Dendrimer-Supported Oligothiophene Synthesis: Aliphatic Ether Dendrimers in the Preparation of Oligothiophenes with Minimal Substitution

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The field of dendrimers has expanded greatly in recent years due in part to their legitimate promise of being used for a variety of applications.[1,2] Similarly, the field of conjugated oligomers[3] and conducting polymers[4] has shown renewed promise with advances such as the fabrication of organic field effect transistors[5] and organic light emitting diodes.[6] Much attention has been devoted to oligothiophenes and the pursuit of well-defined, lengthy "molecular wires".[3,7] Due to the rigid nature of the conjugated backbone, oligo- and polythiophenes must be functionalized with pendant groups, typically linear alkyl chains, to preserve their solubilities.[7,8] Although, regioregular poly(3-alkyl)thiophenes are both soluble in common organic solvents and highly conducting, such functionalization leads to undesired steric interactions that increase the band gap of the polymer, thus affecting their performance.

Dendrimers are well-defined, highly branched structures that can serve as solubilizers for oligothiophenes and polythiophenes. We have recently demonstrated the successful use of poly(benzyl ether)[9] dendrimers as efficient solubilizers for lengthy oligothiophenes.[7g] Unfortunately, this approach required that synthetic intermediates be solubilized with alkyl chains prior to the attachment of the dendrimer. Furthermore, the electron-rich nature of the poly(benzyl ether) dendrimers precludes the use of NBS to activate the oligomer for further coupling. Our main objective in this study was to explore the use of a solubilizing platform for the preparation of lengthy oligothiophenes having no other substituents (i.e., no alkyl chains). For this purpose, we chose the aliphatic ether dendrimers recently developed in our laboratory.[10] The dendrimer affords a pure, monodisperse product that is more easily characterized than a polydisperse polymer while still providing excellent solubility. More importantly, the aliphatic ether dendrimer framework, which is analogous to poly(ethylene glycol) (PEG), is chemically inert toward the reaction conditions used to extend the oligomers.

Herein, we present the synthesis of oligothiophenes tethered to the focal point of a single aliphatic ether dendrimer via an iterative protocol of NBS bromination and Stille coupling reactions. To our knowledge, this is the first example in which a dendrimer is used as a solubilizing platform for the preparation of a normally intractable material.

Scheme 1 depicts the dendrimer-supported synthesis of sexithiophene. Attachment of bithiophene to the focal point of a third-generation [G3] dendrimer was done by reaction of the G3 alcohol with 2,2′-bithiophene-5-carbonyl chloride in the presence of pyridine in CH_2Cl_2 (**1**). The reaction of **1** with 1 equiv of NBS in DMF at room temperature provides the dimer bromide (**2**). Extension to the tetramer was done in DMF using 5-(trimethylstannyl)-2,2′-bithiophene[7g] and $Pd(PPh_3)_2Cl_2$ as the catalyst (**3**). As early as the tetramer stage, unsubstituted oligothiophenes become sparingly soluble; however, the presence of the dendrimer, renders **3** highly soluble, thus allowing both its purification by flash chromatography and its further growth. One more iteration of activation and coupling leads to the dendrimer-supported tetramer bromide (**4**) and sexithiophene (**5**), respectively. A further extension leads to the corresponding octamer, but its sensitivity to oxidation precluded its isolation as it decomposed during chromatography. Nevertheless, all of the materials prepared were found to be highly soluble in common organic solvents such as THF, DMF, CH_2Cl_2, and $CHCl_3$ and could be fully characterized by ^{1}H NMR and ^{13}C NMR. Critical to the success of this approach is the highly stable aliphatic dendrimer framework that allows for the NBS bromination to be selective toward the terminal α-position of the oligothiophene as determined by ^{1}H

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(1) Newkome, G. R.; Moorefield, C. N.; Vogtle, F. *Dendritic Molecules: Concepts, Synthesis, Perspectives*; VCH: Weinheim, New York, 1996.

(2) Bosman, A. W.; Janssen, H. M.; Meijer, E. W. *Chem. Rev.* **1999**, *99*, 1665.

(3) Martin, R. E.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1350. *Electronic Materials: The Oligomer Approach*; Wegner, G., Mullen, K., Eds.; VCH: Weinheim, 1997. Tour, J. M. *Chem. Rev.* **1996**, *96*, 537. Roncali, J. *Chem. Rev.* **1997**, *97*, 173.

(4) *Handbook of Conducting Polymers*, 2nd ed.; Skotheim, T. A., Elsenbaumer, R. L., Reynolds, J. R., Eds; Marcel Dekker: New York 1998. Feast, W. J.; Tsibouklis, J.; Pouwer, K. L.; Groenendaal, L.; Meijer, E. W. *Polymer* **1996**, *37*, 5017.

(5) Garnier, F. *Acc. Chem. Res.* **1999**, *32*, 209. Horowitz, G. *Adv. Mater.* **1998**, *10*, 365. Katz, H. E. *J. Mater. Chem.* **1997**, *7*, 369. Bao, Z.; Dodabalapur, A.; Lovinger, A. J. *Appl. Phys. Lett.* **1996**, *69*, 4108. Sirringhaus, H.; Tessler, N.; Friend, R. H. *Science* **1998**, *280*, 1741. Dodabalapur, A.; Bao, Z.; Makhija, A.; Laquindanum, J. G.; Raju, V. R.; Feng, Y.; Katz, H. E.; Rogers, J. *Appl. Phys. Lett.* **1998**, *73*, 142.

(6) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 402.

(7) (a) Kirschbaum, T.; Azumi, R.; Mena-Osteritz, E.; Bäuerle, P. *New J. Chem.* **1999**, 241. (b) Nakanishi, H.; Sumi, N.; Aso, Y.; Otsubo, T. *J. Org. Chem.* **1998**, *63*, 8632. (c) Bidan, G.; De Nicola, A.; Enee, V.; Guillerez, S. *Chem. Mater.* **1998**, *10*, 1052. (d) Bäuerle, P.; Fisher, T.; Bidlingmeier, B.; Stabel, A.; Rabe, J. P. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 303. (e) ten Hoeve, W.; Wynberg, H.; Havinga, E. E.; Meijer, E. W. *J. Am. Chem. Soc.* **1991**, *113*, 5887. (f) Yassar, A. Delabouglise, D.; Hmyene, M.; Nessak, B.; Horowitz, G.; Garnier, F. *Adv. Mater.* **1992**, *4*, 490. (g) Malenfant, P. R. L.; Groenendaal, L.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1998**, *120*, 10990.

(8) McCullough, R. D. *Adv. Mater.* **1998**, *10*, 93. Chen, T.-A.; Wu, X.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233. McCullough, R. D.; Williams, S. P. *J. Am. Chem. Soc.* **1993**, *115*, 11608. Lévesque, I.; Leclerc, M. *Chem. Mater.* **1996**, *8*, 2843. Bäuerle, P.; Hiller, M.; Scheib, S.; Sokolowshi, M.; Umbach, E. *Adv. Mater.* **1996**, *8*, 214. Bäuerle, P.; Scheib, S. *Adv. Mater.* **1993**, *5*, 848. Arbizzani, C.; Bongini, A.; Mastragostino, M.; Zanelli, A.; Barbarella, G.; Zambianchi M. *Adv. Mater.* **1995**, *7*, 571.

(9) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638. Fréchet, J. M. J. *Science* **1994**, *263*, 1710.

(10) Jayaraman, M.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1998**, *120*, 12996. Grayson, S. M.; Jayaraman, M.; Fréchet, J. M. J. *Chem. Commun.* **1999**, 1329.

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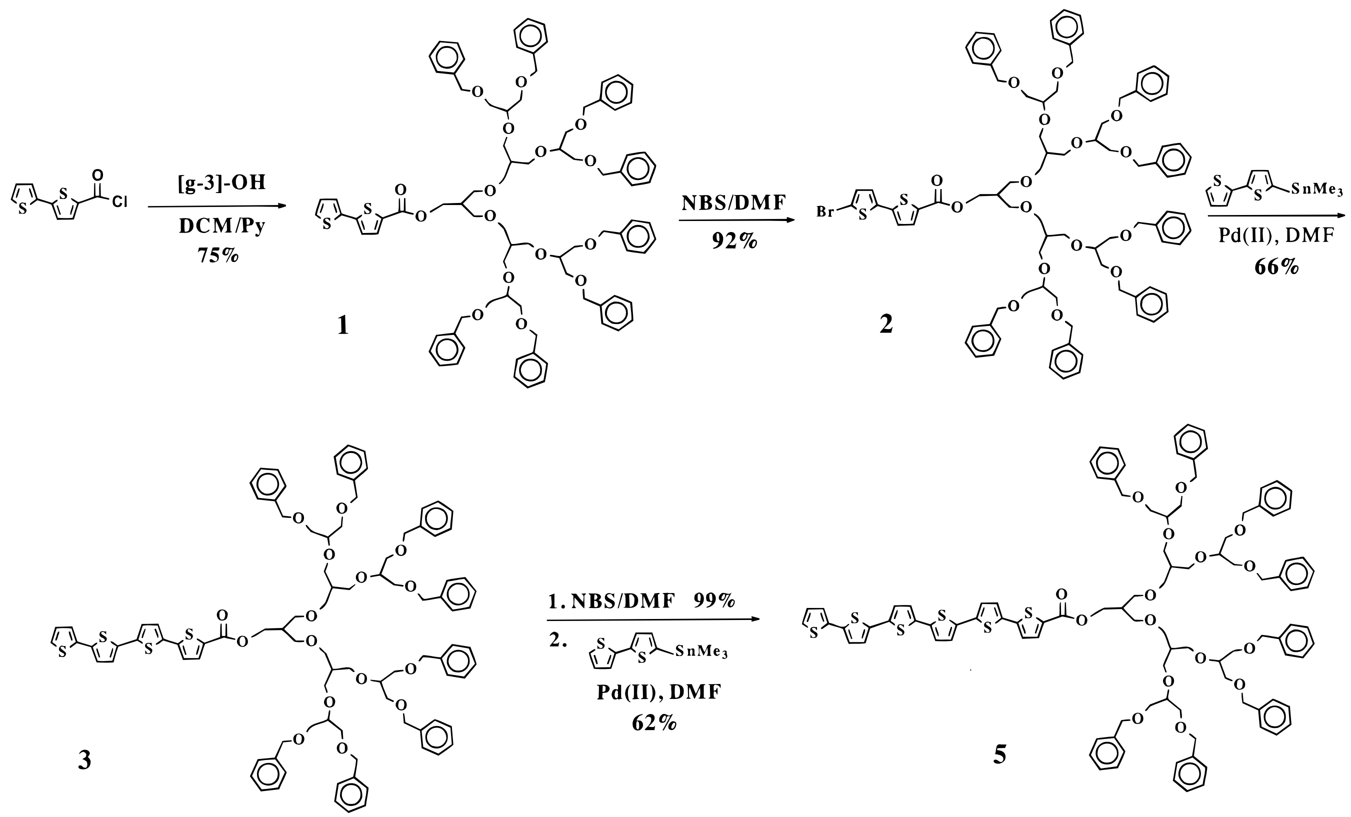
Scheme 1



Scheme 2

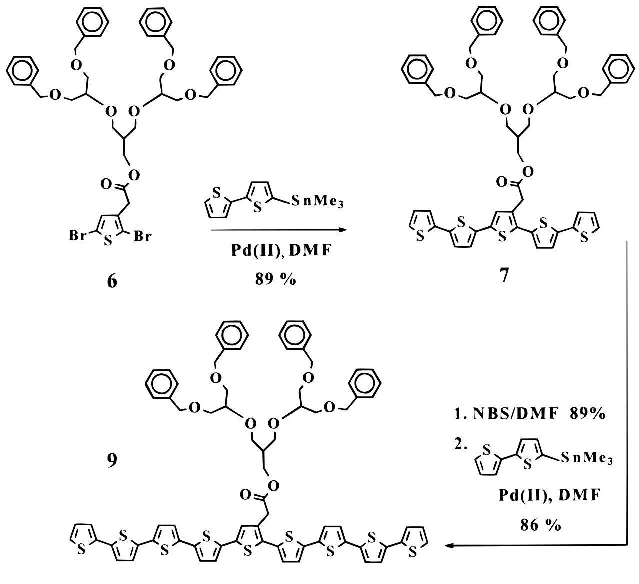


Table 1. Spectroscopic Data for Various Oligomers(Data for ENTRIES 2, 4, and 6 Taken from Ref 7a)

entry	sample	$\lambda_{\max}$ (nm)	melting transition (°C)
1[a]	**1**	336 (5)[c]	<25
2[b]	BnT′2	331	47
3[a]	**3**	412 (21)	<25
4[b]	BnT′4	391	55
5[a]	**5**	446 (32)	<25
6[b]	BnT′6	414	66
7[a]	**7**	400	<25
8[a]	**9**	450 (12)	142
9[a]	BnT′9	438	69

[a] $CHCl_3$. [b] CH_2Cl_2. [c] Values in parentheses represent the difference in nanometers between the dendrimer-supported oligomers and the benzyl ester, regioregular analogues.

NMR and MALDI-TOF spectrometry. In contrast, the electron rich nature of the poly(benzyl ether) dendrimers[9] precludes their use as a solubilizing platform during the activation steps since NBS is an excellent source of Br^+, that can easily brominate the phenolic rings of the poly(benzyl ether) dendrimers.

To accelerate the growth of the oligomers we explored grafting at the β-position of the thiophene ring as depicted in Scheme 2. The β-grafted oligothiophenes were prepared by first attaching 2,5-dibromo-3-thiopheneacetic acid[11] to the focal point of a G2 dendrimer using standard EDC/DMAP conditions (**6**). The first coupling step between **6** and 5-(trimethylstannyl)-2,2′-bithiophene was done in DMF using $Pd(PPh_3)_2Cl_2$ as the catalyst thus providing the bound pentamer (**7**). The pentamer dibromide was prepared by reaction of **7** with 2 equiv of NBS in DMF (**8**). A subsequent Stille coupling reaction between 5-(trimethylstannyl)-2,2′-bithiophene and **8** led to the nonamer **9**. All of the oligomers were soluble in common organic solvents and purified by flash chromatography. Surprisingly, **9** could be purified by chromatography while the α-grafted octamer could not. Clearly, the placement of the dendrimer at the β-position makes **9** less oxidatively sensitive than the α-grafted octamer.

From the UV−vis data presented in Table 1, one can infer that the dendrimer-supported oligomers have a more extended conjugation when compared to similar

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[11] See Supporting Information for synthetic details.

[12] Unpublished results.

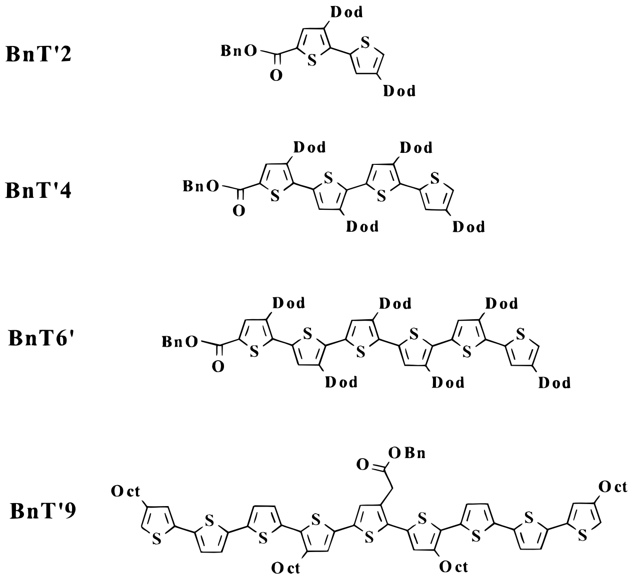

Figure 1.

oligomers having alkyl chain substituents. Recently, Bäuerle and co-workers reported an elegant synthesis of a series of regioregular oligothiophenes having an α-benzyl ester functionality and dodecyl chain solubilizers thus enabling an accurate comparison of the effect of substitution on λ_{max} (see Figure 1). For example **1**, **3**, and **5** have λ_{max} values that are red shifted by 5, 21, and 32 nm respectively when compared to the equivalent regioregular oligomers in solution (see Table 1). Furthermore, the λ_{max} of **9** is red shifted by 12 nm when compared to an analogue having a benzyl ester functionality and four octyl chains along the oligomeric backbone (see Figure 1). Thus, it is clear from the spectroscopic data that minimizing substitution on the oligomers leads to materials with a more extended conjugation even when bulky solubilizers such as G2 and G3 dendrimers are used.

As can be seen in Table 1, the thermal properties of the dendrimer-supported oligomers differ greatly from analogues having a regioregular array of linear alkyl chains as solubilizers. The G2 and G3 dendrimers having an alcohol functionality at the focal point are viscous, colorless oils having glass transition temperatures of −39 and −34 °C, respectively. Similarly, the various oligomers **1** through **5** were all isolated as viscous oils. In the β-grafted series, **7** was also isolated as a viscous oil, while **9** was isolated as a red solid having a melting point of 142 °C, indicating that at a certain oligomer length the thiophene moiety dominates the material properties.

In summary, we have shown that aliphatic ether dendrimers may be successfully used as solubilizing scaffolds for the preparation of well-defined oligothiophenes having a minimum number of points of substitution. Their synthesis was facilitated by the enhanced solubility provided by the dendritic framework that enables the use of unsubstituted building blocks. The dendrimer-bound oligothiophenes obtained were found to have drastically altered thermal properties as well as a more extended conjugation when compared to similar oligomers with more conventional linear alkyl chain solubilizers. We are currently exploring the use of the β-grafted oligomers as macromonomers in the synthesis of novel polythiophenes having only dendritic substituents. We anticipate that polythiophenes with minimal β-substitution should have a more planar backbone thus extending the conjugation and perhaps leading to higher conductivities.

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

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