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A First Synthesis of Thiophene Dendrimers

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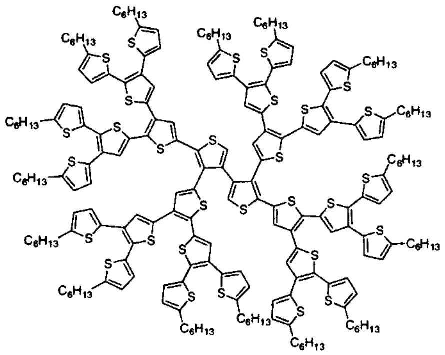
ABSTRACT



Thiophene dendrons and dendrimers were designed and synthesized using a convergent approach. Metal-mediated coupling reactions were used in the synthesis. A rational approach allowed the formation of αα, *ββ*, and α*β* linkages between the dendrons and thiophene units.

During the past several decades, oligothiophenes and polythiophenes have been extensively studied not only for fundamental interest but also for their promising applications in the organic semiconductor field.[1] A large number of substituted derivatives have been designed and synthesized, and their electronic properties have been investigated. Organic electronic devices, such as organic light-emitting diodes (OLEDs)[2] and Field-effect transistors (FETs),[3] based on these derivatives have been fabricated and tested. The optical and electronic properties of oligo- and polythiophene derivatives can be easily tuned by introducing functional substituents to different position on the backbone.[1]

Dendrimers, which are perfect monodispersed macromolecules with a regular and highly branched three-dimensional architecture, represent a key stage in the ongoing evolution of polymer chemistry.[4] Along with flexible backbone dendrimers, conjugated dendrimers with rigid structures, such as phenylacetylene,[5] phenylene vinylene,[6] and polyphenylene[7] dendrimers have also been developed in recent years.

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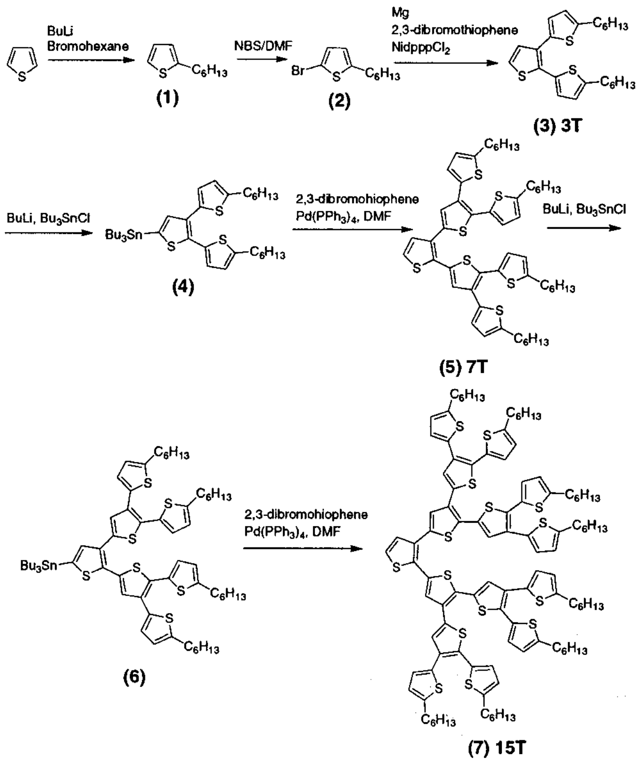
These shape-persistent objects with nanometer sizes exhibit interesting aggregation properties.[8] Some of these compounds can self-assemble into nanowires and other supramolecular structures as a result of $\pi-\pi$ stacking interactions. On the other hand, generational dendrimers containing *all*-thiophene units have not been reported in the literature even though their macrocyclic,[9] tubular,[10] and linear analogues have been extensively studied. However, the optical, electronic, and self-assembly properties of thiophene dendrimers may be intriguing because of their spatial arrangement and microstructure. The intrinsic asymmetric structure can result in different conjugation lengths, resulting in broad absorption, which has been recently observed for another asymmetric polyphenyl acetylene dendrimer.[11]

In this paper, we present our design and synthesis strategy for a series of thiophene dendrons and dendrimers, using mainly a convergent synthesis methodology. The purpose of this macromolecule architecture is to investigate photochemical and physical properties resulting in (1) unusual broad absorption, rendering it a good candidate for an antenna molecule;[12] (2) formation of regular 2-D supramolecular structures on graphite or gold surfaces and conformational change induced through different bias;[13] and (3) formation of self-stacked long-ranged ordered structures.

Scheme 1. Synthesis of Thiophene Dendrons



Scheme 1 shows the synthetic route for the thiophene dendrons. The key starting material for the synthesis is 2,3-dibromothiophene, which is commercially available. In a convergent synthetic sequence, 2,3-dibromothiophene acts as an AB$_2$ type monomer. A C−C bond can form through the C−Br group at the 2,3 positions using metal-mediated coupling. The fifth position can undergo other transformations for further coupling reactions, in our case, Stille coupling. 2-Bromo-5-hexylthiophene was synthesized from thiophene by treating with butyllithium and 1-bromohexane, followed by bromination with NBS/DMF. The pure product was obtained by distillation under reduced pressure; **3T** was made with an excellent yield (90%) using the Kumada method.[14] Although the Grignard coupling could be used to continue the synthesis, the ease of the Stille coupling[15] reaction attracted our attention. As has been well documented, Stille coupling offers efficient C−C bond formation for heterocycles such as thiophenes. The tolerance of a variety of functional groups makes it very useful for modern synthesis. In addition, the reaction is easy to perform. Harmful oxygen can be easily removed by simply doing several freeze−thaw cycles.

Compound **3T** was readily lithiated using butyllithium and reacted with tributyltin chloride to give the stannyl compound for the following Stille coupling. There was no **3T** left after this reaction, and hence, this compound, which is liable to acids, was used without further purification. An excess of the stannyl compound was used to ensure completion of the coupling reaction. No monocoupled product was detected from the NMR. The efficiency of the coupling decreases as the product becomes more crowded around the focal point thiophene, i.e., **7T** was synthesized with 90% yield and **15T**

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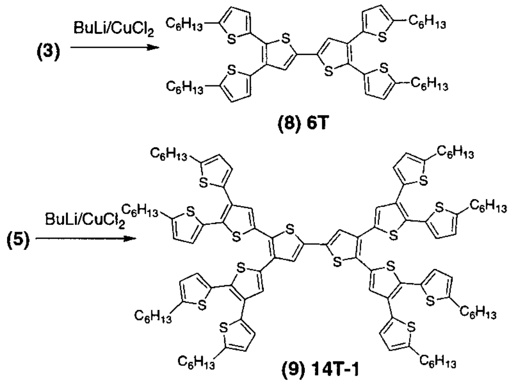
with a lesser 77% yield. Prolonged reaction time did not increase the yield significantly. Attempts on lithiation of **15T** with butyllithium were unsuccessful probably as a result of steric hindrance, which makes the central thiophene inaccessible. In addition, only trace bromination products were isolated when treated with bromine or NBS. Once again, we attribute the inert reactivity mainly to the inaccessibility of the central thiophene.

Direct coupling of these dendrons afforded the dendrimer structures (Scheme 2). Compounds **6T** and **14T-1** were directly coupled from **3T** and **7T**, respectively, through a BuLi/$CuCl_2$ method, which is widely applied for oligothiophene synthesis.[16] However, this coupling is not as efficient as those of linear oligomers and gave only moderate yields, e.g., 54% for **6T** and 40% for **14T-1**. Unfortunately, the coupling of **15T** was not practical because of its poor reactivity (despite several attempts).

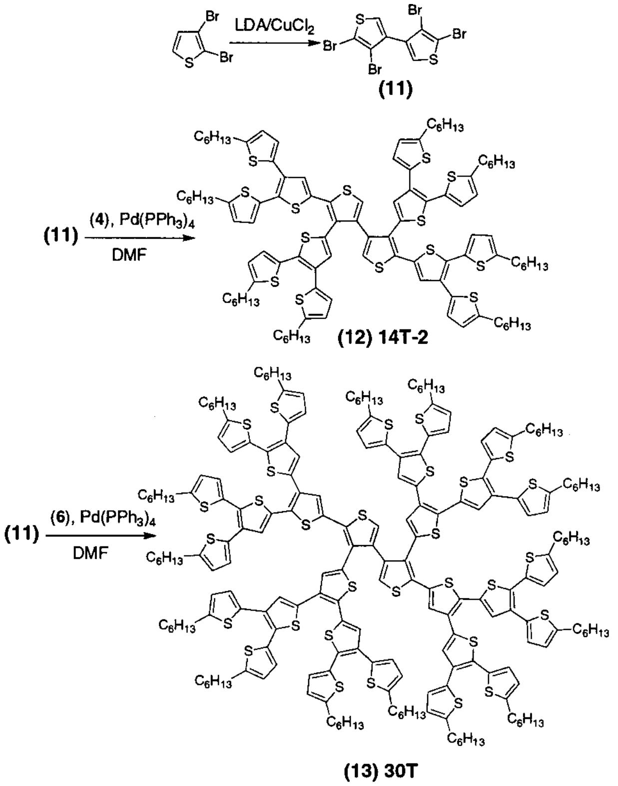
Scheme 2. BuLi/$CuCl_2$ Coupling to Thiophene Dendrimers



For dendrimer synthesis, assembly of dendrons to a core is widely used in order to form functional dendrimers or to simply enlarge the compound. We adopted this method to synthesize **14T-2** and **30T** as shown in Scheme 3. Treating 2,3-dibromothiophene with LDA, followed by $CuCl_2$, gave compound **11**, 4,5,4′,5′-tetrabromo-[3,3′]bithiophene. Instead of abstracting the proton at the fifth position, LDA removed the proton mainly at the fourth position. On the other hand, the lithiation mainly occurred at the fifth position for 2-bromothiophene. Compounds **14T-2** and **30T** were thus made by coupling the tetrabromothiophene with compounds **4** and **6**. The unexpected lithiation allows us to compare the properties of **14T-1** and **14T-2** because they were linked through the α,α- and β,β-position in the central thiophene, respectively. Therefore, they should have different π-conjugation characteristics and also give different NMR spectra.

All of these thiophene dendrons and dendrimers are highly soluble in common solvents such as chloroform, THF, and even hexane. Polar solvents such as DMF and DMSO cannot dissolve compounds bigger than **7T** at room temperature. Only **14T-1** and **30T** solidified after standing for a long time at room temperature; the others are viscous liquids at room temperature. Interestingly, the NMR spectra of compounds bigger than **7T** differed when using different solvents, such as chloroform-*d*, THF-d_8, and methylene chloride-d_2, in both peak positions and split patterns. This phenomenon indicates the association of the molecules in different solvents. Figure 1 shows the aromatic region of the ^{1}H NMR spectra of **6T**,

Scheme 3. Synthesis of Thiophene Dendrimers



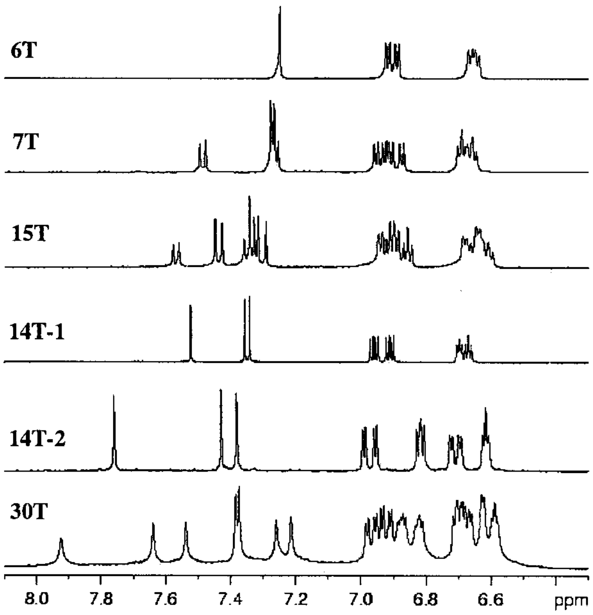


Figure 1. Aromatic region of the ^{1}H NMR spectra of the dendrons and dendrimers.

7T, **15T**, **14T-1**, **14T-2**, and **30T** in THF-d_8 at 290 K. For **6T**, **14T-1**, **14T-2**, and **30T** the interior protons on the thiophene ring show singlets downfield and the exterior protons show doublets upfield. For **7T** and **15T**, two doublets were found for the two protons at the focal thiophene, one at the most downfield and the other hidden in the singlets. Temperature control experiments were also performed for **14T-1**, **14T-2**, and **30T** in THF-d_8. Upon cooling, the resonance of those singlet protons shifted markedly downfield. Only small shifts were observed for the external protons. The association of the dendrimers in solution is under investigation. The MALDI-TOF analysis verified monodispersed masses for **14T-1**, **14T-2**, **15T**, and **30T**, giving 1824.0, 1823.6, 1905.3, and 3809.5, respectively. These are consistent with the calculated values: 1823.6, 1823.6, 1905.6, and 3809.2.

In conclusion, thiophene dendrons and dendrimers have been successfully synthesized by metal-mediated coupling reactions through a convergent approach. All the characterization results, including NMR, elemental analysis, and MALDI-TOF-MS, confirmed the structure proposed in the schemes. The methodology allows for a rational design of generational dendrimers with different conjugation lengths and microstructures. These materials are currently being systematically investigated for their optical properties, redox behavior under potential cycling, aggregation behavior in solution, self-assembly in ultrathin film and bulk state, and possible applications in organic electronics.

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Supporting Information Available: Experimental details and characterization data for all the compounds reported. This material is available free of charge via the Internet at http://pubs.acs.org.

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