 6H, $2CH_3$); 0.81 (m, 35H, $16CH_2$ and 3H of the methyl branch); 1.33 (m, 2H, C<u>H</u>$_2$–CH); 2.78 (t, *J* = 7.3 Hz, 2H, SCH_2); 3.95 (m, 1H, CH of the chiral chain); 6.47 (d, *J* = 8.6 Hz, 2H, arom. H); 6.78 (d, *J* = 8.2 Hz, 2H, arom. H); 7.32 (d, *J* = 8.6 Hz, 2H, arom. H); 7.52 (d, *J* = 8.4 Hz, 2H, arom. H); 7.87 (s, 1H, N=CH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 14.0, 14.1, 19.6, 22.5, 22.6, 25.3, 28.5, 29.0, 29.2, 29.4, 29.6, 31.7, 31.8, 32.6, 36.3 (aliph. C); 74.0 (CH of the chiral chain); 115.7, 121.5, 127.6, 130.9 (arom. C); 114.5, 120.0, 128.2, 131.9, 163.3, 165.0 (quaternary arom. C); 160.7 (CH=N). IR (KBr disc): cm^{-1} = 2919 (Csp^3–H); 1588 (C=C); 1245 (C–O).

IX: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.45 (t, *J* = 6.7 Hz, 6H, $2CH_3$); 0.75–1.36 (m, 39H, $18CH_2$ and 3H of the methyl branch); 2.78 (t, *J* = 7.3 Hz, 2H, SCH_2); 3.06 (m, 2H, OCH_2); 3.32 (m, 1H, CH of the chiral chain); 3.44 (m, 1H, OC<u>H</u>$_2$–CH*); 3.56 (m, 1H, OC<u>H</u>$_2$–CH*); 6.51 (d, *J* = 8.6 Hz, 2H, arom. H); 6.79 (d, *J* = 8.6 Hz, 2H, arom. H); 7.29 (d, *J* = 8.6 Hz, 2H, arom. H); 7.52 (d, *J* = 8.4 Hz, 2H, arom. H); 7.88 (s, 1H, N=CH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 14.0, 14.1, 17.2, 22.5, 26.0, 28.5, 28.9, 29.2, 29.3, 29.5, 29.9, 31.8, 32.5 (aliph. C); 69.6 (OCH_2); 72.0 (<u>C</u>H_2O–Ø); 74.9 (CH of the chiral chain); 114.8, 121.4, 127.6, 130.8 (arom. C); 114.5, 120.0, 128.2, 131.9, 163.3, 165.0 (quaternary arom. C); 161.0 (CH=N). IR (KBr disc): cm^{-1} = 2920 (Csp^3–H); 1598 (C=C); 1248 (C–O).

X: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.68 (t, *J* = 6.1 Hz, 6H, $2CH_3$); 0.86 (m, 35H, $16CH_2$ and 3H of the methyl branch); 1.49 (m, 2H, C<u>H</u>$_2$–CH); 3.56 (t, 2H, C<u>H</u>$_2$O–Ø); 3.84 (m, 1H, CH of the chiral chain); 6.80 (d, 4H, arom. H); 7.00 (d, *J* = 8.6 Hz, 2H, arom. H); 7.30 (d, *J* = 8.6 Hz, 2H, arom. H); 7.91 (d, *J* = 8.7 Hz, 2H, arom. H); 8.18 (d, *J* = 8.7 Hz, 2H, arom. H); 8.40 (s, 1H, N=CH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 14.0, 14.1, 19.0, 22.1, 22.4, 25.1, 28.6, 29.0, 29.1, 29.3, 29.6, 31.7, 31.9, 32.5, 36.1 (aliph. C); 74.0 (CH of the chiral chain); 114.4, 114.8, 121.2, 128.0, 128.5, 130.9 (arom. C); 116.2, 121.0, 158.6, 162.1, 162.4, 163.9, 164.5 (quaternary arom. C); 160.5 (CH=N). IR (KBr disc): cm^{-1} = 2924 (Csp^3–H); 1600 (C=C); 1250 (C–O).

XI: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz): δppm = 0.89 (t, *J* = 6.7 Hz, 6H, $2CH_3$); 1.28–1.84 (m, 39H, $18CH_2$ and 3H of the methyl branch); 3.53 (t, 2H, CH_2O–Ø); 3.79 (m, 2H, OCH_2); 3.85 (m, 1H, CH of the chiral chain); 3.92 (m, 1H, OC<u>H</u>$_2$–CH*); 4.01 (m, 1H, OC<u>H</u>$_2$–CH*); 6.77 (d, 4H, arom. H); 7.03 (d, *J* = 8.5 Hz, 2H, arom. H); 7.34 (d, *J* = 8.5 Hz, 2H, arom. H); 7.86 (d, *J* = 8.7 Hz, 2H, arom. H); 8.08 (d, *J* = 8.7 Hz, 2H, arom. H); 8.42 (s, 1H, N=CH). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz): δppm = 14.0, 14.1, 17.1, 22.6, 25.9, 26.0, 28.5, 29.1, 29.2, 29.3, 29.5, 30.1, 31.8, (aliph. C); 69.6 (CH_2O); 71.8 (<u>C</u>H_2O–Ø); 73.5 (CH of the chiral chain); 114.6, 114.8, 121.5, 128.5, 130.9 (arom. C); 116.3, 121.0, 127.9, 158.5, 161.9, 162.6, 163.9, 164.5 (quaternary arom. C); 160.6 (CH=N). IR (KBr disc):cm^{-1} = 2924 (Csp^3-H); 1603 (C=C); 1251 (C–O).

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