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The Synthesis and Characterisation of Novel Thienyl-Pyrimidine Liquid Crystalline Materials

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The synthesis and transition temperatures of a series of novel thienyl-pyrimidine liquid crystalline materials is described. Palladium catalysed coupling of 5-*n*-alkyl-2-tri-*n*-butylstannyl thiophenes to 5-bromo-2-iodopyrimidine is used to create novel pyrimidine compounds which exhibit lower melting points than similar pyrimidine liquid crystals. These compounds exhibit a variety of phases including smectic A, C, G, B and hexstatic B also they exhibit several as yet unidentifiable phases. Speculation as to hydrogen bonding in the liquid crystalline core is also discussed therein.

Keywords: Thiophene; pyrimidine; smectic; hydrogen bonding

Introduction

Over the last 10 years or so there has been great research activity in the use of ferroelectric liquid crystals because of their potential in fast-switching, high resolution bistable electro-optic display devices (SSFLCDs) [1-3]. Such devices have been developed for commercial applications where high information content and / or fast response times are required, ie, for computer screens, printer heads, spatial light modulators etc. However, ferroelectric display devices do have a number of problems which include alignment, grey scale and sensitivity to shock. With the discovery of MHPOBC (1) by Chandani [4-5] in 1989, a number of antiferroelectric liquid crystals have been synthesised. Although the structure of the phase is very similar to that of the ferroelectric phase, in the antiferroelectric phase the tilt direction alternates through successive layers of the phase and this manifests a phase exhibiting tristate switching. Accordingly, the tristate switching display devices have very good multiplex capabilities, grey scale and better viewing angle [6]. The vast majority of compounds that exhibit the antiferroelectric phase are structurally very similar to MHPOBC figure 1, but because the structure includes an ester group and at least three phenyl rings, the inherent high viscosity associated with these structural features does not permit fast-switching. Additionally, these strucutres also give disadvantageously high melting points.

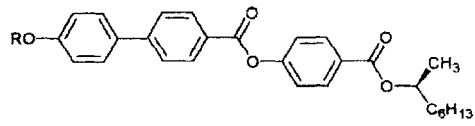
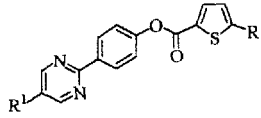


Figure 1. MHPOBC molecule.

In many ferro- and antiferro-electric mixtures a variety of liquid crystals incorporating a pyrimidine ring have been used because of their low viscosity, relatively low melting points and wide-range SmC phases [7-9]. It has also been proposed that the antiferroelectric phase is promoted by a bent molecular structure [10-11] although it is recognised that bent structures are generally not conducive to the formation of liquid crystalline phases. However, Byron [12], Seed [13] and more recently Matharu [14] have clearly shown that compounds based on thiophene, despite the non-linear or slightly bent nature of the 2,5-disubstituted thiophene ring, when suitably substituted will exhibit both ferro- and antiferro-electric phases with relatively low melting points. It seems that the incorporation of pyrimidine and thiophene rings into the structure of mesogens will be conducive to the formation of both ferro- and antiferro-electric liquid crystals for display device applications.
In this paper we report our preliminary results on the synthesis and liquid crystalline properties of novel thiophene / pyrimidine based liquid crystalline materials in order to investigate the effect of the thiophene-pyrimidine ring combination on the liquid crystalline properties of these mesogens. We believe that this is the first time such liquid crystalline compounds have been synthesised which incorporate both thiophene and pyrimidine ring systems, to produce novel liquid crystal cores consisting of a combination of different heterocyclic rings but eliminating phenyl rings which are normally present in liquid crystal cores.

Synthesis and Discussion

Pyrimidine liquid crystals have been widely investigated by a number of group's [15a-c] in the past. There is however, only one example of a thiophene, pyrimidine liquid crystal in the literature [16-17], scheme 1 and table 1.

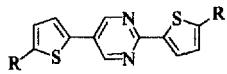


Scheme 1.

Compound No	R	R^1
1a	C_6H_{13} [16]	C_6H_{13}
1b	$C_{12}H_{25}$ [16]	$C_{12}H_{25}$
1c	$C_{12}H_{25}$ [16]	C_6H_{13}
1d	C_6H_{13} [17]	$C_{12}H_{25}$

Table 1. Showing examples of previously synthesised thienyl-pyrimidine liquid crystals in the literature.

We believe that this is the first attempt to synthesise terphenyl liquid crystalline analogues containing both the pyrimidine and thiophene heterocyclic ring systems that do not posses an ester linkage, figure 1.

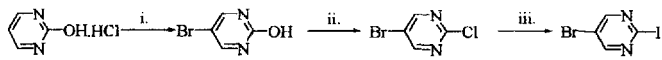


R = alkyl chain

Figure 1. Novel thienyl-pyrimidine liquid crystalline target molecules

The synthesis of materials like that shown in figure 1 involves the synthesis of two key intermediates. The first being 5-bromo-2-iodo-pyrimidine **4** and the second a range of 2-tri-*n*-butyl-5-alkylthiophenes.

5-Bromo-2-iodopyrimidine **4** was first synthesised by Lewis *et al* [18], scheme 2. The *starting material for this synthesis was 2-hydroxypyrimidine hydrochloride* **1**. *This* was reacted with bromine to give 5-bromo-2-hydroxypyrimidine **2** then treated with phosphorous oxy chloride to give 5-bromo-2-chloropyrimidine **3**. This **3**, was reacted with hydroiodoic acid to give the desired intermediate 5-bromo-2-iodopyrimidine **4**. It is possible with the 5-bromo-2-iodopyrimidine intermediate **4** to perform selective palladium catalysed cross coupling reactions using this compound first coupling reaction replacing the iodine, then the second replacing the bromine. However, in this synthesis this selectivity of palladium catalysed cross coupling towards the iodine functionality was not required as both bromine and iodine were to be replaced by thiophene rings.

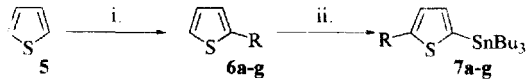


i. Br_2, water, room temperature, 1 h.
ii. $POCl_3$, *N,N*-dimethylanaline, reflux, 5 h.
iii. HI, DCM, 0 °C, 5 h.

Scheme 2. Synthesis of the 5-bromo-2-iodopyrimidine intermediate

The second key intermediate in the synthesis of the bis-thienylpyrimidine materials is 2-tri-*n*-butyl-5-alkyl thiophenes. It was possible to purchase several 2-alkylthiophenes from Lancaster Synthesis however it proved to be simpler to synthesise these intermediates using the method of Wurthner [19]. Initial thiophene **5**

was treated with *n*-butyl lithium then the 2-thienyllithium formed was reacted with iodododecane to give 2-dodecylthiophene **6 g**, see scheme 3. We have extended this to synthesise a range of 2-alkylthiophene intermediates all in high yield see table 2.



i. RI, THF, nBuli, -78 °C, 1 h / room temperature, 24 h.
ii. nBuLi, THF, -78 °C, 1 h / $SnBu_3Cl$, room temperature, 24 h.

Scheme 3. Showing the synthesis of 2-*n*-alkylthiophenes **6a-g** see table 2 and 5-*n*-alkyl-2-tri-*n*-butylstannyl thiophenes **7a-g** see table 3.

R	Boiling point(°C)	Compound No. / yield (%)
C_5H_{11}*		**6a**
C_6H_{13}*		**6b**
C_7H_{15}	121 / 2 mmHg	**6c** (80)
C_8H_{17}*		**6d**
C_9H_{19}	135 / 1.5 mmHg	**6e** (71)
$C_{10}H_{21}$	143 / 1 mmHg	**6f** (82)
$C_{12}H_{25}$	156 / 1 mmHg	**6g** (76)

Table 2. Synthesised 2-*n*-alkylthiophenes **6a-g**.

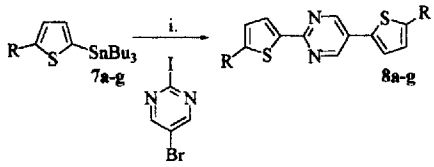
* Indicates the compound was purchased from Lancaster Synthesis.

This method of synthesising 2-alkylthiophene intermediates is far superior to the Friedel-Crafts method, which involves a further reduction step before the 2-alkylthiophene compound is formed. The alkyl thiophene intermediates above were treated a second time with *n*-butyl lithium followed by tri-*n*-butylstannyl chloride, scheme 3. This gave the desired stannylated intermediates in good yield, table 3.

R	Boiling point. (°C)	Compound No. / yield (%)
C_5H_{11}	192 / 1 mmHg	**7a** (54)
C_6H_{13}	208 / 1.5 mmHg	**7b** (51)
C_7H_{15}	212 / 1 mmHg	**7c** (62)
C_8H_{17}	224 / 1.5 mmHg	**7d** (54)
C_9H_{19}	235 / 1.5 mmHg	**7e** (57)
$C_{10}H_{21}$	241 / 1.5 mmHg	**7f** (55)
$C_{12}H_{25}$	252 / 1.5 mmHg	**7g** (47)

Table 3. Synthesised 5-*n*-alkyl-2-tri-*n*-butylstannyl thiophenes, yields and boiling points indicated.

The synthesis of the final materials used the method of Stille [20]. This involves the palladium catalysed coupling reaction between 2 equivalents of the 2-alkyl-5-tri-*n*-butylstannyl thiophene compounds **7a-g**, shown in table 3 and 5-bromo-2-iodopyrimidine **4**. This gave the final liquid crystalline materials in a range of yields see scheme and table 4.



i. DMF, $PdCl_2(PPh_3)_2$, 100 °C, 24 h.

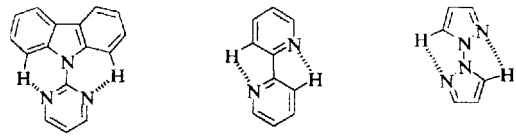
Scheme 4. Synthesis of novel liquid crystalline thienyl-pyrimidine compounds **8a-g**.

R	Transition temperatures (°C)	Compound No. / Yield (%)
C_5H_{11}	K 72.8 (G 46.5) SmA 109.0 I	**8a** (55)
C_6H_{13}	K 50.1 SmA 108.0 I	**8b** (48)
C_7H_{15}	K 61.6 SmC 114.7 I	**8c** (81)
C_8H_{17}	K 56.4 (G 35.7) (SmX_1 51.2) (SmX_2 58.7) SmC 111.6 I	**8d** (65)
C_9H_{19}	K 68.7 (G 32.9) (SmX_1 45.6) (SmX_2 66.5) SmB 75.5 SmC 116.3 I	**8e** (55)
$C_{10}H_{21}$	K 60.0 (G 37.2) SmX_1 67.0 SmB 90.9 SmC 115.9 I	**8f** (62)
$C_{12}H_{25}$	K 71.8 (G 42.4) (SmX_1 70.4) B 107.6 SmC 114.5 I	**8g** (57)

Table 4. Compounds **8a-g** showing phase transition temperatures and isolated yields of final materials.

Optical microscopy of the compounds shown in table 4 was performed using both the thin film and free standing film techniques. Thin film microscopy of compounds **8a** and **8b** showed a typical focal conic texture of a smectic A phase. In the case of **8a** at lower temperatures this compound possess a higher ordered crystal phase which was readily identified as a G phase [21]. Thin film microscopy of compound **8c** showed the presence of a *Schlieren* texture typical of the smectic C phase. It was the longer alkyl-chain compounds **8d-g**, which proved to be the most interesting. Differential scanning calorimetry of these compounds showed the presence several phases with very low enthalpy values in the order of 0.025 J g^{-1}. Thin film microscopy however, only showed that in all these compounds the *Schlieren* texture of the phase was lost and an orthogonal phase was formed this was easily identified as smectic B. The presence of this smectic B phase was confirmed by free standing film of **8e**. However, in compound **8d-g** the phases identified in table 4 as SmX_1 and SmX_2 could not be identified as no change in texture was noted using both the thin film and free standing film techniques. An X-ray study of compound **8d** was performed in order to assist in the assignment of the nature of these phases.

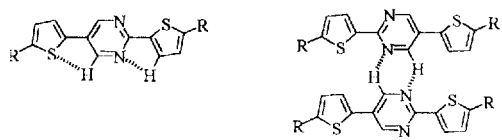
This technique shows that the layer spacing at 60 °C increases considerably on cooling and conversely decreases on heating. Both thin film and free standing film microscopy techniques had shown that this compound does not exhibit a smectic B phase. As this compound does not possess this phase then the tilting of the smectic C phase to the orthogonal smectic B phase and *vice versa* cannot be responsible for this increase / decrease in the layer spacing. Explaining this has proved to be extremely difficult. One possible explanation for this behaviour is that below this temperature there is restricted rotation of the molecular core due to either inter- or intramolecular hydrogen bonding. Other groups have noted this behaviour in other molecules particularly in 9-(2'-pyrimidinyl)carbazoles **11** [22], 2,2'-bipyridines **12** [23]and 1,1'-bipyrazoles [24], see figure 2. However, the possibility of this type of hydrogen has never been extended to thiophene-pyrimidine systems.



11 **12** **13**

Figure 2. IMHB's in **11**, 9'-(2-pyrimidinyl)carbazole, **12**, 2,2'-bipyridine, **13**, 1,1'bipyrazole.

It is easy to see that similar hydrogen bonding interactions either inter- or intramolecular could exist in compounds **8a-g** see figure 3.



Compounds 8a-g

Figure 3. Showing possible IMHB interactions, both inter- and intra-molecular types in compounds **8a-g**.

There are of course several other explanations of this phenomenon however the lack of microscopy evidence on phase changes at these temperatures tends to lead the authors to the conclusion that some other molecular level interactions are occurring in these systems.

The above molecules illustrated in table 4 also exhibit several other interesting physical properties compared to their phenyl-pyrimidine analogues. The first property to note is their low melting points compared to similar three ring terphenyl analogues. Similar compounds have melting points in excess of 100 °C, while compound **8b** exhibits a melting point of only 50 °C. Another physical property of note is the odd even effect this is clearly illustrated by the compounds shown in table 4. The even numbered carbon chain lengths **8b**, **8d** and **8f** exhibiting the lowest melting points whilst the odd number chains **8a**, **8c**, **8e** and **8f** appear to

possess elevated melting points. It is also interesting to note as the alkylchain length of group R is increased the SmC ranges of the compound **8c-g** decreases from 55.2 °C for compound **8d** to just 6.9 °C for compound **8g**. This fall in the smectic C thermal stability is due , in part to th increase in the smectic B thermal stability on increasing the length of the alkylchain R.

Future work on these systems will include electro-optic work and mixture studies in order to determine the usefulness of these materials in ferro- and antiferroelectric host materials. Further work will also be performed on the system using the selective palladium catalysed cross coupling ability of 5-bromo-2-iodopyrimidine in order to vary the lengths of the alkyl-chains on either end of the molecule. Finally work is being performed on these compounds so that chiral end groups can be attached directly to the molecular core, this hopefully will produce liquid crystalline materials with smectic C* phases.

Acknowledgments

The authors wish to thank the EPSRC for funding (P.W. and S.S.) and Dr. Robert Lewis for invaluable advice on the synthesis of some of the intermediate materials. The authors are also grateful to Dr Stephen Cowling for assistance in the assignments of liquid crystalline phase textures.

Experimental

^{1}H Nuclear magnetic resonance spectroscopy (NMR) were carried out on a JMN GX270FT spectrometer or a Jeol JMN-LA 400 FT NMR. ^{13}C NMR was carried out at 100 MHz of the Jeol JMN-LA 400 FT NMR instrument and carbon multiplicity's were established by distortionless enhancement by polarisation transfer (DEPT). ^{118}Sn NMR was carried out at 142.33 MHz using the Jeol JMN-LA 400 FT NMR instrument. All NMR were carried out using per deuterio chloroform as the solvent and tetramethylsilane as the internal standard. Peak types are denoted as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quin.) and multiplet (m).

Infrared spectra were obtained using a Perkin Elmer 487G spectrometer samples were prepared as either potassium bromide disks or thin films between sodium chloride disks.

Mass spectra were obtained using a Finigan Mat 1020 automated GC-MS spectrometer. Results are quoted were M^{+} represents the molecular ion and the base peak by (100 %). Optical microscopy was performed using an Olympus BH2 polarising microscope fitted with a Mettler FP5 controller. Samples were prepared as thin films between a glass cover slip and a glass slide or using the free standing film technique.

Differential Scanning Calorimetry (DSC) thermograms were obtained using a Perkin Elmer DSC 7 with a TAC 7/PC interface and a controlled cooling control accessory. The heating rate was 10 °C min $^{-1}$. Calculations were made using Perkin Elmer PC base software. The instrument was calibrated against an indium standard (melting temperature 156.6 °C, ΔH 28.45 J g^{-1}).

Column chromatography was carried out under flash chromatography conditions [24] unless otherwise stated. The stationary phase used was Sorbsil C60 (40-60 μm).

The compounds outlined in this paper have relatively simple structures and in our view the NMR date, MS and other data are more than adequate to confirm the structure of the compounds. The 5-*n*-alkyl-2-tri-*n*-butylstannyl thiophene

compounds **7a-g** are new materials, all attempts to perform microanalysis on these failed due to insufficient combustibility.
n-Pentylthiophene **6a** (Cat. No. 6735), n-hexylthiophene **6b** (Cat. No. 6695) and n-octylthiophene **6d** (Cat. No. 7966) were all purchased from Lancaster synthesis. 5-Bromo-2-iodopyrimidine **4** was synthesised using the method described by Lewis et al [4].

2-n-Heptylthiophene 6c

Under a nitrogen atmosphere a solution of thiophene **5** (40 g, 437 mmol) was cooled to −78 °C. To this was added dropwise a solution of n-butyllithium (183 ml, 2.5 M) in hexanes whilst maintaining a constant temperature. The reaction mixture was then stirred for 1 h then n-iodoheptane (108 g, 437 mmol) was added and the reaction mixture was allowed to warm to room temperature. The reaction was quenched with water (100 ml) and an organic layer separated, the aqueous layer was extracted with DCM (3 x 100 ml). The combined organic layers were dried and concentrated in vacuo to give a brown oil which was distilled to give a yellow oil 2-n-heptylthiophene **6c** (63.8 g, 80 %); bp. 121 °C / 1.5 mmHg, (lit [1] 110 °C / 1 mmHg); δ_H (400 MHz, $CDCl_3$) 0.87 (t, 3H, CH_3, J 7.2), 1.28 (m, 8H, CH_2), 1.66 (quint., 2H, CH_2, J 7.2), 2.79 (t, 2H, CH_2, J 7.2), 6.74 (dd, 1H, CH, J 0.8, 3.2), 6.87 (dd, 1H, CH, J 3.2, 3.3), 7.05 (dd, 1H, CH, J 0.8, 3.3); δ_C (100 MHz, $CDCl_3$) 14.0 (CH_3), 22.6 (CH_2), 29.0 (CH_2), 29.1 (CH_2), 29.9 (CH_2), 31.7 (CH_2), 32.8 (CH_2), 122.6 (aromatic CH) 123.8 (aromatic CH), 126.5 (aromatic CH), 145.7 (quat. C); m / z (EI) 182 (M^+, 17 %), 143 (10), 111 (14), 97 (100), 84 (6).

2-n-Nonylthiophene 6e

Preparation as in 2-n-heptylthiophene **6c**, distillation gave a yellow oil 2-n-nonylthiophene **6e** (53.2 g, 71 %) bp. 135 °C / 1.5 mmHg, (lit. [1] 128 °C / 1.5 mmHg); δ_H (400 MHz, $CDCl_3$) 0.89 (t, 3H, CH_3, J 7.2), 1.26 (m, 12H, CH_2), 1.67 (quint., 2H, CH_2, J 7.2), 2.79 (t, 2H, CH_2, J 7.2), 6.73 (dd, 1H, CH, J 0.8, 3.2), 6.89 (dd, 1H, CH, J 3.2, 3.3), 7.03 (dd, 1H, CH, J 0.8, 3.3); δ_C (100 MHz, $CDCl_3$) 14.1 (CH_3), 22.6 (CH_2), 29.1 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 29.5 (CH_2), 29.7 (CH_2), 29.9 (CH_2), 31.9 (CH_2), 122.6 (aromatic CH), 123.7 (aromatic CH), 126.5 (aromatic CH), 145.6 (quat. C); m / z (EI) 210 (M^+, 18 %), 139 (5), 111 (12), 97 (100), 84 (5).

2-n-Decylthiophene 6f

Preparation as described in 2-n-heptylthiophene **6c**, distillation gave a yellow oil 2-n-decylthiophene **6f** (58.3 g, 82 %), bp. = 143 °C / 1 mmHg, (lit. [1] 144 °C / 1.5 mmHg); δ_H (400 MHz, $CDCl_3$) 0.89 (t, 3H, CH_3, J 7.2), 1.22 (m, 14H, CH_2), 1.64 (quint., 2H, CH_2, J 7.2), 2.74 (t, 2H, CH_2, J 7.2), 6.75 (dd, 1H, CH, J 0.8, 3.2), 6.88 (dd, 1H, CH, J 3.2, 3.3), 7.04 (dd, 1H, CH, J 0.8, 3.3); δ_C (100 MHz, $CDCl_3$) 14.1 (CH_3), 22.7 (CH_2), 28.5 (CH_2), 29.2 (CH_2), 29.4 (3 x CH_2), 29.6 (CH_2), 29.8 (CH_2), 31.9 (CH_2), 122.6 (aromatic CH), 123.8 (aromatic CH), 126.6 (aromatic CH), 145.9 (quat. C); m / z (EI) 224 (M^+, 30 %), 111 (20), 97 (100), 84 (8).

2-n-Dodecylthiophene 6g

Preparation as in 2-n-heptylthiophene **6c**, distillation gave a yellow oil 2-n-dodecylthiophene **6g** (56.3 g, 76 %), bp. 156 °C / 1 mm Hg, (lit. [1] 159 °C / 1.5 mmHg); δ_H (400 MHz, $CDCl_3$) 0.88 (t, 3H, CH_3, J 7.2), 1.26 (m, 19H, CH_2), 1.67 (quint., 2H, CH_2, J 7.2), 2.80 (t, 2H, CH_2, J 7.2), 6.76 (dd, 1H, CH, J 0.8, 3.2), 6.89 (dd, 1H, CH, J 3.2, 3.3), 7.07 (dd, 1H, CH, J 0.8, 3.3); δ_C (100 MHz, $CDCl_3$) 14.1 (CH_3), 22.7 (CH_2), 28.6 (CH_2), 29.2 (CH_2), 29.4 (3 x CH_2), 29.6 (CH_2), 29.7 (CH_2), 29.8 (CH_2), 29.9 (CH_2), 31.9 (CH_2), 122.7 (aromatic CH), 123.8 (aromatic CH), 126.6 (aromatic CH), 145.9 (quat. C); m / z (EI) 252 (M^+, 25 %), 139 (8), 111 (20), 97 (100), 84 (5).

2-(5-*n*-Octyl)tri-*n*-butylstannyl thiophene 7d

Under a nitrogen atmosphere a solution of *n*-octylthiophene **6d** (10.0 g, 51 mmol) in dry THF was cooled to –78 °C. To this *n*-butyllithium (20.4 ml, 2.5 M solution in hexanes) was added dropwise maintaining a constant temperature. The reaction mixture was stirred for 1 hour then tributylstannyl chloride (16.6 g, 51 mmol) was added dropwise and the reaction mixture was stirred for 1 hour at –78 °C, then allowed to warm to room temperature over a 12 h period. The reaction was quenched with water (100 ml) and an organic layer separated. The aqueous layer was extracted with DCM (3 x 100 ml) and the combined organic extracts were dried and concentrated *in vacuo* to give a yellow oil. Distillation gave a pale yellow oil 2-(5-*n*-octyl)tri-*n*-butylstannyl thiophene **7d** (13.4 g, 54 %), bp 224-225 °C, 1.5 mmHg; δ_H (400 MHz, $CDCl_3$) 0.90 (t, 12H, CH_3 *J* 7.2), 1.02-1.70 (m, 30H, CH_2), 2.85 (t, 2H, CH_2 *J* 7.2), 6.89 (d, 1H, CH, *J* 3.2), 6.98 (d, 1H, CH, *J* 3.2); δ_C (100 MHz, $CDCl_3$) 10.8 (3 x CH_2), 13.6 (3 x CH_3), 14.1 (CH_3), 22.7 (CH_2), 27.3 (CH_2), 29.0 (3 x CH_2), 29.1 (CH_2), 29.3 (CH_2), 29.6 (CH_2), 31.7 (CH_2), 125.3 (aromatic CH), 135.0 (quat. C), 135.4 (aromatic CH), 151.5 (quat. C); δ_{Sn} (142.33 MHz, $CDCl_3$) –42.41 (-$SnBu_3$); *m / z* (EI) 484 (M^+ ^{118}Sn, 1 %), 429 (100), 427 (70), 373 (20), 315 (25).

2-(5-n-Pentyl)tri-n-butylstannyl thiophene 7a

Preparation as in 2-(5-n-octyl)tri-n-butylstannyl thiophene **7d**, distillation gave a yellow oil 2-(5-n-pentyl)tributylstannyl thiophene **7a** (27.8 g, 51 %), bp. 208 °C / 1.5 mmHg; δ_H (400 MHz, $CDCl_3$) 0.88 (t, 12H, CH_3, J 7.2), 1.02-1.73 (m, 24H, CH_2), 2.84 (t, 2 H,CH_2), 6.88 (d, 1H, CH, J 3.2), 6.97 (d, 1H, CH, J 3.2); δ_C (100 MHz, $CDCl_3$) 10.7 (3 x CH_2), 13.7 (3 x CH_3), 14.1 (CH_3), 22.7 (CH_2), 27.3 (CH_2), 29.4 (CH_2), 31,8 (CH_2); δ_{Sn} (142.33 MHz, $CDCl_3$) –42.43 (-$SnBu_3$); m / z (EI) 441 (M^+ ^{118}Sn, 1 %), 401 (100), 345 (41), 289 (58), 115 (10).

2-(5-n-Hexyl)tri-n-butylstannyl thiophene 7b

Preparation as in 2-(5-n-octyl)tri-n-butylstannyl thiophene **7d**, distillation gave a yellow oil 2-(5-n-hexyl)tributylstannyl thiophene **7b** (27.8 g, 51 %), bp. 208 °C / 1.5 mmHg; δ_H (400 MHz, $CDCl_3$) 0.89 (t, 12H, CH_3, J 7.2), 1.04-1.75 (m, 26H, CH_2), 2.84 (t, 2 H,CH_2), 6.87 (d, 1H, CH, J 3.2), 6.97 (d, 1H, CH, J 3.2); δ_C (100 MHz, $CDCl_3$) 10.7 (3 x CH_2), 13.7 (3 x CH_3), 14.1 (CH_3), 22.6 (CH_2), 27.3 (CH_2), 29.0 (CH_2), 29.7 (CH_2), 31,8 (CH_2); δ_{Sn} (142.33 MHz, $CDCl_3$) –42.41 (-$SnBu_3$); m / z (EI) 455 (M^+ ^{118}Sn, 1 %), 401 (100), 345 (45), 289 (55).

2-(5-n-Hexyl)tri-n-butylstannyl thiophene 7b

Preparation as in 2-(5-n-octyl)tri-n-butylstannyl thiophene **7d**, distillation gave a yellow oil 2-(5-n-hexyl)tributylstannyl thiophene **7b** (27.8 g, 51 %), bp. 208 °C / 1.5 mmHg; δ_H (400 MHz, $CDCl_3$) 0.89 (t, 12H, CH_3, J 7.2), 1.04-1.75 (m, 26H, CH_2), 2.84 (t, 2 H,CH_2), 6.87 (d, 1H, CH, J 3.2), 6.97 (d, 1H, CH, J 3.2); δ_C (100 MHz, $CDCl_3$) 10.7 (3 x CH_2), 13.7 (3 x CH_3), 14.1 (CH_3), 22.6 (CH_2), 27.3 (CH_2), 29.0 (CH_2), 29.7 (CH_2), 31,8 (CH_2); δ_{Sn} (142.33 MHz, $CDCl_3$) –42.41 (-$SnBu_3$); m / z (EI) 455 (M^+ ^{118}Sn, 1 %), 401 (100), 345 (45), 289 (55).

2-(5-*n*-Heptyl)tri-*n*-butylstannyl thiophene 7c

Preparation as in 2-(5-*n*-octyl)tri-*n*-butylstannyl thiophene **7d**, distillation gave 2-(5-*n*-heptyl)tri-*n*-butylstannyl thiophene **7c** (32.51 g, 62 %) bp 212 °C / 1.5 mmHg; δ_H (400 MHz, $CDCl_3$) 0.88 (t, 12H, CH_3, *J* 7.2), 1.05-1.71 (m, 28H, CH_2), 2.83 (t, 2H, CH_2, *J* 7.2), 6.87 (d, 1H, CH, *J* 3.2), 6.96 (t, 2H, CH, *J* 3.2); δ_C (100 MHz, $CDCl_3$) 10.7 (3 x CH_2), 13.6 (3 x CH_3), 14.1 (CH_3), 22.6 (CH_2), 27.0 (3 x CH_2), 28.9 (3 x CH_2), 29.1 (CH_2), 29.3 (CH_2), 29.9 (CH_2), 31.8 (CH_2), 31,9 (CH_2), 125.4 (aromatic CH), 133.5 (quat. C), 135.1 (aromatic CH), 151.5 (quat. C); δ_{Sn} (142.33 MHz, $CDCl_3$) –42.39 (-$SnBu_3$); m / *z* (EI) 472 (M^+ ^{118}Sn, 2 %), 415 (100), 359 (30), 301 (54), 97 (30).

2-(5-*n*-Nonyl)tri-*n*-butylstannyl thiophene 7e

Preparation as in 2-(5-*n*-octyl)tri-*n*-butylstannyl thiophene **7d**, distillation gave a yellow oil 2-(5-*n*-nonyl)tributylstannyl thiophene **7e** (36.2, 57 %), bp 235 °C / 1.5 mmHg; δ_H (400 MHz, $CDCl_3$) 0.91 (t, 12H, CH_3, *J* 7.2), 1.07-1.71 (m, 32H, CH_2), 2.84 (t, 2H, CH_2, *J* 7.2), 6.89 (d, 1H, CH, *J* 3.2), 6.97 (d, 1H, CH, *J* 3.2); δ_C (100 MHz, $CDCl_3$) 10.7 (3 x CH_2), 13.6 (3 x CH_3), 14.1 (CH_3), 22.7 (CH_2), 27.2 (3 x CH_2), 28.9 (3 x CH_2), 29.3 (CH_2), 29.5 (CH_2), 29.9 (CH_2), 31.8 (CH_2), 31.9 (CH_2); δ_{Sn} (142.33 MHz, $CDCl_3$) –42.48 (-$SnBu_3$); *m* / *z* (EI) 498 (M^+ ^{118}Sn,5 %), 443 (100), 387 (43), 331 (44) 97 (11).

2-(5-*n*-Decyl)tributylstannyl thiophene 7f

Prepared as in 2-(*n*-octyl)tri-*n*-butylstannyl thiophene **7d**, distillation gave a yellow oil 2-(*n*-decyl)tri-*n*-butylstannyl thiophene **7f** (25.2 g, 55 %), bp. 241 °C / 1.5 mmHg; δ_H (400 MHz, $CDCl_3$) 1.17 (t, 12H, CH_3, *J* 7.2), 1.27-2.00 (m, 34H, CH_2), 3.12 (t, 2H, CH_2, *J* 7.2), 7.12 (d, 1H, CH, *J* 3.2), 7.25 (d, 1H, CH, *J* 3.2); δ_C (100 MHz, $CDCl_3$) 10.7 (3 x CH_2), 13.6 (3 x CH_3), 14.1 (CH_3), 22.7 (CH_2), 27.0 (3 x CH_2), 29.0 (3 x CH_2), 29.1 (CH_2), 29.3 (CH_3), 29.4 (CH_2), 29.6 (CH_2), 29.9 (CH_2), 31.9 (CH_2), 125.2 (aromatic CH), 133.6 (quat. C), 135.1 (aromatic CH), 151.5 (quat. C); δ_{Sn} (142.33 MHz, $CDCl_3$) –42.48 (-$SnBu_3$); *m* / *z* (EI) 512 (M^+ ^{118}Sn, 2 %), 457 (90), 454 (100), 401 (20), 398 (22), 343 (20), 97 (9).

2-(5-*n*-Dodecyl)tri-*n*-butylstannyl thiophene 7g

Prepared as in 2-(5-octyl)tributylstannyl thiophene **7d**, distillation gave a yellow oil 2-(5-*n*-dodecyl)tri-*n*-butylstannyl thiophene **7g** (20.12 g, 47 %), bp. 252 °C / 1.5 mmHg; δ_H (400 MHz, $CDCl_3$) 1.17 (t, 12H, CH_3, *J* 7.2), 1.29-1.99 (m, 38H, CH_2),

3.12 (t, 2H, CH_2, *J* 7.2), 7.16 (d, 1H, CH, *J* 3.2), 7.25 (d, 1H, CH, *J* 3.2); δ_C (100 MHz, $CDCl_3$) 10.7 (3 x CH_2), 13.6 (3 x CH_3), 14.1 (CH_3), 22.7 (CH_2), 27.4 (3 x CH_2), 29.0 (3 x CH_2), 29.1 (2 x CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.6 (CH_2), 29.9 (CH_2), 31.8 (CH_2), 125.2 (aromatic CH), 133.6 (quat. CH), 135.1 (aromatic CH), 151.5 (quat. CH); δ_{Sn} (142.33 MHz, $CDCl_3$) insert data here; *m / z* (EI) (M^+ ^{118}Sn,) insert data here.

Bis 2,5-[2-(5-*n*-octyl)thienyl]pyrimidine 8d

Under a nitrogen atmosphere 2-(5-*n*-octyl)tri-*n*-butylstannyl thiophene **7d** (6.80 g, 14.08 mmol) and 5-bromo-2-iodopyrimidine **4** (2.00 g, 7.04 mmol) were mixed at room temperature in dry DMF (100 ml). To this bis triphenylphosphine palladium dichloride (0.30 g, 3 %mol) was added and the reaction was heated at 100 °C for 24 h. The reaction solvent was removed *in vacuo* and the reaction residue was passed through a pad of silica (DCM, ethyl acetate). The solvent was removed *in vacuo* to give a brown solid which was recrystallised with charcoal decolourisation to give a white powder bis 2,5-[2-(5-*n*-octyl)thienyl]pyrimidine **8d** (2.13 g, 65 %), mp. 54.0-56.4 °C, K 56.4 °C, (SmG 38.2 °C) (SmX_2 51.2 °C), SmX_1 58.7 °C, SmC 111.6 °C I (hexane); (found: C 71.5, H 8.8, N 5.9, S 13.5, $C_{28}H_{40}S_2N_2$ C 71.7, H 8.6, N 6.0, S 13.7); δ_H (400 MHz, $CDCl_3$) 0.87 (t, 6H, CH_3, *J* 7.2), 1.27 (m, 20H, CH_2), 1.69 (quint., 4H, CH_2, *J* 7.2), 2.81 (t, 2H, CH_2, *J* 7.2), 2.84 (t, 2H, CH_2, *J* 7.2), 6.78 (d, 1H, CH, *J* 4.0), 6.81 (d, 1H, CH, *J* 4.0), 7.16 (d, 1H, CH, *J* 4.0), 7.80 (d, 1H, CH, *J* 4.0), 8.78 (s, 2H, CH); δ_C (100 MHz, $CDCl_3$) 14.1 (2 x CH_3), 22.6 (CH_2), 29.1 (2 x CH_2), 29.2 (CH_2), 29.3 (2 x CH_2), 29.4 (2 x CH_2), 30.3 (CH_2), 30.5 (CH_2), 31.5 (CH_2), 31.6 (CH_2), 31.9 (CH_2), 124.1 (aromatic CH), 125.5 (aromatic CH), 125.7 (aromatic CH), 128.8 (aromatic CH), 134.2 (quat. C), 140.1 (quat. C), 147.8 (quat. C), 151.2 (quat. C), 153.1 (2 x aromatic CH), 159.6 (quat. C); *m / z* (EI) 468 (M^+, 8 %), 422 (35), 254 (100), 117 (28).

Bis 2,5-[2-(5-*n*-pentyl)thienyl]pyrimidine 8a

The title compound was synthesised using the method described in bis 2,5-[2-(5-*n*-octyl)thienyl]pyrimidine **8d**, recrystallisation with charcoal decolourisation gave a white solid bis 2,5-[2-(5-*n*-pentyl)thienyl]pyrimidine **8a** (1.61 g, 55 %), mp. 69.0-72.8 °C K 72.8 (SmG 46.5 °C) SmA 109.0 I (hexane), (found: C 68.6, H 7.4, N 7.3, requires C 68.7, H 7.3, N 7.3); δ_H (400 MHz, $CDCl_3$) 0.90 (m, 6H, CH_3), 1.36 (m, 8H, CH_2), 1.74 (m, 4H, CH_2), 2.82 (t, 2H, CH_2, *J* 7.2), 2.85 (t, 2H, CH_2, *J* 7.2), 6.79 (d, 1H, CH, *J* 3.2), 6.83 (d, 1H, CH, *J* 3.2), 7.17 (d, 1H, CH, *J* 3.2), 7.79 (d, 1H, CH, *J* 3.2), 8.79 (s, 2H, CH); δ_C (100 MHz, $CDCl_3$) 14.0 (2 x CH_3), 22.3 (2 x CH_2), 30.1 (CH_2), 30.4 (CH_2), 31.1 (2 x CH_2), 31.3 (2 x CH_2), 124.0 (aromatic CH), 125.4 (quat. C), 125.5 (aromatic CH), 125.7 (aromatic CH), 128.8 (aromatic CH), 134.1 (quat.. CH), 140.0 (quat. C), 147.8 (quat. C), 151.2 (quat. C), 153.1 (2 x aromatic CH), 159.4 (quat. C); *m / z* (EI) 384 (M^+, 75 %), 327 (100), 270 (48), 121 (15).

Bis 2,5-[2-(5-*n*-hexyl)thienyl]pyrimidine 8b

The title compound was synthesised using the method described in bis 2,5-[2-(5-*n*-octyl)thienyl]pyrimidine **8d**, recrystallisation with charcoal decolourisation gave a white solid bis 2,5-[2-(5-*n*-hexyl)thienyl]pyrimidine **8b** (1.62 g, 48 %), mp 47.2-50.1 °C, K 50.1 °C, SmA 108.0 °C I (hexane), (found C 69.9, H 7.9, N 6.8,

requires $C_{24}H_{32}N_2S_2$ C 69.9, H 7.8, N 6.8); δ_H (270 MHz, $CDCl_3$) 0.89 (t, 6H, CH_3, *J* 7.2), 1.20-1.32 (m, 12H, CH_2), 1.66 (m, 4H, CH_2), 2.81 (t, 2H, CH_2, *J* 7.2), 2.84 (t, 2H, CH_2, *J* 7.2), 6.77 (d, 1H, CH, *J* 3.2), 6.81 (d, 1H, CH, *J* 3.2), 7.17 (d, 1H, CH, *J* 3.2), 7.80 (d, 1H, CH, *J* 3.2), 8.78 (s, 2H, CH); δ_C (67.8 MHz, $CDCl_3$), 14.1 (2 x CH_3), 22.6 (2 x CH_2), 28.8 (2 x CH_2), 30.2 (CH_2), 30.5 (CH_2), 31.4 (2 x CH_2), 31.5 (CH_2), 124.1 (aromatic CH), 125.5 (aromatic CH), 125.8 (aromatic CH), 128.8 (aromatic CH), 134.2 (quat. C), 140.1 (quat. C), 147.8 (quat. C), 151.2 (quat. C), 153.1 (2 x aromatic CH), 159.6 (quat. C); *m / z* (EI) 412 (M^+, 98 %), 341 (100), 270 (62), 121 (15).

Bis 2,5-[2-(5-*n*-heptyl)thienyl]pyrimidine 8c

The title compound was synthesised using the method described in bis 2,5-[2-(5-*n*-octyl)thienyl]pyrimidine 8d, recrystallisation with charcoal decolourisation gave a white solid bis 2,5-[2-(5-*n*-heptyl)thienyl]pyrimidine 8c (2.51 g, 81 %), mp. 59.3-61.6 °C, K 61.6, SmC 114.7 °C I (hexane), (found: C 70.8, H 8.3, N 6.4, requires C 70.5, H 8.6, N 6.3, S 14.5); δ_H (400 MHz, $CDCl_3$) 0.88 (t 6H, CH_3, *J* 7.2), 1.28-1.38 (m, 16H, CH_2), 1.69 (m, 4H, CH_2), 2.81 (t, 2H, CH_2, *J* 7.2), 2.83 (t, 2H, CH_2, *J* 7.2), 6.77 (d, 1H, CH, *J* 3.2), 6.82 (d, 1H, CH, *J* 3.2), 7.15 (d, 1H, CH, *J* 3.2), 7.79 (d, 1H, CH, *J* 3.2), 8.78 (s, 2H, CH); δ_C (100 MHz, $CDCl_3$) 14.1 (2 x CH_3), 22.6 (2 x CH_2), 28.9 (CH_2), 29.0 (2 x CH_2), 29.1 (CH_2), 30.2 (CH_2), 30.5 (CH_2), 31.4 (CH_2), 31.5 (CH_2), 31.7 (2 x CH_2), 124.1 (aromatic CH), 125.4 (aromatic CH), 126.7 (aromatic CH), 128.7 (aromatic CH), 134.1 (quat. C), 140.0 (quat. C), 147.7 (quat. C), 151.2 (quat. C), 153.0 (2 x aromatic CH), 159.5 (quat. C); *m / z* (EI) 440 (M^+ 37 %), 390 (43), 277 (71), 178 (100), 165 (91).

Bis 2,5-[2-(5-*n*-nonyl)thienyl]pyrimidine 8e

The title compound was synthesised using the method described in bis 2,5-[2-(5-*n*-octyl)thienyl]pyrimidine 8d, recrystallisation with charcoal decolourisation gave a white solid bis 2,5-[2-(5-*n*-nonyl)thienyl]pyrimidine 8e (1.59 g, 55 %), mp. 68.7 °C, K 68.7 °C, (SmG 35.9 °C), (SmX_1 45.6 °C), (SmX_2 66.5 °C), SmB_{Hex} 75.5 °C, SmC 116.3 °C I (hexane), (found: C 73.0, H 9.2, N 5.7, $C_{30}H_{44}N_2S_2$ requires C 72.5, H 8.9, N 5.6); δ_H (400 MHz, $CDCl_3$) 0.86 (t, 6H, CH_3, *J* 7.2), 1.25-1.36 (m, 24H, CH_2), 1.70 (m, 4H, CH_2), 2.80 (t, 2H, CH_2, *J* 7.2), 2.82 (t, 2H, CH_2, *J* 7.2), 6.77 (d, 1H, CH, *J* 3.2), 6.80 (d, 2H, CH, *J* 3.2), 7.78 (d, 2H, CH, *J* 3.2), 8.77 (s, 2H, CH); δ_C (100 MHz, $CDCl_3$) 14.1 (2 x CH_3), 22.6 (2 x CH_2), 29.1 (CH_2), 29.2 (CH_2), 29.3 (2 x CH_2), 29.4 (CH_2), 29.5 (2 x CH_2), 30.2 (2 x CH_2), 30.5 (2 x CH_2), 31.4 (CH_2), 31.6 (CH_2), 31.9 (CH_2), 124.1 (aromatic CH), 125.5 (aromatic CH), 125.7 (aromatic CH), 128.8 (aromatic CH), 134.1 (quat. C), 140.0 (quat. C), 147.7 (quat. C), 151.2 (quat. C), 153.1 (2 x aromatic CH), 159.6 (quat. C); *m / z* (EI) 496 (M^+ 9 %), 270 (7), 212 (12), 153 (36), 140 (100), 128 (60).

Bis 2,5-[2-(5-*n*-decyl)thienyl]pyrimidine 8f

The title compound was synthesised using the method described in bis 2,5-[2-(5-*n*-octyl)thienyl]pyrimidine **8d**, recrystallisation with charcoal decolourisation gave a white solid bis 2,5-[2-(5-*n*-decyl)thienyl]pyrimidine **8f** (2.30 g, 62 %), mp. 57.0-60.0 °C, K 60.0 °C, (SmG 37.2 °C), SmX_1 62.0 °C, SmB_{Hex} 90.9 °C, SmC 115.9 °C I (hexane), (found: C 70.0, H 9.4, N 5.3, requires C 73.2, H 9.2, N 5.3); δ_H (400 MHz, $CDCl_3$) 0.87 (t, 6H, CH_3, *J* 7.2), 1.26-1.38 (m, 28H, CH_2), 1.72 (m,

4H, CH_2), 2.82 (t, 2H, CH_2, *J* 7.2), 2.84 (t, 2H, CH_2, *J* 7.2), 6.79 (d, 1H, CH, *J* 3.2), 6.82 (d, 1H, CH, *J* 3.2), 7.17 (d, 1H, CH, *J* 3.2),7.79 (d, 1H, CH, *J* 3.2), 8.79 (s, 2H, 2 x CH), δ_C (100 MHz, $CDCl_3$) 14.1 (2 x CH_3), 22.6 (2 x CH_2), 29.0 (CH_2), 29.1 (CH_2), 29.3 (2 x CH_2), 29.4 (CH_2), 29.5 (4 x CH_2), 29.6 (2 x CH_2), 30.2 (CH_2), 30.5 (CH_2), 31.4 (CH_2), 31.6 (CH_2), 31.9 (CH_2), 124.1 (aromatic CH), 125.4 (aromatic CH), 125.5 (aromatic CH), 128.8 (aromatic CH), 134.1 (quat. C), 140.0 (quat. C), 147.8 (quat. C), 151.2 (quat. C), 153.1 (2 x aromatic CH), 159.6 (quat. C); *m* / *z* (EI) 524 (M^+ 100 %), 494 (27), 397 (52), 381 (15), 284 (12), 270 (49).

Bis 2,5-[2-(5-*n*-dodecyl)thienyl]pyrimidine 8g

The title compound was synthesised using the method described in bis 2,5-[2-(5-*n*-octyl)thienyl]pyrimidine **8d**, recrystallisation with charcoal decolourisation gave a white solid bis 2,5-[2-(5-*n*-dodecyl)thienyl]pyrimidine **8g** (2.31 g, 57 %), mp. 69.4-71.8 °C, K 71.8 °C (SmG 42.4 °C), (SmX_1 70.4 °C), SmB 107.6 °C, SmC 114.5 °C I (hexane), (found: C 74.8, H 10.0, N 4.8, S 11.1; $C_{36}H_{56}N_2S_2$ requires C 74.4, H 9.7, N 4.8, S 11.0); δ_H (400 MHz, $CDCl_3$) 0.88 (t, 3H, CH_3, *J* 7.2), 1.25-1.38 (m, 36H, CH_2), 1.71 (m, 4 H, CH_2), 2.82 (t, 2H, CH_2, *J* 7.2), 2.84 (t, 2H, CH_2, *J* 7.2), 6.79 (d, 1H, CH, *J* 3.2), 6.82 (d, 1H, CH, *J* 3.2), 7.17 (d, 1H, CH, *J* 3.2), 7.79 (d, 1H, CH, *J* 3.2), 8.79 (s, 2H, CH); δ_C (100 MHz, $CDCl_3$) 14.1 (2 x CH_3), 22.7 (2 x CH_2), 29.0 (CH_2), 29.1 (2 x CH_2), 29.3 (4 x CH_2), 29.5 (4 x CH_2), 29.6 (2 x CH_2), 29.7 (CH_2), 30.5 (CH_2), 31.4 (CH_2), 31.5 (CH_2), 31.9 (2 x CH_2), 124.1 (aromatic CH), 125.4 (aromatic CH), 125.6 (aromatic CH), 128.8 (aromatic CH), 134.1 (quat. C), 140,0 (quat. C), 147,7 (quat. C), 151.2 (quat. C), 153.1 (2 x aromatic CH), 159.6 (aromatic CH); *m* / *z* (EI) 580 (M^+ 32 %), 425 (55), 283 (35), 270 (100).

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