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Synthesis of D-glucose and L-phenylalanine substituted phenylene–thiophene oligomers

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ABSTRACT

Phenylene–thiophene oligomers bearing peracetylated β-D-glucose or *N*-BOC-L-phenylalanine as chiral substituents were synthesized in good yields by a versatile protocol based on the Suzuki–Miyaura cross-coupling reaction. Aryl iodides bearing the chiral biomolecules as substituents efficiently reacted with pinacol boronates of bi- or terthiophenes leading to the bio-functionalized oligomers in good yields.

1. Introduction

The wide variety of applications of polymeric[1] and oligomeric[2] organic semiconductors in organic electronics[3] largely benefits from the possibility to selectively functionalize the conjugated backbone with several substituents. Side groups not only enable fine tuning of the properties of conjugated materials, but can also confer the specific ability to selectively interact with other molecules, thus opening the way to their use as active materials in highly selective electrical and optical sensors.[4] In this context, biomolecules used as substituents offer the fascinating possibility to combine the recognition ability deriving from their biological role with the semiconducting properties of the conjugated backbone. In fact, efficient and selective biological sensors employing properly functionalized organic semiconductors as transducers have been reported.[5] Many classes of biological molecules, including monosaccharides and amino acids, can also be considered as easily available sources of enantiopure multifunctional compounds for the chiral functionalization of conjugated materials. This would endow organic semiconductors with enantioselective recognition ability towards specific chiral analytes[6] or larger biological molecules like proteins or DNA.[7]

The fast and efficient enantioselective detection of chiral compounds is an issue of primary importance in many research and industrial areas, such as synthetic chemistry, pharmacology, cosmetics, food-monitoring and medical diagnostics. Thus, a growing interest has been devoted to the synthesis of organic semiconductors bearing chiral substituents as enantioselective receptors.[8] Most frequently, chirally functionalized conjugated materials have been used as fluorescence-based enantioselective markers or sensors.[9] Electropolymerized or molecularly imprinted conducting polymers bearing chiral substituents have also been reported as active materials in enantioselective electrochemical sensors.[6a,7a,8e,10] Frequently, chiral substituents described in the literature are biotinylated pendant groups,[8e,10a] monosaccharides,[9b,c] amino acids[7a,9a,b] or chiral hydrocarbon chains.[6a] We reported the synthesis of D-glucose[8f] and L-phenylalanine[8g] substituted poly(*p*-phenyleneethynylene)s and their use as active layers in quartz crystal microbalance enantioselective gravimetric sensors for chiral analytes in the vapour phase.[6c,d] More recently, in the search for chirally substituted organic semiconductors for electrical solid state enantioselective sensors, we have synthesized the D-glucose and L-phenylalanine substituted oligophenylene-thiophenes, **1a** and **1b**, respectively.[11] These oligomers have been used as the sensing layer material in organic thin film transistor (OTFT)-based enantioselective sensors for chiral analytes in the vapour phase, exhibiting outstanding performances including

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a detection threshold three order of magnitude lower than that of any chiral solid state sensors previously reported.[11]

The excellent progress in enantioselective sensing was made possible by the synthesis of **1a** and **1b**. However, in the previous paper we did not systematically investigate the potential of the protocol affording **1a** and **1b** described in the Supplementary information of reference 11. It is important to fully explore the generality of the synthetic methods as tools for fine tuning properties of organic semiconductors by small structural modifications. In particular, changing the sequence of the conjugated backbone and extending the π system impact on electronic and optical properties of the materials while modifying the number and positions of the bio/chiral substituents can affect polarity and eventually recognition capability of the receptors.

The aim of this synthetic paper is to report a full exploration of a simple and effective method to obtain several phenylene–thiophene oligomers functionalized with the required chiral biomolecules. The impact of the structural modifications accessible by our method on the basic spectroscopic properties of this class of molecular semiconductors is also discussed.

2. Results and discussion

Several phenylene–thienylene oligomers have been described in the literature,[12] showing different connections of phenyl or 1,4-phenylene units with 2-thienyl or 2,5-thienylene rings. Alkoxy moieties on the phenyl/phenylene rings are frequently used to easily introduce several side groups on the main backbone in various classes of conjugated oligomers and polymers.[13] In the present study chiral amino acid and glucose molecules were attached to the benzene rings as alkoxy substituents. The oligomers reported in this paper can be divided into three classes (Fig. 1): the structures of the first kind (Type 1, compounds **1**, **2**) are characterized by a dialkoxy-substituted phenylene ring bonded to two oligothiophene blocks; the second class (Type 2, compounds **3**, **4**) consists of oligothienylene segments terminating with two monoalkoxy-substituted phenyl rings; the third type (Type 3, compounds **5**, **6**) consists of linear oligothiophenes terminating on one side with a monoalkoxy-functionalized phenyl ring. The *N*-*tert*-butoxycarbonyl protected L-phenylalanine molecule is attached to the phenyl ring through a six carbon atom alkoxy chain connected to the amino acid carboxylic group by an ester linkage. Conversely, the peracetylated D-glucose molecules are directly bonded to the phenyl rings through β-glucosidic linkage.

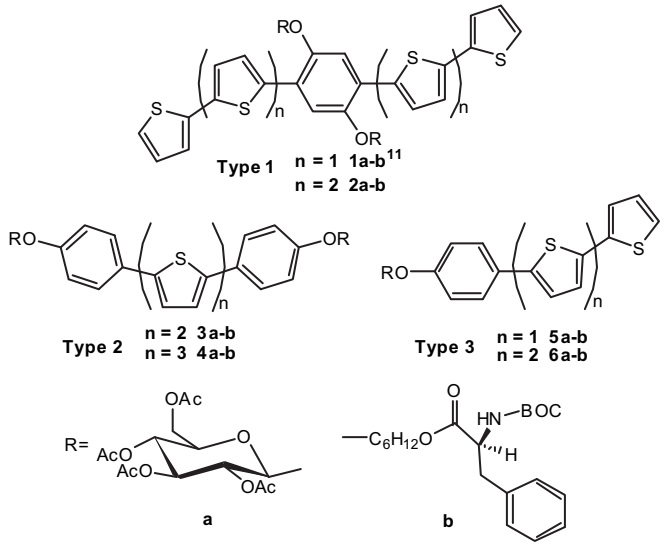
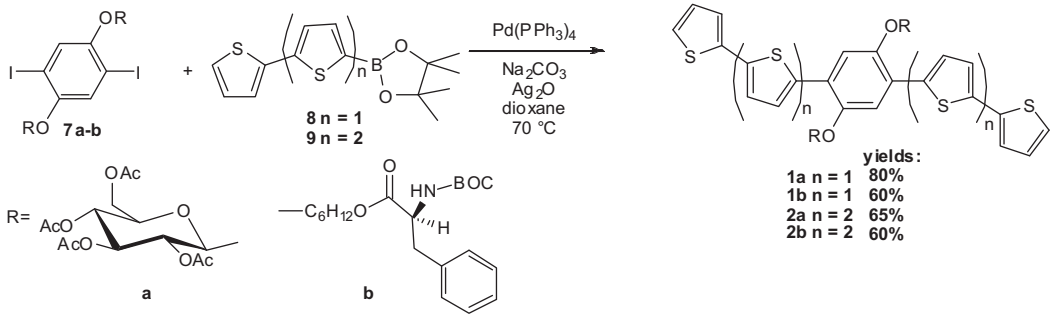


Fig. 1. Structures of the phenylene–thiophene oligomers.

The synthetic approach for building the conjugated system is based on the palladium catalyzed Suzuki–Miyaura cross-coupling reaction[14] between oligothiophene mono- or bis-pinacol boronic esters and the mono- or diiodo-benzenes previously functionalized with the biomolecules. The sequence proposed here offers distinctive advantages compared to a possible alternative protocol involving the synthesis of the conjugated skeleton followed by the functionalization with the glucose or the amino acid substituents. Actually, as the presence of the biomolecules on the organic halides is tolerated in the cross-coupling conditions, our protocol enables the synthesis of a wide variety of structures by simply using different thiophene boronic derivatives, many of which are commercially available. Moreover, the thiophene pinacol boronates are among the most stable and readily available boron-derivatives of thiophene, showing good reactivity in the classical Suzuki–Miyaura cross-coupling conditions and forming low toxicity by-products.[14] In this respect, our experiments further extend the usefulness of thiophene boronic esters as valuable building blocks in the synthesis of functionalized thiophene-based materials, even in the presence of small biomolecules as substituents on the coupling partner.

The cross-coupling reactions were performed in anhydrous dioxane in the presence of Na_2CO_3 as the base and silver oxide[15] at 70 °C; these conditions were also compatible with the presence of both the acetyl and *tert*-butoxycarbonyl protecting groups.

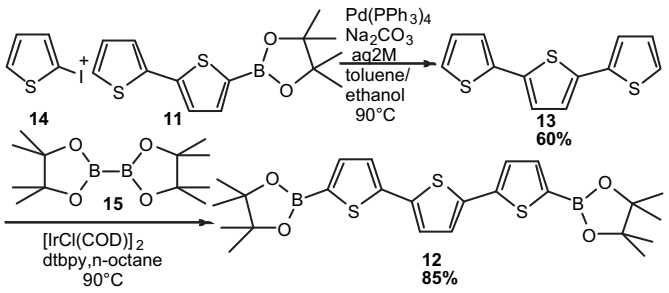
The synthesis of **2a**,**b** represents an extension of the method adopted for **1a**,**b** as we have previously reported:[11] it consists of a single step double cross-coupling reaction between the dihalides **7a** and **7b**, which were prepared according to our previous reports,[8f,g] and the commercially available boronic esters **8** and **9**. The reaction yields are summarized in the Scheme 1, showing that the coupling of **7a**,**b** with 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2′-bithiophene **8** affords products **1a** and **1b** in high yields. Similarly, the oligomers **2a** and **2b**, with a more extended aromatic system given by the two terthiophene blocks were obtained by reaction of **7a**,**b** with the 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[2,2′:5′,2″]-terthiophene **9** (see Scheme 1). Oligomers belonging to the second and third categories, namely compounds **3**, **4**, **5**, **6**, differ from compounds of



Scheme 1. Synthesis of Type 1 compounds.

the first type (**1**, **2**) due to the presence of the biomolecules at one or both ends of the oligoarylene sequence rather than in the center of the molecule.

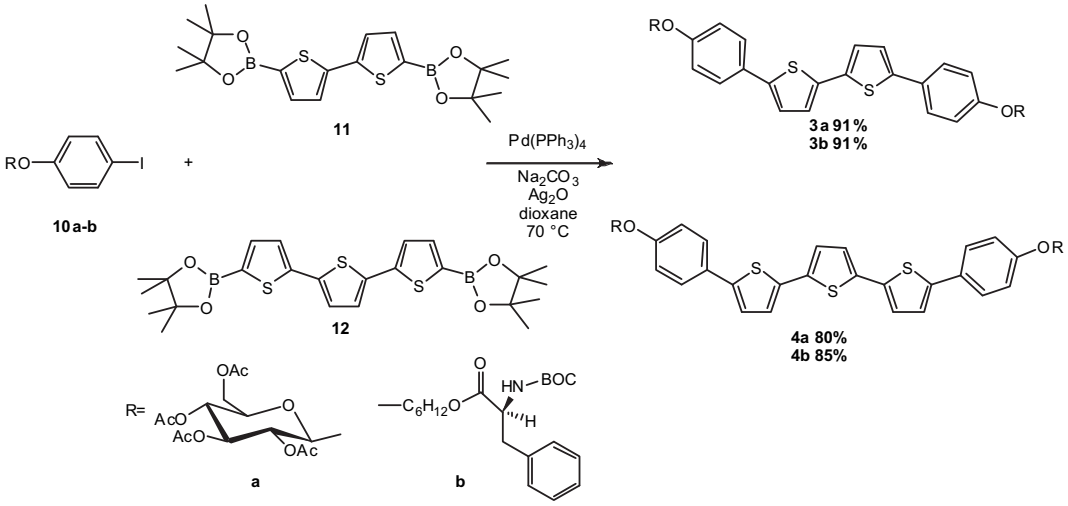
Such structural modifications can cause changes in polarity that may affect solid state organization and processability both via solution casting and via layer by layer technique, such as the Langmuir–Shäfer method.[16] The synthesis of the oligomers **3**, **4**, reported in the Scheme 2, was performed by coupling the diboronic derivatives **11** and **12** with the halides **10a**,**b** and afforded the reaction products with good to excellent yields. Accordingly, the coupling of the halides **10a**,**b** with the monopinacol boronic esters of di- or terthiophene, **8** or **9**, yielded the oligomers **5** and **6** with similar yields (Scheme 3). While the intermediate bis-boronic ester **11** is commercially available, the bis-pinacol boronic ester of terthiophene **12** was prepared for the first time starting from the terthiophene **13** in 60% yield by Ir-catalyzed direct activation of the C–H bond in the α position of the thiophene rings[17] carried out using the complex $[IrCl(COD)]_2$ and 4,4′di-*tert*-butyl-2,2′-bipyridine (dtbpy) the as catalyst and a stochiometric amount of bisdioxaborolane **15**.



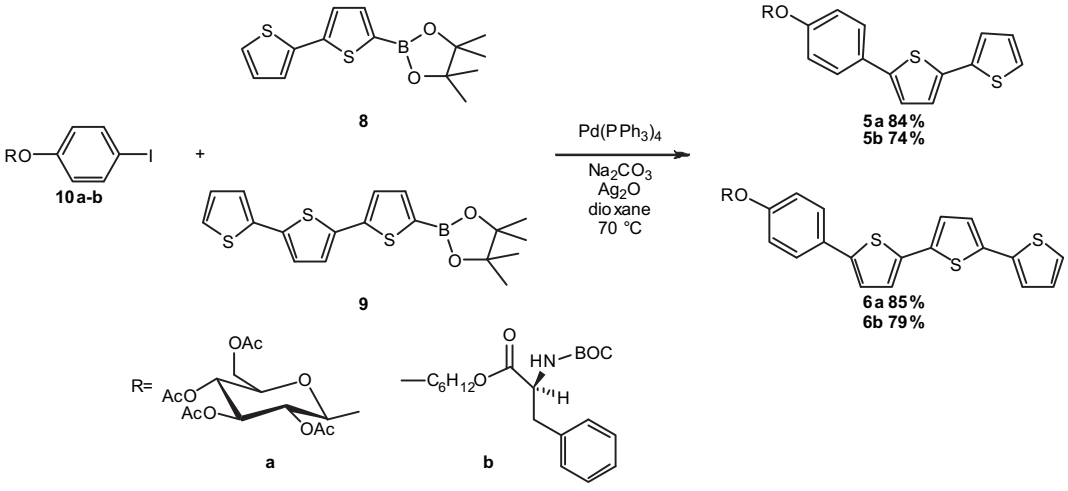
Scheme 4. Synthesis of **12**.

synthesis of molecular structures containing the terthienylene block.

The halides **10a** and **10b** were synthesized in high yields starting from the commercially available 4-iodophenol **16** and the per-

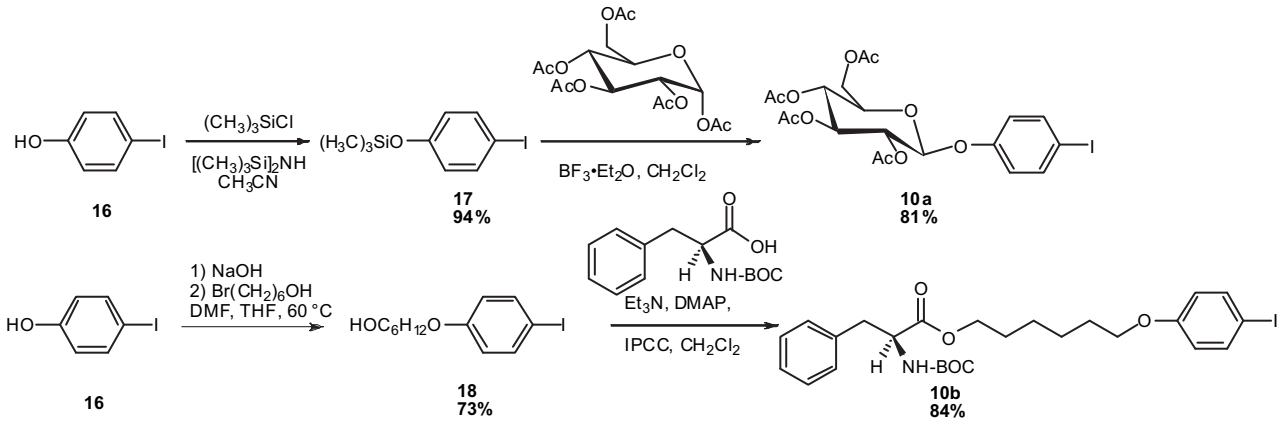


Scheme 2. Synthesis of Type 2 compounds.



Scheme 3. Synthesis of Type 3 compounds.

The starting terthiophene **13** was conveniently synthesized by reacting 2-iodothiophene **14** with the pinacolboronic ester **11**. The reaction sequence leading to **12** is summarized in the Scheme 4. Product **12** can be considered a useful building block for the acetylated α-glucopyranose or *N*-BOC-L-phenylalanine, respectively (Scheme 5). The two-step synthetic approach here proposed afforded the compound **10a** with improved overall yield compared with the literature (76% vs 43%).[18]



Scheme 5. Synthesis of halides **10a** and **10b**.

The reaction of *p*-iodophenol **16** with trimethylchlorosilane in the presence of bis-trimethylsilylamine in acetonitrile afforded the corresponding trimethylsilyl ether **17**,[19] which then reacted with peracetylated glucose. We used modified conditions (see Experimental section) for the glycosidation step with respect to a reference synthetic procedure leading to *O*-phenylglycosides[20] and our procedure resulted in higher reaction yields.

The β configuration of the glycosidic linkage was confirmed by the coupling constant value ($J \approx 7$ Hz) between the protons on C-1 and C-2 of the glucose ring. The value is typical of the axial-axial arrangement in the β anomer.[21]

The reaction of **16** with NaOH, followed by addition of 6-bromohexanol, afforded the derivative **18**. The esterification reaction of the alcohol **18** with the BOC-*N*-protected L-phenylalanine was performed using isopropenyl chlorocarbonate (IPCC) as the condensing agent, according to our previously reported procedure.[8g] The reaction occurs without racemisation of the amino acid unit.[22]

Table 1 summarizes the main spectroscopic properties of the oligomers synthesized (maxima of absorption and emission spectra in solution).

Table 1
Spectroscopic properties of the synthesized oligomers

λ_{max} abs (nm)	$\Delta\lambda_{max}$ abs (nm)	λ_{max} emis. (nm)
(**1a**) 394	33	(**1a**) 457, 485
(**2a**) 427		(**2a**) 497, 529
(**1b**) 411	29	(**1b**) 467, 495
(**2b**) 440		(**2b**) 504, 539
(**3a**) 377	28	(**3a**) 437, 462
(**4a**) 405		(**4a**) 474, 505
(**3b**) 381	29	(**3b**) 444, 470
(**4b**) 410		(**4b**) 479, 508
(**5a**) 345	39	(**5a**) 405, 423
(**6a**) 384		(**6a**) 446, 472
(**5b**) 348	39	(**5b**) 399, 420
(**6b**) 387		(**6b**) 452, 476

As expected, for each type of structures a red shift in absorption and emission maxima is observed moving from the shorter to the longer homologous due to the increase of the conjugation length caused by the addition of one (for Type 2 and Type 3) or two thiophene rings (for Type 1) to the oligoaromatic chain. Quite surprisingly, however, the red shifts measured for compounds of the Type 1 is comparable to and more often slightly smaller than the red shift obtained for the other two types, in spite of the larger increase of the conjugation expected in this case (two thiophene rings are added). This effect may be attributed to a significant distortion of the conjugated backbone in compounds of the Type 1 caused by the presence of the central phenylene ring bearing two bulky substituents that would decrease the effective conjugation between the two oligothiophene arms. In the other two types of compounds the steric hindrance of the bio-substituents, and the consequent reduction of the effective conjugation length is eliminated by bonding them in the external positions of the conjugated backbone.

3. Conclusions

Summing up, we have reported an effective and versatile synthetic method to phenylene–thienylene oligomeric semiconductors bearing *N*-BOC-L-phenylalanine or D-glucose as chiral substituents. The key step of the synthetic protocol is the palladium catalyzed Suzuki–Miyaura cross-coupling reaction of pinacolboronate derivatives of di- or terthiophenes with iodobenzenes functionalized with the glucose or the amino acid moieties, which were found to be tolerated in the cross-coupling reaction conditions.

Our work has also made easily available versatile intermediates (e.g., compound **12**) that in principle can be also used in other synthetic sequences leading to several thiophene-based oligomers eventually bearing pendant biological substituents different from amino acids or monosaccharides.

4. Experimental section

4.1. General

All reactions were carried out under a nitrogen atmosphere in oven-dried glassware, with dry solvents unless otherwise noted. All solvents were distilled immediately prior to use. Tetrahydrofuran, toluene and dioxane were distilled from benzophenone ketyl. Acetonitrile, *n*-octane and dimethylsulfoxide were distilled from 4 Å molecular sieves and dichloromethane from phosphorus pentoxide. All reagents were purchased at the highest commercial quality from Aldrich Chemicals Co, Acros Organics or Fluka, and used without further purification, with the exception of triethylamine, which was distilled from KOH and stored over 4 Å molecular sieves. Compounds **7a** and **7b** were synthesized according to our previous reports.[8f,g] Compounds **17**, **18** and **13** were synthesised and their characterisation data were compared with literature reports.[23–25] Petroleum ether used refers to fraction boiling in the range 40–60 °C. Column chromatography was performed using silica gel 60, 40–63 μm from Merck. Merck silica gel 60 F_{254} aluminum sheets were used for TLC analyses. All new compounds were characterized by ^{1}H NMR, ^{13}C NMR, IR spectroscopy and elemental analysis. GC analyses were performed on a Varian 3900 gas chromatograph

equipped with an SE-30 (methyl silicone, 30 m×0.25 mm id) capillary column and a FID detector. ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively, on Varian Inova 400, or at 500 MHz (^{1}H NMR) and 125 MHz (^{13}C NMR) on Bruker AM 500, using the residual proton peak of $CDCl_3$ at 7.26 ppm as reference for ^{1}H spectra and the signals of $CDCl_3$ at 77 ppm for ^{13}C spectra. Coupling constants values are given in hertz. Melting points (uncorrected) were obtained on a capillary melting point apparatus. IR spectra were recorded on a Perkin–Elmer FTIR BX spectrophotometer. Elemental analyses were performed in our laboratories on a Carlo Erba EA 1108 CHNS Elemental analyzer.

4.1.1. (4-Iodo-phenoxy)-trimethylsilane ***17***. This compound was prepared following a procedure adopted in similar cases.[19] 4-Iodophenol (3.00 g, 13.64 mmol), chlorotrimethylsilane (2.10 mL, 16.37 mmol) and hexamethyldisilazane (3.45 mL, 16.37 mmol) were dissolved in 40 mL of dry acetonitrile. The reaction mixture was stirred under nitrogen at room temperature for 12 h and then the solvent was removed at reduced pressure. The residue was dissolved in petroleum ether and filtered to remove precipitated salts. The solution was washed with saturated aqueous bicarbonate 50 mL×3 and brine 50 mL×2, dried over anhydrous Na_2SO_4 and evaporated to dryness. The final product was obtained as a pale yellow oil (3.17 g, 94% yield). (Found: C, 47.02, H, 4.49. $C_9H_{13}IOSi$ requires C, 47.00, H, 4.48); δ_H ($CDCl_3$, 400 MHz): 0.25 (9H, s, CH_3), 6.57–6.67 (2H, app d, *J* 9 Hz, Ph), 7.48–7.56 (2H, app d, *J* 9 Hz, Ph).

4.1.2. (2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl)-4-iodobenzene ***10a***. This compound was prepared following a procedure adopted in similar cases.[20] β-D-Glucose pentaacetate (3.83 g, 9.82 mmol) and $BF_3\cdot Et_2O$ (1.24 mL, 9.82 mmol), previously dissolved in 15 mL of dry dichloromethane, were added under a nitrogen atmosphere to a solution of (4-iodo-phenoxy)-trimethylsilane **17** (2.39 g, 8.18 mmol) in 15 mL of CH_2Cl_2 kept at room temperature. After 12 h the reaction mixture was washed with saturated aqueous bicarbonate 50 mL×3 and brine 50 mL×2 and dried over anhydrous Na_2SO_4. Evaporation of the solvent at reduced pressure gave the crude product that was purified by column chromatography over silica gel, using a mixture of petroleum ether/ethyl acetate 6:4 as eluent obtaining **10a** as a white solid (3.65 g, 81% yield). (Found: C, 43.61, H, 4.20. $C_{20}H_{23}IO_{10}$ requires C, 43.65, H, 4.21); R_f (petroleum ether/ethyl acetate 6:4) 0.49; mp 144–145 °C (methanol). δ_H ($CDCl_3$, 400 MHz): 1.99 (3H, s, CH_3), 2.00 (3H, s, CH_3), 2.01 (3H, s, CH_3), 2.03 (3H, s, CH_3), 3.78–3.86 (1H, m, CH), 4.12 (1H, dd, *J* 12.3, 2.4 Hz, CH_2), 4.24 (1H, dd, *J* 12.3, 5.4 Hz, CH_2), 5.00 (1H, d, *J* 7.6 Hz, anomeric CH), 5.11 (1H, t, *J* 9.6 Hz, CH), 5.18–5.29 (2H, m, 2CH), 6.70–6.75 (2H, app d, *J* 9.0 Hz, Ph), 7.52–7.57 (2H, app d, *J* 9.0 Hz, Ph). δ_C ($CDCl_3$, 100 MHz) 20.5 (CH_3), 20.6 ($2CH_3$), 20.8 (CH_3), 61.8 (CH_2), 68.1 (CH, glucose ring), 71.0 (CH, glucose ring), 72.0 (CH, glucose ring), 72.5 (CH, glucose ring), 86.2 (C–I, Ph), 98.9 (anomeric CH), 119.2 (C, Ph), 138.4 (C, Ph), 156.6 (C, Ph), 169.2 (C=O), 169.3 (C=O), 170.2 (C=O), 170.5 (C=O). ν_{max}/cm^{-1} (KBr): 818, 1041, 1224 (s, C–O–C), 1432, 1485, 1587, 1750 (s, C=O), 2961.

4.1.3. 1,4-Bis([2,2′]-bithiophen-5-yl)-2,5-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)benzene ***1a***. Na_2CO_3 (0.21 g, 1.98 mmol), Ag_2O (0.45 g, 1.94 mmol) and $Pd(PPh_3)_4$ (0.030 g, 0.03 mmol) were added to a solution of 1,4-bis-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-2,5-diiodobenzene **7a** (1.00 g, 0.98 mmol) and 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2′-bithiophene **8** (0.630 g, 2.16 mmol) in 30 mL of anhydrous dioxane under a nitrogen atmosphere. The reaction mixture was heated at 70 °C overnight and then cooled to room temperature and concentrated under reduced pressure. The crude material obtained was purified by preparative chromatography on silica gel, using a mixture of petroleum ether/ethyl acetate 1:1 as the eluent and then crystallized from dichloromethane–hexane. A bright yellow solid was recovered (0.900 g, 84%). (Found: C 54.49, H 4.52, S 11.63. $C_{50}H_{50}O_{20}S_4$ requires C 54.63, H 4.58, S 11.67); R_f (petroleum ether/ethyl acetate 1:1) 0.56; mp 218–220 °C (dichloromethane/hexane). δ_H ($CDCl_3$, 500 MHz): 1.82 (6H, s, CH_3), 1.98 (6H, s, CH_3), 2.02 (6H, s, CH_3), 2.06 (6H, s, CH_3), 3.97–4.03 (2H, m, CH), 4.21–4.30 (4H, m, $2CH_2$: two diasterotopic protons signals overlapped), 5.18 (2H, t, *J* 9.5 Hz, CH), 5.19 (2H, d, *J* 7.7 Hz, anomeric CH) 5.30 (2H, t, *J* 9.5 Hz, CH), 5.43 (2H, dd, *J* 9.5, 8.3 Hz, CH), 7.05 (2H, dd, *J* 5.1, 3.5 Hz, Th), 7.14 (2H, d, *J* 4.0 Hz, Th), 7.24 (2H, dd, *J* 5.1, 1.0 Hz, Th), 7.27 (2H, dd, *J* 3.5, 1.0 Hz, Th), 7.32 (2H, d, *J* 4.0 Hz, Th), 7.43 (2H, s, Ph). δ_C ($CDCl_3$, 125 MHz) 20.4 (CH_3), 20.6 ($2CH_3$), 20.8 (CH_3), 62.3 (CH_2), 68.3 (CH, glucose ring), 70.9 (CH, glucose ring), 72.4 (CH, glucose ring), 73.0 (CH, glucose ring), 99.9 (anomeric CH), 115.5, 124.0, 124.7, 127.5, 128.1, 136.3, 136.4, 136.9, 138.2, 148.8 (C, Ph), 169.4 (C=O), 169.5 (C=O), 170.2 (C=O), 170.7 (C=O). ν_{max}/cm^{-1} (KBr): 1036, 1218 (s, C–O–C), 1367, 1489, 1753 (s, C=O).

4.1.4. 1,4-Bis([2,2′:5′2″]terthiophen-5-yl)-2,5-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)benzene ***2a***. Na_2CO_3 (0.042 g, 0.39 mmol), Ag_2O (0.091 g, 0.39 mmol) and $Pd(PPh_3)_4$ (0.014 g, 0.012 mmol) were added to a solution of 1,4-bis-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-2,5-diiodobenzene **7a** (0.200 g, 0.20 mmol) and 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[2,2′:5′2″]-terthiophene **9** (0.161 g, 0.43 mmol) in 8 mL of anhydrous dioxane under a nitrogen atmosphere. The reaction mixture was heated at 70 °C overnight and then cooled to room temperature and concentrated under reduced pressure. The crude material obtained was purified by preparative chromatography on silica gel, using a mixture of petroleum ether/ethyl acetate 1:1 as the eluent and then crystallized from dichloromethane–hexane. A orange-yellowish solid was recovered (0.161 g, 65%). (Found: C 55.37, H 4.43, S 15.34. $C_{58}H_{54}O_{20}S_6$ requires C 55.14, H 4.31, S 15.23); R_f (petroleum ether/ethyl acetate 1:1) 0.51; mp 230–231C (dichloromethane/hexane). δ_H ($CDCl_3$, 400 MHz): 1.82 (6H, s, CH_3), 1.94 (6H, s, CH_3), 2.04 (6H, s, CH_3), 2.07 (6H, s, CH_3), 3.98–4.04 (2H, m, CH), 4.22–4.31(4H, m, CH_2, two diasterotopic protons signals overlapped), 5.18 (2H, t, *J* 9.8 Hz, CH), 5.21 (2H, d, *J* 7.8 Hz, anomeric CH), 5.31 (2H, t, *J* 9.4 Hz, CH), 5.45 (2H, t, *J* 9.0 Hz, CH), 7.03 (2H, dd, *J* 5.1, 3.9 Hz, Th), 7.10–7.15 (4H, m, Th), 7.17–7.21 (4H, m, Th), 7.23 (2H, d, *J* 5.1 Hz, Th), 7.33 (2H, d, *J* 3.9 Hz, Th), 7.43 (2H, s, Ph). δ_C ($CDCl_3$, 100 MHz) 20.6 (CH_3), 20.7 ($2CH_3$), 20.8 (CH_3), 62.3 (CH_2), 68.2 (CH, glucose ring), 70.9 (CH, glucose ring), 72.4 (CH, glucose ring), 73.0 (CH, glucose ring), 99.8 (anomeric CH), 115.2, 123.7, 123.8, 124.5, 127.4, 127.8, 135.5, 136.3, 136.4, 136.9, 137.8, 148.7 (C, Ph), 169.2 (C=O), 169.3 (C=O), 170.1 (C=O), 170.5 (C=O). ν_{max}/cm^{-1} (KBr): 1041, 1225 (s, C–O–C), 1374, 1418, 1699, 1717, 1742 (s, C=O), 1791.

4.1.5. 5,5′-Bis-(4-[2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl]phenyl)-[2,2′]-bithiophene ***3a***. Na_2CO_3 (0.038 g, 0.36 mmol), Ag_2O (0.083 g, 0.36) and $Pd(PPh_3)_4$ (0.013 g, 0.011 mmol) were added to a solution of (2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-4-iodobenzene **10a** (0.200 g, 0.36 mmol) and 2,2′-bithiophene-5,5′-diboronic acid bis-(pinacol) ester **11** (0.067 g, 0.16 mmol) in 7 mL of anhydrous dioxane under a nitrogen atmosphere. The reaction mixture was heated at 70 °C overnight and then cooled to room temperature and concentrated under reduced pressure. The crude material obtained was purified by preparative chromatography on silica gel, using a mixture of dichloromethane/diethyl ether 8.5:1.5 as the eluent and then crystallized from dichloromethane/hexane. A bright yellow solid was recovered (0.138. g, 91% yield). (Found: C, 57.04, H, 4.33, S, 6.37. $C_{48}H_{50}O_{20}S_2$ requires C, 57.02, H, 4.98, S, 6.34); R_f (dichloromethane/diethyl ether 8.5:1.5) 0.39; mp 139–140 °C (dichloromethane/hexane). δ_H ($CDCl_3$, 400 MHz): 2.04 (6H, s, CH_3), 2.06 (6H, s, CH_3), 2.08 (6H, s, CH_3), 2.09 (6H, s, CH_3), 3.84–3.91 (2H, m, CH), 4.17 (2H, dd, *J* 12.3, 2.4 Hz, CH_2), 4.30 (2H, dd, *J* 12.3, 5.3 Hz, CH_2), 5.03 (2H, d, *J* 7.6 Hz, anomeric CH), 5.19 (2H,

t, *J* 9.6 Hz, CH), 5.25–5.35 (4H, m, CH), 6.73–6.77 (4H, app d, *J* 9 Hz, Ph), 6.98–7.01 (2H, app d, *J* 9 Hz, Th), 7.50–7.53 (2H, app d, *J* 9 Hz, Th), 7.55–7.59 (4H, app d, *J* 9 Hz, Ph). δ_C ($CDCl_3$, 100 MHz) 20.6 (CH_3), 20.7 ($2CH_3$), 20.8 (CH_3), 61.9 (CH_2), 68.2 (CH, glucose ring), 71.1 (CH, glucose ring), 72.1 (CH, glucose ring), 72.6 (CH, glucose ring), 98.9 (anomeric CH), 117.3, 123.3, 124.3, 126.8, 129.4, 136.2, 142.2, 156.2 (C, Ph), 169.1 (C=O), 169.2 (C=O), 170.0 (C=O), 170.4 (C=O). ν_{max}/cm^{-1} (KBr): 1177, 1253 (s, C–O–C), 1498, 1506, 1731 (s, C=O), 2940.

4.1.6. 5,5″-Bis-(4-[2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl]phenyl)-[2,2′:5′2″]terthiophene ***4a***. Na_2CO_3 (0.038 g, 0.36 mmol), Ag_2O (0.083 g, 0.36) and $Pd(PPh_3)_4$ (0.013 g, 0.011 mmol) were added to a solution of (2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-4-iodobenzene **10a** (0.200 g, 0.36 mmol) and 5,5″-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[2,2′:5′2″]terthiophene **12** (0.080 g, 0.16 mmol) in 7 mL of anhydrous dioxane under a nitrogen atmosphere. The reaction mixture was heated at 70 °C overnight and then cooled to room temperature and concentrated under reduced pressure. The crude material obtained was purified by preparative chromatography on silica gel, using a mixture of petroleum ether/diethyl ether 8.5:1.5 as the eluent and then crystallized from dichloromethane/hexane. A bright yellow solid was recovered (0.127 g, 80% yield). (Found: C, 57.10, H, 4.81, S, 8.78. $C_{52}H_{52}O_20S_3$ requires C, 57.13, H, 4.79, S, 8.80); R_f (petroleum ether/diethyl ether 8.5:1.5) 0.45; mp 247–248 °C (dichloromethane/hexane). δ_H ($CDCl_3$, 400 MHz): 2.04 (6H, s, CH_3), 2.06 (6H, s, CH_3), 2.08 (6H, s, CH_3), 2.10 (6H, s, CH_3), 3.85–3.93 (2H, m, CH), 4.19 (2H, dd, *J* 12.2, 1.9 Hz, CH_2), 4.31(2H, dd, *J* 12.2, 5.2 Hz, CH_2), 5.13 (2H, d, *J* 7.3 Hz, anomeric CH), 5.20 (2H, t, *J* 9.5 Hz, CH), 5.26–5.37 (4H, m, CH), 6.97–7.06 (4H, app d, *J* 9 Hz, Ph), 7.08–7.12 (2H, m, Th), 7.12–7.18 (4H, m, Th), 7.50–7.57 (4H, app d, *J* 9 Hz, Ph). δ_C ($CDCl_3$, 100 MHz) 20.7 ($3CH_3$), 20.8 (CH_3), 61.9 (CH_2), 68.3 (CH, glucose ring), 71.2 (CH, glucose ring), 72.1 (CH, glucose ring), 72.7 (CH, glucose ring), 99.0 (anomeric CH), 117.4, 123.4, 124.1, 124.5, 126.8, 129.4, 136.0, 136.0, 142.4, 156.3 (C, Ph), 169.1 (C=O), 169.2 (C=O), 170.1 (C=O), 170.4 (C=O). ν_{max}/cm^{-1} (KBr): 1038, 1234 (s, C–O–C), 1368, 1406, 1738 (s, C=O), 2951.

4.1.7. 5-(4-[2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl]phenyl)-[2,2′]-bithiophene ***5a***. Na_2CO_3 (0.030 g, 0.28 mmol), Ag_2O (0.065 g, 0.28 mmol) and $Pd(PPh_3)_4$ (0.09 g, 0.01 mmol) were added to a solution of (2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-4-iodobenzene **10a** (0.155 g, 0.28 mmol) and 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2′-bithiophene **8** (0.091 g, 0.31 mmol) in 5 mL of anhydrous dioxane under a nitrogen atmosphere. The reaction mixture was heated at 70 °C overnight and then cooled to room temperature, filtered through a thin pad of silica gel (eluting with dichloromethane/ethyl acetate 1:1) and concentrated under reduced pressure. The crude material obtained was purified by preparative chromatography on silica gel, using a mixture of petroleum ether/ethyl acetate 6:4 as the eluent and then crystallized from dichloromethane/hexane. A bright yellow solid was recovered (0.140 g, 84% yield). (Found: C, 57.16, H, 4.77, S, 10.86. $C_{28}H_{28}O_{10}S_2$ requires C, 57.13, H, 4.79, S, 10.89); R_f (petroleum ether/ethyl acetate 6:4) 0.43; mp 197–198 °C (dichloromethane/hexane). δ_H ($CDCl_3$, 400 MHz): 2.04 (3H, s, CH_3), 2.06 (3H, s, CH_3), 2.08 (3H, s, CH_3), 2.09 (3H, s, CH_3), 3.84–3.91 (1H, m, CH), 4.17 (1H, dd, *J* 12.3, 2.4 Hz, CH_2), 4.30 (1H, dd, *J* 12.3, 5.3 Hz, CH_2), 5.10 (1H, d, *J* 7.6 Hz, anomeric CH), 5.19 (1H, app t, *J* 9.6 Hz, CH), 5.25–5.35 (2H, m, CH), 6.97–7.04 (3H, m, Ph–Th), 7.11–7.15 (2H, m, Th), 7.18 (1H, dd, *J* 3.6, 1.1 Hz, Th), 7.21 (1H, dd, *J* 5.1, 1.1 Hz, Th), 7.49–7.55 (2H, app d, *J* 9 Hz, Ph). δ_C ($CDCl_3$, 100 MHz) 20.8 ($2CH_3$), 20.9 ($2CH_3$), 62.1 (CH_2), 68.4 (CH, glucose ring), 71.3 (CH, glucose ring), 72.3 (CH, glucose ring), 72.9 (CH, glucose ring), 99.2 (anomeric CH), 117.6, 123.6, 123.8, 124.6, 124.8, 127.1, 128.1, 129.7, 136.6, 137.5, 142.5, 156.5 (C, Ph), 169.5 (C=O), 169.6 (C=O), 170.5 (C=O), 170.8 (C=O). ν_{max}/cm^{-1} (KBr): 1045, 1084, 1226 (s), 1235, 1366, 1499, 1747 (s, C=O), 2945.

4.1.8. 5-(4-[2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl]phenyl)-[2,2′:5′2″]terthiophene ***6a***. Na_2CO_3 (0.031 g, 0.29 mmol), Ag_2O (0.068 g, 0.29 mmol) and $Pd(PPh_3)_4$ (0.010 g, 0.009 mmol) were added to a solution of (2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-4-iodobenzene **10a** (0.165 g, 0.29 mmol) and 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[2,2′:5′2″]-terthiophene **9** (0.124 g, 0.33 mmol) in 5 mL of anhydrous dioxane under a nitrogen atmosphere. The reaction mixture was heated at 70 °C overnight and then cooled to room temperature and concentrated under reduced pressure. The crude material obtained was purified by preparative chromatography on silica gel, using a mixture of dichloromethane/ethyl acetate 9:1 as the eluent and then crystallized from dichloromethane/hexane. A bright yellow solid was recovered (0.170 g, 85% yield). (Found: C, 57.32, H, 4.51, S, 14.30. $C_{32}H_{30}O_{10}S_3$ requires C, 57.30, H, 4.51, S, 14.34); R_f (dichloromethane/ethyl acetate 9:1) 0.6; mp 237–238 °C (dichloromethane/hexane). δ_H ($CDCl_3$, 500 MHz): 2.05 (3H, s, CH_3), 2.06 (3H, s, CH_3), 2.08 (3H, s, CH_3), 2.10 (3H, s, CH_3), 3.85–3.91 (1H, m, CH), 4.19 (1H, dd, *J* 12.4, 2.2 Hz, CH_2), 4.30(1H, dd, *J* 12.4, 5.3 Hz, CH_2), 5.11 (1H, d, *J* 7.6 Hz, anomeric CH), 5.18 (1H, t, *J* 9.5, CH), 5.23–5.34 (2H, m, CH), 6.99–7.04 (3H, m, Th–Ph), 7.09(2H, br s, Th), 7.13 (2H, dd, *J* 8.9, 3.8 Hz, Th), 7.18 (1H, dd, *J* 3.6, 1.1 Hz, Th), 7.22 (1H, dd, *J* 5.1, 1.1 Hz, Th), 7.51–7.55 (2H, app d, *J* 9 Hz, Ph). δ_C ($CDCl_3$, 100 MHz) 20.6 (CH_3), 20.7 ($2CH_3$), 20.8 (CH_3), 61.9 (CH_2), 68.2 (CH, glucose ring), 71.1 (CH, glucose ring), 72.1 (CH, glucose ring), 72.7 (CH, glucose ring), 98.9 (anomeric CH), 117.3, 123.4, 123.6, 124.0, 124.3, 124.4, 126.8, 127.8, 129.3, 129.6, 136.0, 136.1, 136.9, 142.7, 156.2 (C, Ph), 169.1 (C=O), 169.2 (C=O), 170.1 (C=O), 170.4 (C=O). ν_{max}/cm^{-1} (KBr): 794, 833, 1043, 1068, 1233 (s), 1368 (w), 1750 (s, C=O).

4.1.9. 6-(4-Iodophenoxy)hexan-1-ol ***18***. 4-Iodophenol (3.0 g, 13.64 mmol) and potassium hydroxide (1.68 g, 30.0 mmol) were dissolved in 15 mL of DMSO. After stirring for 10 min 6-bromo-1-hexanol (1.96 ml, 15.0 mmol) was added dropwise. After 8 h, the reaction was quenched by adding an aqueous solution of 5% HCl. The product was extracted with dichloromethane (3×50 mL). The organic phases were washed thrice with a saturated solution of NaCl and after dried over anhydrous Na_2SO_4. The solvent was evaporated at reduced pressure. The crude product was purified by silica gel column chromatography (dichloromethane/ethyl acetate 7:3 as eluent) obtaining 6-(4-iodo-phenoxy)-hexan-1-ol **18** (3.202 g, 73%) as a colourless oil.[24] (Found: C, 45.04, H, 5.33. $C_{12}H_{17}IO_2$ requires C, 45.02, H, 5.35); R_f (dichloromethane/ethyl acetate 7:3) 0.55; δ_H ($CDCl_3$, 400 MHz): 1.26 (1H, t, *J* 7.1 Hz, OH), 1.33–1.54 (4H, m, CH_2), 1.60 (2H, quintet, *J* 7.1 Hz, CH_2), 1.78(2H, quintet, *J* 6.5 Hz, CH_2), 3.65 (2H, t, *J* 6.6 Hz, CH_2), 3.91 (2H, t, *J* 6.5 Hz, CH_2), 6.61–6.71 (2H, app d, *J* 9 Hz, Ph), 7.50–7.58 (2H, app d, *J* 9 Hz, Ph) ppm.

4.1.10. (S)-4-Iodo-1-(6-(2-tert-butoxycarbonylamino-3-phenylpropanoyl)hexyloxy)benzene ***10b***. Triethylamine (1.70 mL, 12.18 mmol) and DMAP (0.343 g, 2.81 mmol) were added to a solution of *N*-BOC-L-phenylalanine (3.23 g, 12.18 mmol) and 6-(4-iodophenoxy)-hexan-1-ol **18** (3.0 g, 9.37 mmol) in 30 mL of dichloromethane. The mixture was cooled to 0 °C under stirring and isopropenyl chlorocarbonate (IPCC) was added dropwise (1.33 mL, 12.2 mmol) over 30 min. After 1 h, dichloromethane (20 mL) was added, and the organic phases were washed with a saturated aqueous solution of NH_4Cl (20 mL) and brine (20 mL). The organic phases were dried over anhydrous Na_2SO_4 and the solvent evaporated at reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate 8:2 as the eluent) obtaining (*S*)-4-iodo-1-(6-(2-*tert*-butoxycarbonylamino-3-phenylpropanoyl)hexyloxy)benzene **10b** as a pale white solid (4.48 g, 84% yield). (Found: C, 55.00, H, 6.06, N, 2.49. $C_{26}H_{34}INO_5$

requires C, 55.03, H, 6.04, N, 2.47); R_f (petroleum ether/ethyl acetate 8:2) 0.61; mp 45–46 °C (methanol). δ_H ($CDCl_3$, 400 MHz): 1.31–1.50 (13H, m, CH_2–CH_3), 1.57–1.68 (2H, m, CH_2), 1.71–1.80 (2H, m, CH_2), 3.01–3.12 (2H, m, CH_2), 3.90 (2H, t, *J* 6.4 Hz, CH_2), 4.04–4.16 (2H, m, CH_2), 4.52–4.61 (1H, br m, CH), 4.98 (1H, br d, *J* 8.8 Hz, NH), 6.64–6.69 (2H, app d, *J* 8 Hz, Ph), 7.10–7.15 (2H, app d, *J* 7 Hz, Ph), 7.20–7.31 (3H, m, Ph), 7.51–7.56 (2H, app d, *J* 8 Hz, Ph). δ_C ($CDCl_3$, 100 MHz). 25.6 ($2CH_2$), 28.3 (one CH_3 plus one CH_2), 28.9 (CH_2), 38.4 (CH_2), 54.4 (CH_2), 65.2 (aliphatic carbon), 67.8 (aliphatic carbon), 79.8 (C_{quat}), 82.4 (C–I, Ph), 116.8 (Ph), 126.9 (Ph), 128.5 (Ph), 129.3 (Ph), 136 (Ph), 138.1 (Ph), 155.0 (Ph), 158.8 (C=O), 172.0 (C=O). ν_{max}/cm^{-1} (KBr): 1057, 1168, 1248, 1281, 1487, 1529, 1690 (s, C=O), 1732 (s, C=O), 2941, 3366 (N–H).

4.1.11. (2S,2′S)-1,4-Bis-([2,2′]-bithiophen-5-yl)-2,5-bis-(6-(2-tert-butoxycarbonylamino-3-phenylpropanoyl)hexyloxy)benzene ***1b***. Anhydrous Na_2CO_3 (0.066 g, 0.623 mmol), Ag_2O (0.144 g, 0.621 mmol) and $Pd(PPh_3)_4$ (0.011 g, 0.009 mmol) were added to a stirred solution of 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2′-bithiophene **8** (0.198 g, 0.678 mmol) and (2*S*,2′*S*)-1,4-diiodo-2,5-bis-(6-(2-*tert*-butoxycarbonylamino-3-phenylpropanoyl)hexyloxy) benzene **7b** (0.326 g, 0.308 mmol) in 5 mL of dry 1,4-dioxane kept under nitrogen atmosphere. The reaction mixture was heated at 70 °C overnight and then cooled to room temperature and concentrated under reduced pressure. The crude material obtained was purified by preparative chromatography on silica gel, using a mixture of petroleum ether/dichloromethane/ethyl acetate (8:2:2) as eluent and then crystallized from dichloromethane/hexane. A yellow solid was isolated (0.210 g, 60% yield). (Found: C, 65.63; H, 6.36; N, 2.51; S, 11.40. $C_{62}H_{72}N_2O_{10}S_4$ requires C, 65.70; H, 6.40; N, 2.47; S, 11.32); R_f (petroleum ether/dichloromethane/ethyl acetate (8:2:2)) 0.53; mp 121–123 °C (dichloromethane/hexane); δ_H ($CDCl_3$, 500 MHz): 1.34–1.48 (4H, m, CH_2), 1.42 (18H, s, CH_3), 1.61 (4H, quintet, *J* 7.8 Hz, CH_2), 1.63 (4H, quintet, *J* 7.8 Hz, CH_2), 1.93 (4H, quintet *J* 7.8 Hz, CH_2), 3.01–3.14 (4H, m, CH_2), 4.07–4.17 (8H, m, CH_2), 4.53–4.62 (2H, br m, CH), 4.99 (2H, br d, *J* 8 Hz, NH), 7.04 (2H, dd, *J* 3.9, 5.1 Hz, Th), 7.13 (4H, dl, *J* 7.0 Hz, Th), 7.18 (2H, d, *J* 3.9 Hz, Th), 7.19–7.31 (2H, m, Ph), 7.46 (2H, d, *J* 3.9 Hz, Ph) ppm. δ_C ($CDCl_3$, 125 MHz) 25.7 (CH_2), 26.0 (CH_2), 28.3 (one CH_3 plus one CH_2), 29.3 (CH_2), 38.4 (CH_2), 54.4 (CH_2), 65.3 (aliphatic carbon), 69.5 (aliphatic carbon), 79.8 (CH_{quat}), 112.1, 122.7, 123.3, 123.5, 124.3, 125.8, 126.9, 127.9, 128.5, 129.3, 136.0, 137.3, 137.6, 138.0, 149.2, 155.0 (C=O), 172.0 (C=O) ppm. ν_{max}/cm^{-1} (KBr): 1054, 1166, 1214, 1522, 1691 (C=O), 1731 (C=O). 2931, 3365 (m, N–H).

4.1.12. (2S,2′S)-1,4-Bis-([2,2′:5′2″]terthiophen-5-yl)-2,5-bis-(6-(2-tert-butoxycarbonylamino-3-phenylpropanoyl)hexyloxy)benzene ***2b***. Anhydrous Na_2CO_3 (0.042 g, 0.392 mmol), Ag_2O (0.091 g, 0.392 mmol) and $Pd(PPh_3)_4$ (0.014 g, 0.0118 mmol) were added to a stirred solution of 4,4,5,5-tetramethyl-2-[2,2′:5′2″]terthiophen-5-yl-[1,3,2]dioxaborolane **9** (0.161 g, 0.431 mmol) and (2*S*,2′*S*)-1,4-diiodo-2,5-bis-(6-(2-*tert*-butoxycarbonylamino-3-phenylpropanoyl) hexyloxy)benzene **7b** (0.207 g, 0.196 mmol) in 5 mL of dry 1,4-dioxane kept under nitrogen atmosphere. The reaction mixture was heated at 70 °C overnight and then cooled to room temperature and concentrated under reduced pressure. The crude material obtained was purified by preparative chromatography on silica gel, using a mixture of petroleum ether/dichloromethane/ethyl acetate (8:1:2) as eluent and then crystallized from dichloromethane/hexane. A brown-yellow solid was isolated (0.153 g, 60% yield). (Found: C, 46.75, H, 5.93, N, 2.17, S, 15.87. $C_{70}H_{76}N_2O_{10}S_6$ requires C, 64.78; H, 5.90; N, 2.16; S, 14.83); R_f (petroleum ether/dichloromethane/ethyl acetate (7:1:2)) 0.35; mp 121–123 °C (dichloromethane/hexane). δ_H ($CDCl_3$, 400 MHz): 1.38 (18H, s, CH_3), 1.49–1.68 (12H, m, CH_2), 1.92 (4H, quintet, *J* 7.4 Hz, CH_2), 2.97–3.10 (4H, m, CH_2), 4.05–4.15 (8H, m, CH_2), 4.48–4.59 (2H, m, CH), 4.90 (2H, br d, *J* 8.0 Hz, NH), 7.00 (2H, dd, *J* 5.0, 3.7 Hz, Th), 7.05–7.30 (22H, m, Ph–Th), 7.43–7.47 (2H, m, Ph). δ_C ($CDCl_3$, 100 MHz) 25.8 (CH_2), 26.1 (CH_2), 28.4 (CH_3), 28.6 (CH_2), 29.3 (CH_2), 38.5 (CH_2), 54.5 (CH_2), 65.3 (aliphatic carbon), 69.5 (aliphatic carbon), 79.8 (CH_{quat}), 112.0, 122.7, 123.4, 123.6, 123.8, 124.3, 125.9, 126.9, 127.8, 128.4, 129.2, 136.0, 136.4, 136.9, 137.1, 138.0, 149.1, 154.9 (C=O), 171.8 (C=O) ppm. ν_{max}/cm^{-1} (KBr): 791, 1165, 1261, 1458, 1491, 1521, 1692 (C=O), 1718 (C=O). 2852, 2923, 3368 (m, N–H).

4.1.13. (2S,2′S)-5,5′-Bis-(4-(6-(2-tert-butoxycarbonylamino-3-phenylpropanoyl)hexyloxy)phenyl)-[2,2′]-bithiophene ***3b***. Anhydrous Na_2CO_3 (0.038 g, 0.36 mmol), Ag_2O (0.083 g, 0.36) and $Pd(PPh_3)_4$ (0.013 g, 0.011 mmol) were added to a stirred solution of 2,2′-bithiophene-5,5′-diboronic acid bis-(pinacol) ester **11** (0.067 g, 0.16 mmol) and (*S*)-4-iodo-1-(6-(2-*tert*-butoxycarbonylamino-3-phenylpropanoyl)hexyloxy)benzene **10b** (0.204 g, 0.36 mmol) in 5 mL of dry 1,4-dioxane kept under nitrogen atmosphere. The reaction mixture was heated at 70 °C overnight and then cooled to room temperature and concentrated under reduced pressure. The crude material obtained was purified by preparative chromatography on silica gel, using a mixture of petroleum ether/dichloromethane/ethyl acetate (6:3:1) as eluent and then crystallized from dichloromethane/hexane. A pale yellow solid was isolated (0.152 g, 91%). (Found: C, 68.92, H, 6.60, N, 2.69, S, 6.11. $C_{60}H_{72}N_2O_{10}S_2$ requires C, 68.94, H, 6.94, N, 2.68, S, 6.13); R_f (petroleum ether/dichloromethane/ethyl acetate (6:3:1)) 0.65; mp 140–141 °C (dichloromethane/hexane). δ_H ($CDCl_3$, 400 MHz): 1.29–1.51 (26H, m, CH_2, CH_3), 1.52–1.65 (4H, m, CH_2), 1.72–1.81 (4H, m, CH_2), 2.99–3.12 (4H, m, CH_2), 3.95 (4H, t, *J* 6.4 Hz, CH_2), 4.04–4.14 (4H, m, CH_2), 4.50–4.59 (2H, m, CH), 4.96 (2H, br d, *J* 9 Hz, NH), 6.85–6.91 (4H, app d, *J* 9 Hz, Ph), 7.06–7.14 (8H, m, Ph–Th), 7.18–7.30 (6H, m, Ph), 7.46–7.52 (4H, app d, *J* 9 Hz, Ph). δ_C ($CDCl_3$, 100 MHz) 25.6 (CH_2), 25.7 (CH_2), 28.3 (CH_3), 28.4 (CH_2), 29.1 (CH_2), 38.4 (CH_2), 54.4 (CH_2), 65.2 (aliphatic carbon), 67.8 (aliphatic carbon), 79.8 (C_{quat}), 94.3, 114.7, 122.5, 124.0, 126.6, 126.7, 126.8, 128.3, 129.2, 135.6, 135.9, 142.7, 158.5 (C=O), 171.8 (C=O). ν_{max}/cm^{-1} (KBr): 794, 1025, 1095, 1162, 1258 (S, C–O–C), 1465, 1499, 1517, 1686 (C=O), 1730 (C=O), 2925, 3365 (m, N–H).

4.1.14. (2S,2′S)-5,5″-Bis-(4-(6-(2-tert-butoxycarbonylamino-3-phenylpropanoyl)hexyloxy)phenyl)-[2,2′:5′2″]-terthiophene ***4b***. Anhydrous Na_2CO_3 (0.038 g, 0.36 mmol), Ag_2O (0.083 g, 0.36) and $Pd(PPh_3)_4$ (0.013 g, 0.011 mmol) were added to a stirred solution of 5,5″-bis (4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[2,2′:5′2″]terthiophene **12** (0.080 g, 0.16 mmol) and (*S*)-4-iodo-1-(6-(2-*tert*-butoxycarbonylamino-3-phenylpropanoyl)hexyloxy)benzene **10b** (0.204 g, 0.36 mmol) in 5 mL of dry 1,4-dioxane kept under nitrogen atmosphere. The reaction mixture was heated at 70 °C overnight and then cooled to room temperature and concentrated under reduced pressure. The crude material obtained was purified by preparative chromatography on silica gel, using a mixture of petroleum ether/dichloromethane/ethyl acetate (6:3:1) as eluent and then crystallized from dichloromethane/hexane. A pale yellow solid was isolated (0.153 g, 85%). (Found: C, 68.16, H, 6.60, N, 2.50, S, 8.53. $C_{64}H_{74}N_2O_{10}S_3$ requires C, 68.18, H, 6.62, N, 2.48, S, 8.53); R_f (petroleum ether/dichloromethane/ethyl acetate (6:3:1)) 0.39; mp 178–179 °C (dichloromethane/hexane). δ_H ($CDCl_3$, 400 MHz): 1.31–1.52 (26H, m, CH_2, CH_3), 1.57–1.66 (4H, m, CH_2), 1.74–1.83 (4H, m, CH_2), 3.01–3.13 (4H, m, CH_2), 3.96 (4H, t, *J* 6.4 Hz, CH_2), 4.05–4.14 (4H, m, CH_2), 4.53–4.62 (2H, m, CH), 4.96 (2H, br d, *J* 8.5 Hz, NH), 6.67–6.93 (4H, app d, *J* 9 Hz, Ph), 7.05–7.07 (2H, m, Th), 7.09–7.11 (4H, m, Ph), 7.11–7.17 (4H, app d, *J* 7 Hz, Th), 7.20–7.31 (6H, m, Ph), 7.47–7.54 (4H, app d, *J* 9 Hz, Ph). δ_C ($CDCl_3$, 100 MHz) 25.7 ($2CH_2$), 28.3 (CH_3), 28.4 (CH_2), 29.1 (CH_2), 38.5 (CH_2), 54.5 (CH_2), 65.3 (aliphatic carbon), 67.8 (aliphatic carbon), 79.8 (C_{quat}), 114.8, 122.6, 123.8, 124.3, 126.5, 126.7, 126.9, 128.5, 129.2, 135.2, 135.9, 143.1, 154.9, 158.6 (C=O), 171.8 (C=O). ν_{max}/cm^{-1}

(KBr): 791, 1055, 1176, 1250, 1464, 1496, 1694 (C=O), 1730 (C=O), 2930, 3380 (m, N–H).

4.1.15. (S)-5-(4-(6-(2-tert-Butoxycarbonylamino-3-phenylpropanoyl) hexyloxy)phenyl)-[2,2′]-bithiophene ***5b***. Anhydrous Na_2CO_3 (0.056 g, 0.53 mmol), Ag_2O (0.123 g, 0.53 mmol) and $Pd(PPh_3)_4$ (0.018 g, 0.016 mmol) were added to a stirred solution of 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2′-bithiophene **8** (0.170 g, 0.58 mmol) and (*S*)-4-iodo-1-(6-(2-*tert*-butoxycarbonylamino-3-phenylpropanoyl)hexyloxy)benzene **10b** (0.300 g, 0.53 mmol) in 8 mL of dry 1,4-dioxane kept under nitrogen atmosphere. The reaction mixture was heated at 70 °C overnight and then cooled to room temperature and concentrated under reduced pressure. The crude material obtained was purified by preparative chromatography on silica gel, using a mixture of petroleum ether/ethyl acetate 8:2 as the eluent and then crystallized from dichloromethane/hexane. A yellow solid was isolated (0.237 g, 74% yield). (Found: C, 67.42, H, 6.46, N, 2.30, S, 10.57. $C_{34}H_{39}NO_5S_2$ requires C, 67.41, H, 6.49, N, 2.31, S, 10.59); R_f (petroleum ether/ethyl acetate 8:2) 0.43; mp 102–103 °C (dichloromethane/hexane). δ_H ($CDCl_3$, 400 MHz): 1.33–1.53 (13H, m, CH_2, CH_3), 1.57–1.67 (2H, m, CH_2), 1.75–1.83 (2H, m, CH_2), 3.04–3.13 (2H, m, CH_2), 3.98 (2H, t, *J* 6.4 Hz, CH_2), 4.08–4.16 (2H, m, CH_2), 4.54–4.61 (1H, br m, CH), 4.98 (1H, br d, *J* 8 Hz, NH), 6.88–6.92 (2H, app d, *J* 9 Hz, Ph), 7.02 (1H, dd, *J* 5.1, 3.6 Hz, Th), 7.09–7.15 (4H, m, Ph–Th), 7.17 (1H, dd, *J* 3.6, 1.1 Hz, Th), 7.20 (1H, dd, *J* 5.1, 1.2 Hz, Th), 7.23–7.32 (3H, m, Ph), 7.34–7.49 (2H, app d, *J* 9 Hz, Ph). δ_C ($CDCl_3$, 125 MHz) 25.6 (CH_2), 25.7 (CH_2), 28.3 (CH_3), 28.4 (CH_2), 29.1 (CH_2), 38.4 (CH_2), 54.4 (CH_2), 65.3 (CH_2 or CH), 67.8 (aliphatic carbon), 79.8 (C_{quat}), 114.8, 122.5, 123.3, 124.1, 124.5, 126.7, 126.8, 126.9, 127.8, 128.5, 129.3, 135.6, 136.0, 137.6, 143.2, 155.0, 158.7 (C=O), 172.0 (C=O). ν_{max}/cm^{-1} (KBr): 699, 797, 1167, 1180, 1251 (s), 1279, 1499, 1516, 1692 (C=O), 1728 (s, C=O), 2934, 3399 (m, NH).

4.1.16. (S)-5-(4-(6-(2-tert-Butoxycarbonylamino-3-phenylpropanoyl) hexyloxy)phenyl)-[2,2′:5′2″]-terthiophene ***6b***. Anhydrous Na_2CO_3 (0.032 g, 0.30 mmol), Ag_2O (0.070 g, 0.32 mmol) and $Pd(PPh_3)_4$ (0.010 g, 0.008 mmol) were added to a stirred solution of 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2′:5′2″-terthiophene **9** (0.124 g, 0.33 mmol) and (*S*)-4-iodo-1-(6-(2-*tert*-butoxycarbonylamino-3-phenylpropanoyl)hexyloxy)benzene **10b** (0.170 g, 0.30 mmol) in 5 mL of dry 1,4-dioxane kept under nitrogen atmosphere. The reaction mixture was heated at 70 °C overnight and then cooled to room temperature and concentrated under reduced pressure. The crude material obtained was purified by preparative chromatography on silica gel, using a mixture of petroleum ether/dichloromethane/ethyl acetate (8:2:1) as eluent and then crystallized from dichloromethane/hexane. A yellow solid was isolated (0.163 g, 79%). (Found: C, 66.32, H, 6.00, N, 2.02, S, 14.01. $C_{38}H_{41}NO_5S_3$ requires C, 66.34, H, 6.01, N, 2.04, S, 13.98); R_f (petroleum ether/dichloromethane/ethyl acetate (8:2:1)) 0.45; mp 163–164 °C (dichloromethane/hexane). δ_H ($CDCl_3$, 400 MHz): 1.31–1.55 (13H, m, CH_2, CH_3), 1.57–1.71 (2H, m, CH_2), 1.74–1.85 (2H, m, CH_2), 3.00–3.14 (2H, m, CH_2), 3.98 (2H, t, *J* 6.3 Hz, CH_2), 4.05–4.18 (2H, m, CH_2), 4.54–4.63 (1H, br m, CH), 4.99 (1H, br d, *J* 7.7 Hz, NH), 6.87–6.96 (2H, app d, *J* 9 Hz, Ph), 7.03 (1H, dd, *J* 5.1, 3.6 Hz, Th), 7.09–7.19 (7H, m, Ph–Th), 7.21–7.33 (4H, m, Ph–Th), 7.48–7.55 (2H, app d, *J* 9 Hz, Ph). δ_C ($CDCl_3$, 100 MHz) 25.6 (CH_2), 25.7 (CH_2), 28.3 (CH_3), 28.4 (CH_2), 29.1 (CH_2), 38.4 (CH_2), 54.4 (CH_2), 65.3 (aliphatic carbon), 67.8 (aliphatic carbon), 79.9 (C_{quat}), 114.9, 122.6, 123.6, 123.9, 124.3, 124.4, 124.5, 126.7, 1 26.9, 127.0, 127.9, 128.5, 129.3, 135.2, 135.8, 136.0, 136.4, 137.1, 143.3, 155.0, 158.8 (C=O), 172.0 (C=O). ν_{max}/cm^{-1} (KBr): 790, 1169, 1251, 1496, 1691 (C=O), 1731 (C=O), 2934, 3350 (m, N–H).

4.1.17. [2,2′:5′2″]Terthiophene ***13***. A 100 mL three-necked round bottom flask equipped with a stirrer and a water condenser was charged under nitrogen with 2-iodothiophene (0.34 mL, 3.11 mmol) and 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2′-bithiophene **8** (1.00 g, 3.42 mmol). Then 12.5 mL of ethanol, previously degassed by flushing nitrogen for 30 min, the catalyst $Pd(PPh_3)_4$ (0.107 g, 0.093 mmol), toluene (50 mL) and finally 20 mL of a 2 M aqueous solution of Na_2CO_3 (40.4 mmol), previously degassed for 30 min were added. The reaction mixture was heated at 95 °C with vigorous stirring until the aryl halide had been completely consumed (GC). The reaction mixture was then cooled to room temperature and concentrated under reduced pressure. The base excess was neutralized with an aqueous solution of HCl 5%, and the mixture extracted with dichloromethane (3×30 mL). The organic phase was collected, washed three times with saturated aqueous NaCl (3×50 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by preparative column chromatography over silica gel, using a mixture of petroleum ether/dichloromethane 95:5 as the eluent. A white solid was recovered (0.594 g, 60% yield). (Found: C, 58.01, H, 3.25, S, 38.71. $C_{12}H_8S_3$ requires C, 58.03, H 3.25, S, 38.73); R_f (petroleum ether/dichloromethane 95:5) 0.5; mp 90–91 °C (lit.[25] 93–95 °C). δ_H ($CDCl_3$, 400 MHz): 7.01 (2H, dd, *J* 4.8, 3.8 Hz), 7.07 (2H, m), 7.16 (2H, *J* 3.8 Hz), 7.20 (2H, d, *J* 4.8 Hz). δ_C ($CDCl_3$, 100 MHz) 123.7, 124.3, 124.4, 127.8, 136.2, 137.1. ν_{max}/cm^{-1} (KBr): 674, 680, 796, 832, 1055, 1421, 2923, 3063.

4.1.18. 5,5″-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[2,2′:5′2″]terthiophene ***12***. An oven-dried Schlenk tube containing a magnetic stirrer was evacuated and backfilled with nitrogen three times. Then it was charged with $[IrCl(COD)]_2$ (0.020 g, 0.0303mmol), 4,4′di-*tert*-butyl-2,2′-bipyridine (dtbpy) (0.016 g, 0.0606 mmol) and pin_2B_2 (0.307 g, 1.21 mmol). Dry *n*-octane (20 mL) was added to the mixture, that was stirred for few minutes at room temperature. Then, [2,2′:5′2″]terthiophene **13** (0.250 g, 1.01 mmol) was added and the mixture was heated at 90 °C for 12 h. The reaction was monitored by TLC that showed the disappearance of **13**. The reaction mixture was then allowed to reach room temperature and concentrated under reduced pressure. The crude material obtained was purified by preparative chromatography on silica gel eluting with dichloromethane/methanol in volumetric ratio 9.5:0.5. A green solid was recovered (0.422 g, 84% yield). (Found: C, 57.60, H, 6.05, S, 19.25. $C_{24}H_{30}B_2O_4S_3$ requires C, 57.62, H, 6.04, S, 19.23); R_f (dichloromethane/methanol 9.5:0.5) 0.46; mp; 103–104 °C (dichloromethane/hexane). δ_H ($CDCl_3$, 500 MHz): 7.52 (2H, d, *J* 3.8 Hz), 7.23 (2H, *J* 3.8 Hz), 7.14 (2H, s), 1.35 (24H, $8CH_3$). δ_C ($CDCl_3$, 125 MHz) 24.8 ($8CH_3$), 84.2 ($4C_{quat}$), 123.7, 124.9, 125.0, 127.8, 136.5, 137.8. ν_{max}/cm^{-1} (KBr): 850, 1125, 1285, 1350, 1450, 1512, 2925, 2979.

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Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2010.11.004.

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