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Synthesis of Dendritic Oligothiophenes and Their Self-Association Properties by Intermolecular π–π Interactions

**Nobukazu Negishi,[†] Yutaka Ie,[†] Masateru Taniguchi,[†] Tomoji Kawai,[†]
Hirokazu Tada,[‡] Takahiro Kaneda,[†] and Yoshio Aso*,[†,§]**

*The Institute of Scientific and Industrial Research, Osaka University, 8-1,
Mihogaoka, Ibaraki, Osaka 567-0047, Japan, CREST, Japan Science and
Technology Agency (JST), Japan, and The Graduate School of Engineering Science,
Osaka University, Toyonaka, Osaka 560-8531, Japan*

aso@sanken.osaka-u.ac.jp

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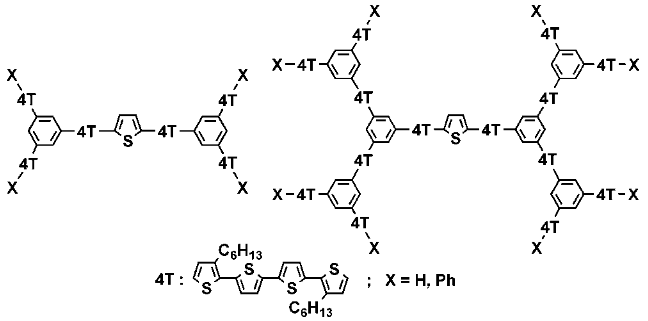
ABSTRACT



The addition of oligothiophene into a dendritic structure causes a self-association behavior by intermolecular π–π interactions in a solution and in a solid state. Increasing the generation of the dendritic structure gives not only a high association constant but also sufficient field-effect hole mobility, which indicates that the charge-transporting passes are formed by the strong π–π interactions.

Oligothiophenes and polythiophenes have been well-studied π-conjugated systems in the past few decades as attractive candidates for active materials for organic thin-film electronic devices such as organic field-effect transistors (OFETs), electroluminescent devices, and solar cells.[1] The performances of these devices largely depend on charge-carrier mobility, which is enhanced by efficient intermolecular charge hopping in the organic materials through $\pi-\pi$ stacking structures achieved by a high degree of intermolecular order or a high crystallinity. These desirable packing structures are generally pursued by fabrication techniques: a precise control of the thermal evaporation conditions for molecular materials or a thermal posttreatment for polymer films.[2] On the other hand, it is more desirable that such a stacking structure is formed by simple solution processes, such as spin coating, drop casting, and ink-jet printing, which are appropriate for fabricating large area and flexible devices.[3] Toward development of such molecular materials, we have designed the incorporation of oligothiophenes into a dendritic highly branched structure in anticipation of self-

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[†] The Institute of Scientific and Industrial Research.

[‡] Graduate School of Engineering Science.

[§] JST-CREST.

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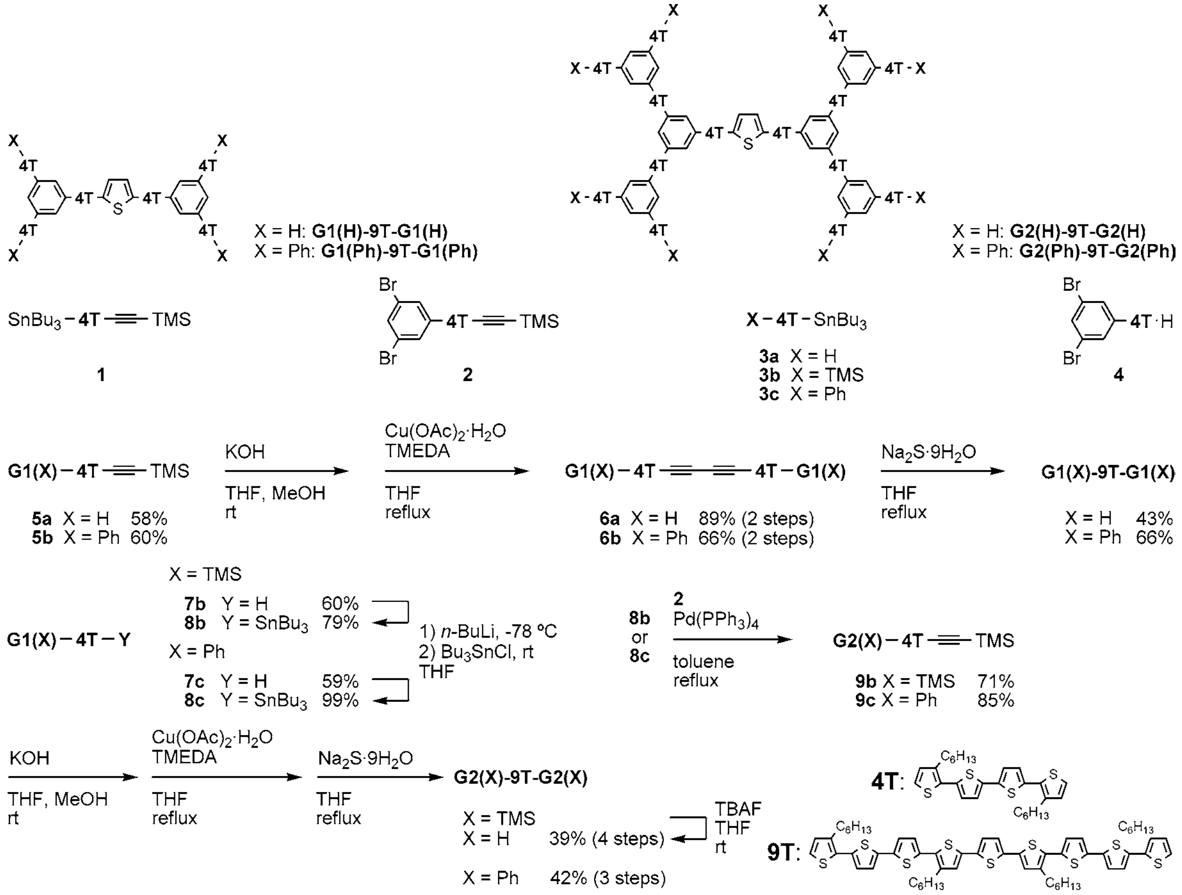
Scheme 1. Synthesis of Dendritic Oligothiophenes



aggregation properties and enhanced $\pi-\pi$ stacking interactions.[4] Recently, a number of star-shaped oligothiophenes[5] and thiophene dendrimers[6] have been prepared, and some of them were applied to OFETs and solar cells. In this communication, we report the synthesis of the dendritic oligothiophenes composed by the thiophene tetramer (4T) and nonamer (9T) with the 1,3,5-trisubstituted benzene juncture unit (Scheme 1) and also report on their self-association properties and the preliminary investigation of the field-effect mobility of holes.

As shown in Scheme 1, our synthetic strategy for the dendritic oligothiophenes relies on a convergent method to reduce the number of reaction sites and on repeating Stille cross-coupling reactions of large building blocks to suppress the formation of byproducts that are not separable by chromatographic techniques. In the beginning, the 4T derivatives **2** and **4** were obtained by a Stille coupling reaction of **1** and **3a** with 3,5-dibromoiodobenzene in 74 and 84% yields, respectively. Then, the G1 unit **5a** was prepared by Stille coupling of **2** with **3a** in 58% yield. Eglinton homocoupling of the deprotected compound of **5a** followed by a treatment of the resulting diyne with Na_2S gave desired **G1(H)-9T-G1(H)** in 38% yield in three steps. To stabilize the chemically active terminal α-positions of the 4T parts, **G1-(Ph)-9T-G1(Ph)** was also synthesized by the same route starting from **3c** and **2**. For the synthesis of **G2(H)-9T-G2-(H)**, the differently substituted G1 unit **7b** was prepared in 60% yield by the coupling of **3b** with **4** and converted to the ethynyl-substituted G2 unit **9b** (71%) via selective formation of monotributylstannyl derivative **8b** (79%). Then, **G2(TMS)-9T-G2(TMS)** was synthesized according to the

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same route as **G1(X)-9T-G1(X)**, and finally, the TMS protecting groups were easily removed by TBAF treatment to provide **G2(H)-9T-G2(H)**. Similarly, **G2(Ph)-9T-G2(Ph)** was prepared by starting from the reaction of **3c** with **4**. All of the new compounds were unambiguously characterized by ^{1}H and ^{13}C NMR spectroscopy and elemental analyses. The dendritic oligothiophenes are soluble in common organic solvents. It is important to note that MALDI-TOF mass spectra of the dendritic oligothiophenes clearly showed a sharp molecular ion peak, indicating complete homogeneity of the dendritic structure, and it was accompanied by several aggregation peaks (vide infra).

The UV−vis absorption and photoluminescence (PL) spectral data of the dendritic oligothiophenes are summarized in Table 1. The absorption bands are considered as the superposition of $\pi-\pi^*$ transitions of the 4T−Ph, Ph−4T−Ph, and Ph−9T−Ph chromophores because π-conjugation between the metasubstituted units does not generally occur.[7] Thus, the observed red shifts of absorption maxima with an increasing number of branch units as well as with conversion of the terminal positions from H to Ph are attributable to the increasing participation of the Ph−4T−Ph chromophores. On the other hand, the observed PL wavelengths of all the dendritic oligothiophenes correspond to the fluorescence only from the 9T moieties regardless of excitation wavelengths,[8] which are considered to have been caused by an efficient photoinduced intramolecular energy transfer. The increase of the number of branching points leads to the drastic decrease of the fluorescent quantum yield and to broadening of the spectrum. This, along with taking into account the tailing absorptions of **G2(X)-9T-G2(X)** to longer wavelengths (Figure S3, see Supporting Information), suggests intermolecular interactions of the 9T units induced by the highly branched structure.

Table 1. Spectroscopic Data of the Dendritic Oligothiophenes in CH_2Cl_2

compound	abs_{max}/nm	flu_{max}/nm^{a}	ϕ^{b}
G1(H)-9T-G1(H)	418	558, 597 (sh)	0.083
G1(Ph)-9T-G1(Ph)	429	557, 597 (sh)	0.080
G2(H)-9T-G2(H)	430	563	0.025
G2(Ph)-9T-G2(Ph)	439	590	0.015

^{a} $\lambda_{ex} = 370$ nm. ^{b}9,10-Diphenylanthracene in cyclohexane as the standard ($\phi = 0.90$).

Aggregation behaviors of **G1(H)-9T-G1(H)** and **G2(H)-9T-G2(H)** were investigated by ^{1}H NMR spectroscopy in $CDCl_3$. As the concentration of sample solutions increased, all the NMR signals in the aromatic region showed notable upfield shifts owing to $\pi-\pi$ stacking aggregation. The chemical shifts of the juncture benzene protons and the terminal thiophene α-protons were plotted against the concentrations in Figure 1.[9] The shifts of the benzene protons exhibit relatively strong concentration dependence, whereas those of the thiophene protons show little concentration dependency. These results indicate that the aggregation of the dendritic oligothiophenes occurs mainly around the star-shaped juncture moieties. Interestingly, ^{1}H NMR signals assigned to the inner and outer benzene rings of **G2(H)-9T-G2(H)** showed almost equal upfield shifts, implying that the dendritic oligothiophenes associate overall with each other. Assuming the dominate association to be monomer−dimer equilibrium in solution, we calculated dimerization constants by using nonlinear least-squares fitting.[10] The highly branched **G2(H)-9T-G2(H)** showed a large K value of 3480 M^{-1} at 30 °C, which is 120 times as large as that of **G1(H)-9T-G1(H)** (29.2 M^{-1}). This is demonstrative of the high self-association potential of the dendritic oligothiophenes as nonpolar π-conjugation systems. Their aggregation is derived from $\pi-\pi$ interactions of the two-dimensionally extended conjugation systems in contrast with self-associations of most reported π-conjugated systems where solvophobic interactions of peripheral polar groups dominate.[11−15] Preferable strong aggregation behavior in a solid state has been supported by MALDI-TOF mass spectroscopy of all the dendritic oligothiophenes,[16] which showed a series of regular-

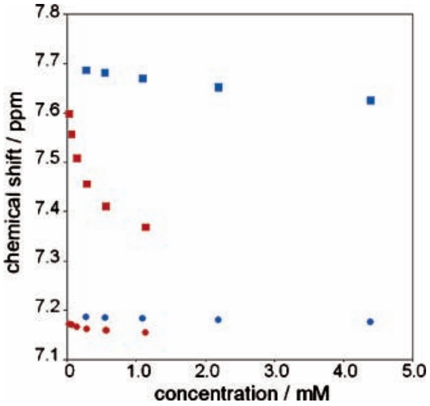

Figure 1. Concentration dependence of ^{1}H NMR chemical shifts for benzene protons (square) and terminal thiophene protons (circle) of **G1(H)-9T-G1(H)** (blue) and **G2(H)-9T-G2(H)** (red) at 30 °C in $CDCl_3$.

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[7] Recently, π-conjugation between the metasubstituted arms has been reported: Yamaguchi, Y.; Ochi, T.; Miyamura, S.; Tanaka, T.; Kobayashi, S.; Wakamiya, T.; Matsubara, Y.; Yoshida, Z.-i. *J. Am. Chem. Soc.* **2006**, *128*, 4504−4505.

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[9] The chemical shifts of juncture benzene protons of **G1(Ph)-9T-G1(Ph)** and **G2(Ph)-9T-G2(Ph)** could not be plotted because their signals were superimposed on those of the terminal benzene protons.

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interval weak but obvious peaks assignable to aggregated monocationic and dicationic species up to 7-mer as shown representatively by **G2(H)-9T-G2(H)** in Figure 2 and summarized in Table S4 (see Supporting Information).

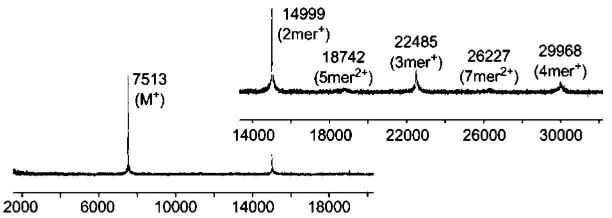

Figure 2. MALDI-TOF mass spectrum of **G2(H)-9T-G2(H)**.

The electrochemical behavior was investigated by cyclic voltammetry. On an anodic voltammetric scan (Figure S5, see Supporting Information), **G1(H)-9T-G1(H)** and **G2(H)-9T-G2(H**) showed ambiguous broad multioxidation waves, which were irreversible when the scan was repeated, and black materials were deposited on the working electrode, indicating that polymerization or decomposition occurred. The phenyl-capped **G1(Ph)-9T-G1(Ph)** also showed irreversible complex oxidation waves, but they became reversible when the scan was repeated within a range of 0−0.5 V (Figure S6, see Supporting Information). On the other hand, the cyclic voltammogram of **G2(Ph)-9T-G2(Ph)** exhibited reversible waves during repeated scans up to 1.3 V (Figure S6, Supporting Information), implying that the phenyl-capped highly branched structure could kinetically stabilize its positively charged states. These properties of high aggregation, low oxidation potential, and stable cationic state of **G2-(Ph)-9T-G2(Ph)** are promising as OFET materials.

The bottom-contact OFET devices fabricated preliminarily by using spin-coated **G1(Ph)-9T-G1(Ph)** and **G2(Ph)-9T-G2(Ph)** thin films as active layers showed typical *p*-channel FET responses as the latter was representatively shown in Figure 3. The field-effect mobility of the **G2(Ph)-9T-G2-(Ph)**-based device is 2.0×10^{-4} cm^2 V^{-1} s^{-1} ($I_{on}/I_{off} = 1 \times 10^4$), the value of which is about 2 orders of magnitude larger than that of the **G1(Ph)-9T-G1(Ph)**-based device (1.2×10^{-6} cm^2 V^{-1} s^{-1}; $I_{on}/I_{off} = 150$). This shows that the high aggregation tendency with $\pi-\pi$ stacking interactions of the highly branched structure contributes to the higher mobility. Because the thin film of **G2(Ph)-9T-G2(Ph)** showed no peak on an XRD measurement, indicating the film is completely amorphous, we presume that the dendritic oligothiophene molecules form multidirectional networks through intermolecular $\pi-\pi$ interactions of the star-shaped conjugated moieties.

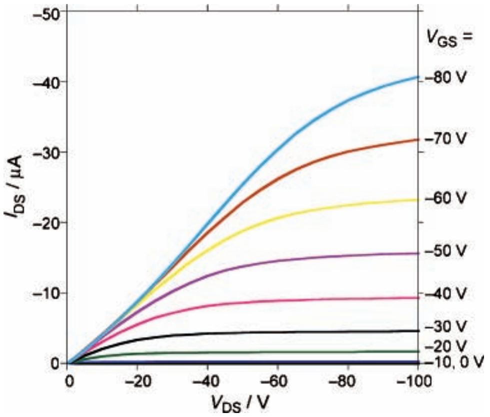

Figure 3. $I_{DS}-V_{DS}$ plot of the **G2(Ph)-9T-G2(Ph)** FET device at various gate voltages (V_{GS}).

In summary, we have synthesized the dendritic oligothiophenes using highly selective reactions and demonstrated their strong self-association behaviors and successful application to OFET devices. We have been currently investigating the development of further intelligent systems based on the dendritic oligothiophenes.

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

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