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Synthesis and mesophase behaviour of rigid rod-like phenylthiophene-based amphiphilic diol derivatives

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Novel amphiphilic block molecules consisting of a rigid 2-phenylthiophene or 5-phenylbithienyl core, with a polar glycerol group attached to the phenyl ring and one or two alkyl chains attached to the thiophene ring on the other side, have been synthesised by using Ni(0) and Pd(0) catalyzed coupling reactions as key steps. The thermotropic and solvent-induced liquid crystalline behaviour of these compounds was investigated by polarising optical microscopy and X-ray diffraction. The influence of the length, number and position of the alkyl chains, and the length of the rigid core, on their mesophase behaviour was investigated. Compounds with one alkyl chain in the terminal 5-position on the thiophene ring form only smectic A phases, compounds with two adjacent alkyl chains attached in the 4- and 5-positions of the thiophene ring exhibit thermotropic columnar mesophases, and those with two long alkyl chains attached to the 3- and 5-positions form columnar LC phases only in the presence of water. Another compound containing the longer 5-phenylbithienyl core unit and two alkyl chains attached in lateral positions to each of the thiophene rings is not mesogenic.

Keywords: thiophene derivatives; amphiphiles; carbon–carbon coupling; mesophase; synthesis

1. Introduction

In recent decades liquid crystalline materials have received much attention. The combination of order and mobility in these systems has led to novel functional materials, which have had a significant impact on the development of mobile information technologies (*1*). Compounds that form liquid crystalline phases are divided into two classes: anisometric mesogens and amphiphilic molecules. Anisometric mesogens, including rod-like and disc-like molecules, in most cases give exclusively thermotropic liquid crystals. Amphiphilic molecules, consisting of hydrophilic and lipophilic parts, could lead to both lyotropic and thermotropic mesophases. Additionally, different molecular structures combining anisometric and amphiphilic structural units have been designed to bridge the gap between thermotropic and lyotropic liquid crystals (amphotropic LCs) (*2*). For example, three block biphenyl based amphotrops were obtained by combining rigid biphenyl rods with flexible and lipophilic alkyl chains at one end and flexible, but polar oligooxyethylene chains terminated with hydroxyl groups at the other end (compounds **A**, see Scheme 1), as designed by Tschierske's group (*3, 4*). Such block molecules show a diversity of different mesophases, including smectic, columnar and cubic, similar to those found in lyotropic systems and in the thermotropic phase sequence of polycatenar compounds (*5*). Shape anisotropy, dipole–dipole interactions, microphase segregation and non-covalent interactions are considered as the most fundamental factors in designing new types of liquid crystalline molecules (*6*).

Thiophene-based derivatives have been widely studied because of their potential charge carrier properties (*7*). Among them, thiophene-based amphiphilic mesogens are considered as excellent candidates for organic field-effect transistors (OFETS), because by a solution process they can form highly ordered mesophases, which can be further transferred into organic thin-film devices with high charge carrier mobility. However, to the best of our knowledge, there are only few reports about thiophene-based amphiphilic mesogens (*8*). In these molecules, oligothiophenes were laterally substituted by lipophilic alkyl groups as well as by hydrophilic oligooxyethylene groups or ionic groups. The aim of this work was threefold: to design new types of amphiphilic thiophene derivatives, in which the thiophene units are incorporated into a rod-like mesogenic unit with a hydrophilic group at one end and alkyl chains in different positions; secondly, to investigate their mesophase behaviour; finally, to understand the relationship between structure and mesomorphic properties of these new amphiphilic thiophene derivatives.

Recently we have reported that 4-(5-bromothien-2-yl)anisole (**5/0**, Scheme 2), which was obtained in the monocoupling reaction between 2,5-dibromothiophene

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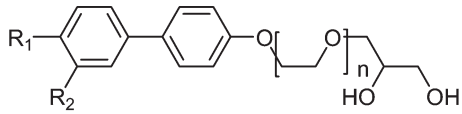
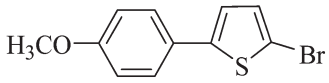


A/a: $R_1 = OC_{12}H_{25}$, $R_2 = H$, $n = 0$: Cr 176 SmA 195 I [3a]
A/b: $R_1 = OC_{16}H_{33}$, $R_2 = H$, $n = 1$: Cr 136 Col_{ob1} 145 Cub 146 Col_{ob2} 148 SmA 170 I [4]
A/c: $R_1 = OC_{12}H_{25}$, $R_2 = OC_{12}H_{25}$, $n = 1$: Cr 87 Col_{hex}135 I [15]

Scheme 1. Structures and phase transition temperatures (°C) of **A** compounds.



Scheme 2. Structure of **5/0**.

and 4-methoxybenzeneboronic acid (*9*), can serve as valuable building block for designing new mesogens (*10*).

In this paper, we describe the extension of the use of compound **5/0** for the design of new amphipilic 2-phenylthiophene-based mesogens (**I–III**, see Table 1) with a polar glycerol (2,3-dihydroxyprop-1-yloxy) terminal group attached at the phenyl ring and one or two alkyl chains attached to the thiophene rings. Compounds **I** could be considered as analogues of the biphenyl amphotrops **A** in the sense that three different molecular blocks (rigid aromatic core, lipophilic chains and polar group) are connected in the same topology as in **A**, but the chemical structure of the aromatic core is different from that in **A** (*3a, e*). Compounds **II** have a second aliphatic chain in a lateral position, whereas compound **III** has an additional thiophene ring and a lateral alkyl chain is fixed to each of the thiophene rings of the bithienyl unit. The liquid crystalline behaviour of these compounds was investigated by polarising optical microscopy (POM) and X-ray diffraction. The influence of the length, number and position of the alkyl chains and the length of the rigid cores on the mesophase behaviour was investigated.

2. Results and discussion

Synthesis

The synthesis of thiophene-based amphiphilic compounds **I/*m*/*n***, **II/6/*n*** and **III/12/12** is shown in Scheme 3. Palladium-catalyzed Suzuki cross-coupling (*11*) between 3-alkyl-2,5-dibromothiophene (**2/*m***) and 4-methoxybenzeneboronic acid with $NaHCO_3$ as base gave a mixture of the monocoupling products **5/*m*** and **8/*m*** in 15.3% and 7.6% yield, respectively. From this mixture, the monocoupling products **5/*m*** and **8/*m*** could be easily separated by column chromatography. Alternatively, **8/*m*** could also be obtained from 3-alkyl-2-bromothiophene (**3/*m***) by Suzuki reaction with 4-methoxybenzeneboronic acid (Scheme 3, right) in 78% yield. Compound **8/*m*** was coupled with *n*-alkyl Grignard reagent or with 3-alkylthiene-2-ylmagnesium bromide reagent (Kumada coupling) resulting in the thiophene compound **9/6/*n*** or the bithienyl derivative **10/12/12**, respectively.

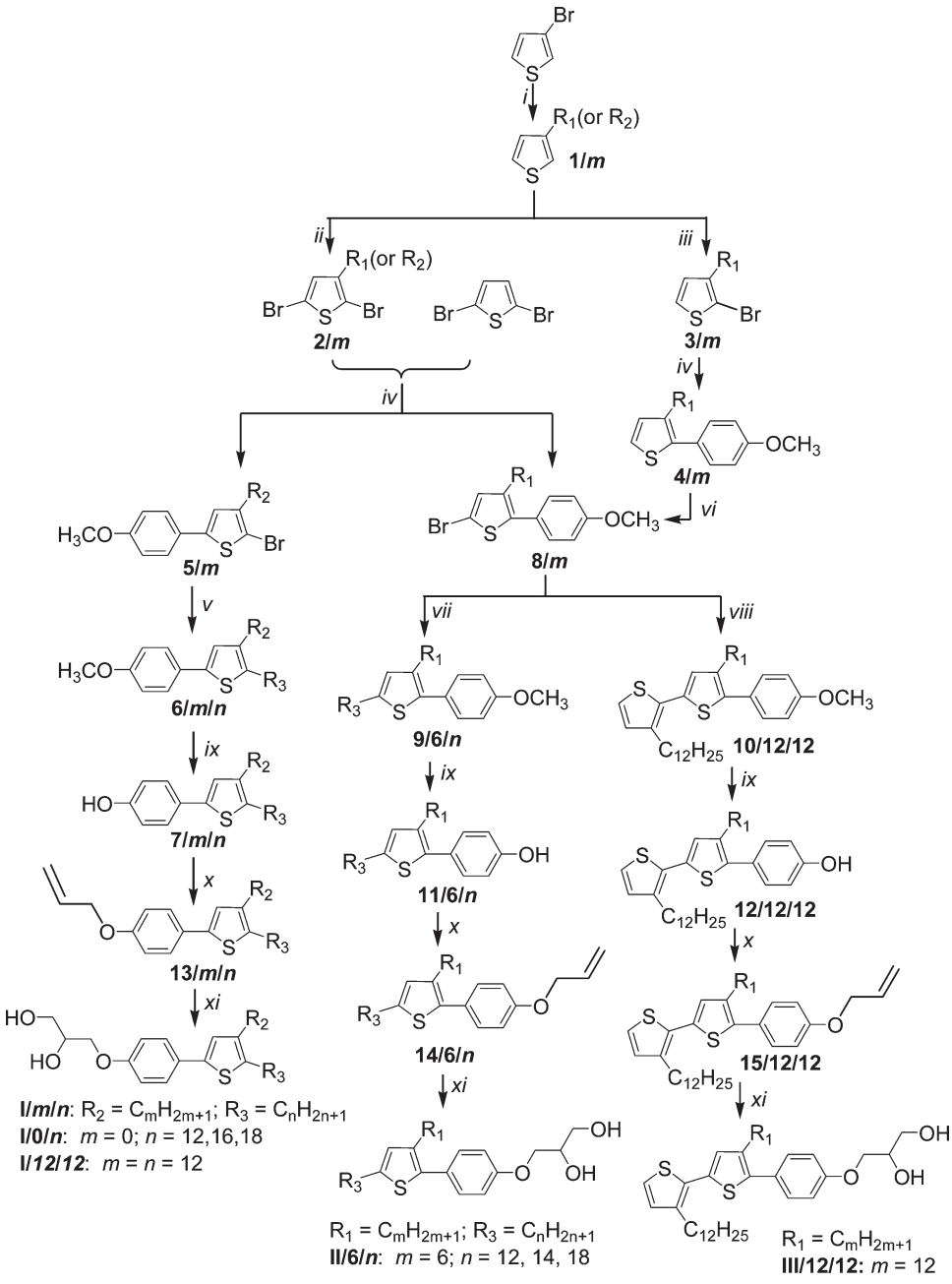
Exchange of Br against Li in compound **5/*m***, followed by coupling with excess bromoalkanes gave compound **6/*m*/*n***. The following steps were the same for compounds **6/*m*/*n***, **9/6/*n*** and **10/12/12**. Demethylation with BBr_3 at −78°C (*12*) yielded the phenols **7/*m*/*n***, **11/6/*n*** and **12/12/12**, respectively, which were etherified with allyl bromide followed by dihydroxylation of the double bonds with catalytic amounts of osmium tetroxide and *N*-methylmorpholine *N*-oxide (NMMNO) as reoxidant (*13*) to yield the diols **I/*m*/*n***, **II/6/*n*** and **III/12/12**, respectively. Purification of these diols was done by crystallisation or column chromatography, the structure and purity of all compounds were confirmed by ^{1}H NMR and HRMS spectroscopy.

Mesophase behaviour

The liquid crystalline properties of compounds **I/*m*/*n***, **II/6/*n*** and **III/12/12** were investigated by POM and for selected compounds by X-ray scattering. Generally, since all compounds contain the 2,3-dihydroxypropyloxy terminal group, the hydrogen bonding between such diol groups leads to strong cohesive forces in the polar regions, which should reinforce microsegregation and contribute to mesophase stability.

Single-chain amphiphiles with a 2-phenylthiophene core.

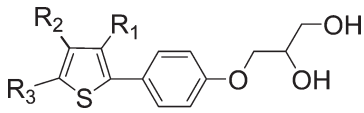
The transition temperatures of the single-chain compounds **I/0/*n*** are collected in Table 1. All of them exhibit only thermotropic smectic A (SmA) phases, as characterised by textures consisting of both focal-conic and pseudo-isotropic regions. The occurrence of focal-conic fans suggests a layered structure, whereas the pseudo-isotropic region indicates an on average orthogonal organisation of the molecules with respect to the layer planes (*14*). The layer spacings in these SmA phases, as determined by X-ray scattering, are d=4.5 nm for **I/0/12** and d=5.0 nm



Scheme 3. Synthesis of compounds **I, II** and **III**. Reagents and conditions: (*i*) $C_nH_{2n+1}MgBr$, THF, reflux, 15 h; (*ii*) NBS, $CHCl_3$, DMF, RT, 12 h; (*iii*) NBS, THF, 0–5°C, 1 h; (*iv*) 4-methoxyphenylboronic acid, $Pd(PPh_3)_4$, $NaHCO_3$, glyme, H_2O, reflux, 6 h; (*v*) *n*-BuLi, −60°C, THF, 1-bromoalkane, RT, 24h; (*vi*) NBS, THF, 0–5°C, 1 h; (*vii*) $C_nH_{2n+1}MgBr$, THF, reflux, 15 h; (*viii*) 3-dodecyl-2-thienylMgBr, THF, reflux, 15 h; (*ix*) BBr_3, −78°C, CH_2Cl_2, RT, 24 h; (*x*) allyl bromide, K_2CO_3, CH_3CN, reflux, 2 h; (*xi*) OsO_4, NMMNO, H_2O, acetone, RT.

for **I/0/18**. Compared with the molecular lengths of these molecules in their most stretched conformations (L=3.0 and 3.8 nm, respectively) this indicates a bilayer structure of the mesophases. With elongation of the terminal alkyl chains, both the melting and the clearing points of **I/0/*n*** decrease. Comparison of the thiophenes **I/0/*n*** with the reported biphenyl analogues with the same chain length (alkyl for compounds **I/0/*n***, alkoxy for the related biphenyl derivatives **A**) indicates that the melting and the clearing points are decreased for the thiophene-based compounds (*3a*). For example, compound **A/a** with n=0 and R=$OC_{12}H_{25}$ (Cr 176°C SmA 195°C I) can be compared with compound **I/0/12** (Cr 137°C SmA 159°C I). This reduction of mesophase stability should be due to the slightly bent shape in the rigid

Table 1. Phase transition temperatures (T/°C) of the compounds investigated.



Compound	R_1	R_2	R_3	T/°C
I/0/12	H	H	$C_{12}H_{25}$	Cr 137 SmA 159 I
I/0/16	H	H	$C_{16}H_{33}$	Cr 135 SmA 155 I
I/0/18	H	H	$C_{18}H_{37}$	Cr 134 SmA 148 I
I/12/12	H	$C_{12}H_{25}$	$C_{12}H_{25}$	Cr 44 Col_{hex} 75 I
II/6/12	C_6H_{13}	H	$C_{12}H_{25}$	liquid
II/6/14	C_6H_{13}	H	$C_{14}H_{29}$	Cr 54 I
II/6/18	C_6H_{13}	H	$C_{18}H_{37}$	Cr 56 I
III/12/12	$C_{12}H_{25}$	H	3-dodecylthienyl	liquid

phenylthiophene core, induced by the thiophene unit (bond angle 147.5°) and due to the replacement of the alkoxy chains by alkyl chains, which provide more flexibility of the lipophilic parts. A major advantage of the thiophene derivatives **I/0/*n*** is that the melting temperatures are also reduced considerably; hence the mesomorphic ranges are approximately the same in both series, whereas all transition temperatures are shifted to lower temperatures.

Double-chain compounds.

Two types of double-chain compounds, **I/12/12** and **II/6/*n***, were synthesised, which differ in the position of the two alkyl chains attached to the thiophene ring. Compound **III/12/12** also has two alkyl chains, but in this compound the length of the rigid core is increased by an additional thiophene ring and the two chains are grafted laterally to different thiophene rings.

Compound **I/12/12**, in which the alkyl chains are located in the neighbouring 4,5-positions of the thiophene ring exhibits a hexagonal columnar (Col_{hex}) phase. The texture observed by POM is characterised by typical spherulitic domains (Figure 1(a)). The hexagonal lattice (Col_{hex}/*P6mm*) of the mesophase was further confirmed by the hexagonal symmetry of the two-dimensional X-ray diffraction pattern of a surface-aligned sample of compound **I/12/12** (Figure 1(b)). The hexagonal lattice parameter is measured to be a=4.26 nm (at T=50°C). Assuming a density of ρ=1 g cm^{-3}, the number n of molecules arranged side by side in a single slice of the columns with a thickness (h) of 0.45 nm (maximum of the diffuse wide-angle scattering) was estimated according to

$$n = \left(a^2/2\right)\sqrt{3}h(N_A/M)\rho, \qquad (1)$$

and using the hexagonal lattice parameter, a, the Avogadro constant, N_A and the molecular mass, M, to give n about 7 (Figure 1(c)).

The introduction of the second alkyl chain induces a change of the molecular shape from rod-like (compounds **I**) to taper shaped, leading to an organisation of the molecules in circular cylindrical aggregates, which can organise into a hexagonal lattice. This is very similar to observations made with other tapered amphipiles (*16*). Comparison of the thiophene **I/12/12** (Cr 44°C Col_{hex} 75°C I) with the reported biphenyl analogue **A/c** (Cr 87°C Col_{hex} 135°C I) having the same chain length (alkyl for compounds **I/12/12**, alkoxy for the related biphenyl derivative) indicates that the melting and the clearing points are decreased for the thiophene-based compounds.

Since the compounds under discussion are amphiphilic, the influence of water on the phase behaviour was studied for selected compounds. The columnar phase of **I/12/12** is significantly stabilised on addition of water. The mesophase is stable up to 100°C, but due to rapid evaporation of the solvent the clearing temperature cannot be determined precisely. The water molecules interact with the diol groups and provide additional hydrogen bonding, which increases the attractive forces between the polar groups. This should also increase the contrast between polar region and non-polar region and therefore enhance the microsegregation of the incompatible parts, both effects stabilising the columnar phase.

Compounds **II/6/*n***, in which one of the alkyl chains is moved to the 3-position of the thiophene ring, are not mesogens in the pure state. This is most likely due to the position of the second alkyl chain in a lateral position, which is likely to disturb the self-assembly of the molecules. Only after adding water could a liquid crystalline phase be observed for the compounds with n=14 and n=18. The textures (Figure 2) suggest that columnar phases are induced. For compound **II/6/14** a maximum of the mesophase

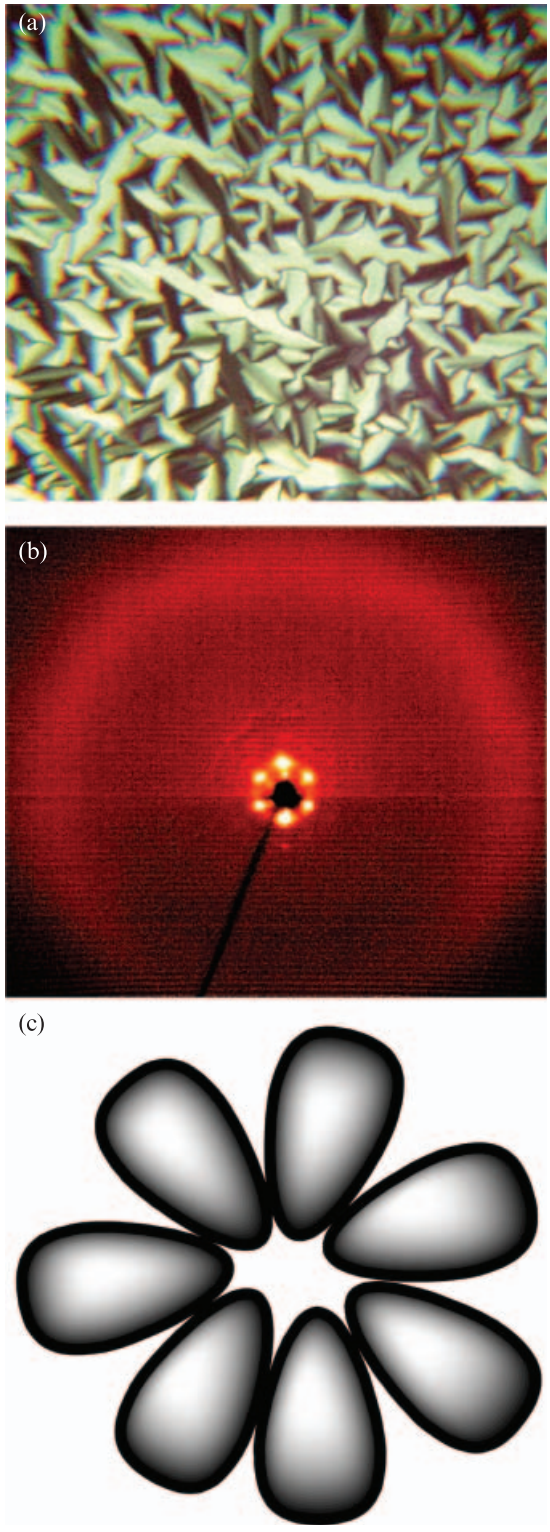


Figure 1. (a) Texture (crossed polarisers) of the Col_{hex} phase of compound **I/12/12** at 70°C; (b) X-ray diffraction pattern of an aligned sample of the $Col_{hex}/P6mm$ phase of compound **I/12/12** at $T=50$°C; (c) Cross-section of a column in the columnar mesophase of compound **I/12/12**.

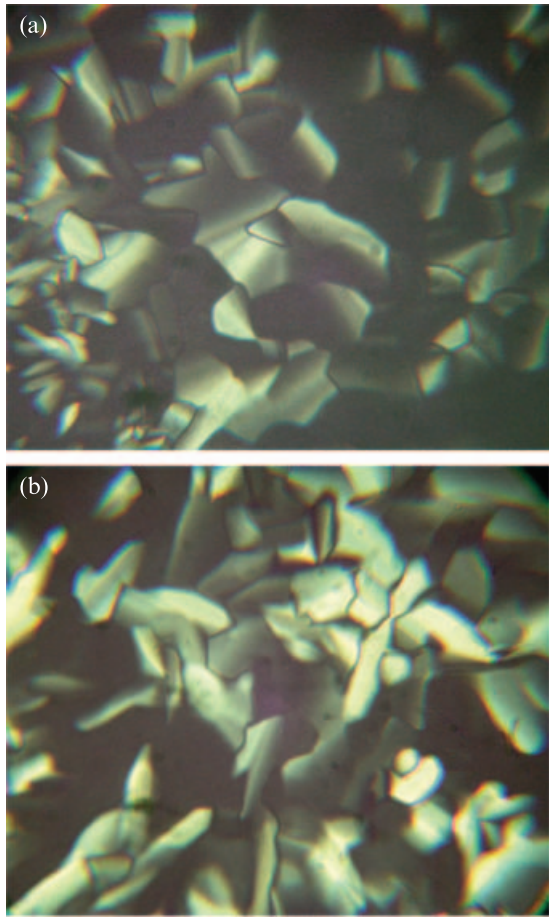


Figure 2. (a) Texture (crossed polarisers) of the induced lyotropic columnar phase of compound **II/6/14** with water ($T=25$°C, water-saturated sample). (b) Textures (crossed polarisers) of the induced lyotropic columnar phase of compound **II/6/18** with water ($T=70$°C, water-saturated sample).

stability of ca. 100°C was obtained for a water concentration of ca. 30 mass %. On further increasing the water concentration the mesophase stability decreases again to $T=51$°C, which corresponds to the water-saturated sample. No change of the texture could be observed in the whole mesomorphic region. For **II/6/18** the clearing temperature of the induced columnar phase is >100°C for the water-saturated sample. No mesophase is induced in the case of the short-chain compound **II/6/12**. Although the water-induced columnar mesophases of compounds **II/6/*n*** are stabilised with increasing chain length from $n=14$ to $n=18$, no thermotropic LC phase can be achieved by elongation of the terminal alkyl chains.

In compound **III/12/12**, in which the rigid core is elongated by introducing an extra thiophene ring, both alkyl chains are located in lateral positions. For this compound neither thermotropic nor solvent-induced mesophases could be observed. The two lateral alkyl chains seem to disfavour the parallel

alignment of the rigid cores, preventing mesophase formation.

3. Conclusion

In summary, we have synthesised the first examples of amphiphilic diol-based mesogens incorporating the phenylthiophene structural motif. The influence of structural variations, such as the number and position of the lateral alkyl chains was investigated. For the single-chain compounds **I/0/*n***, with an alkyl chain in the terminal position of the rigid core, only smectic A phases were found, whereas, for the two-chain compound **I/12/12**, in which the second alkyl chain is grafted directly beside the terminal alkyl chain, a hexagonal columnar phase is observed. In contrast, the connection of a second aliphatic chain to a lateral position closer to the centre of the calamitic core gives rise to a complete loss of the thermotropic mesophase, accompanied by a drastic decrease of the melting temperatures (compounds **II/6/*n***). However, by interaction with water a columnar mesophase can be induced for compounds with long chains. For compound **III/12/12**, in which two alkyl chains are located in lateral position at the rigid core no mesophase can be found. In this molecule, in addition to the steric effect of the lateral substituent, which disfavours the parallel alignment of the rigid cores, also the incompatibility of the lateral alkyl chains with the aromatic cores is important. If the lateral chains are not located close to the terminal chains their segregation into distinct well-defined regions is disturbed and gives rise to disorder.

The new thiophene-based amphiphiles described here can be considered as low molecular weight block molecules. By further changing the topology and volume fraction of different blocks (*17*) new mesogens could be designed in the future that might be useful for application in self-organised functional devices.

4. Experimental

General

Reactions requiring an inert gas atmosphere were conducted under argon and the glassware was oven-dried (140°C). Commercially available chemicals were used as received. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker–DRX-500 spectrometer. High resolution MS (HRMS) data were recorded on a Finnigan MAT 90 spectrometer at an ionisation potential of 70 eV. Field-desorption (FD) mass spectra were recorded on a VG ZAB 2-SE-FPD spectrometer. Column chromatography was performed with silica gel 60 (230–400 mesh) from Merck.

The compounds **1/6**, **1/12, 2/12** were recently synthesised (*9, 17e*).

Procedures

*General procedure for 2-bromo-3-alkylthiophenes (**3/m**).*

All 2-bromo-3-alkylthiophene derivatives were prepared according to a modified procedure of Pham *et al.* (*18*). At 0–5°C under an argon atmosphere, NBS powder (5.0 g, 28 mmol) was added slowly to a stirred solution of 3-alkylthiophene (28 mmol) dissolved in THF (50 ml). The mixture was stirred for 1 h, quenched with water and then was extracted with Et_2O. The organic layer was separated, washed with 10% aqueous $Na_2S_2O_3$, 10% aqueous NaOH, and H_2O, dried over anhydrous magnesium sulfate, the solvent was removed *in vacuo* and the residue was purified by column chromatography (petroleum ether). The NMR data of 2-bromo-3-hexylthiophene **3/6** (*19*) and 2-bromo-3-dodecylthiophene **3/12** (*20*) corresponded to those reported in the literature.

*2-Bromo-3-hexylthiophene (**3/6**).*

Yield 81%, as pale yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.89 (t, J=6.5 Hz, 3H, CH_3), 1.32–1.25 (m, 6H, $3CH_2$), 1.61–1.53 (m, 2H, $ArCH_2C\mathbf{H}_2$), 2.58 (t, J=7.4 Hz, 2H, $ArCH_2$), 6.79 (d, J=5.5 Hz, 1H, ArH), 7.18–7.17 (d, J=5.5 Hz, 1H, ArH).

*2-Bromo-3-dodecylthiophene (**3/12**).*

Yield 81%, as pale yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.90 (t, J=6.7 Hz, 3H, CH_3), 1.32–1.25 (m, 18H, $9CH_2$), 1.57–1.60 (m, 2H, $ArCH_2C\mathbf{H}_2$), 2.57 (t, J=7.5 Hz, 2H, $ArC\mathbf{H}_2$), 6.79 (d, J=5.6 Hz, 1H, ArH), 7.18 (d, J=5.6 Hz, 1H, ArH).

General procedure for Pd(0)-catalyzed cross-coupling of aryl bromides with 4-methoxybenzeneboronic acid.

A mixture of the appropriate bromo-substituted thiophene derivative **3/*n*** (1.82 mmol), 4-methoxybenzeneboronic acid (0.31 g, 2.00 mmol), $Pd(PPh_3)_4$ (46 mg, 2 mol. %), ethylene glycol dimethyl ether (5 ml) and saturated $NaHCO_3$ solution (5 ml) was refluxed for 15 h under an argon atmosphere. After leaving it overnight at RT, the reaction mixture was extracted with chloroform (10 ml × 3). The combined chloroform solution was dried over anhydrous magnesium sulfate, the solvent was evaporated and the product was purified by

column chromatography (eluent: petroleum ether/ethyl acetate V:V=15:1).

*3-Hexyl-2-(4-methoxyphenyl)thiophene (**4l6**).*

Synthesised from **3/6**. Yield 80%, as a colourless liquid. HRMS: calculated for $C_{17}H_{22}OS$ $(M+H)^+$, 275.1391; found, 275.1287. ^1H NMR ($CDCl_3$, 500 MHz): δ 0.87 (t, J=6.2 Hz, 3H, CH_3), 1.23–1.27 (m, 6H, $3CH_2$), 1.55–1.58 (m, 2H, $ArCH_2C\mathbf{H}_2$), 2.62 (t, J=7.4 Hz, 2H, $ArCH_2$), 3.84 (s, 3H, OCH_3), 6.93–6.96 (m, 3H, ArH), 7.17 (d, J=5.0 Hz, 1H, ArH), 7.35 (d, J=8.5 Hz, 2H, ArH). IR (ν_{max}/cm^{-1}): 2923, 2853, 1608, 1508, 1458, 1374,1291, 1248, 1177, 1040, 831, 722.

*3-Dodecyl-2-(4-methoxyphenyl)thiophene (**4l12**).*

Synthesised from **3/12**. Yield 80%, as a colourless liquid. HRMS: calculated for $C_{23}H_{34}OS$ $(M+H)^+$, 359.2330; found, 359.2327. ^1H NMR ($CDCl_3$, 500 MHz): δ 0.88 (t, 3H, J=6.5Hz, CH_3), 1.23–1.26 (m, 18H, $9CH_2$), 1.54–1.58 (m, 2H, $ArCH_2C\mathbf{H}_2$), 2.60 (t, J=7.7 Hz, 2H, $ArC\mathbf{H}_2$), 3.82 (s, 3H, $OC\mathbf{H}_3$), 6.91–6.95 (m, 3H, ArH), 7.16 (d, 1H, J=5.2 Hz, ArH), 7.34 (d, 2H, J=7.9 Hz, ArH). IR (ν_{max}/cm^{-1}): 2923, 2853, 1608, 1508, 1458, 1374,1291, 1248, 1177, 1040, 831, 722.

*2-Bromo-5-(4-methoxyphenyl)thiophene (**5l0**) (21).*

Synthesised from 2,5-dibromothiophene. Yield 65%, as a colourless crystal; m.p. 110–112°C. ^1H NMR (500 MHz, $CDCl_3$): δ 3.83 (s, 3H, CH_3), 6.90 (d, J=8.8 Hz, 2H, ArH), 6.93 (d, J=3.8 Hz, 1H, ArH), 6.98 (d, J=3.9 Hz, 1H, ArH), 7.43 (d, J=8.8 Hz, 2H, ArH). IR (ν_{max}/cm^{-1}): 2954, 2835, 1608, 1539, 1504, 1434, 1311, 1287,1258, 1180, 1113, 1067, 1032, 978, 945, 828, 793.

*2-Bromo-3-dodecyl-5-(4-methoxyphenyl)thiophene (**5l12**) and 5-bromo-3-dodecyl-2-(4- methoxyphenyl)thiophene (**8l12**).*

5/12 was synthesised from **2/12**. Yield 15%, as a colourless crystal; m.p. 38–40°C. HRMS: calculated for $C_{23}H_{33}BrOS$ $(M+H)^+$, 437.1435; found, 437.1391. ^1H NMR ($CDCl_3$, 500 MHz): δ 0.87 (t, J=7.1 Hz, 3H, CH_3), 1.25–1.32 (m, 18H, $9CH_2$), 1.56–1.59 (m, 2H, $ArCH_2C\mathbf{H}_2$), 2.54 (t, J=7.8 Hz, 2H, $ArCH_2$), 3.84 (s, 3H, OCH_3), 6.87 (s, 1H, ArH), 6.89 (d, J=8.8 Hz, 2H, ArH), 7.42 (d, J=8.8 Hz, 2H, ArH). IR (ν_{max}/cm^{-1}): 2918, 2849, 1605, 1558, 1514, 1471, 1292, 1255, 1180, 1110, 1028, 824, 720.

8/12 was synthesised from **2/12**. Yield 7%, as a colourless liquid. HRMS: calculated for $C_{23}H_{33}BrOS$ $(M+H)^+$, 437.1435; found, 437.1411. ^1H NMR (500 MHz; $CDCl_3$): 0.87 (t, J=6.3 Hz, 3H, CH_3), 1.22–1.24 (m, 18H, $9CH_2$), 1.53–1.55 (m, 2H, $ArCH_2C\mathbf{H}_2$), 2.52 (t, J=7.0 Hz, 2H, $ArCH_2$), 3.79 (s, 3H, OCH_3), 6.87 (s, 1H, ArH), 6.89 (d, J=8.2 Hz, 2H, ArH), 7.26 (d, J=8.4 Hz, 2H, ArH). IR (ν_{max}/cm^{-1}): 2924, 2856, 1609, 1557, 1507, 1452, 1378,1291, 1248, 1178, 1107, 1037, 829.

*5-Bromo-3-alkyl-2-(4-methoxyphenyl)thiophenes (**8l*** ***m**).*

Synthesised from **4/*m*** according to the general procedure for **3/*m***, **8/*m*** were purified by column chromatography (eluent: petroleum ether/ethyl acetate V:V=15:1).

For 5-bromo-3-hexyl-2-(4-methoxyphenyl)thiophene (**8/6**): yield 95%, as a colourless liquid. HRMS: calculated for $C_{17}H_{21}BrOS$ $(M+H)^+$, 353.0496; found, 353.0483. ^1H NMR ($CDCl_3$, 500 MHz): δ 0.85 (t, J=6.3 Hz, 3H, CH_3). 1.28–1.24 (m, 6H, $3CH_2$), 1.55–1.51 (m, 2H, $ArCH_2C\mathbf{H}_2$), 2.53 (t, J=7.7 Hz, 2H, $ArCH_2$), 3.84 (s, 3H, OCH_3), 6.90 (s, 1H, ArH), 6.92 (d, J=8.6 Hz, 2H, ArH), 7.29–7.27 (d, J=8.6 Hz, 2H, ArH). IR (ν_{max}/cm^{-1}): 2924, 2856, 1609, 1557, 1507, 1452, 1378,1291, 1248, 1178, 1107, 1037, 829.

For 5-bromo-3-dodecyl-2-(4-methoxyphenyl)thiophene (**8/12**): yield 92%, as a colourless liquid. HRMS: calculated for $C_{23}H_{33}BrOS$ $(M+H)^+$, 437.1435; found, 437.1411. ^1H NMR (500 MHz; $CDCl_3$): δ 0.87 (t, J=6.3 Hz, 3H, CH_3), 1.22–1.24 (m, 18H, $9CH_2$), 1.53–1.55 (m, 2H, $ArCH_2C\mathbf{H}_2$), 2.52 (t, J=7.0 Hz, 2H, $ArCH_2$), 3.79 (s, 3H, OCH_3), 6.87 (s, 1H, ArH), 6.89 (d, J=8.2 Hz, 2H, ArH), 7.26 (d, J=8.4 Hz, 2H, ArH). IR (ν_{max}/cm^{-1}): 2924, 2856, 1609, 1557, 1507, 1452, 1378, 1291, 1248, 1178, 1107, 1037, 829.

*General procedure for synthesis of **6l**m**l**n**.*

5/0 or **5/12** (1 mmol) was dissolved in dry THF (1.5 ml) and cooled to −60°C. *n*-BuLi (1.6M solution in *n*-hexane, 1.25 ml, 2 mmol) was added and the solution was stirred for 30 min, then the corresponding 1-bromoalkane (2 mmol) was added and the mixture was stirred at RT overnight. The crude product was purified by column chromatrography (eluent: petroleum ether), then crystallised from ethanol.

*2-Dodecyl-5-(4-methoxyphenyl)thiophene (**6l0l12**).*

Synthesised from **5/0**. Yield 61%, as a colourless crystal; m.p. 72–73°C. HRMS: calculated for $C_{23}H_{34}OS$ $(M+H)^+$, 359.2330; found, 359.2314. ^1H NMR (500 MHz; $CDCl_3$): δ 0.88 (t, J=7.1 Hz, 3H, CH_3), 1.38–1.42 (m, 18H, $9CH_2$), 1.67–1.68 (m, 2H, $ArCH_2C\mathbf{H}_2$), 2.79 (t, J=7.6 Hz, 2H, $ArCH_2$), 3.82 (s, 3H, OCH_3). 6.7 (d, J=3.3 Hz, 1H, ArH), 6.88 (d,

J=8.8 Hz, 2H, ArH), 6.99 (d, J=3.5 Hz, 1H, ArH), 7.47 (d, J=8.8 Hz, 2H, ArH). IR (ν_{max}/cm^{-1}): 2952, 2919, 2848, 1608, 1516, 1471, 1288,1255, 1182, 1114, 1032, 1032, 939, 834, 797, 727.

*2-Hexadecyl-5-(4-methoxyphenyl)thiophene (**6l0l16**).*

Synthesised from **5/0**. Yield 47%, as a colourless crystal; m.p. 75–76°C. HRMS: calculated for $C_{27}H_{42}OS$ $(M+H)^+$, 415.2956; found, 415.2950. ^{1}H NMR (500 MHz; $CDCl_3$): δ 0.88 (t, J=7.1 Hz, 3H, CH_3), 1.35–1.39 (m, 26H, $13CH_2$), 1.67–1.70 (m, 2H, $ArCH_2CH_2$), 2.79 (t, J=7.4 Hz, 2H, $ArCH_2$), 3.83 (s, 3H, OCH_3). 6.7 (d, J=3.4 Hz, 1H, ArH), 6.88 (d, J=8.7 Hz, 2H, ArH), 6.99 (d, J=3.3 Hz, 1H, ArH), 7.47 (d, J=8.8 Hz, 2H, ArH). IR (ν_{max}/cm^{-1}: 2952, 2919, 2848, 1608, 1572, 1548, 1515, 1472, 1288, 1255, 1182, 1114, 1032, 1032, 939, 834, 797, 719 (*22*).

*2-Octadecyl-5-(4-methoxyphenyl)thiophene (**6l0l18**).*

Synthesised from **5/0**. Yield 49%, as a colourless crystal; m.p. 78–79°C. HRMS: calculated for $C_{29}H_{46}OS$ $(M+H)^+$, 443.3269; found, 443.3232. ^{1}H NMR (500 MHz; $CDCl_3$): δ 0.88 (t, J=7.1 Hz, 3H), 1.36–1.39 (m, 30H, $15CH_2$), 1.65–1.7 (m, 2H, $ArCH_2CH_2$), 2.79 (t, J=7.5 Hz, 2H, $ArCH_2$), 3.82 (s, 3H, OCH_3). 6.7 (d, J=3.4 Hz, 1H, ArH), 6.88 (d, J=8.8 Hz, 2H, ArH), 6.99 (d, J=3.5 Hz, 1H, ArH), 7.47 (d, J=8.8 Hz, 2H, ArH). IR (ν_{max}/cm^{-1}): 2952, 2919, 2848, 1608, 1548, 1516, 1471, 1288, 1255, 1182, 1114, 1032, 1032, 939, 834, 797, 727 (*22*).

*2,3-Didodecyl-5-(4-methoxyphenyl)thiophene (**6l12l12**).*

Synthesised from **5/12**. Yield 62%, as a colourless crystal; m.p. 32–34°C. HRMS: calculated for $C_{35}H_{58}OS$ $(M+H)^+$: 527.4208 found 527.4186; ^{1}H NMR (500 MHz; $CDCl_3$): δ 0.88 (t, J=7.0 Hz, 3H, CH_3), 0.95 (t, J=7.6 Hz, 3H, CH_3), 1.26–1.42 (m, 36H, $18CH_2$), 1.56–1.64 (m, 4H, $2ArCH_2CH_2$), 2.48 (t, J=7.9 Hz, 2H, $ArCH_2$), 2.70 (t, J=7.5 Hz, 2H, $ArCH_2$), 3.81 (s, 3H), 6.87 (d, J=7.1 Hz, 2H, ArH), 6.92 (s, 1H, ArH), 7.47 (d, J=7.2 Hz, 2H, ArH). IR (ν_{max}/cm^{-1}): 2923, 2852, 1609, 1513, 1460, 1294, 1249,1178, 1112, 1038, 823.

*5-Alkyl-3-hexyl-2-(4-methoxyphenyl)thiophene (**9l6l n**) and 4,3′-didodecyl-5-(4-methoxyphenyl)[2,2′]-bithienyl (**10l12l12**).*

These compounds were prepared by a modified literature procedure of Kumada, as outlined by Pham *et al.* (*18*). Accordingly, magnesium turnings (0.85 g, 35 mmol) were covered by dry THF (10 ml) and alkyl bromide (or 2-bromothiophene, **3/12**) (0.32 mmol) was added. After the reaction had started, the remaining alkyl bromide (or 2-bromothiophene **3/12**) (31.7 mmol) dissolved in dry THF (20 ml) was added dropwise, maintaining the Grignard solution under reflux. Stirring was continued under reflux for 2 h, and then the mixture was cooled to RT, and added dropwise to a mixture of **8/m** (16.0 mmol) and Ni(dppp)Cl_2 (120 mg) in THF (35 ml) at 0°C, maintaining the temperature of the solution below 5°C. Stirring of the mixture was continued for additional 3 h under reflux, and the reaction mixture was cooled to room temperature, quenched with crushed ice (50 g), and 6N HCl was added until the precipitate was dissolved. The mixture was extracted with diethyl ether (3×100 ml). The combined organic phase was dried over anhydrous magnesium sulfate, and the solvent was removed *in vacuo*. The crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate V:V=20:1).

*3-Hexyl-2-(4-methoxyphenyl)-5-dodecylthiophene (**9l6l12**).*

Yield 15%, as a colorless liquid. HRMS: calculated for $C_{29}H_{46}OS$ $(M+H)^+$, 443.3269; found, 443.3258. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.89–0.84 (m, 6H, $2CH_3$), 1.38–1.26 (m, 24H, $12CH_2$), 1.56–1.54 (m, 2H, $ArCH_2CH_2$), 1.68–1.65 (m, 2H, $ArCH_2CH_2$),. 2.54 (t, J=7.5 Hz, 2H, $ArCH_2$), 2.75 (t, J=7.3 Hz, 2H, $ArCH_2$), 3.83 (s, 3 H, OCH_3), 6.62 (s, 1H, ArH), 6.91 (d, J=7.6 Hz, 2H,ArH), 7.32 (d, J=7.6 Hz, 2H, ArH). IR (ν_{max}/cm^{-1}): 2924, 2854, 1609, 1565, 1514, 1461, 1372, 1291, 1247, 1177, 1109, 1039, 830, 725.

*3-Hexyl-2-(4-methoxyphenyl)-5-tetradecylthiophene (**9l6l14**).*

Yield 15%, as a colourless liquid. HRMS: calculated for $C_{31}H_{50}OS$ $(M+H)^+$, 471.3582; found, 471.3584. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.89–0.84 (m, 6H, $2CH_3$), 1.37–1.25 (m, 28H, $14CH_2$), 1.56–1.54 (m, 2H, $ArCH_2CH_2$), 1.68–1.65 (m, 2H, $ArCH_2CH_2$), 2.54 (t, J=7.5 Hz, 2H, $ArCH_2$), 2.75 (t, J=7.3 Hz, 2H, $ArCH_2$), 3.82 (s, 3 H, OCH_3), 6.62 (s, 1H, ArH), 6.92 (d, J=7.6 Hz, 2H,ArH), 7.33 (d, J=7.6 Hz, 2H, ArH). IR (ν_{max}/cm^{-1}): 2924, 2854, 1608, 1508, 1458, 1374, 1292, 1248, 1177, 1039, 831, 723.

*3-Hexyl-2-(4-methoxyphenyl)-5-octadecylthiophene (**9l6l18**).*

Yield 12%, as a colourless crystal; m.p. 35–37°C. HRMS: calculated for $C_{35}H_{58}OS$ $(M+H)^+$, 527.4208;

found, 527.4218. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.89–0.84 (m, 6H, $2CH_3$), 1.38–1.25 (m, 36H, $18CH_2$), 1.56–1.54 (m, 2H, $ArCH_2CH_2$), 1.68–1.65 (m, 2H, $ArCH_2CH_2$), 2.54 (t, J=7.6 Hz, 2H,$ArCH_2$), 2.76 (t, J=7.3 Hz, 2H, $ArCH_2$), 3.83 (s, 3H, OCH_3), 6.62 (s, 1H, ArH), 6.91 (d, J=8.5 Hz, 2H, ArH), 7.31 (d, J=8.7 Hz, 2H, ArH). IR (ν_{max}/cm^{-1}): 2924, 2854, 1607, 1508, 1514, 1461, 1372, 1291, 1247, 1177, 1109, 1039, 830, 725.

*4,3′-Didodecyl-5-(4-methoxyphenyl)[2,2′]bithienyl (**10/12/12**).*

Yield 92%, as a colourless liquid. HRMS: calculated for $C_{39}H_{60}OS_2$ $(M+H)^+$, 609.4086; found, 609.4082. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.96–0.89 (m, 6H, $2CH_3$), 1.34–1.24 (m, 36H, $18CH_2$), 1.7 (m, 6H, $2CH_2$), 2.69 (t, 2H, J=7.5 Hz, $ArCH_2$), 2.86 (t, 2H, J=7.5 Hz, $ArCH_2$), 3.89 (s, 3H, OCH_3), 6.97 (d, 1H, J=5.0 Hz, Ar-H), 7.00 (d, 2H, J=7.0 Hz, ArH), 7.06 (s, 1H, ArH), 7.17 (d, 1H, J=5.0 Hz, ArH), 7.45 (d, 2H, J=6.9 Hz, Ar-H). IR (ν_{max}/cm^{-1}): 2924, 2854, 16079, 1565, 1514, 1461, 1372, 1291, 1247, 1177, 1109, 1039, 830, 725.

General procedure for cleavage of methyl ethers.

The appropriate methyl ether (**6/*m*/*n***, **9/6/*n*** or **10/12/12**) (4.7 mmol) was dissolved in CH_2Cl_2 (45 ml) and cooled to −78°C. BBr_3 (0.49 ml, 5.17 mmol) was added and the solution was stirred at RT overnight. Water (30 ml) was carefully added, the precipitate was filtered and washed with water (10 ml) and petroleum ether (20 ml), respectively, dried in *vacuo* at 40°C for 4 h. The obtained product was used directly for the next step without further purification. Yields of **7/*m*/*n***, **11/6/*n*** and **12/12/12** were 99, 98 and 99%, respectively.

*General procedure for etherification of **7/*m*/*n**, **11/6/*n*** and **12/12/12**.*

Allyl bromide (6.6 mmol) was added to a mixture of the appropriate compound **7/*m*/*n***, **11/6/*n*** or **12/12/12** (6 mmol) and K_2CO_3 (12 mmol) in dry CH_3CN (20 ml) under an argon atmosphere. The mixture was refluxed for 2 h. The solvent was evaporated *in vacuo*. Water (50 ml) and diethyl ether (50 ml) were added to the residue. The layers were separated, and the aqueous layer was extracted with Et_2O (3 × 75 ml), and the combined organic layers were washed with H_2O (3 × 50 ml) and dried over Na_2SO_4. Finally the solvent was evaporated in *vacuo*. Purification of the product was done by column chromatography (eluent: petroleum ether/ethyl acetate V:V=20:1).

*2-(4-Allyloxyphenyl)-5-dodecylthiophene (**13/0/12**).*

Synthesised from **7/0/12**. Yield 87%, as colourless crystals; m.p. 71–72°C. HRMS: calculated for $C_{25}H_{36}OS$ $(M+H)^+$, 385.2487; found, 385.2482. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.88 (t, J=7.2 Hz, 3H, CH_3), 1.36–1.38 (m, 18H, $9CH_2$), 1.65–1.71 (m, 2H, $ArCH_2CH_2$), 2.79 (t, J=7.7 Hz, 2H, $ArCH_2$), 4.55–4.56 (m, 2H, OCH_2), 5.28–5.44 (m, 2H, CH_2=), 6.02–6.1 (m, 1H, CH=), 6.7 (d, J=3.4 Hz, 1H, ArH), 6.89 (d, J=8.8 Hz, 2H, ArH), 6.99 (d, J=3.5 Hz, 1H, ArH), 7.47 (d, J=8.8 Hz, 2H, ArH). IR (ν_{max}/cm^{-1}) 2955, 2920, 2850, 1603, 1514, 1465, 1428, 1282, 1247, 1181, 1114, 1016, 994, 940, 830, 798.

*2-(4-Allyloxyphenyl)-5-hexadecylthiophene (**13/0/16**).*

Synthesised from **7/0/16**. Yield 83%, as colourless crystals; m.p. 74–75°C. HRMS: calculated for $C_{29}H_{44}OS$ $(M+H)^+$, 441.3113; found, 441.3106. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.88 (t, J=7.0 Hz, 3H, CH_3), 1.36–1.38 (m, 26H. $13CH_2$), 1.67–1.70 (m, 2H, $ArCH_2CH_2$), 2.79 (t, J=7.6 Hz, 2H, $ArCH_2$), 4.55–4.56 (m, 2H, OCH_2), 5.29–5.44 (m, 2H, CH_2=), 6.04–6.09 (m, 1H, CH=), 6.70 (d, J=3.4 Hz, 1H, ArH), 6.89 (d, J=8.8 Hz, 2H, ArH), 6.99 (d, J=3.4 Hz, 1H, ArH), 7.47 (d, J=8.8 Hz, 2H, ArH). IR (ν_{max}/cm^{-1}): 2955, 2920, 2850, 1603, 1514, 1465, 1428, 1282, 1247, 1181, 1114, 1016, 994, 940, 830, 798.

*2-(4-Allyloxyphenyl)-5-octadecylthiophene (**13/0/18**).*

Synthesised from **7/0/18**. Yield 82%, as colourless crystals; m.p. 75–77°C. HRMS: calculated for $C_{31}H_{48}OS$ $(M+H)^+$, 469.3426; found, 469.3412. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.88 (t, J=7.1 Hz, 3H, CH_3), 1.36–1.38 (m, 30H, $15CH_2$), 1.65–1.70 (m, 2H, $ArCH_2CH_2$), 2.79 (t, J=7.5 Hz, 2H, $ArCH_2$), 4.55–4.56 (m, 2H, OCH_2), 5.29–5.44 (m, 2H, CH_2=), 6.03–6.10 (m, 1H, CH=), 6.70 (d, J=3.5 Hz, 1H, ArH), 6.89 (d, J=8.8 Hz, 2H, ArH), 6.99 (d, J=3.5 Hz, 1H, ArH), 7.46 (d, J=8.8 Hz, 2H, ArH). IR (ν_{max}/cm^{-1}) 2955, 2920, 2850, 1603, 1514, 1465, 1428, 1282, 1247, 1181, 1114, 1016, 994, 940, 830, 798.

*5-(4-Allyloxyphenyl)-2,3-didodecylthiophene (**13/12/12**).*

Synthesised from **7/12/12**. Yield 71%, as colourless crystals; m.p. 33–34°C. HRMS: calculated for $C_{37}H_{60}OS$ $(M+H)^+$, 553.4365; found, 553.4298. ^{1}H NMR (500 MHz; $CDCl_3$): δ 0.88 (t, J=7.0 Hz, 3H, CH_3), 0.95 (t, J=7.6 Hz, 3H, CH_3), 1.23–1.29 (m,

36H, 18CH_2), 1.56–1.64 (m, 4H, 2ArCH_2C**H**$_2$), 2.48 (t, J=7.9 Hz, 2H, ArCH_2), 2.70 (t, J=7.5 Hz, 2H, ArCH_2), 4.55–4.56 (m, 2H, OCH_2), 5.29–5.44 (m, 2H, CH_2=), 6.04–6.09 (m, 1H, CH=), 6.88 (d, J=8.6 Hz, 2H, ArH), 6.92 (s, 1H, ArH), 7.46 (d, J=8.4 Hz, 2H, ArH). IR (ν_{max}/cm^{-1}): 2919, 2851, 1620, 1608, 1515, 1465, 1292, 1249, 1182, 1114, 1026, 921, 821, 717.

*2-(4-Allyloxyphenyl)-3-hexyl-5-dodecylthiophene (**14/6/12**).*

Synthesised from **11/6/12**. Yield 78%, as a colourless liquid. HRMS: calculated for $C_{31}H_{48}OS$ $(M+H)^+$, 469.3426; found, 469.3364. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.89–0.79 (m, 6H, 2CH_3), 1.38–1.26 (m, 24H, 12CH_2), 1.68–1.51 (m, 4H, 2ArCH_2C**H**$_2$), 2.53 (t, J=7.7 Hz, 2H, ArCH_2), 2.75 (t, J=7.5 Hz, 2H, ArCH_2), 4.57–4.55 (m, 2H, OCH_2), 5.29–5.31 (m, 2H, CH_2=), 5.41–5.45 (m, 1H, CH=), 6.62 (s, 1H, ArH), 6.92 (d, J=8.6 Hz, 2H, ArH), 7.31 (d, J=8.6 Hz, 2H, ArH). IR (ν_{max}/cm^{-1}): 2920, 2854, 1620, 1607, 1513, 1463, 1374, 1286, 1241, 1174, 1111, 1028, 928, 828, 722.

*2-(4-Allyloxphenyl)-3-hexyl-5-tetradecylthiophene (**14/6/14**).*

Synthesised from **11/6/14**. Yield 94%, as a colourless liquid. HRMS: calculated for $C_{33}H_{52}OS$ $(M+H)^+$, 497.3739; found, 497.3712. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.89–0.84 (m, 6H, 2CH_3), 1.38–1.26 (m, 28H, 14CH_2), 1.68–1.63 (m, 2ArCH_2C**H**$_2$), 2.55 (t, J=7.7 Hz, 2H, ArCH_2), 2.76 (t, J=7.5 Hz, 2H, ArCH_2), 4.57–4.55 (m, 2H, OCH_2), 5.45–5.29 (m, 2H, CH_2=), 6.10–6.04 (m, 1H, CH=), 6.63 (s, 1H, ArH), 6.93 (d, J=8.1 Hz, 2H, ArH), 7.31 (d, J=8.3 Hz, 2H, ArH). IR (ν_{max}/cm^{-1}): 2920, 2854, 1620, 1607, 1513, 1463, 1374, 1286, 1241, 1174, 1111, 1028, 928, 828, 722.

*2-(4-Allyloxphenyl)-3-hexyl-5-octadecylthiophene (**14/6/18**).*

Synthesised from **11/6/18**. Yield 94%, as colourless crystals; m.p. 33–34°C. HRMS: calculated for $C_{37}H_{60}OS$ $(M+H)^+$, 553.4365; found, 553.4342. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.89–0.79 (m, 6H, 2CH_3), 1.38–1.26 (m, 36H, 18CH_2), 1.68–1.51 (m, 2ArCH_2C**H**$_2$), 2.55 (t, J=7.7 Hz, 2H, ArCH_2), 2.76 (t, J=7.5 Hz, 2H, ArCH_2), 4.57 (m, 2H, OCH_2), 5.29–5.45 (m, 2H, CH_2=), 6.12–6.02 (m, 1H, CH=), 6.63 (s, 1H, ArH), 6.93 (d, J=8.1 Hz, 2H, ArH), 7.31 (d, J=8.1Hz, 2H, ArH). IR (ν_{max}/cm^{-1}): 2920, 2854, 1620, 1607, 1513, 1463, 1374, 1286, 1241, 1174, 1111, 1028, 928, 828, 722.

*5-(4-Allyloxyphenyl)-4,3′-didodecyl[2,2′]bithienyl (**15/12/12**).*

Synthesised from **12/12/12**. Yield 71%, as a colourless liquid. HRMS: calculated for $C_{41}H_{62}OS_2$ $(M+H)^+$, 635.4242; found, 635.4212. ^{1}H NMR (500 MHz; $CDCl_3$): δ 0.89 (m, 6H, 2CH_3), 1.24–1.35 (m, 36H, 18CH_2), 1.65–1.63 (m, 4H, 2 ArCH_2C**H**$_2$), 2.62 (t, J=7.6 Hz, 2H, ArCH_2), 2.79 (t, J=7.6 Hz, 2H, ArCH_2), 4.58 (d, J=5.0 Hz, 2H OCH_2), 5.32–5.45 (m, 2H, CH_2=), 6.12 (m, 1H, CH=), 6.93 (d, J=5.1 Hz, 1H, ArH), 6.96–6.98 (m, 3H, ArH), 7.14 (d, J=5.1 Hz, 1H, ArH), 7.38 (d, J=8.5 Hz, 2H, ArH). IR (ν_{max}/cm^{-1}): 2922, 2853, 1620, 1606, 1507, 1464, 1377, 1286, 1244, 1176, 1111, 1027, 998, 924, 829, 721.

*General procedure for dihydroxylation of **13/m/n**, **14/6/n** or **15/12/12**.*

The appropriate **13/*m*/*n***, **14/6/*n*** or **15/12/12** (1.4 mmol), and NMMNO (1.2 ml, 7.1 mmol of 60% solution in water) were dissolved in acetone (20 ml). Osmium tetroxide (1.25 ml of a 0.004M solution in *tert*-butanol) was added, and the solution was stirred 2 h at RT. Afterwards, saturated aqueous Na_2SO_3 solution (5 ml) was added and the mixture was stirred for 30 min at RT. The mixture was filtered over a silica bed. The residue was carefully washed twice with acetone (50 ml), and the solvent was evaporated *in vacuo*. The residue was dissolved in ethyl acetate (100 ml). The solution was washed with 10% aqueous H_2SO_4 (30 ml), saturated $NaHCO_3$ solution (30 ml) and H_2O (30 ml). The organic layer was dried over Na_2SO_4, and the solvent was evaporated *in vacuo*.

*3-[4-(5-Dodecylthien-2-yl)phenoxy]propane-1,2-diol (**1l/0/12**).*

Synthesised from **13/0/12**, crystallised twice from ethyl acetate. Yield 56%, as colourless crystals. HRMS: calculated for $C_{25}H_{38}O_3S$ $(M+H)^+$, 419.2542; found, 419.2544. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (t, J=6.8 Hz, 3H, CH_3), 1.35–1.38 (m, 18H, 9CH_2), 1.65–1.70 (m, 2H, ArCH_2C**H**$_2$), 2.75 (t, J=7.6 Hz, 2H, ArCH_2), 3.66–4.23 (m, 5H, O**H**$_2$C**H**OHC**H**$_2$OH), 6.70 (d, J=2.8 Hz, 1H, ArH), 6.90 (d, J=8.2 Hz, 2H, ArH), 6.99 (d, J=3.2 Hz, 1H, ArH), 7.44 (d, J=8.2 Hz, 2H, ArH). ^{13}C NMR (500 MHz, $CDCl_3$): δ 13.91, 22.57, 29.05–31.85 (multicarbon in alkyl chain), 63.71, 69.59, 70.44, 115.04(2C), 121.84, 124.77, 126.85 (2C), 141.34, 144.96, 157.79. IR (ν_{max}/cm^{-1}): 3385, 2955, 2918, 2848, 1606, 1515, 1471, 1285, 1254, 1180, 1113, 1060, 954, 823, 798, 783.

*3-[4-(5-Hexadecylthien-2-yl)phenoxy]propane-1,2-diol (**II0/16**).*

Synthesised from **13/0/16**, crystallised twice from ethyl acetate. Yield 49%, as colourless crystals. HRMS: calculated for $C_{29}H_{46}O_3S$ $(M+H)^+$, 475.3168; found, 475.3171. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.87 (t, J=6.5 Hz, 3H, CH_3), 1.36–1.39(m, 26H, 13H), 1.67–1.69 (m, 2H, $ArCH_2CH_2$), 2.75 (t, J=7.3 Hz, 2H, $ArCH_2$), 3.75–4.08 (m, 5H, $OCH_2CHOHCH_2OH$), 6.69 (d, J=2.8 Hz, 1H, ArH), 6.90 (d, J=8.4 Hz, 2H, ArH), 6.98 (d, J=3.2 Hz, 1H, ArH), 7.46 (d, J=8.3 Hz, 2H, ArH). ^{13}C NMR (500 MHz, $CDCl_3$): δ 13.89, 22.56, 29.05–31.84 (multicarbon in alkyl chain), 63.77, 69.61, 70.48, 115.06 (2C), 121.82, 124.76, 126.85 (2C), 128.61, 141.35, 144.94, 157.83. IR (ν_{max}/cm^{-1}): 3385, 2955, 2918, 2848, 1606, 1515, 1471, 1285, 1254, 1180, 1113, 1060, 954, 823, 798, 783.

*3-[4-(5-Octadecylthien-2-yl)phenoxy]propane-1,2-diol (**II0/18**).*

Synthesised from **13/0/18**, crystallised twice from ethyl acetate. Yield 42%, as colourless crystals. HRMS: calculated for $C_{31}H_{50}O_3S$ $(M+H)^+$, 503.3481; found, 503.3477. ^{1}H NMR (500 MHz, DMSO): δ 0.87 (t, J=6.9 Hz, 3H, CH_3), 1.34–1.37(m, 30H, $15CH_2$), 1.63–1.66 (m, 2H, $ArCH_2CH_2$), 2.78 (t, J=7.4 Hz, 2H, $ArCH_2$), 3.84–4.66 (m, 5H, $OCH_2CHOHCH_2OH$), 6.76 (d, J=3.3 Hz, 1H, ArH), 6.96 (d, J=8.6 Hz, 2H, ArH), 7.10 (d, J=3.4 Hz, 1H, ArH), 7.47 (d, J=8.6 Hz, 2H, ArH). ^{13}C NMR (500 MHz, $CDCl_3$): δ 13.66, 21.90, 28.29–31.15 (multicarbon in alkyl chain), 62.90, 70.07, 70.11, 115.26 (2C), 121.90, 125.21, 126.30 (2C), 127.01, 140.81, 143.83, 158.30. IR (ν_{max}/cm^{-1}): 3418, 2954, 2917, 2848, 1607, 1515, 1472, 1463, 1285, 1254, 1181, 1113, 1054, 950, 832, 797, 719.

*3-[4-(4,5-Didodecylthien-2-yl)phenoxy]propane-1,2-diol (**II12/12**).*

Synthesised from **13/12/12**, purified by column chromatography (eluent: petroleum ether/ethyl acetate V:V=1:1) and then crystallised twice from ethyl acetate. Yield 66%, as colourless crystals. HRMS: calculated for $C_{37}H_{62}O_3S$ $(M+H)^+$, 587.4420; found, 587.4421. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (t, J=7.0 Hz, 3H, CH_3), 0.95 (t, J=7.6 Hz, 3H, CH_3), 1.24–1.31 (m, 36H, $18CH_2$), 1.56–1.64 (m, 4H, $2ArCH_2CH_2$), 2.48 (t, J=7.9 Hz, 2H, $ArCH_2$), 2.70 (t, J=7.5 Hz, 2H, $ArCH_2$), 3.16–4.11 (m, 5H, $OCH_2CHOHCH_2OH$), 6.87 (d, J=6.8 Hz, 2H, ArH), 6.93 (s, 1H, ArH), 7.46 (d, J=7.3 Hz, 2H, ArH). ^{13}C NMR (500 MHz, $CDCl_3$): δ 14.10, 22.70, 27.92, 28.40, 29.37–31.94 (multicarbon in alkyl chain), 63.67, 69.32, 70.45, 114.83, 123.98, 126.62, 128.52, 138.08, 138.81, 139.09, 157.52. IR (ν_{max}/cm^{-1}): 3419,2955, 2918,2850, 1606, 1516, 1469, 1289, 1251, 1179, 1113, 1050, 821, 714.

*3-[4-(-3-Hexyl-5-dodecylthien-2-yl)phenoxy]propane-1,2-diol (**III6/12**).*

Synthesised from **14/6/12**, purified twice by column chromatography (eluent: ethyl acetate). Yield 81%, as a colourless liquid. HRMS: calculated for $C_{31}H_{50}O_3S$ $(M+H)^+$, 503.3481; found, 503.3482. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.89–0.84 (m, 6H, $2CH_3$). 1.38–1.26 (m, 24H, $12CH_2$) 1.68–1.51 (m, 4H, $2ArCH_2CH_2$), 2.54 (t, J=7.7 Hz, 2H, $ArCH_2$), 2.76 (t, J=7.6 Hz, 2H, $ArCH_2$), 3.79–4.13 (m, 5H, $OCH_2CHOHCH_2OH$), 6.63 (s, 1H, ArH), 6.93 (d, J=8.6 Hz, 2H, ArH), 7.32 (d, J=8.6 Hz, 2H, ArH). ^{13}C NMR (500 MHz, $CDCl_3$): δ 14.00, 22.50, 22.60, 28.71–31.85 (multicarbon in alkyl chain), 63.62, 69.16, 70.43, 114.39, 114.49, 126.38, 128.33, 130.35 (2C), 134.43, 137.69, 143.44, 157.42. IR (ν_{max}/cm^{-1}): 3388, 2922, 2853, 1607, 1561, 1513, 1463, 1374,1289, 1244, 1180, 1117, 1050, 936, 878, 830, 718.

*3-[4-(-3-Hexyl-5-tetradecylthien-2-yl)phenoxy]propane-1,2-diol (**III6/14**).*

Synthesised from **14/6/14**, purified twice by column chromatography (eluent: ethyl acetate). Yield 83%, as a colourless liquid. HRMS: calculated for $C_{33}H_{54}O_3S$ $(M+H)^+$, 531.3794; found, 531.3794. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.89–0.84 (m, 6H, $2CH_3$), 1.38–1.26 (m, 28H, $14CH_2$) 1.68–1.51 (m, 4H, $2ArCH_2CH_2$), 2.54 (t, J=7.7 Hz, 2H, $ArCH_2$), 2.76 (t, J=7.6 Hz, 2H, $ArCH_2$), 3.79–4.13 (m, 5H, $OCH_2CHOHCH_2OH$), 6.63 (s, 1H, ArH), 6.93 (d, J=8.6 Hz, 2H, ArH), 7.32 (d, J=8.6 Hz, 2H, ArH). ^{13}C NMR (500 MHz, $CDCl_3$): δ 14.01, 22.51, 22.60, 28.71–31.85 (multicarbon in alkyl chain), 63.60, 69.16, 70.43, 114.39, 114.37, 126.39, 128.31, 130.36(2C), 134.42, 137.71, 143.48, 157.39. IR (ν_{max}/cm^{-1}): 3388, 2922, 2853, 1607, 1561, 1513, 1463, 1374,1289, 1244, 1180, 1117, 1050, 936, 878, 830, 718.

*3-[4-(3-Hexyl-5-octadecylthien-2-yl)phenoxy]propane-1,2-diol (**III6/18**).*

Synthesised from **14/6/18**, purified twice by column chromatography (eluent: ethyl acetate). Yield 84%, as colourless crystals. HRMS: calculated for $C_{37}H_{62}O_3S$ $(M+H)^+$, 587.4420; found, 587.4420. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.89–0.84 (m, 6H, $2CH_3$), 1.38–1.26 (m, 36H, $18CH_2$), 1.68–1.51 (m, 4 H,

$2ArCH_2CH_2$), 2.54 (t, J=7.5 Hz, 2H, $ArCH_2$), 2.75 (t, J=7.5 Hz, 2H, $ArCH_2$), 3.76–4.13 (m, 5H, $OCH_2CHOHCH_2OH$), 6.63 (s, 1H, ArH), 6.93 (d, J=7.8 Hz, 2H, ArH), 7.32 (d, J=7.8 Hz, 2H, ArH). ^{13}C NMR (500 MHz, $CDCl_3$): δ 14.00, 22.50, 22.60, 28.71–31.85 (multicarbon in alkyl chain), 63.62, 69.16, 70.43, 114.39, 114.49, 126.38, 128.33, 130.35 (2C), 134.43, 137.69, 143.44, 157.42. IR (ν_{max}/cm^{-1}): 3384, 2918, 2850, 1607, 1514, 1470, 1376,1284, 1246, 1179, 1117, 1046, 933, 831, 718.

*3-[4-(4,3′-Didodecyl[2,2′]bithienyl-5-yl)phenoxy]-propane-1,2-diol (**III/12/12**).*

Synthesised from **15/12/12**, purified twice by column chromatography (eluent: ethyl acetate). Yield 93%, as colourless crystals. HRMS: calculated for $C_{41}H_{64}O_3S_2$ $(M+H)^+$, 669.4297; found, 669.4287. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.89–0.91 (m, 6H, $2CH_3$), 1.25–1.35 (m, 36H, $18CH_2$), 1.63–1.66 (m, 4H, $2ArCH_2CH_2$), 2.62 (t, J=7.4 Hz, 2H, $ArCH_2$), 2.80 (t, J=7.5 Hz, 2H $ArCH_2$), 3.79–4.16 (m, 5H, $OCH_2CHOHCH_2OH$), 6.93 (d, J=5.2 Hz, 1H ArH), 6.96–6.98 (m, 3H, ArH), 7.14 (d, J=5.2 Hz, 1H, ArH), 7.39 (d, J=8.6 Hz, 2H, ArH). ^{13}C NMR (500 MHz, $CDCl_3$): δ 14.06, 22.64, 28.67–31.87 (multicarbon in alkyl chain), 63.65, 69.13, 70.52, 114.53 (2C), 123.18, 127.51, 128.18, 129.90, 130.42 (2C), 130.86, 133.75, 137.17, 138.44, 139.14, 157.79. IR (ν_{max}/cm^{-1}): 3373, 2921, 2852, 1607, 1509, 1461, 1248, 1180, 1117, 1053, 937, 878, 830, 723.

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