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Synthesis and thermal behaviour of α,α′-didecyloligothiophenes

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α,α′-Didecylquater-, -quinque- and -sexi-thiophenes were synthesized by Kumada cross-coupling and oxidative coupling reactions. For the former reaction Pd(dppf)Cl_2 was found to be a more efficient catalyst than the usually applied Ni(dppp)Cl_2. Thermal behaviour of all new oligothiophenes was investigated by differential scanning calorimetry and polarizing optical microscopy. It was shown that all these compounds possess not only crystal phases but also high temperature ordered smectic mesophases and that the clearing point increases linearly with the number of conjugated thiophene rings. A degree of order in the crystal phase was estimated on the basis of thermodynamic data. The highest degree of order was proposed for α,α′-didecylquaterthiophene, which explains why the mobility of end-α,α′-capped quaterthiophenes in FET (field effect transistor) devices is comparable or sometimes better than those of corresponding quinque- and sexi-thiophene derivatives.

Introduction

Oligothiophenes are a promising class of organic semiconducting materials, which are considered to be realistic candidates for industrial use in the production of solution processed organic field effect transistors (FETs) for cheap, large area smart electronic devices.[1] It has already been shown that TFTs (thin film transistors) made from α,α′-oligothiophenes as the active layer possess not only high field effect mobility [up to 0.23 cm^2 $(Vs)^{-1}$],[2] but also small off currents (on/off ratios in the range 10^4–10^6).[3] Moreover, it has been noted that end-capped oligothiophenes usually show better electronic characteristics than unsubstituted oligothiophenes due to their better structural organisation in the crystal phase.[4] However, only a few examples of end-capped oligothiophenes have been synthesized and investigated up to now.[1] Since the first examples (*i.e.* α,α′-dihexylsexithiophene,[5,6] α,α′-bidodecylsexithiopnene[7] and α,α′-dihexylquaterthiophene[2,8]) have shown very promising characteristics, it is worth synthesizing different compounds of this type in order to optimise the properties and to clarify the structure–property relationship. Since it is known that the field effect mobility depends not only on the chemical structure of the molecular semiconductor, but also on their structural organisation in the bulk, *i.e.* on morphology and a degree of order in the crystal phase,[3] the relationship between phase order and chemical structure needs to be further clarified. Indeed, it is already known that oligothiophene derivatives could form different mesophases.[9–11] Complex phase behaviour has also been observed for several α,α′-dialkyloligothiophenes.[7,8] However, only a few papers devoted to the systematic investigation of the thermal behaviour of α,α′-dialkyloligothiophenes have been published up to now. Dependence of the phase behaviour of 5,5″-dialkyl-2,2′:5′,2″-terthiophenes[12] and different alkyl-capped quaterthiophene derivatives[13] on the length of the terminal alkyl substituent have been reported. In the present paper, for the first time a relationship between the thermal behaviour of α,α′-didecyloligothiophenes and the length of the central oligothiophene unit, *i.e.* on the number of conjugated thiophene rings in the molecule, is considered.

Experimental

Materials

All solvents and reagents used were purchased from Aldrich and were used as received unless otherwise stated.

Methods

^{1}H NMR spectra were recorded on a Bruker DPX 400 spectrometer, equipped with a QNP Probehead, operating at 400.13 MHz for ^{1}H, in $CDCl_3$ solutions unless otherwise stated. Phase transitions were studied by differential scanning calorimetry (DSC) with a Mettler TA-4000 thermosystem at a scanning rate of 10 K min^{-1} and 1 K min^{-1}. The polarizing microscopic investigations were performed using a Mettler FP-90 central processor equipped with a hot stage Mettler FP-82 and control unit in conjunction with a Zeiss polarizing microscope.

Synthesis

2-Decylthiophene (1). Anhydrous THF (60 ml) was added to a solution of 0.08 mol butyllithium in 32 ml of hexane (2.5 M solution) with cooling below 0 °C. Thiophene (8.08 g, 0.096 mol) was added within 10 min and the temperature was kept between 0 and 10 °C. The cooling bath was then removed and the temperature was allowed to rise to 20 °C. Decyl bromide (23.0 g, 0.104 mol) was added in one portion without external cooling. The temperature of the yellow-orange solution rose slowly to 32 °C within 2 h. The solution was refluxed overnight and 200 ml of ice water were added with vigorous stirring. After separation of the layers, the aqueous layer was extracted twice with diethyl ether. The combined organic solutions were dried over magnesium sulfate and subsequently concentrated under vacuum to give 22.63 g of raw product. The product was then purified by distillation in high vacuum (0.2 mBar, 85 °C) to give 13.1 g (73%) of 99.9% pure (GC–MS) product as a colorless liquid. Isolated yield: 73%; reaction yield 88%. MS *m*/*z* 224 ($M^{\bullet +}$).

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2-Bromo-5-decylthiophene (2). In the absence of light, a solution of 7.93 g (45 mmol) *N*-bromosuccinimide (NBS) in 50 ml of anhydrous DMF was added dropwise at 0 °C to a solution of 10.0 g (45 mmol) of 2-decylthiophene in 50 ml of anhydrous DMF within 30 min. The reaction mixture was stirred for 4 h at room temperature. It was then poured on to ice and extracted twice with dichloromethane. The organic phases were combined, washed with water and dried over sodium sulfate. The solvent was evaporated on a Rotavapor to give 14.1 g of crude product. After removing the residual DMF by heating at 40 °C under high vacuum (0.2 mBar) for 2 h, 13.32 g of the product as a yellowish liquid was obtained. Isolated yield: 98.5%; reaction yield (GC–MS): 99.9%. MS *m*/*z* 304 (M$^{\bullet+}$).

5-Decyl-2,2′-bithiophene (3). To a suspension of 0.793 g (33 mmol) of magnesium in 5 ml of anhydrous diethyl ether a solution of 4.89 g (30 mmol) of 2-bromothiophene in 30 ml of anhydrous diethyl ether was added dropwise under nitrogen. The solution of the Grignard reagent was refluxed for 2 h, then cooled to room temperature and transferred to the dropping funnel of a second apparatus *via* syringe. In the second apparatus the foregoing solution was added dropwise to an ice-cooled suspension of 6.05 g (20 mmol) of 2-bromo-5-decylthiophene and 140 mg (0.2 mmol) of Pd(dppf)$\mathrm{Cl_2}$ in 30 ml of anhydrous diethyl ether. The reaction mixture was stirred for 1 h at room temperature. It was then hydrolysed with 20 ml of a saturated aqueous ammonium chloride solution followed by the addition of 100 ml of anhydrous pentane. Then 500 ml of diethyl ether were added and the organic layer was washed three times with 200 ml of water and dried over sodium sulfate. After removal of the solvent, the residue (6.47 g, containing 99% of the product and 1% of bithiophene according to GC–MS analysis) was purified by column chromatography (silica gel, hexane) to give 5.4 g of pure material as a white solid. Reaction yield (GC–MS): 99%; isolated yield: 88%. MS *m*/*z* 306 (M$^{\bullet+}$). ^{1}H NMR ($\mathrm{CDCl_3}$, TMS/ppm): 0.88 (t, 3H, ^3J = 6.9 Hz), 1.20–1.45 (overlapped peaks, 14 H), 1.67 (m, 2H), 2.78 (t, 2H, J = 7.8 Hz), 6.67 (d, 1H, ^3J = 3.4 Hz), 6.97 (d, 1H, ^3J = 3.4 Hz), 6.98 (dd, 1H, ^3J = 3.4 Hz, ^4J = 5.9 Hz), 7.089 (dd, 1H, ^3J = 3.4 Hz, ^4J = 1.0 Hz), 7.156 (dd, 1H, ^3J = 4.9 Hz, ^4J = 1.0 Hz).

5-Bromo-5′-decyl-2,2′-bithiophene (4). Synthesis was as described for compound (**2**) using 4.53 g (25 mmol) NBS and 7.79 g (25 mmol) of **3** to give 8.57 g of the product as a yellow solid. Isolated yield: 88%; reaction yield (GC–MS): 99.9%. MS *m*/*z* 385 (M$^{\bullet+}$). ^{1}H NMR ($\mathrm{CDCl_3}$, TMS/ppm): 0.88 (t, 3H, ^3J = 6.9 Hz), 1.20–1.45 (overlapped peaks, 14 H), 1.67 (m, 2H), 2.77 (t, 2H, J = 7.6 Hz), 6.66 (d, 1H, ^3J = 3.4 Hz), 6.82 (d, 1H, ^3J = 3.9 Hz), 6.91 (d, 1H, ^3J = 3.4 Hz), 6.93 (d, 1H, ^3J = 3.4 Hz).

5-Decyl-2,2′:5′,2″-terthiophene (5). Synthesis was as described for compound (**3**) using 0.65 g (27 mmol) of magnesium, 3.98 g (24 mmol) of 2-bromothiophene, 8.57 g (22 mmol) of 5-bromo-5′-decyl-2,2′-bithiophene and 154 mg (0.22 mmol) of Pd(dppf)$\mathrm{Cl_2}$. After recrystallisation from hexane 5.61 g (65%) of pure product was obtained as a yellow solid. MS *m*/*z* 388 (M$^{\bullet+}$). ^{1}H NMR ($\mathrm{CDCl_3}$, TMS/ppm): 0.88 (t, 3H, ^3J = 6.9 Hz), 1.20–1.45 (overlapped peaks, 14 H), 1.67 (m, 2H), 2.79 (t, 2H, J = 7.6 Hz), 6.68 (d, 1H, ^3J = 3.9 Hz), 6.99 (dd, 2H, ^3J = 3.4 Hz, ^4J = 5.4 Hz), 7.02 (dd, 1H, ^3J = 4.2 Hz, ^4J = 4.2 Hz), 7.05 (d, 1H, ^3J = 3.4 Hz), 7.15 (dd, 1H, ^3J = 3.4 Hz, ^4J = 1.0 Hz), 7.20 (dd, 1H, ^3J = 5.1 Hz, ^4J = 1.2 Hz).

5,5‴-Didecyl-2,2′:5′,2″:2‴-quaterthiophene (6). 5-Decyl-2,2′-bithiophene (1.0 g, 3.3 mmol) in anhydrous THF (10 ml) was added dropwise to a solution of lithium diisopropylamide (LDA; 1.95 ml of 2 M solution, 3.9 mmol) in 10 ml of anhydrous THF at −78 °C under nitrogen. A white-yellowish suspension was formed. It was stirred for 30 min at −78 °C, and anhydrous powdered $\mathrm{CuCl_2}$ (440 mg, 3.3 mmol) was added in one portion, upon which the colour of the solution changed to black. The mixture was stirred until it returned to room temperature (the colour changed from black to green and a yellow precipitate formed gradually) and then for an additional 30 min at 30 °C. The mixture was poured into 200 ml of water, containing 10 ml of 1 M hydrochloric acid. Then 300 ml of diethyl ether were added and a yellow solid formed in the ether phase, which was washed three times with 200 ml of water and filtered to give a yellow precipitate, which was washed with diethyl ether and dried under vacuum to give 669 mg (67%) of yellow crystals. ^{1}H NMR ($\mathrm{CDCl_3}$, TMS/ppm): 0.88 (t, 6H, ^3J = 7.1 Hz), 1.20–1.45 (overlapped peaks, 28 H), 1.68 (m, 4H), 2.79 (t, 4H, J = 7.6 Hz), 6.68 (d, 2H, ^3J = 3.9 Hz), 6.97 (d, 2H, ^3J = 3.4 Hz), 6.99 (d, 2H, ^3J = 3.9), 7.03 (d, 2H, ^3J = 3.4 Hz). Calc. for $\mathrm{C_{36}H_{50}S_4}$ (693.2): C, 70.76; H, 8.25; S, 20.99. Found: C, 70.57; H, 8.40; S, 21.0%.

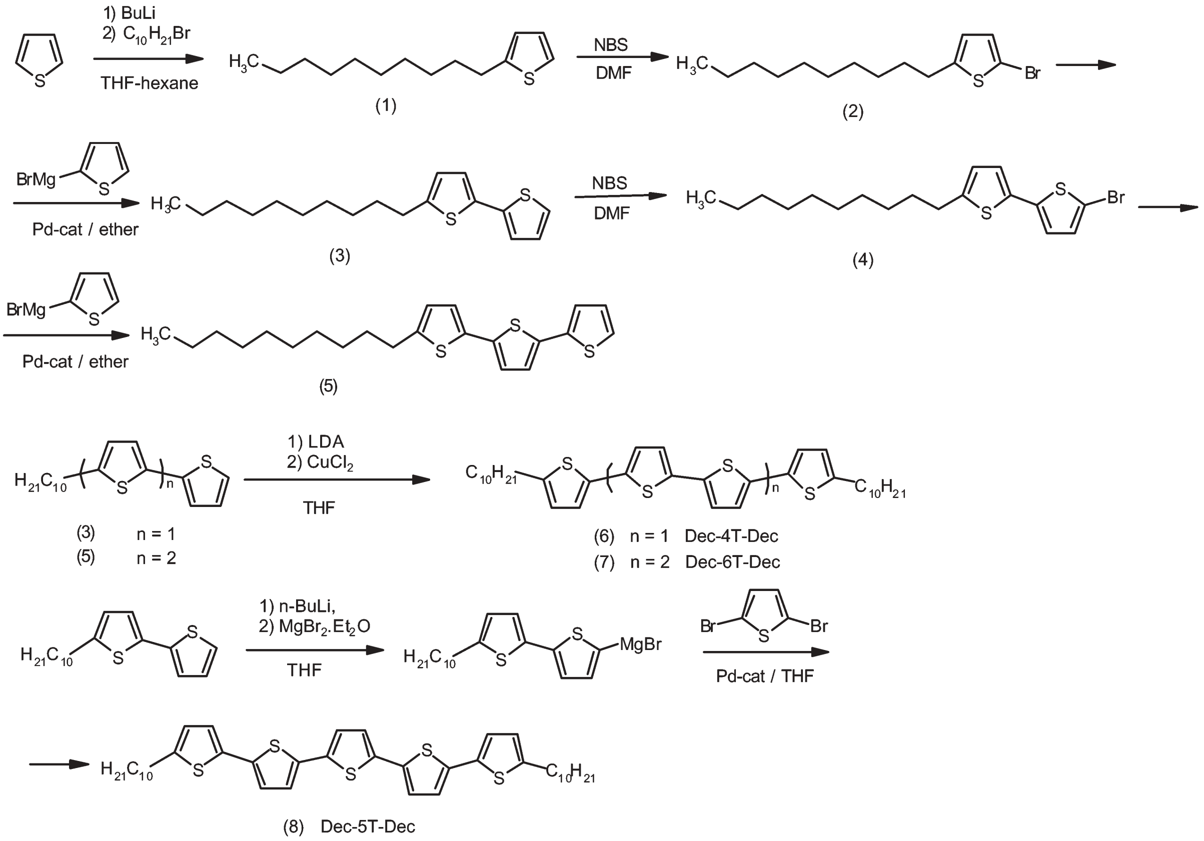
5,5′′′′′-Didecyl-2,2′:5′,2″:5″,2‴:5‴,2′′′′:5′′′′,2′′′′′-sexithiophene (7). Synthesized was according to the procedure described for compound **6** from 1.0 g (2.6 mmol) of 5-decyl-2,2′,5′,2″-terthiophene (**5**), 1.55 ml of 2 M LDA solution (3.1 mmol) and 350 mg (2.6 mmol) of $\mathrm{CuCl_2}$. The product was filtered from the solution to yield orange-red crystals. Isolated yield: 495 mg (50%). ^{1}H NMR (1,2-dichloroethane-d$_4$, 85 °C, TMS/ppm): 0.88 (t, 6H), 1.20–1.45 (overlapped peaks, 28 H), 1.68 (m, 4H), 2.78 (t, 4H), 6.69 (d, 2H), 7.02 (overlapped peaks, 4H), 7.08 (overlapped peaks, 6H). Calc. for $\mathrm{C_{44}H_{54}S_6}$ (775.3): C, 68.17; H, 7.02; S, 24.81. Found: C, 67.90; H, 7.00; S, 25.0%. FD MS *m*/*z*: 774, 775, 776 (M$^{\bullet+}$, three most intense peaks of the isotope pattern).

5,5′′′′-Didecyl-2,2′:5′,2″:5″,2‴:5‴,2′′′′-quinquethiophene (8). n-Butyllithium (1.6 M in hexane, 2.4 ml, 3.9 mmol) was added dropwise *via* syringe to a stirred solution of **3** (1.20 g, 3.9 mmol) in absolute THF (15 ml) at 0 °C under nitrogen. Upon completion of the addition, the solution was stirred at 0 °C for 30 min, then it was allowed to warm to room temperature and stirred for 30 min. Then it was cooled again to 0 °C, 1.03 g of $\mathrm{MgBr_2{\cdot}Et_2O}$ were added in one portion and the solution was stirred at 0 °C for 30 min and for an additional 30 min without a cooling bath. The solution of the Grignard reagent was transferred to the dropping funnel of a second apparatus *via* syringe. The previous solution was added dropwise to an ice-cooled solution of 2,5-dibromothiophene (363 mg, 1.5 mmol) and Pd(dppf)$\mathrm{Cl_2}$ (21 mg, 0.03 mmol) in 15 ml of absolute THF. After stirring for 16 h at room temperature the reaction mixture was hydrolysed with 1 M hydrochloric acid. Then it was poured on to 100 ml of ice water and extracted twice with 200 ml of diethyl ether. The combined organic layers were washed with water and filtered on glass filter G4 to yield the product as orange crystals. Yield: 0.98 g (94%). ^{1}H NMR (500 MHz,[14] $\mathrm{CDCl_3}$, TMS/ppm): 0.88 (t, 6H, ^3J = 7.0 Hz), 1.20–1.45 (overlapped peaks, 28 H), 1.68 (m, 4H), 2.79 (t, 4H, J = 7.5 Hz), 6.68 (d, 2H, ^3J = 3.6 Hz), 6.97 (d, 2H, ^3J = 3.6 Hz), 6.99 (d, 2H, ^3J = 3.6), 7.04 (d, 2H, ^3J = 3.6 Hz), 7.05 (s, 2H). Calc. for $\mathrm{C_{40}H_{52}S_5}$ (693.2): C, 69.31; H, 7.56; S, 23.13. Found: C, 69.20; H, 7.65; S, 23.0%.

Results and discussion

Synthesis

Choice of synthetic strategy (see Scheme 1) for the synthesis of the target compounds was based on the ‘minimal price–highest yield’ approach, implying that the minimal price for initial reagents, which could be converted through a number of (not necessarily minimal) high yield reactions to the desired products.



Scheme 1

Thiophene, 2-bromothiophene, 2,5-dibromothiophene and 10-bromodecane were selected as the starting reagents.

Lithiation of thiophene followed by its reaction with 10-bromodecane, adapted from the synthesis of 2-buthylthiophene,[15] led to 2-decylthiophene (**1**) in 88% reaction yield (73% isolated yield) after 2 h of stirring. Bromination of 2-decylthiophene with NBS in DMF in the absence of light[16] was quantitative, leading to formation of 2-bromo-5-decylthiophene (**2**) after stirring at room temperature for 4 h in 98% isolated yield.

For the next step – Kumada cross-coupling between 2-bromo-5-decylthiophene and the Grignard reagent made from 2-bromothiophene and magnesium in diethyl ether – the Ni(dppp)Cl_2 catalyst, used usually in the similar synthesis,[16] was found to be less efficient than Pd(dppf)Cl_2.[17] In the former case, even a two-fold excess of the Grignard reagent did not lead to complete consumption of the 2-bromo-5-decylthiophene after 48 h under reflux. In the latter case, reaction was usually complete within 30 min of stirring at room temperature, using only a 10% excess of Grignard reagent, leading up to 83% isolated yield of 5-decyl-2,2′-bithiophene (**3**). This compound was used as a key precursor for synthesis of the target compounds: α,α′-didecylquater- and α,α′-didecylquinque-thiophenes.

For the synthesis of α,α′-didecylsexithiophene (**6**) another precursor, namely 5-decyl-2,2′:5′,5″-terthiophene (**5**) was synthesized. For this purpose the same reaction sequence, including bromination of 5-decyl-2,2′-bithiophene with NBS in DMF followed by Kumada cross-coupling with 2-thienylmagnesium bromide using the Pd(dppf)Cl_2 catalyst, was continued. Isolated yields were 87 and 65%, respectively. The chemical structures of both precursors as well as all intermediate compounds were confirmed by GC–MS analysis as well as ^{1}H NMR spectrometry (see Experimental part).

α,α′-Didecylquater- and α,α′-didecylsexi-thiophenes [Dec-4T-Dec (**6**) and Dec-6T-Dec (**7**)] were synthesized by oxidative coupling of 5-decyl-2,2′-bithiophene (**3**) and 5-decyl-2,2′:5′,5″-terthiophene (**5**), respectively, in the presence of equimolar amount of $CuCl_2$. Isolated yields were 67 and 50%, respectively. In this case the reaction conditions were not optimised, so it is believed that careful optimisation of them allows further increase of the reaction yield.

α,α′-Didecylquinquethiophene [Dec-5T-Dec, (**8**)] was synthesized by the Kumada cross-coupling reaction between 2,5-dibromothiophene and a Grignard reagent, freshly prepared from 5-decyl-2,2′-bithiophene (**3**) by lithiation with n-butyllithium followed by lithium exchange with a magnesium dibromide etherate complex in THF, using the Pd(dppf)Cl_2 catalyst. This reaction led to formation of Dec-5T-Dec in 94% isolated yield. Such a high reaction yield can be explained by the fact that the product is the most insoluble compound in the reaction mixture and it precipitates during the reaction in its pure form since the initial and all intermediate compounds and by-products remain dissolved in the reaction solvent (THF at room temperature).

As expected, the solubility of the oligothiophenes synthesized (Dec-4T-Dec, Dec-5T-Dec and Dec-6T-Dec) decreases from Dec-4T-Dec to Dec-6T-Dec, *i.e.* with increasing the number of conjugated thiophene rings. Even Dec-4T-Dec is already almost insoluble in diethyl ether and dichloromethane (solubility $<10^{-2}$ mg ml^{-1}), but its solubility is quite good in chloroform, THF and toluene (solubility *ca.* 1 mg ml^{-1} at room temperature and >10 mg ml^{-1} at 50 °C). Dec-5T-Dec is almost insoluble in all of these solvents at room temperature (solubility $<10^{-2}$ mg ml^{-1}), but it is soluble at elevated temperatures in chloroform, THF and toluene (solubility *ca.* 1 mg ml^{-1} at 50 °C). Dec-6T-Dec is the most insoluble compound. It is only soluble at elevated temperatures (above 50 °C) in chloroform, dichloroethane and other chlorinated solvents, as well as in toluene, chlorobenzene, dichlorobenzene, *etc.* concentrations of *ca.* 10^{-1} mg ml^{-1}.

Table 1 Transition temperatures and enthalpies of transitions for α,α′-oligothiophenes[a]

Oligothiophene	Transition temperatures (°C) and enthalpies of transitions (in parentheses, kJ mol^{-1})						
Dec-4T-Dec	K	98 (41.8)	SmX	168 (36.9)	I		
Dec-5T-Dec	K	72 (10.7)	SmX	225 (41.5)	I		
Dec-6T-Dec	K	108 (21.9)	SmX	281 (34.0)	SmX1	290 (17.3)	I

[a] Note: K = crystalline phase; SmX and SmX1 = undefined smectic ordered phases; I = isotropic liquid. Onset of the transition temperatures from the second heating curves are shown.

Thermal behaviour

The thermal behaviour of all the oligothiophenes synthesized was investigated by means of polarizing optical microscopy (POM) and differential scanning calorimetry (DSC) methods. The results are summarized in Table 1.

As can be seen from the data obtained, all three oligothiophenes in question (Dec-4T-Dec, Dec-5T-Dec and Dec-6T-Dec) possess not only crystal phases, but also high temperature liquid crystal, most probably ordered smectic, mesophases. Isotropisation temperature increases linearly with the number of conjugated thiophene rings, while the enthalpy of this transition has the reverse tendency.

The most interesting results were obtained for oligothiophene Dec-4T-Dec. POM showed that cooling from the isotropic melt to 170 °C leads to formation of a mosaic texture [Fig. 1(a)], characteristic for either columnar or for ordered smectic mesophases.[18] Since the chemical structure of this molecule does not favour the formation of columnar phases [Fig. 2(a)],[19] it is meaningful to suggest the formation of one of the ordered smectic mesophases in this temperature region. Further cooling to 92 °C leads to crystallisation [Fig. 1(b)]. Data of DSC measurements confirm these observations. DSC curves for a sequence of heating, cooling and second heating of this compound are shown in Fig. 3. The high value of the enthalpy of transition at 168 °C (37 kJ mol^{-1}) is typical for ordered smectic mesophases. It is worth noting the good reproducibility of the values of the temperatures and enthalpies of both transitions at all heating and cooling curves even at rather high scanning rates (10 K min^{-1}). It indicates a fast speed of the phase transitions as well as good thermal stability of the compound (all of the measurements were made at normal atmospheric conditions). Both of these findings are very important for the application of this compound as a FET. Moreover, the rather large interval of the crystal phase (from room temperature to 98 °C) makes α,α′-didecylquaterthiophene a more promising material for FET application as compared with the α,α′-dihexylquaterthiophene[2,8] with the crystal-to-mesophase transition at 84 °C, since it was shown that the field effect mobility in the liquid crystal mesophase is lower than in the crystal phase.[20]

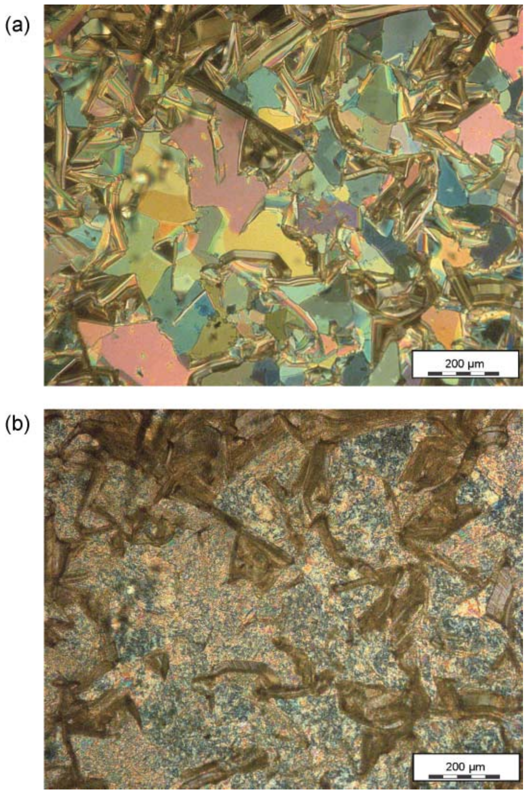


Fig. 1 Polarizing optical micrograph of Dec-4T-Dec on cooling: (a) 170 °C, and (b) 90 °C.

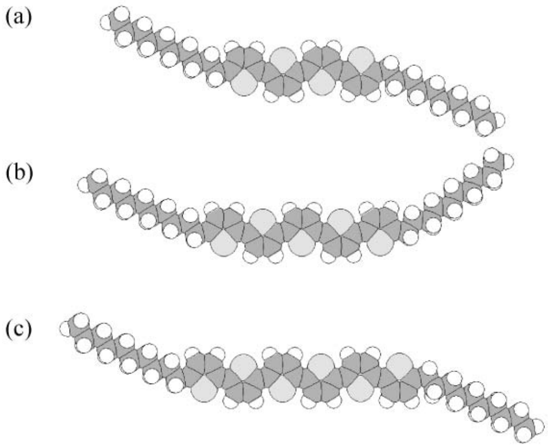


Fig. 2 Molecular models of oligothiophenes based on Molecular Mechanic Calculations (HyperChem, MM+Force Field): (a) Dec-4T-Dec, (b) Dec-5T-Dec, and (c) Dec-6T-Dec.

DSC of the quinquethiophene derivative Dec-5T-Dec showed two phase transitions: at 72 °C with the enthalpy 10.7 kJ mol^{-1}, and at 225 °C with the enthalpy of 41.5 kJ mol^{-1} (see Table 1). However, reproducibility of the transition at 72 °C was achieved only at rather slow scanning rates (1 K min^{-1}) that indicate some hindering during the crystallisation process. Polarizing optical microscopy of Dec-5T-Dec does not show formation of any typical textures that could also be attributed to hindered phase transitions. Nevertheless, mechanical shear in the upper phase showed its fluidity, so it was referred to a liquid crystal mesophase. Bearing in mind the high value of isotropisation enthalpy (see Table 1), which is

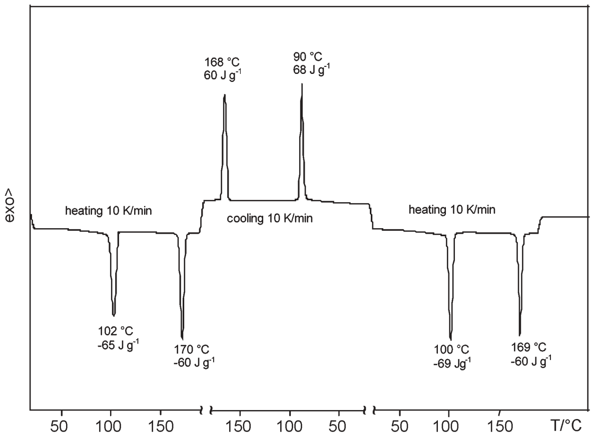


Fig. 3 DSC thermogram of Dec-4T-Dec. A sequence of heating, cooling and second heating at the rate of 10 K min^{-1} is shown. Peaks of the transition temperatures together with the enthalpies of transition are indicated.

very close to that of Dec-4T-Dec, as well as molecular symmetry of Dec-5T-Dec (Fig. 2b), it was also attributed to an ordered smectic mesophase.

DSC of the sexithiophene derivative Dec-6T-Dec showed three phase transitions: at 108 °C with the enthalpy 21.9 kJ mol^{-1}, at 281 °C with the enthalpy 34 kJ mol^{-1}, and at 290 °C with the enthalpy of 17.3 kJ mol^{-1} (see Table 1). Again, as in the case of Dec-5T-Dec, reproducible values of the transition enthalpies were obtained at low scan rates only (1 K min^{-1}). Polarizing optical microscopy showed melting at 281 °C and isotropisation at 290 °C. This observation allowed us to attribute the upper phase between 281 and 290 °C to a liquid crystal mesophase. Unfortunately, the high temperature of this mesophase accompanied by sublimation of the chemical did not allow us to obtain any pronounced texture, therefore it was not possible to make a more exact attribution of this mesophase on the basis of POM. However, the relatively high value of the isotropisation enthalpy (17.3 kJ mol^{-1}) allowed us to suggest that it is smectic rather than a nematic mesophase. Moreover, this value is more than twice lower than those for the transitions SmX-I for Dec-4T-Dec and Dec-5T-Dec (see Table 1) which also indicate its different ordering. That is why it was marked as 'SmX1'.[21] As far as the mesophase in the temperature region between 108 and 281 °C is concerned, ii is reasonable to suggest that it is similar to SmX found for Dec-4T-Dec and Dec-5T-Dec. It follows from the fact that not only are the transitions from the K phase to the SmX mesophase close for all three compounds in question (98, 72 and 108 °C), but also the enthalpies of their 'melting' are similar (36.9, 41.5 and 34 kJ mol^{-1}).

In order to estimate an average degree of order in the crystalline phase (or how well crystals could form a particular compound) for all three oligothiophenes under study, we compared the total values of entropies (ΔS_Σ) lost by each chemical during the transitions from the isotropic melt to the low temperature crystal phase. These are in particular: $\Delta S_\Sigma = \Sigma \Delta S_i$, where ΔS_i are entropies of the transitions from the isotropic melt to the LC mesophase, from the LC mesophase to the crystal phase as well as from one mesophase to another. Of course, such an approach could not give us exact quantitative results since the dependence of the entropy $\Delta S(T)$ on the temperature within each phase should be taken into account. But since such changes are much smaller within the temperature interval under consideration than the changes that happen during the phase transitions, it could give us at least qualitative results for comparison reasons. Such dependence is presented as a diagram in Fig. 4. One can see that the highest value of ΔS_Σ corresponds to the oligothiophene with four conjugated thiophene rings, Dec-4T-Dec. This fact indicates that the degree of order in the crystal phase decrease with increasing the number of thiophene rings from 4 to 6 in the series of oligothiophenes under consideration. Such findings might give an explanation as to why similar quaterthiophene derivatives show comparable or even better values of field effect mobility than the corresponding sexithiophene compounds[22] by the following way. On the one hand, one should expect a higher value of the mobility with an increasing the number of thiophene rings in oligothiophenes due to the larger conjugation length of the molecules. This could be true for molecular semiconductors, *i.e.* if one measures the properties of individual molecules or at least a monolayer. However, a usual FET consists of a thin film of the material (at least several monolayers), so intermolecular interactions and the order within the molecular layer rather than the properties of single molecules are responsible for the mobility. That is why a decrease of the degree of order in the crystal phase compensates or even exceeds the gain connected with the increase in the conjugation length.

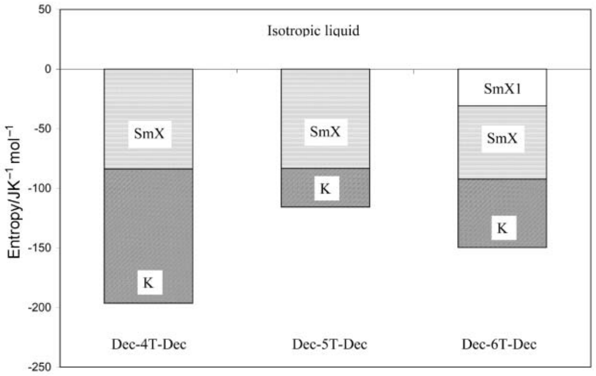


Fig. 4 Diagram, showing the lost of entropy ΔS by each chemical during the transitions from the isotropic melt to the low temperature crystal phase.

Conclusions

A new series of oligothiophenes, namely α,α′-didecylquater-, α,α′-didecylquinque- and α,α′-didecylsexi-thiophenes, has been synthesized and characterized. The phase behaviour of these compounds was investigated by combination of POM and DSC methods. It was shown that all of these compounds possess not only crystal phases, but also high temperature liquid crystal, most probably ordered smectic, mesophases. Combination of the results obtained, including solubility properties, ease of LC mesophase and crystal phase formation as well as estimation of the degree of order in the crystal phase, indicate that α,α′-didecylquaterthiophene has the highest order in its crystalline phase and therefore might be the most promising material for solution processed FET application as compared with the corresponding quinque- and sexi-thiophene derivatives. Measurements of field effect mobility for all the new compounds synthesized will be published elsewhere.[23]

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References and notes

1 C. D. Dimitrakopoulus and D. J. Mascaro, *IBM J. Res. Dev.*, 2001, **45**, 11.
2 H. E. Katz, A. J. Lovinger and J. G. Laquindanum, *Chem. Mater.*, 1998, **10**, 457.
3 *Handbook of Oligo- and Poly-thiophenes*, D. Fichou, ed., Wiley-VCH, Weinheim, 1999, p. 469.
4 G. Horowitz, *Adv. Mater.*, 1998, **10**, 365.
5 F. Garnier, A. Yassar, R. Hajlaoui, G. Horowitz, F. Deloffre, B. Servet, S. Ries and P. Alnot, *J. Am. Chem. Soc.*, 1993, **115**, 8716.
6 C. D. Dimitrakopoulus, B. K. Furman, T. Graham, S. Hegde and S. Purushothaman, *Synth. Met.*, 1998, **92**, 47.
7 H. E. Katz, J. G. Laquindanum and A. J. Lovinger, *Chem. Mater.*, 1998, **10**, 633.
8 F. Garnier, R. Hajlaoui, A. El Kassami, G. Horowitz, L. Laigre, W. Porzio, M. Armanini and F. Provasoli, *Chem. Mater.*, 1998, **10**, 3334.
9 S. Inoue, S. Nishiguchi, S. Murakami, Y. Aso, T. Otsubo, V. Vill, A. Mori and S. Ujiie, *J. Chem. Res.*, 1999, (S)596.
10 T. Yamada, R. Azumi, H. Tashibana, H. Sakai, M. Abe, P. Bäuerle and M. Matsumoto, *Chem. Lett.*, 2001, 1022.
11 P. Liu, H. Nakao and Y. Shirota, *Liq. Cryst.*, 2001, **28**, 581.
12 D. Byron, A. Matharu, R. Wilson and G. Wright, *Mol. Cryst. Liq. Cryst.*, 1995, **265**, 61.
13 R. Azumi, G. Götz and P. Bäuerle, *Synth. Met.*, 1999, **101**, 544.

14 Obtained on a Bruker DRX 500 spectrometer, equipped with a TXI Cryo-Probehead, operating at 500.13 MHz for ^{1}H NMR.

15 L. Brandsma and H. Verkruijsse, *Preparative Polar Organometallic Chemistry 1*, Springer-Verlag, Berlin/Heidelberg/New York, 1987, p. 124.

16 P. Bäuerle, F. Würthner, G. Götz and F. Effenberger, *Synthesis*, 1993, 1099.

17 G. Zotti, G. Schiavon, A. Berlin and G. Pagani, *Chem. Mater*, 1993, **5**, 430.

18 D. Demus and L. Richter, *Textures of Liquid Crystals*, VEB Deutsche Verlag für Grungstoffinustrie, Leipzig, 1980.

19 HyperChem™, Hypercube, Inc., Gainesville, FL, USA, 1997.

20 B. Wegewijs, M. P. de Haas, D. M. de Leeuw, R. Wilson and H. Sirringhaus, *Synth. Met.*, 1999, **101**, 534.

21 SmX and SmX1 are different, undefined smectic mesophases.

22 H. E. Katz, Z. Bao and S. L. Gilat, *Acc. Chem. Res.*, 2001, **34**, 359.

23 M. Halik, H. Klauk, U. Zschieschang, G. Schmid, W. Radlik, S. Ponomarenko, S. Kirchmeyer and W. Weber, *J. Appl. Phys.*, submitted.