Regiospecifically Alkylated Oligothiophenes via Structurally Defined Building Blocks

Fredrik von Kieseritzky,[a] Jonas Hellberg,*[a] Xiangjun Wang,[b] Olle Inganäs[b]

[a] Department of Chemistry, Organic Chemistry, Royal Institute of Technology, 100 44 Stockholm, Sweden
Fax +46(879)12333; E-mail: jhel@kth.se

[b] Biomolecular and Organic Electronics, Department of Physics and Measurement Technology, Linköping University, 581 83 Linköping, Sweden

Received 25 April 2002

Abstract: We have developed a new synthetic protocol for the unsymmetrically alkylated and halogenated terthiophenes **5** and **10**. To demonstrate their usefulness as building blocks for well-defined oligothiophenes, we synthesized a series of seven new sexi-, septi- and octithiophenes. Terthiophene **5** could be dimerized to the didecylsexithiophene **In6** and terthiophene **10** to sexithiophene **Out6**, respectively, by the use of nickel catalysis. Together with the bisstannylated thiophenes **11** and **12**, the septithiophenes **In7** and **Out7** as well as the octithiophenes **In8** and **Out8** could be obtained via Stille coupling methodology. We could also obtain the unsymmetrical sexithiophene **Unsym6** by selective heterocoupling between one equivalent of terthiophene **5** and **10** each. All new sexi-, septi- and octithiophenes show high photoluminescence in solution, but the quantum yield drops sharply in thin films of the materials.

Key words: regioselectivity, halogenation, alkylations, coupling, oligothiophenes, luminescence

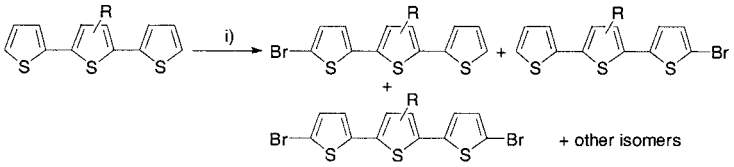
Oligomers and polymers of substituted thiophenes have received considerable attention in the last years owing to potential applications of both scientific and economic value.[1] Alkyl substitution enhances molecular systems' solubilities, thereby enabling the creation of applications that demand processability. The alkyl substitution can also alter the conjugation length of the thiophene chain by causing the thiophene units to assume separate planes from each other.[2]

The main application for oligo- and polythiophenes has traditionally been the electroactive component in light-emitting diodes (LEDs) and field-effect transistors (FETs). Thiophenes synthesized for FET-applications are typically substituted in the free peripheral α-positions,[3] whereas LED-thiophenes have substituents in the β-positions.[2] The latter substitution pattern opens up the possibility of different regioisomers, both in oligomers and polymers. While 3-alkylated thiophene monomers have been successfully polymerized regioselectively,[4] there is a lack of synthetic procedures that generate regioselectively alkylated oligomers, both for use as such, and for further functionalization–polymerization.

Since the stability of a light-emitting diode depends on the number of coupling defects in the constituting polymer (among other things),[5] it should be of interest to synthesize well-defined longer oligomers. Furthermore, as the diode efficiency is a function of several structural parameters, it should also be worthwhile to investigate different regioselectively alkylated oligomers, where different alkyl 'dilutions' of the π-system are possible. In addition to creating different conjugation lengths, different proportions of sp^3-chains should also affect solubility, which previously has been proposed as a way of optimizing the photoluminescence yield.[6]

Terthiophenes can be considered key building blocks for oligothiophenes. We therefore anticipated that it should be valuable to develop synthetic routes to terthiophenes, with regioselective alkyl and halogen substitution, thereby facilitating further regioselective oligomerization–functionalization. We chose the unsymmetrically substituted terthiophenes **5** and **10** as useful, and until now, unknown targets for synthesis. We also chose a decyl group as the alkyl chain for our systems, since we thought it would be of sufficient length to solubilize the higher oligomers, and because starting materials are easily available.

Previous syntheses of terthiophenes have usually consisted of organometallic coupling of two thiophene subunits to one central substituted unit,[7] or ring-closure of disubsti-



Scheme 1 *Reactions and conditions:* i) Bromine, NBS or other brominating reagent

Synthesis 2002, No. 9, Print: 01 07 2002.
Art Id.1437-210X,E;2002,0,09,1195,1200,ftx,en;C12302SS.pdf.
© Georg Thieme Verlag Stuttgart · New York
ISSN 0039-7881

Downloaded by: Florida State University Libraries. Copyrighted material.

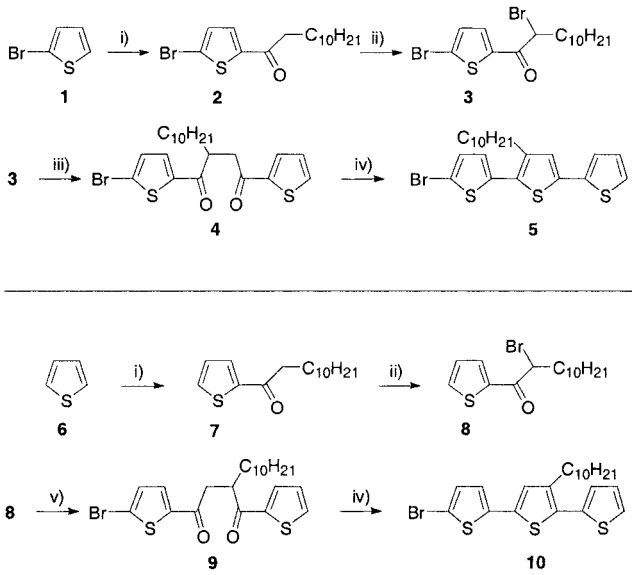
tuted 1,3-diacetylene[8] or 1,4-butadione segments[9] by different thionating reagents. None of these methods have been successful for the synthesis of β-alkylsubstituted terthiophenes with regioselective halogen attachment. Reported brominations of unsymmetrically alkylsubstituted terthiophenes have not been selective (Scheme 1).[10]

We therefore anticipated that a useful synthesis must include a halogenated building block, which is assembled to the desired terthiophene without scrambling. Our synthesis is depicted in Scheme 2. 2-Bromothiophene (**1**) was acylated with *n*-dodecanoyl chloride in quantitative yield to give **2**, which conveniently and quantitatively could be brominated α to the ketone, with elemental bromine to give compound **3**. We adopted the method of Kelin and Kulinkovich[11] to transform **3** and 2-acetylthiophene to the corresponding unsymmetrically substituted 1,4-dithienylbutandione **4** in moderate yield (63%). The ring-closure of **4** to the corresponding thiophene proved a more demanding task than first expected. The common reagents for this transformation, like phosphorus pentasulfide or Lawesson's reagent, gave high yields of debrominated, reduced terthiophene, despite claims in the literature that these reagents are inert toward aryl bromides.[12] We are not sure if this debromination occurs before the cyclization, or whether it is the thionating reagent or one of its reaction products that is the active species in this undesired side-reaction. Noteworthy is however that reduction of the target terthiophenes (**5** or **10**) does not occur with either phosphorus pentasulfide or Lawesson's reagent under similar conditions. In addition, we could somewhat suppress reduction by using very large excess of thionating reagent, leading to the assumption that the reduction is caused by one of the reaction products from the phosphorus reagent.

The desired non-reductive cyclization could, on the other hand, conveniently be carried out by the phosphorus-free procedure of Freeman et al. and Steliou et al.,[13] where hexamethyldisilathiane is reacted with a 1,4-butanedione in the presence of boron trichloride (in situ creating borontrisulfide as the thionating reagent). This reaction afforded the target terthiophene **5** in 51% yield of excellent purity. Analogously, the second target terthiophene **10** could be synthesized from thiophene (**6**).

Once we had created these valuable building blocks, we could proceed to synthesize a series of regio-defined oligothiophenes (Figure 1). Since the systematic names of these oligomers are rather inconvenient, we decided to give them more graphic acronyms than what is usual. The position of the alkyl chain is always at the second peripheral thiophene unit. Thus the position of the alkyl chain can be viewed as being either 'In' or 'Out' depending on its position on the thiophene. Accordingly, the word 'In' or 'Out' is followed by the number of thiophene units, making an acronym like **In6** for the first oligothiophene in the series.

We synthesized the didecyl-substituted sexithiophene **In6** via a nickel-catalyzed dimerization of **5** in the presence of



Scheme 2 *Reactions and conditions:* i) *n*-Dodecanoyl chloride, aluminium chloride; ii) bromine; iii) diethylamino magnesium bromide, 2-acetylthiophene; iv) hexamethyldisilathiane, boron trichloride; v) diethylaminomagnesium bromide, 5-bromo-2-acetylthiophene

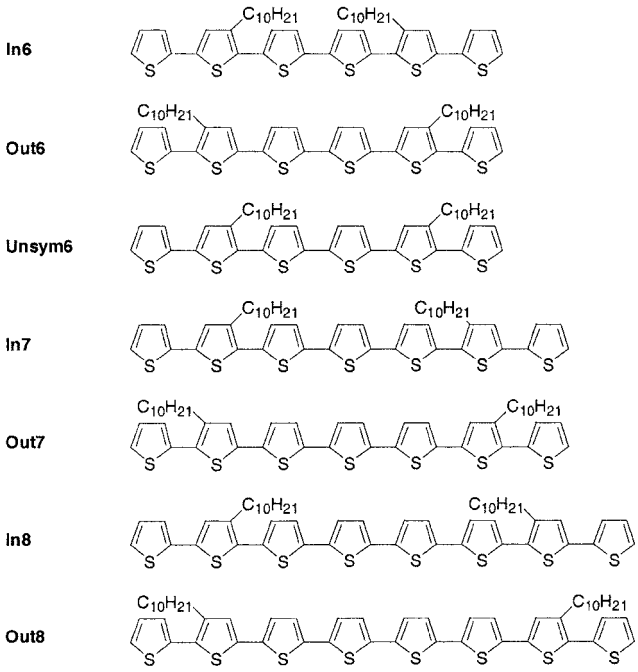


Figure 1 Series of regio-defined oligothiophenes

2,2′-bipyridine.[14] It is interesting to note that zinc had to be added after the addition of the substrate **5** in order to get the reaction to proceed. Analogously the other regioisomeric sexithiophene **Out6** could be obtained by dimerization of terthiophene **10**.

Next, we were able to transform **5** to its corresponding trimethylstannyl derivative, and react it with **10** in a one-pot palladium-catalyzed procedure to yield the unsymmetri-

Downloaded by: Florida State University Libraries. Copyrighted material.

cally substituted sexithiophene **Unsym6**, with a very unusual substitution pattern.

In order to obtain longer oligomers, we chose the tin-based Stille procedure, since the central bis-stannylated bridging units **11** and **12** (Figure 2) are easily obtainable.[15] Terthiophene **5** and thiophene **11** conveniently gave septithiophene **In7**. Analogously **10** and **11** could be assembled to give **Out7**. Additionally, bithiophene **12** could be reacted with terthiophene **5** to yield **In8** and in a similar procedure with **10** to give **Out8**. We found this Stille methodology most useful as attempted syntheses of the same targets, employing boron-based procedures (such as Suzuki coupling) gave inconsistent and unsatisfactory results.

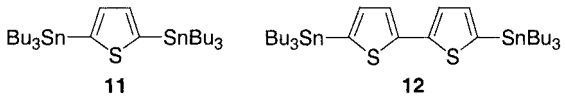


Figure 2 Bis-stannylated building blocks

All oligothiophenes were collected in 60–90% yield with these procedures. We could not distinguish any reliable trends in yields with respect to oligomer lengths or substitution patterns. However, we did observe that one crucial factor for high yields was the freshness of the stannylated building blocks. Although no deterioration of compounds **11** and **12** was detectable by NMR, oligomer yields were consistently higher when using freshly prepared material. The title compounds, terthiophenes **5** and **10**, could on the other hand be stored at ambient temperature and atmosphere for several months without any detectable degradation or loss of reactivity.

We investigated the optical properties of the new oligomers (Table) and found that all 'Out'-oligomers show a small bathochromic shift compared to their 'In'-isomers. All oligomers display high luminescence in chloroform solution, as expected for soluble thiophene oligomers. The emission wavelengths were identical for all oligomers of the same length, showing that the position of the alkyl group does not alter the emissive state's energy levels. The photoluminescence efficiencies in solution are a few percent higher for the 'Out'-isomers, compared to the corresponding 'In'-isomers, meaning that the alkyl chain in the 'Out'-isomers is more effective in hindering the interchain luminescence quenching. The photoluminescence efficiencies in films are only a few percent for all oligomers, which clearly shows that there is not enough 'sp^3-dilution' of the π-system to prevent the interchain luminescence quenching in the solid state. The octimers **In8** and **Out8** are rather insoluble in chloroform, which clearly limits the measurements.

We have developed an efficient synthesis of two new versatile building blocks, terthiophenes **5** and **10**. With these as starting materials, we have synthesized a series of new and hitherto unavailable sexi- septi- and octithiophenes in high purity, useful on a preparative scale. All oligomers show high photoluminescence in solution, whereas interchain quenching drastically reduces the photoluminescence efficiency in the solid state. Further synthetic applications of building blocks **5** and **10** are now pursued in our laboratory and will be reported in due course.

All operations except where indicated were performed in ambient atmosphere, without any special care taken for the exclusion of air or moisture. ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, on a Bruker AM 400. ^{13}C NMR spectra could not be collected for the sexi-, septi- or octithiophenes, even at prolonged experiment times (18 h), due to their relatively low solubility in $CDCl_3$, or any other deuterated solvent. Mass spectra were recorded on a Finnegan SSQ 7000 (electron impact) and on a Perseptive Biosystems Voyager-De STR (MALDI-TOF). Elemental analyses were performed by Analytische Laboratorien GmbH, Germany. THF was freshly distilled from sodium benzophenone ketyl, and DMF was distilled from P_2O_5 and stored over molecular sieves. All other commercial reagents and solvents were used as received. In the optical measurements, the oligomer was dissolved in $CHCl_3$ with concentrations adjusted to give an optical density 0.2 or lower in a 10 mm optical glass cell. Thin films were spin-coated from $CHCl_3$ solution, 5–10 mg/mL, on a 24×40 mm^2 quartz substrate giving optical densities of 0.1–0.3. The optical absorption spectra of samples were measured on a Perkin Elmer λ9 spectrometer, and the emission spectra were measured with an Oriel Instaspec IV diode matrix spectrometer. Photoluminescence (PL) yields and spectra were measured in a custom built integrating sphere made by Lab-

Table Optical Properties of Oligothiophenes

	Absorption Maxima (nm)		Emission Maxima (nm)		PL Quantum Efficiency (%)	
Compound	Solution	Film	Solution	Film	Solution	Film
In6	415	445, 473, 613	515, 555	580, 630	24	3.7
Out6	427	425, 501	515, 555	580, 630	31	1.9
Unsym6	422	445, 473, 512	515, 555	580, 630	28	2.3
In7	434	457, 482, 523	530, 570	625, 670, 710	29	3.5
Out7	444	438	530, 570	625, 710	33	2.2
In8	444	476, 508, 554	545, 585	625, 675, 710	22	4.7
Out8	451	447	545, 585	625, 675, 710	25	~

Downloaded by: Florida State University Libraries. Copyrighted material.

sphere, together with Oriel Instapec IV diode matrix spectrometer. Exciting light was a chromatic beam and the beam wavelength was selected according to absorption spectra of each sample.

1-(5-Bromothien-2-yl)-dodecan-1-one (2)
2-Bromothiophene (**1**) (8.16 g, 50 mmol) and *n*-dodecanoyl chloride (13.67 g, 62.5 mmol) were dissolved in benzene (75 mL). $AlCl_3$ (8.33 g, 62.5 mmol) was added in portions, with stirring, over 10 min. The resulting black solution was refluxed for 30 min and left to cool to r.t.. The reaction was quenched by very cautious (excessive frothing!) addition of aq HCl (2 M; 75 mL), affording a yellow slurry that was rinsed into a separating funnel with benzene (50 mL) and aq HCl (2 M; 50 mL). The mixture was gently shaken and the phases separated. The organic phase was washed with aq HCl (2 M; 2 × 75 mL), aq NaOH (2 M; 2 × 75 mL) and H_2O (2 × 75 mL) and passed through a silica column (3 cm diameter, 8 cm long), followed by CH_2Cl_2 (100 mL). Evaporation of the solvent gave pure **2**.

Yield: 17.27 g (quantitative); white solid.

^{1}H NMR ($CDCl_3$): δ = 0.88 (t, *J* = 6.4 Hz, 3 H), 1.22–1.40 (m, 16 H), 1.71 (q, *J* = 7.2 Hz, 2 H), 2.80 (t, *J* = 7.2 Hz, 2 H), 7.08 (d, *J* = 4.0 Hz, 1 H), 7.43 (d, *J* = 4.0 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 14.5, 23.1, 25.1, 29.6, 29.7, 29.8, 29.8, 30.0, 32.3, 39.2, 122.6, 131.5, 132.1, 146.4, 192.8.

2-Bromo-1-(5-bromothien-2-yl)-dodecan-1-one (3)
The ketone **2** (17.27 g, 50 mmol) was dissolved in CH_2Cl_2 (300 mL). With stirring, Br_2 (8.15 g, 51 mmol) was added dropwise. The solution was refluxed for 45 min and left to cool to r.t. The dark solution was washed with sat. aq $Na_2S_2O_3$ (100 mL) and H_2O (100 mL), and the organic phase was directly passed through a silica column (3 cm diameter, 10 cm long), followed by CH_2Cl_2 (150 mL). Evaporation of the solvent left pure **3**.

Yield: 21.21 g (quantitative); yellow oil.

^{1}H NMR ($CDCl_3$): δ = 0.87 (t, *J* = 6.8 Hz, 3 H), 1.21–1.40 (m, 16 H), 2.01–2.22 (m, 2 H), 4.86 (t, *J* = 6.8 Hz, 1 H), 7.13 (d, *J* = 4.0 Hz, 1 H), 7.56 (d, *J* = 4.0 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 14.5, 23.1, 27.8, 29.4, 29.6, 29.7, 29.8, 29.9, 32.3, 34.1, 48.0, 124.4, 131.8, 133.5, 143.1, 186.0.

1-(5-Bromothien-2-yl)-2-decyl-4-thien-2-ylbutane-1,4-dione (4)
To a solution of commercial MeMgBr (3 M in Et_2O; 25 mL) in toluene (150 mL), was added diethylamine (4.39 g, 60 mmol) in one portion. The reaction was stirred at r.t. for 15 min, with apparent release of methane. The solution was cooled to 0 °C and a separate solution of bromo ketone **3** (21.21 g, 50 mmol) and 2-acetylthiophene (6.31 g, 50 mmol) in toluene (a few mL), was added over 5 min. The resulting solution was stirred at 0 °C for 3 h, and the organic phase was subsequently gently shaken with aq H_2SO_4 (5% v/v; 100 mL) and washed with H_2O (100 mL). To the clear, orange organic phase, Et_3N (5.06 g, 50 mmol) was added, and the reaction was left at r.t. to proceed overnight. The organic phase was washed with aq HCl (2 M; 2 × 100 mL) and H_2O (2 × 100 mL), dried ($MgSO_4$) and evaporated to a dark oil (24.5 g). This crude product was purified by flash chromatography (3 cm diameter, 15 cm long silica column; heptane–EtOAc, 9:1) (R_f 0.3). On evaporation, the pooled desired fractions afforded **4**.

Yield: 14.88 g (63%); orange oil.

^{1}H NMR ($CDCl_3$): δ = 0.87 (t, *J* = 6.8 Hz, 3 H), 1.17–1.34 (m, 16 H), 1.54–1.63 (m, 1 H), 1.74–1.84 (m, 1 H), 3.09 (dd, *J* = 17.6 Hz, *J* = 4.4 Hz, 1 H), 3.56 (dd, *J* = 17.6, 9.2 Hz, 1 H), 3.78–3.85 (m, 1 H), 7.11–7.14 (m, 2 H), 7.59 (d, *J* = 4 Hz, 1 H), 7.63 (dd, *J* = 5.2, 1.2 Hz, 1 H), 7.75 (dd, *J* = 4, 1.2 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 14.5, 23.1, 27.8, 29.7, 29.8, 29.9, 29.9, 30.0, 32.3, 33.4, 41.9, 43.1, 123.2, 128.6, 131.8, 132.6, 132.7, 134.3, 144.0, 146.1, 191.6, 195.4

5-Bromo-3′-decyl-[2,2′;5′,2″]terthiophene (5)
The 1,4-butadione **4** (7.04 g, 15 mmol) was dissolved in toluene (150 mL) and hexamethyldisilathiane (5.34 g, 30 mmol) was added in one portion at r.t., directly followed by BCl_3 (1 M in hexanes; 22.5 mL). After 1 h, TLC (EtOAc–heptane, 9:1) indicated total consumption of the starting material, and H_2O (100 mL) was added. The organic phase was separated, washed with a further amount of H_2O (2 × 150 mL), dried ($MgSO_4$) and evaporated to a dark crude product that was purified by flash chromatography (heptane) (R_f 0.4). This afforded **5** of excellent purity,

Yield: 3.55 g (51%); yellowish crystalline product.

^{1}H NMR ($CDCl_3$): δ = 0.88 (t, *J* = 6.4 Hz, 3 H), 1.22–1.39 (m, 14 H), 1.63 (q, *J* = 7.6 Hz, 2 H), 2.68 (t, *J* = 7.6 Hz, 2 H), 6.86 (d, *J* = 3.6 Hz, 1 H), 6.99 (s, 1 H), 7.00–7.02 (m, 2 H), 7.15 (dd, *J* = 3.6, 1.2 Hz, 1 H), 7.22 (dd, *J* = 4.8, 1.2 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 14.9, 23.5, 30.0, 30.1, 30.2, 30.3, 30.3, 30.4, 31.4, 32.7, 112.5, 124.6, 125.4, 126.9, 127.2, 128.6, 129.3, 131.0, 136.5, 137.8, 138.2, 141.7.

MS (EI): *m*/*z* = 468, 466 (M^+, 100).

Anal. Calcd for $C_{22}H_{27}BrS_3$: C, 56.51; H, 5.82. Found: C, 56.37; H, 5.97.

1-Thien-2-yldodecan-1-one (7)[16]
Using the procedure for the synthesis of **2**, with thiophene (**6**) substituted for **1**, the desired product was obtained.

Yield: quantitative; yellow oil.

^{1}H NMR ($CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 3 H), 1.21–1.39 (m, 16 H), 1.70–1.78 (m, 2 H), 2.89 (t, *J* = 7.6 Hz, 2 H), 7.12 (dd, *J* = 4.8, *J* = 4 Hz, 1 H), 7.61 (d, *J* = 4.8 Hz, 1 H), 7.70 (d, *J* = 4 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 14.6, 23.1, 25.2, 29.4, 29.7, 29.7, 29.8, 29.9, 30.0, 32.3, 39.9, 128.4, 132.0, 133.7, 145.0, 194.0.

2-Bromo-1-thien-2-yldodecan-1-one (8)
Using the procedure for the synthesis of **3**, with the ketone **7** substituted for **2**, the desired product was obtained.

Yield: quantitative; orange oil.

^{1}H NMR ($CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 3 H), 1.20–1.43 (m, 16 H), 2.04–2.25 (m, 2 H), 4.96 (t, *J* = 6.8 Hz, 1 H), 7.16 (dd, *J* = 4.8, 4.0 Hz, 1 H), 7.70 (d, *J* = 4.8 Hz, 1 H), 7.83 (d, *J* = 4.0 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 14.5, 23.1, 27.9, 29.5, 29.7, 29.8, 29.9, 30.0, 32.3, 34.3, 48.8, 128.7, 133.3, 135.3, 141.8, 187.2.

4-(5-Bromothien-2-yl)-2-decyl-1-thien-2-ylbutane-1,4-dione (9)
Using the procedure for the synthesis of **4**, with α-bromo ketone **8** substituted for **3** and with commercial 5-bromo-2-acetythiophene instead of 2-acetylthiophene (more toluene was required to make a solution of these two reagents, compared to the synthesis of compound **4**), the desired product was obtained.

Yield: 47%; orange oil.

^{1}H NMR ($CDCl_3$): δ = 0.87 (t, *J* = 7.2 Hz, 3 H), 1.17–1.33 (m, 16 H), 1.53–1.62 (m, 1 H), 1.75–1.84 (m, 1 H), 3.00 (dd, *J* = 17.2, 4.4 Hz, 1 H), 3.50 (dd, *J* = 17.2, 9.2 Hz, 1 H), 3.85–3.92 (m, 1 H), 7.07 (d, *J* = 4.0 Hz, 1 H), 7.14 (dd, *J* = 4.8, 4.0 Hz, 1 H), 7.49 (d, *J* = 4 Hz, 1 H), 7.63 (dd, *J* = 4.8, 1.0 Hz, 1 H), 7.82 (dd, *J* = 4.0, 1.0 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 14.5, 23.1, 27.7, 29.7, 29.8, 30.0, 30.0, 32.3, 33.5, 41.0, 43.7, 123.2, 128.6, 131.7, 132.6, 132.8, 134.3, 144.5, 145.7, 190.8, 196.0.

Downloaded by: Florida State University Libraries. Copyrighted material.

5-Bromo-4′-Decyl-[2,2′;5′,2″]terthiophene (10)
Using the procedure for the synthesis of **5**, with the 1,4-dione **9** substituted for **4**, the desired product was obtained in slightly diminished yield (38%), as a yellow material, that required several days to crystallize.

^{1}H NMR ($CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 3 H), 1.20–1.39 (m, 14 H), 1.64 (q, 2 H, *J* = 7.6 Hz), 2.71 (t, *J* = 7.6 Hz, 2 H), 6.89 (d, *J* = 4 Hz, 1 H), 6.94 (s, 1 H), 6.96 (d, *J* = 4 Hz, 1 H), 7.06 (dd, *J* = 5.2, 3.6 Hz, 1 H), 7.12 (dd, *J* = 3.6, 1.0 Hz, 1 H), 7.31 (dd, *J* = 5.2, 1.0 Hz, 1 H).

^{13}C NMR ($CDCl_3$): δ = 14.6, 23.1, 29.7, 29.8, 29.9, 30.0, 30.0, 30.1, 31.0, 32.4, 111.3, 124.0, 126.0, 126.5, 127.2, 127.9, 130.5, 131.1, 134.5, 136.1, 139.2, 140.8.

MS (EI): *m*/*z* = 468, 466 (M^+, 100).

Anal. Calcd for $C_{22}H_{27}BrS_3$: C, 56.51; H, 5.82. Found: C, 56.40; H, 5.91.

Purification of the Sexi-, Septi- and Octithiophenes; General Procedure
After evaporation of the solvent, the crude product was treated with boiling Et_2O (ca. 10 mL) and then rapidly cooled down to 0 ºC by immersing the flask in an ice bath, whereupon the oligothiophene precipitated as flakes. Cold MeOH (a few mL) was added and the solids were collected by vacuum-filtration and washed with a little cold MeOH and acetone. The solids were then adsorbed on ~0.5 g silica gel and put on top of a dry silica column (1 cm diameter, 5 cm high). The column was then flushed with hexanes (50 mL) (to remove non-polar byproducts), pumped dry, flushed with MeOH (50 mL) (to remove polar byproducts) and again pumped dry. The desired oligomer was then eluted with CH_2Cl_2 (sexi- and septithiophenes) or THF (octithiophenes) and the analytically pure product was collected upon evaporation of the solvent, typically in 60–90% yield, in the form of a brick red amorphous solid.

4′,3‴″-Didecyl-[2,2′;5′,2″;5″,2‴;5‴,2⁗;5⁗,2⁗′]sexithiophene (In6)
To a dry 25 mL 3-necked round-bottom flask, anhyd $NiCl_2$ (13 mg, 0.1 mmol), PPh_3 (131 mg, 0.5 mmol) and 2,2′-bipyridine (16 mg, 0.1 mmol) were added. The system was flushed with argon for a few min, dry DMF (1 mL) was added and the solution stirred at 70 °C for 1 h. A solution of terthiophene **5** (234 mg, 0.5 mmol) in anhyd THF (2.5 mL) was added in one portion, 3 min later followed by Zn (82 mg, 1.25 mmol, 300 mesh). (Note: No reaction took place if the zinc was added before the terthiophene!) The mixture was stirred at 70 °C overnight, diluted with CH_2Cl_2 (50 mL) and vacuum-filtered through Celite. The clear organic phase was washed with H_2O (3 × 50 mL) water, dried ($MgSO_4$) and evaporated. The crude product was purified according to the general purification procedure.

^{1}H NMR ($CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 6 H), 1.21–1.43 (m, 28 H), 1.68 (q, *J* = 7.6 Hz, 4 H), 2.77 (t, *J* = 7.6 Hz, 4 H), 7.00–7.05 (m, 6 H), 7.13 (d, *J* = 4.0 Hz, 2 H), 7.17 (d, *J* = 3.6 Hz, 2 H), 7.22 (d, *J* = 4.8 Hz, 2 H).

Anal. Calcd for $C_{44}H_{54}S_6$: C, 68.16; H, 7.02. Found: C, 68.28; H, 7.08.

MS (EI): *m*/*z* = 774 (M^+, 100).

3′,4‴″-Didecyl-[2,2′;5′,2″;5″,2‴;5‴,2⁗;5⁗,2⁗′]sexithiophene (Out6)
The procedure for synthesis of **In6, 13**, with terthiophene **10** substituted for **5**, afforded the desired product.

^{1}H NMR ($CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 6 H), 1.21–1.43 (m, 28 H), 1.66 (q, *J* = 7.6 Hz, 4 H), 2.73 (t, *J* = 7.6 Hz, 4 H), 7.02 (s, 2 H), 7.05–7.09 (m, 6 H), 7.13 (d, *J* = 3.6 Hz, 2 H), 7.32 (d, *J* = 5.2 Hz, 2 H).

MS (EI): *m*/*z* = 774 (M^+, 100).

Anal. Calcd for $C_{44}H_{54}S_6$: C, 68.16; H, 7.02. Found: C, 68.02; H, 7.18

3′,3‴′-Didecyl-[2,2′;5′,2″;5″,2‴;5‴,2⁗;5⁗,2⁗′;5⁗′,2⁗″]sexithiophene (Unsym6)
A mixture of terthiophene **5** (467 mg, 1 mmol), hexamethylditin (656 mg, 2 mmol), and $Pd(PPh_3)_4$ (29 mg, 0.025 mmol) in anhyd THF (5 mL) was heated to reflux under argon for 6 h. To the in situ formed arylstannane was added terthiophene **10** (467 mg, 1 mmol) in anhyd THF (5 mL), followed by a second portion of $Pd(PPh_3)_4$ (58 mg, 0.050 mmol). After another 18 h of reflux, the solvent was evaporated, leaving a dark semi-solid. This crude product was purified according to the general purification procedure.

^{1}H NMR ($CDCl_3$): δ = 0.88 (m, 6 H), 1.20–1.43 (m, 28 H), 1.62–1.72 (m, 4 H), 2.71–2.79 (m, 4 H), 7.00–7.05 (m, 4 H), 7.06–7.09 (m, 3 H), 7.11–7.14 (m, 2 H), 7.17 (d, *J* = 3.6 Hz, 1 H), 7.22 (d, *J* = 5.2 Hz, 1 H), 7.32 (d, *J* = 5.2 Hz, 1 H).

MS (MALDI-TOF): *m*/*z* = 774 (M^+, 100).

Anal. Calcd for $C_{44}H_{54}S_6$: C, 68.16; H, 7.02. Found: C, 68.32; H, 6.89.

4′,3⁗″-Didecyl-[2,2′;5′,2″;5″,2‴;5‴,2⁗;5⁗,2⁗′;5⁗′,2⁗″;5⁗″,2⁗‴]septithiophene (In7)
To a dry 25 mL 3-necked round-bottom flask, terthiophene **5** (234 mg, 0.5 mmol), 2,5-bistributylstannylthiophene (**11**) (166 mg, 0.25 mmol) and $Pd(PPh_3)_4$ (58 mg, 0.05 mmol) were added. The system was flushed with argon for a few min, anhyd DMF (5 mL) was added and the solution stirred at 80 °C overnight. The product was precipitated by addition of cold MeOH (50 mL), collected by vacuum-filtration and then purified according to the general purification procedure.

^{1}H NMR ($CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 6 H), 1.21–1.43 (m, 28 H), 1.68 (q, *J* = 7.6 Hz, 4 H), 2.77 (t, *J* = 7.6 Hz, 4 H), 7.00–7.05 (m, 6 H), 7.10 (s, 2 H), 7.13 (d, *J* = 4.0 Hz, 2 H), 7.17 (d, *J* = 3.6 Hz, 2 H), 7.22 (d, *J* = 4.8 Hz, 2 H).

MS (MALDI-TOF): *m*/*z* = 856 (M^+, 100).

Anal. Calcd for $C_{48}H_{56}S_7$: C, 67.24; H, 6.58. Found: C, 67.05; H, 6.54.

3′,4⁗″-Didecyl-[2,2′;5′,2″;5″,2‴;5‴,2⁗;5⁗,2⁗′;5⁗′,2⁗″;5⁗″,2⁗‴]septithiophene (Out7)
The procedure for synthesis of **In7, 16**, with terthiophene **10** substituted for **5**, afforded the desired product.

^{1}H NMR ($CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 6 H), 1.21–1.43 (m, 28 H), 1.66 (q, *J* = 7.6 Hz, 4 H), 2.73 (t, *J* = 7.6 Hz, 4 H), 7.02 (s, 2 H), 7.05–7.09 (m, 8 H), 7.13 (d, *J* = 3.6 Hz, 2 H), 7.32 (d, *J* = 5.2 Hz, 2 H).

MS (MALDI-TOF): *m*/*z* = 856 (M^+, 100).

Anal. Calcd for $C_{48}H_{56}S_7$: C, 67.24; H, 6.58. Found: C, 66.78; H, 6.42

4′,3⁗′-Didecyl-[2,2′;5′,2″;5″,2‴;5‴,2⁗;5⁗,2⁗′;5⁗′,2⁗″;5⁗″,2⁗‴;5⁗‴,2⁗⁗′]octithiophene (In8)
The procedure for synthesis of **In7, 16**, with 5,5′-bistributylstannyl[2,2′]bithiophene (**12**) substituted for the bis-stannylated thiophene **11**, afforded the desired product.

^{1}H NMR ($CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 6 H), 1.21–1.43 (m, 28 H), 1.68 (q, *J* = 7.6 Hz, 4 H), 2.77 (t, *J* = 7.6 Hz, 4 H), 7.00–7.05 (m, 6 H), 7.10 (s, 4 H), 7.13 (d, *J* = 4.0 Hz, 2 H), 7.17 (d, *J* = 3.6 Hz, 2 H), 7.22 (d, *J* = 4.8 Hz, 2 H).

MS (MALDI-TOF): *m*/*z* = 938 (M^+, 100).

Downloaded by: Florida State University Libraries. Copyrighted material.

Anal. Calcd for $C_{52}H_{58}S_8$: C, 66.47; H, 6.22. Found: C, 66.25; H, 6.11.

3′,4‴″‴′-Didecyl-[2,2′;5′,2″;5″,2‴;5‴,2⁗;5⁗,2⁗′;5⁗′,2⁗″;5⁗″,2⁗‴;5⁗‴,2⁗⁗′]octithiophene (Out8)

The procedure for the synthesis of **In7, 16**, with 5,5′-bistributylstannyl[2,2′]bithiophene (**12**) substituted for the bis-stannylated thiophene **11** and tertiophene **10** substituted for **5**, afforded the desired product.

^{1}H NMR ($CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 6 H), 1.21–1.43 (m, 28 H), 1.66 (q, *J* = 7.6 Hz, 4 H), 2.73 (t, *J* = 7.6 Hz, 4 H), 7.02 (s, 2 H), 7.05–7.09 (m, 10 H), 7.13 (d, *J* = 3.6 Hz, 2 H), 7.32 (d, *J* = 5.2 Hz, 2 H).

MS (MALDI-TOF): *m*/*z* = 938 (M^+, 100).

Anal. Calcd for $C_{52}H_{58}S_8$: C, 66.47; H, 6.22. Found: C, 65.41; H, 6.05.

Acknowledgements

Financial support from TFR and Carl Tryggers Stiftelse is gratefully acknowledged. We specially thank Kurt Benkestock for performing the MALDI-TOF experiments. Baron Jonas Leijonhufvud is thanked for his wholehearted proof reading of the manuscript.

References

(1) For example, see: Neugebauer, H.; Sariciftci, N. S.; Kuzmany, H.; Resel, R.; Leising, G. *Synth. Met.* **2001**, *120*, 663–1092.
(2) Andersson, M. R.; Thomas, O.; Mammo, W.; Svensson, M.; Theander, M.; Inganäs, O. *J. Mater. Chem.* **1999**, *9*, 1933.
(3) (a) Garnier, F.; Yassar, A.; Hajlaoui, R.; Horowitz, G.; Deloffre, F.; Servet, B.; Ries, S.; Alnot, P. *J. Am. Chem. Soc.* **1993**, *115*, 8716. (b) Garnier, F.; Hajlaoui, R.; Yassar, A.; Srivastava, P. *Science* **1994**, *265*, 1684.
(4) (a) McCullough, R. D.; Ewbank, P. C. In *Handbook of Conducting Polymers*, 2nd ed.; Skotheim, T. A.; Elsenbaumer, R. L.; Reynolds, J. R., Eds.; Marcell Dekker: New York, **1998**, Chap. 9, 225–258. (b) McCullough, R. D. *Adv. Mater.* **1998**, *10*, 1. (c) McCullough, R. D.; Lowe, R. D. *J. Chem. Soc., Chem. Commun.* **1992**, 70. (d) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. *J. Org. Chem.* **1993**, *58*, 904. (e) McCullough, R. D.; Tristram-Nagle, S.; Williams, S. P.; Lowe, R. D.; Jayaraman, M. *J. Am. Chem. Soc.* **1993**, *115*, 4910. (f) McCullough, R. D.; Williams, S. P. *J. Am. Chem. Soc.* **1993**, *115*, 11608. (g) McCullough, R. D.; Jayaraman, M. *J. Chem. Soc., Chem. Commun.* **1995**, 135. (h) Chen, T.-A.; Rieke, R. D. *J. Am. Chem. Soc.* **1992**, *114*, 10087. (i) Chen, T.-A.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233. (j) Wu, X.; Chen, T.-A.; Rieke, R. D. *Macromolecules* **1995**, *28*, 2101. (k) Bouman, M. M.; Meijer, E. W. *Adv. Mater.* **1995**, *7*, 385. (l) Loewe, R. S.; Ewbank, P. C.; Liu, J.; Zhai, L.; McCullough, R. D. *Macromolecules* **2001**, *34*, 4324.
(5) Johansson, D. M.; Theander, Y. M.; Srdanov, G.; Yu, G.; Inganäs, O.; Andersson, M. R. *Macromolecules* **2001**, *34*, 3716.
(6) Theander, Y. M.; Svensson, M.; Ruseckas, A.; Zigmantas, D.; Sundström, V.; Andersson, M. R.; Inganäs, O. *Chem. Phys. Lett.* **2001**, *337*, 277.
(7) For example, see: (a) Gronowitz, S.; Peters, D. *Heterocycles* **1990**, *30*, 645. (b) Charloner, P. A.; Gunatunga, S. R.; Hitchcock, P. B. *J. Chem. Soc., Perkin Trans. 2* **1997**, *8*, 1597. (c) Rossi, R.; Carpita, A.; Ciofalo, M.; Houben, J. L. *Gazz. Chim. Ital.* **1990**, *120*, 793.
(8) For example, see: (a) Beny, J.-P.; Dhawan, S. M.; Kagan, J.; Sundlass, S. *J. Org. Chem.* **1982**, *47*, 2201. (b) Perrine, D. M.; Kagan, J. *Heterocycles* **1986**, *24*, 365.
(9) For example, see: (a) Merz, A.; Ellinger, F. *Synthesis* **1991**, 462. (b) Wynberg, H.; Metselaar, J. *Synth. Commun.* **1984**, *14*, 1. (c) Kagan, J.; Arora, S. K. *Heterocycles* **1983**, *20*, 1941.
(10) For example, see: (a) Eachern, A. M.; Soucy, C.; Leitch, L. C.; Arnason, J. T.; Morand, P. *Tetrahedron* **1988**, *44*, 2403. (b) Nakayama, J.; Konishi, T.; Murabayashi, S.; Hoshino, M. *Heterocycles* **1987**, *26*, 1793. (c) Effenberger, F.; Grube, G. *Synthesis* **1998**, 1372. (d) Jones, C. L.; Higgins, S. J. *J. Mater. Chem.* **1999**, *4*, 865. (e) Bäuerle, P.; Pfau, F.; Schlupp, H.; Würthner, F.; Gaudl, K.-U.; Caro, M. B.; Fisher, P. *J. Chem. Soc., Perkin Trans. 2* **1993**, *3*, 489.
(11) Kelin, A. V.; Kulinkovich, O. G. *Synthesis* **1996**, 330.
(12) *Encyclopedia of Reagents for Organic Synthesis*, Vol 1; Wiley: New York, **1995**, 530–533; and references cited therein.
(13) (a) Freeman, F.; Kim Darrick, S. H. L.; Rodriguez, E. *J. Org. Chem.* **1992**, *57*, 1722. (b) Steliou, K.; Mrani, M. *J. Am. Chem. Soc.* **1982**, *104*, 3104.
(14) Destri, S.; Ferro, D. R.; Khotina, I. A.; Porzio, W.; Farrina, A. *Macromol. Chem. Phys.* **1998**, *199*, 1973.
(15) Wei, Y.; Yang, Y.; Yeh, J.-M. *Chem. Mater.* **1996**, *8*, 2659.
(16) Galli, C. *Synthesis* **1979**, 303.

Downloaded by: Florida State University Libraries. Copyrighted material.