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Liquid crystalline properties of all symmetric p-phenylene and 2,5-thiophene pentamers

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In order to understand the mesophase behaviour of the p-phenylene pentamer p-quinquephenylene (PPPPP), all symmetric pentamers composed of p-phenylene (P) and 2,5-thiophene (T) have been synthesised and investigated. The effects of substituting 1,4-phenylene by 2,5-thiophene units are the introduction of kinks along the main axis of the molecule, often resulting in mixtures of stable conformers, and planarisation of the molecule by avoiding twisted PP sequences. The mesophase behaviour of the compounds was determined by optical polarised microscopy and differential scanning calorimetry. Nematic phases were found for six out of eight compounds, but some of these compounds are monotropic. Quinquephenylene has the highest phase transition temperatures at 393°C and 426°C, for the crystal to nematic and nematic to isotropic phase transition, respectively. Introduction of one or two kinks in the pentamers lowers the phase transition temperatures, typically by 60 and 130°C, respectively. It was also observed that 2,5-thiophene units at the positions 1 and 5 widens the nematic window for these compounds. The two compounds with three successive thiophene units in the middle of the pentamer, which possess three stable conformations, did not show liquid crystal behaviour.

Keywords: mesophase characterisation; nematic liquid crystals; quinquephenylene derivates; synthesis

1. Introduction

Organic conductors are interesting materials for opto-electronic applications, such as light emitting diodes, solar cells and field-effect transistors, due to their flexibility, low weight and low production costs (*1*). Despite these advantages, applications for these materials are limited by low charge carrier mobility and instability of the organics in the atmosphere (*2*). The charge carrier mobility of materials can be increased by a better ordering of the molecules (*3–6*). Long-range ordering in a material can be obtained by exploiting liquid crystalline states (*7*). It has been reported that p-quinquephenylene (I), the 1,4-phenylene pentamer (PPPPP), exhibits liquid crystalline phases at very high temperatures (*8*). Recently, it was reported that various derivatives of **I**, in which a single phenyl group has been replaced by an aromatic heterocycle, form liquid crystalline phases as well (*9–11*). Quinquephenylene can be seen as the simplest liquid crystalline material, because it does not have any polar groups or alkyl tails and its shape can be considered as a rigid rod.

Polythiophenes are an important class of electron conductive polymers, and therefore we decided to conduct a systematic investigation of the pentamers of p-phenylene and 2,5-thiophene. All symmetric pentamers of p-phenylene and 2,5-thiophene were synthesised. Some of these pentamers have multiple stable conformations, because the exocyclic bond angle for a 2,5-substituted thiophene is 148°. Therefore, a kink is introduced in the molecules that contain a thiophene in position 2–4 and multiple conformations will exist for molecules that contain more than one thiophene at these positions. A single thiophene will induce a boomerang shape, whereas multiple thiophene units will give rise to multiple non-linear conformations, containing several kinks in the backbone. Another consequence of introducing thiophene moieties in **I** is planarisation of the molecule, giving rise to extensive intramolecular conjugation (*12, 13*). A reduced steric interaction between the thiophene protons and those of its neighbours enables the molecule to adapt a stable planar conformation. In fact, only adjacent phenylene groups will adapt a non-planar twisted conformation, so avoiding the presence of these structural elements will result in planar molecules (*14*).

In this paper, we describe the synthesis and properties of all eight linear symmetric pentamers containing p-phenylene and 2,5-thiophene moieties depicted in Figure 1. We focus our attention on the relationship between molecular structure and the physical properties of these molecules, especially on the liquid crystalline phase transitions.

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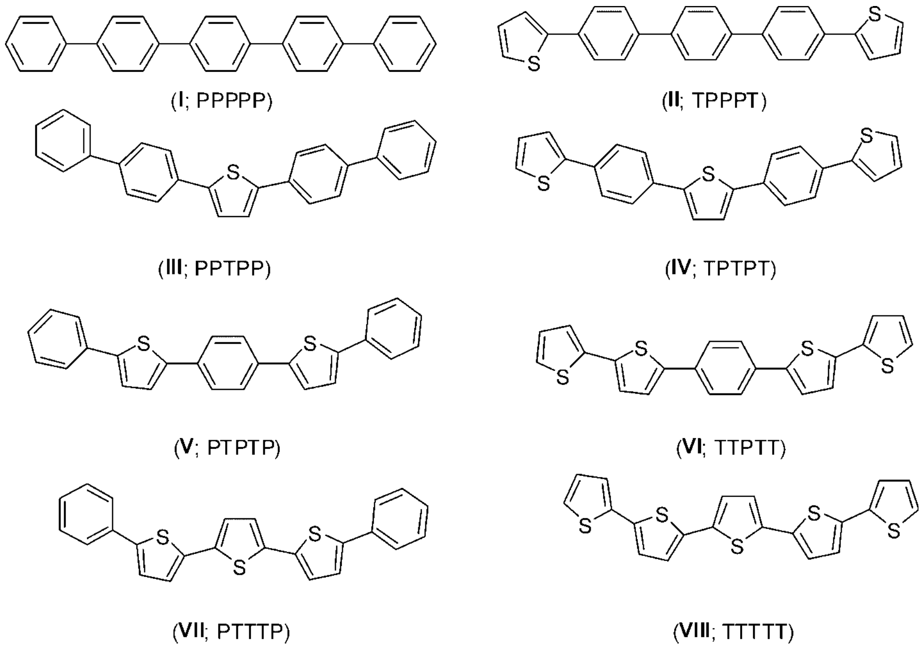


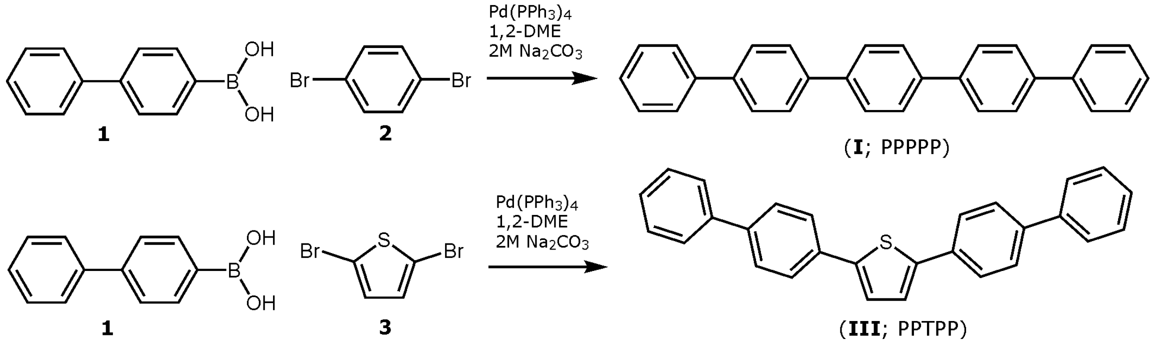
Figure 1. All symmetric linear pentamers composed of p-phenylene and 2,5-thiophene units.

2. Results and discussion

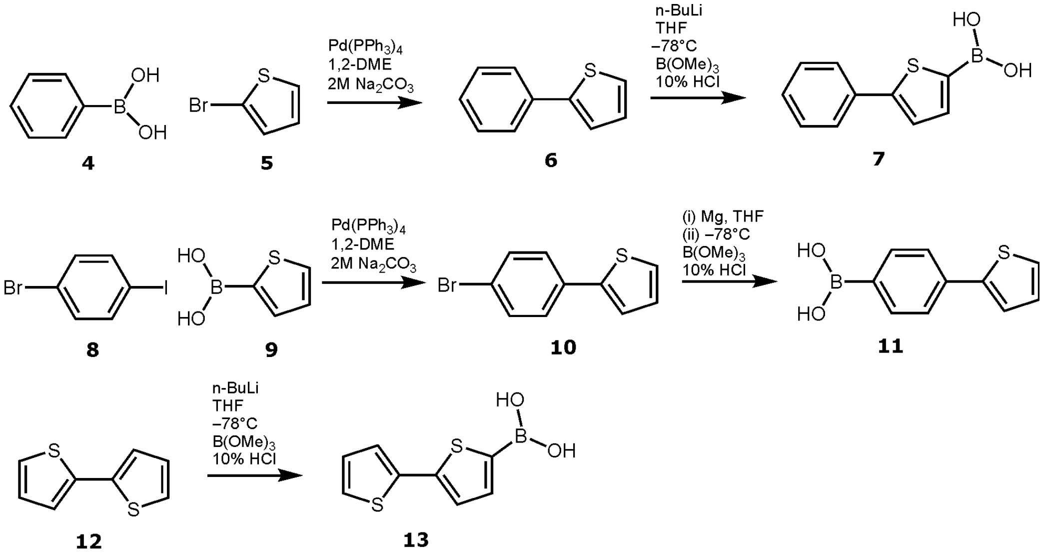
All symmetric p-phenylene and 2,5-thiophene pentamers **I–VIII**, have been synthesised via Suzuki coupling reactions, as is shown for **I** and **III** in Scheme 1. In all cases, two dimers containing a boronic acid were coupled with a dibromide in a Palladium-catalysed reaction. The resulting unfunctionalised pentamers were crystalline highly insoluble compounds that were purified by crystallisation from trichlorobenzene. In all cases, satisfactory yields ranging from 65–78% were obtained for this coupling reaction. The synthesis of the dimers that are required for the synthesis of **III–VIII** is illustrated in Scheme 2.

The mesophase behaviour of **I–VIII** has been investigated by optical polarisation microscopy (OPM) and differential scanning calorimetry (DSC). OPM is used to identify the liquid crystalline phases, as is shown in Figure 2. The phase transitions of these compounds are presented in Figure 3. A typical DSC trace, in which sublimation close to the melting and crystallisation temperature is visible, is shown in Figure 4. The mesophase behaviour of PPPPP (**I**) and PPTPP (**III**) has been reported in the literature (*2*). Our results, as presented in Figure 3, are in good agreement with the reported values. For PPTPP, the phase transitions are found to be approximate 60°C lower than for PPPPP, and this has been attributed to the geometry of the central thiophene ring, which causes the molecule to adopt a boomerang shape. In general boomerang-shaped molecules, as compared with javelin-shaped counterparts, tend to have significantly lower transition temperatures.

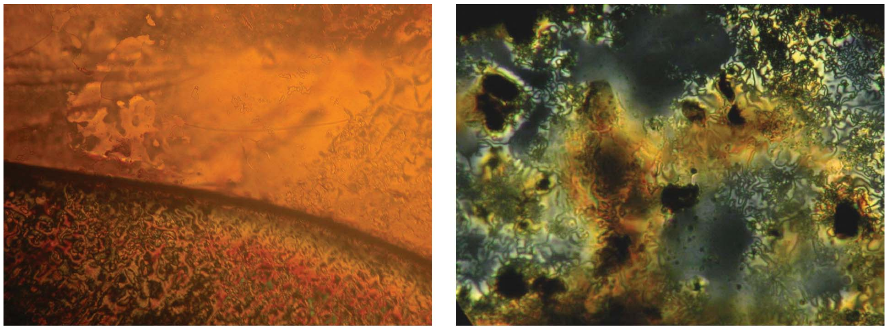
Quinquephenylene shows a nematic phase between 393°C and 426°C upon heating and from 419°C to

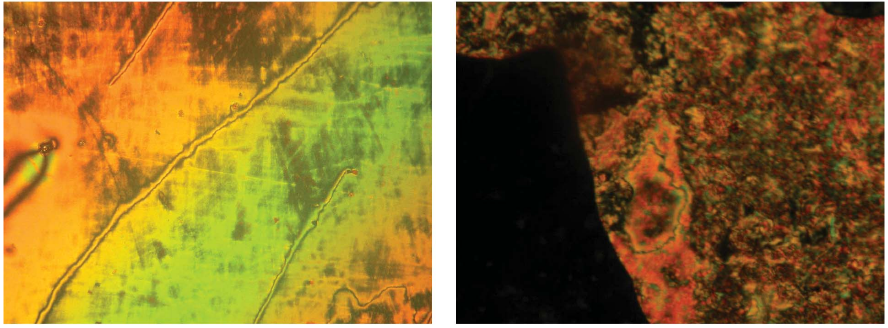


Scheme 1. Synthesis of PPPPP (**I**) and PPTPP (**III**).



Scheme 2. Synthesis of the boronoc acids **7**, **10** and **12**, required for the synthesis of **III-VIII**.


PPPPP (magnification 100x) TPPPT (magnification 100x)


PPTPP (magnification 100x) TPTPT (magnification 100x)

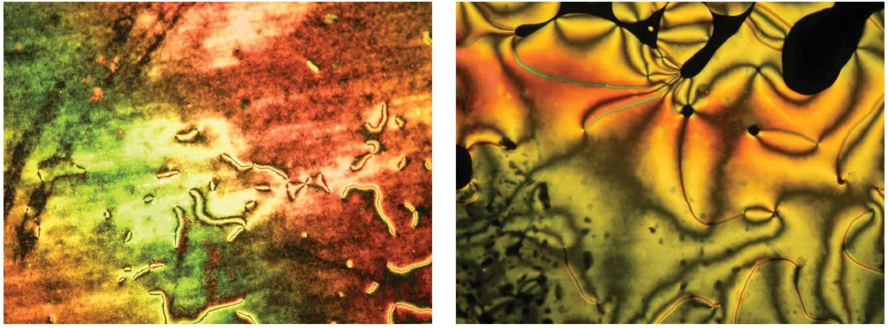

PTPTP (magnification 100x) TTPTT (magnification 200x)

Figure 2. Optical polarised microscope pictures in the nematic phase.

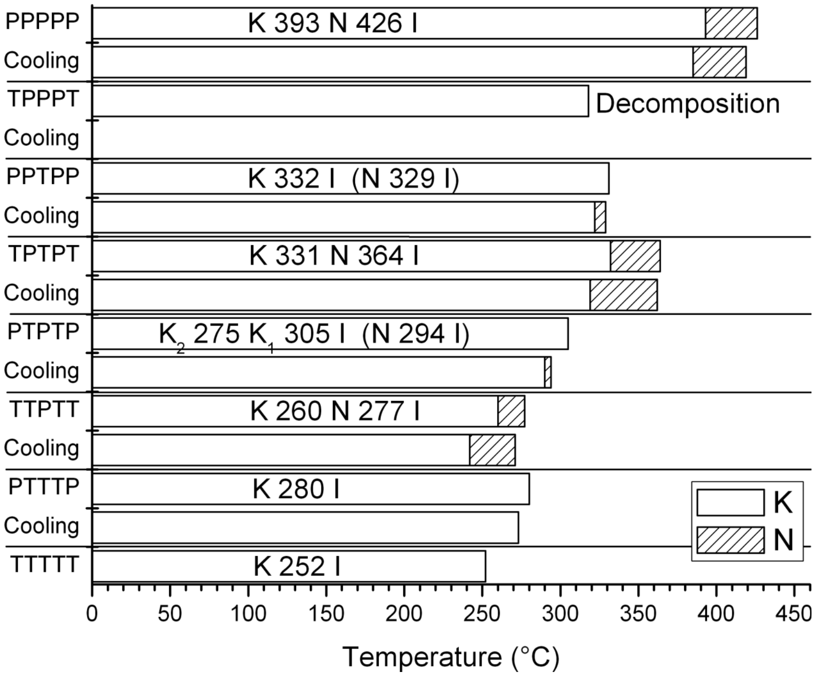


Figure 3. Phase-transitions of pentamers **I-VIII**, determined by OPM measurements.

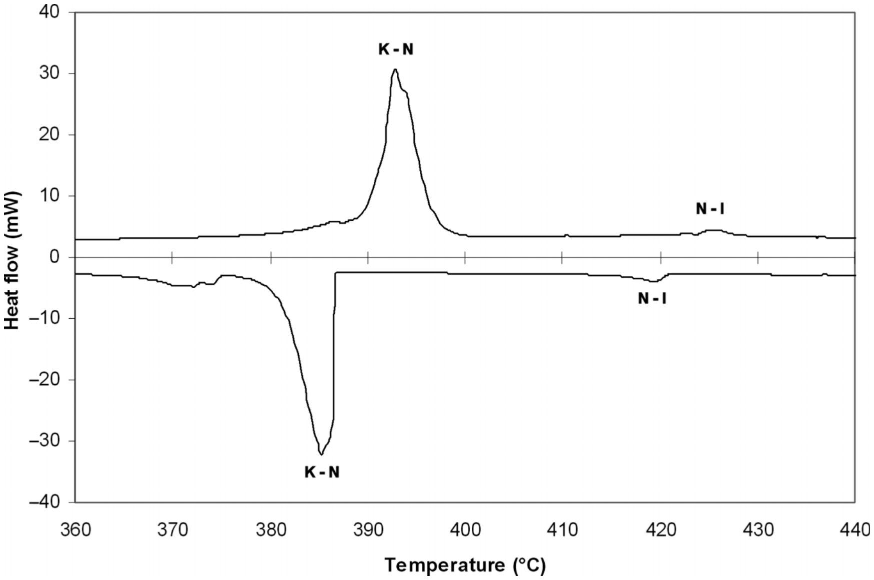


Figure 4. DSC curve of **I-PPPPP** taken in a high-pressure DSC sample capsule at 10 K min^{-1}.

385°C when the sample is cooled from the isotropic phase. Replacement of the outer phenyl groups by thiophene moieties results in molecules with similar conformations. Therefore, as far as geometrical arguments apply, the substitution of a p-phenylene by a 2,5-thiophene should not inflict drastic changes in the mesophase behaviour. A fair comparison between the mesophase behaviour of TPPPT and PPPPP, however, is not possible due to the thermal instability of TPPPT. For TPPPT a nematic phase seems to emerge at 318°C, but a simultaneous formation of gas bubbles due to decomposition at these temperatures is observed. Instability of thiophenes and furanes that lack substituents at the 2 and 5 positions is well known (*15, 16*). Adding substituents to the outer thiophenes would most likely result in more stable compounds.

PPTPP shows a similar phase behaviour as has been reported (*9*). Upon heating only a K–I phase transition was found at 332°C and upon cooling a nematic phase was found between 329°C and 322°C. TPTPT is also boomerang shaped and has a similar shape to PPTPP. The K–N phase transition at 332°C is at virtually the same temperature as the K–I phase transition temperature of PPTPP. TPTPT shows a wide nematic window until 364°C where it becomes isotropic. Upon cooling the I–N transition is found at 362°C and it crystallises at 319°C.

For PTPTP and TTPTT two 'active' thiophene units are incorporated and these molecules form mixtures of two different conformations. In Figure 5, the two conformations of PTPTP, which are Z- and U-shaped, are depicted. The phase transitions temperatures are further decreased compared with PPPPP and PPTPP. Upon heating the PTPTP shows only a K–I phase transition at 305°C. Upon cooling, a nematic phase transition is observed at 294°C and crystallisation occurs at 290°C. TTPTT exhibits a nematic phase between 260°C and 277°C. When the sample is cooled from the isotropic phase, an I–N phase transition is observed at 271°C and the sample crystallises at 242°C.

Compounds PTTTP and TTTTT can adopt three different conformations, due to the presence of three 'active' thiophene units. Neither shows a liquid crystalline phase. The Cr–I phase transition temperatures can be found at 282°C and 252°C for PTTTP and TTTTT, respectively. TTTTT decomposed during heating, so no crystallisation was found when cooling the sample. PTTTP show a crystallisation peak at 273°C when cooling from the isotropic phase.

The results obtained from our research, as shown in Table 1, reveal a rather consistent and predictable mesophase behaviour of the related pentamers **I–VIII**. First of all, as was reported previously, linear rigid molecules such as PPPPP exhibit the highest phase transition temperatures. Introducing a kink in the molecule, by placing a thiophene unit at position 3, transforms a javelin-shaped molecule into a boomerang-shaped molecule, and lowers the phase transition temperatures, typically by 60°C. Introducing two thiophene units at the positions 2–4 introduces two kinks and results in mixtures of non-linear Z- and U-conformers. These molecules exhibit transition temperatures that are lowered by 130°C, as compared with PPPPP. Upon increasing the number of kinks the nematic mesophase disappears and the melting and crystallisation temperatures decrease further.

Thiophene units at the 1 and 5 position are not expected to change the overall shape of the molecules, but do play a role in their phase behaviour. The boomerang-shaped TPTPT has a much more stable nematic phase than the boomerang-shaped PPTPP. For this compound, the thiophene units at the 1 and 5 position enable the molecule to adapt a planar conformation with full conjugation. This might explain the stability of the nematic phase. For PTPTP and TTPTT a similar behaviour, being broad(er) nematic temperature windows for TTPTT, was observed. In this case both molecules are planar, and other factors must be responsible for the increased nematic windows of TTPTT.

3. Conclusions

We have synthesised all symmetric pentamers composed of p-phenylene (P) and 2,5-thiophene (T) and have investigated the effects of substituting 1,4-phenylene by 2,5-thiophene units on the mesophase behaviour of these compounds. All compounds, with the notable exception of PTTTP and TTTTT, exhibited nematic phases at significantly reduced temperatures, as compared with p-quinquiphenylene (PPPPP). Introduction of thiophenes at the position 2–4, which changes the shape of the molecule along its main axis and may allow the molecule to adopt multiple stable conformations, has the most pronounced effect on the phase transition temperatures. A single thiophene at position 3 results in boomerang-shaped molecules, for which phase transition temperatures are reduced by about 60°C. Introducing thiophenes at positions 2 and 4 results in mixtures of Z- and U-shaped molecules, and phase transition temperatures are lowered by approximately 100–150°C, as compared with quinquiphenylene (PPPPP). With three thiophenes at the positions 2–4, no nematic phases are found. Introduction

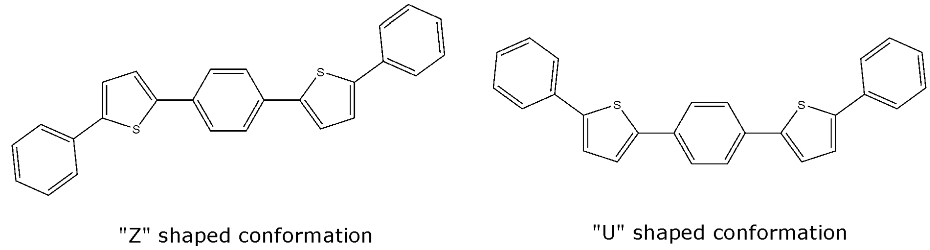
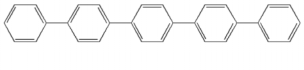
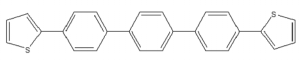
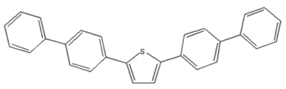
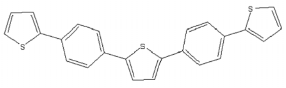
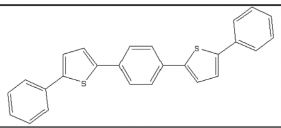
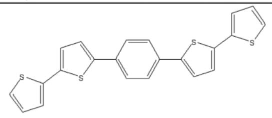
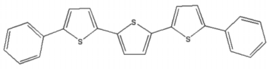
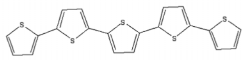


Figure 5. Two stable conformations of PTPTP (**V**).

Table 1. Phase transition temperatures and enthalpies for compounds **I**–**VIII**.

Compound	Structure	Phase Map [°C – (J/g)]
(**I**)-PPPPP		$K \underset{385(-110)}{\overset{393(123)}{\rightleftharpoons}} N \underset{419(-4)}{\overset{426(3)}{\rightleftharpoons}} I$
(**II**)-TPPPT		Decomposition
(**III**)-PPTPP		$K \xrightarrow{332(110)} I$ $K \xleftarrow[322(-113)]{} N \xleftarrow[329(-2)]{} I$
(**IV**)-TPTPT		$K \underset{319(-75)}{\overset{331(86)}{\rightleftharpoons}} N \underset{362(-0.4)}{\overset{364(1.2)}{\rightleftharpoons}} I$
(**V**)-PTPTP		$K \xrightarrow{305(127)} I$ $K \xleftarrow[290(-131)]{} N \xleftarrow[294(-)]{} I$
(**VI**)-TTPTT		$K \underset{242(-84)}{\overset{260(83)}{\rightleftharpoons}} N \underset{271(-0.6)}{\overset{277(0.6)}{\rightleftharpoons}} I$
(**VII**)-PTTTP		$K \underset{273(-129)}{\overset{282(132)}{\rightleftharpoons}} I$
(**VIII**)-TTTTT		$K \underset{\text{Decomposed}}{\overset{252(65)}{\rightleftharpoons}} I$

* T_{NI} could only be observed using optical microscopy

of thiophenes at the outer part of the pentamers, at positions 1 and 5, generally increases the stability of the nematic phase. While the phenyl-terminated compounds PPTPP and PTPTP are monotropic, their thiophene terminated analogues TPTPT and TTPTT have a 17–32°C nematic window upon heating.

4. Experimental details

4.1 General

Tetrahydrofuran (THF) was dried over and distilled from sodium/benzophenone prior to use. Reagents were purchased from commercial sources and were used without further purification. Tetrakis(triphenylphosphine) palladium(0) was purchased from Aldrich Chemical Co. Transition temperatures were determined by using a Perkin Elmer DSC differential scanning calorimeter. The scans were done at a heating and cooling rate of 10°C min^{-1}. To prevent the liquid crystals from subliming out of the sample pans we used high-pressure DSC sample capsules. Mesophases were identified with a Nikon polarising microscope equipped with a Mettler hotstage.

4.2 2-Phenyl-5-thiopheneboronic acid

A 500 ml round bottom flask equipped with magnetic stir bar, reflux condenser, and argon inlet was charged (under argon atmosphere) with 2-bromothiophene (**5**) (15 g, 123 mmol) and tetrakis(triphenylphosphine) palladium(0) (1 g). A volume of 100 ml of dimethoxyethane (DME) was added and this yellow solution was stirred for 10 min at room temperature. Phenylboronic acid (**4**) (20 g, 123 mmol) and 100 ml of 2 M Na_2CO_3 were added and this mixture was refluxed under argon atmosphere overnight. After cooling to room temperature the mixture was extracted with diethyl ether (three times 100 ml) and the organic layer was washed with water. The solvent was removed by distillation and the resulting crude product was recrystallised from EtOH to obtain 16.1 g (82%) 2-phenylthiophene (**6**) as slight yellow platelets.

2-Phenylthiophene (**6**) (6.0 g, 37.5 mmol) in 75 ml of dry THF under argon atmosphere was cooled to –78°C and 24 ml of 1.6 M *n*-BuLi in hexanes (37.5 mmol) was added over 10 min. The mixture was stirred for 1 h. A solution of trimethyl borate (2.6 g, 25 mmol) in 12.5 ml dry THF was added dropwise at –78°C. The mixture was allowed to warm up to room temperature overnight, acidified with 10% HCl, and stirred for 1 h. The aqueous mixture was extracted with diethyl ether (three times 100 ml) and the organic layer was washed with water. The solvent was removed by distillation and the resulting crude product was recrystallised from water/ethanol (95/5). Yield was 3.9 g (51%) of 2-phenyl-5-thiopheneboronic acid (**7**).

4.3 *2-(4-Phenylboronic acid) thiophene*

A 250 ml round bottom flask equipped with magnetic stir bar, reflux condenser, and argon inlet was charged (under argon atmosphere) with 1-iodo-4-bromo-benzene (**9**) (12.0 g, 60 mmol) and tetrakis(triphenylphosphine) palladium(0) (1.0 g). A volume of 100 ml of DME was added and this yellow solution was stirred for 10 min at room temperature. 2-Thiophene boronic acid (**8**) (10 g, 48 mmol) and 100 ml of 2 M Na_2CO_3 were added and this mixture was refluxed under argon atmosphere overnight. After cooling to room temperature the mixture was extracted with diethyl ether (two times 100 ml) and the organic layer was washed with water. The solvent was removed by distillation and the resulting crude product was recrystallised from EtOH to obtain 8.4 g (58%) 2-(4-bromophenyl) thiophene (**10**) as slight yellow platelets.

2-(4-Bromophenyl) thiophene (**10**) (2.5 g, 10.5 mmol) was treated with magnesium (0.29 g, 12 mmol) in 30 ml of dry THF under argon. After the initial reaction subsided the mixture was refluxed for 6 h and cooled to room temperature. This Grignard solution was added dropwise to a cooled (–78°C) trimethyl borate solution (2.2 g, 21 mmol in THF 20 ml) and was allowed to warm up overnight. The resulting mixture was acidified with 10 ml of a 10% HCl solution and stirred for 1 h at room temperature. The crude product was extracted into diethyl ether (three times 50 ml), washed successively with a concentrated sodium carbonate solution, and water. The ether was removed by distillation and the crude was recrystallised from water/ethanol (95/5) and used immediately. The yield was 1.1 g (51%) of 2-(4-phenylboronic acid) thiophene (**11**).

4.4 *([2,2′-Bithiophene]-5-yl)boronic acid*

2,2′-bithiophene (**12**) (5 g, 30.1 mmol) in 100 ml of dry THF under argon atmosphere was cooled to –78°C and 19 ml of 1.6 M *n*-BuLi in hexanes (30 mmol) was added over 10 min. The mixture was stirred for 1 h. A solution of trimethyl borate (6.2 g, 60 mmol) in 40 ml dry THF was added dropwise at –78°C. The mixture was allowed to warm up to room temperature overnight, acidified with 10% HCl, and stirred for 1 h. The aqueous mixture was extracted with diethyl ether (three times 100 ml) and the organic layer was washed with water. The solvent was removed by distillation and the resulting crude product was recrystallised from water/ethanol (95/5). Yield was 1.4 g (22%) of 5-boronic acid 2,2′-bithiophene (**13**).

4.5 *Quinquephenylene*

A 100 ml two-neck flask equipped with magnetic stir bar, reflux condenser, and argon inlet was charged (under argon atmosphere) with 1,4-dibromobenzene (**2**) (1.18 g, 5 mmol) and tetrakis(triphenylphosphine)-palladium(0) (0.36 g). A volume of 20 ml of DME was added and this yellow solution was stirred for 10 min at room temperature. 4-Biphenylboronic acid (**1**) (2.97 g, 15 mmol) and 20 ml of 2 M Na_2CO_3 were added and this mixture was refluxed under argon atmosphere for 24 h. After cooling to room temperature the reaction mixture was diluted with 50 ml of water and filtered. The solids were washed with acetone and dichloromethane and vacuum-dried overnight at 60°C. Pure p-quinquephenyl (**I**), 1.38 g (72%), was obtained as colourless platelets after three recrystallisations from hot 1,2,4-trichlorobenzene.

Compound **III** (PPTPP) quantities were as follows: 2.97 g (15 mmol) of 4-biphenylboronic acid (**1**) was used and 1.18 g (5 mmol) of 2,5-dibromothiophene (**3**), resulting in 1.32 g (68%) of compound **III**.

Compound **V** (PTPTP) quantities were as follows: 1.2 g (6 mmol) of 2-phenyl-5-thiopheneboronic acid (**7**) was used and 0.4 g (1.6 mmol) of 1,4-dibromobenzene (**2**), resulting in 0.61 g (78%) of compound **V**.

Compound **VII** (PTTTP) quantities were as follows: 1.2 g (6 mmol) of 2-phenyl-5-thiopheneboronic acid (**7**) was used and 0.4 g (1.6 mmol) of 2,5-dibromothiophene (**3**), resulting in 0.61 g (70%) of compound **VII**.

Compound **II** (TPPPT) quantities were as follows: 0.50 g (2.5 mmol) of -(4-phenylboronic acid) thiophene (**11**) was used and 0.2 g (0.8 mmol) of 1,4-dibromobenzene (**2**), resulting in 0.21g (65%) of compound **II**.

Compound **IV** (TPTPT) quantities were as follows: 0.50 g (2.5 mmol) of -(4-phenylboronic acid) thiophene (**11**) was used and 0.2 g (0.8 mmol) of 2,5-dibromothiophene (**3**), resulting in 0.24g (73%) of compound **IV**.

Compound **VI** (TTPTT) quantities were as follows: 0.50 g (2.4 mmol) of ([2,2′-bithiophene]-5-yl)boronic acid (**13**) was used and 0.2 g (0.8 mmol) of

1,4-dibromobenzene (**2**), resulting in 0.22g (68%) of compound **VI**.

Compound **VIII** (TTTTT) quantities were as follows: 0.50 g (2.4mmol) of ([2,2′-bithiophene]-5-yl)boronic acid (**13**) was used and 0.2 g (0.8mmol) of 2,5-dibromothiophene (**3**), resulting in 0.25 (76%) of compound **VIII**.

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