JOURNAL OF
Materials
CHEMISTRY

The synthesis and mesomorphism of di-, tetra- and hexa-catenar liquid crystals based on 2,2′-bipyridine

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2,2′-Bipyridines are known to coordinate to a wide variety of metal centres. In this paper, liquid-crystalline two-chained (dicatenar), four-chained (tetracatenar) and six-chained (hexacatenar) bipyridines are synthesised and their mesomorphism is described. For the tetracatenar bipyridines, a full homologous series, from tetramethoxy to tetratetradecyloxy, was synthesised, and the phase diagram showed a classic progression from nematic and smectic C phases at short chain length, through a cubic phase to a columnar phase.

2,2′-Bipyridines are some of the most versatile ligands used in the construction of metal coordination complexes,[1] having been used to make dendrimers,[2] helical structures,[3] photoactive systems,[4] and a wide range of other supramolecular structures.[5] Their attractiveness comes form their synthetic versatility and from their ability to coordinate to a very wide variety of metal centres.

In recent publications, we have reported that by suitable choice of anisotropic ligand, it is possible to form rod-like liquid crystals based on metals with octahedral stereochemistry.[6] The approach is based on the assumption that such a high coordination number metal centre perturbs the anisotropy of the ligand to which it binds and leads to complexes with low aspect ratios. Consequently, it is necessary to use rather highly anisotropic ligands to screen out the perturbing effects of the metal complex. We have demonstrated that this is possible with imines orthometallated to $\mathrm{Mn^I}$[7] and $\mathrm{Re^I}$,[8] and with diazabutadienes coordinated to $\mathrm{Re^I}$.[9] It is, however, of interest to note that low aspect ratios appear not to be so much of a disadvantage in the design of columnar mesogens, as evidenced by the synthesis by Swager[10] of mesomorphic complexes based on octahedral metal centres bound to polysubstituted β-diketones.

Subsequently, we used the same approach in an effort to incorporate bipyridines as ligands in metal-based liquid crystals.[11] Thus, we reported the synthesis and mesomorphism of diesters of 2,2′-bipyridine-5,5′-dicarboxylic acid,[12] simultaneously with reports of mesomorphic bipyridines based on unsymmetrically substituted 5,5′-disubstituted bipyridines.[13] However, when complexed to a whole range of metal centres, the liquid crystallinity of the bipyridines was lost.[14] Curious to understand the absence of mesomorphism in these systems, we reasoned that by comparison with our own work and with that of Deschenaux with 1,3-disubstituted ferrocenes,[15] it seemed necessary to have, in addition to the core of the molecules, an additional four phenyl rings in order to realise mesomorphic metal complexes. Thus, when complexed, the 2,2′-bipyridine unit represented part of the core and, according to our idea, four extra rings were required. It was therefore necessary to synthesise a six-ring bipyridine to fulfil this design criterion, and subsequent complexation to $\mathrm{Re^I}$ eventually led to a liquid crystalline complex.[16]

Having shown that two-chained, six-ring derivatives of 2,2′-bipyridine could lead to mesomorphic complexes of $\mathrm{Re^I}$, we were keen to pursue the synthesis of further examples as bipyridines have enormous potential for coordination to a very wide range of metal centres. Therefore, we proceeded to synthesise several more examples and in particular, we examined tetracatenar (four-chain) and hexacatenar (six-chain) derivatives. The syntheses and liquid crystal properties of these new bipyridines are now described.

Synthesis of the bipyridines

Four different types of bipyridine were synthesised, shown in Scheme 1, and their synthesis is now described. Reaction of methyl 4-hydroxybenzoate, or ethyl 3,4-dihydroxy- or 3,4,5-trihydroxybenzoate with bromoalkane under basic conditions led to the related mono-, di- or tri-alkoxybenzoic acid, after alkaline hydrolysis and an acidic workup. For the mono- and di-alkylations, butanone was used as the solvent, while pentanone was preferred for the trialkylation reaction. These acids were then esterified with hydroquinone which was monoprotected with either tetrahydropyran (THP) or with a benzyl group. Benzyl protection was initially used and was subsequently readily removed by hydrogenolysis. However, hydrogenolysis of the di- and tri-alkoxy esters was painfully slow, which led us to change to THP-protection, where the deprotection using oxalic acid in methanol at reflux gave essentially quantitative yields. However, we subsequently found that addition of a small amount of triethylamine during the hydrogenolysis of the benzyl-protected system led to complete deprotection within minutes for any of the systems we studied, indicating a clearly preferential route, especially as mono THP-protected hydroquinone is obtained in four steps from hydroquinone. After deprotection, the resulting phenol was then esterified with 2,2′-bipyridine-5,5′-dicarbonyl dichloride. This was the lowest-yielding step of the whole procedure and despite our best efforts which included evaluation of other possible esterification methods, we could not obtain more than about 30% yield for this reaction. However, we would recommend making the diacid chloride just before it is required as under these circumstances, yields were consistently higher.

For the sake of later clarity, the bipyridines (Scheme 1) will be abbreviated as follows. The two-chain (or dicatenar) bipyridines, will be labelled **D*n***, where *n* denotes the number of carbon atoms in the alkoxy chains. Similarly, the four-chain (tetracatenar) and six-chain (hexacatenar) bipyridines will be abbreviated as **T*n*** and **H*n***, respectively.

The two-chained bipyridines were found to be highly insoluble making purification difficult, and while an analytically pure sample was obtained for the octyloxy derivative, **D8**, the other derivatives gave carbon values which were low by approximately 1%, despite numerous recrystallisations; compound **R8** behaved in a similar fashion. Further purification involved attempts to convert the dicatenar ligands to the

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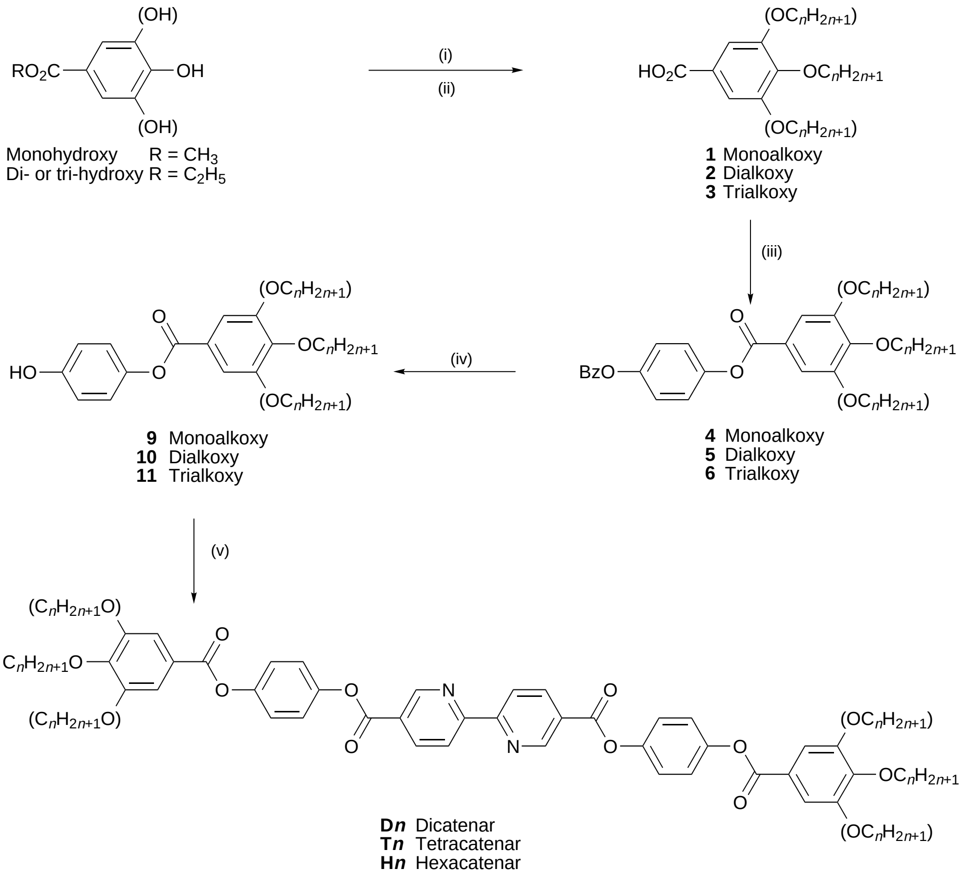


Scheme 1 Synthesis of the polycatenar bipyridines. *Reagents and conditions*: (i) $C_nH_{2n+1}Br$, $KHCO_3$; (ii) KOH/EtOH; (iii) BzOH, DCC, DMAP; (iv) H_2, Pd/C; (v) 2,2′-bipyridine-5,5′-dicarbonyl dichloride, toluene, Et_3N.

corresponding hydrochloride salt, in order to achieve higher solubility thus aiding purification. Unfortunately this was also accompanied by decomposition, and so was unsuitable. Compound **T1** was also very insoluble and we could not obtain good analytical data. However, we are not unduly disturbed by this as neither of the first two homologues was mesomorphic.

Synthesis of bipyridine, R8

One example of a bipyridine with one of the ester groups reversed was synthesised to examine the effect on mesomorphism. The route is shown in Scheme 2. Thus, benzyl 4-hydroxybenzoate was first protected with 3,4-dihydro-2*H*-pyran under acid-catalysed conditions at room temperature in ethyl acetate, before the benzyl group was cleaved, in quantitative yield, with hydrogen over a palladium-on-charcoal catalyst. This carboxylic acid **11** was reacted with 4-octyloxyphenol, using a standard DCC–DMAP esterification, and the THP group was subsequently cleaved under acidic conditions, at reflux in methanol. The resulting phenol **13** was reacted with 2,2′-bipyridine-5,5-dicarbonyl dichloride at reflux in toluene containing a few drops of triethylamine, to give the reversed ester, **R8**. In common with the dicatenar bipyridines above, this compound was found to be highly insoluble, again making purification difficult.

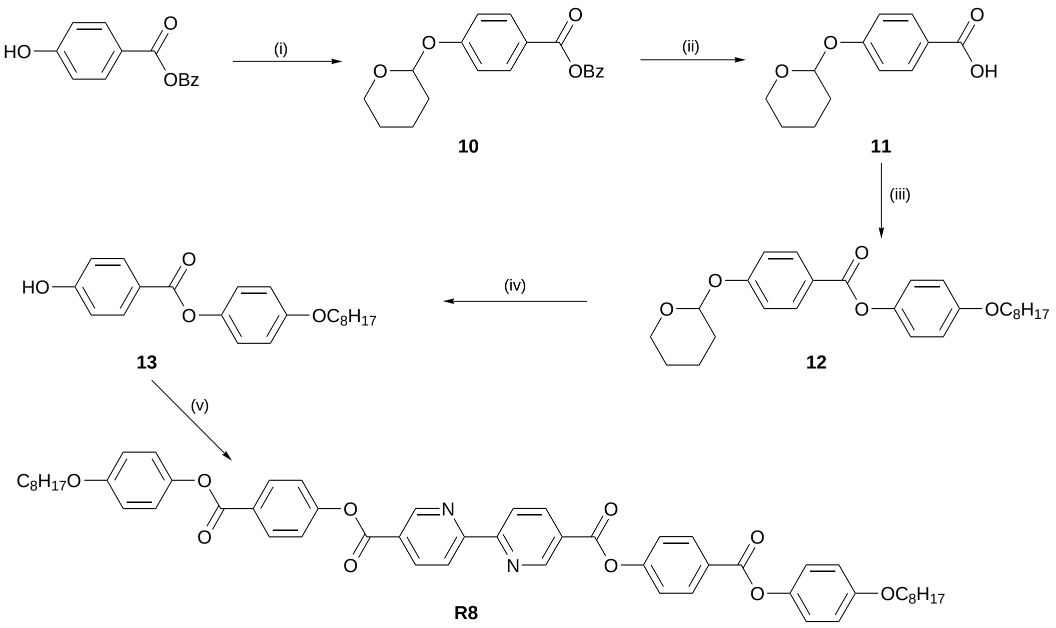
Mesomorphism of the dicatenar bipyridines, D*n*

Five dicatenar 2,2′-bipyridine ligands were synthesised with $n=1$, 4, 8, 12 and 14; the thermal data for these compounds are collected in Table 1. The methoxy derivative was found to exhibit two mesophases, the upper one being nematic, but the lower phase (M_1) being unidentified. However due to decomposition occurring at these elevated temperatures it was not possible to obtain a clear texture of the lower mesophase on cooling making identification impossible. Furthermore, this meant that only data from the first DSC cycle could be used.

The butoxy bipyridine, **D4**, showed only a nematic phase, while the longer chain length derivatives, **D8**, **D12** and **D14**, showed a smectic C phase before giving way to the nematic phase at higher temperatures. The temperature of the S_C–N transition was found to vary with heating rate, which is attributed to decomposition occurring in the upper reaches of the S_C phase and rapidly accelerating in the nematic phase. Despite this, the S_C phase range was found to increase with increasing chain length, as is expected with calamitic materials.

On both the heating and cooling cycles of the DSC, **D12** showed another mesophase (M_2) between the crystal and S_C phase. By microscopy, with careful cooling, this transition was observed, but persisted for only a degree or so before crystallisation occurred. Due to decomposition occurring in the nematic phase, it was not possible to obtain a good optical texture for the S_C phase, and therefore for the M_2 phase, too. However, the relative magnitude of both the entropy and enthalpy changes (obtained on cooling) leads to a tentative assignment as a crystal smectic phase.

As this additional phase first appeared in the dodecyloxy derivative it was hoped that its phase range would increase with increasing alkoxy chain length. Hence, the tetradecyloxy derivative, **D14**, was subsequently synthesised as a direct attempt to elucidate the nature of this mesophase. Unfortunately, the range of the phase was found to be equally short and once more, a good optical texture could not be obtained, leaving the mesophase unidentified.



Scheme 2 The synthesis of the 'reversed ester' ligand. *Reagents and conditions*: (i) 3,4-dihydro-2*H*-pyran, HCl(g); (ii) H_2, Pd/C; (iii) 4-octyloxyphenol, DCC, DMAP; (iv) oxalic acid, MeOH; (v) 2,2′-bipyridine-5,5′-dicarbonyl dichloride, toluene, Et_3N.

Table 1 Thermal data for the dicatenar bipyridines

n	Transition[a]	T°/C	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}
1	Cr→M_1	237	—[b]	—[b]
	M_1→N	264	—[b]	—[b]
	N→decomp.	>264	—	—
4	Cr→N	269	45.8	84
	N→decomp.	350	—	—
8	Cr→S_C	231	52.3	104
	S_C→N	328[c]	—[b]	—[b]
	N→decomp.	>328	—	—
12	Cr→M_2	210	2.1[d]	4[d]
	M_2→S_C	212	35.5[d]	75[d]
	S_C→N	341[c]	—[b]	—[b]
	N→decomp.	>341	—	—
14	Cr→M_2	209	0.5[d]	1[d]
	M_2→S_C	211	49.0	102
	S_C→N	355[c]	4.2	7
	N→I	368[c]	—[b]	—[b]

[a] M_1 and M_2 are unidentified mesophases (see text).
[b] Not seen by DSC.
[c] These temperatures are sensitive to the thermal history of the sample due to decomposition occuring in the S_C phase.
[d] The thermodynamic data for these transitions are taken from the cooling cycles on the DSC.

Mesomorphism of the tetracatenar bipyridines, T*n*

Polycatenar liquid crystals[17,18] are those which contain, typically, three or more chains and a rather extended core. They are classified both by the number of terminal chains they possess (tri-, tetra-, penta- and hexa-catenar) and also by the way these are distributed on the terminal benzene rings.

The hexa- and penta-catenar compounds are found to exhibit columnar phases, while the tricatenar compounds show lamellar and cubic mesophases. The columnar phases result from a strong curvature at the aromatic–aliphatic interface in a way similar to that observed in lyotropic liquid crystals. The structure of the columnar mesophase formed from polycatenar species has been shown by dilatometry studies and X-ray measurements to be slightly different from those formed by conventional discoid molecules. Conventional disc shaped molecules stack on top of each other to form a column, these columns being packed in a two-dimensional array. However, in the polycatenar systems, between two and four molecules come together to form what is, in effect, a disc-like repeat unit representing a slice through the columns, which are then themselves packed in a two-dimensional array.

Probably the most interesting of the polycatenar systems are the tetracatenar compounds which can display lamellar, cubic and columnar mesophases. Generally, lamellar mesophases are observed at short chain lengths while columnar mesophases are observed at longer chain lengths. At intermediate chain lengths, this competition can result in the formation of a frustrated phase, namely the cubic phase. This polymorphism arises due to the fact that in the mesophase, segregation of the aromatic and aliphatic parts of the molecule occurs, and as such these molecules can be regarded as amphiphilic in nature. Indeed, their observed polymorphism is similar to that of lyotropic systems in the sense that two-dimensional oblique or rectangular columnar phases, or three-dimensional cubic phases can be inserted in between lamellar and hexagonal columnar phases. Also, like lyotropic systems, this segregation of molecular parts results in curvature at the aromatic–aliphatic interface. This helps to explain the correlation between mesophase type and the length of the aliphatic chain, for as the chain length is increased so the curvature is increased, resulting in the columnar mesophases being stabilised at the expense of the lamellar mesophases.

Because of the potential for such rich mesomorphism in these systems, we undertook the synthesis of a complete homologous series from $n = 1$–14. We believe that this is the first time that such an homologous series has been investigated for tetracatenar mesogens, and the results are presented as a phase diagram in Fig. 1, while the thermal data are collected in Table 2.

This series of compounds exhibits a phase behaviour that is very typical for tetracatenar species, namely nematic and lamellar phases at short chain lengths, columnar at long chain lengths, with the changeover being accompanied by the observation of a cubic phase at intermediate chain lengths.

Until the pentyloxy derivative, **T5**, only nematic phases were observed at elevated temperatures, with decomposition

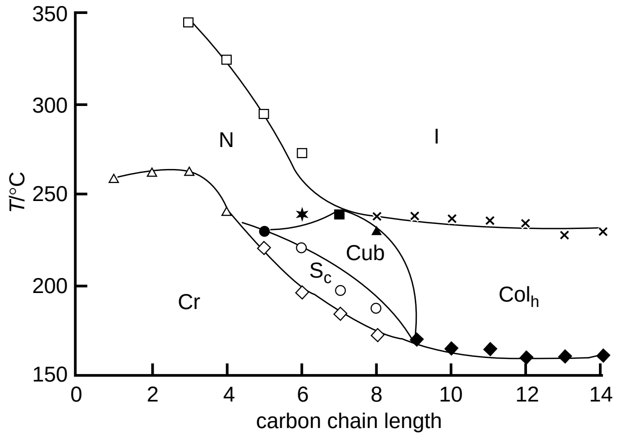


Fig. 1 Phase diagram for the tetracatenar bipyridines (Cr = crystal; N = Nematic, S_C = smectic C; Cub = cubic and Col_h = columnar hexagonal); Δ, Cr–N; ◇, Cr–S_C; ◆, Cr–Col_h; ●, S_C–N; ○, S_C–Cub; *, Cub–N; ▲, Cub–Col_h; □, N–I; ■, Cub–I; x, Col_h–I

Table 2 Thermal data for the tetracatenar bipyridines

n	Transition	T/°C	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}
1	Cr→N	259	62.6	117
	N→decomp.	>300	—	—
2	Cr→N[a]	262	52.4	99
	N→decomp.	>300	—[c]	—[c]
3	Cr→N[a]	263	55.7	104
	N→I[b]	345	—[c]	—
4	Cr→N*a*	242	55.6	109
	N→I*b*	325	—[c]	—[c]
5	Cr→S_C	221	61.8	126
	S_C→N	229	3.2	6
	N→I	294	1.0	2
6	Cr→S_C	196	55.8	120
	S_C→Cub	220	1.7	14
	Cub→N	239	4.0	8
	(Cub→S_C)	(203)	—[c]	—[c]
	(S_C→Cub)	(224)	—[c]	—[c]
	(N→S_C)	(229)	—[c]	—[c]
	N→I	272	0.5	1.0
7	Cr→S_C	184	59.2	130
	S_C→Cub	197	2.9	6
	(Col→Cub)	(228)	(3.6)	(7.0)
	(I→Col)	(234.5)	—[c]	—[c]
	Cub→I	239	3.8	7
8	Cr→S_C	173	56.0	126
	S_C→Cub	188	2.4	5
	Cub→Col_{hd}	229	—	—
	Col_{hd}→I	237	4.0	8
9	Cr→Col_{hd}	171	35.6	4
	Col_{hd}→I	238	3.9	8
10	Cr→Col_{hd}	166	45.2	103
	Col_{hd}→I	237	4.3	9
11	Cr→Col_{hd}	165	48.2	110
	Col_{hd}→I	236	5.31	11
12	Cr→Col_{hd}	161	48.6	112
	Col_{hd}→I	234	5.8	11
13	Cr→Col_{hd}	161	47.7	110
	Col_{hd}→I	229	6.6	12
14	Cr→Col_{hd}	161	48.9	113
	Col_{hd}→I	230	6.5	13

[a] The DSC data are only approximate due to an incomplete crystal–crystal transition immediately prior to melting.
[b] These temperatures are sensitive to the thermal history of the sample due to decomposition occurring in the upper regions of the nematic phase.
[c] Not seen by DSC.

occurring in the upper regions of these phases, beginning above 300 °C and accelerating rapidly above 350 °C. Thus, for the methoxy (**T1**) and ethoxy (**T2**) derivatives, no clearing point was observed. While the propoxy (**T3**) and butoxy (**T4**) derivatives did clear to the isotropic, this temperature was not found to be reproducible on subsequent runs as it was accompanied by extensive decomposition. Nevertheless, the clearing point decreased quite markedly as the chain length increased. In initial microscopy studies, it appeared that **T2–T4** melted over a large temperature range. DSC data showed that there was a crystal–crystal transition immediately prior to melting into the nematic mesophase. Further microscopy allowed the melting temperature to be ascertained; however by DSC the first transition was almost complete before the compounds melted into the nematic phase; hence, the thermodynamic data associated with these melting points are only approximate.

An additional phase, namely $S_{C,}$ was introduced at the pentyloxy chain length and was readily characterised by its optical texture. Thus, the aliphatic chain was now of sufficient length to stabilise lamellar mesophases. The derivatives **T6–T8** represent the change over from lamellar to hexagonal columnar mesophases, and as is often typical in tetracatenar systems this is achieved *via* the cubic phase. Thus, the cubic phase (characterised by its optical anisotropy, by the slow formation of such a texture *via* the characteristic appearance of square edges growing across the preceding texture, its high viscosity and the accompanying appearance of misshapen air bubbles) first appears in the hexyloxy derivative, between the S_C and N phases, giving one of very few well-authenticated examples of a cubic phase below a nematic.[19] In the heptyloxy derivative, a monotropic columnar hexagonal phase was observed and by the octyloxy derivative we had a compound that exhibited enantiotropic lamellar, cubic and hexagonal columnar phases. We believe that this is also unique in tetracatenar systems.

From **T9** onwards, only columnar mesomorphism was observed, with both the melting and clearing temperatures remaining remarkably constant, irrespective of chain length. The optical textures of these hexagonal columnar phases was highly characteristic, exhibiting beautiful focal conic monodomains and areas of homeotropic orientation. These columnar mesophases have been identified as disordered hexagonal columnar mesophases by X-ray diffraction studies which will be published in due course as part of a much larger structural study of the phase diagram.[20] Thus, spacings in the ratio 1, $\sqrt{3}$, $\sqrt{4}$ were seen and, for example, **T12** gave $d_{001} = 43.8$ Å.

This phase diagram is absolutely 'text-book' for the behaviour of tetracatenar mesogens and is, to our knowledge, the first time that a full homologous series of tetracatenar mesogens, from methoxy upwards, has been synthesised. Thus, the nematic and smectic C phases observed at short chain lengths pass through an 'intermediate' cubic phase before giving way to a columnar phase. By contrast, in a related piece of work where we complexed two dicatenar alkoxystilbazoles in a *trans* fashion across a $PtCl_2$ centre, the mesomorphism changed suddenly from smectic C to columnar on passing from the dodecyloxy derivative (S_C only) to the tridecyloxy derivatice (columnar only), without any sign of a cubic phase and without any of the homologues showing both lamellar and columnar phases.[21] The sensitivity of polycatenar mesogens to their core structure has been commented on previously.[22]

Close examination of the phase diagram reveals some interesting possibilities. For example, there is a direct nematic–cubic transition which ought to allow for the production of a cubic monodomain from an aligned nematic, leading to unequivocal assignment of the symmetry of the cubic phase, as reported previously by us for mesomorphic complexes of silver(I).[23] Furthermore, we have in **T8**, a compound with the enantiotropic phase sequence $Col_h \rightleftharpoons Cub \rightleftharpoons S_C$, previously found only monotropically and not before in symmetric, tetracatenar systems.[20] We have recently carried out a detailed investigation of polycatenar complexes of silver(I)[24] using X-ray scattering, freeze–fracture electron microscopy,[25] and dilatometry, in which we confirmed an epitaxial relationship between the columnar and cubic phase, and have proposed a model for the columnar-to-cubic transition.[26] We now have the possibility of extending this approach to look at the epitaxy of the columnar-to-cubic-to-smectic C transitions in the same material, which we hope will give further information on transitions to cubic phases. These studies are already underway and will be reported in due course.

The mesomorphism of the hexyloxy and heptyloxy derivatives were found to be particularly interesting and are now discussed in some detail. Thus, on heating, **T6** showed the following phase sequence:

$$\mathrm{Cr} \rightarrow \mathrm{S_C} \rightarrow \mathrm{Cub} \rightarrow \mathrm{N} \rightarrow \mathrm{I}$$

However, on cooling the nematic phase gives way to a S_C phase rather than a cubic phase. A cubic phase then grows into the S_C phase and persists until the S_C phase reappears once more. Thus, the phase sequence on cooling is:

$$\mathrm{I} \rightarrow \mathrm{N} \rightarrow \mathrm{S_C} \rightarrow \mathrm{Cub} \rightarrow \mathrm{S_C} \rightarrow \mathrm{Cr}$$

We were initially perplexed by this behaviour, but following discussions with Dr Antoine Skoulios of the IPCMS in Strasbourg, we feel we can offer an explanation. The behaviour is best explained by considering a schematic free energy diagram for the system as shown in Fig. 2.

Thus, on increasing the temperature and minimising G, transitions would be expected (and are observed) from S_C→Cub→N→I. On cooling, the reverse would clearly be expected, but the behaviour is modified due to the very slow kinetics generally found for the formation of cubic phases. Thus, while on cooling from the nematic phase the cubic phase is thermodynamically preferred, the nematic can supercool due to these slow kinetics, allowing the appearance of the S_C phase. As this phase is thermodynamically unstable with respect to the cubic, then the latter eventually appears, once more giving way to the (now thermodynamically stable) S_C phase on further cooling.

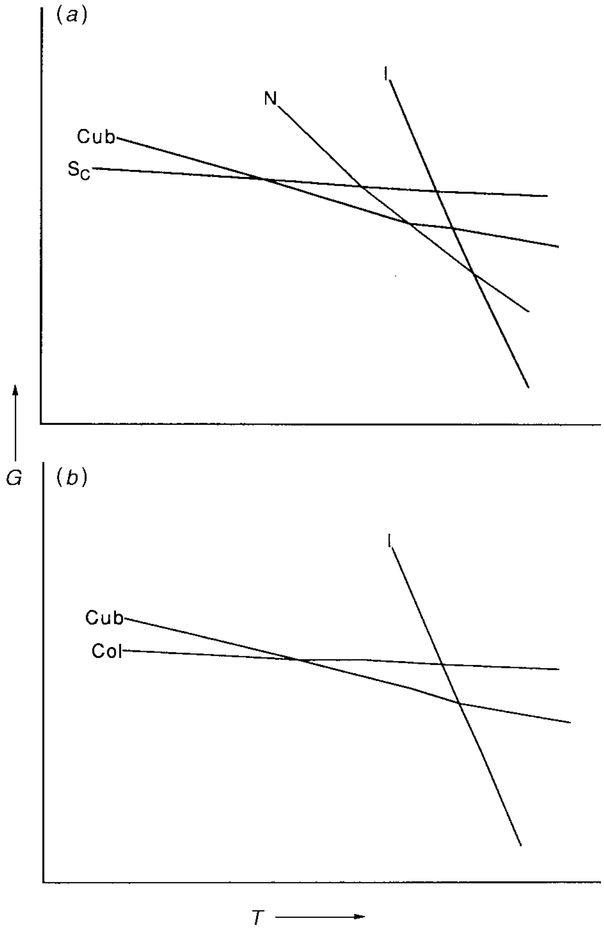


Fig. 2 Schematic representation to show the thermodynamic relationship between the mesophases in compounds **T6** (*a*) and **T7** (*b*)

A similar situation exists with **T7**, where the heating and cooling phase sequences are as shown below:

Col→Cub→I Heating

I→Col→Cub→Col Cooling

Very similar arguments can be invoked here, with a thermodynamically unstable columnar phase appearing on cooling the isotropic due to the slow kinetics of cubic phase formation.

Mesomorphism of the hexacatenar 2,2′-bipyridines

As the mesomorphism displayed with the hexacatenar 2,2′-bipyridine systems was found to be predominantly columnar, only four ligands were synthesised with $n=1$, 4, 8 and 12. Thermal data are collected in Table 3.

The mesomorphism observed in these compounds is typical of hexacatenar systems, namely columnar mesophases, with the exception of the methoxy derivative which exhibits a rather different phase sequence. Thus, the butoxy derivative was found to show a columnar phase. The cooling cycle of the DSC only gave the isotropic–columnar transition, but the crystal–columnar transition was reproducibly obtained on subsequent heating cycles, following a cold crystallisation exotherm. The octyloxy and dodecyloxy derivatives exhibited similar mesomorphism. In both derivatives, the first heating cycle on the DSC gave two transitions prior to clearing into the isotropic. On cooling, neither sample crystallised, and consequently on subsequent heating cycles, the melting transition was no longer observed, but the other transitions were reproducibly obtained. By microscopy, these samples were also observed not to crystallise, with the texture that first appeared from the isotropic remaining until solidification. As a result, the mesophase–mesophase transition (reproducible obtained by DSC), was not initially observed by microscopy. On careful reexamination of the dodecyloxy derivative by microscopy, it was possible on the first heat to see a subtle textural change in the highly birefringent sample, from a smooth to a finely grained, less focused surface. However, the textures observed by the first heat were not sufficient for characterisation. The natural texture of the upper phase observed on cooling was characteristic of a columnar phase, and the small change in enthalpy required in the mesophase–mesophase transition combined with the lack of any observed textural change on cooling, suggests that the lower phase is also columnar. X-Ray

Table 3 Thermal data for the hexacatenar bipyridines

n	Transition	T/°C	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}
1	Cr→Cub	203	—[a]	—[a]
	Cub→S_A	211	—[a]	—[a]
	S_A→N	217	—[a]	—[a]
	N→I	292	—[a]	—[a]
4	Cr→Col	143	26.7	64
	Col→I	176	3.5	8
8	Cr→Col[b]	85	45.2	126
	Col→Col′	157	0.2	1
	Col→I	165	6.4	15
12	Cr→Col[b]	54	38.6	114
	Col→Col′	142	0.3	1
	Col′→I	151	5.7	14

[a]Not seen by DSC. [b]This transition is only observed on the first heat.

studies are now in progress in order to ascertain the exact nature of these mesophases (and the other analogues in this series).

The methoxy derivative was remarkable in showing the phase sequence:

$$\mathrm{Cr}\rightarrow\mathrm{Cub}\rightarrow\mathrm{S_A}\rightarrow\mathrm{N}\rightarrow\mathrm{I}$$

While transitions from both S_A to cubic and nematic to cubic are known, we are not aware of the $\mathrm{I}\rightarrow\mathrm{N}\rightarrow\mathrm{S_A}\rightarrow\mathrm{Cub}$ phase sequence having been observed before. All of the phases were readily assigned on the basis of optical microscopy, although bizarrely, no thermal changes could be observed by DSC. We have come across this problem before in other studies and have usually found that by changing the experimental method slightly, it was possible to obtain reproducible data. However, in this case it was to no avail.

Mesomorphism of ligand, R8

Thermal data for **R8** and **D8** are collected in Table 4. It is well known that the direction of an ester functionality can have a profound effect on the observed mesomorphism.[27] The six-ring 2,2′-bipyridines described so far have their ester groups arranged so that their dipoles oppose one another (see Fig. 3), leading to net lateral dipoles which can be regarded as being mutually repulsive and therefore, promoting nematic phases, as observed. However, if the outer ester groups are reversed, then the dipoles would be arranged as a kind of ‘outboard’ dipole which should promote smectic phases. Similar effects are seen on the introduction of fluoro substituents into mesomorphic systems.[28]

Reversal of the terminal ester group was found to promote S_C phase formation by destabilising both the crystal and the nematic phase. Nematic phase formation was suppressed to the extent that it was no longer observed and the melting point was lowered by some 34 °C. This is unsurprising as the dipole moments of the ester functionalities are now no longer opposing each other, therefore they are now serving to stabilise lamellar interactions.

Table 4 Thermal data for **D8** and the ‘reversed’ ester, **R8**

Comp.	Transition	T/°C	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}
R8	$\mathrm{Cr}\rightarrow\mathrm{S_C}$	197	37.3	80
	$\mathrm{S_C}\rightarrow$decomp.	>280	—	—
D8	$\mathrm{Cr}\rightarrow\mathrm{S_C}$	231	52.3	104
	$\mathrm{S_C}\rightarrow\mathrm{N}^a$	328	—	—
	$\mathrm{N}\rightarrow$decomp.^{a}	>328	—	—

[a] These temperatures are sensitive to the thermal history of the sample due to decomposition occurring in the S_C phase.

Conclusions

A number of di-, tetra- and hexa-catenar six-ring 2,2′-bipyridines have been synthesised. These were found to be novel liquid-crystalline materials that exhibited a rich polymorphism.

Thus, the dicatenar compounds were found to exhibit nematic and S_C phases, with the S_C phase being stabilised at the expense of the nematic phase with increasing chain length. This was the only lamellar phase observed, leading to the observation reported previously[15] that the 2,2′-bipyridine core seems to strongly promote S_C phase formation in these types of compounds. This observation was also borne out when the direction of the terminal ester functionality was reversed, as only a S_C phase was observed.

The tetracatenar system, in particular displayed the most interesting mesomorphism as these compounds were found to exhibit nematic and lamellar phases at short chain lengths, and hexagonal columnar phases at long chain lengths, with a cubic phase appearing at intermediate chain lengths at the transferral point between the lamellar and columnar mesophases.

Finally, the mesomorphism of hexacatenar species synthesised was found to be essentially columnar, with the exception of the methoxy derivative which behaved as a calamitic mesogen.

Experimental

Elemental analysis were determined by the University of Sheffield Microanalysis Service. Mass spectra were recorded using the Fast Atom Bombardment technique (FAB), at the University of Sheffield. Infrared spectra were measured using a Nicolet MAGNA 550 FTIR infrared spectrometer; UV–VIS spectroscopy was carried out using a ATI Unicam UV4 machine. NMR spectra were recorded on either a Bruker ACF-300 or a Bruker DRX-400 spectrometer, where the chemical shifts are reported relative to the internal standard of the deuterated solvent used. J values are in Hz. Analysis by DSC was carried out on a Perkin-Elmer DSC7 instrument using heating and cooling rates of either 5 or 10 K min^{-1}. Analysis by hot stage microscopy was carried out using a Zeiss Labpol, or Olympus BH40 microscope equipped with a Link-Am HFS91 hot stage, TMS92 controller and LNP2 colling unit. Silica gel particle size was 40–63 µm.

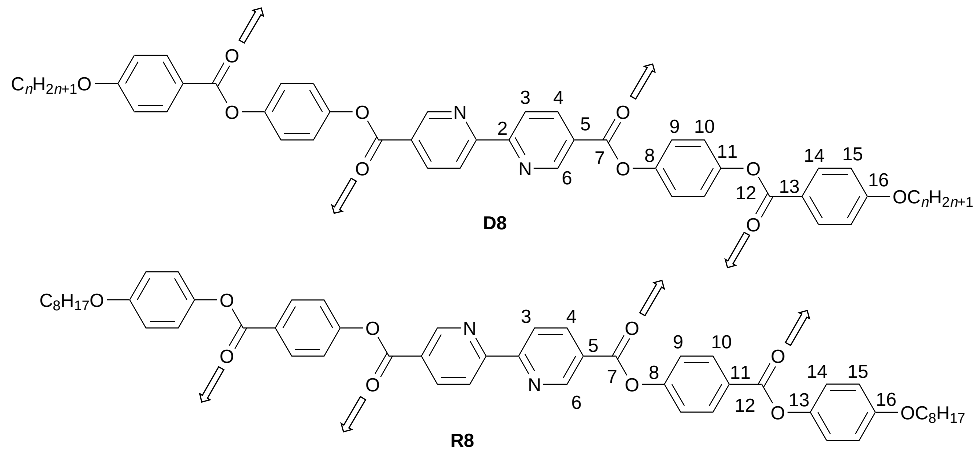
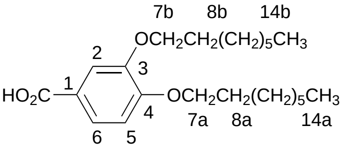


Fig. 3 Diagram to show the relative dispositions of dipoles in the dicatenar compounds and the related ‘reversed ester’

Synthesis of the 3,4-dialkoxybenzoic acids

All derivatives were prepared similarly and one example is given. All other derivatives were obtained in yields ranging from 80–95%.

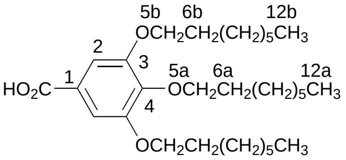


2h

3,4-Bis(octyloxy)benzoic acid 2h. Ethyl-3,4-dihydroxybenzoate (5 g, 0.027 mol), potassium carbonate (15.15 g, 0.1 mol) and 1-bromooctane (10.6 g, 0.055 mol) were placed in butanone (150 cm^{3}), and the reaction heated at reflux for 84 h. Water (100 cm^{3}) was added and the aqueous phase extracted against dichloromethane (3 × 100 cm^{3}). The organic extracts were combined, dried over $MgSO_4$, filtered and evaporated to give a brown solid. A solution of potassium hydroxide (3.07 g, 0.055 mol) in ethanol (95%, 100 cm^{3}) was added and the reaction heated at reflux for 2.5 h. Water (100 cm^{3}) was added and the solution acidified with HCl (conc., 10 cm^{3}). The resulting colourless precipitate was collected and crystallised twice from ethanol to give 3,4-bis(octyloxy)benzoic acid as a colourless solid. Yield: 9.12 g (88%); δ_{H} ($CDCl_3$): 7.72 (1H, dd, H^{6}, $^{3}J_{\mathrm{HH}}$ 8.5, $^{4}J_{\mathrm{HH}}$ 2), 7.60 (1H, d, H^{2}, $^{4}J_{\mathrm{HH}}$ 2), 6.89 (1H, d, H^{5}, $^{3}J_{\mathrm{HH}}$ 8.5), 4.07 and 4.05 (4H, t, H$^{7a\ \mathrm{and}\ b}$), 1.85 (4H, qt, H^{8}), 1.30 (20H, m, H$^{8-13}$), 0.90 (6H, t, H^{14})

Synthesis of the 3,4,5-trialkoxybenzoic acids

All derivatives were prepared similarly and one example is given. All other derivatives were obtained in yields ranging from 55–70%.

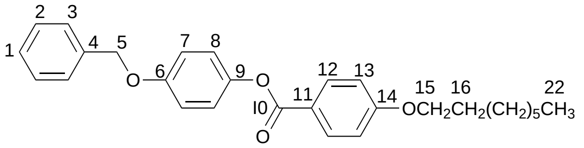


3c

3,4,5-Tris(octyloxy)benzoic acid 3c. Methyl 3,4,5-trihydroxybenzoate (5 g, 0.027 mol), potassium carbonate (22.5 g, 0.16 mol) and 1-bromooctane (15.65 g, 0.082 mol), were placed in pentan-3-one (150 cm^{3}), and the reaction heated at reflux for 84 h. Water (100 cm^{3}) was added and the aqueous phase extracted against dichloromethane (3 × 150 cm^{3}). The organic extracts were combined dried over $MgSO_4$, filtered and evaporated to give a brown oil. A solution of potassium hydroxide (3.04 g, 0.054 mol) in 95% ethanol (150 cm^{3}) was added and the reaction heated at reflux for 2.5 h. Water (100 cm^{3}) was added and the solution acidified with conc. hydrochloric acid (20 cm^{3}). The resulting colourless precipitate was collected and crystallised (2 ×) from ethanol to give 3,4,5-tris(octyloxy)benzoic acid as a colourless solid. Yield 11 g (54%); δ_{H} ($CDCl_3$): 7.30 (2H, s, H^{2}), 4.00 and 4.03 (6H, t, H$^{5a\ \mathrm{and}\ b}$), 1.84 (6H, qt, H^{6}), 1.50 (6H, m, H^{7}), 1.30 (24H, m, H$^{8-11}$), 0.85 (9H, t, H^{12}); δ_{C} ($CDCl_3$): 172.0(CO_2H), 152.8(C^{3}), 143.1(C^{4}), 123.7(C^{1}), 108.5(C^{2}), 73.6(C^{5a}), 6.2(C^{5b}), 31.9, 31.8, 30.3, 29.5, 29.4, 29.3, 26.1, 22.7 (C$^{6-11}$), 14.1(C^{12}).

Synthesis of the 4-(4-alkoxybenzoyloxy)-1-benzyloxybenzenes

All derivatives were prepared similarly and one example is given. All other derivatives were obtained in yields ranging from 70–83%.

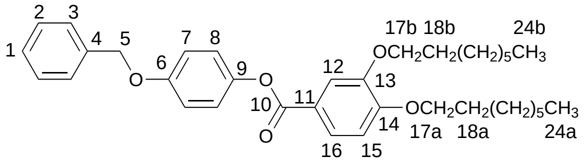


4c

4-(4-Octyloxybenzoyloxy)-1-benzyloxybenzene 4c. 4-Octyloxybenzoic acid (5 g, 0.02 mol), 4-benzyloxyphenol (4 g 0.02 mol), and dicyclohexylcarbodiimide (4.1 g, 0.02 mol), were dissolved in dichloromethane. To this *N,N*-dimethylaminopyridine (0.25 g 0.002 mol) was added and the reaction was stirred at room temp. for 24 h. The colourless precipitate was removed by filtration and the solvent was evaporated. Crystallisation from ethanol (2 ×) gave the product as a colourless solid. Yield: 6.8 g (80%); δ_{H} ($CDCl_3$): 8.05 (2H, AA′XX′, H^{12}, $J_{\mathrm{AA'XX'}}$ 9), 7.35 (5H, m, H$^{1-3}$), 7.05 (2H, AA′XX′, H^{8}, $J_{\mathrm{AA'XX'}}$ 9), 7.05 (2H, AA′XX′, H^{13}, $J_{\mathrm{AA'XX'}}$ 9), 6.87 (2H, AA′XX′, H^{7}, $J_{\mathrm{AA'XX'}}$ 9), 5.00 (2H, s, H^{5}), 3.95 (2H, t, H^{15}, $^{3}J_{\mathrm{HH}}$ 6.5), 1.75 (2H, qt, H^{16}), 1.40 (2H, m, H^{17}), 1.25 (8H, m, H$^{18-21}$), 0.80 (3H, t, H^{22}); δ_{C} ($CDCl_3$): 165.3(C^{10}), 163.5(C^{14}), 156.4(C^{6}), 144.8(C^{9}), 136.9(C^{4}), 132.3(C^{12}), 128.6, 128.0, 127.5(C$^{1-3}$), 122.6(C^{8}), 121.6(C^{11}), 115.5(C^{7}), 114.3(C^{13}), 70.5(C^{5}), 68.3(C^{15}), 31.8, 29.4, 29.3, 29.1, 26.0, 22.7(C$^{16-21}$), 14.1(C^{22}).

Synthesis of the 4-(3,4-dialkoxybenzoyloxy)-1-benzyloxybenzenes

All derivatives were prepared similarly and one example is given. All other derivatives were obtained in yields ranging from 58% to quantitative.

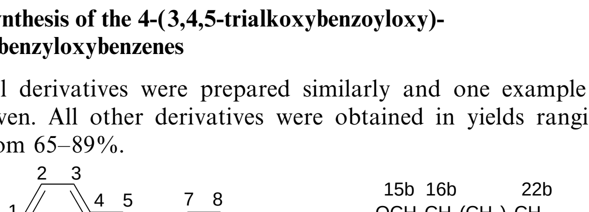


5h

4-[3,4-Bis(octyloxy)benzoyloxy]-1-benzyloxybenzene 5h. This was prepared from 3,4-bis(octyloxy)benzoic acid using the procedure given for **4c**. This gave the product as a colourless solid. Yield: 3 g (80%); δ_{H} ($CDCl_3$): 7.82 (1H, dd, H^{16}, $^{3}J_{\mathrm{HH}}$ 8.5, $^{4}J_{\mathrm{HH}}$ 2), 7.68 (1H, d, H^{12}, $^{4}J_{\mathrm{HH}}$ 2), 7.40 (5H, m, H$^{1-3}$), 7.13 (2H, AA′XX′, H^{8}, $J_{\mathrm{AA'XX'}}$ 9), 7.01 (2H, AA′XX′, H^{7}, $J_{\mathrm{AA'XX'}}$ 9), 6.93 (1H, d, H^{15}, $^{3}J_{\mathrm{HH}}$ 8.5), 5.09 (2H, s, H^{5}), 4.09 and 4.08 (4H, t, H$^{17a\ \mathrm{and}\ b}$), 1.87 and 1.86 (4H, qt, H$^{18a\ \mathrm{and}\ b}$), 1.51 (4H, m, H^{19}), 1.35 (16H, m, H$^{20-23}$), 0.91 (6H, t, H^{24}); δ_{C}($CDCl_3$): 165.4(C^{10}), 156.4(C^{6}), 153.8(C^{14}), 148.7(C^{13}), 144.8(C^{9}), 136.9(C^{4}), 128.6, 128.0, 127.5(C$^{1-3}$), 124.3(C^{8}), 122.6(^{16}C), 121.8(C^{11}), 115.5(C^{7}), 114.7(C^{12}), 112.1(C^{15}), 70.5(C^{5}), 69.4&69.1(C$^{17a\ \mathrm{and}\ b}$), 31.8, 29.4, 29.3, 29.2, 29.1, 26.0, 22.7(C$^{18-23}$), 14.1(C^{24}).

Synthesis of the 4-(3,4,5-trialkoxybenzoyloxy)-1-benzyloxybenzenes

All derivatives were prepared similarly and one example is given. All other derivatives were obtained in yields ranging from 65–89%.

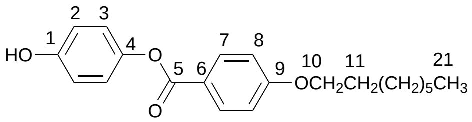


6c

4-[3,4,5-Tris(octyloxy)benzoyloxy]-1-benzyloxybenzene 6c. This was prepared from 3,4,5-tris(octyloxy)benzoic acid using the procedure described for **4c**. The crude product was purified by crystallisation from ethanol (250 cm^3), to give the pure product as a colourless solid. Yield: 0.88 g (65%); δ_H (CDCl$_3$): 7.40 (5H, m, H$^{1-3}$), 7.38 (2H, s, H^{12}), 7.10 (2H, AA′XX′, H^8, $J_{AA'XX'}$ 9), 7.00 (2H, AA′XX′, H^7, $J_{AA'XX'}$ 9), 5.06 (2H, s, H^5), 4.05 (6H, m, H^{15}), 1.82 and 1.80 (6H, qt, H$^{16a\ and\ b}$), 1.50 (6H, m, H^{17}), 1.30 (24H, m, H$^{18-21}$), 0.85 (9H, t, H^{22}).

Synthesis of the 4-(4-alkoxybenzoyloxy)phenols

All derivatives were prepared similarly and one example is given. All other derivatives were obtained in yields ranging from 76% to quantitative.

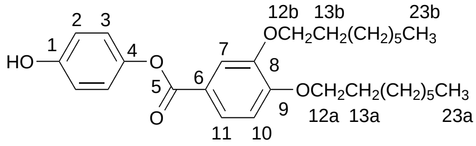


9c

4-(4-Octyloxybenzoyloxy)phenol 9c. 4-(4-Octyloxybenzoyloxy)-1-benzyloxybenzene (6.6 g, 0.015 mol) was dissolved in freshly distilled THF (150 cm^3) and triethylamine (1 cm^3), and 10% wet Degassu Pd/C catalyst (0.05 g) was added. The reaction flask was evacuated and placed under hydrogen (repeated three times), before being stirred at room temp. under an atmosphere of hydrogen. After 223 cm^3 of hydrogen had been taken up the catalyst was removed by filtration through Celite and the solvent was evaporated, to give a colourless solid as the product. Yield: 4.7 g (90%); δ_H (CDCl$_3$): 8.12 (2H, AA′XX′, H^7, $J_{AA'XX'}$ 9), 7.02 (2H, AA′XX′, H^3, $J_{AA'XX'}$ 9), 6.95 (2H, AA′XX′, H^8, $J_{AA'XX'}$ 9), 6.80 (2H, AA′XX′, H^2, $J_{AA'XX'}$ 9), 5.38 (1H, s, OH), 4.02 (2H, t, H^{10}, $^3J_{HH}$ 6.5), 1.80 (2H, qt, H^{11}), 1.45 (2H, m, H^{12}), 1.30 (8H, m, H$^{13-16}$), 0.85 (3H, t, H^{17}); δ_C (CDCl$_3$): 166.2(C^5), 163.7(C^9), 153.7(C^1), 144.2(C^4), 132.4(C^7) 122.5(C^3), 121.4(C^6), 116.3(C^2), 114.3(C^8), 68.4(C^{10}), 31.8, 29.3, 29.2, 29.1, 26.0, 22.7(C$^{11-16}$), 14.1(C^{17}).

Synthesis of the 4-(3,4-dialkoxybenzoyloxy)phenols

All derivatives were prepared similarly and one example is given. All other derivatives were obtained in yields ranging from 80–95%.

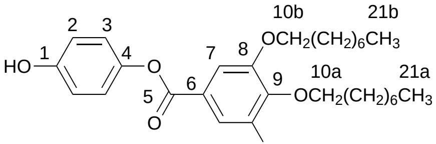


10h

4-[3,4-Bis(octyloxy)benzoyloxy]phenol 10h. Compound **5h** (6.6 g, 0.0118 mol) was dissolved in freshly distilled THF (150 cm^3) and triethylamine (1 cm^3) and 10% wet Degassu Pd/C catalyst (0.05 g) was added. The reaction flask was evacuated and placed under hydrogen (three times), before being stirred at room temp. under an atmosphere of hydrogen. After the calculated amount of hydrogen had been taken up the catalyst was removed by filtration through Celite and the solvent was evaporated. The crude product was purified by crystallisation from ethanol, to give a colourless solid as the product. Yield: 5.25 g (95%); δ_H (CDCl$_3$): 7.74 (1H, dd, H^{11}, $^3J_{HH}$ 8.5, $^4J_{HH}$ 2), 7.57 (1H, d, H^7, $^4J_{HH}$ 2), 6.95 (2H, AA′XX′, H^3, $J_{AA'XX'}$ 9), 6.85 (1H, d, H^{10}, $^3J_{HH}$ 8.5), 6.75 (2H AA′XX′, H^2, $J_{AA'XX'}$ 9), 5.15 (1H, s, OH), 4.01 and 4.00 (4H, t, H^{12}), 1.80 (4H, qt, H^{13}), 1.40 (4H, m, H^{14}), 1.25 (16H, m, H$^{15-18}$), 0.83 (6H, t, H^{19}); δ_C (CDCl$_3$): 166.1(C^5), 153.9(C^1), 153.7(C^9), 148.6(C^8), 144.2(C^4), 124.5(C^3), 122.5(C^{11}), 121.5(C^6), 116.2(C^2), 114.6(C^7), 112.0(C^{10}), 69.4 and 69.1(C$^{12a\ and\ b}$), 31.8, 29.4, 29.3, 29.2, 29.0, 26.0, 22.7(C$^{13-18}$), 14.1(C^{19}).

Synthesis of the 4-(3,4,5-trialkoxybenzoyloxy)phenols

All derivatives were prepared similarly and one example is given. All other derivatives were obtained in yields ranging from 80–95%.



11c

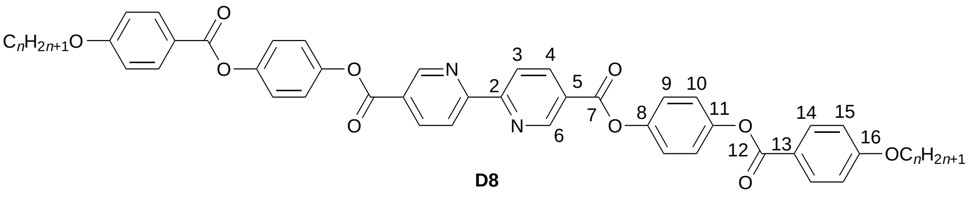
4-[3,4,5-Tris(octyloxy)benzoyloxy]phenol 11c. Compound **6c** (3.9 g, 5.7 mmol) was dissolved in freshly distilled THF (150 cm^3) and triethylamine (1 cm^3) and 10% wet Degassu Pd/C catalyst (0.05 g) was added. The reaction flask was evacuated and placed under hydrogen (three times), before being stirred at room temp. under an atmosphere of hydrogen. After the calculated amount of hydrogen had been taken up the catalyst was removed by filtration through Celite and the solvent was evaporated. The crude product was purified by flash chromatography on silica gel using THF as the eluent. Yield: 3.37 g (quantitative); δ_H (CDCl$_3$) 7.38 (2H, s, H^7), 7.03 (2H, AA′XX′, H^3, $J_{AA'XX'}$ 9), 6.83 (2H, AA′XX′, H^2, $J_{AA'XX'}$ 9), 5.18 (1H, s, OH), 4.02 (6H, t, H^{10}), 1.80 and 1.75 (6H, qt, H$^{11a\ and\ b}$), 1.45 (6H, m, H^{12}), 1.30 (24H, m, H$^{13-16}$), 0.85 (9H, t, H^{17}); δ_C (CDCl$_3$): 166.2(C^5), 153.8(C^1), 152.9(C^8), 144.1(C^4), 142.8(C^9), 123.9(C^6), 122.5(C^3), 116.2(C^2), 108.5(C^7), 73.7(C^{10a}), 69.3(C^{10b}), 31.9, 31.8, 31.6, 30.3, 29.5, 29.4, 29.3, 26.9, 26.1, 22.7 (C$^{11-16}$), 14.1(C^{17}).

Synthesis of the bis[4-(4-alkoxybenzoyloxy)phenyl] 2,2′-bipyridine-5,5′-dicarboxylates

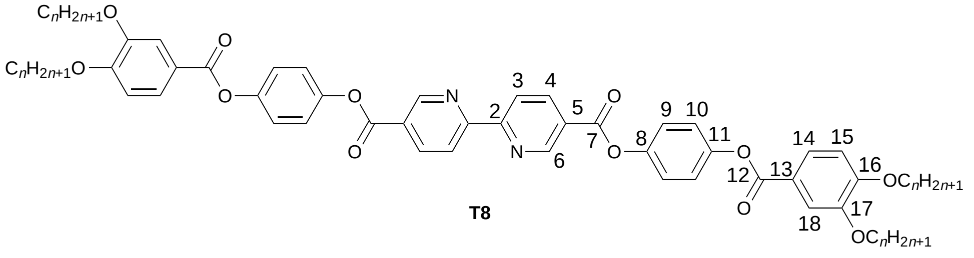
All derivatives were prepared similarly and one example is given. Yields and elemental analyses are collected in Table 5. No ^{13}C NMR data could be obtained for any of these materials due to poor product solubility.

Table 5 Yields and analytical data

		(Calc. %)		Found %			
n	Yield (%)	C		H		N	
D1	20	(69.0)	67.6	(4.1)	4.0	(4.0)	4.2
D4	15	(70.8)	69.5	(5.2)	5.2	(3.6)	3.5
D8	18	(72.6)	72.4	(6.3)	6.3	(3.1)	3.0
D12	12	(74.1)	73.2	(7.2)	7.2	(2.8)	2.8
D14	12	(74.7)	74.3	(7.6)	7.5	(2.6)	2.7
T1	20	(66.7)	64.4	(4.3)	4.2	(3.7)	3.6
T2	15	(68.0)	67.4	(5.0)	5.0	(3.5)	3.3
T3	8	(69.1)	68.9	(5.6)	5.6	(3.2)	3.2
T4	18	(70.1)	69.6	(6.1)	6.1	(3.0)	3.0
T5	8	(71.0)	71.0	(6.6)	6.7	(2.9)	2.8
T6	22	(71.8)	71.8	(6.9)	7.1	(2.7)	2.6
T7	22	(72.5)	72.3	(7.4)	7.2	(2.5)	2.5
T8	25	(73.1)	73.3	7.7	7.9	(2.4)	2.5
T9	19	(73.7)	73.4	(8.0)	7.9	(2.3)	2.3
T10	10	(74.3)	74.0	(8.3)	8.2	(2.2)	2.2
T11	32	(74.9)	74.6	(8.6)	8.5	(2.1)	2.1
T12	5	(75.2)	75.0	(8.8)	8.7	(2.0)	2.0
T13	5	(75.2)	75.2	(9.2)	9.0	(2.0)	2.0
T14	18	(76.0)	75.7	(9.2)	9.0	(1.9)	1.8
H1	20	(64.7)	64.4	(4.4)	4.5	(3.4)	3.5
H4	12	(69.6)	69.4	(6.8)	6.9	(2.6)	2.6
H8	18	(72.6)	72.4	(6.3)	6.3	(3.1)	3.0
H12	12	(73.5)	73.2	(8.6)	8.9	(2.0)	2.0
R8	24	(72.6)	71.6	(6.3)	6.1	(3.1)	3.4



D8



T8

Bis[4-(4-octyloxybenzoyloxy)phenyl] 2,2′-bipyridine-5,5′-dicarboxylate D8. The apparatus was flame dried prior to use. 2,2′-Bipyridine-5,5′-dicarboxylic acid dichloride (2.4 g, 3.6 mmol), and 4-(4-octyloxybenzoyloxy)phenol (1.74 g 7.1 mmol) were placed in freshly distilled toluene (50 cm^3). Triethylamine (1 cm^3) was added and the reaction heated at reflux, under nitrogen overnight. The solvent was evaporated and dichloromethane added. This was extracted against 10% ammonia solution. The aqueous phase was then extracted with dichloromethane (2 × 100 cm^3), the organic extracts combined and the solvent evaporated to give a crude dark brown solid. The solid was placed in ethyl acetate, heated to reflux, allowed to cool to room temp. and the solid collected by centrifugation (× 2). The solid was then heated to reflux in 1,4-dioxane and collected (× 2), giving the product as a cream solid. δ_H (CDCl$_3$) 9.40 (2H, dd, H^6, $^4J_{HH}$ 2.5, $^5J_{HH}$ 1), 8.64 (2H, dd, H^3, $^3J_{HH}$ 8.5, $^5J_{HH}$ 1), 8.54 (2H, dd, H^4, $^3J_{HH}$ 8.5, $^4J_{HH}$ 2.5), 8.06 (4H, AA′XX′, H^{14}, $J_{AA'XX'}$ 9), 7.22 (8H, AA′XX′, H$^{9\text{ and }10}$), 6.90 (4H, AA′XX′, H^{15}, $J_{AA'XX'}$ 9); The alkyl region was unresolvable.

Synthesis of the bis[4-(3,4-dialkoxybenzoyloxy)phenyl] 2,2′-bipyridine-5,5′-dicarboxylates

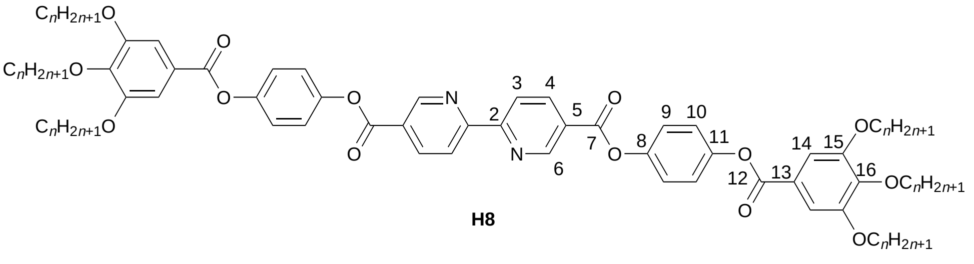
All derivatives were prepared similarly and one example is given. Yields and elemental analyses are collected in Table 5.

Bis{4-[3,4-bis(octyloxy)benzoyloxy]phenyl} 2,2′-bipyridine-5,5′-dicarboxylate T8. The apparatus was flame dried prior to use. 2,2′-Bipyridine-5,5′-dicarboxylic acid dichloride (0.9 g, 3.2 mmol), and 4-[3,4-bis(octyloxy)benzoyloxy]phenol (3 g, 6.4 mmol) were placed in freshly distilled toluene (50 cm^3). Triethylamine (1 cm^3) was added and the reaction heated at reflux, under nitrogen overnight. The solvent was evaporated and dichloromethane added. This was extracted against 10% ammonia solution. The aqueous phase was then extracted with dichloromethane (2 × 100 cm^3), the organic extracts combined and the solvent evaporated to give a crude dark brown solid. The solid was placed in ethyl acetate, heated to reflux, allowed to cool to room temp. and the solid collected by centrifugation (× 2), before being crystallised from 1,4-dioxane. The crude product was placed in chloroform, heated to reflux and filtered hot through Celite. The colourless solution was evaporated and the solid recrystallised (× 2) from 1,4-dioxane, giving the product as a cream solid. Yield: 0.62 g (17%); δ_H (CDCl$_3$): 9.43 (2H, dd, H^6, $^4J_{HH}$ 2, $^5J_{HH}$ 1), 8.65 (2H, dd, H^3, $^3J_{HH}$ 8.5, $^5J_{HH}$ 1), 8.55 (2H, dd, H^4, $^3J_{HH}$ 8.5, $^4J_{HH}$ 2), 7.78 (2H, dd, H^{18}, $^3J_{HH}$ 8.5, $^4J_{HH}$ 2), 7.60 (2H, d, H^{14}, $^4J_{HH}$ 2), 7.29 and 7.22 (8H, AA′XX′, H$^{9\text{ and }10}$, $J_{AA'XX'}$ 9), 6.88 (2H, d, H^{17}, $^3J_{HH}$ 8.5), 4.03 and 4.02 (8H, t, H$^{19a\text{ and }b}$), 1.60 (8H, m, H^{20}), 1.43 (8H, m, H^{21}), 1.30 (32H, m, H$^{22-25}$), 0.95 (12H, t, H^{26}); δ_C (CDCl$_3$): 164.9(C^{12}), 163.7(C^7), 158.7(C^2), 153.9(C^{16}), 151.2(C^6), 148.9 and 148.6, 147.8(C$^{8,11\text{ and }15}$), 138.8(C^4), 125.8(C^5), 124.4(C^3), 122.9 and 122.5(C$^{9\text{ and }10}$), 121.6(C^{18}), 121.2(C^{13}), 114.5(C^{14}), 111.9(C^{17}), 69.3 and 69.1(C$^{19a\text{ and }b}$), 31.8, 29.4, 29.3, 29.1, 29.0, 26.0, 22.7 (C$^{20-25}$), 14.1(C^{26}).

The synthesis of the bis[4-(3,4,5-trialkyloxybenzoyloxy)-phenyl] 2,2′-bipyridine-5,5′-dicarboxylates

All derivatives were prepared similarly and one example is given. Yields and elemental analyses are collected in Table 5.

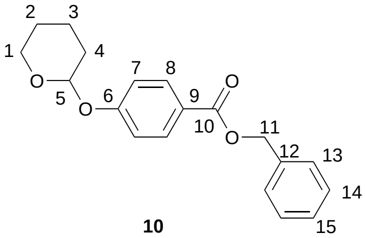
Bis{4-[3,4,5-tris(octyloxy)benzoyloxy]phenyl} 2,2′-bipyridine-5,5′-dicarboxylate H8. The apparatus was flame dried prior to use. 2,2′-Bipyridine-5,5′-dicarboxylic acid dichloride (0.25 g, 0.9 mmol), and 4-[3,4,5-tris(octyloxy)benzoyloxy]-phenol (10.6 g 1.8 mmol) were placed in freshly distilled toluene (50 cm^3). Triethylamine (1 cm^3) was added and the reaction heated at reflux, under nitrogen overnight. The solvent was evaporated and dichloromethane added. This was extracted against 10% ammonia solution. The aqueous phase was then extracted with dichloromethane (2 × 100 cm^3), the organic extracts combined and the solvent evaporated to give a crude dark brown solid. The solid was placed in ethyl acetate, heated to reflux, allowed to cool to room temp. and the solid collected by centrifugation (× 2), before being crystallised from 1,4-dioxane. The crude product was placed in chloroform, heated to reflux and filtered hot through Celite. The colourless solution was evaporated and the solid recrystallised (× 2) from 1,4-dioxane, giving the product as a cream solid. Yield: 0.23 g (19%); δ_H (CDCl$_3$): 9.50 (2H, dd, H^6, $^4J_{HH}$ 2, $^5J_{HH}$ 1), 8.73 (2H, dd, H^3, $^3J_{HH}$ 8.5, $^5J_{HH}$ 1), 8.63 (2H, dd, H^4, $^3J_{HH}$ 8.5, $^4J_{HH}$



H8

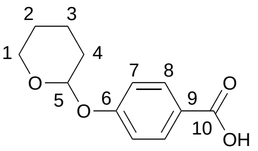
2), 7.42 (4H, s, H^{14}), 7.35 and 7.30 (8H, AA′XX′, $H^{9 \text{ and } 10}$, $J_{AA'XX'}$ 9), 4.08 and 4.06 (12H, t, $H^{17a \text{ and } b}$), 1.86 and 1.80 (12H, m, $H^{18a \text{ and } b}$), 1.49 (12H, m, H^{19}), 1.30 (48H, m, H^{20-23}), 0.90 (18H, t, H^{24}); δ_C ($CDCl_3$): 164.9(C^{12}), 163.6(C^7), 158.8(C^2), 153.0(C^{15}), 151.1(C^6), 148.8 and 148.0($C^{8 \text{ and } 11}$), 143.3(C^{16}), 138.7(C^4), 125.9(C^5), 123.6(C^{13}), 122.9 and 122.5($C^{9 \text{ and } 10}$), 121.7(C^3), 108.7(C^{14}), 73.6(C^{17a}), 69.3(C^{17b}), 31.9, 31.8, 30.4, 29.5, 29.4, 29.3, 26.1, 22.7 (C^{18-23}), 14.1(C^{24}).

Synthesis of the reversed ester, R8



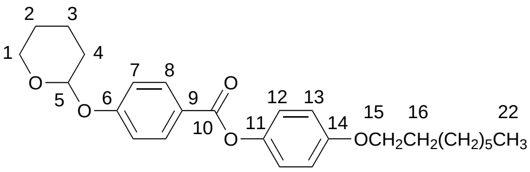
10

Benzyl 4-(tetrahydropyran-2-yloxy)benzoate 10. 3,4-Dihydro-2*H*-pyran (20 cm^3, 0.22 mol) and ethyl acetate saturated with HCl(g) (3.5 cm^3) was added to a solution of benzyl 4-hydroxybenzoate (10 g, 0.044 mol) in ethyl acetate (100 cm^3). The reaction was stirred at room temp. for 12 h before the solvent was removed. Flash chromatography on neutral alumina using dichloromethane as the eluent gave the product as a colourless oil which solidified on standing. Yield: 12 g (88%); mp 68–71 °C (decomp.); δ_H ($CDCl_3$): 8.03 (2H, AA′XX′, H^8, $J_{AA'XX'}$ 9), 7.40 (5H, m, H^{13-17}), 7.06 (2H, AA′XX′, 7^H, $J_{AA'XX'}$ 9), 5.50 (1H, t, H^5, $^3J_{HH}$ 3), 3.88 (1H, m, H^{1eq}), 3.62 (1H, m, H^{1ax}), 2.01, 1.90 and 1.70 (6H, m, $H^{2,3 \text{ and } 4}$); δ_C ($CDCl_3$): 166.2(C^{10}), 161.0(C^6), 136.4(C^{12}), 131.6(C^8), 128.6, 128.12 and 128.07(C^{13-15}), 123.3(C^9), 115.9(C^7), 96.1(C^5), 66.4(C^{11}), 62.0(C^1), 30.1(C^4), 25.1(C^2), 18.5(C^3).



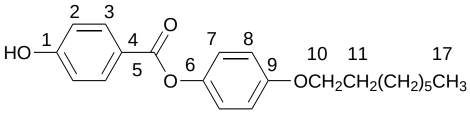
11

4-(Tetrahydropyran-2-yloxy)benzoic acid 11. To a solution of compound **10** (11.5 g, 0.037 mol) in freshly distilled THF, wet Degassu Pd/C catalyst was added (10%, 50 mg). The reaction was placed under vacuum and hydrogen (× 3) before being left to stir under an atmosphere of hydrogen at room temp. After hydrogen (900 cm^3) had been used the reaction was filtered through Celite and the solvent evaporated. The crude product was crystallised from ethanol to give a colourless solid as the product. Yield: 6 g (73%); mp 159 °C (decomp.); δ_H ($CDCl_3$): 8.05 (2H, AA′XX′, H^8, $J_{AA'XX'}$ 9), 7.10 (2H, AA′XX′, 7^H, $J_{AA'XX'}$ 9), 5.55 (1H, t, H^5, $^3J_{HH}$ 3), 3.88 (1H, dt, H^{1eq}), 3.62 (1H, m, H^{1ax}), 2.01, 1.90 and 1.70 (6H, m, $H^{2,3 \text{ and } 4}$); δ_C ($CDCl_3$): 172.0(C^{10}), 161.6(C^6), 132.2(C^8), 122.4(C^9), 116.0(C^7), 96.1(C^5), 66.4(C^{11}), 62.1(C^1), 30.1(C^4), 25.1(C^2), 18.5(C^3).



12

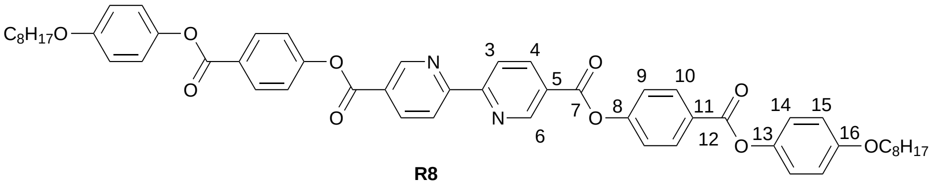
4-Octyloxyphenyl 4′-(tetrahydropyran-2-yloxy)benzoate 12. Compound **11** (2.5 g, 0.012 mol), 4-octyloxyphenol (2.5 g 0.012 mol), and dicyclohexylcarbodiimide (DCC) (2.32 g 0.012 mol) were dissolved in dichloromethane (80 cm^3). 4-(*N,N*-Dimethylamino)pyridine (0.14 g 1.2 mmol) was then added and the reaction stirred at room temp. overnight. The colourless precipitate was removed by filtration and the solvent evaporated. Crystallisation from ethanol (× 2) gave the product as a colourless solid. Yield: 4 g (84%); mp 81 °C (sublimes); δ_H ($CDCl_3$): 8.13 (2H, AA′XX′, H^8, $J_{AA'XX'}$ 9), 7.10 (2H, AA′XX′, H^7, $J_{AA'XX'}$ 9), 7.15 (2H, AA′XX′, H^{13}, $J_{AA'XX'}$ 9), 6.90 (2H, AA′XX′, H^{12}, $J_{AA'XX'}$ 9), 5.55 (1H, t, H^5, $^3J_{HH}$ 3), 3.95 (2H, t, H^{15}, $^3J_{HH}$ 6.5), 3.88 (1H, m, H^{1eq}), 3.62 (1H, m, H^{1ax}), 2.05, 1.90 and 1.70 (6H, m, $H^{2,3 \text{ and } 4}$), 1.78 (2H, m, H^{16}), 1.45 (2H, m, H^{17}), 1.30 (8H, m, H^{18-21}), 0.90 (3H, t, H^{22}); δ_C ($CDCl_3$): 165.3(C^{10}), 161.4(C^6), 156.8(C^{14}), 144.4(C^{11}), 132.1(C^8), 122.7(C^9), 122.4(C^{12}), 116.1(C^7), 115.1(C^{13}), 96.1(C^5), 68.5(C^{15}), 62.0(C^1), 30.1(C^4), 25.1(C^2), 18.5(C^3), 31.8, 29.4, 29.3, 29.2, 26.1, 22.7(C^{16-21}), 14.1(C^{22}).



13

4-Octyloxyphenyl 4-hydroxybenzoate 13. Compound **12** (4 g, 9.4 mmol) and oxalic acid (50 mg) were placed in methanol–water (100 cm^3; 9 : 1), and the reaction was heated at reflux for 72 h. The reaction was cooled to room temp. and the resulting colourless needles collected and washed with ethanol–water (1 : 1), to give the pure product. The mother liquor was evaporated and the resulting colourless solid crystallised from ethanol–water to give more product as colourless needles. Yield: 2.95 g (95%); mp 159 °C; δ_H ($CDCl_3$): 8.10 (2H, AA′XX′, H^3, $J_{AA'XX'}$ 9), 7.10 (2H, AA′XX′, H^7, $J_{AA'XX'}$ 9), 6.89 and 6.93 (4H, AA′XX′, $H^{2 \text{ and } 8}$, $J_{AA'XX'}$ 9), 5.80 (1H, s, OH), 3.95 (2H, t, H^{10}, $^3J_{HH}$ 6.5), 1.78 (2H, qt, H^{11}), 1.45 (2H, m, H^{12}), 1.30 (8H, m, H^{13-16}), 0.90 (3H, t, H^{17}); δ_C ($CDCl_3$): 165.5(C^5), 162.3(C^1), 156.7(C^9), 144.5(C^6), 132.3(C^3), 122.5(C^7), 120.6(C^4), 115.5, 115.0($C^{2 \text{ and } 8}$), 68.4(C^{10}), 31.8, 29.3, 29.2, 26.0, 22.6(C^{11-16}), 14.1(C^{17}).

Bis[(4-octyloxybenzoyloxy)phenyl] 2,2′-bipyridine-5,5-dicarboxylate R8. This was prepared from compound **13** using the procedures for esterification with 2,2′-bipyridine-5,5′-dicarboxylic acid dichloride described above. This gave the product as a cream solid. Analytical data are found in Table 5. δ_H ($CDCl_3$): 9.51 (2H, dd, H6, $^4J_{HH}$ 2, $^5J_{HH}$ 1), 8.75 (2H, dd, H3, $^3J_{HH}$ 8.5, $^5J_{HH}$ 1), 8.64 (2H, dd, H4, $^3J_{HH}$ 8.5, $^4J_{HH}$ 2), 8.33 (4H, AA′XX′, H10, $J_{AA'XX'}$ 9), 7.44 (4H, AA′XX′, H9, $J_{AA'XX'}$ 9),



R8

7.14 (4H, AA′XX′, H14, $J_{AA'XX'}$ 9), 6.95 (4H, AA′XX′, H15, $J_{AA'XX'}$ 9), 3.98 (4H, t, H17, $^3J_{HH}$ 6.5), 1.85 (4H, qt, H18), 1.50 (4H, m, H19), 1.27 (16H, m, H20–23), 0.90 (12H, t, H24); MS *m/z:* [M+] 892.39; no ^{13}C NMR data could be obtained due to the product's insolubility.

Support from the EPSRC and the University of Exeter is gratefully acknowledged.

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Paper 7/06400D; *Received* 2nd *September*, 1997