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Oligothiophene-substituted arenetricarbonylchromium complexes

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Abstract

The synthesis of oligothiophene-substituted arenetricarbonylchromium complexes using efficient palladium and nickel-catalyzed coupling reactions is reported. ***To cite this article: G. Loire et al., C. R. Chimie 6 (2003)***

Résumé

Des complexes arènetricarbonylchrome substitués par des oligothiophènes ont été synthétisés via une méthodologie basée sur des réactions de couplage catalysées par des complexes de palladium et de nickel. ***Pour citer cet article : G. Loire et al., C. R. Chimie 6 (2003)***

Keywords: thiophenes; tricarbonylchromium arenes; Stille reaction; *ipso* nucleophilic aromatic substitution

Mots clés : thiophènes ; complexes arènetricarbonylchrome ; réaction de Stille ; substitution nucléophile aromatique *ipso*

1. Introduction

α-Coupled polythiophenes have unusual properties and have attracted substantial interest [1–3]. In particular, oligothiophenes are of major importance in the second order non-linear optic field because molecules containing the sequence electron donor-spacer-electron acceptor present a higher hyperpolarizability when a thienyl spacer replaces a classical phenyl group [4–7]. Thus, we developed an access to functionalized oligothiophenes using transition-metal-catalyzed coupling reactions [8]. This approach enabled an easy synthesis of well-defined oligothiophenes that could be readily functionalized. In particular, we intended to prepare ortho- and meta-disubstituted arenetricarbonylchromium complexes in order to study their influence on the optoelectronic properties of the molecules.

2. Results and discussion

In the first part of this paper, we will describe the synthesis of oligothiophenes using Stille coupling re-

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action. In the second part, we will show how to modify them with arenetricarbonylchromium complexes.

The preparation of the key synthons **2a** and **2b** is depicted in Fig. 1. Commercially available 2-(3-thienyl)ethanol **1** was quantitatively O-benzylated according to a standard procedure [9] and regiospecifically brominated at the 2 position using *N*-bromosuccinimide in DMF owing to an aromatic electrophilic substitution [10–11]. Stannylation firstly required lithium–halogen exchange at low temperature, followed by addition of trimethyl or tributylstannyl chloride. Two different stannyl chlorides were used in order to compare their reactivity in the subsequent coupling reactions (Fig. 1).

As trialkylstannylthiophenes exhibit low stability upon silica-gel-chromatography purification [12] and as they were pure enough for being used as raw material, they were directly involved in the coupling reactions without any purification (Fig. 2).

Combination of Pd_2dba_3 as a catalyst precursor and $AsPh_3$ as ligand was used to generate the catalytic species required for the Stille reaction [13–17]. As shown in Fig. 2, compound **2a** reacted with the 2-bromothiophene **6**, 2,5-dibromothiophene **7** as well as 5,5'-dibromobithiophene **8** in DMF under the above-mentioned catalytic conditions, affording oligothiophenes **3**, **4** and **5** in reasonable yields. Optimizing the coupling conditions led to the use of low catalyst loading. Indeed, it has been determined that only 1.5% of palladium source and 3% of ligand are sufficient to ensure completion of the coupling reaction. Comparing the reactivity of tributyl and trimethylstannylthiophene proved that the reaction proceeds in comparable yields but is faster with **2a**. According to this result, the trimethylstannyl derivative **2a** was preferentially chosen for further reactions.

Moreover, we have shown that for the same reaction time (24 h), the temperature required for the coupling

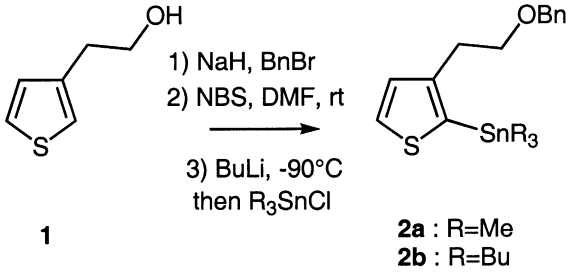


Fig. 1. Preparation of the key building blocks **2a** and **2b**.

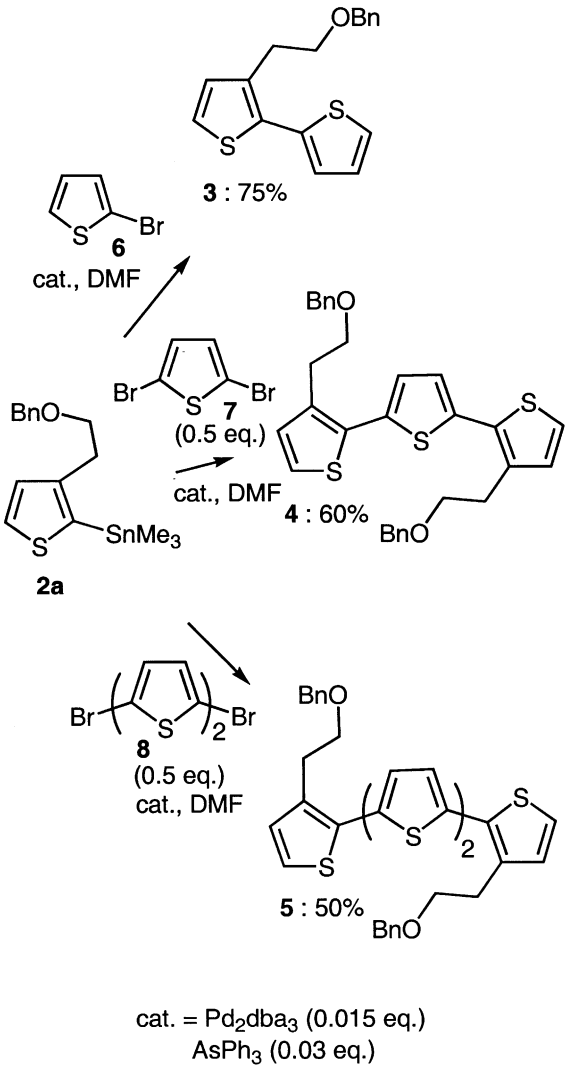


Fig. 2. Synthetic approach to oligothiophenes **3**–**5**.

varies from room temperature to 153 °C. It is interesting to note that the 2,5-dibromothiophene **7** only reacts at high temperature. In contrast, 5,5'-dibromobithiophene **8** behaves like two independent bromothiophene units, and the reaction proceeds at room temperature in 50% yield.

Using this approach, compound **5** could be selectively and quantitatively brominated at the α position [18] and accordingly coupled with stannane **2a**, affording sexithiophene **9** in 60% yield (Fig. 3). As already related for 5,5'-dibromobithiophene **8**, the independent character of the 5 and 5''' bromide atoms allowed the

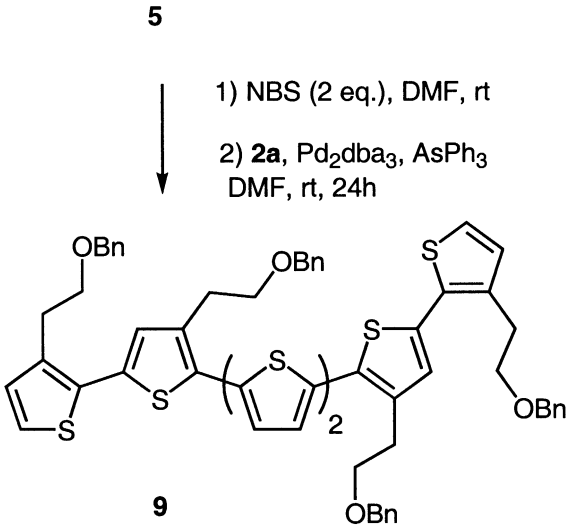


Fig. 3. Synthesis of sexithiophene **9**.

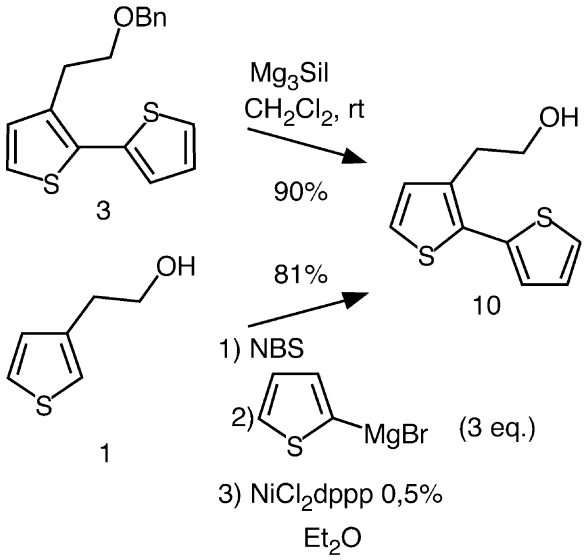


Fig. 4. Preparation of compound **10** by two different pathways.

reaction to be carried out at room temperature (Table 1).

Having in hands an efficient strategy for the preparation of well-defined oligothiophenes, we then investigated an access to more elaborated systems. The synthetic approach that we chose involved the deprotection of the benzyl ether. Preliminary attempts were carried out using the more readily available bithiophene **3** as model compound.

While hydrogenolysis did not afford the expected alcohol **10**, compound **3** was quantitatively debenzylated during 10 min using iodotrimethylsilane at room temperature in freshly distilled dichloromethane (Fig. 4) [19].

Alternatively, we also investigated a straightforward preparation of **10** based on the so-called Kumada coupling reaction [20–22]. This one-pot strategy involves bromination of thiophene **1** and coupling of the latter with 2-thienylmagnesium bromide in the presence of $NiCl_2$dppp (dppp = 1,3-bis(diphenylphosphino)propane). Interestingly, this approach led to **10** in 81% yield. In contrast to the Stille reaction (Fig. 2), the new pathway rapidly completed in a few minutes and required an easy purification step. Thus, using this very efficient method, we were able to prepare compound **10** in gram-scale quantity, allowing further functionalization.

Table 1
Summarized data for the coupling reactions

Oligothiophene	Temperature	Yield (%)
3	60 °C	75
4	153 °C	60
5	rt	50
9	rt	60

Considering our expertise in arene-chromium chemistry [23–24], we intended to link ortho- and meta-disubstituted arene-chromium complexes with planar chirality [25] to bithiophene **10** via an *ipso* substitution [26–33] (Fig. 5), in order to study the potential response of the resulting molecules in NLO [6].

The method involves an *ipso* nucleophilic aromatic substitution of the fluorine atom of *ortho*-fluorotoluene **11a** or *meta*-fluoroanisole **11b** chromium complexes [34] by the alcoholate derived from **10**. Alcohol **10** could either be deprotonated with *n*-butyllithium or sodium hydride without noticeable difference in the chemical yield. In a first attempt, the use of equimolar amounts of alcoholate and arene-chromium afforded an unsatisfying 30% yield. Fortunately, the use of an excess of alcoholate (2 equiv) led to a huge improvement as the coupled compounds **12a** and **12b** were isolated in 85 and 90% yield respectively.

Noteworthy, ^{1}H NMR data of compound **12a** showed interesting features. The proton signals of the ethoxy chain in compound **12a** exhibit the expected apparent triplet for H_a and H_b (Fig. 6a). However, the multiplicity of the signal corresponding to H_c and H_d

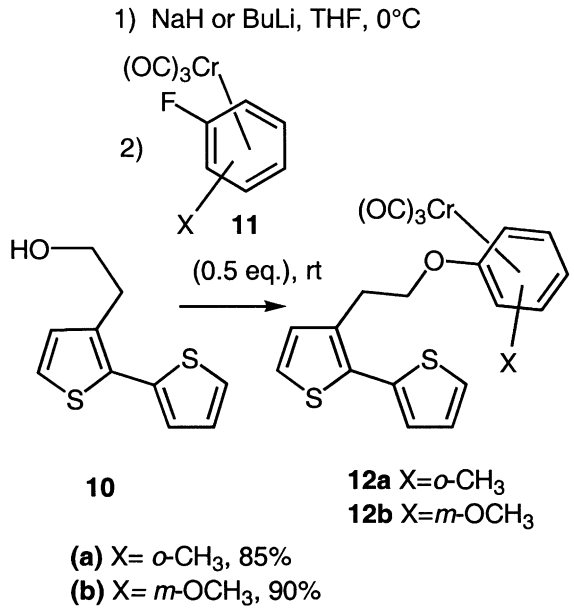


Fig. 5. *Ipso* substitution leading to organometallic bithiophenes **12a** and **12b**.

appears as a doublet of doublet of doublet, due to the fact that they are diastereotopic because of the presence of the stereogenic ortho-disubstituted arenetricarbonylchromium moiety. Selective irradiation of the upfield triplet confirmed the presence of two diastereotopic protons (Fig. 6b).

Interestingly, the ^{1}H NMR spectrum of complex **12b** revealed two triplets, corresponding to the ethoxy chain. In comparison with **12a**, the influence of the

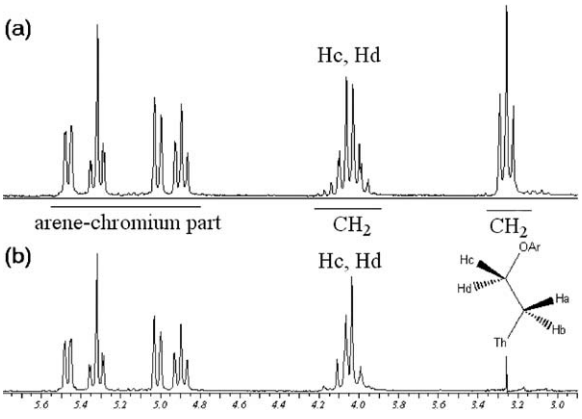


Fig. 6. Irradiation of Ha and Hb, protons of **12a** (Th = thiophene; Ar = arenetricarbonylchromium complexes).

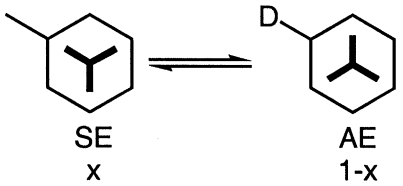


Fig. 7. Equilibrium between two conformers SE and AE.

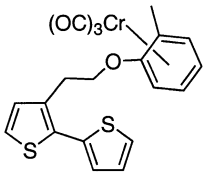
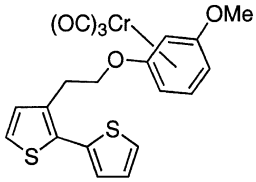
planar chirality on the multiplicity of the C_2H_4O unit can easily be explained by the fact that the diastereotopic H_c and H_d protons resonance frequencies are accidentally equal (isochronous).

It has been reported that in solution a substituted arenetricarbonylchromium complex can be considered to be in equilibrium between two conformations: the syn-eclipsed SE conformation with an (x) population and the anti-eclipsed AE conformation with an ($1 - x$) population (Fig. 7). Thus, if D is an electron-donor substituent, the major conformer is the SE one and if D is an electron-withdrawing group, the major conformer is the AE one [36].

The conformation of the $Cr(CO)_3$ tripod of complexes **12a** and **12b** can be studied in solution by analysing the ^{1}H NMR spectra. Indeed, in both cases the conformation of the major conformer was eclipsed with respect to the alkoxy group according to the data gathered in Table 2. The resonances of these eclipsed protons H_3 and H_5 occur, as expected, at high frequency [35]. The largest difference of chemical shift was 0.57 in the case of complex **12a** and reached 0.77 in the case of complex **12b**. Thus, it was possible to calculate the population x of the major isomer (Table 2) [36–40].

In conclusion, we have described a selective and efficient small-scale method for accessing bi-, tri-, quater- and sexithiophenes. The nickel-catalyzed method allowed us to prepare bithiophene **10** in quantitative yield from commercially available compounds. We also reported the first examples of arene-chromium complexes associated to oligothiophenes prepared in high yield by *ipso*-nucleophilic aromatic substitution S_NAr of the fluorine atom of *o*-fluorotoluene or *m*-fluoroanisole chromium complexes. Further insights on the non-linear properties of the molecules are currently in progress.

Table 2
Selected ^{1}H NMR data of complexes **12a** and **12b**. [a] $\delta H_3 - \delta H_4 = 0.57$; [b] $\delta H_5 - \delta H_4 = 0.43$; [c] $\delta H_5 - \delta H_6 = 0.31$; [d] $\delta H_5 - \delta H_4 = 0.77$; [e] $\delta H_i - \delta H_{i-1} = (2\,x - 1)\,\Delta\delta_{max}$, see refs [36–40]. The maximum difference $\Delta\delta_{max}$ used in this reference is 0.84 ppm in $CDCl_3$, which represents the difference of chemical shifts between the eclipsed 1,3,5-tri-methylbenzene and the anti eclipsed 1,3,5-tri-*tertio*-butylbenzene arenetricarbonylchromium complexes.

Complex	H_2	H_3	H_4	H_5	H_6	x[e]
	—	5.46	4.89[a]	5.32[b]	5.01[c]	68%
	5.13	—	4.78[d]	5.55	4.78	92%

3. Experimental part

3.1. General information

2-(3-thienyl)ethanol, 2-bromothiophene, Pd_2dba_3, *N*-bromosuccinimide were purchased from ACROS. Tributylstannyl chloride, $AsPh_3$, benzyl bromide, are available from Aldrich Chemical Co. Organic solvents were dried using standard procedures. Additionally, DMF was degassed with N_2 bubbling. Analysis apparatus: NMR spectrum on Brüker AC200 and ARX400, Infrared spectrum on Nicolet-Avatar 320 FT-IR, UV spectrum on UVIKON 923, MS/HRMS on Applied Biosystem Voyager DE-STR MALDI-TOF MS.

3.2. Bromination of 3-(2-benzyloxy-ethyl)-thiophene

To a solution of 7.012g (32mmol) of benzyloxy-2-(3-thienyl)ethanol in 100 ml of DMF was added dropwise during 1 h a solution of 5.77 g (32 mmol) of *N*-bromosuccinimide in 50 ml of DMF sheltered from light, the mixture was stirred overnight. The mixture was poured into 200 ml of water and extracted three times with diethylether. The organic layer was treated with a 10% solution of KOH and washed with water. The organic layer was dried over $MgSO_4$ and evaporated under reduced pressure. The crude product (8.905 g) was distilled under vacuum (E_1 = 110 °C, yellow oil, 7.132 g, 75%). The crude product can be also purified by silica-gel-column chromatography using a mixture of cyclohexane/dichloromethane: 80:20 (yield = 75%). ^{1}H NMR (200 MHz, $CDCl_3$) δ, ppm: 7.33 (m, 5H, H_{ar}); 7.20 (d, 1H, H_5, J = 5.9 Hz); 6.88 (d, 1H, H_4, J = 5.9 Hz); 4.54 (s, 2H, H_{benz}); 3.67 (t, 2H, H_{alk}, J = 6.9 Hz); 2.92 (t, 2H, H_{alk}, J = 6.9 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ, ppm: 138.4; 128.9; 128.5; 127.7; 125.5; 110.1; 73.0; 69.3; 30.2. Anal. calc. for $C_{13}H_{13}BrOS$: C 52.53, H 4.41; found: C 52.42, H 4.43.

*3.3. Stannylation of 3-(2-benzyloxy-ethyl)-2-bromo-thiophene, synthesis of **2a***

To a solution of 300 mg (1 mmol) of 3-(2-benzyloxy-ethyl)-2-bromo-thiophene in anhydrous diethylether at –90 °C was added dropwise 630 µl (1 mmol) of a solution of *n*-BuLi (1.6 M) in hexane. After 10 min, 1 ml (1 mmol) of a solution of Me_3SnCl (1M) in THF was added dropwise and the mixture was stirred for 1h at –90°C. Then, water was added directly at –90°C and the mixture was allowed to warm up at room temperature, then extracted with diethylether, washed with water, dried over $MgSO_4$ and evaporated under reduced pressure. The [3-(2-benzyloxy-ethyl)-thiophen-2-yl]-trimethyl-stannane **2a** was obtained in 90% yield and 10% yield of debrominated thiophene measured by NMR were recovered. The crude product is used without further purification. ^{1}H NMR (200 MHz, $CDCl_3$) δ, ppm: 7.5 (d, 1H, H_5, J = 4.9 Hz); 7.32 (m, 5H, H_{ar}); 7.13 (d, 1H, H_4, J = 4.9 Hz); 4.54 (s, 2H, H_{benz}); 3.67 (t, 2H, H_{alk}, J = 6.9 Hz); 2.92 (t, 2H, H_{alk},

J = 6.9 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ, ppm: 146.6; 138.6; 133.3; 131.0; 130.0; 128.6; 127.9; 127.8; 73.2; 71.5; 33.2; –7.6.

3.4. General procedure: coupling reactions

To a solution of [3-(2-benzyloxy-ethyl)-thiophen-2-yl]-trimethyl-stannane **2a** in DMF, was added a solution of brominated thiophene (1 or 0.5 equiv according to the coupling reaction), Pd_2dba_3 (0.015 equiv), $AsPh_3$ (0.03 equiv) in DMF. The mixture was stirred at the appropriated temperature (Table 1). After 24 h, the mixture was poured into water and extracted three times with diethylether. The combined organic phases were dried over $MgSO_4$ and evaporated under reduced pressure.

*3.5. Synthesis of 3-(2-benzyloxy-ethyl)-[2,2']bithiophenyl (**3**)*

Compound **3** was prepared according to the general procedure at 60 °C. The crude product can be also purified by silica-gel-column chromatography using a mixture of cyclohexane/dichloromethane: 70:30 then 60:40 (yellow oil, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 7.32 (m, 5H, H_{ar}); 7.30 (dd, 1H, $H_{5'}$, J = 5.2 Hz, J = 1.2 Hz); 7.19 (d, 1H, H_5, J = 5.2 Hz); 7.12 (dd, 1H, $H_{3'}$, J = 3.6 Hz, J = 1.2 Hz); 7.05 (dd, 1H, $H_{4'}$, J = 5.2 Hz, J = 3.6 Hz); 7.00 (d, 1H, H_4, J = 5.2 Hz); 4.53 (s, 2H, H_{benz}); 3.71 (t, 2H, H_{alk}, J = 7.1 Hz); 3.10 (t, 2H, H_{alk}, J = 7.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 138.4; 135.8; 135.6; 131.8; 130.1; 128.4; 127.6; 127.5; 127.4; 126.3; 125.6; 124.0; 72.9; 70.1; 29.6. UV/Visible ($CHCl_3$): λ (nm) = 293, ε = 8614 cm^{-1} mol^{-1} l. HRMS (MALDI-TOF) *m/z*: calculated for $C_{17}H_{16}OS_2$ (+Na) = 323.0549; found (+Na) = 323.0535.

*3.6. Synthesis of 3,3''-bis-(2-benzyloxy-ethyl)-[2,2';5',2'']terthiophene (**4**)*

Compound **4** was prepared according to the general procedure at 153 °C. The crude product was chromatographed on silica gel using a mixture of cyclohexane/dichloromethane: 65:35, 55:45 and then 45:55 (orange oil, 60% yield). ^{1}H NMR (200 MHz, $CDCl_3$) δ, ppm: 7.30 (m, 10H, H_{ar}); 7.20 (d, 2H, H_5, $H_{5''}$, J = 5.1 Hz); 7.05 (s, 2H, $H_{3'}$, $H_{4'}$); 7.00 (d, 2H, H_4, $H_{4''}$, J = 5.1 Hz); 4.53 (s, 4H, H_{benz}); 3.72 (t, 4H, H_{alk}, J = 6.9 Hz); 3.11 (t, 4H, H_{alk}, J = 6.9 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ, ppm: 138.4; 136.0; 135.9; 131.6; 130.3; 128.4; 127.7; 126.7; 124.2; 73.0; 70.2; 29.8. UV/visible ($CHCl_3$): λ (nm) = 334, ε = 17 000 cm^{-1} mol^{-1} l. HRMS (MALDI-TOF) *m/z*: calculated for $C_{30}H_{28}O_2S_3$ = 516.1423; found = 516.1246.

*3.7. Synthesis of 3,3'''-bis-(2-benzyloxy-ethyl)-[2,2';5',2'';5'',2''']quaterthiophene (**5**)*

Compound **5** was prepared according to the general procedure at room temperature. The crude product can be also purified by silica-gel-column chromatography using a mixture of cyclohexane/dichloromethane: 65:35 then 55:45 and then 45:55 (orange solid, 50% yield). ^{1}H NMR (200 MHz, $CDCl_3$) δ, ppm: 7.34 (m, 10H, H_{ar}); 7.20 (d, 2H, H_5, $H_{5'''}$, J = 5.2 Hz); 7.01 (d, 2H, H_4, $H_{4'''}$, J = 5.2 Hz); 7.12 (d, 2H, $H_{4'}$, $H_{3''}$, J = 3.9 Hz); 7.05 (d, 2H, $H_{3'}$, $H_{4''}$, J = 3.9 Hz); 4.56 (s, 4H, H_{benz}); 3.75 (t, 4H, H_{alk}, J = 6.9 Hz); 3.14 (t, 4H, H_{alk}, J = 6.9 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ, ppm: 138.5; 137.1; 135.9; 135.1; 131.7; 130.5; 128.6; 127.8; 127.1; 124.3; 124.2; 73.1; 70.2; 30.0. UV/visible ($CHCl_3$): λ (nm) = 377, ε = 28 000 cm^{-1} mol^{-1} l. HRMS (MALDI-TOF) *m/z*: calculated for $C_{34}H_{30}O_2S_4$ = 598.1123; found = 598.1044.

3.8. Bromination of 3,3'''-bis-(2-benzyloxy-ethyl)-[2,2';5',2'';5'',2''']quaterthiophene; preparation of 3'''-(2-benzyloxy-ethyl)-5,5'''-dibromo-3-(2-phenoxy-ethyl)-[2,2';5',2'';5'',2''']quaterthiophene

According to the bromination of **2**, the workup was done on 50 mg (0.083 mmol) of **5** and 30 mg of NBS (2 equiv) (orange solid, 60mg, 95% yield). ^{1}H NMR (200 MHz, $CDCl_3$) δ, ppm: 7.31 (m, 10H, H_{ar}); 7.07 (d, 2H, $H_{4'}$, $H_{3'''}$, J = 3.9 Hz); 6.98 (d, 2H, $H_{3'}$, $H_{4''}$, J = 3.9 Hz); 6.95 (s, 2H, H_4, $H_{4'''}$); 4.53 (s, 4H, H_{benz}); 3.68 (t, 4H, H_{alk}, J = 6.4 Hz); 3.03 (t, 4H, H_{alk}, J = 6.4 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ, ppm: 138.2; 137.2; 136.6; 133.7; 133.1; 128.5; 127.7; 127.4; 124.2; 110.9; 73.1; 69.7; 29.8. HRMS (MALDI-TOF) *m/z*: calculated for $C_{34}H_{28}Br_2O_2S_4$ = 755.9314; found = 755.9266.

*3.9. Synthesis of 3,4',3'''',3''''''-tetrakis-(2-benzyloxy-ethyl)-[2,2';5',2'';5'',2''';5''',2'''';5'''', 2''''']sexithiophene (**9**)*

Compound **9** was prepared according to the general procedure at room temperature. The crude product can

be also purified by silica-gel-column chromatography using a mixture of cyclohexane/dichloromethane: 50:50 (orange oil, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 7.35 (m, 20H, H_{ar}); 7.20 (d, 2H, H_5, H"", $H_{4''''}$); 7.02 (d, 2H, H_4, $H_{4''''}$, J = 5.1 Hz); 4.58 (s, 4H, H_{benz}); 4.56 (s, 4H, H_{benz}); 3.78 (t, 4H, H_{alk}, J = 7.1 Hz); 3.76 (t, 4H, H_{alk}, J = 7.1 Hz); 3.16 (t, 8H, H_{alk}, J = 7.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 138.5; 138.4; 137.1; 136.3; 135.9; 134.7; 134.3; 131.7; 131.7; 130.4; 129.5; 128.5; 127.7; 126.9; 126.8; 124.2; 124.1; 73.1; 70.2; 70.0; 30.1; 29.9; 29.8. UV/visible ($CHCl_3$): λ (nm) = 411; ε = 27 292 cm^{-1} mol^{-1} l. HRMS (MALDI–TOF) *m/z*: calculated for $C_{60}H_{54}O_4S_6$ = 1030.2316; found = 1030.2341.

*3.10. Synthesis of 2-[2,2']bithiophenyl-3-yl-ethanol (**10**) from 3-(2-benzyloxy-ethyl)-[2,2']bithiophenyl (**3**)*

To a 2-M solution of **3** (50 mg, 0.166 mmol) in freshly distilled dichloromethane (84 µl) was added dropwise 32 µl (0.166mmol) of iodotrimethylsilane. The reaction was stirred under nitrogen for 1 hour. The mixture is poured into water, extracted with dichloromethane, dried over Na_2SO_4 and evaporated under reduced pressure. The crude product can be also purified by silica-gel-column chromatography using dichloromethane (colourless oil, 32mg, 90% yield). ^{1}H NMR (200 MHz, $CDCl_3$) δ, ppm: 7.28 (dd, 1H, $H_{5'}$, J = 5.2 Hz, J = 1.5 Hz); 7.19 (d, 1H, H_5, J = 5.2 Hz); 7.15 (dd, 1H, $H_{3'}$, J = 3.7 Hz, J = 1.5 Hz); 7.04 (dd, 1H, $H_{4'}$, J = 5.2 Hz, J = 3.7 Hz); 6.96 (d, 1H, H_4, J = 5.2 Hz); 3.81 (t, 2H, H_{alk}, J = 6.9 Hz); 3.00 (t, 2H, H_{alk}, J = 6.9 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ, ppm: 135.7; 135.4; 132.3; 130.1; 127.6; 126.6; 125.8; 124.4; 62.8; 32.4. HRMS (MALDI–TOF) *m/z*: calculated for $C_{10}H_{10}OS_2$ (+Na) = 233.0065; found (+Na) = 233.0059. Anal. calc. for $C_{10}H_{10}OS_2$: C 57.11, H 4.79; found: C 56.95, H 4.99.

*3.11. Synthesis of 2-[2,2']bithiophenyl-3-yl-ethanol (**10**) from 2-(3-thienyl)-ethanol (**1**)*

Brominated thienylethanol was prepared according to the bromination of **2** from 2-(3-thienyl)-ethanol (2 g, 15.6 mmol) in 50 ml of DMF and NBS (2.387 g, 15.6 mmol) to yield 2.536 g (93%) of a colourless oil. A solution of 2.99 g (18 mmol) of 2-bromothiophene **6** and 446 mg of magnesium in anhydrous diethylether was stirred until complete dissolution of the metal; the brominated thienylethanol (1.27 g, 6.13 mmol) was added dropwise to the Grignard reagent. 0.5% of the nickel catalyst (17mg) was then added to the reaction. The reaction was stirred under N_2 for 30 min. The mixture was poured into water, extracted with diethylether, dried over $MgSO_4$ and evaporated under reduced pressure. The crude product can be also purified by silica-gel-column chromatography using dichloromethane (colourless oil, 1.16g, 90% yield). ^{1}H NMR (200 MHz, $CDCl_3$) δ, ppm: 7.28 (dd, 1H, $H_{5'}$, J = 5.2 Hz, J = 1.5 Hz); 7.19 (d, 1H, H_5, J = 5.2 Hz); 7.15 (dd, 1H, $H_{3'}$, J = 3.7 Hz, J = 1.5 Hz); 7.04 (dd, 1H, $H_{4'}$, J = 5.2 Hz, J = 3.7 Hz); 6.96 (d, 1H, H_4, J = 5.2 Hz); 3.81 (t, 2H, H_{alk}, J = 6.9 Hz); 3.00 (t, 2H, H_{alk}, J = 6.9 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ, ppm: 135.7; 135.4; 132.3; 130.1; 127.6; 126.6; 125.8; 124.4; 62.8; 32.4. HRMS (MALDI–TOF) *m/z*: calculated for $C_{10}H_{10}OS_2$ (+Na) = 233.0065; found (+Na) = 233.0059. Anal. calc. for $C_{10}H_{10}OS_2$: C 57.11, H 4.79; found: C 56.95, H 4.99.

*3.12. Synthesis of (**12a**) and (**12b**)*

Compounds **12a** and **12b** are light sensitive, usual precautions must be taken. To a solution of 329 mg (1.6 mmol) of **10** in 5 ml of dried THF was added dropwise, at 0 °C, 980 µl (1.6 mmol) of *n*-BuLi (1.6 M in hexane) or 61.1 mg of NaH (60% in mineral oil). The mixture was stirred for 10 min at 0 °C. A solution of 0.5 equiv of arenetricarbonylchromium **11a** [41] or **11b** [34] in THF was added to the reaction at 0 °C. The reaction was stirred at 0 °C for 10 min and at room temperature for four days. The mixture was poured into water, extracted with diethylether, dried over $MgSO_4$ and evaporated under reduced pressure. The crude products can be also purified by silica-gel-column chromatography using a mixture of cyclohexane/dichloromethane: 50:50 for both products to yield 85% of **12a** and 90% for **12b. Compound 12a**: ^{1}H NMR (200 MHz, $CDCl_3$) δ, ppm: 7.33 (dd, 1H, $H_{5'}$, J = 4.9 Hz, J = 1.5 Hz); 7.23 (d, 1H, H_5, J = 4.9 Hz); 7.15 (dd, 1H, $H_{3'}$, J = 3.4 Hz, J = 1.5 Hz); 7.07 (dd, 1H, $H_{4'}$, J = 4.9 Hz, J = 3.4 Hz); 7.02 (d, 1H, H_4, J = 4.9 Hz); 5.46 (dd, 1H, H_{ArCr}, J = 6.4 Hz, J = 1.5 Hz); 5.32 (td, 1H, H_{ArCr}, J = 6.4 Hz, J = 1.5 Hz); 5.01 (d, 1H, H_{ArCr}, J = 6.4 Hz); 4.89 (t, 1H, H_{ArCr}, J = 6.4 Hz); 4.04 (m, 2H, H_{alk}); 3.26 (t, 2H, H_{alk}, J = 6.9 Hz). ^{13}C NMR (50

MHz, $CDCl_3$) δ, ppm: 233.8; 140.5; 135.3; 134.0; 132.6; 130.1; 127.7; 126.8; 126.0; 124.6; 98.5; 97.0; 92.8; 86.6; 68.8; 28.7; 16.3. UV/visible ($CHCl_3$): λ (nm) = 300; ε = 13 082 cm^{-1} mol^{-1} l. IR (KBr): 1867, 1954 cm^{-1} (ν_{CO}). **Compound 12b**: ^{1}H NMR (200 MHz, $CDCl_3$) δ, ppm: 7.33 (dd, 1H, $H_{5'}$, J = 5.4 Hz, J = 0.98 Hz); 7.22 (d, 1H, H_5, J = 5.4 Hz); 7.14 (dd, 1H, $H_{3'}$, J = 3.4 Hz, J = 0.98 Hz); 7.07 (dd, 1H, $H_{4'}$, J = 5.4 Hz, J = 3.4 Hz); 7.00 (d, 1H, H_4, J = 5.4 Hz); 5.55 (t, 1H, H_{ArCr}, J = 6.9 Hz); 5.13 (t, 1H, H_{ArCr}, J = 2 Hz); 4.78 (td, 2H, H_{ArCr}, J = 6.9 Hz, J = 2 Hz); 4.05 (t, 2H, H_{alk}, J = 6.9 Hz); 3.71 (s, 3H, CH_3); 3.23 (t, 2H, H_{alk}, J = 6.9 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ, ppm: 233.6; 143.9; 143.1; 133.7; 130.0; 127.7; 126.7; 126.0; 124.6; 93.2; 73.4; 73.0; 69.7; 68.6; 55.8; 28.7. UV/Visible ($CHCl_3$): λ (nm) = 302; ϵ = 14325 cm^{-1} mol^{-1} l. IR (KBr): 1870, 1952 cm^{-1}(ν_{CO}).

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