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Synthesis and optical properties of soluble sexithiophenes with one central head-to-head junction

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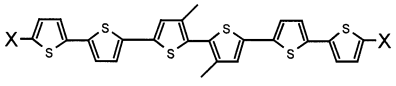
Abstract—The regioselective synthesis of three sexithiophenes characterized by the presence of one central 3,3′-dimethyl-2,2′-bithiophene subsystem is described. One of these compounds was obtained under mild conditions by microwave-mediated synthesis. All sexithiophenes were soluble in organic solvents and displayed 30–40% fluorescence quantum yields in solution. In thin films the fluorescence quantum yields dropped to 1–2%, indicating conformational changes and strong intermolecular interactions in the solid state.

It is known that thiophene oligomers are among the most promising organic materials for electronic and electro-optical applications.[1–3] Sexithiophene is one of the best organic semiconducting materials for the fabrication of thin film field effect transistors (FETs).[4] It has been demonstrated that high purity and high molecular ordering in the film are essential to obtain high charge mobilities.[5] The highest charge mobilities, comparable to those of amorphous silicon, have been obtained by using single crystals for FET fabrication.[6] Single crystals represent the upper limit attainable in terms of purity and molecular ordering for organic molecules. However, preparing single crystals of thiophene oligomers of a sufficient size for device application is a very difficult task. Thus, an ambitious goal is to take advantage of spontaneous self-assembly properties of these oligomers and obtain in thin films a degree of molecular ordering comparable to that reached in single crystals.

Achieving this objective is hindered by synthetic difficulties, solubility problems and by the ultrapurity standards required for applications in microelectronics.

Unsubstituted sexithiophene is scarcely soluble and difficult to obtain in a pure form.[4,5] Solubility can be achieved by inserting appropriate substituents into the aromatic skeleton of sexithiophene but the substituents modify the self-organization properties of the molecule in ways that are difficult to predict.[7]

The search for structural elements helping solubility and processability yet not altering the self-organization properties of thiophene oligomers is the rationale underlying the present work, which describes the synthesis and the optical properties of the three sexithiophenes depicted in Fig. 1.



X = H (**4**), $(CH_2)_5CH_3$ (**16**), $S(CH_2)_{11}CH_3$ (**17**)

Figure 1. Molecular structure of the title compounds.

The fluorescence spectra of all compounds in solution and in thin films were investigated in order to get some insight into their conformation and self-assembly modalities.

1. Results and discussion

The synthesis of functionalized thiophene oligomers is generally carried out by reacting thienyl bromides with thienylstannanes or organoboron derivatives—Stille[8,9] and Suzuki–Miyaura reaction,[10,11] respectively—in the presence of palladium(0) catalysts. Both reactions are greatly dependent on the steric and electronic characteristics of reagents and catalysts and require careful adjustment of the experimental conditions case by case.

We have demonstrated that sexithiophene **4** is characterized by high FET mobility.[7] However, so far, we have only been able to obtain this compound in low yield via the Stille coupling.[7] Given its good electrical characteristics, we were then checking alternative ways to synthesize this compound in better yields.

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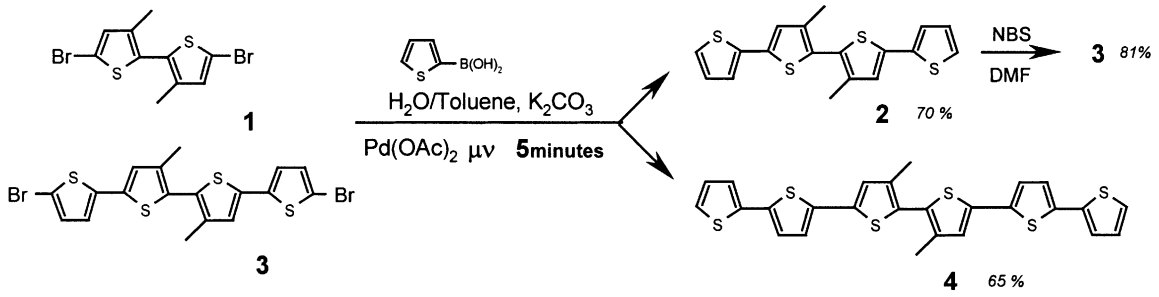


Scheme 1.

In the last few years, the use of microwaves has been found to be expedient for a great variety of organic reactions both in solution or in the absence of solvents.[12–15]

Scheme 1 summarizes the synthetic method followed to prepare sexithiophene **4** in good yield under mild conditions through the use of microwaves. The yields reported in the scheme are relative to isolated products after chromatography.

As shown in Scheme 1, 2,5′-dibromo-3,3′-dimethyl-2,2′-bithiophene[7] **1** was coupled to 2-thiophene boronic acid under the action of microwaves using H_2O/toluene as the solvent, a quaternary salt (Bu_4NBr), K_2CO_3 and $Pd(OAc)_2$ as the catalyst. The reaction afforded quaterthiophene **2** in 70% yield within a reaction time not exceeding 5 min. Besides **2**, only the starting material was present in the reaction mixture, making the purification procedures straightforward. Bromination of **2** with *N*-bromosuccinimide afforded dibromo quaterthiophene **3** in high yield. Compound **3** was then reacted with 2-thiophene boronic acid in the same conditions as **1** under microwave action. The reaction afforded sexithiophene **4** in high yield. In this case, besides the starting material, the reaction mixture also contained some monobromo quinquethiophene that did not react further with 2-thiophene boronic acid even on changing reaction conditions and times. In consequence, for **4** the purification procedures were slightly more elaborate than for **2** and the yields of isolated product lower (65%).

These results show that the use of microwaves is very efficient in the synthesis of sexithiophene **4** via Suzuki coupling under mild conditions. The reaction occurs in very short times, with high yields and can be carried out using the same experimental conditions for the preparation of both tetramer **2** and hexamer **4**.

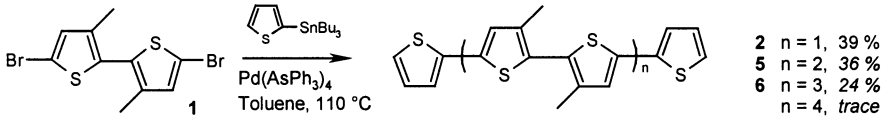
For comparison, and with the aim of achieving a better understanding of the reactions we were dealing with, we reacted dibromo **1** in the absence of microwaves: (a) with 2-thiophene boronic acid using experimental conditions typical of the Suzuki–Miyaura reaction and (b) with 2-thiophene tributylstannyl using experimental conditions typical of the Stille reaction.

In the first case we succeeded in obtaining tetramer **2** in the same yield (70%) by reacting **1** for a few hours with 2-thiophene boronic acid in refluxing tetrahydrofuran, K_2CO_3 and $Pd(PPh_3)_4$. However, several attempts to react dibromo **3** with 2-thiophene boronic acid using the same experimental conditions failed. Only traces of the desired hexamer were detected by mass spectrometry and most of the product recovered was made of polymeric chains. Nevertheless we were able to identify (by mass spectrometry and ^1H NMR) the formation of a dibromo-octathiophene, a monobromo nonamer and of a quaterthiophene having $B(OH)_2$ groups at both the terminal positions.

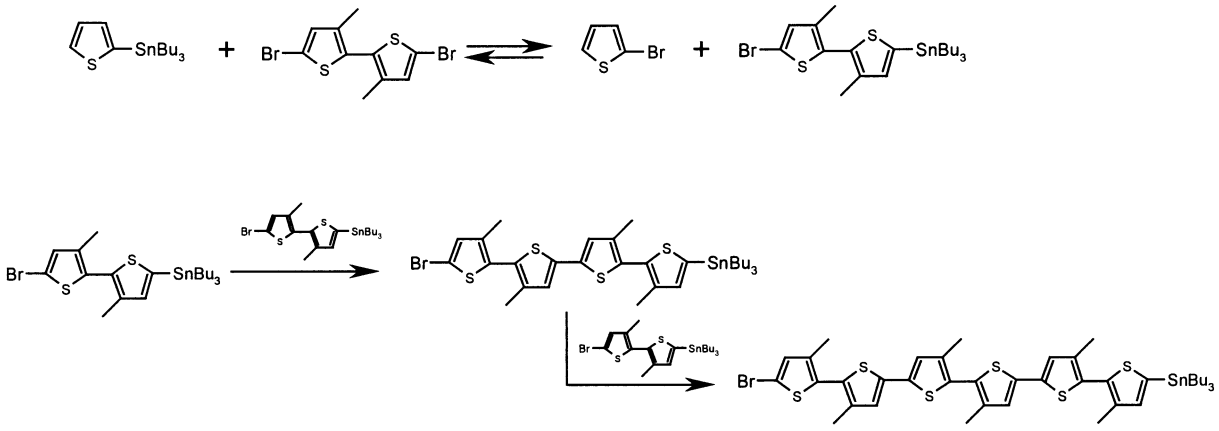
The formation of polymeric chains indicates that in the Suzuki reaction metal–halogen exchange may become competitive with the cross-coupling when the size of the oligomer increases. By contrast, the fact that the use of microwaves led to the formation of **4** in high yield suggests that the use of microwaves causes a large acceleration of the cross-coupling reaction with respect to that of metal–halogen exchange.

The results of the Stille coupling of dibromo **1** with 2-tributylstannyl thiophene are reported in Scheme 2. It is seen that in this case the yield of quaterthiophene **2** is low and there is the formation of longer oligomers containing repeated 3,3-dimethyl-2,2′-bithiophene subunits that we were able to isolate and purify. Several attempts to improve the yield of this reaction in quaterthiophene **2** by use of microwaves were unsuccessful but we cannot exclude that this is only due to our inability to find the appropriate conditions.

The formation of oligomers **5** and **6** containing repeating 3,3-dimethyl-2,2′-bithiophene subunits can be explained by assuming that the metal–halogen exchange reaction and the subsequent coupling of the metallated–halogenated intermediates (Scheme 3) are competitive with the cross-coupling reaction leading to the desired quaterthiophene **2**.



Scheme 2.



Scheme 3.

It is reasonable to assume that the degree of competition between the halogen–metal exchange reaction and the cross-coupling reaction depends on the reactivity of the brominated–metallated intermediate species that is formed, which in turn should depend on the oligomer size and on the metal used. A better knowledge of these aspects of the Stille and Suzuki reactions should make it possible to pilot these reactions in the direction of the exclusive (or near so) formation of short or, in alternative, of long oligomers or polymers.

The synthesis of sexithiophenes **16** and **17** was carried out via conventional Stille coupling according to the method shown in Scheme 4.

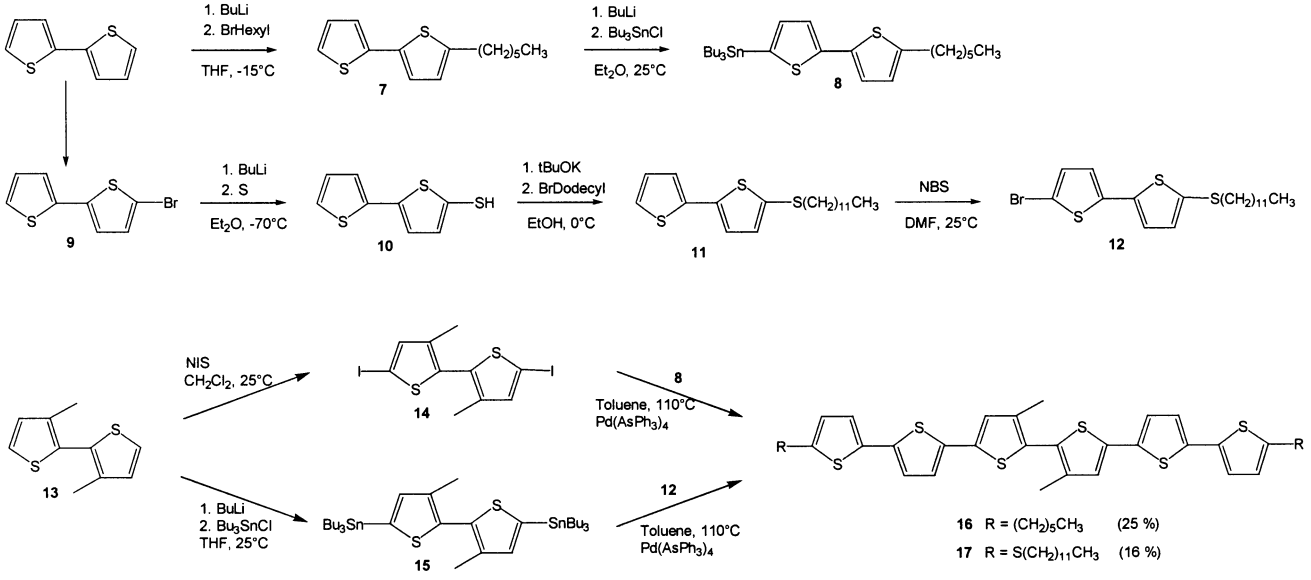
Compound **16** was synthesized through the coupling of 5,5′-diiodo-3,3′dimethyl-2,2′-bithiophene **14** with the appropriate stannanes in the presence of $Pd(AsPh_3)_4$ prepared in situ,[16] while product **17** was obtained using 5,5′-bis-(tributylstannyl)-3,3′dimethyl-2,2′-bithiophene **15** with the corresponding monobromo derivative under the same conditions.

The crude reaction products contained large amounts of byproducts which were separated from the desired hexamers by silica gel chromatography. The reaction yields of isolated **16** and **17** were in consequence rather low, 25 and 16%, respectively. Again we ascribed the low reaction yields to the metal–halogen exchange reaction leading to a mixture of longer oligomers, for which we had spectroscopic evidence but that we did not try to isolate and purify.

The absorption and photoluminescence spectra of compounds **4**, **16**, **17** in THF are shown in Fig. 2.

The maximum wavelength absorptions (λ_{max}) of **4**, **16**, **17** are 390, 400 and 410 nm, respectively. These values are markedly blue shifted with respect to the λ_{max} of unsubstituted sexithiophene (432 nm[17]) and are explained by the lower $\pi-\pi$ overlap associated with the presence of the methyl groups, i.e. of a head-to-head 'rotational defect'.

The photoluminescence wavelengths (λ_{PL}) of **4**, **16**, **17** upon UV irradiation (λ_{exc}=370 nm) are in the range 500–510 nm with Stokes shifts between absorption and emission



Scheme 4.

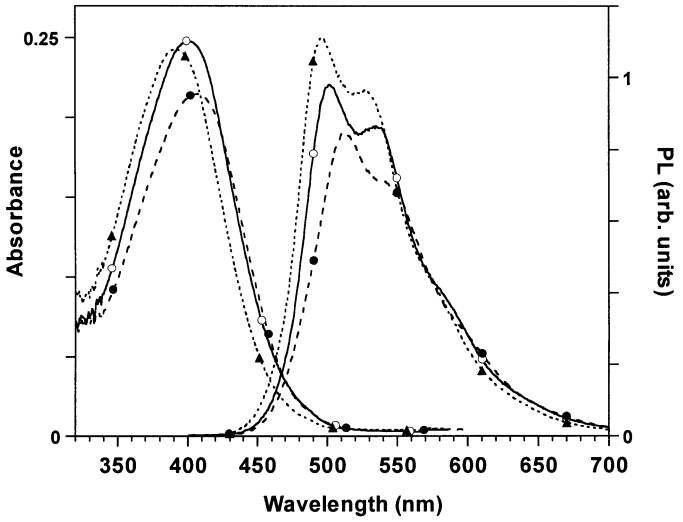


Figure 2. Absorption and photoluminescence spectra of sexithiophenes **4** (triangle), **16** (open circle) and **17** (solid circle), 10^{-5} M in THF. Absorbances are measured for 1 cm optical path cells.

wavelengths amounting to more than 100 nm. These values are similar to that measured for unsubstituted sexithiophene, for which a λ_{PL}=508 nm has been reported.[18,19] It is worth noting that while the absorption wavelengths are markedly blue shifted with respect to that of unsubstituted sexithiophene, the emission wavelengths are nearly the same, suggesting that in spite of the head-to-head junction the excited state is planar. In agreement with this,[18–20] the emission bands show some vibronic structure while the absorption bands are shapeless.

The fluorescence quantum yields (QY, namely the ratio between absorbed and emitted photons under UV irradiation), in chloroform were 33, 42 and 34% for **4**, **16**, **17**, respectively. For unsubstituted sexithiophene, a QY value of 40–42% in solution has been reported.[18,20]

After deposition as thin films by spin-coating from chloroform, the fluorescence QY of **4**, **16**, **17** dropped to 1–2%, i.e. to values more than one order of magnitude smaller than those in solution. Once again, this behaviour is in agreement with what has been observed for unsubstituted thiophene oligomers[20] and indicates that in the solid state, the molecules assume a planar conformation despite the head-to-head 'rotational' defect and give rise to strong intermolecular interactions.

This conclusion is strongly supported by the single crystal X-ray structure of sexithiophene **4** showing that the inner head–head groups are in the *trans*-orientation and the molecules have a planar conformation favoured by packing forces.[7] Measurements of the absolute QY of single crystals of **4** using an integrated sphere gave a value of 3%.[21] The fact that in thin film, a very similar QY value was measured indicates that the arrangement of **4** is of the same type as that that in the single crystal. By analogy, the same is likely to be true for **16** and **17**, the planarization process in this case being assisted by the long terminal alkyl chains.[22] It is known that in the solid state, strong intermolecular interactions increase the probability of non-radiative decay and that these processes are strictly correlated to the molecular geometry and to the supramolecular structure. In unsubstituted thiophene oligomers, planar conformations and strong intermolecular interactions in the solid state lead to photoluminescence quenching.[23]

Recently, high level ab initio calculations of 3,3′-dimethyl-2,2-bithiophene have been reported.[24] According to the calculations, the rotational profile is very flat indicating the existence of a large number of equienergetic conformations with slightly different inter-ring rotation angles.

It is probably the existence of a large family of rotational conformers that explains the great solubility of these compounds. The large entropy increase in solution compared to the solid state together with the lack of formation of aggregates for steric reasons explains why sexithiophene **16** is very soluble while its non-methylated counterpart—namely (α,ω-dihexyl sexithiophene,[22] is even less soluble than unsubstituted sexithiophene itself.

2. Conclusions

The remarkable improvement obtained in the synthesis of sexithiophene **4** shows that there is room for developing microwave-mediated synthetic methodologies leading to the preparation of long thiophene oligomers rapidly and in high yields. The comparison of the results obtained by the use of microwaves and those obtained with conventional heating suggests that the microwaves cause the acceleration of the cross-coupling reaction compared to the metal–halogen exchange reaction which is at the origin of the formation of a variety of undesired products.

Finally, we have shown that the presence of one inner dimethyl head-to-head 'rotational defect' into the skeleton of sexithiophene makes it very soluble and does not prevent a planar arrangement in the solid state, which leads to strong intermolecular interactions and fluorescence quenching.

3. Experimental

3.1. General information

2-Tributylstannylthiophene, $Pd(PPh_3)_4$, 2-thiophene boronic acid, K_2CO_3, Pd_2dba_3, $AsPh_3$, $Pd(OAc)_2$, 2,2′-bithiophene, hexyl bromide, dodecyl bromide, butyllithium, tributyltin chloride, sulfur, potassium *tert*-butoxide, *N*-iodosuccinimide were available from Aldrich Chemical Co. Tetrabutylammonium bromide and *N*-bromosuccinimide were obtained from Carlo Erba and Lancaster, respectively. Organic solvents were dried by standard procedures. Flash chromatographies were carried out using silica gel (200–300 mesh ASTM) or LiChroprep RP-8 and RP-18 40–63 μm (Merck). Analytical thin layer chromatographies (TLCs) with 0.2 mm silica gel plates (Merck). Stille and Suzuki reactions with conventional heating were carried out under nitrogen. Microwave assisted reactions were carried out under air and they were performed using a commercial system Synthewave 402 manufactured by Prolabo.

The characteristics of compounds **1**–**5**, **9**, **13** have already been reported.[7]

3.1.1. 4′,3″-Dimethyl-2,2′:5′,2″:5″,2‴-quaterthiophene, 2, via microwave assisted Suzuki method. A 20 mL reactor for a microwave oven was charged with 0.1 g (0.28 mmol) of 5,5′-dibromo-3,3′-dimethyl-2,2′-bithiophene (**1**), 0.08 g (0.62 mmol) of commercial 2-thiophene boronic acid, 3 mg (0.013 mmol) of $Pd(OAc)_2$, 0.193 g (1.4 mmol) of K_2CO_3, 0.09 g (0.28 mmol) of Bu_4NBr, and 0.31 mL of water in 5 mL of toluene as the solvent. The reaction mixture was stirred and then irradiated for 5 min at 25 W. After cooling to room temperature the mixture was quenched with 1 mL of 2 M HCl, washed twice with brine, dried with Na_2SO_4 and evaporated. The residue was chromatographed on silica gel with petroleum ether/CH_2Cl_2 95:5 as eluent and 0.072 g (72% yield) of **5** as yellow microcrystalline solid was recovered. Elemental analysis, melting point, λ_{max}, mass spectrum, NMR were in agreement with those reported in Ref. 7.

3.1.2. 4′,3″-Dimethyl-2,2′:5′,2″:5″,2‴-quaterthiophene, 2, via conventional Suzuki method. A mixture of 0.1 g (0.28 mmol) of 5,5′-dibromo-3,3′-dimethyl-2,2′-bithiophene (**1**), 0.08 g (0.62 mmol) of commercial 2-thiophene boronic acid, 0.014 mmol of commercial $Pd(PPh_3)_4$ in 5 mL of dry THF was refluxed for 0.5 h. Then 0.31 mL of H_2O and 0.193 g (1.4 mmol) of K_2CO_3 were added to the reaction mixture. The reaction was followed by thin layer chromatography (TLC) using petroleum ether/CH_2Cl_2 95:5 as the eluent. The mixture was refluxed for 3 h, and quenched with 1 mL of 2 M HCl. After the usual workup the residue was chromatographed on silica gel using the same eluent. A total of 0.071 g (71% yield) of **5** was recovered. Elemental analysis, melting point, λ_{max}, mass spectrum, NMR were in agreement with those reported in Ref. 7.

3.1.3. 4″,3‴-Dimethyl-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2⁗′-sexithiophene, 4, via microwave assisted Suzuki method. A 5 mL toluene solution containing 0.1 g (0.19 mmol) of 5,5‴-dibromo-4′,3″-dimethyl-2,2′:5′,2″:5″,2‴-quaterthiophene, **3**, 0.056 g (0.44 mmol) of commercial 2-thiophene boronic acid, 0.131 g (0.95 mmol) of K_2CO_3, 0.064 g (0.19 mmol) of Bu_4NBr and 0.22 mL of water in the presence of 2 mg (0.01 mmol) of $Pd(OAc)_2$. The reaction mixture was stirred and was carried out under microwave irradiation for 5 min at 25 W. After usual workup the residue was chromatographed on silica gel with hexane as eluent to give 0.067 g (yield 67%) of hexamer **4**. Elemental analysis, melting point, λ_{max}, mass spectrum, NMR were in agreement with those reported in Ref. 7.

3.1.4. 4′,3″,4‴,3⁗,4⁗′,3⁗″-Hexamethyl-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2⁗′:5⁗′2⁗″:5⁗″,2⁗″octithiophene, 6. A 40 mL toluene solution containing 85 mg (0.082 mmol) of Pd_2dba_3 and 202 mg (0.66 mmol) of $AsPh_3$[3] was refluxed for 10 min. Then 2.90 g (8.24 mmol) of 5,5′-dibromo-3,3′-dimethyl-2,2′-bithiophene (**4**) dissolved in 30 mL of toluene was added. 5.50 mL (17.30 mmol) of commercial 2-tributylstannylthiophene was added dropwise to the refluxed mixture. After 45 h the reaction mixture was evaporated, and the residue was chromatographed on silica gel with hexane as eluent to give 1.15 g (39% yield) of tetramer **2**,[7] 0.81 g (36% yield) of hexamer **5**[7] and 0.71 g (24% yield) of octamer **6** as dark red microcrystalline solid. Anal. calcd for **6**, $C_{38}H_{30}S_8$: C, 61.42; H, 4.07. Found: C, 61.37; H, 4.09. MS *m/e* 742 ($M^{\cdot+}$); λ_{max} (CH_2Cl_2) 383 nm; mp 164°C. ^1H NMR ($CDCl_3$, TMS/ppm) δ 7.22 (dd, $^3J_{HH}$=5.0 Hz, $^3J_{HH}$=1.0 Hz, 2H), 7.16 (dd, $^3J_{HH}$=3.5 Hz, $^3J_{HH}$=1.0 Hz, 2H), 7.01 (m, 8H), 2.22 (m, 18H); ^{13}C NMR ($CDCl_3$, TMS/ppm) δ 137.4, 137.3, 137.2, 136.7, 136.4, 128.2, 128.1, 127.8, 126.8, 126.6, 124.4, 123.6, 15.04, 15.01.

3.1.5. 5-Hexyl-2,2′-bithiophene, 7. To a solution of 2,2′-bithiophene (2.07 g, 0.012 mol) in THF (50 mL) was added a 2.5 M solution of *n*-BuLi (5.0 mL, 0.012 mol) in hexane at −70°C. After 30 min, the mixture was heated to −15°C and 1-bromohexane (2.06 g, 0.012 mol) was added. The mixture was heated at room temperature and stirred for 2 h. Then it was hydrolyzed with a saturated solution of NH_4Cl and extracted with diethyl ether. The organic layer was dried and evaporated, the residue was chromatographed on RP-18 silica gel column with MeOH/CH_2Cl_2 (9:1) as eluent to give 1.96 g (63%) of a yellow oil. MS *m/e* 250 ($M^{\cdot+}$); λ_{max} (CH_2Cl_2) 324 nm; ^1H NMR ($CDCl_3$, TMS/ppm) δ 7.19 (m, 2H), 7.04 (m, 2H), 6.73 (m, 1H), 2.85 (t, 2H, $^3J_{HH}$=7.5 Hz), 1.75 (m, 2H), 1.41 (m, 6H), 0.98 (t, 3H, $^3J_{HH}$=5.5 Hz); ^{13}C NMR ($CDCl_3$, TMS/ppm) δ 145.2, 137.9, 134.7, 127.6, 124.6, 123.6, 123.3, 122.9, 31.5, 30.1, 28.7, 22.5, 14.0. Proton and carbon-13 NMR spectra of **7** are given as supplementary material.

3.1.6. 5-Tributylstannyl-5′-hexyl-2,2′-bithiophene, 8. To a solution of 1.82 g (7.3 mmol) of 5-hexyl-2,2′-bithiophene in 40 mL of dry ether at room temperature was added a 2.5 M solution of BuLi in hexane (3.2 mL, 8.0 mmol). After 30 min, 2.60 g (8.0 mmol) of tributyltin chloride was added dropwise. The reaction was stirred for 2 h, hydrolyzed with water, extracted with ether, dried over Na_2SO_4 and evaporated. A total of 3.68 g (94%) of product as a yellow oil was isolated. MS *m/e* 539 ($M^{\cdot+}$); ^1H NMR ($CDCl_3$, TMS/ppm) δ 7.27 (d, $^3J_{HH}$=3.5 Hz, 1H), 7.11 (d,

$^3J_{HH}$=3.5 Hz, 1H), 7.02 (d, $^3J_{HH}$=3.5 Hz, 1H), 6.72 (d, $^3J_{HH}$=3.5 Hz, 1H), 2.82 (t, $^3J_{HH}$=7.5 Hz, 2H), 1.68 (m, 8H), 1.40 (m, 12H), 1.18 (m, 6H), 0.98 (m, 12H); ^{13}C NMR ($CDCl_3$, TMS/ppm) δ 145.5, 143.8, 136.6, 136.3, 135.5, 125.2, 124.6, 123.5, 32.1, 30.6, 29.5, 29.3, 27.8, 23.1, 14.4, 14.0, 11.3. Proton and carbon-13 NMR spectra of **8** are given as supplementary material.

3.1.7. 5-Dodecylsulfanyl-2,2′-bithiophene, 11. To a solution of 5-bromo-2,2′-bithiophene (5.22 g, 0.021 mol) in dry ether (30 mL) was added a 2.5 M solution of *n*-BuLi (8.4 mL, 0.021 mol) in hexane at −70°C. After 20 min, 0.68 g (0.021 mol) of sublimed sulfur was added and the mixture was stirred at −70°C for 2 h, then the reaction mixture was hydrolyzed with a 1 M solution of NaOH (120 mL). The aqueous layer was acidified with a 2 M solution of HCl and extracted with ether (3×50 mL). The organic layer was dried over Na_2SO_4 and evaporated to give 3.80 g (91%) of a red brown oil identified as being 5-mercapto-2,2′-bithiophene (**10**). MS *m/e* 198 ($M^{\cdot+}$); ^{1}H NMR ($CDCl_3$, TMS/ppm) δ 7.24 (m, 2H), 7.06 (m, 3H), 3.55 (s, 1H); ^{13}C NMR ($CDCl_3$, TMS/ppm) δ 144.1, 140.6, 136.7, 136.6, 134.6, 127.8, 124.6, 123.9. Proton and carbon-13 NMR spectra of **10** are given as supplementary material. To a solution of *t*-BuOK (2.60 g, 0.023 mol) in ethyl alcohol (10 mL) was added dropwise a solution of **10** (2.97 g, 0.015 mol) in CH_2Cl_2 (7 mL) at 0°C. After 20 min, 3.73 g (0.015 mol) of dodecyl bromide was added. Then the reaction mixture was refluxed for 2 h and treated by water (3×30 mL) and extracted with CH_2Cl_2 (2×30 mL), dried and evaporated. The crude product was chromatographed on RP-8 silica gel column with hexane/CH_2Cl_2 (9:1) as eluent to give 3.73 g (68%) of a deep yellow oil. MS *m/e* 366 ($M^{\cdot+}$); ^{1}H NMR ($CDCl_3$, TMS/ppm) δ 7.21 (m, 1H), 7.13 (m, 1H), 7.01 (m, 3H), 2.77 (t, $^3J_{HH}$=7.5 Hz, 2H), 1.60 (m, 2H), 1.25 (m, 18H), 0.95 (m, 3H); ^{13}C NMR ($CDCl_3$, TMS/ppm) δ 140.4, 137.1, 134.0, 133.9, 127.8, 124.5, 123.8, 38.9, 31.9, 29.6, 29.57, 29.5, 29.4, 29.3, 29.1, 28.4, 22.7, 14.1. Proton and carbon-13 NMR spectra of **11** are given as supplementary material.

3.1.8. 5-Bromo-5′-dodecylsulfanyl-2,2′-bithiophene, 12. To a solution of 5-dodecylsulfanyl-2,2′-bithiophene (2.20 g, 0.006 mol) in DMF (50 mL) was added stepwise 1.10 g (0.006 mol) of NBS at room temperature. Then the mixture was stirred for 2 h and treated with ice. The organic compound was extracted with CH_2Cl_2 (1×30 mL) and washed with saturated solution of NaCl (3×30 mL). The organic layer was dried and evaporated and the residue was chromatographed on silica gel using cyclohexane/CH_2Cl_2 (9:1) as eluent. The product was isolated as a yellow oil (2.40 g, yield 90%). MS *m/e* 445 ($M^{\cdot+}$); ^{1}H NMR ($CDCl_3$, TMS/ppm) δ 6.97 (d, $^3J_{HH}$=3.8 Hz, 1H), 6.94 (d, $^3J_{HH}$=3.6 Hz, 1H), 6.92 (d, $^3J_{HH}$=3.8 Hz, 1H), 6.85 (d, $^3J_{HH}$=3.6 Hz, 1H), 2.75 (t, $^3J_{HH}$=7.5 Hz, 2H), 1.58 (m, 2H), 1.25 (m, 18H), 0.85 (m, 3H); ^{13}C NMR ($CDCl_3$, TMS/ppm) δ 139.1, 138.6, 135.1, 133.7, 130.6, 124.0, 123.8, 111.2, 38.9, 31.9, 29.6, 29.56, 29.5, 29.4, 29.3, 29.1, 28.4, 22.7, 14.1.

3.1.9. 5,5′-Diiodo-3,3′-dimethyl-2,2′-bithiophene, 14. To a solution of 3,3′-dimethyl-2,2′-bithiophene (1.94 g, 0.01 mol) in CH_2Cl_2 (30 mL) was added 4.5 g (0.02 mol) of NIS at −20°C. Then the mixture was stirred at room temperature overnight and treated with 10% solution of KOH (1×20 mL) and water (1×20 mL). After usual workup the residue was chromatographed on silica gel with pentane as eluent to give 4.37 g (yield 98%) of a white powder: mp 94–96°C. MS *m/e* 446 ($M^{\cdot+}$); ^{1}H NMR ($CDCl_3$, TMS/ppm) δ 7.07 (s, 2H), 2.14 (s, 6H); ^{13}C NMR ($CDCl_3$, TMS/ppm) δ 139.8, 138.8, 134.1, 73.6.

3.1.10. 5,5′-Bis(tributylstannyl)-3,3′-dimethyl-2,2′-bithiophene, 15. To a solution of 3,3′-dimethyl-2,2′-bithiophene (1.94 g, 0.01 mol) in dry ether (20 mL) at room temperature was added a 2.5 M solution of BuLi in hexane (8 mL, 0.02 mol). After 1 h, 6.50 g (0.02 mol) of tributyltin chloride was added dropwise. The reaction mixture was stirred 2 h, hydrolyzed with water, extracted with diethyl ether, dried over Na_2SO_4 and evaporated. The crude compound was chromatographed on silica gel column with petroleum ether as eluent to give 6.35 g (yield 82 %) of a yellow oil. MS *m/e* 774 ($M^{\cdot+}$); ^{1}H NMR (acetone-d_6, TMS/ppm) δ 7.03 (s, 2H), 2.18 (s, 6H), 1.61 (m, 12H), 1.32 (m, 12H), 1.12 (m, 12H), 0.89 (m, 18H); ^{13}C NMR (acetone-d_6, TMS/ppm) δ 143.5, 139.4, 137.4, 128.5, 29.6, 27.7, 14.3, 13.8, 11.3.

3.1.11. 5,5‴″-Dihexyl-4″,3‴-dimethyl-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2⁗′:5⁗′,2‴′-sexithiophene, 16. To a 20 mL toluene solution containing 0.03 mmol of $(Ph_3As)_4Pd$ prepared in situ was added 0.45 g (1 mmol) of **14** and 1.08 g (2 mmol) of **8**. The mixture was refluxed for 15 h. After evaporation of toluene the residue was chromatographed on RP-18 silica gel column with CH_2Cl_2/MeOH (6:4) as eluent to give 172 mg (yield 25 %) of a deep red polycrystalline solid: mp 123–124°C. MS *m/e* 690 ($M^{\cdot+}$); λ_{max} (CH_2Cl_2) 414 nm; ^{1}H NMR ($CDCl_3$, TMS/ppm) δ 7.00 (m, 8H), 6.68 (m, 2H), 2.79 (t, 4H), 2.21 (s, 6H), 1.68 (m, 4H), 1.33 (m, 12H), 0.89 (m, 6H); ^{13}C NMR ($CDCl_3$, TMS/ppm) δ 145.7, 137.4, 136.9, 136.5, 135.2, 134.5, 128.0, 126.5, 124.8, 124.1, 123.6, 123.4, 31.6, 30.2, 28.7, 22.6, 15.0, 14.1. Anal. calcd for $C_{38}H_{42}S_6$: C, 66.04; H, 6.13. Found: C, 65.87; H, 6.11.

3.1.12. 5,5⁗′-Bis(dodecylsulfanyl)-4″,3‴-dimethyl-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2⁗′:5⁗′,2‴′-sexithiophene, 17. To a 20 mL toluene solution containing 0.045 mmol of $(Ph_3As)_4Pd$ prepared in situ was added 1.33 g (3 mmol) of **12** and 1.16 g (1.5 mmol) of **15**. The mixture was refluxed for 16 h. After evaporation of toluene the residue was chromatographed on silica gel column with cyclohexane/CH_2Cl_2 (9:1) as eluent. A total of 221 mg (yield 16%) of pure **17** as a deep red polycrystalline solid: mp 103–105°C. MS *m/e* 922 ($M^{\cdot+}$); λ_{max} (CH_2Cl_2) 400 nm; ^{1}H NMR ($CDCl_3$, TMS/ppm) δ 7.03 (m, 8H), 7.01 (s, 2H), 2.82 (t, 4H), 2.22 (s, 6H), 1.62 (m, 4H), 1.30 (m, 36H), 0.88 (m, 6H); ^{13}C NMR ($CDCl_3$, TMS/ppm) δ 140.0, 137.5, 136.3, 136.1, 135.9, 134.5, 133.9, 128.3, 126.8, 124.4, 124.2, 123.7, 39.0, 31.9, 29.64, 29.58, 29.5, 29.4, 29.3, 29.1, 28.4, 22.7, 15.0, 14.1. Anal. calcd for $C_{50}H_{66}S_8$: C, 65.02; H, 7.20. Found: C, 64.93; H, 7.22.

3.2. Optical measurements

Photoluminescence measurements were performed with a

SPEX 270 M polychromator equipped with a cooled CCD detector by exciting the sample with a monochromated Xe lamp. PL QY were determined for 10^{-5} M solutions in dry THF by using quinine sulfate monohydrate as the reference,[24,25] exciting at 370 nm. Absorption spectra were obtained with a Lambda 20 UV/vis spectrometer.

3.3. Supplementary material

Proton and carbon-13 NMR spectra of 5-hexyl-2,2′-bithiophene (**7**); 5-tributylstannyl-5′-hexyl-2,2′-bithiophene (**8**); 5-mercapto-2,2′-bithiophene (**10**); 5-dodecylsulfanyl-2,2′-bithiophene (**11**).

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References

1. *Handbook of Conductive Polymers*, Skotheim, T. A., Elsenbaumer, R. L., Reynolds, J. R., Eds.; Marcel Dekker: New York, 1998; p. 23.
2. *Electronic Materials: The Oligomer Approach*, Müllen, K., Wegner, G., Eds.; Wiley–VCH: New York, 1998.
3. *Hanbook of Oligo and Polythiophenes*, Fichou, D., Ed.; Wiley–VCH: New York, 1999.
4. Bao, Z.; Rogers, J. A.; Katz, H. E. *J. Mater. Chem.* **1999**, *9*, 1895.
5. Garnier, F. *Acc. Chem. Res.* **1999**, *32*, 209.
6. Schön, J. H.; Kloch, C.; Laudise, R. A.; Batlogg, B. *Appl. Phys. Lett.* **1998**, *73*, 3574.
7. Barbarella, G.; Zambianchi, M.; Antolini, L.; Ostoja, P.; Maccagnani, P.; Bongini, A.; Marseglia, E. A.; Tedesco, E.; Gigli, G.; Cingolani, R. *J. Am. Chem. Soc.* **1999**, *121*, 8920.
8. Stille, J. K. *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 508.
9. Farina, V.; Krishnamurthy, V.; Scott, W. J. *The Stille Reaction*; Wiley: Chichester, 1998.
10. Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.
11. Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147.
12. Caddick, S. *Tetrahedron* **1995**, *38*, 10403–10432.
13. Badone, D.; Baroni, M.; Cardamone, R.; Ielmini, A.; Guzzi, U. *J. Org. Chem.* **1997**, *62*, 7170.
14. Blettner, C. G.; König, W. A.; Stenzel, W.; Schotten, T. *J. Org. Chem.* **1999**, *64*, 3885.
15. Larhed, M.; Hallberg, A. *J. Org. Chem.* **1996**, *61*, 9582.
16. Barbarella, G.; Zambianchi, M.; Sotgiu, G.; Bongini, A. *Tetrahedron* **1997**, *53*, 9401.
17. Van Pham, C.; Burkhardt, A.; Shabana, R.; Cunningham, D. D.; Mark Jr., H. B.; Zimmer, H. *Phosphorus Sulfur Silicon* **1989**, *46*, 153.
18. Chosrovian, H.; Rentsch, S.; Grebner, D.; Dahm, U.; Birckner, E. *Synth. Met.* **1993**, *60*, 23.
19. Kanemitsu, Y.; Suzuki, K.; Masumoto, Y.; Tomiuchi, Y.; Shiraishi, Y.; Kuroda, M. *Phys. Rev. B* **1994**, *50*, 2301.
20. Oelkrug, D.; Egelhaaf, H. J.; Gierschner, J.; Tompert, A. *Synth. Met.* **1996**, 249.
21. Gigli, G. Private communication.
22. Garnier, F.; Yassar, A.; Hajlaoui, R.; Horowitz, G.; Deloffre, F.; Servet, B.; Ries, S.; Alnot, P. *J. Am. Chem. Soc.* **1993**, *115*, 8716.
23. Cornil, J.; Beljonne, D.; Calbert, J. P.; Brédas, J. L. *Adv. Mater.* **2001**, *13*, 1053.
24. Bongini, A.; Bottoni, A. *J. Phys. Chem. A* **1999**, *103*, 6800.
25. Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.