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# Synthesis of Dendrimers Based on Tetrakis(thiophene-2-yl)ethene as New Dendron

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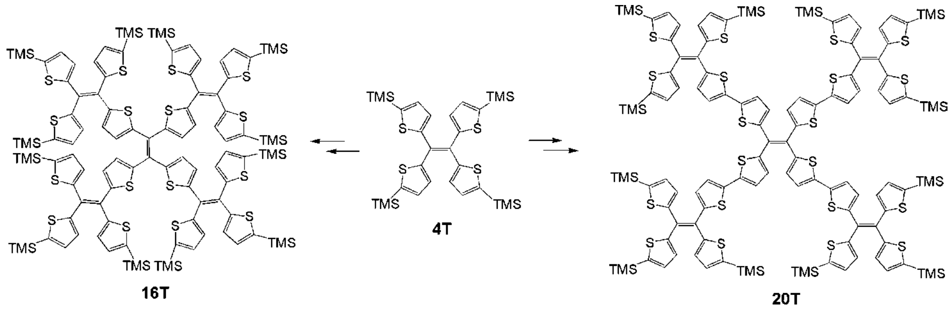
## ABSTRACT



**Two novel dendrimers, 16T and 20T, based on 1,1,2,2-tetra(thiophen-2-yl)ethene (4T) as a new dendron, were efficiently synthesized via carbonylation, Suzuki, and McMurry reactions. All intermediates and title compounds were fully characterized by $^1$H NMR, $^{13}$C NMR, and HRMS. 4T and 16T were confirmed by X-ray single crystal analyses. In addition, the absorption behaviors of two titled dendrimers are also described.**

Oligothiophenes and polythiophenes have remained one of the most well-studied organic semiconductors over the past decade.[1] Owing to their outstanding optical, electrical, redox, photoluminescence, and charge-transport properties, most of the materials were utilized in organic field-effect transistors (OFETs),[2] light-emitting diodes (LEDs),[3] and photovoltaic (PV) applications.[4]

With a single molecular weight and three-dimensional spreading structure, dendrimers could be precisely tailored with discrete and designated functionality to create multifunctional materials.[5] Among the dendritic macromolecules, thiophene-containing dendrimers as an important class of promising materials have received tremendous attention in recent decades.[6] Since the first all-thiophene dendrimers up to a 15- and a 30-mer were prepared by Advicula and co-workers;[7] various oligothiophene-based dendrimers having different cores and branches have also

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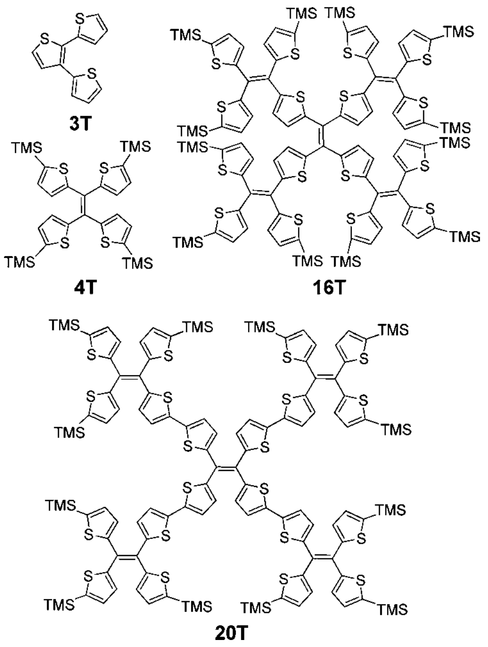
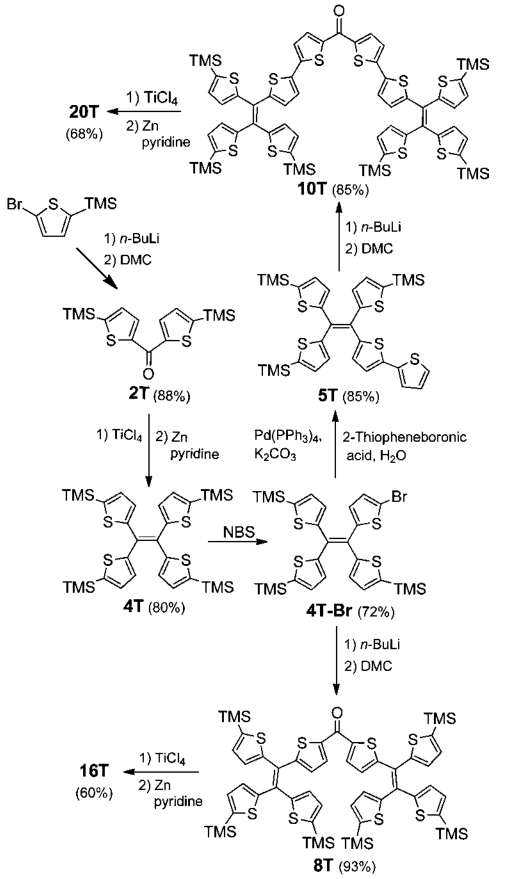


**Figure 1.** Structures of two dendrons, **3T** and **4T**, and the designed dendrimers, **16T** and **20T**.

been reported.[8–11] Most of these dendrimers were synthesized with the dendron of terthiophene (**3T**).[8,10a–c] Since, π-conjugated branched oligothiophenes showed tremendous challenges in synthetic organic chemistry and a promising outcome in organic electronics.[10f,g] To design and construct a new class of dendritic architectures, two novel and hyperbranched dendrimers, **16T** and **20T** (Figure 1), based on tetrakis(thiophene-2-yl)ethene (**4T**)[12] as a dendron, were synthesized using carbonylation, Suzuki, and McMurry reactions in our work. In addition, preliminary spectroscopic and electrochemical data are discussed.

**Scheme 1.** Synthetic Route to Dendrimers **16T** and **20T**



The synthetic route to **16T** and **20T** is outlined in Scheme 1. 2-Bromo-5-trimethylsilyl thiophene was prepared according to the literature method.[13] The Br/Li exchange on 2-bromo-5-trimethylsilyl thiophene occurred in the presence of *n*-BuLi, and *N*,*N*-dimethylcarbamyl chloride (DMC) was added into the reaction mixture to afford bis(5-(trimethylsilyl)thiophen-2-yl)methanone (**2T**) in 88% yield. The intermolecular McMurry reaction of **2T** was employed to generate the modular building block, tetrakis(5-(trimethylsilyl)-thiophene-2-yl)ethene (**4T**) in 80% yield. *N*-Bromo-succinimide (NBS) was used for monobromination of **4T**, and the **4T-Br** was successfully obtained in a good yield of 72%. The prepared **4T-Br** is the key intermediate for the synthesis of both **16T** and **20T**. On the one hand, after the Br/Li exchange of **4T-Br** with *n*-BuLi, the corresponding monolithium, **4T-Li**, was quenched with DMC to afford a ketone, **8T**, in 93% yield. The novel dendrimer **16T** was efficiently obtained by an intermolecular McMurry reaction of **8T** under conditions of $TiCl_4$–Zn powder–pyridine in dry THF with a yield of 60%. On the other hand, dendron **5T** could be generated from **4T-Br** and

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2-thiopheneboronic acid via a Suzuki reaction in 85% yield. The deprotonation of **5T** was performed using *n*-BuLi, and the monolithiated intermediate, **5T-Li**, was subsequently treated with DMC to afford another ketone, **10T**, in 85% yield. Another novel dendrimer, **20T**, was also efficiently obtained in 68% yield under the same conditions as those in making **16T**. In summary, with 2-bromo-5-trimethylsilyl thiophene as starting material, the overall yields for **16T** and **20T** could be obtained in ca. 28.3% and ca. 24.9% isolated yields, respectively.

Both the crystal structures of **4T** and **16T** are confirmed by single-crystal X-ray crystallography. **4T** belongs to monoclinic, space group $P2(1)/n$, and **16T** belongs to triclinic, space group $P\bar{1}$. The inversion symmetry is clearly observed in the crystals of both **4T** and **16T**. In **4T**, the four C−C bonds linked to the cored double bond are almost planar. The angle of C2−C4−C3 is 114.16(45)°, and the dihedral angle of C2−C4−C4−C3 is 2.14(64)°. However, the four thiophene rings and the cored ethylene are not planar. There are two interplanar angles of 77.09(17)° (**T**-S1 and C═C bond) and 30.74(18)° (**T**-S2 and C═C bond) observed between the thiophene rings and the cored ethylene, and the interplanar angle of two neighboring thiophenes is 69.83(21)° (**T**-S1 and **T**-S2, Figure 2a). In the crystal of **16T**, there are eight molecules located at the eight corners of a cell (Figure 2d) and some short intermolecular interaction could be observed as 2.9211(11) Å (C37-H53B), 2.8547(64) Å (H37A-C53), 2.3604(11) Å (H37A-H53B), and 2.2127(13) Å (H44C-H30A) (Figure 2c and cif file of **16T** in Supporting Information).

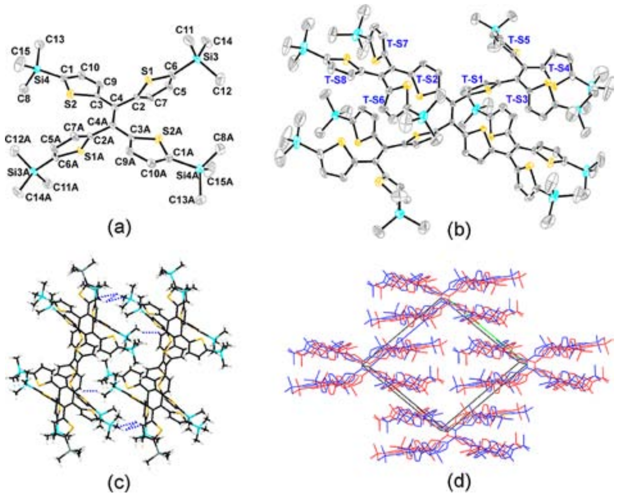

**Figure 2.** Molcular structures and conformations for **4T** (a) and **16T** (b). Carbon, silicon, and sulfur atoms are depicted with thermal ellipsoids set at the 30% probability level, and all hydrogen atoms are omitted for clarity. Crystal packing of **16T**: the intermolecular interactions (c) and the packing in a cell (d).

Both **16T** and **20T** are typical dendrimers, in which **4T** is employed as building blocks. **20T** is a quintamer of **4T**, in which four **4T**s linked to the center **4T** in an uncrowded linkage with four C−C bonds. On the one hand, **16T** could be taken as a tetramer of **4T**, in which four **4T**s link to the cored ethylene (marked as four blue cycles, Figure 3). On the other hand, **16T** could also be taken as a quintamer of **4T**, in which four outside **4T**s share four inner thiophene rings, which linked to the cored ethylene to form the cored **4T** (marked as red cycle, Figure 3).

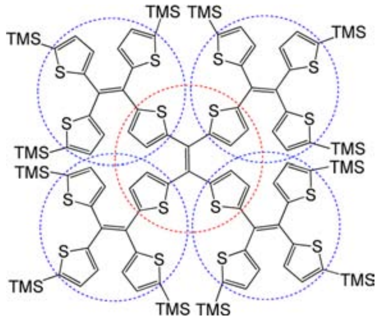

**Figure 3.** Structure of **16T**, a tetramer of **4T** (marked as four blue cycles) or a quintamer of **4T** (marked as four blue cycles and one red cycle).

Different from the case of an uncrowded molecular structure in **20T**, the repulsion between the terminal TMS groups and thiophenes makes **16T** more crowded. Compared with the case of **4T**, the center **4T** in **16T** gives two interplanar angles of 87.459(105)° (**T**-S1 and C═C bond) and 11.640(86)° (**T**-S2 and C═C bond) observed between the thiophene rings and the cored ethylene (Figure 2b). That means two inversion symmetric thiophene rings are conjugated pretty well with the cored ethylene, but another two inversion symmetric thiophene rings are not. This fact of good conjugation in the cored **4T** can explain why **16T** shows a high bathochromic shift in its UV−vis spectrum, compared with that of **4T** (Figure 4). There are five interplanar angles of two thiophenes connecting to the three types of C═C double bonds in **16T**. These interplanar angles are observed as 77.956(12)° (**T**-S1 and **T**-S2), 59.623(99)° (**T**-S1 and **T**-S5), 54.891(123)° (**T**-S3 and **T**-S4), 71.158(111)° (**T**-S2 and **T**-S6), and 74.846(121)° (**T**-S7 and **T**-S8), respectively, which indicate the high repulsion and poor conjugation among **16T**. This idea could also be observed from the C═C double bond length difference between **4T** and **16T**. The bond lengths of the three C═C double bonds in **16T** are 1.348(6), 1.330(5), and 1.328(4) Å for C5−C5A, C15−C19, and C16−C27, respectively, which are shorter than that of 1.355(13) Å (C4−C4A) in **4T**. In addition, this conclusion provides an explanation for the obvious absorption difference between **16T** and **20T**, in which **20T** shows both a significant bathochromic shift and strong absorption (Figure 4).

The UV/vis spectra for **4T**, **16T**, and **20T** are shown in Figure 4. There are three major absorption bands in the range of 220−275 nm (Band-I), 275−340 nm (Band-II), and 340−450 nm (Band-III). All three compounds show the same peaks at 246 nm in Band-I. A slight bathochromic shift could be observed for Band-II with increased units of **4T**. The absorption peaks at 301, 305, and 309 nm are

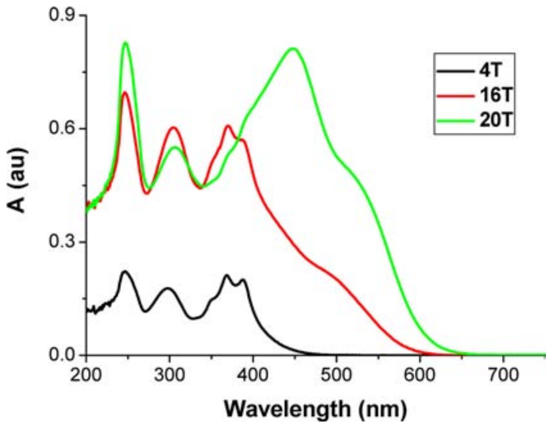

**Figure 4.** UV/vis spectra for dendron **4T** (black), dendrimers **16T** (red), and **20T** (green) in chloroform at room temperature ([C] = $1 \times 10^{-5}$ M).

found for **4T**, **16T**, and **20T**, respectively. From the crystal analysis of **16T**, the high repulsion among the thiophene rings in **16T** could be observed, so its absorption peaks (370 and 388 nm) in Band-III are similar to that of **4T** (369 and 388 nm). However, the integrated absorbance in **16T** is approximately 4-fold that of **4T**, and an additional shoulder peak at 500 nm is clearly observed due to its increased $\pi$-electron delocalization from its distorted conjugation. **20T** is a quintamer of **4T**, in which five **4T**s linked together in an uncrowded linkage with higher $\pi$-conjugation. Therefore, the absorption of **20T** shows a significant bathochromic shift with peaks at 448 and 520 nm (shoulder peak). Compared with the case of **16T**, **20T** gives higher integrated absorbance, about 6-fold that of **4T**.

In addition, the electrochemical parameters of **4T**, **16T**, and **20T** were measured in $CH_2Cl_2$ with the Ag/AgCl electrode as the reference electrode (see Supporting Information). The HOMO (highest occupied molecular orbits) and LUMO (lowest unoccupied molecular orbits) values of these compounds were calculated according to the empirical formula[14] and summarized in Table 1. These values indicate that **16T** and **20T** might be used as electron donors in organic photovoltaics.[15]

**Table 1.** Optical and Redox Data of Dendron **4T**, Dendrimers **16T** and **20T**[a]

| compd | $\lambda_{onset}$ [nm] | $E_{g\ (opt)}$ [eV] | $E_{HOMO}$[b] [eV] | $E_{LUMO}$[c] [eV] |
|---|---|---|---|---|
| **4T** | 453 | 2.74 | −5.30 | −2.56 |
| **16T** | 605 | 2.05 | −4.99 | −2.94 |
| **20T** | 650 | 1.91 | −5.01 | −3.10 |

[a] Measured in anhydrous $CH_2Cl_2/Bu_4F_6NP$ (0.1 M), [C] = $1 \times 10^{-3}$ mol $L^{-1}$, vs Ag/AgCl. [b] $E_{HOMO} = -[E_{ox\ (onset)} - E_{(Fc/Fc+)} + 4.8]$. [c] $E_{LUMO} = E_{g(opt)} + E_{HOMO}$.

In summary, the novel and hyperbranched dendrimers, **16T** and **20T**, with 1,1,2,2-tetra(thiophen-2-yl)ethane (**4T**) as a dendron, were first constructed in high yields. The different molecular skeletons of **16T** and **20T** result in varying performance in absorption properties. This work gives interesting examples in the design of thiophene-based dendrimers with new dendrons such as **4T**. Based on the absorption behaviors in a range of 350−600 nm and the energy gaps of **16T** and **20T**, the title comounds may also show their possible application in organic photovoltaics.

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**Supporting Information Available.** Synthesis and characterization of all compounds; cyclic voltammetry (CV) of **4T**, **16T**, and **20T**; and crystallographic CIF files of **4T** and **16T**. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.