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The synthesis and liquid crystalline behaviour of alkoxy-substituted derivatives of 1,4-bis(phenylethynyl)benzene

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Despite the prevalence of organised 1,4-bis(phenylethynyl)benzene derivatives in molecular electronics, the interest in the photophysics of these systems and the common occurrence of phenylethynyl moeties in molecules that exhibit liquid crystalline phases, the phase behaviour of simple alkoxy-substituted 1,4-bis(phenylethynyl)-benzene derivatives has not yet been described. Two series of 1,4-bis(phenylethynyl)benzene derivatives, i.e. 1-[(4′-alkoxy)phenylethynyl]-4-(phenylethynyl)benzenes (**5a**–**5f**) and methyl 4-[(4″-alkoxy)phenylethynyl-4′-(phenylethynyl)] benzoates (**18a**–**18f**) [alkoxy=*n*-C_4H_9 (**a**), *n*-C_6H_{13} (**b**), *n*-C_9H_{19} (**c**), *n*-$C_{12}H_{25}$ (**d**), *n*-$C_{14}H_{29}$ (**e**), *n*-$C_{16}H_{33}$ (**f**)] have been prepared and characterised. Both series have good chemical stability at temperatures up to 210°C, the derivatives featuring the methyl ester head-group (**18a**–**18f**) offering rather higher melting points and generally stabilising a more diverse range of mesophases at higher temperatures than those found for the simpler compounds (**5a**–**5f**). Smectic phases are stabilised by the longer alkoxy substituents, whereas for short and intermediate chain lengths of the simpler system (**5a**–**5c**) nematic phases dominate. Diffraction analysis was used to identify the SmB_{hex} phase in (**5d**–**5f**) that is stable within a temperature range of approximately 120–140°C. The relationships between the organisation of molecules within these moderate temperature liquid crystalline phases and other self-organised states (e.g. Langmuir-Blodgett films) remain to be explored.

Keywords: alkyne; alkoxy; liquid crystal; X-ray diffraction

1. Introduction

Molecular structures based on the phenylene ethynylene moiety (Figure 1) have been widely studied, with the rigid linear molecular framework and extended π-conjugated electronic structures coupled with their ease of preparation (*1*) making them attractive research objects. The combination of shape persistent linear molecular structures and extended π-conjugation makes oligo(phenylene ethynylene)s attractive candidates for molecular wires (*2*) and for opto-electronic applications (*3*). Consequently, numerous studies have been conducted on the wire-like (*2*–*4*) and photophysical properties of phenylene ethynylene based materials (*5*).

A good deal of synthetic work has been directed towards decoration of the parent molecular system with a view to the preparation of functional molecular systems. For example, the introduction of polar head-groups leads to amphiphiles capable of Langmuir film formation (*6*), whereas the incorporation of surface binding groups affords test systems suitable for measurements of electron transport in these prototypical molecular devices (*7*). Recently, some relatively fundamental studies of the molecular framework have been reported, such as measurements of the torsional motion about the aryl–alkyne single bond and the impact of this conformational flexibility on the physical properties of the system discussed (*8*).

Liquid crystal (LC) materials derived from the phenylene ethynylene motif are well known. For example, rigid-rod oligo(phenylene ethynylenes) (*9*) and buta-1,3-diynes (*10*) exhibit calamitic LC phases, while disc-like molecules based on pentakis(phenylethynyl)benzene derivatives exhibit the nematic discotic phase (*11*). Moreover, the versatile phenylene ethynylene motif has also been incorporated into metallomesogens (*12*), and both side-chain and main-chain polymeric LC materials (*13*). Non-conventional phenylene ethynylene-based mesogens incorporating the sterically demanding triptycene group form glassy phases, whereas V-shaped mesogens with shape persistent phenylene ethynylene arms exhibit the nematic phase (*14*). The improved mesophase behaviour of fluorinated LC materials, and their enhanced dielectric anisotropy (*15*) has driven the investigation of fluorinated phenylene ethynylenes for use as dopants in liquid crystal hosts (*16*). Non-fluorinated compounds have found application as dopants in polymer LC hosts to form dichroic photoluminescent materials (*17*).

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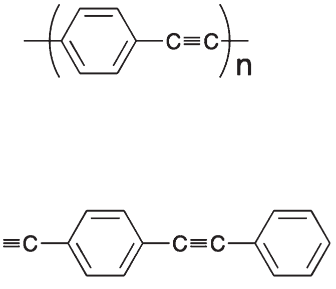


A

Figure 1. The phenylene ethynylene motif, and the 1,4-bis(phenylethynyl)benzene structure **A**.

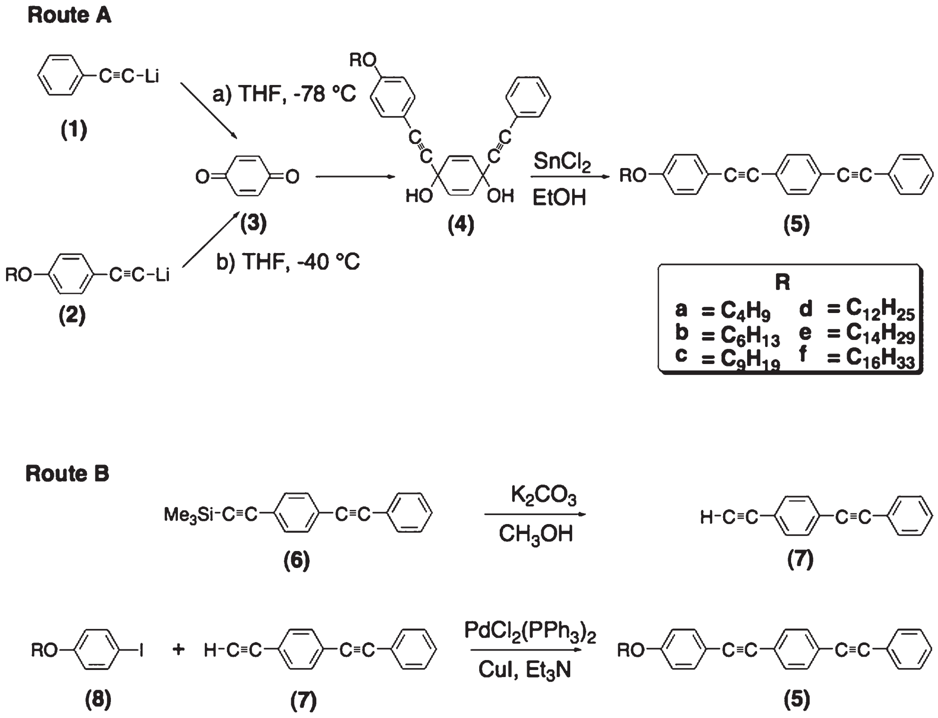
Many of the phenylene ethynylene systems that exhibit liquid crystalline properties feature alkyl or alkoxy chains in addition to the aromatic core; the effect of introduction of alkynyl-based tail groups into such systems having also been highlighted (*18*). Somewhat surprisingly, given the predominance of alkoxy chains in LC materials, simple mono-alkoxy derivatives of 1,4-bis(phenylethynyl)benzene (**A**, Figure 1) have not been studied. Equally, terminal ester groups in low molecular weight LCs are known to promote smectic behaviour due to the presence of a dipole acting across the molecular long axis, yet, to the best of our knowledge, little work has been reported on the influence of simple functional groups on the mesomorphic behaviour of the elementary rigid-rod scaffold offered by **A** (*5g, 5h, 19*). The enhancement of interactions between molecules arising from manipulation of the molecular dipole has the capacity to stabilise layered assemblies and give rise to novel mesomorphic behaviour (*20*).

In this paper we report the preparation of two representative series of mono-alkoxy derivatives of bis(phenylethynyl)benzene, 1-[(4′-alkoxyphenyl)ethynyl]-4-(phenylethynyl)benzenes and methyl 4-[(4″-alkoxy)phenylethynyl-4′-(phenylethynyl)]benzoates, and describe their liquid crystalline phase behaviour.

2. Results

Synthesis

Several routes to compounds such as **5** can be envisioned, two of which are illustrated in Scheme 1 (*21*). We chose to utilise the selective and sequential addition of lithiated acetylide anions to benzoquinone as the key steps in the assembly of the carbon-scaffold in compounds **5a**–**5f** (Scheme 1, route A) (*22*). Thus, sequential reaction of benzoquinone with lithium phenylacetylide and the appropriate lithium 4-alkoxyphenylacetylide gave the unsymmetrical dienediols, which were then reduced with tin(II) chloride in ethanol to give the desired 1-[(4′-alkoxyphenyl)ethynyl]-4-(phenylethynyl)benzenes in moderate overall yield (ca. 35%). An alternative route (route B) was also explored. The ethynyl tolan **7** (*23*) was



Scheme 1. Preparation of 1-[(4′-alkoxyphenyl)ethynyl]-4-(phenylethynyl)benzenes.

prepared from sequential reaction of lithium trimethylsilyl acetylide and lithium phenyl acetylide with benzoquinone, Sn(II) reduction of the intermediate diol and protiodesilylation (K_2CO_3/MeOH) in 61% yield, which is comparable with that reported for alternative procedures elsewhere (*23*). Cross-coupling of 4-alkoxyiodobenzenes with **7** also gave **5**, however, the yield for the final coupling step was relatively poor (25%).

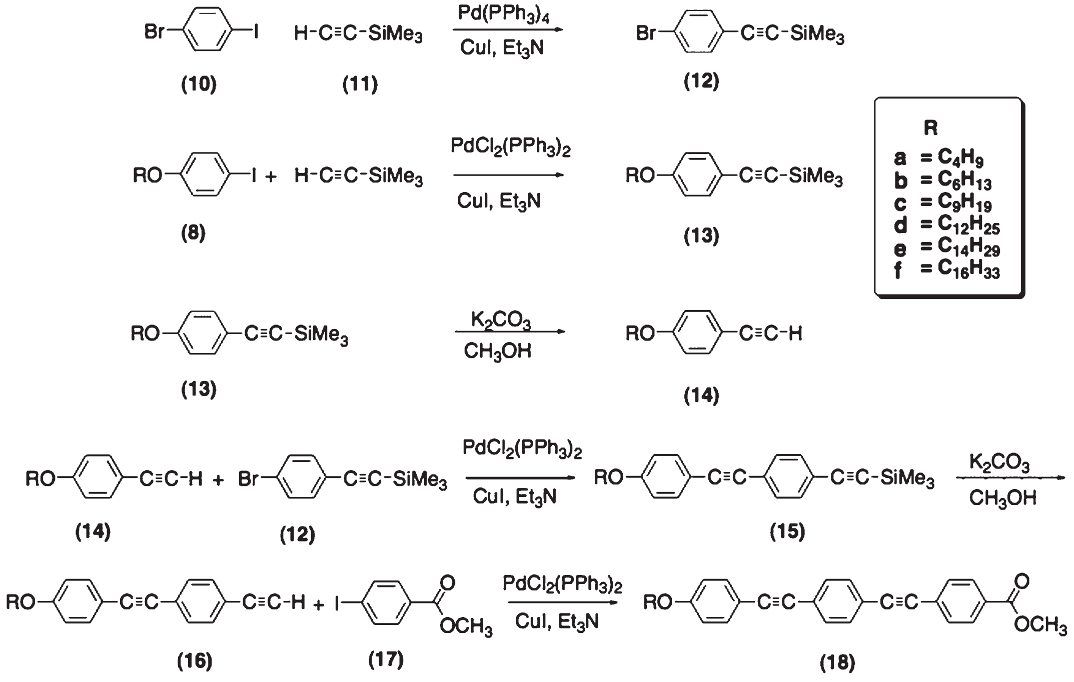
The ester derivatives **18a–18f** were synthesised using classical metal-catalysed cross-coupling methods (see Scheme 2), due to the electrophilic and reducible nature of the ester group. The intermediate alkoxyethynyl tolan precursors **16a–16f** were readily obtained from Sonogashira cross-coupling of 4-alkoxylphenylacetylenes with 1-bromo-4-(trimethylsilylethynyl)benzene (*24, 26*), and removal of the silyl protecting group. This synthesis is somewhat more expeditious than the route described by Armaroli et al. (*24a*). A second cross-coupling with 4-iodomethyl benzoate gave **18a–18f** in good overall yield.

Thermal behaviour

Alkoxy-substituted rigid-rods represent one of the largest classes of LC materials. The LC properties of **5a–5f** are detailed in Table 1, and summarised in graphical format in Figure 2. The transition temperatures were obtained by differential scanning calorimetry (DSC) and correspond to the observed onset temperatures of the phase transitions.

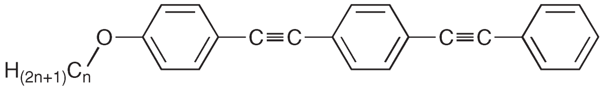
Each compound in the series **5a–5f** exhibited rich phase behaviour. In each case, two or three crystalline phase changes preceded the onset of liquid crystalline behaviour. The nematic phase observed for the early members of the series, **5a–5c**, was identified from two and four point brushes in the Schlieren texture and flashing of the sample upon application of a mechanical pressure. An enthalpy change of *ca.* 1 kJ mol^{-1} for the nematic to isotropic transition was observed by DSC in each case.

As the alkoxy chain length is increased through the series **5a–5f**, the clearing points decrease and the nematic phases give way to SmB_{hex} phases. For example, a SmB_{hex} phase was observed by polarized optical microscopy (POM) over approximately 1°C for compound **5c** before the formation of the nematic phase, whereas compounds **5d** and **5e** both exhibit a SmB_{hex} phase in addition to a smectic phase, Sm_1, at lower temperatures. The enthalpy change for the transition from the lower temperature smectic phase, Sm_1, to the SmB_{hex} phase is of the order of 1 kJ mol^{-1}, indicating that only a small modification to the structure occurs during this phase transition. The last member of the series **5f** again exhibits the SmB_{hex} phase, and, on cooling, the smectic phase Sm_1 was observed at 117°C, as a monotropic transition. The SmB_{hex} phase exists over a broader temperature range for longer chain lengths despite the monotonic decrease in clearing point with increasing chain length. For compounds **5e** and **5f**, the crystal–crystal transition between the K_1 and K_2 phases occurred



Scheme 2. Preparation of methyl 4-[(4″-alkoxy)phenylethynyl-4′-(phenylethynyl)]benzoates.

Table 1. Phase transition temperatures and enthalpies of **5a**–**5f** on heating.



Compound	*n*	Phase transition temperatures/°C (enthalpies/kJ mol^{-1})
5a	4	K_1 128.6 (0.80) K_2 149.7 (26.92) N 168.23 (1.19) I
5b	6	K_1 135.5 (4.89) K_2 141.2 (16.42) N 163.8 (1.30) I
5c	9	K_1 96.4 (2.00) K_2 117.5 (18.04) K_3 144.7 (16.63) SmB_{hex} 145[a] N 152.6 (1.25) I
5d	12	K_1 111.8 (16.31) K_2 118.1 (16.63) Sm_1 132.1 (1.56) SmB_{hex} 145.4 (17.61) I
5e	14	$K_1$115.1 (33.11) $K_2$118.4 (14.39) Sm_1 125.5 (1.17) SmB_{hex} 143.4 (18.15) I
5f	16	K_1 116.8 (41.41) K_2 119.4 (29.01) SmB_{hex} 140.3 (20.45) I

[a] Transition observed by optical microscopy.

14°C and 11°C lower on cooling than on heating, and aside from the monotropic Sm_1 phase in **5f**, all transitions were fully reversible.

The optical textures observed with hot-stage POM for each SmB_{hex} phase are similar in each case, manifested as focal conic-like texture together with large areas of homeotropic texture (Figure 3). These two observations may at first suggest a smectic A (SmA) phase; however, X-ray diffraction studies suggest the formation of a SmB_{hex} phase (vide infra). One interpretation of this apparent anomaly could be the presence of a transient SmA phase, which forms the focal conic texture before rapid transition into the SmB_{hex} phase. The transition from the SmB_{hex} phase to the Sm_1 phase can be detected by optical microscopy from the observation of characteristic lines that grow across the focal conic domains (Figure 4).

A platelet-type texture was also observed for the Sm_1 phase of **5e**, which on reheating above 126°C to the SmB_{hex} phase, formed a texture with birefringent streaks. This texture was found to be viscous when subjected to mechanical shear with a probe (Figure 5).

In order to characterise more fully the more highly ordered phases, X-ray diffraction experiments were conducted on compunds **5d**–**5f**, which offer the greatest temperature range for these phases. A sample of **5e** was studied with a Guinier X-ray camera, capable of recording small-angle (SAXS) and wide-angle (WAXS) X-ray scattering patterns, and subjected to a cycle of heating and cooling (10°C h^{-1} between 90–160–90°C). Two crystal phases, two smectic phases and the isotropic phase were observed for both the heating and cooling stages of the cycle. The crystal–crystal phase transition occurred at a

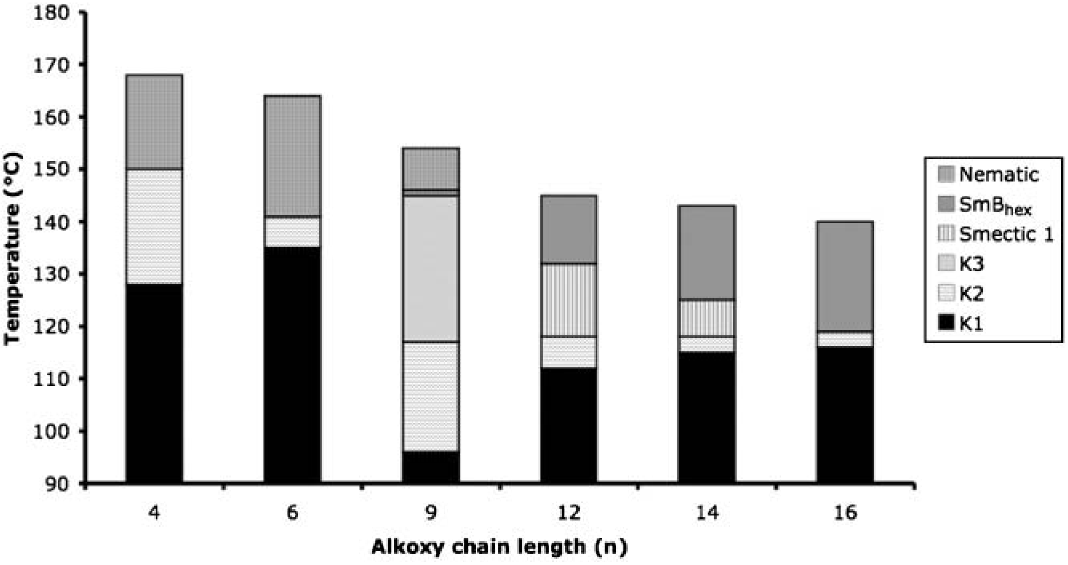


Figure 2. Graphical representation of the thermal phase behaviour of **5a**–**5f** on heating.

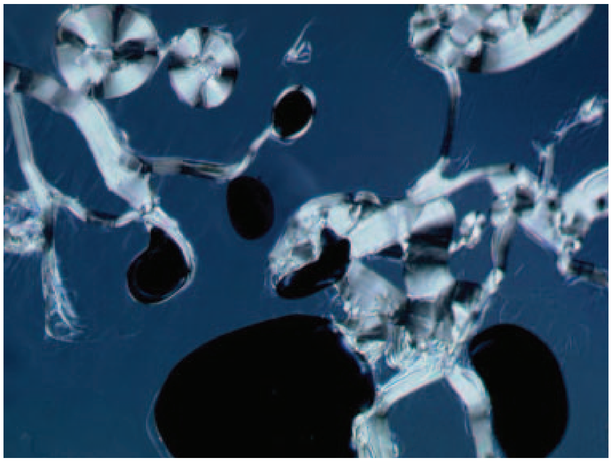


Figure 3. Homeotropic and focal-conic texture observed for the SmB_{hex} phase of **5f** at 130°C.

lower temperature during the cooling run than during the heating run, consistent with the DSC results. The layer spacing from the small angle region of the higher temperature smectic phase was found to be 38.4 Å, consistent with the estimated molecular length, while a single, fairly sharp and quite symmetrical peak at 4.37 Å in the wide-angle region (Figure 6) indicated a locally hexagonal order within the plane of the layers, with the molecules untilted, indicative of a SmB_{hex} phase.

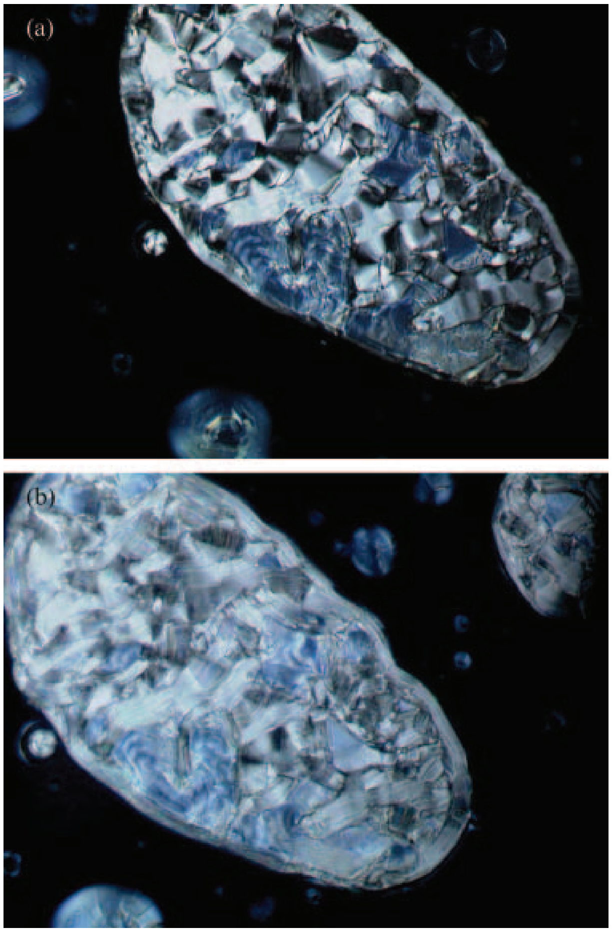


Figure 4. The transition from SmB_{hex} (a) to Sm_1 (b) as observed using optical microscopy for **5f** between 126 and 121°C.

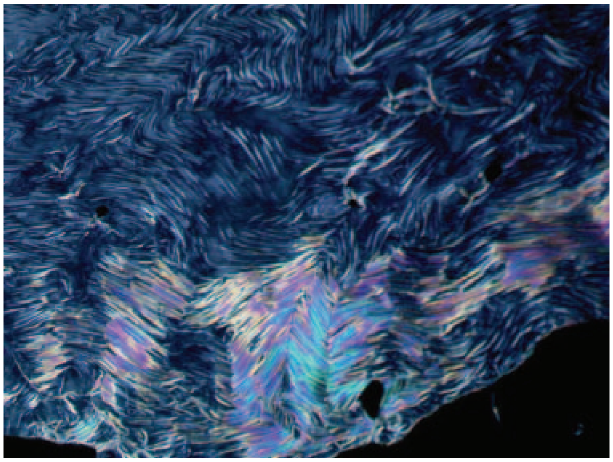


Figure 5. The viscous birefringent texture observed by reheating **5e** from Sm_1 to SmB_{hex} phase.

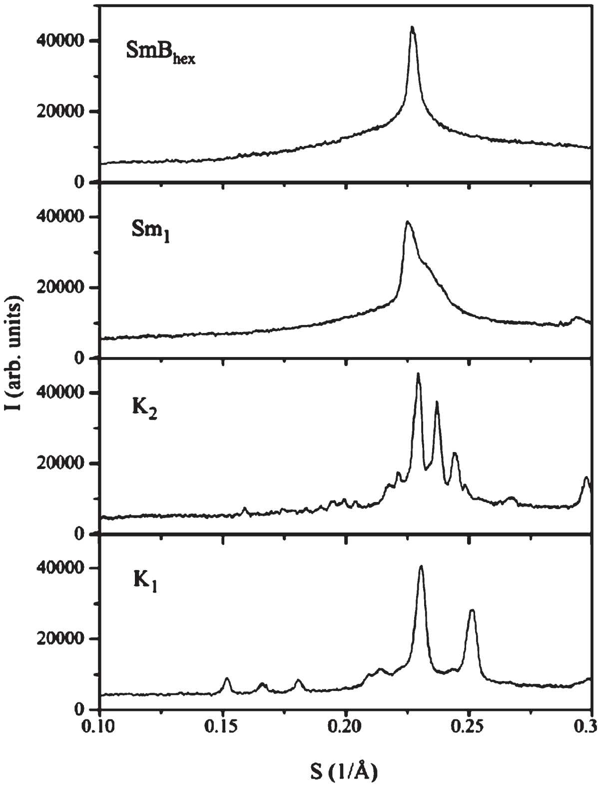


Figure 6. The WAXS patterns of the K_1, K_2, Sm_1 and SmB_{hex} phases of compound **5e**.

The lower temperature smectic Sm_1 phase shows a single peak centred at 4.40 Å with a broad shoulder to higher angles that is consistent with a tilting of the layers (*25*). The layer spacing measured from the small-angle region (not shown) of 37.3 Å is slightly smaller than that of the SmB_{hex} phase, consistent with a small molecular tilt angle relative to the layer normal. The wide-angle X-ray data indicate that there is only a slight rearrangement of the packing of the molecules in the transition from the SmB_{hex} to this lower temperature smectic phase, characterised by a shift of the wide angle peak to a smaller angle and a diffuse shoulder to higher angles. Such a pattern could imply a smectic F/I phase, where the tilting leads to a broadening of the wide-angle peak. However, this interpretation should be viewed with some caution as the extent of broadening seems rather too large, and furthermore, another weak peak could be observed at higher angle, and therefore a longer exposure of 5 h was undertaken in order to clarify the structure of this phase. A peak at 3.38 Å was duly observed after this long exposure study. This is not consistent with a two-dimensional hexagonal in-plane packing of molecules, implying that this lower temperature smectic phase has lower symmetry, but apparently with poorly developed long-range in-plane order, perhaps indicating tilted herringbone domains. The crystal phases K_1 and K_2 gave characteristic patterns of wide-angle reflections (Figure 6), and from the low-angle patterns (not shown), layer spacings of 64.6 Å and 61.4 Å, respectively, were measured, implying that the molecules are packed into bilayers rather than monolayers.

The phase behaviour of the hexadecyloxy derivative **5f** was also examined by X-ray diffraction from a sample cooled from the isotropic melt at 160°C to 90°C and reheated to 160°C at $15°C\,h^{-1}$. On cooling, **5f** exhibited a smectic phase below 140°C, with a layer spacing of 43 Å, in agreement with the length of the molecule. A single relatively sharp peak in the wide-angle region (4.38 Å) of the diffraction pattern is observed, which is again consistent with a SmB_{hex} phase. Further cooling to 118°C leads to the formation of the second smectic phase, Sm_1, with a broader wide-angle peak at 4.40 Å and a layer spacing of 41.6 Å. The sample was re-measured while increasing the temperature from 90 to 160°C. The most important observation from this experiment is that the lower temperature smectic phase Sm_1 is not observed upon heating in the X-ray pattern; rather, the crystal phase K_2 transforms directly to the SmB_{hex} phase. The crystal phases K_1 and K_2 gave wide-angle diffraction patterns that were qualitatively similar to those of compound **5e**, and the layer spacings were measured from the low-angle patterns as 69.6 Å and 65.4 Å, respectively.

An X-ray heating and cooling scan was also run on the dodecyloxy compound **5d**, and the results were very similar to those seen with the tetradecyloxy compound **5e**, with crystal phases K_1 and K_2, and smectic phases Sm_1 and SmB_{hex} observed on both heating and cooling scans. The layer spacings measured for this compound are plotted, together with those from compounds **5e** and **5f**, in Figure 7.

A linear dependence on alkoxy chain length is seen, with a gradient of 2.05 Å per methylene (CH_2) group for the crystal phases K_1 and K_2, 0.9 Å per CH_2 for the Sm_1 phase, and 1.05 Å per CH_2 for the SmB_{hex} phase. Comparison with the value of 2.54 Å for the next-nearest neighbour carbon–carbon distance for an all-trans hydrocarbon chain provides further evidence that the two crystal phases have a bilayer packing, and yields an estimate for the tilt angle of the molecules with respect to the layer normal of approximately 35° (this assumes that the mesogenic cores are colinear with the alkoxy chains, which is not necessarily true). The incremental spacing values for the two smectic phases are consistent with a monolayer packing for both of these phases. The fact that the increment for the SmB_{hex} phase (1.05 Å per CH_2) is less than 1.27 Å (the value for an untilted, fully extended chain in a monolayer packing) is probably due to some conformational disorder being present in the chains when packed in a hexatic phase. The somewhat lower

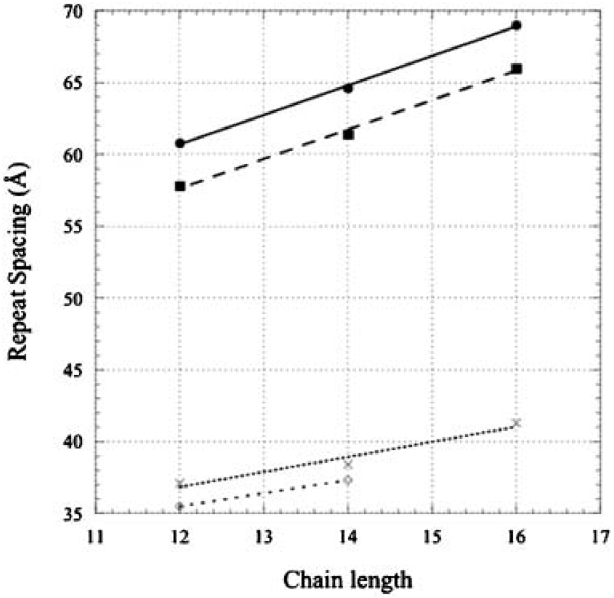


Figure 7. The layer spacings as a function of the alkoxy chain length for the four phases (SmB_{hex} X; Sm_1 ♦; K_2 ■; K_1 ●) observed in compounds **5d**–**5f**. The data are taken from X-ray heating scans.

increment of 0.9 Å per CH_2 for the Sm_1 phase compared with the SmB_{hex} phase is probably a further consequence of tilt.

The thermal phase behaviour of the series (**18a**–**18f**) bearing methoxy ester head groups was studied by optical microscopy and DSC. Each member of the series was found to exhibit LC behaviour (Table 2, Figure 8).

The early members of the series (**18a**, **18b**) exhibit nematic phases at relatively high temperatures (clearing point >280°C), whereas a progression towards lower transition temperatures is seen for the later members of the series (**18c**–**18f**), as a result of increasing chain length. This leads to a marked reduction in the nematic phase range for **18e** and **18f**. However, for the later members of the series bearing longer alkyl chains, melting points also decrease, ultimately leading to the formation of a greater number of smectic phases, with lower transition temperatures than seen for **18a**.

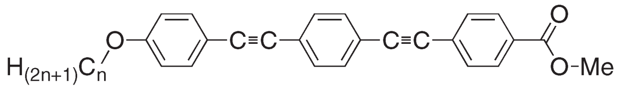
Compound **18a** exhibits a nematic phase between 210°C and 308°C, identified by the presence of two and four point brushes and flashing behaviour in the optical texture. A SmB_{hex} phase was identified between 202°C and 210°C from the observation of large platelet type texture (Figure 9). Compound **18b** exhibits a nematic phase between 212°C and 283°C, again identified by the presence of two and four point brushes in the Schlieren texture. A SmA phase was identified by the presence of a homeotropic texture between 198°C and 212°C. Furthermore, a phase exhibiting a platelet type texture between 194°C and 198°C was observed similar to that of **18a**, suggesting that this phase is a SmB_{hex} phase. In the case of **18c**, a nematic phase is observed on cooling from the isotropic phase at 258°C, using hot-stage microscopy. The texture is homeotropic but flashes brilliantly on probing mechanically, with a Schlieren texture observed close to the clearing point. Below 223°C, a mylenic texture was observed together with small focal conic texture implying a SmA phase. At 202°C a greyish, marble texture that displayed birefringent streaks upon applying pressure to the sample with a mechanical probe was observed. This texture is similar to the viscous birefringent texture observed for the SmB_{hex} phase in **5e** (Figure 5).

When cooled from the isotropic phase, **18d** exhibited a nematic phase, confirmed by flashing of the texture below 237°C. Further cooling led to the formation of a SmA phase at 227°C, assigned from the observation of homeotropic texture and small focal conic domains. Cooling the sample from 200°C to 190°C results in the formation of smooth platelets that on reheating leads to the formation of a dark homeotropic texture at 193°C, characteristic of the orthogonal SmB_{hex} phase.

When cooled from the isotropic phase, compound **18e** forms a nematic phase at 234°C, identified by two and four point brushes in its Schlieren texture and flashing when examined with a mechanical probe. On cooling below 223°C, the homeotropic, polygonal and fan textures of the SmA phase were observed. Below 190°C, paramorphotic polygonal texture with very smooth fan texture was observed, in addition to regions of homeotropic texture, suggesting it is an orthogonal phase. The smooth fan texture leads to the assignment of a SmB_{hex} phase. A marble texture was observed on cooling sample below 176°C. When pressure was exerted on the sample with a mechanical probe to cause shear flow, regions of the birefringent viscous texture were observed, similar that seen for the SmB_{hex} phases in **5e** and **5f**.

Compound **18f** exhibits a transient nematic phase below 217°C, with subsequent formation of a SmA phase, identified again by the presence of very well formed polygonal and focal conic textures. Thin samples exhibited regions of homeotropic texture, which persisted following a transition to a more

Table 2. Phase transition temperatures and enthalpies of **18a**–**18f** on heating.



Compound	*n*	Phase transition temperatures/°C (enthalpies/kJ mol^{-1})
18a	4	K_1 202 (9.70) SmB_{hex} 210 (18.9) N 308 I[a]
18b	6	K_1 177 (29.9) Sm_1 194 (1.57) SmB_{hex} 198 (5.49) SmA 212 (1.26) N 283 (1.00) I[a]
18c	9	K_1 153 (1.17) K_2 163 (16.43) Sm_1 193 (3.26) SmB_{hex} 202 (9.21) SmA 223 (1.98) N 258 I[a]
18d	12	K_1 101 (9.53) K_2 154 (27.9) Sm_1 190 (3.24) SmB_{hex} 200 (9.08) SmA 227 (2.07) N 237 I[a]
18e	14	K_1 122 (12.9) K_2 147 (34.68) Sm_1 180 (2.95) SmB_{hex} 191 (7.27) SmA 219 (5.51) N 224 I[a]
18f	16	K_1 119 (18.6) K_2 143 (36.64) Sm_1 176 (0.88) SmB_{hex} 186 (9.48) SmA 215 (6.84) N 216 I[a]

[a] Transition observed by optical microscopy.

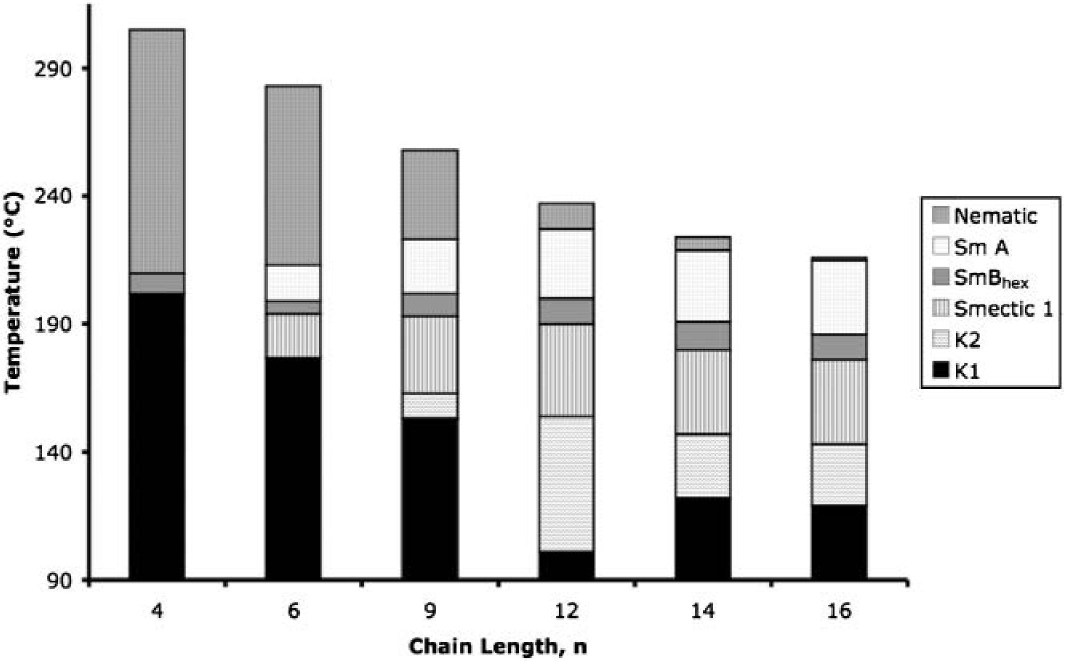


Figure 8. Graphical representation of the thermal phase behaviour of **18a**–**18f** on heating.

ordered phase at 186°C. No change in the focal conic/polygonal textures was observed to accompany this phase transition, suggesting that a SmB$_{hex}$ phase was formed. Cooling the sample below 181°C leads to the formation of what is thought to be a smectic F phase on the basis of platelet texture formation. This mosaic texture was disrupted with shear flow leading to a viscous birefringent texture similar to that observed for **5e**, **5f** and **18e** (Figure 5). Crystallization occurs below 143°C.

3. Discussion

Some interesting trends are apparent when the thermal phase behaviour of series **5a**–**5f** and **18a**–**18f** are compared. The 1-[(4′-alkoxyphenyl)ethynyl]-4-(phenylethynyl)benzenes (**5a**–**5f**) have lower transition temperatures and the later members of this group of compounds exclusively form smectic phases. The effect of the alkoxy donor group combined with the benzoate acceptor group leads to a strong molecular dipole along the mesogenic core in **18a**–**18f**. This leads to strong intermolecular dipole–dipole interactions with the ability to sustain mesomorphic behaviour at high temperatures (>250–300°C), well in excess of the highest clearing point observed for series **5a**–**5f**. In addition, the ester-substituted compounds have a high tendency to form the more fluid SmA and nematic phases. Early members of the series exhibit very broad nematic phase ranges; for example, in the case of **18a**, the nematic phase persists for almost 100°C. Equally, for **18f**, a SmA phase is found between 186°C and about 215°C with a transient nematic phase observed as it approaches the clearing point. In general, it can be seen from Table 2 and Figure 8 that these molecules interact with sufficient strength to stabilise lamellar assemblies at temperatures up to 60°C higher than was observed in series **5a**–**5f**. This stabilisation is again due to the strong interactions between the dipole moments of the donor–acceptor system, combined with the strong tendency to form layered phases with longer chains lengths. However, the entropic contribution of the terminal chains becomes dominant at high temperatures reducing the clearing point as the chain length increases. The combined result of these trends is to decrease the nematic phase range to 1°C in the case of **18f**.

The unusual texture observed for this SmB$_{hex}$ phase in **5c**–**5f** can be explained by the occurrence of a transient SmA phase that, though not detected by DSC, microscopy nor X-ray diffraction, nonetheless influences the formation of observed texture (Figure 10). Indeed, the presence of a distinct SmA phase can be ruled out by the observation of sharp peaks in the wide-angle region of the diffraction patterns for **5e** and **5f**. Similar apparent anomalies in the observed texture have been described previously by Gray *et al.* (*26a, 26b*), and attributed to isotropic to smectic AB transitions, where an infinitely narrow SmA phase results in the moss-like texture observed for the SmB$_{hex}$ phase (*26c*).

In contrast, in the methyl ester series **18a**–**18f**, the natural platelet texture of the SmB_{hex} phase is observed for **18a** between 202–210°C (Figure 9), whereas subsequent homologues **18b**–**18f** exhibit the paramorphotic fan or polygonal texture arising from a distinct and long lived SmA phase, which on cooling forms the SmB_{hex} phase.

4. Conclusion

Mono-alkoxy-substituted 1,4-bis(phenylethynyl)benzene derivatives exhibit a rich thermal behaviour and good chemical stability at temperatures in excess of 200°C. The introduction of a methyl ester head group gives rise to an enhanced dipole moment coincident with the long molecular axis leading to a diverse range of mesophases at higher temperatures. Smectic phases are stabilised by the longer alkoxy substituents, whereas for short and intermediate chain lengths of the simpler system nematic phases dominate. X-ray diffraction analysis has been used to identify a SmB_{hex} phase in three members of the simple alkoxy-substituted 1,4-bis(phenylethynyl)benzene series, which is stable over a relatively small thermal range (~120–140°C).

Figure 9. The platelet texture of the SmB_{hex} phase of **18a** at 208°C.

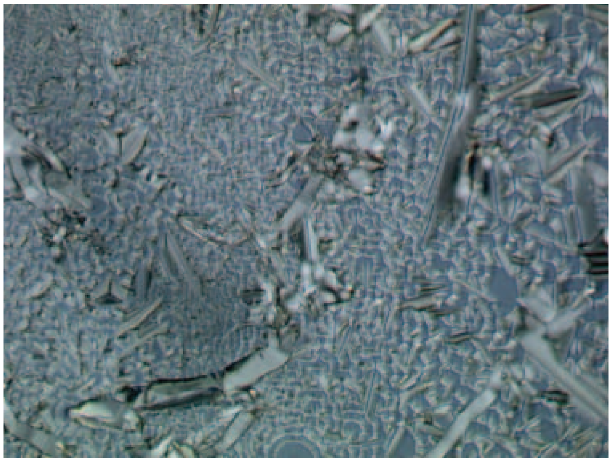


Figure 10. The optical texture of **5f** at 124°C showing large regions of moss-type texture associated with the SmB_{hex} phase.

5. Experimental

General conditions

Reactions involving lithium reagents were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. Benzoquinone, copper(I) iodide (Strem Chemicals), phenylacetylene (Aldrich), trimethylsilylacetylene (Fluorochem) and *n*-butyllithium (1.6M in hexanes, Acros) were purchased and were used as received. Solvents were dried using a solvent purification system (Innovative Technologies Inc.), and deoxygenated prior to use. Dichlorobis(triphenylphosphine)palladium(II) was prepared according to a literature method (*27a*). The 4-alkoxyphenylacetylenes were prepared by minor modification of the literature methods (*27b*), (*c*). The procedures detailed below are representative of the general methods employed. Full details are given in the supporting information available online.

IR spectra were recorded on a Nicolet Avatar spectrometer from nujol mulls supported between NaCl plates. NMR spectra were recorded from $CDCl_3$ solutions on a Bruker Avance 400 spectrometer, and referenced against solvent resonances. Mass spectra were recorded on Autospec EI and Micromass Quattro II spectrometers. A Perkin Elmer Pyris 1 DSC operating at a heating rate of $10^{\circ}C\,min^{-1}$, and fitted with a Cryofill cooling system was used to record the thermal behaviour of the sample and an Olympus BX51 microscope fitted with Linkam THMS 600 hot-stage and a Linkam TMS 94 temperature controller was used to examine the phase behaviour of the materials. Melting points were obtained using the same apparatus. The variable temperature X-ray studies were carried out using a using a Huber Guinier X-ray camera with a Philips PW1140 X-ray generator and fixed-anode Cu X-ray tube. The experimental data were collected on Kodak BioMax MS film housed in a motorised film carrier operating with the sample temperature controlled by a Eurotherm temperature controller cycling between 100–160–100°C at $10^{\circ}C\,h^{-1}$ for compound **5e** with the film carrier moving at a speed of $0.06\,mm\,min^{-1}$ and for compound **5f**, cycling between 160–100–160°C at $15^{\circ}C\,h^{-1}$ with the film carrier moving at a speed of $0.15\,mm\,min^{-1}$.

Syntheses

*Preparation of 1-([4′-hexyloxyphenyl)ethynyl]-4-(phenylethynyl)-2,5-cyclohexa-diene-1,4-diol (**4b**).*

Phenylacetylene (2.84 g, 27.8 mmol) in tetrahydrofuran (30 ml) at −78°C was treated with *n*-butyllithium (17.3 ml, 27.8 mmol) and allowed to warm slowly to 0°C. The lithium phenylacetylide solution was then cooled again to −78°C resulting in a cream coloured suspension and a solution of benzoquinone (3.00 g, 27.8 mmol) in tetrahydrofuran (30 ml) was added dropwise forming a deep blue coloured solution. The reaction was allowed to stir for one hour at −78°C. A solution of 4-hexyloxyphenylacetylene (5.62 g, 27.8 mmol) in tetrahydrofuran (40 ml) at −78°C was treated with *n*-butyllithium (17.3 ml, 27.8 mmol) and allowed to stir for one hour while warming to 0°C, cooling once more to −78°C followed by the dropwise addition of this solution to the original lithium phenylacetylide/benzoquinone solution. After stirring overnight, the reaction mixture was quenched at 0°C with aqueous ammonium chloride and then extracted with ethyl acetate. The solvent was removed and the crude product was then purified by column chromatography using dichloromethane as the eluent (11.0 g, 26.7 mmol, 94%). ^{1}H NMR: δ 7.42 (m, 2H, Ar*H*); 7.34 (m, 2H, Ar*H*); 7.28 (m, 2H, Ar*H*); 6.78 (m, 2H, Ar*H*); 6.11 (m, 4H, $C_6H_4(OH)_2$); 3.91 [t, ^3J(H,H)=6.8 Hz, 2H, OCH_2R]; 3.55 (s, br 2H, $C_6H_4(OH)_2$); 1.75, 1.47 (m, 8H, –CH_2–aliphatic); 0.89 [t, ^3J(H,H)=6.8 Hz, 3H, CH_3]. ^{13}C NMR: δ 159.9, 133.7, 133.25, 132.75, 132.2, 132.1, 129.5, 129.0, 128.6, 122.5, 114.8 (Ar); 89.1, 87.6, 85.8, 85.5 (–*C*≡*C*–); 68.4 (O*C*H); 61.7 (*C*–OH); 31.9, 29.5, 26.0, 22.9, (aliphatic); 14.3 (–CH_3). MS (EI): m/z (%) 412 (2.12) [M]$^+$; 394 (74) [M-H_2O]$^+$; 378 (33) [M-$(HO)_2$]$^+$; 302 (91) [M-$C_6H_4(OH)_2$]; 218 (100) [M-$C_6H_{13}OC_6H_5$].

*Preparation of 1-[(4-hexyloxyphenyl)ethynyl]-4-(phenylethynyl)benzene (**5b**).*

Compound **4b** (11.0 g, 26.7 mmol) in EtOH (20 ml) was added to $SnCl_2.2H_2O$ (6.00 g, 26.7 mmol) in 50% aqueous acetic acid (20 ml) and heated to 60°C. The crude product precipitated and was collected by filtration and allowed to dry in air. The product was purified by column chromatography on silica gel, eluting with hexane (2.12 g, 5.60 mmol 36%). ^{1}H NMR: δ 7.55 (m, 8H, Ar*H*); 7.35 (m, 3H, Ar*H*); 6.87 (m, 2H, Ar*H*); 3.97 [t, ^3J(H,H)=6.8 Hz, 2H, OCH_2R]; 1.77, (m, 2H, –CH_2 aliphatic) 1.48 (m, 2H, –CH_2 aliphatic); 1.35 (m, 4H, –CH_2 aliphatic); 0.89 [t, ^3J(H,H)=6.8 Hz, 3H, –CH_3]. ^{13}C NMR: δ 159.8, 133.5, 131.98, 131.9, 131.7, 128.7, 123.9, 123.5, 123.0, 115.2, 114.9 (Ar); 91.9, 91.4, 89.6, 88.2 (–*C*≡*C*–); 68.5 (OCH_2–aliphatic); 31.9, 29.5, 26.1, 22.9 (aliphatic); 14.4 (CH_3). MS (EI): *m*/*z* (%) 378 (48) [M]$^+$; 294 (100) [M-C_6H_{12}]$^+$. Elemental analysis: found C 88.97, H 6.82; $C_{28}H_{26}O$ requires C 88.85, H 6.92%.

*Preparation of 1-iodo-4-hexyloxybenzene (**8b**).*

Potassium carbonate (20.00 g, 1.45×10^{-1} mol) and 1-bromohexane (8.25 g, 5.00×10^{-2} mol) were added to 4-iodophenol (10.00 g, 4.55×10^{-2} mol) dissolved in acetone (150 ml) and the reaction mixture was then heated under reflux (48 h). The excess potassium carbonate was removed by filtration, and the solvent was then removed from the filtrate to give the crude product. The crude product was then purified by flash chromatography on silica gel, eluting with hexane to yield the product as a colourless oil (11.6 g, 3.81×10^{-2} mol, 84%). ^{1}H NMR δ 7.55 (m, 2H, Ar*H*); 6.67 (m, 2H, Ar*H*); 3.91 [t, ^3J(H,H)=6.4 Hz, 2H, OCH_2R]; 1.75 (m, 2H, –CH_2 aliphatic); 1.33 (m, 6H, –CH_2 aliphatic); 0.89 [t ^3J(HH)=6.8 Hz 3H, –CH_3]. ^{13}C NMR: δ 159.4, 138.1, 117.3, 82.7 (Ar); 68.5 (OCH_2R); 31.9, 29.5, 26.1, 22.9, (aliphatic); 14.4 (–CH_3). EI-MS 304.0 (37) [M]$^+$, 219.8 (100) [M–I]$^+$. Elemental analysis: found C 47.06, H 5.58; $C_{12}H_{17}IO$ requires C 47.39, H 5.63.

*Preparation of (4-bromophenylethynyl)trimethylsilane (**12**).*

The compound 1-bromo-4-iodobenzene (10.0 g, 3.54×10^{-2} mol), CuI (0.135 g, 7.08×10^{-4} mol) and $Pd(PPh_3)_4$ (0.409 g, 3.54×10^{-4} mol) were added to toluene (40 ml) and NEt_3 (40 ml). The reaction flask was cooled in an ice bath and trimethylsilylacetylene (5.5 ml, 3.28 g, 3.89×10^{-2} mol) was then added and the reaction mixture was allowed to warm slowly to room temperature while stirring. When the reaction was complete (24 h) the precipitate formed was removed by filtration, and washed with toluene. The organic fractions were combined and evaporated to dryness under reduced pressure. The crude product was purified by flash chromatography on silica gel with hexane as the eluent to yield the product as a white solid (7.44 g, 2.94×10^{-2} mol, 83 %). ^{1}H NMR δ 7.43 (AA′XX′, 2H, Ar*H*); 7.35 (AA′XX′, 2H, Ar*H*); 0.26 [s, 9H, –Si$(CH_3)_3$]. ^{13}C NMR: δ, 133.7, 131.8, 123.1, 122.5 (Ar); 104.2, 95.9, (–*C*≡*C*–); 0.28 (–Si$(CH_3)_3$). IR (KBr): ν(C≡C) 2158 cm^{-1}. EI-MS 254.0 (68), 252 (66) [M]$^+$, 237 (100) [M-CH_3]$^+$, 239 (98) [M-CH_3]. Elemental analysis: found C 52.18, H 5.24; $C_{11}H_{13}BrSi$ requires C 52.18, H 5.17%.

*Preparation of 1-ethynyl-4-hexyloxybenzene (**14b**).*

Trimethylsilylacetylene (2.67 g, 2.77×10^{-2} mol), was added to a Schlenk flask containing **8b** (7.44 g, 2.47×10^{-2} mol), CuI (0.047 g, 2.47×10^{-4} mol) and $PdCl_2(PPh_3)_2$ (0.173 g, 2.47×10^{-4} mol) in NEt_3 (50 ml) and allowed to stir overnight. The salt formed was filtered off and washed with toluene and the washings were combined with the filtrate and then evaporated under reduced pressure to yield the crude product as oil. The crude product was passed through a silica gel pad, eluting with hexane to yield colourless oil. The oil was then stirred in a suspension of potassium carbonate in methanol (6 h) and extracted into diethyl ether. The ether phase was then evaporated to give an oily mixture that was taken up in dichloromethane and separated from a residual aqueous phase to give the desired product (4.1 g, 2.03×10^{-2} mol, 82%). ^{1}H NMR: δ 7.42 (AA′XX′, 2H, Ar*H*); 6.83 (AA′XX′, 2H, Ar*H*); 3.94 [t, ^3J(H,H)=6.4 Hz, 2H, OC*H*$_2$R]; 3.00, (s, 1H, –C≡C*H*); 1.77 (m, 2H, –C*H*$_2$ aliphatic); 1.33 (m, 6H, –C*H*$_2$ aliphatic); 0.89 [t, ^3J(HH)=6.8 Hz 3H, –C*H*$_3$]. ^{13}C NMR: δ 159.9, 133.8, 114.8, 114.2, (Ar); 84.1, 75.9, (–*C*≡*C*–); 68.4 (O*C*H$_2$R); 31.9, 29.4, 26.0, 22.9, (aliphatic); 14.4 (–*C*H$_3$). IR (KBr plates, neat) ν(C≡C–H) 3316, 3291; ν(C≡C) 2107 cm^{-1}. EI-MS 202.1 (30) [M]$^+$, 117.8 (100) [M-C_6H_{12}]$^+$.

*Preparation of 1-ethynyl-4-[(4′-hexyloxy)phenylethynyl]benzene (**16b**).*

A Schlenk flask was charged with **12** (3.00 g, 1.19×10^{-2} mol) and a solution of **14b** (2.43 g, 1.20×10^{-2} mol) in NEt_3 (40 ml) added, followed by CuI (0.045 g, 2.38×10^{-4} mol) and $PdCl_2(PPh_3)_2$ (0.167 g, 2.38×10^{-4} mol). The reaction was heated under reflux (16 h). The reaction was then allowed to cool and the solvent was removed under reduced pressure. The reaction mixture was extracted into chloroform and washed with water (2 × 50 ml) and aqueous sodium chloride solution (1 × 50 ml). The chloroform was removed under reduced pressure and the crude product purified on a pad of silica, eluting with hexane to give **15b**. This product was treated with a suspension potassium carbonate in methanol (100 ml) and stirred (6 h). The product was extracted into ether, the solvent evaporated and the residue taken up in dichloromethane. The organic phase was separated from the aqueous residue and evaporated under reduced pressure to yield the product as an off white waxy solid (2.00 g, 7.18×10^{-3} mol, 60%). ^{1}H NMR: δ 8.02 (m, 6H, Ar*H*); 6.87 (AA′XX′, 2H, Ar*H*); 3.97 [t, ^3J(H,H)=6.4′Hz, 2H, OC*H*$_2$R]; 3.17, (s, 1H, –C≡C*H*); 1.76 (m, 2H, –C*H*$_2$ aliphatic); 1.45 (m, 2H, –C*H*$_2$ aliphatic); 1.33 (m, 4H, –C*H*$_2$ aliphatic); 0.89 [t, ^3J(HH)=6.8 Hz 3H, –C*H*$_3$]. ^{13}C NMR: δ 159.8, 133.4, 132.4, 131.6, 124.6, 121.8, (Ar); 91.9, 87.9, 83.7, 79.0 (–*C*≡*C*–); 68.5 (O*C*H$_2$R); 31.9, 29.5, 26.0, 22.9, (–*C*H$_2$ aliphatic); 14.4 (–*C*H$_3$). IR (KBr): ν(–C≡C–H) 3298, 3271 cm^{-1}; ν(C≡C) 2214 cm^{-1}. EI-MS 302.1 (26) [M]$^+$, 218.1 (100) [M-C_6H_{12}]. Elemental analysis: found C 86.90, H 7.30; $C_{22}H_{22}O$ requires C 87.38, H 7.33%.

*Preparation of methyl [4-{(4″-hexyloxy)phenylethynyl-4′-(phenylethynyl)}] benzoate (**18b**).*

A solution of methyl 4-iodobenzoate (0.47 g, 1.79×10^{-3} mol) in NEt_3 (60 ml), was treated with compound **16b** (0.54 g, 1.79×10^{-3} mol), $PdCl_2(PPh_3)_2$ (0.025 g, 3.56×10^{-5} mol) and CuI (0.007 g, 3.56×10^{-5} mol) and allowed to stir overnight. The solvent was then removed and the reaction mixture was dissolved in chloroform (100 ml) and extracted with water (2 × 100 ml). The aqueous layer was separated, extracted again with chloroform (70 ml), the organic fractions were combined and the solvent was then removed. The crude product was then passed through a column of silica gel, eluting with hot toluene to yield the pure compound (0.51 g, 1.17×10^{-3} mol, 65%). ^{1}H NMR δ 8.02 (AA′XX′, 2H, Ar*H*); 7.58 (AA′XX′, 2H, Ar*H*); 7.50 (s, 4H, Ar*H*); 7.46 (AA′XX′, 2H, Ar*H*); 6.87 (AA′XX′, 2H, Ar*H*); 3.98 [t, ^3J(H,H)=6.4′Hz, 2H, OC*H*$_2$R]; 3.93 (s, 1H, –CO$_2$C*H*$_3$); 1.76 (m, 2H, –C*H*$_2$– aliphatic); 1.45 (m, 2H, –C*H*$_2$– aliphatic); 1.33 (m, 4H, –C*H*$_2$– aliphatic); 0.89 [t, ^3J(HH)=6.8 Hz 3H, –C*H*$_3$]. ^{13}C NMR: δ 166.9 (C=O), 159.8, 133.5, 131.9, 131.85, 131.75, 129.9, 129.8, 128.15, 124.45, 122.3, 115.0, 114.9, (Ar); 92.5, 98.1, 90.6, 88.0, (–*C*≡*C*–); 68.4 (O*C*H$_2$R); 52.6 (–C(O)O*C*H$_3$); 31.9, 29.5, 26.04, 22.9 (aliphatic); 14.4 (–*C*H$_3$). IR (KBr): ν(C≡C) 2210 cm^{-1}; ν(C=O) 1721 cm^{-1}. EI MS 436 (13) [M]$^+$, 352.2 (8)[M-C_6H_{12}]$^+$. Elemental analysis: found C 82.47, H 6.52; $C_{30}H_{28}O_3$ requires C 82.54, H 6.46%.

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