Tetrahedron 68 (2012) 5599–5605

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Bridged 3,3‴-didodecylquaterthiophene-based dimers: design, synthesis, and optoelectronic properties

Claude Niebel [a,*], Maud Jenart [a], Christelle Gautier [b], Yves Henri Geerts [a]

[a] Université Libre de Bruxelles (ULB), Laboratory of Polymer Chemistry, C.P. 206/01, Boulevard du Triomphe, 1050 Brussels, Belgium
[b] Université d'Angers, Laboratoire MOLTECH-Anjou, CNRS UMR 6200, 2 boulevard Lavoisier, 49045 Angers, France

ARTICLE INFO

Article history:
Received 29 February 2012
Received in revised form 13 April 2012
Accepted 19 April 2012
Available online 26 April 2012

Keywords:
Oligothiophene synthesis
Organic electronics
Mitsunobu coupling
Reductive amination
Optoelectronic properties

ABSTRACT

Five functionalized quaterthiophene dimers including a non-conjugated bridge have been designed and efficiently synthesized. The synthetic pathways explored toward these dimers revealed unexpected features, such as the direct formation of secondary and tertiary quaterthiophene amines through a procedure initially developed for the preparation of primary amine exclusively. All these dimers possess a promising potential for the elaboration of semiconducting materials with a charge transport of higher dimensionality compared to quaterthiophene.

1. Introduction

Charge transfer in π-conjugated oligomers is a crucial mechanism in the field of organic electronics.[1–3] Numerous studies have been made on organic and organometallic donor–bridge–acceptor systems to determine the parameters influencing the charge transfer.[4–6] These fundamental understandings have also lead to the distinction between two intramolecular charge transfer mechanisms: the superexchange, also named charge-tunneling, and the hopping mechanism.[4,6,7] The charge-tunneling is predominant when the transient reduction of the bridging moiety is thermodynamically impossible. The distance decay constant (β) and tunneling-energy gap ($\Delta\varepsilon$) appear of pivotal importance for superexchange charge transfer.[8] Indeed, in their study of the photoinduced charge transfer in synthetic DNA hairpin, Wasiliewski et al. have shown the exponential decrease of its rate constant with increasing the distance between donor–acceptor, made of guanine and stilbene, respectively.[9] Beratan et al. have also investigated the electron transfer in synthetic DNA hairpin with an additional focus on the influence of donor–acceptor energetics relative to the bridge separating both redox centers. Their results show the strong dependence of DNA electron superexchange not on the donor–acceptor distance but rather on the tunneling-energy gap.[10] In addition, most of the numerous investigations made on the superexchange charge transfer in organic and organometallic donor–bridge–acceptor systems have involved the one-step tunneling through a uniform and rectangular barrier. Wenger et al. have extended this study using metal complex based dyads with a molecular bridge composed of *p*-dimethoxybenzene, which imposes a so called double barrier to hole transfer.[11] In this particular donor–bridge–acceptor system, the photoinduced hole transfer has been measured to be one order of magnitude more rapid than hole transfer across a comparable uniform barrier, emphasizing even further the importance of the tunneling-energy gap $\Delta\varepsilon$.

Besides, dyads composed of two identical organic redox centers separated by a bridging unit have also been studied for charge delocalization purposes.[12,13] If most of these investigations have been made on systems with a π-conjugated bridge, some attention has also been paid on dyads incorporating a non-conjugated spacer. For instance, Müllen et al. have shown that the mode of linking two anthryl electrophores through a non-conjugated bridge drastically affects the rate of the intramolecular electron transfer.[14] Our group has recently reported on the interest of introducing a non-conjugated ethylene bridge between two 3,3‴-didodecylquaterthiophene cores (**B1**) to enhance the charge transport dimensionality in this type of semiconducting materials (Fig. 1).[15] Indeed, 3,3‴-didodecylquaterthiophene (**1**) is known to form a lamellar-type structure with a one-dimensional charge transport ability.[16] The ethylene bridge in **B1** allows an additional electronic coupling between the two oligothiophenes cores, pushing the solid state charge transport dimensionality from 1D to 2D.[15]

* Corresponding author. Tel.: +32 2650 5390; fax: +32 2650 5410; e-mail address: claude.niebel@ulb.ac.be (C. Niebel).

0040-4020/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2012.04.072

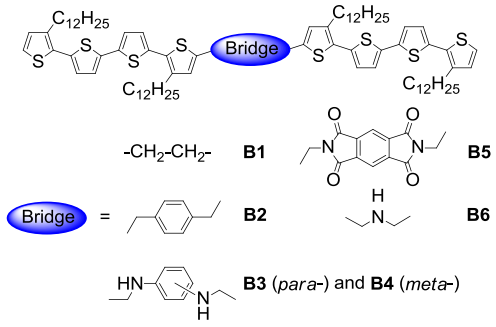


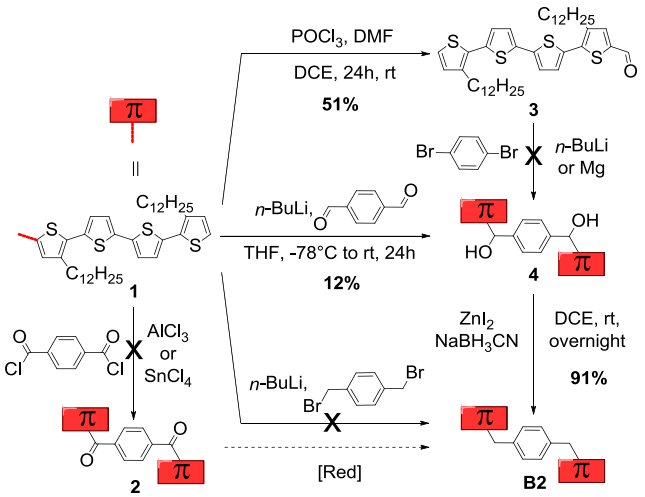
Fig. 1. Bridged didodecylquaterthiophene dimers **B1**–**B6**.

The derivatization of the non-conjugated spacer in **B1** is thought to analogously affect the charge transport properties of this type of semiconducting materials. The presence of an additional organic moiety within the bridge will provide the quaterthiophene dimer with a supplementary functional group together with modifying the β and Δε of the system. The dimers **B2**, **B3**/**B4** and **B5** incorporate, respectively a phenylene, diamino phenylene, and pyromellitic diimine units within the bridge (Fig. 1), which obviously enlarge the distance between the two oligothiophene cores and thus increase the β coefficient compared to the reference **B1**. The introduction of a heteroatom, such as nitrogen in the non-conjugated spacer is however thought to conduct to an energetic double barrier, potentially shifting the tunneling-energy gap Δε in favor of a promoted intramolecular charge transfer comparable to the one observed by Wenger et al.[11] (See Fig. S12 in Supplementary data). This feature would also allow an enhancement of the charge transport dimensionality from 1D to 2D in such materials. Quaterthiophene dimers **B6** and **B3**/**B4** present such an amino-functionalization within the bridge compared to **B1** and **B2**, respectively. The dimers **B2**–**B6**, in addition to **B1**, therefore represent some valuable oligothiophenes for the production of functionalized semiconducting materials with a higher charge transport dimensionality compared to quaterthiophene **1**. In this purpose, we have decided to prepare the 3,3‴-didodecylquaterthiophene-based dimers **B2**–**B6**.

In this synthetic paper, we report on the synthetic pathways explored for the preparation of quaterthiophene bridged dimers **B2**–**B6**. The optoelectronic properties of all these dimers will then be discussed, together with the references **1** and **B1** ones.

2. Synthesis

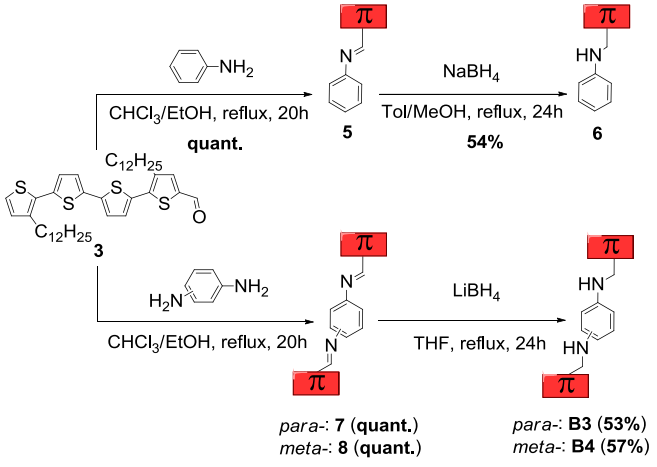
The bridged quaterthiophene reference **B1** was prepared from the mono-formylated derivative **3** in two steps.[15] Several different synthetic pathways were investigated to produce the phenylene derivative **B2**. First of all, a typical $AlCl_3$ or $SnCl_4$ mediated Friedel and Crafts acylation was tried using terephthaloyl dichloride as acylating agent.[17] The aim was to produce the intermediate **2**, which could further be reduced into target **B2** (Scheme 1). This acylation was however unsuccessful and led to the complete recovery of unreacted quaterthiophene **1**. The attempt of direct dinucleophilic substitution of 1,4-bis(bromomethyl)benzene by a mono-lithiated thiophene intermediate also resulted in the complete recovery of starting quaterthiophene **1**. Moreover, the addition of *para*-bis-lithiated benzene, prepared from *para*-dibromobenzene,[18] to a solution of quaterthiophene mono-aldehyde **3** engendered the partial decompostion of the starting aldehyde without any traces of the expected diol **4** (Scheme 1).



Scheme 1. Explored synthetic pathways toward quaterthiophene dimer **B2**.

The diol intermediate **4** was finally prepared by the dinucleophilic attack of mono-lithiated quaterthiophene on terephthaldicarboxaldehyde. The low yield of this reaction (12%) can be explained by the relatively low reactivity of **1** mono-lithiated intermediate. This low reactivity is also illustrated by the poor yield obtained for the preparation of the mono-aldehyde **3** following a conventional *n*-BuLi/DMF procedure.[15] The subsequent reductive deoxygenation of diol **4** toward **B2** was carried out using the convenient and efficient ZnI_2–$NaCNBH_3$ procedure described by Lau et al.[19]

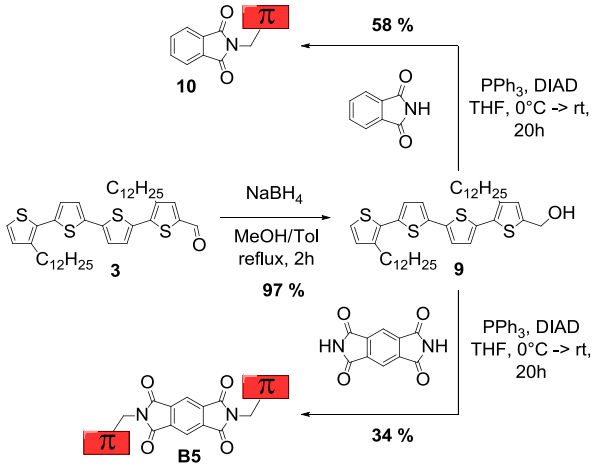
Concerning the preparation of the phenylenediamine derivatives **B3** and **B4**, synthetic investigations were firstly tried on simple aniline (Scheme 2). The condensation of aniline with the mono-quaterthiophene aldehyde **3** went smoothly, even without the use of a Dean Stark apparatus to remove the water formed during the reaction. The reduction of the imine **5** needed hard conditions. Indeed, 20 h of reflux in the presence of about 5 equiv of sodium borohydride were not sufficient to totally reduce **5**, and the addition of a new portion of sodium borohydride (~5 equiv) was necessary to complete the reaction. The commonly extracted crude product appeared to be almost pure looking at its ^1H NMR, and is obtained in nearly quantitative yield. Nevertheless, its further purification by chromatography resulted in partial decomposition of the target amine **6** on silica gel, which explains its isolated yield of only 54%. As for the aniline, the condensations of *para*- and *meta*-penylenediamine with mono-aldehyde **3** allowed the preparation of imines **7** and **8**, respectively in quantitative yield. The same



Scheme 2. Synthesis of quaterthiophene derivatives **6**, **B3** and **B4**.

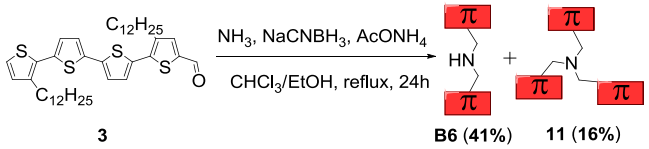
procedure was also applied to *ortho*-phenylenediamine, but in this case the reaction didn't proceed to the formation of the expected diimine. This feature is certainly explained by sterical hindrance effects due to the spatial proximity of the two amino functions in *ortho*-phenylenediamine. It is also worth to notice that both diimine derivatives **7** and **8** are used further without any additional purification. Indeed, an attempt of purification by chromatography shows, in both cases, the partial hydrolysis of the diimine on silica gel, even after neutralization of silica gel acidity with triethylamine. The reduction of both diimines required even stronger conditions than the one used for **5**. The crude product obtained after a 24 h reflux of **7** and **8**, respectively, in the presence of 10 equiv of sodium borohydride was actually composed of a mixture of mono- and direduced species. The use of lithium borohydride in large excess (30 equiv) was finally sufficient to get a complete reduction leading to target **B3** and **B4**. As in the case of **6**, both bridged dimers **B3** and **B4** were collected nearly quantitatively as crude products. However, their purification by chromatography on silica gel again induced a loss of isolated compounds due to partial decomposition.

The bridged quaterthiophene derivative **B5** was thought to be produced through a Mitsunobu coupling involving the quaterthiophene primary alcohol **9** (Scheme 3). **9** was nearly quantitatively obtained by a simple reduction of the corresponding aldehyde **3** using sodium borohydride. Concerning the coupling step, synthetic investigations were firstly tried on phthalimide before going to its pyromellitic analog. Typical Mitsunobu conditions,[20] including the slow addition of diisopropyl azodicarboxylate to a mixture of the other reagents, allowed the synthesis of the imide **10** in an acceptable yield of 58%. The same synthetic procedure was then used to prepare the target bridged derivative **B5** in 34% yield using pyromellitic diimide as nucleophilic agent.



Scheme 3. Synthesis of quaterthiophene derivatives **10** and **B5**.

Finally, the bridged amino-derivative **B6** was surprisingly obtained through a direct reductive amination of the mono-aldehyde **3** using aqueous ammonia (Scheme 4). The reaction conditions used here were the same as the one described by Dangerfield et al. for the synthesis of primary amines from furanoside and analogs.[21] However, in our case, the reductive amination didn't stop to the primary amine and proceeded to the secondary (**B2**) and also tertiary amine **11**. This feature can be explained by the formation of aldehyde **3** π-stacks or aggregates, which would therefore promote the subsequent reaction of the amine just formed with neighboring aldehyde. The conversion was nearly quantitative looking at the crude product ^{1}H NMR, but the yield of the isolated compounds decreased significantly due to their partial decomposition on silica gel during the purification step, even after neutralization of silica gel acidity.



Scheme 4. Reductive amination of quaterthiophene aldehyde **3** using aqueous ammonia.

3. Optoelectronic properties in dilute solution

The absorption and fluorescence properties of quaterthiophene **1** and its the six bridged derivatives **B1**–**B6** were recorded in THF solutions (See Fig. S9 and S10 in Supplementary data). All the absorption spectra present an analog predominant absorption band, which is known to correspond to the quaterthiophene HOMO–LUMO transition.[22,23] The structureless feature of all these absorption bands shows the flexibility of the two oligothiophene cores in the ground state. A small red shift of the λ_{max}(abs) is observed when going from the quaterthiophene **1** to its bridged derivatives **B1**–**B6**, which is certainly due to inductive effect of the bridge. Moreover, the λ_{max}(abs) of each bridged dimers are closely the same indicating that the nature of the non-conjugated bridge has no influence on the quaterthiophene electronic transitions. The extinction coefficients of the dimers **B1**–**B6** are of the same order of magnitude and correspond to the double of their precursor **1** one, as expected (Table 1). Besides, all the fluorescence spectra of these compounds show vibrational structure due to the known rigid quinoid form adopted by oligothiophenes in S_1 excited state.[24–26] A light bathochromic shift is again observed when going from λ_{max}(em) of **1** to the dimers **B1**–**B6**. As it is the case for the UV–vis absorption, the λ_{max}(em) of the derivatives **B1**–**B6** are almost equal, which confirms the absence of influence of the bridge on the quaterthiophene electronic transition (Table 1).

Table 1
Molar extinction coefficients ε_{max}, absorption (λ_{max}(abs)) and fluorescence (λ_{max}(em)) maximum of quaterthiophene **1** and its bridged derivatives **B1**–**B6** in 10^{-5} M solution in THF

	ε_{max} (M^{-1} cm^{-1})	λ_{max}(abs) (nm/eV)	λ_{max}(em) (nm/eV)
1	30,000	376/3.30	453/2.74
B1	61,000	384/3.23	458/2.71
B2	59,000	383/3.24	460/2.70
B3	64,000	384/3.23	459/2.70
B4	63,000	386/3.22	460/2.70
B5	64,000	382/3.25	458/2.71
B6	59,000	384/3.23	459/2.70

Noteworthy, the electrochemical properties of **1** and its derivatives **B1**–**B6** were investigated by cyclic voltammetry (CV). CVs were achieved in 0.1 M Bu_4NPF_6/CH_2Cl_2 solutions containing 1 mM of compounds. The CV of **1** shows an expected fast electropolymerization initiated by the oxidation of the quaterthiophene core. Unfortunately, all the bridge derivatives **B1**–**B6** follow the same oxidative polymerization, even after only one cycle, which makes the calculation and comparison of their oxydation potentials unfeasable (See Fig. S11 in Supplementary data).

4. Conclusion

In conclusion, we successfully synthesized the target bridged quaterthiophene dimers **B2**–**B6** starting from easily available 3,3‴-didodecylquaterthiophene **1**. The synthetic pathways explored toward these dimers revealed some unexpected features, such as the

low reactivity of **1** mono-lithiated intermediate or the direct formation of secondary (**B6**) and tertiary amine (**11**) through a procedure initially developed for the preparation of primary amine exclusively. The synthetic procedure developed for the preparation of **B3**, **B4**, and **B6** is easily adaptable to scale up the production of large amounts of materials, however those three dimers appeared to be quite unstable on silica gel. All the synthesized dimers **B2**–**B6** possess a high potential for the elaboration of semiconducting materials with a charge transport of higher dimensionality compared to **1**. The next steps beyond the scope of this synthetic paper involve the fabrication and characterization of thin films made of these dimers, to measure and compare the charge carrier mobility in field-effect transistors.

5. Experimental section

5.1. Materials and methods

Unless otherwise noted, all chemicals were purchased from Aldrich or Acros and used without further purification. THF was dried by conventional method (Na/benzophenone distillation procedure under argon) and collected with glass syringes. TLC: SiO_2 Silica gel $60F_{254}$ on aluminum sheet (Merck). Column chromatography: Silica gel 60 (particle size 0.063–0.200 mm, Merck). ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) were recorded on Bruker Avance 300 at room temperature. Chemical shifts are given in parts per million and coupling constants *J* in Hertz. The residual signal of the solvent was taken as internal reference standard. EI-HRMS measurements were made on a Waters AutoSpec 6 and MALDI-ToF experiments on a Waters QToF Premier. Absorption spectra were recorded on an Agilent 8453 spectrophotometer in a quartz cell (optical path of 1 cm) in tetrahydrofuran (concentration solutions of 10^{-5} M were used). Emission spectra were measured on an Aminco Bowman series 2 luminescence spectrophotometer.

5.2. Synthetic procedures for the preparation of B2

*5.2.1. 1,4-Phenylenebis((3,3‴-didodecyl-[2,2′:5′,2″:5″,2‴-quaterthiophen]-5-yl)methanol) (**4**).* To a solution of quaterthiophene **1** (0.170 g, 0.25 mmol) in dry THF (15 mL) was added dropwise a 1.6 M solution of *n*-butyllithium in hexanes (0.19 ml, 0.31 mmol) at −30 °C under an argon atmosphere. The reaction mixture was warmed to 0 °C and stirred at this temperature for 1 h. It was then cooled down to −78 °C, and a solution of terephthaldicarboxaldehyde in dry THF (3 mL) was added in one portion. The reaction mixture was allowed to warm up slowly to room temperature overnight. The reaction was then quenched by the addition of water (10 mL). The mixture was extracted with dichoromethane (2*50 mL). The combined organic layers were washed with water and brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluant: petroleum ether/ethyl acetate 8/2 v/v) affording the target bridged quaterthiophene **4** (0.066 g, 0.04 mmol, 12%) as a yellowish oil. R_f (petroleum ether/ethyl acetate 4/1 v/v): 0.57; ^1H NMR ($CDCl_3$, 300 MHz) δ: 7.50 (s, 4H, $-C_6H_4-$), 7.17 (d, 2H, J=5.2 Hz, H5‴), 7.10 (d, 2H, J=3.7 Hz, H3″ or H4′), 7.09 (d, 2H, J=3.7 Hz, H4′ or H3″), 7.00 (d, 2H, J=3.8 Hz, H4″), 6.97 (d, 2H, J=3.8 Hz, H3′), 6.93 (d, 2H, J=5.2 Hz, H4‴), 6.76 (s, 2H, H4), 5.99 (s, 2H, $-CH$OH−), 2.81–2.65 (m, 8H, $C_{thiophene}-CH_2-$), 2.65 (br s, 2H, -O*H*), 1.70–1.55 (m, 8H, $C_{thiophene}-CH_2-CH_2-$), 1.42–1.20 (m, 72H, $-(CH_2)_9-CH_3$), 0.92–0.83 (m, 12H, $-CH_3$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 145.9, 142.8, 140.0, 139.6, 137.0, 136.9, 135.5, 135.2, 130.6, 130.4, 130.2, 128.1, 126.7, 126.62, 126.56, 124.0, 123.9, 72.4, 32.1, 30.8, 30.7, 29.82, 29.76, 29.75, 29.7, 29.61, 29.59, 29.5, 29.4, 22.9, 14.3; HRMS (MALDI-ToF): [$M^{+\bullet}$] calcd for $C_{88}H_{122}O_2S_8$ *m*/*z* 1466.7211, found 1466.7186.

*5.2.2. 1,4-Bis((3,3‴-didodecyl-[2,2′:5′,2″:5″,2‴-quaterthiophen]-5-yl)methyl)benzene (**B2**).* Sodium cyanoborohydride (0.042 g, 0.67 mmol) was added at room temperature to a suspension of zinc iodide (0.043 g, 0.14 mmol) and **4** (0.066 g, 0.05 mmol) in 1,2-dichloroethane (10 mL). The reaction mixture was stirred overnight at room temperature. It was then filtered over silica gel using dichloromethane as eluant to give **B2** (0.059 g, 0.04 mmol, 91%) as a yellow waxy solid. R_f (petroleum ether/dichloromethane 4/1 v/v): 0.60; ^1H NMR ($CDCl_3$, 300 MHz) δ: 7.25 (s, 4H, $-C_6H_4-$), 7.17 (d, 2H, J=5.2 Hz, H5‴), 7.10 (d, 2H, J=3.6 Hz, H3″ or H4′), 7.09 (d, 2H, J=3.6 Hz, H4′ or H3″), 7.01 (d, 2H, J=3.8 Hz, H4″), 6.96–6.92 (m, 4H, H3′, H4‴), 6.66 (s, 2H, H4), 4.08 (s, 4H, $C_{thiophene}-CH_2-C_6H_4$), 2.82–2.66 (m, 8H, $C_{thiophene}-CH_2-$), 1.71–1.55 (m, 8H, $C_{thiophene}-CH_2-CH_2-$), 1.42–1.20 (m, 72H, $-(CH_2)_9-CH_3$), 0.92–0.83 (m, 12H, $-CH_3$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 142.6, 140.0, 139.8, 138.4, 137.0, 136.5, 135.7, 135.3, 130.5, 130.2, 129.0, 128.5, 126.6, 126.1, 123.93, 123.88, 123.8, 77.6, 77.2, 76.7, 36.0, 32.1, 30.81, 30.75, 29.82, 29.76, 29.7, 29.6, 29.5, 29.4, 22.9, 14.3; HRMS (MALDI-ToF): [$M^{+\bullet}$] calcd for $C_{88}H_{122}S_8$ *m*/*z* 1434.7312, found 1434.7319.

5.3. Synthetic procedures for the preparation of 6, B3, and B4

*5.3.1. N-((3,3‴-Didodecyl-[2,2′:5′,2″:5″,2‴-quaterthiophen]-5-yl) methylene)aniline (**5**).* A solution of quaterthiophene aldehyde **3** (0.100 g, 0.14 mmol) and aniline (0.013 g, 0.14 mmol) in an equivolume mixture (4 ml) of chloroform and absolute ethanol was gently refluxed for 20 h under inert atmosphere. The reaction mixture was then cooled down to room temperature and concentrated under reduced pressure. The residue was washed several times with methanol to afford the expected imine **5** (0.011 g, 0.14 mmol, quantitative) as a dark red oil. This crude product was used directly in the next step without further purification. R_f (toluene): 0.90; ^1H NMR ($CDCl_3$, 300 MHz) δ: 8.48 (s, 1H, $-CH$=N−), 7.42–7.35 (m, 2H, $-CH$=CH−C*H*=), 7.31 (s, 1H, H4), 7.25–7.14 (m, 7H, H3″, H4′, H5‴, −CH=C*H*−*C*−*N*=, −CH=C*H*−CH=), 7.03 (d, 1H, J=3.8 Hz, H3′), 6.95 (d, 1H, J=5.2 Hz, H4‴), 2.86–2.75 (m, 4H, $C_{thiophene}-CH_2-$), 1.76–1.59 (m, 4H, $C_{thiophene}-CH_2-CH_2-$), 1.44–1.22 (m, 36H, $-(CH_2)_9-CH_3$), 0.88 (t, 7H, J=6.7 Hz, $-CH_3$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 152.5, 151.5, 140.1, 140.02, 139.97, 138.0, 136.5, 135.9, 135.8, 135.2, 134.8, 130.3, 130.2, 129.4, 129.2, 127.4, 126.6, 126.1, 124.3, 124.1, 124.0, 121.2, 115.2, 32.1, 30.8, 30.4, 29.8, 29.7, 29.6, 29.5, 29.4, 22.8, 14.3.

*5.3.2. N-((3,3‴-Didodecyl-[2,2′:5′,2″:5″,2‴-quaterthiophen]-5-yl) methyl)aniline (**6**).* To a solution of quaterthiophene imine **5** (0.100 g, 0.13 mmol) in a mixture of toluene (5 ml) and methanol (10 ml) was added sodium borohydride (0.025 g, 0.65 mmol) at room temperature. The reaction mixture was refluxed for 20 h under an inert atmosphere. A TLC of the reaction medium showed the presence of the expected aniline **6** together with unreacted starting imine **5**. A new portion of sodium borohydride (0.025 g, 0.65 mmol) was then added to the reaction mixture and 4 additional hours of reflux were necessary to complete the reduction. The mixture was then cooled down to room temperature, poured into ice/water and extracted with dichloromethane (2*50 mL). The combined organic layers were washed with water and brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluant: toluene/petroleum ether 1/1 v/v) affording the target quaterthiophene aniline **6** (0.054 g, 0.07 mmol, 54%) as a yellowish oil, which solidifies upon cooling. R_f (toluene/petroleum ether 1/1 v/v): 0.57; mp: 49.1–52.9 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ: 7.24–7.15 (m, 3H, H5‴, $-CH$=CH−C*H*=), 7.11 (d, 2H, J=3.7, H3″ or H4′), 7.10 (d,

2H, J=3.7, H4′ or H3″), 7.01 (d, 1H, J=3.8 Hz, H4″), 6.97 (d, 1H, J=3.8 Hz, H3′), 6.94 (d, 1H, J=5.2 Hz, H4‴), 6.85 (s, 1H, H4), 6.76 (t, 1H, J=7.3 Hz, −CH=C*H*−CH=), 6.72–6.67 (m, 2H, −CH=C*H*−*C*−*N*=), 4.46 (s, 2H, −CH_2−NH−), 4.07 (br s, 1H, −N*H*−), 2.82–2.68 (m, 4H, $C_{thiophene}$−CH_2−), 1.70–1.56 (m, 4H, $C_{thiophene}$−CH_2−CH_2−), 1.41–1.19 (m, 36H, −$(CH_2)_9$−CH_3), 0.87 (t, 6H, J=6.7 Hz, −CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 147.7, 141.4, 140.0, 139.8, 136.9, 136.8, 135.5, 135.4, 130.5, 130.2, 129.6, 129.5, 128.2, 126.7, 126.4, 124.0, 123.9, 118.3, 113.3, 43.9, 32.1, 30.82, 30.75, 29.82, 29.76, 29.7, 29.62, 29.58, 29.5, 29.4, 22.9, 14.3; HRMS (MALDI-ToF): [$M^{+\bullet}$] calcd for $C_{47}H_{65}NS_4$ m/z 771.4000, found 771.3996.

*5.3.3. General procedure for the preparation of the diimine derivatives **7** and **8**.* A solution of quaterthiophene aldehyde **3** (1 equiv) and phenylenediamine (2 equiv) in an equivolume mixture (6 ml) of chloroform and absolute ethanol was gently refluxed for 20 h under inert atmosphere. The reaction mixture was cooled down to room temperature and concentrated under reduced pressure. The residue was then washed several times with methanol (3*5 ml) to afford the expected crude diimine as a red oil, which solidifies upon cooling. This crude product was used directly in the next step without further purification.

*5.3.3.1. N^1,N^4-Bis((3,3‴-didodecyl-[2,2′:5′,2″:5″,2‴-quaterthiophen]-5-yl)methylene)benzene-1,4-diamine (**7**).* This compound was prepared starting from **3** (0.310 g, 0.45 mmol) and *para*-phenylenediamine (0.024 g, 0.22 mmol). **7** (0.321 g, 0.22 mmol, quantitative) was isolated as a red solid. R_f (toluene): 0.71; mp: 92.2–95.9 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.52 (s, 2H, −C*H*=N−), 7.31 (s, 2H, H4), 7.28 (s, 4H, −C_6H_4−), 7.20–7.14 (m, 8H, H5‴, H3″, H4′, H4″), 7.03 (d, 2H, J=3.8 Hz, H3′), 6.95 (d, 2H, J=5.2 Hz, H4‴), 2.86–2.75 (m, 8H, $C_{thiophene}$−CH_2−), 1.76–1.59 (m, 8H, $C_{thiophene}$−CH_2−CH_2−), 1.44–1.20 (m, 72H, −$(CH_2)_9$−CH_3), 0.91–0.84 (m, 12H, −CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 151.8, 149.5, 140.1, 138.0, 136.6, 135.9, 135.8, 135.2, 134.9, 130.4, 130.3, 127.4, 126.7, 124.3, 124.2, 124.1, 122.2, 32.1, 30.8, 30.5, 29.82, 29.76, 29.7, 29.6, 29.5, 29.4, 22.9, 14.3.

*5.3.3.2. N^1,N^3-Bis((3,3‴-didodecyl-[2,2′:5′,2″:5″,2‴-quaterthiophen]-5-yl)methylene)benzene-1,3-diamine (**8**).* This compound was prepared starting from **3** (0.200 g, 0.29 mmol) and *meta*-phenylenediamine (0.015 g, 0.14 mmol). **8** (0.199 g, 0.14 mmol, quantitative) was isolated as a red oil. R_f (toluene/petroleum ether 8/2 v/v): 0.83; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.53 (s, 2H, −C*H*=N−), 7.42–7.35 (m, 1H, −CH=C*H*−CH=), 7.32 (s, 2H, H4), 7.21–7.14 (m, 8H, H5‴, H3″, H4′, H4″), 7.13–7.07 (m, 3H, −C*H*=CH−C*H*=, =N−C=C*H*−*C*−*N*=), 7.03 (d, 2H, J=3.8 Hz, H3′), 6.95 (d, 2H, J=5.2 Hz, H4‴), 2.86–2.75 (m, 8H, $C_{thiophene}$−CH_2−), 1.76–1.59 (m, 8H, $C_{thiophene}$−CH_2−CH_2−), 1.44–1.20 (m, 72H, −$(CH_2)_9$−CH_3), 0.91–0.84 (m, 12H, −CH_3); ^{13}C NMR (CDCl3, 75 MHz) δ: 153.0, 152.5, 140.2, 139.9, 138.1, 136.6, 136.00, 135.95, 135.5, 134.8, 130.34, 130.27, 127.5, 126.7, 124.4, 124.2, 124.1, 32.1, 30.8, 30.5, 29.82, 29.76, 29.7, 29.6, 29.5, 29.4, 22.9, 14.3.

*5.3.4. General procedure for the reduction of the diimine derivatives **B3** and **B4**.* A 2 M $LiBH_4$ solution (30 equiv) in THF was added at room temperature to a solution of quaterthiophene diimine **7** or **8** (1 equiv) in THF (10 ml), under inert atmosphere. The reaction mixture was refluxed for 24 h. It was then cooled down to room temperature, poured into ice/water and extracted twice with dichloromethane. The combined organic layers were washed with water and brine, dried over $MgSO_4$ and concentrated under reduced pressure affording the expected crude diamine. This crude product was purified by column chromatography on silica gel (eluant: toluene).

*5.3.4.1. N^1,N^4-Bis((3,3‴-didodecyl-[2,2′:5′,2″:5″,2‴-quaterthiophen]-5-yl)methyl)benzene-1,4-diamine (**B3**).* This compound was prepared starting from **7** (0.311 g, 0.21 mmol) and a 2 M $LiBH_4$ solution in THF (3.19 ml, 6.38 mmol). **B3** (0.165 g, 0.11 mmol, 53%) was isolated as a yellow solid. R_f (toluene): 0.51; mp: 67.7–71.2 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.17 (d, 2H, J=5.2 Hz, H5‴), 7.12–7.08 (m, 4H, H3″, H4′), 7.01 (d, 2H, J=3.8 Hz, H4⁗), 6.97 (d, 2H, J=3.8 Hz, H3′), 6.94 (d, 2H, J=5.2 Hz, H4‴), 6.84 (s, 2H, H4), 6.66 (s, 4H, −C_6H_4−), 4.40 (s, 4H, −CH_2−NH−), 2.82–2.67 (m, 8H, $C_{thiophene}$−CH_2−), 1.70–1.55 (m, 8H, $C_{thiophene}$−CH_2−CH_2−), 1.43–1.18 (m, 72H, −$(CH_2)_9$−CH_3), 0.87 (t, 12H, J=6.5 Hz, −CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 142.0, 140.7, 140.0, 139.7, 137.0, 136.7, 135.6, 135.4, 130.5, 130.2, 129.4, 129.2, 128.4, 128.0, 126.7, 126.4, 125.5, 124.0, 123.93, 123.90, 115.3, 45.1, 32.1, 30.82, 30.76, 29.84, 29.82, 29.76, 29.71, 29.68, 29.6, 29.5, 29.4, 22.9, 14.3; HRMS (MALDI-ToF): [$M^{+\bullet}$] calcd for $C_{88}H_{124}N_2S_8$ m/z 1464.7530, found 1464.7521.

*5.3.4.2. N^1,N3-Bis((3,3‴-didodecyl-[2,2′:5′,2″:5‴,2⁗-quaterthiophen]-5-yl)methyl)benzene-1,3-diamine (**B4**).* This compound was prepared starting from **8** (0.150 g, 0.10 mmol) and a 2 M $LiBH_4$ solution in THF (1.54 ml, 3.08 mmol). **B4** (0.086 g, 0.06 mmol, 57%) was isolated as a yellow oil. R_f (toluene): 0.68; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.18 (d, 2H, J=5.2 Hz, H5‴), 7.12–7.09 (m, 4H, H3″, H4′), 7.04 (t, 1H, J=8.0 Hz, −CH=C*H*−CH=), 7.01 (d, 2H, J=3.8 Hz, H4″), 6.97 (d, 2H, J=3.8 Hz, H3′), 6.94 (d, 2H, J=5.2 Hz, H4‴), 6.84 (s, 2H, H4), 6.15 (dd, 2H, J=8.0 and 2.0 Hz, −C*H*=CH−C*H*=), 6.04 (t, 1H, J=2.0 Hz, =N−C=C*H*−*C*−*N*=), 4.43 (s, 4H, =CH_2−NH−), 4.00 (br s, 2H, −N*H*−), 2.83–2.67 (m, 8H, $C_{thiophene}$−CH_2−), 1.72–1.56 (m, 8H, $C_{thiophene}$−CH_2−CH_2−), 1.45–1.19 (m, 72H, −$(CH_2)_9$−CH_3), 0.93–0.83 (m, 12H, −CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 148.9, 141.6, 140.0, 139.7, 137.0, 136.7, 135.5, 135.4, 130.5, 130.3, 130.2, 129.5, 128.1, 126.6, 126.4, 123.94, 123.90, 104.0, 98.0, 43.9, 32.1, 30.8, 29.84, 29.82, 29.78, 29.75, 29.72, 29.68, 29.6, 29.5, 29.4, 22.9, 14.3; HRMS (MALDI-ToF): [$M^{+\bullet}$] calcd for $C_{88}H_{124}N_2S_8$ m/z 1464.7530, found 1464.7507.

5.4. Synthetic procedures for the preparation of 10 and B5

*5.4.1. (3,3‴-Didodecyl-[2,2′:5′,2″:5‴,2⁗-quaterthiophen]-5-yl) methanol (**9**).* To a solution of quaterthiophene aldehyde **3** (0.710 g, 1.02 mmol) in MeOH/Tol (2/1 v/v, 60 ml) was added sodium borohydride (0.077 g, 2.04 mmol). The reaction mixture was stirred under reflux for 2 h. It was then cooled down to room temperature, poured into water/ice and extracted with toluene (2*100 ml). The combined organic layers are washed with water and brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude product obtained was purified by recrystallization in n-hexane to give **9** (0.690 g, 0.99 mmol, 97%) as an orange solid. R_f (toluene): 0.18; mp: 54.5–56.7 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.18 (d, 1H, J=5.2 Hz, H5‴), 7.13 (d, 1H, J=3.7 Hz, H3″ or H4′), 7.12 (d, 1H, J=3.7 Hz, H4′ or H3″), 7.02 (d, 1H, J=3.8 Hz, H4″), 7.01 (d, 1H, J=3.8 Hz, H3′), 6.94 (d, 1H, J=5.2 Hz, H4‴), 6.86 (s, 1H, H4), 4.77 (s, 2H, −CH_2−OH), 2.83–2.69 (m, 4H, $C_{thiophene}$−CH_2−), 1.85 (br s, 1H, −O*H*), 1.71–1.58 (m, 4H, $C_{thiophene}$−CH_2−CH_2−), 1.43–1.20 (m, 36H, −$(CH_2)_9$−CH_3), 0.88 (t, 6H, J=6.6 Hz, −CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 142.2, 140.0, 139.8, 137.0, 136.8, 135.5, 135.3, 130.6, 130.4, 130.2, 128.6, 126.6, 124.0, 123.9, 60.3, 32.1, 30.81, 30.76, 29.84, 29.81, 29.75, 29.7, 29.6, 29.5, 29.4, 22.8, 14.3; HRMS (MALDI-ToF): [$M^{+\bullet}$] calcd for $C_{41}H_{60}OS_4$ m/z 696.3527, found 696.3524.

*5.4.2. 2-((3,3‴-Didodecyl-[2,2′:5′,2″:5″,2‴-quaterthiophen]-5-yl) methyl)isoindoline-1,3-dione (**10**).* To a solution of quaterthiophene alcohol **9** (0.350 g, 0.50 mmol), triphenylphosphine (0.171 g, 0.65 mmol) and phthalimide (0.096 g, 0.65 mmol) in dry THF (25 ml) was added diisopropyl azodicarboxylate (0.132 g, 0.65 mmol) at 0 °C and under inert atmosphere. The reaction mixture was then allowed to warm up to room temperature and was stirred further for 24 h. The mixture was concentrated under reduced pressure and directly purified by column chromatography

on silica gel (eluant: toluene/dichloromethane 9/1 v/v) to give **10** (0.240 g, 0.29 mmol, 58%) as a yellow solid. R_f (toluene): 0.53; mp: 50.1–52.3 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.90–7.83 (m, 2H, –CO–C–CH=C*H*–), 7.75–7.68 (m, 2H, –CO–C–C*H*=CH–), 7.17 (d, 2H, *J*=5.2 Hz, H5‴), 7.11–7.07 (m, 4H, H3″, H4′), 7.01 (d, 2H, *J*=3.8 Hz, H4″), 6.98 (s, 1H, H4), 6.97 (d, 1H, *J*=3.8 Hz, H3′), 6.93 (d, 2H, *J*=5.2 Hz, H4‴), 4.95 (s, 2H, –C*H*$_2$–N–), 2.82–2.65 (m, 4H, $C_{thiophene}$–C*H*$_2$–), 1.70–1.55 (m, 4H, $C_{thiophene}$–CH$_2$–C*H*$_2$–), 1.41–1.19 (m, 36H, –(C*H*$_2$)$_9$–CH$_3$), 0.92–0.83 (m, 6H, –C*H*$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 167.7, 140.0, 139.7, 137.0, 136.9, 136.3, 135.5, 135.0, 134.2, 132.2, 130.94, 130.87, 130.4, 130.2, 126.7, 126.6, 123.94, 123.88, 123.6, 36.0, 32.1, 30.8, 30.7, 29.8, 29.74, 29.72, 29.66, 29.60, 29.57, 29.5, 29.4, 22.8, 14.3; HRMS (MALDI-ToF): [M^{+}•] calcd for $C_{49}H_{63}NO_2S_4$ *m*/*z* 825.3742, found 825.3759.

*5.4.3. 2,6-Bis((3,3‴-didodecyl-[2,2′:5′,2″:5″,2‴-quaterthiophen]-5-yl)methyl)pyrrolo[3,4-f]isoindole-1,3,5,7(2H,6H)-tetraone (**B5**).* To a solution of quaterthiophene alcohol **9** (0.464 g, 0.67 mmol), triphenylphosphine (0.192 g, 0.73 mmol) and pyromellitic diimide (0.072 g, 0.33 mmol) in dry THF (25 ml) was added diisopropyl azodicarboxylate (0.148 g, 0.73 mmol) at 0 °C and under inert atmosphere. The reaction mixture then allowed to warm up to room temperature and was stirred further for 24 h. The mixture was then concentrated under reduced pressure and directly purified by column chromatography on silica gel (eluant: toluene/dichloromethane 9/1 v/v) to give **B5** (0.198 g, 0.13 mmol, 38%) as a yellow solid. R_f (toluene): 0.20; mp: 96.4–101.9 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.30 (s, 2H, –CO–C–C*H*=C–), 7.17 (d, 2H, *J*=5.2 Hz, H5‴), 7.11–7.06 (m, 4H, H3″, H4′), 7.02–6.98 (m, 4H, H4″, H4), 6.96 (d, 2H, *J*=3.8 Hz, H3′), 6.93 (d, 2H, *J*=5.2 Hz, H4‴), 4.99 (s, 4H, –C*H*$_2$–N–), 2.80–2.65 (m, 8H, $C_{thiophene}$–C*H*$_2$–), 1.70–1.53 (m, 8H, $C_{thiophene}$–CH$_2$–C*H*$_2$–), 1.41–1.17 (m, 72H, –(C*H*$_2$)$_9$–CH$_3$), 0.92–0.82 (m, 12H, –C*H*$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz) 165.5, 140.0, 139.8, 137.4, 137.2, 136.7, 135.6, 135.1, 134.7, 131.5, 131.4, 130.4, 130.2, 126.8, 126.6, 124.04, 123.9, 118.8, 36.6, 32.1, 30.8, 30.7, 29.8, 29.74, 29.71, 29.66, 29.60, 29.56, 29.5, 29.4, 22.8, 14.3; HRMS (MALDI-ToF): [M^{+}•] calcd for $C_{92}H_{120}N_2O_4S_8$ *m*/*z* 1572.7014, found 1572.7003.

5.5. Reaction of quaterthiophene mono-aldehyde 3 with ammonia in reductive medium

To a solution of quaterthiophene aldehyde **3** (0.200 g, 0.29 mmol) in a saturated solution of NH_4OAc in $CHCl_3$/EtOH (1/1 v/v, 20 ml) were added $NaCNBH_3$ (0.055 g, 0.87 mmol) and 30% aq NH_3 (2.4 ml). The reaction mixture was stirred under reflux for 20 h. It was then cooled down to room temperature, poured into ice/water and extracted with dichoromethane (2*50 ml). The combined organic layers were washed with water and brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude brown oil obtained was purified by column chromatography on silica gel (eluant: toluene/petroleum 7/3+1% of NEt_3 v/v) affording the secondary amine **B6** (0.082 g, 0.06 mmol, 41%) as a yellowish waxy solid, and the tertiary amine **11** (0.031 g, 0.01 mmol, 16%) as a yellowish oil.

*5.5.1. Bis((3,3‴-didodecyl-[2,2′:5′,2″:5″,2‴-quaterthiophen]-5-yl)methyl)amine (**B6**).* R_f (toluene): 0.62; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.18 (d, 2H, *J*=5.2 Hz, H5‴), 7.13–7.10 (m, 4H, H3″, H4′), 7.01 (d, 2H, *J*=3.8 Hz, H4″), 7.00 (d, 2H, *J*=3.8 Hz, H3′), 6.94 (d, 2H, *J*=5.2 Hz, H4‴), 6.79 (s, 2H, H4), 4.00 (s, 4H, –C*H*$_2$–NH–), 2.81–2.69 (m, 8H, $C_{thiophene}$–C*H*$_2$–), 1.71–1.58 (m, 8H, $C_{thiophene}$–CH$_2$–C*H*$_2$–), 1.43–1.20 (m, 72H, –(C*H*$_2$)$_9$–CH$_3$), 0.91–0.84 (m, 12H, –C*H*$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 140.0, 139.6, 137.0, 136.7, 135.7, 135.4, 130.5, 130.2, 129.6, 128.5, 126.7, 126.3, 124.0, 123.9, 47.4, 32.1, 30.82, 30.78, 29.9, 29.82, 29.76, 29.74, 29.68, 29.65, 29.6, 29.5, 29.4, 22.9, 14.3; HRMS (MALDI-ToF): [M^{+}•] calcd for $C_{82}H_{119}NS_8$ *m*/*z* 1373.7108, found 1373.7073.

*5.5.2. Tris((3,3‴-didodecyl-[2,2′:5′,2″:5″,2‴-quaterthiophen]-5-yl)methyl)amine (**11**).* R_f (toluene/petroleum ether 1/1 v/v): 1.0; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.17 (d, 3H, *J*=5.1 Hz, H5‴), 7.15–7.08 (m, 6H, H3″, H4′), 7.06–6.98 (m, 6H, H4″, H3′), 6.94 (d, 3H, *J*=5.1 Hz, H4‴), 6.82 (s, 3H, H4), 3.89 (s, 6H, –C*H*$_2$–NH–), 2.83–2.68 (m, 12H, $C_{thiophene}$–C*H*$_2$–), 1.72–1.59 (m, 12H, $C_{thiophene}$–CH$_2$–C*H*$_2$–), 1.41–1.20 (m, 108H, –(C*H*$_2$)$_9$–CH$_3$), 0.92–0.82 (m, 18H, –C*H*$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 140.6, 140.0, 139.4, 137.1, 136.7, 135.8, 135.3, 130.5, 130.2, 130.1, 129.3, 126.6, 126.4, 123.93, 123.86, 51.9, 32.1, 30.8, 29.83, 29.75, 29.7, 29.6, 29.5, 29.4, 22.9, 14.3; HRMS (MALDI-ToF): [M^{+}•] calcd for $C_{123}H_{177}NS_{12}$ *m*/*z* 2052.0530, found 2052.0588.

Acknowledgements

This work has been financially supported by the Belgian Federal Science Policy Office (PAI SF2), by a concerted research action of the French Community of Belgian (ARC N° 20061), and by the Belgian National Fund for Scientific Research (FNRS). The authors also would like to thank Pr. Pascal Gerbaux for his help with the mass spectrometry.

Supplementary data

^{1}H and ^{13}C spectra of quaterthiophene derivatives **6**, **10** and the bridged compounds **B2**–**B6** are shown in Supplementary data. Absorption and fluorescence spectra of **1** and its bridged derivatives **B1**–**B6** as well as CVs of **B4** are also depicted in Supplementary data. Supplementary data associated with this article can be found in online version. Supplementary data related to this article can be found online at doi:10.1016/j.tet.2012.04.072.

References and notes

1. Martin, R. E.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1350–1377.
2. Bendikov, M.; Wudl, F.; Perepichka, D. F. *Chem. Rev.* **2004**, *104*, 4891–4946.
3. (a) Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028–5048; (b) Anthony, J. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 452–483.
4. Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3047–3049.
5. *Stimulating Concepts in Chemistry*; Paddon-Row, M. N., Ed.; Wiley-VCH GmbH: KGaA: Weinheim, 2005; pp 267–291.
6. Ricks, A. B.; Solomon, G. C.; Colvin, M. T.; Scott, A. M.; Chen, K.; Ratner, M. A.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2010**, *132*, 15427–15434.
7. Paulson, B. P.; Miller, J. R.; Gan, W.-X.; Closs, G. *J. Am. Chem. Soc.* **2005**, *127*, 4860–4868.
8. (a) Wenger, O. S. *Acc. Chem. Res.* **2010**, *44*, 25–35; (b) Wenger, O. S. *Chem. Soc. Rev.* **2011**, *40*, 3538–3550.
9. Lewis, F. D.; Wu, T.; Liu, X.; Letsinger, R. L.; Greenfield, S. R.; Miller, S. E.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 2889–2902.
10. (a) Lewis, F. D.; Liu, J.; Weigel, W.; Rettig, W.; Kurnikov, I. V.; Beratan, D. N. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 12536–12541; (b) Tong, G. S. M.; Kurnikov, I. V.; Beratan, D. N. *J. Phys. Chem. B* **2002**, *106*, 2381–2392.
11. Hanss, D.; Walther, M. E.; Wenger, O. S. *Chem. Commun.* **2010**, 7034–7036.
12. Hankache, J.; Wenger, O. S. *Chem. Rev.* **2011**, *111*, 5138–5178.
13. Lloveras, V.; Vidal-Gancedo, J.; Figueira-Duarte, T. M.; Nierengarten, J.-F. o.; Novoa, J. J.; Mota, F.; Ventosa, N.; Rovira, C.; Veciana, J. *J. Am. Chem. Soc.* **2011**, *133*, 5818–5833.
14. Becker, B.; Bohnen, A.; Ehrenfreund, M.; Wohlfarth, W.; Sakata, Y.; Huber, W.; Muellen, K. *J. Am. Chem. Soc.* **1991**, *113*, 1121–1127.
15. Jenart, M.; Niebel, C.; Balandier, J.-Y.; Leroy, J.; Mignolet, A.; Stas, S.; Van Vooren, A.; Cornil, J.; Geerts, Y. H. *Tetrahedron* **2012**, *68*, 349–355.
16. Azumi, R.; Götz, G.; Debaerdemaeker, T.; Bäuerle, P. *Chem.—Eur. J.* **2000**, *6*, 735–744.
17. For a description of typical conditions used for a Friedel and Crafts acylation using terephthaloyl dichloride, see: (a) Hendy, B. N.; Patterson, K. H.; Smith, D. M.; Gardner, S. E.; Nicolson, N. J. *J. Mater. Chem.* **1995**, *5*, 199–204; (b) Chiechi, R. C.; Sonmez, G.; Wudl, F. *Adv. Funct. Mater.* **2005**, *15*, 427–432.
18. Shin, K.; Yu, B. S.; Goff, H. M. *Inorg. Chem.* **1990**, *29*, 889–890.
19. Lau, C. K.; Dufresne, C.; Belanger, P. C.; Pietre, S.; Scheigetz, J. *J. Org. Chem.* **1986**, *51*, 3038–3043.

20. For a description of typical conditions used for a Mitsunobu coupling involving phthalimide derivatives, see: (a) Iijima, T.; Vignon, S. A.; Tseng, H.-R.; Jarrosson, T.; Sanders, J. K. M.; Marchioni, F.; Venturi, M.; Apostoli, E.; Balzani, V.; Stoddart, J. F. *Chem.—Eur. J.* **2004**, *10*, 6375–6392; (b) Wulff, J. E.; Siegrist, R.; Myers, A. G. *J. Am. Chem. Soc.* **2007**, *129*, 14444–14451.
21. Dangerfield, E. M.; Plunkett, C. H.; Win-Mason, A. L.; Stocker, B. L.; Timmer, M. S. M. *J. Org. Chem.* **2010**, *75*, 5470–5477.
22. Egelhaaf, H. J.; Oelkrug, D.; Gebauer, W.; Sokolowski, M.; Umbach, E.; Fischer, T.; Bäuerle, P. *Opt. Mater.* **1998**, *9*, 59–64.
23. Facchetti, A.; Yoon, M.-H.; Stern, C. L.; Hutchison, G. R.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **2004**, *126*, 13480–13501.
24. Sotgiu, G.; Zambianchi, M.; Barbarella, G.; Botta, C. *Tetrahedron* **2002**, *58*, 2245–2251.
25. Romanazzi, G.; Marinelli, F.; Mastrorilli, P.; Torsi, L.; Sibaouih, A.; Räisänen, M.; Repo, T.; Cosma, P.; Suranna, G. P.; Nobile, C. F. *Tetrahedron* **2009**, *65*, 9833–9842.
26. Chosrovian, H.; Rentsch, S.; Grebner, D.; Dahm, D. U.; Birckner, E.; Naarmann, H. *Synth. Met.* **1993**, *60*, 23–26.