Extended conjugated mesogens: synthesis and mesomorphic properties of H-shaped mesogens based on 3,3′,5,5′-tetrasubstituted 2,2′-bithiophene with oligo(1,4-phenyleneethynylene) arms

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ABSTRACT
A new class of extended conjugated mesogens, namely H-shaped mesogens based on 3,3′,5,5′-tetrasubstituted 2,2′-bithiophene with oligo(1,4-phenyleneethynylene) arms, have been synthesised, and the relationships between molecular structures and mesomorphic properties investigated. Tetraalkyl, tetraalkoxy and dialkyldialkoxy derivatives, \[\text{R}_1\text{C}_6\text{H}_4\text{CCC}_6\text{H}_2(\text{C}_2\text{H}_5)_2\text{CC}_2\text{C}_8\text{H}_2\text{S}_2\] \[\text{R}_2\text{C}_6\text{H}_4\text{CCC}_6\text{H}_2(\text{C}_2\text{H}_5)_2\text{CC}_2\text{C}_8\text{H}_2\text{S}_2\] where \(\text{R}_1\) and \(\text{R}_2\) = alkyl and alkoxy chains of different lengths, exhibit nematic phases. The length, number and position of the terminal chains strongly affect the mesomorphic properties. The tetraalkyl derivatives in which \(\text{R}_1 = \text{R}_2\) = pentyl to heptyl exhibit enantiotropic mesophases, whereas the derivatives with octyl or nonyl chains exhibit monotropic mesophases. The tetraalkoxy derivatives in which \(\text{R}_1 = \text{R}_2\) = pentyloxy to nonyloxy all exhibit enantiotropic nematic phases. The mesophase range increases with increasing alkoxy chain length, except that the octyloxy and nonyloxy derivatives have almost the same temperature range. The dialkyldialkoxy derivatives in which \(\text{R}_1\) = alkyl; \(\text{R}_2\) = alkoxy and in which \(\text{R}_1\) = alkoxy; \(\text{R}_2\) = alkyl (\(\text{R}_1\) and \(\text{R}_2\) = heptyl, nonyl, hexyloxy or nonyloxy) exhibit enantiotropic mesophases. The derivatives in which \(\text{R}_1\) = alkoxy have a significantly lower crystal–nematic transition temperature than the corresponding derivatives (\(\text{R}_2\) = alkoxy), although the two types of derivatives have a similar nematic–isotropic transition temperature.

1. Introduction
Extended conjugated mesogens have been the subject of considerable interest not only because of their optical and electrical properties \([1–5]\) but also in terms of their mesomorphic properties (e.g. rod-like,\([6–10]\) V-shaped,\([11–13]\) star-shaped \([14,15]\) and discotic \([16–20]\) mesogens). The mesogens generally consist of a conjugated core and aliphatic chains. The shape and size of the core, and the length, number and position of the flexible chains are structural factors that affect or control the mesomorphic properties. However, the relationship between molecular structure and mesomorphic properties remains incompletely understood. Studies of the structure–property relationship have an
important role to play in research on liquid crystalline conjugated materials.

The size of the cores of conjugated mesogens is a determining factor in their mesomorphic behaviour (e.g. rod-like,[6,8,10,21–25] V-shaped,[26] star-shaped [27] and discotic [16,20] cores). Any extension of the core generally causes a significant increase in the transition temperatures. Nevertheless, in some cases the attachment of flexible chains to an extended core (e.g. to a rod-like core in lateral positions [8–10,21,22,28]; to a V-shaped core in the lateral positions [11,12]; to a three-armed star-shaped core in internal positions [29]) is a useful method for reducing or controlling the transition temperatures. We recently synthesised alkyl-substituted derivatives of phenyl-terminated 1,4-phenyleneethynylene hexamer (H(C_6H_4CC)_6C_6H_6) that exhibit nematic phases.[9] Hexamer derivatives containing diethyl-substituted oligo(phenyleneethynylene) parts (C_6H_4CC_6H_2(C_6H_2)_{2}CC, Figure 1) have a significantly lower transition temperature than the corresponding derivatives without ethyl chains at the lateral positions.

Very recently, we synthesised H-shaped conjugated mesogens, that is, tetraalkyl-, tetraalkoxy- and dialkyldialkoxy-substituted derivatives of 3,3',5,5'-tetrakis(phenylethynyl)-2,2'-bithiophene (4PE2T) (1a–e, 2a–e, 3a, 3b, 4a and 4b, Figure 2).[30] The conjugated moiety is a mesogenic core, and the derivatives exhibit enantiotropic or monotropic nematic phases. The terminal chains play an important part in their mesomorphic behaviour. Among the tetraalkyl derivatives, the pentyl and heptyl derivatives exhibit enantiotropic mesophase. In contrast, all the tetraalkoxy and dialkyldialkoxy derivatives exhibit enantiotropic mesophases and, moreover, have a wide mesophase range.

To further our studies of extended conjugated mesogens and to investigate the effect of extending the 4PE2T core on mesomorphic behaviour, we have synthesised bithiophene derivatives that have oligo(1,4-phenyleneethynylene) substituents instead of phenylethynyl groups. The extended core, that is, 3,3',5,5'-tetrakis[4-(phenylethynyl)phenylethynyl]-2,2'-bithiophene (4(PE)_22T), has four internal phenyl rings, and eight ethyl groups are attached to the rings (Figure 3);
that is, 4(PE)$_2$T derivatives contain four diethyl-substituted oligo(phenyleneethynylene) arms similarly to the (PE)$_x$P derivatives shown in Figure 1. The ethyl-substituted 4(PE)$_2$T derivatives are designed to have a lower transition temperature and, moreover, to exhibit a higher solubility in a common organic solvent than 4(PE)$_2$T derivatives without side chains (or derivatives with only terminal chains) would do.

In this paper, we report the synthesis and mesomorphic properties of 4(PE)$_2$T derivatives 5a–e, 6a–e, 7a, 7b, 8a and 8b. Derivatives 5a–e contain four terminal alkyl chains, whereas derivatives 6a–e have alkoxy chains instead. Derivatives 7a, 7b, 8a and 8b have two alkyl and two alkoxy chains at the terminal positions, but the positions of the alkyl and alkoxy chains in derivatives 7a and 8a are different from those in derivatives 7b and 8b. For tetraalkyl-, tetraalkoxy- and dialkyldialkoxy-substituted 4(PE)$_2$T derivatives, the effects of the length, number and position of the alkyloxy chains on the mesomorphic properties are discussed, and the structure–property relationships in the 4(PE)$_2$T derivatives are compared with those in the corresponding 4PE2T derivatives. Additionally, the entropy change of the N–I transition for the 4(PE)$_2$T mesogen is described in comparison with those found for the related mesogens.

2. Results and discussion

2.1. Synthesis

The synthesis of tetraalkyl- and tetraalkoxy-substituted 4(PE)$_2$T 5a–e and 6a–e is illustrated in Scheme 1. The 4(PE)$_2$T were synthesised by the Sonogashira coupling of 3,3’,5,5’-tetraido-2,2’-bithiophene (9a) with phenyleneethynylene dimers 10a–e and 11a–e.

**Scheme 1.** Synthesis of 4(PE)$_2$T derivatives 5a–e and 6a–e.
in good yields. Dialkyldialkoxy-substituted 4(PE)_2T derivatives 7a, 7b, 8a and 8b were synthesised in a two-step reaction involving a regioselective Sonogashira coupling (Scheme 2). The cross-coupling of 3,3',5,5'-tetrabromo-2,2'-bithiophene (9b) with the phenyleneethynylene dimers (2.6 equiv.) at room temperature gave 5,5'-disubstituted 3,3'-dibromo-bithiophenes 12a, 12b, 13a and 13b in good yields. The dibromobithiophenes were cross-coupled with the phenyleneethynylene dimers at 85°C to give the desired products.

The 4(PE)_2T derivatives are red-orange solids, soluble in common organic solvents such as chloroform, tetrahydrofuran or hexane. A hexane–ethanol or a chloroform–ethanol mixture is found to be a suitable recrystallisation solvent.

### 2.2. Mesomorphic properties

#### 2.2.1. Tetraalkyl-substituted 4(PE)_2Ts

Derivatives 5a–e have four terminal alkyl chains of the same length, from pentyl to nonyl. These derivatives exhibit enantiotropic or monotropic nematic phases. Nematic Schlieren textures are observed for the derivatives (Figure 4). Their thermotropic data are summarised in Table 1.

Derivatives 5a–c, with pentyl, hexyl and heptyl chains, respectively, exhibit enantiotropic mesophases. The N–I transition temperature decreases significantly

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**Scheme 2.** Synthesis of 4(PE)_2T derivatives 7a, 7b, 8a and 8b.

**Figure 4.** Photomicrographs of the nematic phases of tetraalkyl derivatives 5c (a) and 5d (b).
with increasing terminal chain length (5a: 157°C; 5b: 139°C; 5c: 134°C). The change in the Cr–N transition temperature (5a: 133°C; 5b: 122°C; 5c: 123°C) is slightly different from that in the N–I transition temperature. The replacement of the pentyl chains with hexyl chains causes a significant decrease in the Cr–N transition temperature, but the transition temperatures of the hexyl and heptyl derivatives are almost the same. As a result of these changes, a significant decrease is observed in the mesophase range (5a: 24°C; 5b: 17°C; 5c: 11°C). Derivatives 5d and 5e, with octyl and nonyl chains, respectively, exhibit monotropic mesophases. For the octyl derivative, the Cr–I transition occurs at 118°C, and the mesophase is observed from 118°C to 62°C on cooling. For the nonyl derivative, the Cr–I transition occurs at 122°C, and the mesophase is found between 113°C and 81°C.

These results show that the 4(PE)2T unit is a mesogenic core, and that the mesomorphic properties of the tetraalkyl-substituted 4(PE)2Ts are strongly affected by the length of the alkyl chains. The derivatives with pentyl, hexyl or heptyl chains, 5a–c, exhibit enantiotropic mesophases, whereas the derivatives with octyl or nonyl chains, 5d and 5e, exhibit monotropic mesophases. For derivatives 5a–c, the mesophase range decreases significantly with increasing alkyl chain length. Interestingly, the enantiotropic or monotropic behaviour of derivatives 5a–e is the same as that of the corresponding 4PE2T derivatives, 1a–e, except that hexyl derivative 1b exhibit a monotropic nematic phase (Figure 5). Both of pentyl derivatives 1a and 5a and both of heptyl derivatives 1c and 5c exhibit enantiotropic nematic phases. The replacement of the heptyl chains of derivatives 1c and 5c by octyl or nonyl chains results in monotropic nematic phases (derivatives 1d, 1e, 5d and 5e). This is probably because the longer chains stabilise further the crystalline phase by additional Van der Waals interactions.

Interestingly, 1,2,4,5-tetrakis(4′-alkyl-biphenyl-4-ethynyl)benzenes where alkyl = butyl, hexyl, octyl and decyl, X-shaped nematogens that have a molecular structure similar to these of derivatives 5a–e, exhibit enantiotropic nematic phases with a wide temperature range (15°C, 40°C, 36°C and 41°C, respectively). [15] The longer alkyl chains of the X-shaped mesogens do not stabilise the crystalline

### Table 1. Phase transition temperatures (°C) and transition enthalpies (in square brackets, kJ mol⁻¹) of compounds 5a–e.

| Compound | R     | Phase transition |
|----------|-------|------------------|
| 5a       | C₅H₁₁ | Cr 133 [59.9] N 157 [0.3] I |
| 5b       | C₆H₁₃ | Cr 122 [62.1] N 139 [0.3] I |
| 5c       | C₇H₁₅ | Cr 123 [69.1] N 134 [0.4] I |
| 5d       | C₈H₁₇ | Cr 118 [77.0] I |
| 5e       | C₉H₁₉ | Cr 122 [89.1] I |

Notes: Cr = crystal phase; N = nematic phase; I = isotropic phase.
* Determined by POM.
phase but assist the formation of the mesophase. The X-shaped core, based on 1,2,4,5-tetrasubstituted benzene, has a high symmetry, whereas the 4(PE)₂T core, containing 2,2ʹ-bithiophene, has a skewed H-shape. It appears that the difference of the shape of the core causes the difference of the behaviour of the longer chains between the X- and H-shaped mesogens. For a better understanding of these structure–property relationships, it will be necessary to investigate the crystal structures of the 4(PE)₂T derivatives.

2.2.2. Tetraalkoxy-substituted 4(PE)₂T Ts

Derivatives 6a–e contain four terminal alkoxy chains of the same length, from pentyloxy to nonyloxy. All the alkoxy derivatives exhibit enantiotropic nematic phases. Optical textures characteristic of a nematic phase are observed both on heating and cooling (Figure 6). The thermotropic data are summarised in Table 2, and the changes in the transition temperatures are illustrated in Figure 7.

The N–I transition temperature decreases significantly with increasing alkoxy chain length (190°C, 183°C, 170°C, 165°C and 154°C for 6a–e, respectively). The Cr–N transition temperature also decreases; however, the replacement of the heptyloxy chains with octyloxy chains causes a great decrease (184°C, 172°C, 154°C, 114°C and 105°C for 6a–e, respectively). As a result of these changes, the mesophase range increases with increasing alkoxy chain length, except that the ranges of the octyloxy and nonyloxy derivatives, 6d and 6e, are almost the same (6°C, 11°C, 16°C, 51°C and 49°C for 6a–e, respectively). In addition, the ranges of derivatives 6d and 6e are much broader than those of derivatives 6a–c.

These results show that the alkoxy chains are important constituents of the 4(PE)₂T mesogen. All the alkoxy derivatives exhibit enantiotropic nematic phases, unlike the corresponding alkyl derivatives. The results also show that length of the alkoxy chains strongly affects the mesomorphic properties. The Cr–N and N–I transition temperatures decrease with increasing alkoxy chain length, and the use of octyloxy or nonyloxy chains gives rise to a wide mesophase range. Interestingly, these effects of the alkoxy chain length on the mesomorphic properties are quite different from the observations for the alkyl derivatives. For alkyl derivatives 5a–c, the mesophase range decreases with increasing terminal chain length; for alkoxy derivatives 6a–c, the mesophase range increases, although the Cr–N and N–I transition temperatures of the alkoxy derivatives are much higher than those of the corresponding alkyl derivatives. Alkyl derivatives 5d and 5e exhibit monotropic mesophases; alkoxy derivatives 6d and 6e exhibit enantiotropic mesophases with a wide temperature range.

The mesomorphic properties of derivatives 6a–e are very similar to those of the corresponding 4PE2T derivatives, 2a–e, except that the Cr–N transition temperatures of derivatives 6a–c are much higher than those of the corresponding derivatives (derivatives 6a–c have a narrower mesophase range than derivatives 2a–c). Both
the octyloxy derivatives, 2d and 6d, and both the nonyloxy derivatives, 2e and 6e, exhibit enantiotropic mesophases with a wide temperature range. This is quite different from the corresponding alkyl derivatives, 1d, 1e, 5d and 5e, which exhibit monotropic mesophases. Interestingly, the mesomorphic properties of tetraalkoxy derivatives 6a–e are similar to those of the X-shaped mesogens mentioned in the previous section. In both cases, the longer chains assist the formation of the mesophase with a wide temperature range. This indicates that the O atoms attached to the H-shaped core have an important role to play in stabilising the mesophase. For a better understanding of the structure–property relationship in 4(PE)₂T derivatives, it will be necessary to investigate the mesomorphic properties of derivatives with two alkyl and two alkoxy chains. The mesomorphic properties of 4(PE)₂T derivatives that have the same terminal chains as 4PE2T derivatives 3a, 3b, 4a and 4b are discussed in the following section.

2.2.3. Dialkyldialkoxy-substituted 4(PE)₂Ts

Derivatives 7a and 7b have two heptyl and two hexyloxy chains at the terminal positions similarly to derivatives 3a and 3b, respectively. Derivatives 8a and 8b have nonyl and nonyloxy chains similarly to derivative 4a and 4b, respectively. With the two types of derivatives, that is, 7a and 8a (R¹ = alkyl; R² = alkoxy) and 7b and 8b (R¹ = alkoxy; R² = alkyl), the effects of the number and position of the alkoxy chains on the mesomorphic properties have been investigated. The thermotropic data of these derivatives are listed in Table 3.

Derivatives 7a and 7b exhibit enantiotropic nematic phases with a wide temperature range. The N–I

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**Table 2.** Phase transition temperatures (°C) and transition enthalpies (in square brackets, kJ mol⁻¹) of compounds 6a–e.

| Compound | R           | Phase transition         |
|----------|-------------|--------------------------|
| 6a       | OC₅H₁₁      | Cr 184 [87.8] N 190 [0.7] Ipd |
| 6b       | OC₆H₁₃      | Cr 172 [81.0] N 183 [0.8] Ipd |
| 6c       | OC₇H₁₅      | Cr 154 [77.3] N 170 [0.8] I  |
| 6d       | OC₈H₁₇      | I 167 [−0.8] N 50 °Cr    |
| 6e       | OC₉H₁₉      | Cr 114 [92.6] N 165 [0.8] I  |

Notes: Cr = crystal phase; N = nematic phase; I = isotropic phase. pd = partial decomposition. * Determined by POM.

**Figure 7.** Changes in the transition temperatures of tetraalkoxy derivatives 6a–e.

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The octyloxy derivatives, 2d and 6d, and both the nonyloxy derivatives, 2e and 6e, exhibit enantiotropic mesophases with a wide temperature range. This is quite different from the corresponding alkyl derivatives, 1d, 1e, 5d and 5e, which exhibit monotropic mesophases. Interestingly, the mesomorphic properties of tetraalkoxy derivatives 6a–e are similar to those of the X-shaped mesogens mentioned in the previous section. In both cases, the longer chains assist the formation of the mesophase with a wide temperature range. This indicates that the O atoms attached to the H-shaped core have an important role to play in stabilising the mesophase. For a better understanding of the structure–property relationship in 4(PE)₂T derivatives, it will be necessary to investigate the mesomorphic properties of derivatives with two alkyl and two alkoxy chains. The mesomorphic properties of 4(PE)₂T derivatives that have the same terminal chains as 4PE2T derivatives 3a, 3b, 4a and 4b are discussed in the following section.

2.2.3. Dialkyldialkoxy-substituted 4(PE)₂Ts

Derivatives 7a and 7b have two heptyl and two hexyloxy chains at the terminal positions similarly to derivatives 3a and 3b, respectively. Derivatives 8a and 8b have nonyl and nonyloxy chains similarly to derivative 4a and 4b, respectively. With the two types of derivatives, that is, 7a and 8a (R¹ = alkyl; R² = alkoxy) and 7b and 8b (R¹ = alkoxy; R² = alkyl), the effects of the number and position of the alkoxy chains on the mesomorphic properties have been investigated. The thermotropic data of these derivatives are listed in Table 3.

Derivatives 7a and 7b exhibit enantiotropic nematic phases with a wide temperature range. The N–I
transition temperatures of derivatives 7a and 7b are similar (157°C and 164°C, respectively), whereas the Cr–N transition temperature of derivative 7b (114°C) is significantly lower than that of derivative 7a (131°C). As a result, derivative 7b has a wider mesophase range than derivative 7a (7a: 26°C; 7b: 50°C). Derivatives 8a and 8b also exhibit enantiotropic nematic phases with a wide temperature range (8a: 113–136°C; 8b: 100–141°C). The effects of the position of the nonyloxy chains on the Cr–N and N–I transition temperatures are the same as the observations for derivatives 7a and 7b, and derivative 8b has a wider mesophase range than the other derivative.

As shown in Figure 8, the Cr–N transition temperatures of 7a and 7b are significantly lower than the average of those of derivatives 5c and 6b, although the N–I transition temperatures of derivatives 7a and 7b are almost the same as the average of those of derivatives 5c and 6b. Similar features are found for a series of derivatives 8a, 8b, 5e and 6e. Derivative 8b has the lowest Cr–N transition temperature and exhibits almost the same mesophase range as derivative 6c.

These results indicate that the alkoxy chains of the dialkyldialkoxy derivative have a crucial role to play in their mesomorphic behaviour. The replacement of the two alkyl chains of the tetraalkyl derivative by alkoxy chains causes an enantiotropic mesophase with a wide temperature range. Thanks to the two alkoxy chains,
the derivative has a significantly lower N–I transition temperature than the corresponding tetraalkoxy derivative. The results also show that the position of the alkoxy chains (R\(^1\) or R\(^2\) = alkoxy) is an important factor in mesomorphic behaviour. Although the N–I transition temperatures of the derivatives are hardly affected by the position, the Cr–N transition temperatures are strongly affected. The Cr–N temperature of the derivative in which R\(^1\) = alkoxy is significantly lower than those of the other derivative.

These effects of the number and position of the alkoxy chains on the transition temperatures are the same as the observations for the corresponding 4PE2T mesogens. For the both H-shaped mesogens, the attachment of alkyl and alkoxy chains in the R\(^1\) and R\(^2\) positions is a useful method for controlling the mesomorphic properties, and the attachment of alkoxy chains in the R\(^1\) positions is more favourable for an increase in the mesophase range. The mesogenic core has a skewed H-shape. The long rod includes the terminal (5- and 5') positions of 2,2'-bithiophene and therefore is linear, whereas the short rod, including the lateral (3- and 3') positions, is not linear. The observations indicate that the attachment of alkoxy chains at the ends of the long rod causes a wider mesophase range. For a better understanding of the effects of such attachment, it will be necessary to investigate the mesomorphic properties of different H-shaped mesogens, for example, derivatives of 3,3',5,5'-tetraakis(4-(phenylethynyl)phenylethynyl)-2,2'-bithiophene (2PE2(PE)\(_2\)T) and 3,3'-bis[4-(phenylethynyl)phenylethynyl]-5,5'-bis(phenylethynyl)-2,2'-bithiophene (2(PE)\(_2\)2T).

Derivatives 7a, 7b, 8a and 8b, tetraalkyl derivatives 5a–c and tetraalkoxy derivatives 6a–e have entropy values (AS/R) of 0.1–0.2 for the N–I transition (5a–c: 0.1; 6a–e, 7a, 7b, 8a and 8b: 0.2). These entropy changes are significantly smaller than standard values [33,34] and almost the same as those of hockey-stick compounds (0.1–0.3),[12] V-shaped mesogens (0.2–0.5) [12] or 1,2,4,5-tetrakis(4'-alkyl-biphenyl-4-ethynyl)benzenes (0.2 and 0.3).[15] The small entropy values can be attributed to the shape of the molecule. The biaxial nature of the molecule reduces the orientational order in the nematic phase and hence the entropy change at the N–I transition. Such effect of side groups has been observed in the mesogens mentioned above.[12] For the hockey-stick compounds, a derivative with two methyl side groups has a smaller value (0.1) than a derivative without side groups (0.2). For the V-shaped mesogens, the value decreases with increasing number of the methyl side groups (none, 0.4; two, 0.3; four, 0.2).

Nevertheless, a 4(PE)\(_2\)2T molecule with terminal chains (without side chains) has a length-to-breadth-to-width ratio (L:B:W) of about 5.4:1.7:0.45 (nm), estimated using a molecular model. The aspect ratio is similar to an ideal ratio calculated for biaxial particles to form a biaxial phase (L:B:W = 10:1/2:1, or 4.50:1.45:0.45).[37,38] This will require the study of the crystal structure and phase biaxiality of 4(PE)\(_2\)2T mesogens.

3. Conclusion

A new class of extended conjugated mesogens that exhibit nematic phases, that is, H-shaped mesogens based on 3,3',5,5'-tetrasubstituted 2,2'-bithiophene with oligo(1,4-phenyleneethynylene) arms, have been synthesised, and the relationship between molecular structure and mesomorphic properties has been studied. The results show that the length, number and position of the alkyl and alkoxy terminal chains strongly affect the mesomorphic properties. Tetraalkyl derivatives 5a–c, which have pentyl, hexyl and heptyl chains, respectively, exhibit enantiotropic mesophases, whereas derivatives 5d and 5e, with octyl and nonyl chains, respectively, exhibit monotropic mesophases. For the C5–C7 derivatives, the mesophase range decreases with increasing alkyl chain length. The replacement of the heptyl chains of derivative 5c with octyl or nonyl chains destroys the mesophase on heating.

Tetraalkoxy derivatives 6a–e, with alkoxy chains from pentyloxy to nonyloxy, respectively, exhibit enantiotropic mesophases. The mesophase range increases with increasing alkoxy chain length, except that the octyloxy and nonyloxy derivatives, 6d and 6e, have almost the same temperature range. The ranges of the two derivatives are much broader than those of derivatives 6a–c.

Diheptyldihexyloxy derivatives 7a and 7b and dinonyldinonyloxy derivatives 8a and 8b exhibit enantiotropic mesophases. Derivatives 7b and 8b (R\(^2\) = alkyl; R\(^1\) = alkoxy) have a significantly lower Cr–N transition temperature than derivatives 7a and 8a (R\(^1\) = alkyl; R\(^2\) = alkoxy), respectively. The two types of derivatives, 7a and 7b; and 8a and 8b, have a similar N–I transition.
temperature, and the temperatures are significant lower than those of the corresponding tetraalkoxy derivatives.

The structure–property relationships of the newly synthesised mesogens should prove useful for the molecular design of both H-shaped mesogens and other types of mesogens with extended conjugations. We believe that systematic studies of these conjugated mesogens will play an important role in research on liquid crystalline conjugated materials.

4. Experimental section

4.1. Methods

Silica gel column chromatography was carried out using Wakogel C–200 (0.075–0.15 mm, Wako Pure Chemical Industries, Ltd (Wako)). Recycling gel permeation chromatography (GPC) was performed using an HPLC system equipped with a HPLC pump (JASCO PU–2086), two columns in series (Shodex K–2002 and K–2002.5), a refractive index detector (JASCO RI–2031) and a recycle valve (GL Science HPV–Rc). Chloroform was used as eluent at a flow rate of 3.0 ml min⁻¹.

The chemical structures of the compounds were confirmed by their ¹H and ¹³CNMR spectra, recorded on a Bruker Avance 500 MHz NMR spectrometer (Fällanden, Switzerland) in CDCl₃ with TMS as internal standard. Matrix-assisted laser desorption/ionisation time-of-flight mass spectrometry (MALDI–TOF–MS) was performed on a Bruker Daltonics Autoflex Speed MALDI–TOF/TOF mass spectrometer (Billerica, MA, USA), using 2,5-dihydroxybenzoic acid as the matrix. Elemental analyses were carried out on a CE Instruments EA 1110.

The mesomorphic properties of the compounds were investigated by differential scanning calorimetry (DSC) and polarising optical microscopy (POM). Phase transition temperatures and enthalpies were determined on a Perkin–Elmer DSC 7 instrument (Norwalk, CT, USA), operated at a scanning rate of 5°C min⁻¹ for heating and cooling cycles. Optical textures were observed using a Leitz Orthoplan–Pol polarising microscope (Wetzlar, Germany) equipped with a Mettler FP82HT hot stage. Photomicrographs were taken using a Nikon Coolpix 5000 digital camera.

4.2. Materials

Bis(benzonitrile)palladium(II) dichloride, copper(I) iodide and triphenylphosphine were purchased from Tokyo Chemical Industry Co., Ltd (TCI), Wako and Fluka, respectively. 3,3’,5,5’-Tetrabromo-2,2’-bithiophene (9b) was purchased from Wako and recrystallised from dichloromethane–ethanol. 3,3’,5,5’-Tetraiodo-2,2’-bithiophene (9a) was prepared from 2,2’-bithiophene (TCI) using a modified literature procedure.[30] Phenyleneethynylene dimers 10a–e and 11a–e were prepared from 1,4-dibromo-2,5-diethylenzene (Junsei Chemical Co., Ltd) in a manner similar to that described for 1,4-dimethoxy-2-ethyl-5-(phenylethenyl)benzene.

[39] Diisopropylamine (Wako) was deoxygenated by bubbling with nitrogen for 30 min prior to use.

4.3. Synthesis

Synthetic procedures and characterisation data for compound 9a, 12a, 12b, 13a and 13b are described in the Supplemental Information.

4.3.1. Compounds 5a–e

To a solution of compound 9a and the corresponding phenyleneethynylene dimer in i–Pr₂NH (25 ml) were added Pd(PhCN)₂Cl₂, PPh₃ and CuI. The mixture was stirred for 18 h at room temperature. MeOH (80 ml) was added to the reaction mixture, and the solid was filtered and washed with MeOH (20 ml). The resulting solid was chromatographed on silica gel using hexane–CH₂Cl₂ (4:1). Recrystallisation from hexane–EtOH gave the desired product. An analytical sample was obtained by recycling GPC followed by recrystallisation from CHCl₃–EtOH.

Compound 5a

Quantities: 9a (136 mg, 0.203 mmol), 10a (381 mg, 1.16 mmol), Pd(PhCN)₂Cl₂ (27 mg, 0.070 mmol), PPh₃ (58 mg, 0.22 mmol) and CuI (23 mg, 0.12 mmol). Yield: 86% (257 mg) of 5a as a red-orange solid.

¹H NMR (CDCl₃): δ = 0.90 (t, J = 6.9 Hz, 12 H), 1.25–1.37 (m, 40 H), 1.58–1.66 (m, 8 H), 2.62 (t, J = 7.7 Hz, 8 H), 2.80 (q, J = 7.6 Hz, 4 H), 2.85 (q, J = 7.6 Hz, 4 H), 2.91 (q, J = 7.6 Hz, 4 H), 7.18 (AA’BB’, 8 H), 7.34 (s, 2 H), 7.35 (s, 2 H), 7.38 (s, 2 H), 7.42 (s, 2 H), 7.44 (AA’BB’, 4 H), 7.45 (AA’BB’, 4 H), 7.51 (s, 2 H). ¹³C NMR (CDCl₃): δ = 14.03, 14.67, 14.70, 15.21, 22.54, 27.19, 30.97, 31.45, 35.91, 86.37, 87.51, 87.52, 89.31, 94.53, 94.76, 94.78, 95.72, 119.90, 120.52, 121.44, 121.86, 122.24, 123.29, 123.34, 128.53, 131.40, 131.45, 131.51, 131.59, 131.62, 134.75, 137.83, 143.43, 143.59, 143.62. Anal. Calcd for C₁₀₇H₈₁N₂S₂: C, 88.11; H, 7.53. Found: C, 87.92; H, 7.50. MALDI–TOF–MS: m/z = 1470.69 (M⁺, calcd 1470.80).

Compound 5b

Quantities: 9a (141 mg, 0.210 mmol), 10b (435 mg, 1.26 mmol), Pd(PhCN)₂Cl₂ (27 mg, 0.073 mmol), PPh₃...
(42 mg, 0.16 mmol) and CuI (27 mg, 0.14 mmol). Yield: 85% (272 mg) as a red-orange solid.

\[ ^1H \text{NMR (CDCl}_3\text{): } \delta = 0.89 \text{ (t, } J = 6.9 \text{ Hz, 12 H), 1.25–1.37 (m, 48 H), 1.58–1.66 (m, 8 H), 2.62 (t, } J = 7.7 \text{ Hz, 8 H), 2.80 (q, } J = 7.6 \text{ Hz, 4 H), 2.85 (q, } J = 7.6 \text{ Hz, 4 H), 2.87 (q, } J = 7.6 \text{ Hz, 4 H), 2.91 (q, } J = 7.6 \text{ Hz, 4 H), 7.18 (AA'BB', 8 H), 7.34 (s, 2 H), 7.35 (s, 2 H), 7.38 (s, 2 H), 7.42 (s, 2 H), 7.44 (AA'BB', 4 H), 7.45 (AA'BB', 4 H), 7.51 (s, 2 H). \]

\[ ^{13}C \text{ NMR (CDCl}_3\text{): } \delta = 14.10, 14.67, 14.69, 15.21, 22.67, 27.19, 28.94, 31.25, 31.71, 35.95, 86.37, 87.51, 87.52, 89.32, 94.53, 94.77, 94.78, 95.73, 119.89, 120.51, 121.44, 121.86, 122.23, 122.29, 123.33, 123.37, 128.52, 131.40, 131.44, 131.51, 131.58, 131.62, 134.75, 134.83, 143.43, 143.59, 143.61. \]

Analysis: Calcld for C\text{_{12}H\text{_{13}S}_{2}}: C, 88.02; H, 7.78. Found: C, 87.92; H, 7.75. MALDI–TOF–MS: \( m/z = 1526.80 \) (M\(^+\), calcld 1526.87).

**Compound 5e**

Quantities: 9a (141 mg, 0.210 mmol), 10e (490 mg, 1.27 mmol), Pd(PhCN)\text{Cl}_2 (26 mg, 0.068 mmol), PPh\text{$_3$} (46 mg, 0.17 mmol) and CuI (23 mg, 0.12 mmol). Yield: 90% (322 mg) as a red-orange solid.

\[ ^1H \text{NMR (CDCl}_3\text{): } \delta = 0.88 \text{ (t, } J = 6.9 \text{ Hz, 12 H), 1.24–1.37 (m, 72 H), 1.58–1.66 (m, 8 H), 2.62 (t, } J = 7.7 \text{ Hz, 8 H), 2.80 (q, } J = 7.6 \text{ Hz, 4 H), 2.85 (q, } J = 7.6 \text{ Hz, 4 H), 2.87 (q, } J = 7.6 \text{ Hz, 4 H), 2.91 (q, } J = 7.6 \text{ Hz, 4 H), 7.18 (AA'BB', 8 H), 7.34 (s, 2 H), 7.35 (s, 2 H), 7.38 (s, 2 H), 7.42 (s, 2 H), 7.44 (AA'BB', 4 H), 7.45 (AA'BB', 4 H), 7.50 (s, 2 H). \]

\[ ^{13}C \text{ NMR (CDCl}_3\text{): } \delta = 14.12, 14.67, 14.70, 15.21, 22.69, 27.19, 29.27, 29.33, 29.50, 29.55, 31.30, 31.50, 35.95, 86.37, 87.52, 89.32, 94.53, 94.77, 94.78, 95.73, 119.90, 120.51, 121.45, 121.87, 122.24, 122.30, 123.34, 123.53, 131.40, 131.45, 131.51, 131.59, 131.63, 134.76, 137.83, 143.43, 143.60, 143.62. \]

Analysis: Calcld for C\text{_{12}H\text{_{14}S}_{2}}: C, 87.78; H, 8.44. Found: C, 87.47; H, 8.39. MALDI–TOF–MS: \( m/z = 1694.98 \) (M\(^+\), calcld 1695.06).

### 4.3.2. Compounds 6a–e

Synthesised using the procedure described for 5a–e, except for the eluent of column chromatography (hexane/CH\text{Cl}_2 = 2:1)

**Compound 6a**

Quantities: 9a (136 mg, 0.203 mmol), 11a (441 mg, 1.28 mmol), Pd(PhCN)\text{Cl}_2 (28 mg, 0.073 mmol), PPh\text{$_3$} (48 mg, 0.18 mmol) and CuI (32 mg, 0.17 mmol). Yield: 90% (280 mg) as a red-orange solid.

\[ ^1H \text{NMR (CDCl}_3\text{): } \delta = 0.94 \text{ (t, } J = 7.2 \text{ Hz, 12 H), 1.27 (t, } J = 7.6 \text{ Hz, 6 H), 1.31 (t, } J = 7.6 \text{ Hz, 6 H), 1.32 (t, } J = 7.6 \text{ Hz, 6 H), 1.34 (t, } J = 7.6 \text{ Hz, 6 H), 1.36–1.49 (m, 16 H), 1.76–1.84 (m, 8 H), 2.80 (q, } J = 7.6 \text{ Hz, 4 H), 2.84 (q, } J = 7.6 \text{ Hz, 4 H), 2.86 (q, } J = 7.6 \text{ Hz, 4 H), 2.91 (q, } J = 7.6 \text{ Hz, 4 H), 3.98 (t, } J = 6.6 \text{ Hz, 8 H), 6.89 (AA'BB', 8 H), 7.33 (s, 2 H), 7.35 (s, 2 H), 7.36 (s, 2 H), 7.40 (s, 2 H), 7.45 (AA'BB', 4 H), 7.46 (AA'BB', 4 H), 7.50 (s, 2 H). \]

\[ ^{13}C \text{ NMR (CDCl}_3\text{): } \delta = 14.03, 14.65, 14.70, 15.21, 22.47, 27.18, 28.18, 28.90, 68.11, 86.33, 86.81, 86.82, 89.28, 94.57, 94.72, 95.79, 114.60, 115.23, 115.26, 119.89, 121.24, 121.66, 122.23, 123.47, 123.51, 131.37, 131.48, 131.55, 132.97, 134.71, 137.79, 143.26, 143.40, 143.60, 159.34. \]

Analysis: Calcld for C\text{_{108}H\text{_{110}O}_{4}S}_{2}: 94.77, 94.79, 95.73, 119.91, 120.51, 121.45, 121.87, 122.25, 123.30, 123.35, 128.53, 131.40, 131.45, 131.52, 131.59, 131.63, 134.75, 134.43, 143.60, 143.62.
C, 84.44; H, 7.22. Found: C, 84.36; H, 7.15. MALDI-TOF–MS: m/z = 1534.69 (M⁺, calc 1534.78).

**Compound 6b**

Quantities: 9a (141 mg, 0.210 mmol), 11b (483 mg, 1.30 mmol), Pd(PhCN)₂Cl₂ (28 mg, 0.073 mmol), PPh₃ (49 mg, 0.19 mmol) and Cul (30 mg, 0.16 mmol).

Yield: 92% (308 mg) as a red-orange solid.

¹H NMR (CDCl₃): δ = 0.91 (t, J = 7.1 Hz, 12 H), 1.24–1.40 (m, 40 H), 1.42–1.51 (m, 8 H), 1.76–1.83 (m, 8 H), 2.80 (q, J = 7.6 Hz, 4 H), 2.84 (q, J = 7.6 Hz, 4 H), 2.86 (q, J = 7.6 Hz, 4 H), 2.91 (q, J = 7.6 Hz, 4 H), 3.98 (t, J = 6.6 Hz, 8 H), 6.89 (AA'BB', 8 H), 7.33 (s, 2 H), 7.35 (s, 2 H), 7.36 (s, 2 H), 7.40 (s, 2 H), 7.45 (AA'BB', 4 H), 7.46 (AA'BB', 4 H), 7.50 (s, 2 H). ¹³C NMR (CDCl₃): δ = 14.04, 14.65, 14.70, 15.22, 22.61, 25.71, 27.18, 29.17, 31.59, 68.12, 86.32, 86.80, 88.29, 94.56, 94.72, 95.79, 114.60, 115.23, 115.25, 119.89, 121.24, 121.66, 122.23, 123.46, 123.51, 131.37, 131.48, 131.55, 132.96, 137.79, 143.26, 143.40, 143.60, 159.34. Anal. Calcld for C₁₁₂H₁₁₄O₃S₂: C, 84.48; H, 7.47. Found: C, 84.33; H, 7.41. MALDI–TOF–MS: m/z = 1590.78 (M⁺, calc 1590.85).

**Compound 6d**

Quantities: 9a (137 mg, 0.205 mmol), 11c (455 mg, 1.22 mmol), Pd(PhCN)₂Cl₂ (23 mg, 0.060 mmol), PPh₃ (37 mg, 0.14 mmol) and Cul (21 mg, 0.11 mmol).

Yield: 92% (309 mg) as a red-orange solid.

¹H NMR (CDCl₃): δ = 0.90 (t, J = 6.9 Hz, 12 H), 1.24–1.40 (m, 48 H), 1.42–1.50 (m, 8 H), 1.76–1.83 (m, 8 H), 2.80 (q, J = 7.6 Hz, 4 H), 2.84 (q, J = 7.6 Hz, 4 H), 2.86 (q, J = 7.6 Hz, 4 H), 2.91 (q, J = 7.6 Hz, 4 H), 3.98 (t, J = 6.6 Hz, 8 H), 6.89 (AA'BB', 8 H), 7.33 (s, 2 H), 7.35 (s, 2 H), 7.36 (s, 2 H), 7.40 (s, 2 H), 7.45 (AA'BB', 4 H), 7.46 (AA'BB', 4 H), 7.50 (s, 2 H). ¹³C NMR (CDCl₃): δ = 14.10, 14.65, 14.70, 15.22, 22.62, 25.99, 27.18, 29.07, 29.21, 31.79, 68.12, 86.32, 86.81, 86.82, 89.27, 94.56, 94.72, 95.78, 114.60, 115.23, 115.25, 119.89, 121.24, 121.66, 122.23, 123.46, 123.51, 131.37, 131.48, 131.55, 132.97, 137.79, 143.26, 143.40, 143.60, 159.34. Anal. Calcld for C₁₁₂H₁₁₄O₃S₂: C, 84.52; H, 7.70. Found: C, 84.51; H, 7.67. MALDI–TOF–MS: m/z = 1646.79 (M⁺, calc 1646.91).

**4.3.3. Compounds 7a, 7b, 8a and 8b**

To a solution of the corresponding dibromomobithio-phene and phenylethynylene dimer in i-Pr₂NH (25 ml) were added Pd(PhCN)₂Cl₂, PPh₃ and Cul. The mixture was stirred 85°C for 16 h. The reaction mixture was cooled to room temperature and MeOH (100 ml) was added. The resulting solid was filtered, washed with MeOH (25 ml) and chromatographed (SiO₂, hexane/CH₂Cl₂ 2:1). Recrystallisation from hexane–EtOH gave the desired product. An analytical sample was obtained by recycling GPC followed by recrystallisation from CHCl₃–EtOH.

**Compound 7a**

Quantities: 12a (207 mg, 0.200 mmol), 11b (572 mg, 1.60 mmol), Pd(PhCN)₂Cl₂ (34 mg, 0.089 mmol), PPh₃ (62 mg, 0.24 mmol) and Cul (35 mg, 0.18 mmol).

Yield: 93% (297 mg) as a red-orange solid.
\[ \text{H NMR (CDCl}_3\): } \delta = 0.89 (t, J = 7.1 \text{ Hz, 6 H}), 0.91 (t, J = 7.1 \text{ Hz, 6 H}), 1.24–1.38 (m, 48 H), 1.43–1.51 (m, 4 H), 1.58–1.65 (m, 4 H), 1.76–1.83 (m, 4 H), 2.62 (t, J = 7.7 \text{ Hz, 4 H}), 2.81 (q, J = 7.6 \text{ Hz, 4 H}), 2.85 (q, J = 8.0 \text{ Hz, 4 H}), 2.86 (q, J = 8.0 \text{ Hz, 4 H}), 2.91 (q, J = 7.6 \text{ Hz, 4 H}), 3.98 (t, J = 6.6 \text{ Hz, 4 H}), 6.89 (AA'BB', 4 H), 7.18 (AA'BB', 4 H), 7.34 (s, 2 H), 7.35 (s, 2 H), 7.38 (s, 2 H), 7.40 (s, 2 H), 7.44 (AA'BB', 4 H), 7.46 (AA'BB', 4 H), 7.50 (s, 2 H). 13C NMR (CDCl3): \delta = 14.13, 14.64, 14.68, 14.70, 15.22, 22.69, 26.03, 27.19, 29.21, 29.27, 29.33, 29.41, 29.51, 29.55, 31.30, 31.89, 35.95, 68.11, 86.40, 86.82, 87.51, 89.27, 94.51, 94.74, 94.76, 95.81, 114.59, 115.24, 119.89, 120.49, 121.45, 121.65, 122.19, 123.28, 123.51, 128.52, 131.39, 131.43, 131.48, 131.50, 131.55, 132.97, 134.75, 137.81, 134.25, 143.41, 143.44, 143.60, 159.33. Anal. Calcd for C12H14Cl2O2S: C, 86.16; H, 8.28. Found: C, 86.20; H, 8.30. MALDI–TOF–MS: \text{m/z = 1727.96 (M}^+, \text{calcld 1728.05).}

**Compound 7b**

Quantities: 13a (212 mg, 0.204 mmol), 10c (581 mg, 1.63 mmol), Pd(PhCN)2Cl2 (38 mg, 0.099 mmol), PPh3 (59 mg, 0.22 mmol) and Cul (41 mg, 0.22 mmol).

Yield: 92% (297 mg) as a red-orange solid.

\[ \text{H NMR (CDCl}_3\): } \delta = 0.88 (t, J = 7.2 \text{ Hz, 6 H}), 0.91 (t, J = 7.0 \text{ Hz, 6 H}), 1.24–1.38 (m, 48 H), 1.43–1.51 (m, 4 H), 1.58–1.65 (m, 4 H), 1.76–1.83 (m, 4 H), 2.62 (t, J = 7.7 \text{ Hz, 4 H}), 2.80 (q, J = 7.6 \text{ Hz, 4 H}), 2.84 (q, J = 7.5 \text{ Hz, 4 H}), 2.87 (q, J = 7.5 \text{ Hz, 4 H}), 2.91 (q, J = 7.6 \text{ Hz, 4 H}), 3.98 (t, J = 6.6 \text{ Hz, 4 H}), 6.89 (AA'BB', 4 H), 7.18 (AA'BB', 4 H), 7.33 (s, 2 H), 7.35 (s, 2 H), 7.36 (s, 2 H), 7.42 (s, 2 H), 7.45 (AA'BB', 8 H), 7.50 (s, 2 H). 13C NMR (CDCl3): \delta = 14.04, 14.11, 14.66, 14.70, 15.21, 22.61, 22.67, 25.71, 27.18, 27.21, 29.17, 29.23, 31.30, 31.59, 31.82, 35.95, 68.11, 86.31, 86.80, 87.53, 89.34, 94.58, 94.72, 94.78, 95.73, 114.59, 115.23, 119.87, 120.51, 121.23, 121.87, 122.25, 123.33, 123.47, 128.53, 131.37, 131.43, 131.45, 131.57, 131.62, 132.96, 134.72, 137.81, 143.26, 143.39, 143.42, 143.58, 143.61, 159.33. Anal. Calcd for C11H12Cl2O2S: C, 86.21; H, 7.74. Found: C, 86.56; H, 7.74. MALDI–TOF–MS: \text{m/z = 1587.81 (M}^+, \text{calcld 1587.89).}

**Compound 8a**

Quantities: 12b (222 mg, 0.204 mmol), 11e (682 mg, 1.70 mmol), Pd(PhCN)2Cl2 (33 mg, 0.086 mmol), PPh3 (58 mg, 0.22 mmol) and Cul (35 mg, 0.18 mmol).

Yield: 93% (328 mg) as a red-orange solid.

\[ \text{H NMR (CDCl}_3\): } \delta = 0.88 (t, J = 7.0 \text{ Hz, 6 H}), 0.89 (t, J = 7.0 \text{ Hz, 6 H}), 1.23–1.38 (m, 68 H), 1.42–1.50 (m, 4 H), 1.58–1.65 (m, 4 H), 1.76–1.83 (m, 4 H), 2.62 (t, J = 7.7 \text{ Hz, 4 H}), 2.81 (q, J = 7.6 \text{ Hz, 4 H}), 2.85 (q, J = 8.0 \text{ Hz, 4 H}), 2.86 (q, J = 8.0 \text{ Hz, 4 H}), 2.91 (q, J = 7.6 \text{ Hz, 4 H}), 3.98 (t, J = 6.6 \text{ Hz, 4 H}), 6.89 (AA'BB', 4 H), 7.18 (AA'BB', 4 H), 7.34 (s, 2 H), 7.35 (s, 2 H), 7.38 (s, 2 H), 7.40 (s, 2 H), 7.44 (AA'BB', 4 H), 7.46 (AA'BB', 4 H), 7.50 (s, 2 H). 13C NMR (CDCl3): \delta = 14.13, 14.64, 14.68, 14.70, 15.22, 22.69, 26.03, 27.19, 29.21, 29.27, 29.33, 29.41, 29.51, 29.55, 31.30, 31.89, 35.95, 68.11, 86.40, 86.82, 87.51, 89.27, 94.51, 94.74, 94.76, 95.81, 114.59, 115.24, 119.89, 120.49, 121.45, 121.65, 122.19, 123.28, 123.51, 128.52, 131.39, 131.43, 131.48, 131.50, 131.54, 132.97, 134.75, 137.81, 143.25, 143.40, 143.43, 143.60, 159.33. Anal. Calcd for C12H14Cl2O2S: C, 86.16; H, 8.28. Found: C, 86.20; H, 8.30. MALDI–TOF–MS: \text{m/z = 1727.96 (M}^+, \text{calcld 1728.05).}

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