Well-Defined Triblock Hybrid Dendrimers Based on Lengthy Oligothiophene Cores and Poly(benzyl ether) Dendrons

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π-Conjugated oligomers such as oligothiophenes have been the subject of intense research.[1] Their high environmental stability makes them good candidates for electronic and photonic applications such as field effect transistors, photoswitches, photovoltaic cells, or light modulators.[2]

Recently, block copolymers composed of conjugated and nonconjugated linear blocks have been prepared as a means of controlling the nanoscale molecular organization of these materials.[3] We are interested in preparing a new class of optoelectronic materials based on hybrid structures containing oligothiophenes and dendrimers.[4] For this purpose we have developed a high-yielding synthesis of lengthy oligothiophenes that may be attached to the focal point of the convergent poly(benzyl ether) dendrimers developed earlier in our laboratory.[5] These versatile dendrimers can be further functionalized at the periphery[6] to introduce specific properties such as adhesion, solubility, energy harvesting, or other optoelectronic characteristics in a convenient fashion. To date, oligothiophenes have been constructed mainly through the use of Kumada, Suzuki, Negishi, and Stille reactions and copper-promoted oxidative couplings;[1a,7] however, the yields of these different types of reactions vary greatly. In the case of the Stille reaction, only moderate yields have been reported up to now. Herein, we report the high-yield synthesis of oligothiophenes up to 17 units long via a repetitive sequence of brominations and Stille reactions. Key to our approach is a synthetic design that affords unsymmetrically substituted oligothiophenes with both a terminal carboxylate functionality and an unsubstituted thiophene end. The presence of the terminal carboxylate functionality allows the simple attachment of dendritic blocks to the oligothiophenes. As an example, a symmetric undecathiophene "dumbbell" bearing two-third generation poly(benzyl ether) dendrons was prepared. Dendrimer-based materials employing oligothiophenes as functional cores provide a class of soluble optoelectronic materials having a highly controlled macromolecular architecture with a well-defined electronic substructure.

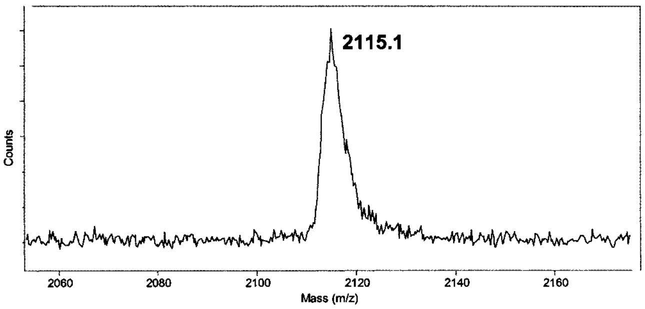

Figure 1. MALDI-TOF spectrum of heptadecamer **12**.

Scheme 1 depicts the synthesis of octamer **10** starting from 2,2′-bithiophene. Carboxylation of 2,2′-bithiophene via lithiation with *n*-butyllithium in tetrahydrofuran (THF) followed by quenching with carbon dioxide provides **1** (80%). To grow the oligomers, the carboxylate functionality of **1** was protected with a benzyl ester group through reaction with benzyl bromide in the presence of 18-crown-6 in THF to provide **2** (95%). Selective bromination of dimer **2** at the α-position with *N*-bromosuccinimide (NBS) in *N*,*N*-dimethylformamide (DMF) was performed at room temperature, thus providing dimer bromide **3** (99%). A Stille reaction between **3** and 2-(trimethylstannyl)-4-octylthiophene[8a,3b] with $Pd(PPh_3)_2Cl_2$ as the catalyst in DMF afforded trimer **4** (95%). Bromination of **4** with NBS in DMF led to the α-brominated trimer bromide **5** (99%). A Stille reaction between **5** and 5-(trimethylstannyl)-2,2′-bithiophene[8b] afforded pentamer **6** (90%). Pentamer **6** and hexamer **8** were brominated at higher temperatures (40−50 °C) due to their lower solubility at room temperature in DMF, thus providing pentamer bromide **7** (97%) and hexamer bromide **9** (98%), respectively. Hexamer **8** (91%) and octamer **10** (89%) were obtained via a Stille reaction as described for **4** and **6**, respectively. The overall yield of the eight-step sequence from dimer **2** up to octamer **10** is 65%.

These oligothiophenes can serve as building blocks for longer, symmetric oligomers. For example, bromination of octamer **10** led to bromide **11** (92%) that was coupled to 2,5-bis(trimethylstannyl)thiophene[9] to provide heptadecamer **12** in 78% yield (Scheme 2). The MALDI-TOF spectrum of **12** (Figure 1) shows a monodisperse product that is the longest oligothiophene reported to date. More importantly, the efficiency of the coupling reactions is illustrated by the better than 47% overall yield of heptadecamer **12** from dimer **2**, which is the equivalent of having a 93% yield at every step.[10a] Also, one can easily envision the use of different building blocks along the synthesis to fine-tune the properties of the lengthy oligomers. Although **12** is not soluble in common organic solvents, dilute solutions can be prepared in hot carbon disulfide (λ_{max} = 492 nm, shoulder at 590 nm). A ^1H NMR spectrum was collected in CS_2 at 45 °C. Unfortunately, due to the low solubility of **12** a ^{13}C NMR spectrum could not be obtained. Nevertheless, a four-point probe measurement of a pressed pellet of **12** doped with iodine yielded a conductivity of

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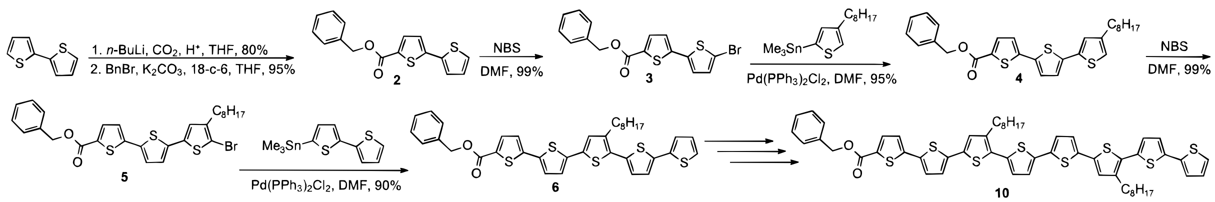
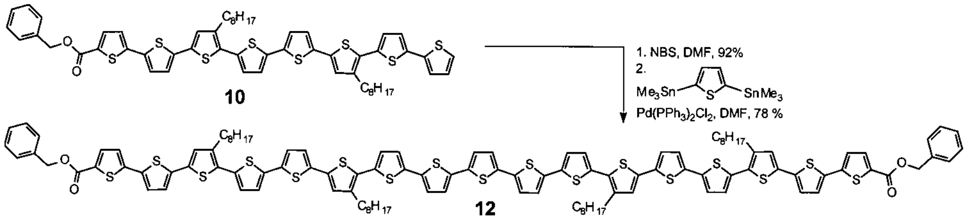
Scheme 1. Synthesis of Octamer **10** from 2,2′-bithiophene[a]

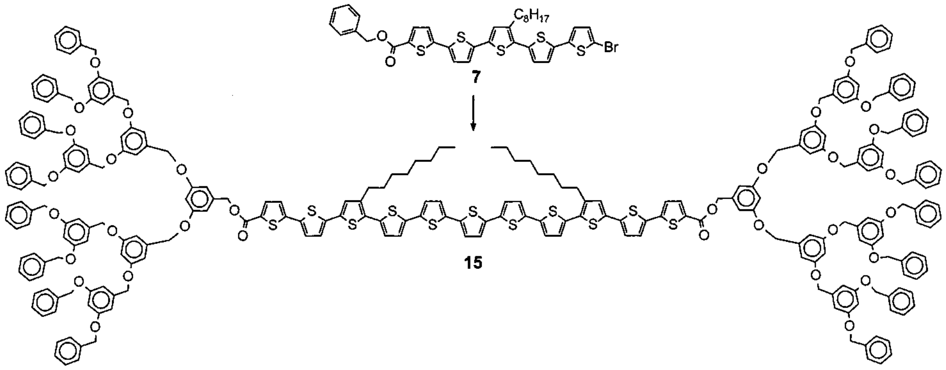


[a] Overall yield for sequence **2**−**10**:65%.

Scheme 2



Scheme 3



33−100 S/cm, which is of the same order of magnitude as poly(3-alkylthiophenes).[11]

Scheme 3 depicts the preparation of the dendrimer-terminated undecamer **15**. Pentamer bromide **7** was first saponified with KOH in a mixture of THF and water and the resulting carboxylic acid **13** was converted to the acid chloride by using oxalyl chloride in THF with catalytic amounts of DMF. The acid chloride was subsequently coupled to a third generation poly(benzyl ether) dendron[5a] containing a benzyl alcohol group at the focal point ([G-3]-OH) thus providing the monodendron functionalized pentamer bromide **14** (80%). A final Stille reaction between **14** and 2,5-bis(trimethylstannyl)thiophene afforded the symmetric undecamer dumbbell **15** in 84% yield. Hybrid dendrimer **15** is monodisperse as assessed by size exclusion chromatography (SEC) ($M_n = 5064$; PDI = 1.01; MALDI-TOF spectrum m/z calcd for ($C_{272}H_{236}O_{32}S_{11}$) 4369.50, found 4371.20). It is highly conjugated ($\lambda_{max} = 472$ nm in $CHCl_3$) and soluble in common organic solvents such as dichloromethane, chloroform, and tetrahydrofuran. Upon addition of methanol to a chloroform solution of **15**, the λ_{max} is bathochromically shifted to 496 nm and a shoulder is observed at 570 nm. These spectral characteristics are also observed in the solid-state thin-film absorption spectrum of **15** and result from aggregation which decreases the inter-ring conformational disorder of the oligomer.[3a] Upon exposing a solution of **15** in CH_2Cl_2 to $NOBF_4$, the oligothiophene core is oxidized and the visible absorbance at 472 nm disappears and two new absorption bands are observed at 744 and 1242 nm. The third-generation dendrons are effective solubilizing groups, thus enabling us to fully characterize the dumbbell-shaped oligothiophene-core dendrimer by ^{1}H and ^{13}C NMR.[10b] Undoubtedly, in the absence of the dendritic groups, **15** would be insoluble.[10b] This material is rather unique in that it is, for the most part, solubilized by substituents at the α and ω positions.[12]

In conclusion, we have presented the synthesis of lengthy oligothiophenes via a high-yielding route that may conceivably allow for a variety of building blocks to be incorporated into the oligomers. The end functionalization of the oligomer allows their incorporation into nanometer-size dendritic moieties in which the conducting oligomer is partially encapsulated by solubilizing dendrons. We are currently using an analogous synthetic protocol to develop a solid-phase method for the expeditious synthesis of oligothiophenes. Also, we have shown the synthesis of a new hybrid linear-dendritic material consisting of a well-defined oligothiophene core and poly(benzyl ether) dendrons. Further study of the optical and redox properties of these dendrimers as well as their application to the design of light-emitting devices or field-effect transistors is underway.

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Supporting Information Available: Experimental details pertaining to the synthesis and characterization (13 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(12) In ref 2b, substitution of sexithiophene at the α and ω position with hexyl chains does not lead to a significant increase in solubility. In ref 3a, α,ω-substitution of undecithiophene with polystyrene blocks leads to a soluble triblock copolymer.