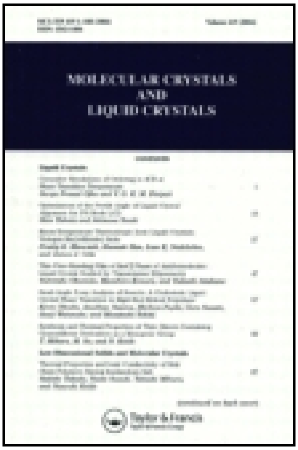

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The Liquid-Crystalline Properties of Copper(II) Complexes of β-Diketones

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The Liquid-Crystalline Properties of Copper(II) Complexes of β-Diketones†

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The preparation of several novel copper(II) complexes of β-diketones is described. Complexes of increasing molecular width have been prepared and the effect of molecular shape on the mesophase types and transition temperatures is discussed. All the liquid-crystalline complexes-exhibit nematic mesophases (monotropic for three-ring ligands and enantiotropic for four-ring ligands) with one exception which shows a smectic A phase. The liquid crystalline properties of the ligands are also discussed with respect to the way in which their molecular geometry affects the type of mesophase formed.

Keywords: Copper(II) complexes, β-diketones, metallo-mesogens

INTRODUCTION

Over the past ten years increasing interest has been aroused in the field of metal-containing liquid-crystals and many mesogenic compounds have been prepared containing a variety of transition metals.

Copper(II) complexes of β-diketones have been reported extensively by Ohta *et al.*[1–7] and by Giroud-Godquin *et al.*[8–11] Many of the complexes described have the general Structure A and some of these are reported to show discotic lamellar phases. The complex with R = $C_{12}H_{25}O$ has been studied by X-ray diffraction and is reported to show a "discotic lamellar phase" with a focal-conic texture analogous to the smectic A phase shown by calamitic systems.[7] The crystal structure of the complex in which R = $C_8H_{17}O$ has also been studied by X-ray diffraction.[12,13]

A most unusual feature of some copper(II) complexes of β-diketones was reported a few years ago by Chandrasekhar *et al.*[14–16] who produced unsymmetrical complexes of general Structure B which exhibit biaxial, paramagnetic, monotropic nematic phases. The nematic phase shown by the complex in which R = OEt was completely miscible with 4-cyano-4″-pentyl-*p*-terphenyl (5CT, a calamitic nematogen) and so the molecules could be regarded as having "an elongated structure

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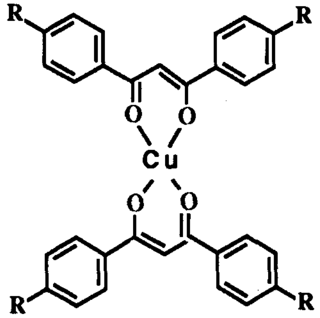
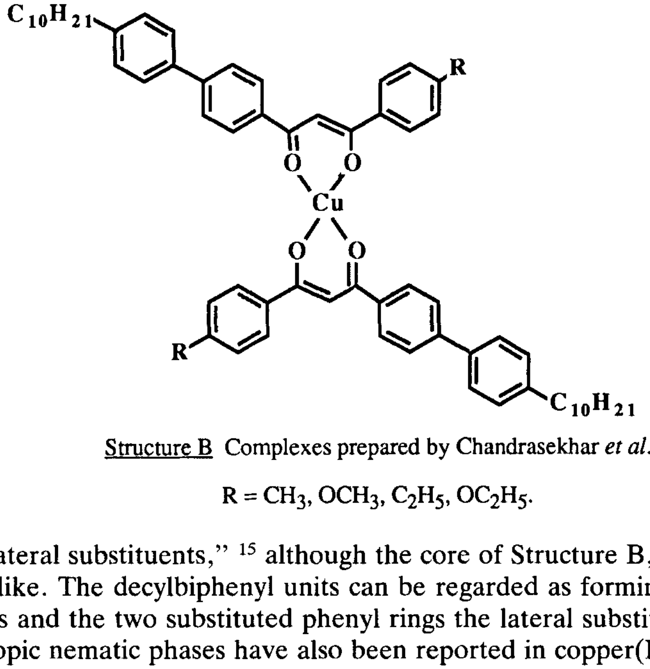
† Presented at The Thirteenth International Liquid Crystal Conference, Vancouver, B.C., Canada, 22–27th July, 1990.



Structure A R= alkyl or alkoxy



Structure B Complexes prepared by Chandrasekhar *et al.*[15-17]

R = CH_3, OCH_3, C_2H_5, OC_2H_5.

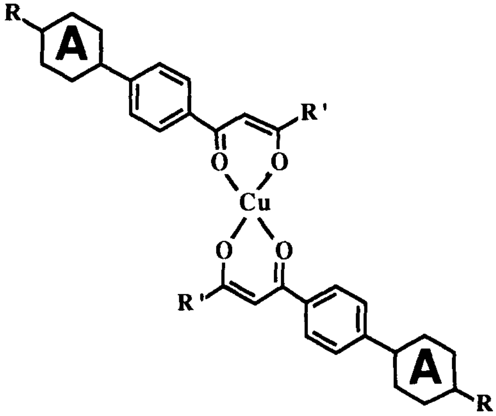
with two lateral substituents,"[15] although the core of Structure B, as in Structure A, is disc-like. The decylbiphenyl units can be regarded as forming the long molecular axis and the two substituted phenyl rings the lateral substituents.

Monotropic nematic phases have also been reported in copper(II) β-diketonate complexes of the type bis-(1-[4-(*trans*-4-alkylcyclohexyl)phenyl]-3-alkylpropane-1,3-dionato)copper(II)[17], i.e., as shown in Structure C with A = cyclohexyl, R = heptyl, pentyl or propyl and R′ = methyl to octyl. All nematic phases reported for those compounds and for all the copper(II) complexes of β-diketones reported to date have been monotropic, although at the recent Thirteenth International Liquid Crystal Conference in Vancouver, enantiotropic nematic phases for some copper(II) complexes of β-diketones were reported by Ohta.[18]

Copper(II) complexes of β-diketones generally have melting points in the range 150–250°C and at these temperatures thermal decomposition usually occurs. The decomposition is slow for material protected between a microscope slide and a cover-slip, but is more rapid for exposed material. Such high temperatures make it difficult to study the properties of the complexes in their mesophase and an additional common problem is that many complexes show monotropic phases and recrystallisation at unpredictable temperatures occurs. The investigations we report here have two main aims designed to overcome these problems and so permit additional physical measurements to be carried out. Firstly, an attempt was made to alter Structure B in order to produce complexes with lower melting points without appreciably affecting the clearing points (N-I transition temperatures). In this way it was hoped to obtain complexes showing enantiotropic nematic phases. Secondly, the length-to-breadth ratios of the complexes were altered by changing the size of the lateral substituent to make the molecules more 'rod-like' or more 'disc-like' (Structures C and D respectively). The complexes with an increased length-to-breadth ratio were expected to be more likely to form calamitic nematic phases while those with a decreased length-to-breadth ratio should be less likely to form calamitic nematic phases and more inclined to generate discotic phases[2,4,5,8,18] and so it was hoped that the change from calamitic to discotic character could be identified.

It was found that the novel series of copper(II) complexes based on Structure B still exhibited monotropic nematic phases and, surprisingly, the mesomorphic complexes of Structure C also exhibited monotropic nematic phases only, but when the molecule was broadened (Structure D), enantiotropic phases were generated exclusively.

The synthetic routes to the ligands are outlined in Schemes 1, 2, and 3. The ligands in Schemes 1 and 3 were prepared by reacting the appropriate methyl ketone and methyl ester with sodium hydride according to the method of Kopecky *et al.*[19] Scheme 2 shows the route to the butane-1,3-diones which were prepared from substituted benzoic acids. The acid chlorides were prepared by the method of Barton *et al.*[20] and were not purified before use. The ligands were prepared by the method described by Kunieda *et al.*[21]

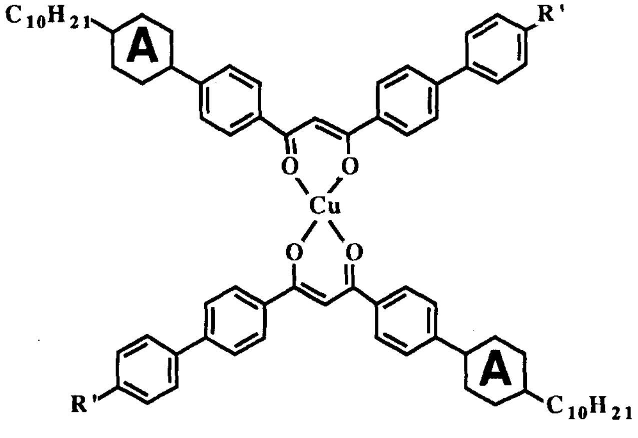


Structure C Complexes with a more 'rod-like' structure

Ring A = phenyl, R = $C_{10}H_{21}$ and R' = H or CH_3

Ring A = 3-fluorophenyl, R = $C_8H_{17}O$ and R' = CH_3

Ring A = cyclohexyl, R = C_7H_{15} and R' = CH_3



Structure D Complexes with a more 'disc-like' structure

Ring A = phenyl and R' = $C_{10}H_{21}$, CH_3, C_2H_5 and F.

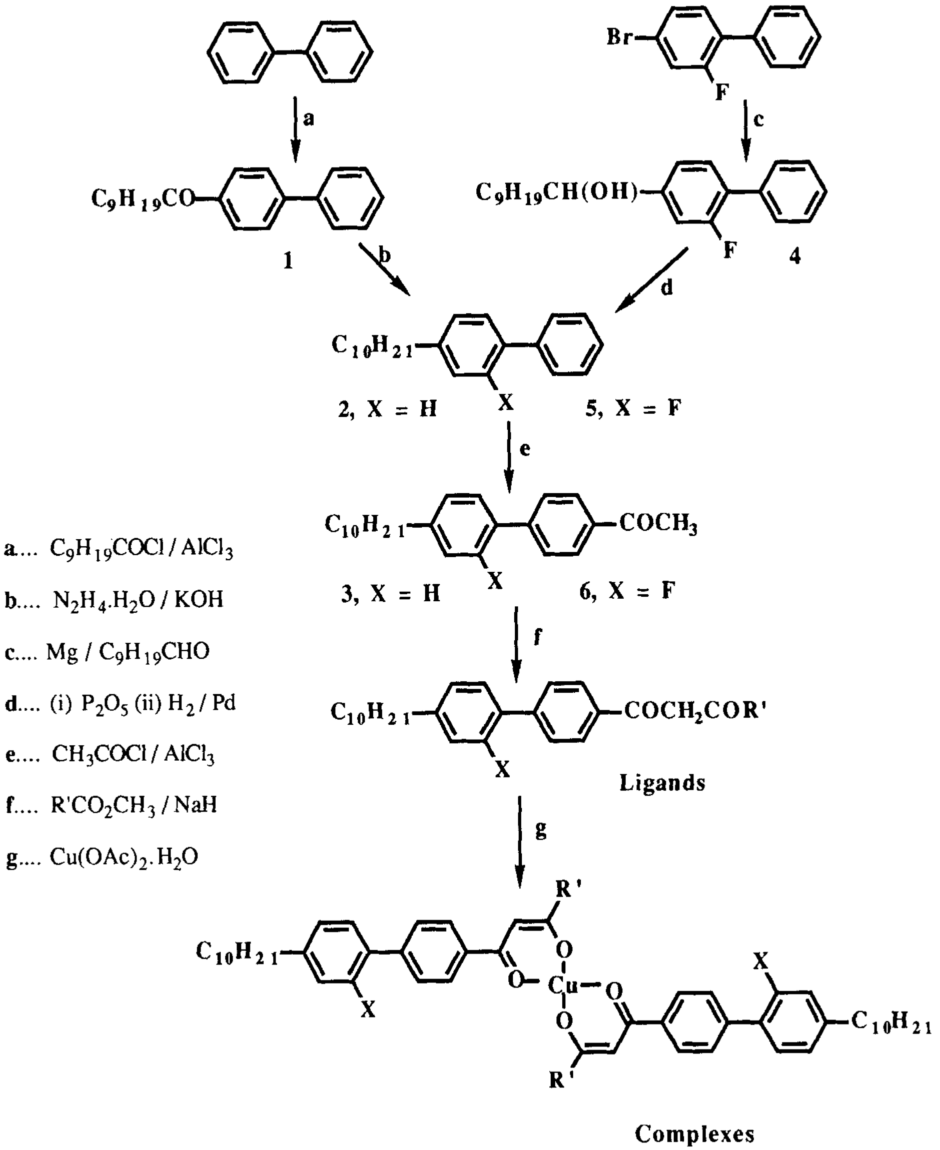
Ring A = cyclohexyl and R' = OCH_3.

The copper(II) complexes were all prepared by reaction of the β-diketone ligand with copper(II) acetate monohydrate in tetrahydrofuran (THF). The crude complexes were purified by recrystallisation from acetone, THF or acetone/THF mixtures, depending on their solubility. Mass spectral values are not quoted for the complexes as the compounds decompose and a molecular ion peak for the ligand is obtained. ^1H nmr spectra are also not given for the complexes because of the paramagnetic nature of the copper atom.

RESULTS AND DISCUSSION

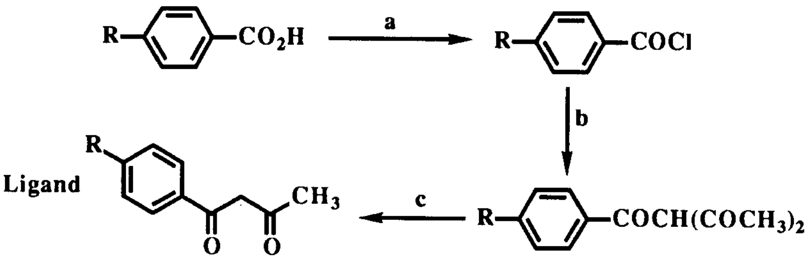
Many of the β-diketone ligands show mesomorphic properties and their transition temperatures are given in the Table. Those β-diketones of the type shown in Structure E in which R′ is methyl are all mesomorphic regardless of the nature of the R group or the ring system A (see compounds **21–23**).

These compounds have a major core system with the diketone unit as a terminal group and, although direct internal comparison within this set is impossible because of the multiple changes in types of ring A and group R, their clearing points (135, 97 and 142°C) are moderately high; the cyclohexyl-containing compound **22** shows a nematic phase whereas the biphenyl-based compounds (**21** and **23**) show orthogonal smectic phases. When a phenyl unit is incorporated into the 'terminal' group R′ (compare compounds **10** and **21**) the smectic clearing point is markedly *depressed*; normally the introduction of a phenyl group into a linear molecule would have caused a significant elevation of the clearing point, possibly by more than 100–150°C. One might conclude from this that the R′ group, although it can conjugatively interact with the rest of the molecule and so increase molecular



X	R'	Ligand	Complex
H-	-H	9	15
H-	$-PhCH_3$	10	16
H-	$-PhOCH_3$	11	17
H-	$-PhPhC_{10}H_{21}$	12	18
H-	$-PhPhC_2H_5$	13	19
F-	$-PhCH_3$	14	20

Scheme 1



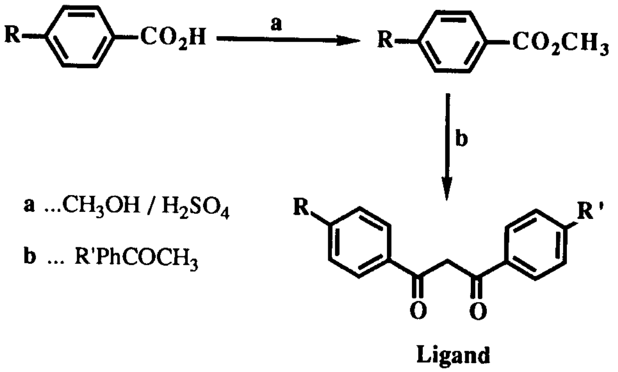
a ... $(COCl)_2$

b ...NaH / $(CH_3CO)_2CH_2$

c ... NH_4Cl / H_2O / NH_3 (aq)

R	Ligand	Complex
$C_{10}H_{21}Ph$-	21	24
$C_7H_{15}Ch$-	22	25
(4-$C_8H_{17}O$)(3-F)Ph-	23	26

Scheme 2



a ...CH_3OH / H_2SO_4

b ... $R'PhCOCH_3$

R	R'	Ligand	Complex
$C_7H_{15}Ch$-	-OCH_3	31	38
$C_7H_{15}Ch$-	-$PhOCH_3$	32	39
$C_{10}H_{21}Ph$-	-$PhCH_3$	33	40
$C_{10}H_{21}Ph$-	-H	34	41
$C_{10}H_{21}Ph$-	-F	35	42
$C_{10}H_{21}Ph$-	-PhF	36	43
(4-$C_8H_{17}0$)(3-F)Ph-	-OCH3	37	44

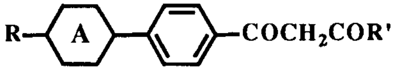
Scheme 3

TABLE

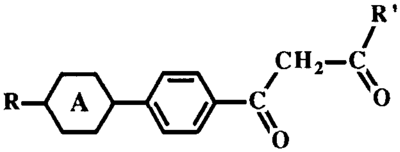
Transition temperatures (°C) for β-dicarbonyl ligands and their copper(II) complexes†

Ligand Structure.	Ligand No.	Transition Temperatures of Ligands.							Complex No.	Transition Temperatures of Complexes.				
		K_1	K_2	S_E	S_B	S_A	N	I		K_1	K_2	S_A	N	I
$C_{10}H_{21}PhPhCOCH_2CHO$	**9**	impure							**15**	*160(d)				*
$C_{10}H_{21}PhPhCOCH_2COCH_3$[a]	**21**	* 86		* 97	* 107	* 135		*	**24**	* 191			[*160]	*
$C_{10}H_{21}PhPhCOCH_2COPhCH_3$	**10**	* 84	* 97			(*93)		*	**16**	* 197/221			(*167)	*
$C_{10}H_{21}PhPhCOCH_2COPhPhCH_3$	**33**	* 186						*	**40**	* 195			* 206	*
$C_{10}H_{21}PhPhCOCH_2COPhOCH_3$[a]	**11**	* 114						*	**17**	* 188/192			(* 172)	*
$C_{10}H_{21}(2\text{-}F)PhPhCOCH_2COPhCH_3$	**14**	* 44/54					* 60	*	**20**	* 157/192			(* 146)	*
$C_9H_{19}OPhPhCOCH_2COPhCH_3$	**45**	* 140/147					(*133)	*	**46**	* 219/230			(* 202)	*
$C_7H_{15}ChPhCOCH_2COPhOCH_3$	**31**	* 37	* 113				(*106)	*	**38**	* 254			(* 212)	*
$C_{10}H_{21}PhPhCOCH_2COPhH$	**34**	* 60				* 98		*	**41**	* 198			(* 156)	*
$C_{10}H_{21}PhPhCOCH_2COPhF$	**35**	* 88				* 122		*	**42**	* 189/193			(* 175)	*
$C_8H_{17}O(3\text{-}F)PhPhCOCH_2COPhOCH_3$	**37**	* 125				(* 119	*121)	*	**44**	* 225	* 231		(* 202)	*
$C_{10}H_{21}PhPhCOCH_2COPhPhC_{10}H_{21}$	**12**	* 188						*	**18**	* 255				*
$C_{10}H_{21}PhPhCOCH_2COPhPhC_2H_5$	**13**	* 185						*	**19**	* 226			* 228	*
$C_7H_{15}ChPhCOCH_2COPhPhOCH_3$	**32**	* 173					* 178	*	**39**	* 247			* 280	*
$C_{10}H_{21}PhPhCOCH_2COPhPhF$	**36**	* 199						*	**43**	* 155		* 250		*
$C_7H_{15}ChPhCOCH_2COCH_3$	**22**	* 68					* 97	*	**25**	* 140	* 193		(*192)	*
$C_8H_{17}O(3\text{-}F)PhPhCOCH_2COCH_3$	**23**	* 99				* 142		*	**26**	* 180	* 198		(*191)	*

† Ch = *trans*-1,4-disubstituted cyclohexyl ring; Ph = 1,4-disubstituted benzene ring; (d) = decomposes. ( ) monotropic transition; [ ] virtual value. An entry such as 197/221 denotes two crystal forms melting at 197 and 221°C respectively. [a] Compound also reported in Reference 15.



Structure E β-diketone ligand; R=alkyl or alkoxy, A=phenyl or cyclohexyl and R'=methyl or 4-substituted phenyl/biphenyl.



Structure F

polarisability, is structurally held almost like a lateral group, as shown in Structure F, to give a bent molecule. [A comparison, similar to but less exact than that made for compounds **10** and **21**, can be made between compounds **22** and **31** and between compounds **23** and **37**. In the first case, the phenyl group introduced into the R′ group gives only a 9°C increase in clearing point, but the substituent on the phenyl ring has been changed to methoxy. In the second case, the introduction of the phenyl group into R′ has caused the clearing point to *decrease* by 21°C and the stability of the smectic phase to *decrease* by 23°C; a nematic phase has been revealed showing that the stability of the smectic phase has been affected more than that of the nematic phase.] The incorporation of a second phenyl ring into R′ (to give compound **33**) gives a high melting ligand which only supercools to 182°C without a mesophase being detected. However, another indication of the effect caused by a second phenyl ring in the R′ group is revealed by comparison of the values for compounds **31** and **32** which shows that, surprisingly, the nematic clearing point is increased by 72°C. As the size of the 'lateral' substituent, R′, has increased so the stability of the smectic phase has decreased (cf, compounds **10/21** and **23/37**), but for nematogenic molecules with an even greater bend (cf, compounds **31** and **32**) the mesophase stability has increased.

A possible explanation for this phenomenon could be that as the ligand molecules become increasingly bent and banana-shaped, so they can less easily be incorporated within a layer structure, and smectogenicity is depressed.[22] A bent structure, however, can be more easily accommodated in a less ordered nematic phase, and so the nematic phase stability increases in the typical fashion with the incorporation of a phenyl unit.

Comparison of the values for compounds **11** and **10** again shows the decreased stability of the smectic phase, because the methoxy compound (**11**) would normally have been expected to have a significantly higher clearing point than the methyl analogue (**10**). In this instance the increase is less than 11°C, since compound **11** supercools to 104°C before crystallisation and the increase in the size of the lateral group has more than offset the advantage of increased polarisability.

Comparing the values for compounds **10, 34** and **35** shows that both H and F, which are smaller than CH_3, are better groups in R′, and F, although slightly bigger than H, has the advantage of electronic interaction with the aromatic ring.

Some other comparisons of transition temperatures for the ligands are also of interest: (a) the depression in smectic character and the revelation of a nematic phase by a lateral fluoro substituent (compare compounds **10** and **14**), (b) the expected enhanced mesogenicity conferred by a long alkoxy rather than a long alkyl group (see compounds **10** and **45**).

The transition temperatures of the copper(II) complexes derived from these ligands are also given in the Table. The first group of four complexes (**15, 24, 16,** and **40**) shows the effect on transition temperatures of making the complex gradually more disc-like by increasing the length of group R′ in structure C. Compound **15** is a thermally unstable complex which decomposes at 160°C and compound **24** does not show a mesophase, but a virtual $T_{N\text{-}I}$ value, obtained from mixtures with 5CT (up to 32% wt/wt), has a value of 160°C, which is below the crystallisation temperature of 182°C. Compounds **25** and **26** are similar to compound **24** in having a 'rod-like' structure, and they exhibit monotropic nematic phases at higher temperatures and the nematic phase for complex **25** is almost enantiotropic. Compound **16**, (initially reported by Chandrasekhar *et al.*[14–16]), also shows a monotropic nematic phase with a clearing point of 167°C and the clearing point is slightly higher than the virtual value for compound **24**. However, compound **40** shows an enantiotropic nematic phase with an increase in clearing point of 39°C compared to compound **16**. This is surprising, but similar to some of the results for the ligands which were discussed earlier in that as the size of the 'lateral substituent' is increased and the compound becomes a double biphenyl molecule, so the thermal stability of the nematic phase increases, leading to an enantiotropic nematic phase in compound **40**. It is clear that this trend is not consistent with the molecules of the complex being regarded as 'rod-like' systems carrying lateral substituents.

The miscibilities of representative examples of each type of nematogenic complex (compounds **16, 26** and **19,** corresponding to structures B, C and D respectively) have been tested with 5CT (the non-polar host I35 was also considered for use with compounds **16** and **40,** but they were both immiscible even as 5% wt/wt mixtures). All of the complexes are completely miscible across the phase diagram and at least five mixtures of varying composition were considered in each case. Complexes **16, 26** and **19** were also found to be miscible with each other. Although more detailed miscibility studies are being undertaken, this evidence implies that the nematic phases of the complexes are of the same nature as each other and also of the same nature as the nematic phase of 5CT; however, such a conclusion conflicts with the observations discussed in the previous paragraph.

The six complexes comprising the second group in the table show the transition temperatures for complexes based on structure B. In each case the molecular structure of the ligand has been altered in an attempt to obtain an enantiotropic phase by either reducing the melting point or increasing the stability of the nematic phase compared to that of compound **16**. Lateral fluoro substitution in calamitic systems is known to reduce melting points, and frequently the smectic character of compounds, quite significantly and to affect the nematic character to a lesser extent. The incorporation of a lateral fluoro substituent (compare compounds **20** and **16**) reduces the melting point by 29°C but the clearing point of compound **20** is reduced by 21°C and no dramatic improvement in the nematic window is achieved.

Compound **17**, containing a terminal methoxy group on the phenyl ring, has a melting point 29°C lower than that of compound **16** and its clearing point is 5°C higher. Compound **46,** with a long alkoxy chain on the biphenyl unit, has an increased melting point (by 9°C) and clearing point (by 35°C). Both of these alkoxy substituted systems show changes in melting point and transition temperatures in the desired direction but the effects are too small to give the required result.

Compound **38** shows the effect of a cyclohexyl ring replacing the outer phenyl ring and although the alkyl chain lengths in **38** and **17** are different so that precise comparison is not possible, the indication is that a cyclohexane ring increases the clearing point significantly, but increases the melting point to a greater extent. Compound **41,** without a terminal substituent, has both a lower melting point (by 23°C) and a lower clearing point (by 11°C) than compound **16,** and the terminal fluoro substituent (compound **42**) improves the situation a little further.

The changes made to the structures of complexes with Structure B have proved unsuccessful in generating enantiotropic nematic phases and it appears unlikely that such complexes are capable of providing enantiotropic phases at significantly lower temperatures by minor modifications to structure B.

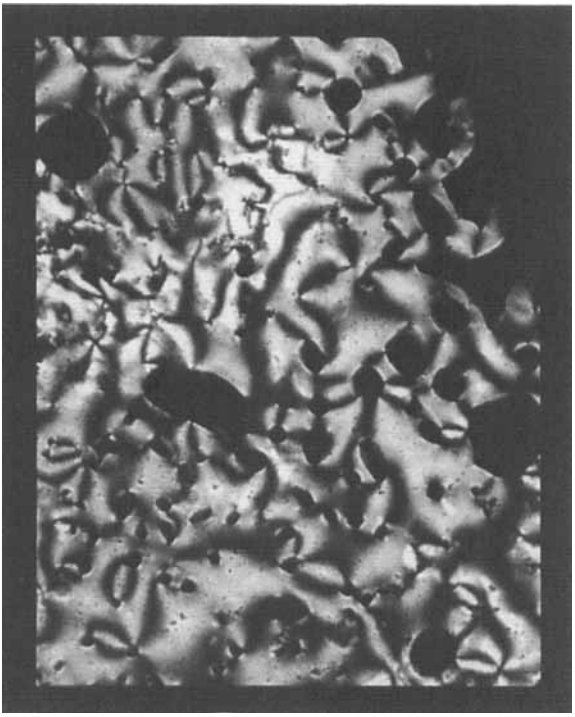
However, enantiotropic phases have been observed exclusively in complexes of Structure D (see **19, 39,** and **43**), except for the results for compound **18** which is a symmetrically substituted complex and gives a high melting crystal. This result is quite unexpected because the eight-ring complexes corresponding to Structure D appear to have a disc-like core. The nematic phases observed for these complexes show a typical *schlieren* texture (as do the monotropic nematic phases for complexes with Structure B, see Photomicrographs 1 and 2).

A further surprising observation for this set of compounds is that compound **43** shows a smectic A phase. The textures observed for the compound are typical of those for smectic A phases and show both homeotropic and focal-conic characteristics (see Photomicrographs 3 and 4). Complex **43** has a drastically reduced melting point compared to other complexes of this set. Compounds **40, 19** and **39** supercool considerably in the nematic phase before crystallisation occurs and show no tendency to form a smectic phase. This anomalous behaviour appears to be due to the polarity of the terminal fluoro substituent, a feature absent from complexes **40, 19** and **39**; we are investigating this phenomenon further.

Ohta *et al.*[2,4,5] have reported complexes with Structure A (R = $C_6H_{13}O$ to $C_{12}H_{25}O$) which exhibit "lamellar (discotic smectic)" phases[7] and Ribiero *et al.*[11] have reported a similar complex (Structure A, R = $C_{10}H_{21}$) which exhibits a "relatively rigid" smectic phase. We have studied by microscopy a sample of the complex in which R = $C_8H_{17}O$ and the mesophase it exhibits also appears to be extremely viscous. In contrast to this, the smectic A phase exhibited by compound **43** is a very fluid phase and we think that it is of a different nature to the phases described above. As with the complexes forming nematic phases, when considering Structure D, compound **43** would appear to be unlikely to be a rod-like molecule.

From the results reported here, two conflicting observations have been made in connection with the generation of nematic complexes.

(a) When the structure of the complex is broadened, the thermal stability of the nematic phase is increased; generally in calamitic systems, the larger the lateral substituent, the greater is the depression of phase stability.[23,24] If the



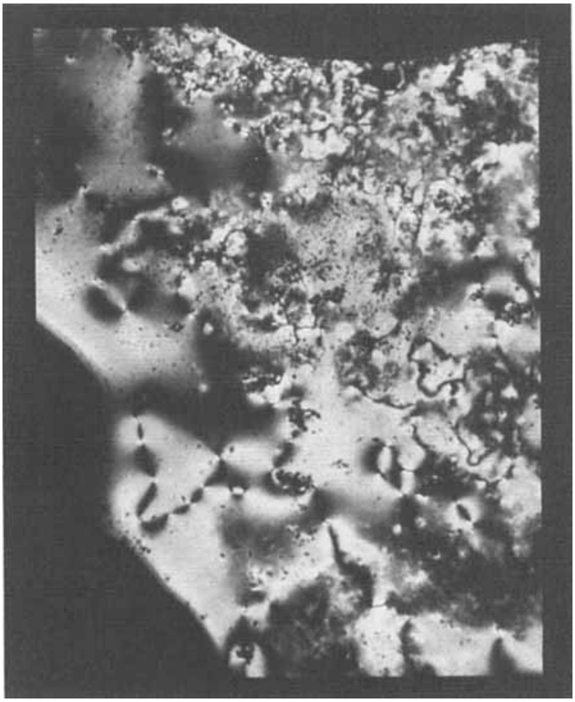
PHOTOMICROGRAPH 1 Schlieren texture of compound **17** in the nematic phase at 168°C. See Color Plate II.

complexes are viewed as 'rod-like' molecules with lateral substituents, then this trend in nematic stability is contrary to the accepted behaviour in 'rod-like' systems, since the nematic phase stability would be expected to decrease as the length-to-breadth ratio of the molecule is decreased.

(b) When the complexes have a broadened structure, they are still miscible with 5CT. This supports the existence of a 'rod-like' structure, unless the miscibility of the complexes with 5CT arises as a result of the cyano group interacting with the complex in some special way.

On the assumption that the miscibility of the complexes with 5CT is not caused by exceptional factors, the assignment of the phases of a molecule to a 'discotic' or 'calamitic' class purely based on the shape of the molecule is clearly an unsatisfactory approach.

If both points (a) and (b) are accepted then the terms 'rod-like' (calamitic) and 'disc-like' (discotic) are misleading terms to use to describe extremes of molecular shape. If, at one extreme, a 'rod-like' shape is gradually broadened through ellipses of increasing width, there will come a point at the other extreme when a disc shape is obtained. Chandrasekhar[16] described complex **16** as 'bridging the gap between rod-like and disc-like molecules' and this seems to be a reasonable description of the molecular shape. As the essentially planar molecules are broadened they become more 'disc-like' (but are not discotic), so that they appear to be in the elliptical, grey area between rods and discs.



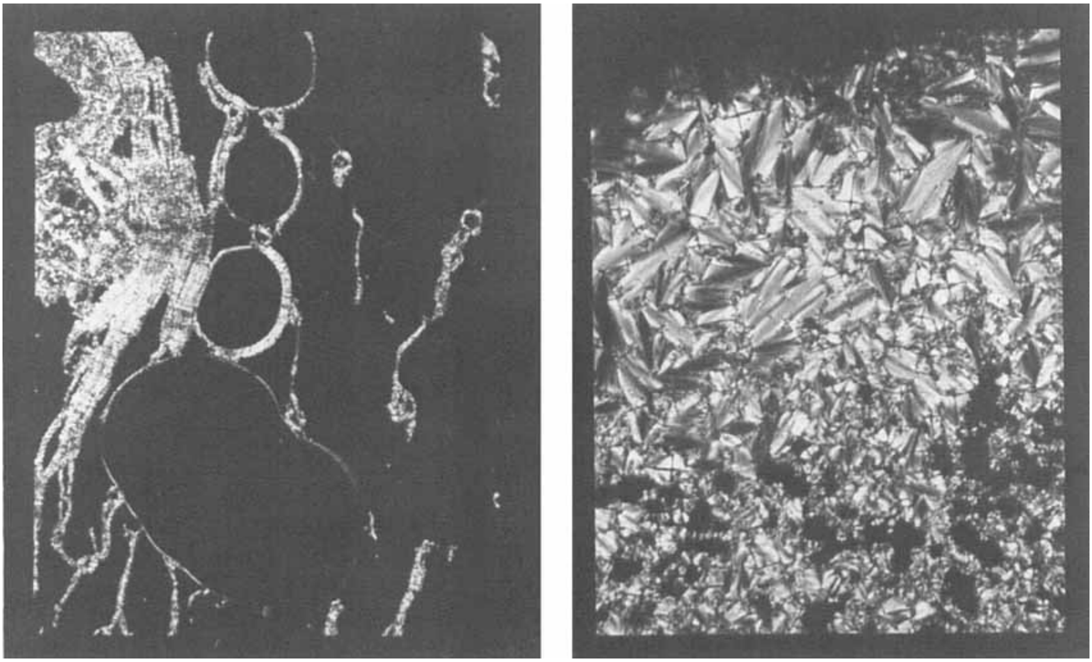
PHOTOMICROGRAPH 2 Schlieren texture of compound **39** in the nematic phase at 265°C. See Color Plate III.

EXPERIMENTAL

The transition temperatures and natures of the phases were obtained using an Olympus BH 2 polarising microscope fitted with a Mettler FP 52 heating stage and temperature controller. These were confirmed using a Perkin Elmer DSC-2C differential scanning calorimeter calibrated with a pure indium sample; the measured latent heat and the onset temperature for the melting point of indium were close to standard values. ^{1}H nmr spectra were obtained using a JEOL JNM-GX270 spectrometer. Infra-red spectra were obtained using a Perkin-Elmer 457 grating spectrophotometer and mass spectra were obtained using a Finnigan-MAT 1020 GC/MS spectrometer. The progress of reactions was monitored by thin layer chromatography (Merck, silica gel 60 F_{254} coated on aluminum sheets) or by gas chromatography (Perkin-Elmer 8310 capillary gas chromatograph fitted with a 12m QC2/BP1-1.0 SGE column). Compounds were purified, where specified, by column chromatography using silica gel 60–120 mesh or by flash chromatography using silica gel 40–60 mesh.

Scheme 1

4-Decanoylbiphenyl (**1**). Powdered aluminium chloride (43.5 g, 312 mmol) was added to a cooled (0°C), stirred solution of biphenyl (40.0 g, 260 mmol) in dry



PHOTOMICROGRAPHS 3 and 4 Homeotropic and focal-conic textures of compound **43** in the S_A phase. See Color Plates IV and V.

dichloromethane (150 ml). A solution of decanoyl chloride (50.0 g, 260 mmol) in dry dichloromethane (150 ml) was added dropwise during 1.5 h. The reaction mixture was allowed to reach room temperature and was stirred for 48 h. The mixture was poured onto ice and the organic material was extracted into ether (3 × 250 ml). The combined ethereal extracts were washed with water (200 ml), 10% aqueous sodium hydroxide (200 ml) and again with water until the aqueous washings were neutral. The organic layer was dried ($MgSO_4$) and the solvent was removed under reduced pressure. The crude product was recrystallised (ethanol) to give colourless crystals. Yield 54.7 g, 68%; mp 102–104°C; ^1H nmr ($CDCl_3$) δ 0.90 (t, 3H), 1.35 (m, 12H), 1.75 (m, 2H), 3.00 (t, 2H), 7.45 (m, 3H), 7.60 (m, 2H), 7.70 (d, 2H), 8.05 (d, 2H); ν_{max} (KCl) 2922, 2858, 1685, 1605, 1460, 1402, 1260, 1190, 760, 740 cm^{-1}; *m/z* 308 (M^+), 196 (100%), 181, 152.

4-Decylbiphenyl (**2**). Compound **1** (54.0 g, 175 mmol), hydrazine hydrate (16.8 g, 526 mmol) and potassium hydroxide (6.8 g, 123 mmol) were mixed in diethylene glycol (200 ml). The reaction mixture was heated at 110°C for 2 h. The excess of hydrazine hydrate was distilled off and the temperature was raised to 200°C for a further 2 h. The reaction mixture was allowed to cool and poured into water. The organic material was extracted into ether (2 × 250 ml) and the combined ethereal extracts were washed with water (200 ml), dilute hydrochloric acid (200 ml) and water (200 ml). The ethereal extracts were dried ($MgSO_4$), the solvent was removed under reduced pressure and the crude product was recrystallised (ethanol) to give yellow crystals. Yield 52.5 g, 98%; mp 55–55.8°C; ^{1}H nmr ($CDCl_3$) δ 0.90 (t, 3H), 1.30 (m, 14H), 1.65 (m, 2H), 2.65 (t, 2H), 7.25 (d, 2H), 7.42 (m, 3H), 7.50 (d, 2H), 7.60 (d, 2H); ν_{max} (KCl) 2925, 2860, 1490, 1470, 760, 750, 690 cm^{-1}; *m/z* 294 (M^+), 167 (100%).

4-Acetyl-4'-decylbiphenyl (**3**). This compound was prepared from compound **2** using a similar procedure to that described for the preparation of compound **1**. The crude product was purified by column chromatography (silica gel/petroleum spirit [bp 60–80°C]); the eluent was changed to chloroform after the first component had been collected and the pure product was obtained as yellow crystals. Yield 12.55 g, 73%; mp 84–86°C; ^{1}H nmr ($CDCl_3$) δ 0.90 (t, 3H), 1.30 (m, 14H), 1.65 (m, 2H), 2.60 (t and s, 5H), 7.25 (d, 2H), 7.55 (d, 2H), 7.65 (d, 2H), 8.00 (d, 2H); ν_{max} (KCl) 2928, 2860, 1685, 1602, 1468, 1270, 812 cm^{-1}; *m/z* 336 (M^+), 294, 209, 167 (100%).

2-Fluoro-4-(1-hydroxydecyl)biphenyl (**4**). A portion of a solution of 2-fluoro-4-bromobiphenyl (45.00 g, 197 mmol) in dry THF (100 ml) was added to magnesium turnings (4.70 g, 197 mmol) in dry THF (15 ml). One crystal of iodine was added and steam heat was used to initiate the reaction. The remainder of the biphenyl solution was added during 40 min with stirring and heating under reflux. The reaction mixture was heated under reflux for a further 1 h and cooled to room temperature. A 10 ml portion of a solution of decanal (33.60 g, 215 mmol) in dry THF (70 ml) was added immediately and the remainder of the solution was added over 30 min and the reaction mixture was heated under reflux for 1 h. The mixture was cooled to room temperature and poured into dilute hydrochloric acid (200 ml). The organic material was extracted into ether (3 × 200 ml) and the combined ethereal extracts were washed with water (200 ml). The organic layer was dried ($MgSO_4$) and the solvent was removed under reduced pressure to give a pale yellow waxy solid as the crude product, which was not purified. Yield 60.70 g, >100%; ^{1}H nmr ($CDCl_3$) δ 0.90 (t, 3H), 1.30 (m, 14H), 1.80 (m, 2H), 4.70 (t, 1H), 7.15 (m, 2H), 7.45 (m, 5H), 7.55 (m, 2H); ν_{max} (KCl) 3230, 2930, 2860, 1480, 1462, 1420, 700 cm^{-1}; *m/z* 328 (M^+), 201 (100%), 153.

2-Fluoro-4-decylbiphenyl (**5**). Phosphorus pentoxide (68.10 g, 480 mmol) was added to a stirred solution of compound **4** (60.50 g, 185 mmol) in heptane (400 ml). The reaction mixture was stirred for 48 h and the phosphorus pentoxide was filtered off and washed thoroughly with heptane. Palladium (5% on charcoal, 2.00 g) was added to the filtrate and the alkene was hydrogenated at atmospheric pressure. The charcoal/palladium catalyst was filtered off when the hydrogen uptake had ceased; the solvent was then removed from the filtrate under reduced pressure, and the crude product distilled under reduced pressure (0.5 mm Hg), collecting the fraction boiling between 160–180°C. The product was a colourless, low melting solid. Yield 28.70 g, 50%; ^{1}H nmr ($CDCl_3$) δ 0.90 (t, 3H), 1.30 (m, 14H), 1.65 (m, 2H), 2.60 (t, 2H), 6.95 (t, 2H), 7.32 (m, 2H), 7.42 (m, 2H), 7.54 (m, 2H); ν_{max} (KCl) 2930, 2860, 1625, 1585, 1485, 1420, 1270, 1132, 768, 700 cm^{-1}; *m/z* 312 (M^+, 100%), 185, 43.

2-Fluoro-4-decyl-4′-acetylbiphenyl (**6**). This compound was prepared from compound **5** using a similar procedure to that described for the preparation of compound **1**. The crude product was purified by column chromatography (silica gel/dichloromethane-petroleum spirit [bp 60–80°C], 1:1) to give pale orange crystals. Yield 10.60 g, 47%; mp 45–46.2°C; ^{1}H nmr ($CDCl_3$) δ 0.90 (t, 3H), 1.25 (m, 14H), 1.65 (m, 2H), 2.65 (s and t, 5H), 7.05 (dd, 2H), 7.35 (t, 1H), 7.65 (d, 2H), 8.05 (d, 2H); ν_{max} (KCl) 2922, 2860, 1684, 1610, 1470, 1400, 1360, 1270, 820, 605 cm^{-1}; *m/z* 354 (M$^+$), 339 (100%), 227, 185.

Methyl 4′-decylbiphenyl-4-carboxylate (**7**). A mixture of 4′-decylbiphenyl-4-carboxylic acid (10.00 g, 30 mmol), concentrated sulphuric acid (3 ml) and methanol (300 ml) was heated under reflux for 4 h. The mixture was allowed to cool and the excess of methanol was removed under reduced pressure. The organic material was extracted into chloroform (2 × 150 ml) and the combined organic extracts were washed with saturated aqueous sodium bicarbonate (200 ml) (the washing was repeated until evolution of carbon dioxide had ceased) and then with water (2 × 200 ml). The organic layer was dried ($MgSO_4$) and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel/dichloromethane) to give colourless crystals. Yield 9.80 g, 90%; mp 79–80.5°C; ^{1}H nmr ($CDCl_3$) δ 0.85 (t, 3H), 1.30 (m, 14H), 1.65 (m, 2H), 2.65 (t, 2H), 3.95 (s, 3H), 7.28 (d, 2H), 7.54 (d, 2H), 7.66 (d, 2H), 8.10 (d, 2H); ν_{max} (KCl) 2920, 2850, 1722, 1610, 1470, 1440, 1290, 1278 cm^{-1}; *m/z* 352 (M$^+$), 225 (100%).

Methyl 4′-ethylbiphenyl-4-carboxylate (**8**). This compound was prepared from 4′-ethylbiphenyl-4-carboxylic acid using a similar procedure to that described for the preparation of compound **7**. The crude product was purified by column chromatography (silica gel/dichloromethane) to give colourless crystals. Yield 9.45 g, 89%; mp 118.6–119.3°C; ^{1}H nmr ($CDCl_3$) δ 1.30 (t, 3H), 2.75 (q, 2H), 3.95 (s, 3H), 7.30 (d, 2H), 7.55 (d, 2H), 7.65 (d, 2H), 8.10 (d, 2H); ν_{max} (KCl) 2970, 1725, 1610, 1445, 1405, 1290, 1278, 1115, 835, 765 cm^{-1}; *m/z* 240 (M$^+$, 100%), 225, 209, 165, 82.

3-(4′-Decylbiphenyl-4-yl)-3-ketopropanal (**9**). Sodium hydride (60% in oil, 0.28 g, 14 mmol) was added to a stirred solution of compound **3** (2.35 g, 7 mmol) and methyl methanoate (0.42 g, 7 mmol) in dry 1,2-dimethoxyethane (100 ml). The reaction mixture was heated under reflux for 3 h under nitrogen and allowed to cool to room temperature. A few drops of water were added cautiously followed by concentrated hydrochloric acid (5 ml) and water (200 ml). The organic material was extracted into ether (3 × 50 ml) and the combined organic extracts were washed with water (2 × 100 ml). The organic layer was dried ($MgSO_4$) and the solvent was removed under reduced pressure. The crude product was not purified before complexation due to concerns regarding its stability. Yield 2.70 g, >100% crude; ^{1}H nmr ($CDCl_3$) δ 0.90 (t, 3H), 1.30 (m, 14H), 1.65 (m, 2H), 2.65 (t, 2H), 6.25 (d, 1H), 7.30 (d, 2H), 7.55 (d, 2H), 7.70 (d, 2H), 8.00 (d, 2H), 8.30 (d, 1H), 15.40 (s broad, 1H), with an impurity at δ 3.0–4.0; ν_{max} (KCl) 2925, 2850, 1608, 1500, 1470, 1405, 1250, 820, 780 cm^{-1}; *m/z* 364 (M$^+$, 100%), 336, 321, 237, 209.

1-(4'-Decylbiphenyl-4-yl)-3-(4-methylphenyl)propane-1,3-dione (**10**). This compound was prepared from compound **3** and methyl 4-methylbenzoate using a similar procedure to that described for the preparation of compound **9**. The crude product was purified by column chromatography (silica gel/dichloromethane-petroleum spirit [bp 40–60°C], 1:1) to give pale yellow crystals. Yield 8.70 g, 65%; transitions (°C) K_1 84 K_2 97 (S_A 93) I; ^{1}H nmr ($CDCl_3$) δ 0.90 (t, 3H), 1.35 (m, 14H), 1.65 (m, 2H), 2.45 (s, 3H), 2.65 (t, 2H), 6.90 (s, 1H), 7.35 (dd, 4H), 7.60 (d, 2H), 7.75 (d, 2H), 7.90 (d, 2H), 8.05 (d, 2H), 17.00 (s, 1H); ν_{max} (KCl) 2915, 2850, 1608, 1588, 1498, 1470 1190, 820, 785 cm^{-1}; *m/z* 454 (M$^+$, 100%), 321, 119, 69.

1-(4'-Decylbiphenyl-4-yl)-3-(4-methoxyphenyl)propane-1,3-dione (**11**). This compound was prepared from compound **3** and methyl 4-methoxybenzoate using a similar procedure to that described for the preparation of compound **9**. The crude product was purified by column chromatography (silica gel/dichloromethane-petroleum spirit [bp 40–60°C], 1:1) to give pale yellow crystals. Yield 3.50 g, 63%; mp 114–114.3°C; ^{1}H nmr ($CDCl_3$) δ 0.90 (t, 3H), 1.20 (m, 14H), 1.70 (m, 2H), 2.60 (t, 2H), 3.95 (s, 3H), 6.82 (s, 1H), 7.00 (d, 2H), 7.30 (d, 2H), 7.58 (d, 2H), 7.70 (d, 2H), 8.00 (d, 2H), 8.05 (d, 2H), 17.00 (s, 1H); ν_{max} (KCl) 2920, 2850, 1610, 1590, 1512, 1492, 1310, 1255, 1178, 782 cm^{-1}; *m/z* 470 (M$^+$, 100%), 343, 135.

1,3-Di-(4'-decylbiphenyl-4-yl)-propane-1,3-dione (**12**). This compound was prepared from compounds **3** and **7** using a similar procedure to that described for the preparation of compound **9**. The crude product was recrystallised twice (acetone) to give fine yellow crystals. Yield 3.20 g, 20%; mp 188.2–189.2°C; ^{1}H nmr ($CDCl_3$) δ 0.90 (t, 6H), 1.30 (m, 28H), 1.65 (m, 4H), 2.70 (t, 4H) 6.95 (s, 1H), 7.30 (d, 4H), 7.58 (d, 4H), 7.72 (d, 4H), 8.07 (d, 4H), 17.00 (s, 1H); ν_{max} (KCl) 2920, 2855, 1608, 1588, 1470, 980 cm^{-1}; *m/z* 656 (M$^+$, 100%), 321.

1-(4'-Decylbiphenyl-4-yl)-3-(4'-ethylbiphenyl-4-yl)propane-1,3-dione (**13**). This compound was prepared from compounds **3** and **8** using a similar procedure to that described for the preparation of compound **9**. The crude product was purified by flash column chromatography (silica gel/dichloromethane-petroleum spirit [bp 40–60°C], 1:1) to give pale yellow crystals. Yield 2.81 g, 58%; mp 185–186°C; ^{1}H nmr ($CDCl_3$) δ 0.90 (t, 3H), 1.30 (m, 17H), 1.65 (m, 2H), 3.70 (m, 4H), 6.94 (s, 1H), 7.29 (d, 2H), 7.32 (d, 2H), 7.58 (dd, 4H), 7.72 (dd, 4H), 8.08 (d, 4H), 17.00 (s, 1H); ν_{max} (KCl) 2950, 2860, 1608, 1595, 1572, 1535, 1520, 1495, 1250, 810 cm^{-1}; *m/z* 544 (M$^+$), 530 (100%), 403, 321, 195.

1-(4'-Decyl-2'-fluorobiphenyl-4-yl)-3-(4-methylphenyl)propane-1,3-dione (**14**). This compound was prepared from compound **6** and methyl 4-methylbenzoate using a similar procedure to that described for the preparation of compound **9**. The crude product was recrystallised twice (ethanol) to give orange/yellow crystals.

Yield 1.70 g, 63%; transitions (°C) K_1 44 N 60 I and K_2 54 N 60 I; ^{1}H nmr ($CDCl_3$) δ 0.90 (t, 3H), 1.35 (m, 14H), 1.65 (m, 2H), 2.45 (s, 3H), 2.70 (t, 2H), 6.90 (s, 1H), 7.04 (q, 2H), 7.30 (d, 2H), 7.40 (t, 1H), 7.68 (d, 2H), 7.92 (d, 2H), 8.05 (d, 2H), 16.95 (s, 1H); ν_{max} 2950, 2875, 1620, 1598, 1505, 1480, 1240, 1200, 1135, 798 cm^{-1}; *m/z* 472 (M$^+$), 344, 339, 185, 119.

Bis[3-(4′-decylbiphenyl-4-yl)-3-ketopropanalato]copper(II) **(15)**. A solution of copper(II) acetate monohydrate (0.73 g, 3.7 mmol) in warm THF (150 ml) was added rapidly to a stirred solution of compound **9** (2.65 g, 7.3 mmol) in THF (80 ml). The mixture was stirred at room temperature for 4 h and the solvent was removed under reduced pressure. The crude product was recrystallised (THF) to give green crystals. Yield 0.70 g, 12%; ν_{max} (KCl) 2925, 2860, 1600, 1510, 1492, 1440, 1362, 820, 778 cm^{-1}.

Bis-[1-(4′-decylbiphenyl-4-yl)-3-(4-methylphenyl)propane-1,3-dionato]-copper(II) **(16)**. This compound was prepared from compound **10** using a similar procedure to that described for the preparation of compound **15**. The crude product was recrystallised (acetone) to give green crystals. Yield 1.08 g, 51%; ν_{max} (KCl) 2930, 2860, 1612, 1590, 1568, 1535, 1492, 1390, 1320, 780 cm^{-1}.

Bis-[1-(4′-decylbiphenyl-4-yl)-3-(4-methoxyphenyl)propane-1,3-dionato]-copper(II) **(17)**. This compound was prepared from compound **11** using a similar procedure to that described for the preparation of compound **15**. The crude product was recrystallised (acetone) to give green crystals. Yield 0.80 g, 37%; ν_{max} (KCl) 2920, 2855, 1610, 1590, 1515, 1310, 1260, 1180, 1030, 985 cm^{-1}.

Bis-[1,3-di-(4′-decylbiphenyl-4-yl)propane-1,3-dionato]copper(II) **(18)**. This compound was prepared from compound **12** using a similar procedure to that described for the preparation of compound **15**. The crude product was recrystallised (THF) to give green crystals. Yield 1.52 g, 73%; ν_{max} (KCl) 2930, 2855, 1610, 1590, 1535, 1518, 1490, 1390, 1010, 782 cm^{-1}.

Bis-[1-(4′-decylbiphenyl-4-yl)-3-(4′-ethylbiphenyl-4-yl)propane-1,3-dionato]copper(II) **(19)**. This compound was prepared from compound **13** using a similar procedure to that described for the preparation of compound **15**. The crude product was recrystallised (THF/acetone) to give green crystals. Yield 0.73 g, 38%; ν_{max} (KCl) 2930, 2860, 1610, 1590, 1535, 1520, 1490, 1410, 830, 780 cm^{-1}.

Bis-[1-(4′-decyl-2′-fluorobiphenyl-4-yl)-3-(methylphenyl)propane-1,3-dionato]copper(II) **(20)**. This compound was prepared from compound **14** using a similar procedure to that described for the preparation of compound **15**. The crude product was recrystallised (acetone) to give green crystals. Yield 0.80 g, 51%; ν_{max} (KCl) 2930, 2860, 1612, 1590, 1538, 1490, 1420, 1390, 1320, 780 cm^{-1}.

Scheme 2

Acid chlorides. In each case, the acid chlorides were prepared immediately prior to use by treating the corresponding 4-substituted benzoic acid in dry benzene with 2 moles of oxalyl chloride and 1 drop of DMF at room temperature with stirring overnight.[20] The solvent was removed under reduced pressure and the residual acid chloride was mixed with a small portion of dry benzene which was again removed under reduced pressure to give the crude chloride which was used without further purification.

1-(4'-Decylbiphenyl-4-yl)butane-1,3-dione (**21**).[21] A solution of acetylacetone (1.40 g, 14 mmol) in dry ether (50 ml) was treated with sodium hydride (60% in oil; 0.60 g, 15 mmol) at 0°C under nitrogen and the mixture was stirred for a further 30 min at 0°C. A solution of 4-(4-decylphenyl)benzoyl chloride (5.30 g, 15 mmol) in dry ether (50 ml) was added and the mixture was stirred at room temperature for 6 h. After the addition of water (15 ml), the solution was acidified with concentrated hydrochloric acid (10 ml) and the organic material was extracted into ether (2 × 200 ml). The combined organic phases were washed with water (200 ml) and the solvent was removed under reduced pressure. Water (10 ml), a solution of ammonium chloride (0.40 g, 7 mmol) in water (10 ml) and aqueous ammonia (4 ml, 30%) were mixed and warmed to 50°C. This solution was added quickly to the crude product and the mixture was warmed at 50°C for 30 min and cooled (ice bath). The organic material was extracted into ether (3 × 200 ml) and the combined ethereal extracts were washed with water (200 ml) and dried ($MgSO_4$). The crude product was recrystallised (ethanol) to give pale orange crystals. Yield 3.60 g, 63%; transitions (°C) K 86 S_E 97 S_B 107 S_A 135 I; ^1H nmr ($CDCl_3$) δ 0.90 (t, 3H), 1.30 (m, 14H), 1.65 (m, 2H), 2.30 (s, 3H), 2.65 (t, 2H), 6.20 (s, 1H), 7.30 (d, 2H), 7.55 (d, 2H), 7.70 (d, 2H), 7.95 (d, 2H), 16.20 (s, 1H); ν_{max} (KCl) 2920, 2858, 1610, 1570, 1495, 1468, 820, 790 cm^{-1}; m/z 378 (M^+), 233 (100%), 151, 81.

1-[4-(trans-4-Heptylcyclohexyl)phenyl]butane-1,3-dione (**22**). This compound was prepared using a similar procedure to that described for the preparation of compound **21**. The organic material was not very soluble in ether and it was extracted into dichloromethane (2 × 200 ml). The crude product was recrystallised (ethanol) to give pale yellow crystals. Yield 6.07 g, 67%; transitions (°C) K 68 N 97 I; ^1H nmr ($CDCl_3$) δ 0.90 (t, 3H), 1.10 (m, 2H),1.20 (m, 13H), 1.45 (m, 2H), 1.90 (m, 4H), 2.20 (s, 3H), 2.50 (m, 1H), 6.15 (s, 1H), 7.25 (d, 2H), 7.80 (d, 2H), 16.20 (s, 1H); ν_{max} (KCl) 2925, 2855, 1650, 1610, 1470, 1450, 1288, 1190, 850, 790 cm^{-1}; m/z 342 (M^+), 327, 285 (100%), 161, 85.

1-[4'-Octyloxy-3'-fluorobiphenyl-4-yl]butane-1,3-dione (**23**). This compound was prepared using a similar procedure to that described for the preparation of compound **21**. The organic material was extracted into dichloromethane (2 × 150 ml). The crude product was purified by column chromatography (silica gel/dichloromethane-petroleum spirit [bp 40–60°C], 1:1) to give pale yellow crystals. Yield

3.70 g, 68%; transitions (°C) K 99 S_A 142 I; ^{1}H nmr ($CDCl_3$) δ 0.90 (t, 3H), 1.45 (m, 10H), 1.85 (m, 2H), 2.22 (s, 3H), 4.10 (t, 2H), 6.20 (s, 1H), 7.04 (t, 1H), 7.36 (m, 2H), 7.60 (d, 2H), 7.93 (d, 2H), 16.20 (s, 1H); ν_{max} (KCl) 2930, 2860, 1610, 1585, 1540, 1510, 1315, 1288, 1140, 785 cm^{-1}; m/z 384 (M^+), 272 (100%), 257, 215, 69, 43.

Bis-[1-(4'-decylbiphenyl-4-yl)-butane-1,3-dionato]copper(II) (**24**). This compound was prepared from compound **21** using a similar procedure to that described for the preparation of compound **15**. The crude product was recrystallised (THF) to give green wool-like crystals. Yield 0.80 g, 66%; ν_{max} (KCl) 2925, 2855, 1610, 1590, 1572, 1550, 1520, 1498, 1410, 1010, 780 cm^{-1}.

Bis-[1-(4-(trans-4-heptylcyclohexyl)phenyl)butane-1,3-dionato]copper(II) (**25**). This compound was prepared from compound **22** using a similar procedure to that described for the preparation of compound **15**. The crude product was recrystallised (acetone) to give pale green crystals. Yield 1.10 g, 52%; ν_{max} (KCl) 2925, 2855, 1612, 1588, 1558, 1528, 1504, 1020, 770, 710 cm^{-1}.

Bis-[1-(4'-octyloxy-3'-fluorobiphenyl-4-yl)butane-1,3-dionato]copper(II) (**26**). This compound was prepared from compound **23** using a similar procedure to that described for the preparation of compound **15**. The crude product was recrystallised (THF/acetone) to give green crystals. Yield 1.64 g, 76%; ν_{max} (KCl) 2940, 2862, 1612, 1580, 1552, 1530, 1500, 1140, 858, 782 cm^{-1}.

Scheme 3

Methyl 4-(trans-4-heptylcyclohexyl)benzoate (**27**). This compound was prepared from 4-(*trans*-4-heptylcyclohexyl)benzoic acid using a similar procedure to that described for the preparation of compound **7**. The crude product was purified by column chromatography (silica gel/dichloromethane) to give a colourless crystalline solid. Yield 9.64 g, 92%; transitions (°C) K 45 N 57 I; ^{1}H nmr ($CDCl_3$) δ 0.90 (t, 3H), 1.05 (m, 2H), 1.30 (m, 13H), 1.45 (m, 2H), 1.90 (m, 4H), 2.50 (m, 1H), 3.90 (s, 3H), 7.30 (d, 2H), 7.95 (d, 2H); ν_{max} (KCl) 2920, 2855, 1722, 1610, 1440, 1280, 1180, 1110, 760, 710 cm^{-1}; m/z 316 (M^+, 100%), 176, 162, 149, 131.

4-Acetyl-4'-fluorobiphenyl (**28**). This compound was prepared from 4-fluorobiphenyl using a similar procedure to that described for the preparation of compound **1**. The crude product was purified by column chromatography (silica gel/dichloromethane) to give colourless crystals. Yield 4.38 g, 73%; mp 103.4–104°C; ^{1}H nmr ($CDCl_3$) δ 2.65 (s, 3H), 7.16 (t, 2H), 7.58 (m, 2H), 7.64 (d, 2H), 8.02 (d, 2H); ν_{max} (KCl) 1685, 1605, 1532, 1500, 1364, 1270, 1258, 1200, 825, 645 cm^{-1}; m/z 214 (M^+), 199 (100%), 170.

4-Acetyl-4'-methoxybiphenyl (**29**). This compound was prepared from 4-methoxybiphenyl using a similar procedure to that described for the preparation of compound **1**. The crude product was purified by column chromatography (silica gel/dichloromethane) to give colourless crystals. Yield 9.0 g, 40%; mp 153.2–154°C;

^{1}H mmr ($CDCl_3$) δ 2.60 (s, 3H), 3.85 (s, 3H), 7.00 (d, 2H), 7.57 (d, 2H), 7.65 (d, 2H), 8.00 (d, 2H); ν_{max} (KCl) 2970, 2840, 1680, 1608, 1590, 1535, 1260, 1205, 1038, 820 cm^{-1}; *m/z* 226 (M^+), 211 (100%), 183, 168, 139.

4-Acetyl-4'-methylbiphenyl (**30**). This compound was prepared from 4-methylbiphenyl using a similar procedure to that described for the preparation of compound **1**. The crude product was purified by column chromatography (silica gel/dichloromethane) to give colourless crystals. Yield 4.5 g, 72%; mp 114–115°C; ^{1}H nmr ($CDCl_3$) δ 2.40 (s, 3H), 2.65 (s, 3H), 7.30 (d, 2H), 7.55 (d, 2H), 7.65 (d, 2H), 8.05 (d, 2H); ν_{max} (KCl) 3040, 2935, 1680, 1608, 1405, 1365, 1270, 965, 810 cm^{-1}; *m/z* 210 (M^+), 195 (100%), 165, 152.

1-[4-(trans-Heptylcyclohexyl)phenyl]-3-(4-methoxyphenyl)propane-1,3-dione (**31**).This compound was prepared from compound **27** and 4-methoxyacetophenone using a similar procedure to that described for the preparation of compound **9**. The crude product was purified by column chromatography (silica gel/dichloromethane-petroleum spirit [bp 40–60°C], 1:1) to give a colourless crystalline solid. Yield 3.84 g, 56%; transitions (°C) K_1 37 K_2 113 (N 106) I; ^{1}H nmr ($CDCl_3$) δ 0.90 (t, 3H), 1.10 (m, 2H), 1.30 (m, 13H), 1.50 (m, 2H), 1.85 (m, 4H), 2.50 (m, 1H), 3.90 (s, 3H), 6.80 (s, 1H), 7.00 (d, 2H), 7.30 (d, 2H), 7.90 (d, 2H), 7.95 (d, 2H), 17.00 (s, 1H); ν_{max} (KCl) 2920, 2850, 1605, 1510, 1460, 1260, 1235, 1182, 1030, 788 cm^{-1}; *m/z* 434 (M^+), 285, 233, 135 (100%).

1-[4-(trans-4-Heptylcyclohexyl)phenyl]-3-(4'-methoxybiphenyl-4-yl)propane-1,3-dione (**32**). This compound was prepared from compounds **27** and **29** using a similar procedure to that described for the preparation of compound **9**. The crude product was purified by column chromatography (silica gel/dichloromethane-petroleum spirit [bp 40–60°C], 1:1) to give colourless crystals. Yield 4.38 g, 60%; transitions (°C) K 173 N 178 I; ^{1}H nmr ($CDCl_3$) δ 0.90 (t, 3H), 1.20–1.50 (m, 17H), 1.90 (m, 4H), 2.50 (m, 1H), 3.85 (s, 3H), 6.85 (s, 1H), 7.00 (d, 2H), 7.35 (d, 2H), 7.60 (d, 2H), 7.67 (d, 2H), 7.95 (d, 2H), 8.05 (d, 2H), 16.95 (s, 1H); ν_{max} (KCl) 2930, 2860, 1610, 1500, 1300, 1258, 1200, 1040, 834, 795 cm^{-1}; *m/z* 510 (M^+, 100%), 458, 285, 272, 211.

1-(4'-Decylbiphenyl-4-yl)-3-(4'-methylbiphenyl-4-yl)propane-1,3-dione (**33**). This compound was prepared from compounds **7** and **30** using a similar procedure to that described for the preparation of compound **9**. The crude product was purified by column chromatography (silica gel/dichloromethane-petroleum spirit [bp 40–60°C], 2:1) to give pale yellow crystals. Yield 4.89 g, 65%; mp 186–186.5°C; ^{1}H nmr ($CDCl_3$) δ 0.90 (t, 3H), 1.30 (m, 14H), 1.70 (m, 2H), 2.40 (s, 3H), 2.65 (t, 2H), 6.90 (s, 1H), 7.30 (d, 4H), 7.56 (d, 2H), 7.58 (d, 2H), 7.72 (d, 4H), 8.70 (d, 4H), 17.00 (s, 1H); ν_{max} (KCl) 2935, 2860, 1610, 1590, 1570, 1500, 1475, 1408, 1010, 828, 790 cm^{-1}; *m/z* 530 (M^+, 100%), 403, 321, 195, 167.

1-(4'-Decylbiphenyl-4-yl)-3-phenylpropane-1,3-dione (**34**). This compound was prepared from compound **7** and acetophenone using a similar procedure to that described for the preparation of compound **9**. The crude product was purified by column chromatography (silica gel/petroleum spirit [bp 40–60°C]-dichloromethane, 2:1) to give pale orange crystals. Yield 3.58 g, 57%; transitions (°C) K 60 S_A 98 I; ^{1}H nmr ($CDCl_3$) δ 0.90 (t, 3H), 1.30 (m, 14H), 1.65 (m, 2H), 2.70 (t, 2H), 6.90 (s, 1H), 7.29 (d, 2H), 7.48–7.52 (m, 3H), 7.58 (d, 2H), 7.72 (d, 2H), 8.02 (d, 2H), 8.05 (d, 2H), 16.90 (s, 1H); ν_{max} (KCl) 2920, 2850, 1608, 1570, 1492, 1470, 1235, 810, 770, 690 cm^{-1}; *m/z* 440 (M^+, 100%), 321, 313, 105.

1-(4′-Decylbiphenyl-4-yl)-3-(4-fluorophenyl)propane-1,3-dione (**35**). This compound was prepared from compound **7** and 4-fluoroacetophenone using a similar procedure to that described for the preparation of compound **9**. The crude product was purified by column chromatography (silica gel/dichloromethane-petroleum spirit [bp 40–60°C], 1:1) to give pale yellow crystals. Yield 3.38 g, 52%; transitions (°C) K 88 S_A 122 I; ^{1}H nmr ($CDCl_3$) δ 0.90 (t, 3H), 1.30 (m, 14H), 1.65 (m, 2H), 2.70 (t, 2H), 6.85 (s, 1H), 7.18 (t, 2H), 7.29 (d, 2H), 7.58 (d, 2H), 7.72 (d, 2H), 8.04 (dd, 4H), 16.90 (s, 1H); ν_{max} (KCl) 2930, 2860, 1608, 1570, 1512, 1472, 1238, 1160, 855, 786 cm^{-1}; *m/z* 458 (M^+, 100%), 331, 321, 168, 123.

1-(4′-Decylbiphenyl-4-yl)-3-(4′-fluorobiphenyl-4-yl)propane-1,3-dione (**36**). This compound was prepared from compounds **7** and **28** using a similar procedure to that described for the preparation of compound **9**. The crude product was purified by flash column chromatography (silica gel/dichloromethane-petroleum spirit [bp 40–60°C], 1:1) to give pale yellow crystals. Yield 1.12 g, 37%; mp 199–200°C; ^{1}H nmr ($CDCl_3$) δ 0.90 (t, 3H), 1.15 (m, 14H), 1.75 (m, 2H), 2.70 (t, 2H), 6.95 (s, 1H), 7.18 (t, 2H), 7.30 (d, 2H), 7.58 (d, 2H), 7.64 (m, 2H), 7.68 (d, 2H), 7.72 (d, 2H), 8.08 (dd, 4H), 17.00 (s, 1H); ν_{max} (KCl) 2930, 2860, 1604, 1498, 1470, 1312, 1250, 1202 838, 790 cm^{-1}; *m/z* 534 (M^+, 100%), 510, 407, 321, 199.

1-(4-Methoxyphenyl)-3-(4′-octyloxy-3′-fluorobiphenyl-4-yl)propane-1,3-dione (**37**). This compound was prepared from compound **47** and 4-methoxyacetophenone using a similar procedure to that described for the preparation of compound **9**. The crude product was purified by column chromatography (silica gel/dichloromethane-petroleum spirit [bp 60–80°C], 2:1) to give pale yellow crystals. Yield 2.87 g, 54%; transitions (°C) K 125 (S_A 119 N 121) I; ^{1}H nmr ($CDCl_3$) δ 0.90 (t, 3H), 1.30 (m, 8H), 1.50 (m, 2H),1.80 (m, 2H), 3.90 (s, 3H), 4.10 (t, 2H), 6.81 (s, 1H), 6.95 (d, 2H), 7.02 (m, 1H), 7.36 (m, 2H), 7.64 (d, 2H), 8.00 (d, 2H), 8.05 (d, 2H), 16.90 (s, 1H); ν_{max} (KCl) 2920, 2860, 1610, 1540, 1502, 1310, 1260, 1178, 1135, 788 cm^{-1}; *m/z* 476 (M^+, 100%), 364, 215, 135.

Bis-{1-[4-(trans-4-heptylcyclohexyl)phenyl]-3-(4-methoxyphenyl)-propanedionato}copper(II) (**38**). This compound was prepared from compound **31** using a similar procedure to that described for the preparation of compound **15**. The crude product was recrystallised (acetone) to give green needles. Yield 1.87 g, 87%; ν_{max} (KCl) 2925, 2855, 1610, 1590, 1530, 1495, 1430, 1390, 1172, 790 cm^{-1}.

Bis-{1-[4-(trans-4-heptylcyclohexyl)phenyl]-3-(4'-methoxybiphenyl-4-yl)propanedionato}-copper(II) (**39**). This compound was prepared from compound **32** using a similar procedure to that described for the preparation of compound **15**. The crude product was recrystallised (THF/acetone) to give green crystals. Yield 3.16 g, 41%; ν_{max} (KCl) 2935, 2860, 1610, 1595, 1530, 1490, 1434, 1390, 1255, 792 cm^{-1}.

Bis-[1-(4'-decylbiphenyl-4-yl)-3-(4'-methylbiphenyl-4-yl)propane-1,3-dionato]copper(II) (**40**). This compound was prepared from compound **33** using a similar procedure to that described for the preparation of compound **15**. The crude product was recrystallised (THF/acetone) to give green crystals. Yield 0.31 g, 32%; ν_{max} (KCl) 2940, 2860, 1612, 1590, 1570, 1535, 1520, 1492, 1390, 790 cm^{-1}.

Bis-[1-(4'-decylbiphenyl-4-yl)-3-phenylpropane-1,3-dionato]copper(II) (**41**). This compound was prepared from compound **34** using a similar procedure to that described for the preparation of compound **15**. The crude product was recrystallised (THF/acetone) to give green crystals. Yield 1.50 g, 70%; ν_{max} (KCl) 2920, 2855, 1592, 1565, 1530, 1488, 1408, 1390, 1315, 770 cm^{-1}.

Bis-[1-(4'-decylbiphenyl-4-yl)-3-(4-fluorophenyl)propane-1,3-dionato]copper(II) (**42**). This compound was prepared from compound **35** using a similar procedure to that described for the preparation of compound **15**. The crude product was recrystallised (THF/acetone) to give green crystals. Yield 1.30 g, 83%; ν_{max} (KCl) 2935, 2862, 1608, 1568, 1538, 1494, 1435, 1392, 1232, 790 cm^{-1}.

Bis-[1-(4'-decylbiphenyl-4-yl)-3-(4'-fluorobiphenyl-4-yl)propane-1,3-dionato]copper(II) (**43**). This compound was prepared from compound **36** using a similar procedure to that described for the preparation of compound **15**. The crude product was recrystallised (THF/acetone) to give green crystals. Yield 0.48 g, 70%; ν_{max} (KCl) 2940, 2865, 1610, 1588, 1555, 1540, 1490, 1010, 845, 785 cm^{-1}.

Bis-[1-(4-methoxyphenyl)-3-(4'-octyloxy-3'-fluorobiphenyl-4-yl)propanedionato]-copper(II) (**44**). This compound was prepared from compound **37** using a similar procedure to that described for the preparation of compound **15**. The crude product was recrystallised (THF/acetone) to give green crystals. Yield 0.35 g, 58%; ν_{max} (KCl) 2940, 2860, 1610, 1590, 1538, 1495, 1390, 1312, 1268, 790 cm^{-1}.

Methyl 4'-octyloxy-3'-fluorobiphenyl-4-carboxylate (**47**). This compound was prepared from 4'-octyloxy-3'-fluorobiphenyl-4-carboxylic acid using a similar procedure to that described for the preparation of compound **7**. The crude product was purified by column chromatography (silica gel/dichloromethane) to give colourless crystals. Yield 4.93 g, 95%; mp 91–92°C; ^{1}H nmr (CDCl$_3$) δ 0.90 (t, 3H), 1.30 (m, 8H), 1.50 (m, 2H), 1.85 (m, 2H), 3.92 (s, 3H), 4.05 (t, 2H), 7.02 (t, 1H), 7.35 (m, 2H), 7.60 (d, 2H), 8.07 (d, 2H); ν_{max} (KCl) 2930, 2860, 1730, 1610, 1540, 1330, 1295, 1200, 1140, 770 cm^{-1}; *m/z* 358 (M$^+$), 246 (100%), 215, 57, 43.

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