

New Synthetic Approaches to Multifunctional π -Conjugated Oligomers for Molecular Scale Electronics

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A new synthetic approach to a series of precisely defined 5-10 nm long oligoheterocycles, using N-silyl-protected 3,4-diaminothiophene as a key building unit, has been developed.

Keywords: molecular scale electronics, molecular wire, oligothiophene

1. INTRODUCTION

Current information devices based on semiconductors and magnetic/photoactive materials are predicted to confront the limits of capabilities within a decade. Single molecular devices have generated a great deal of interest, because they are one of the promising candidate to overcome the limitations [1-2]. At the present stage of the development, however, little is known about the practical architecture in future molecular-scale electronics. Much more systematic researches for long-distance electron transport through a single molecule on the surface of bulk materials should be carried out.

A detailed knowledge of long-distance electron transport through a single molecule on the surface of bulk materials is an essential requisite to establish the system architecture in future molecular-scale electronics [3]. In order to elucidate the structural parameters controlling this type of electron transport, various types of functionalized π -conjugated oligomers with dimension comparable to the present limit of nano-patterning techniques (~ 10 nm gap regime) have been developed over the past decade [4-5]. In general the chain extension of oligomers up to 5-10 nm dimension would be hampered severely by the solubility problems. Long alkyl substituents can improve the solubility of oligomers, however, this modification often induces rotational conjugation defects due to the enhanced inter-unit steric repulsions. Here we report a new synthetic approach to construct "processable" and "multifunctional" 5-10 nm long oligoheterocycles with highly extended π -systems.

2. SYNTHETIC STRATEGY

We have adopted 3,4-diaminothiophene (**1**) as the key unit for the multi-functionalization of oligomers as shown in Scheme 1 [6-9]. Heterocycle **1** is a fruitful synthetic precursor, from which we have synthesized i) a series of "low energy-gap" conjugated oligomers, ii) "insulated" molecular wires, and multistage redox switching systems

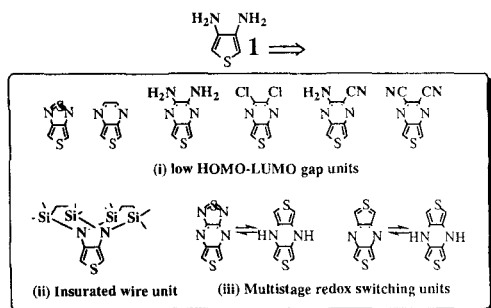
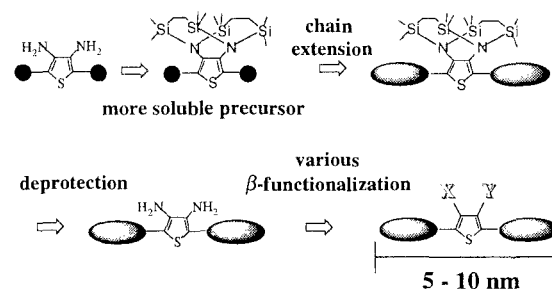


Fig. 1. Chemical modifications of **1**.

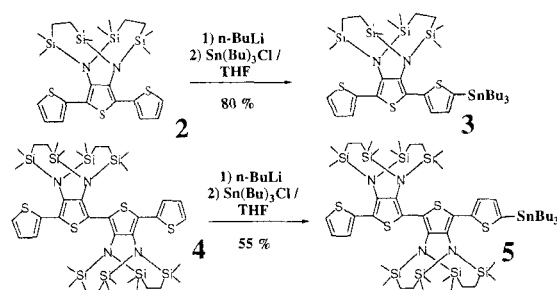
(Fig. 1). So far the instability of **1** prevented the synthesis of well-defined long oligomers containing this heterocycle, however, the N-silylation of the amino groups has been found to improve the stability during a series of reactions giving highly oligomers (α -brominations, lithiations, stanylations, and transition-metal-catalyzed Ar-Ar' couplings). Scheme 1 represents a general chain extension process based on our strategy.



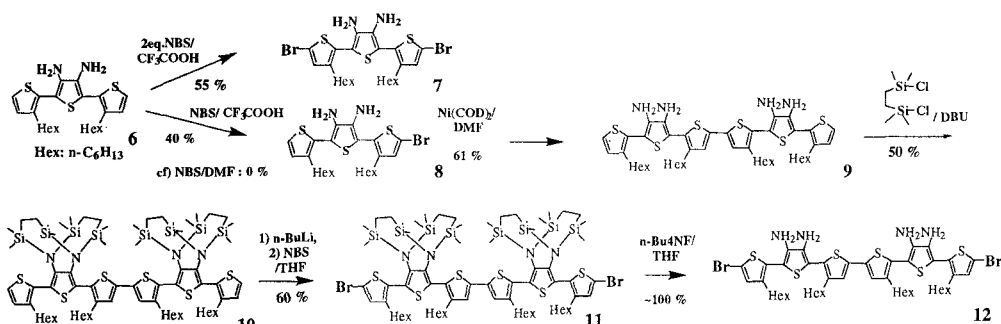
Scheme 1: General synthetic strategy

3. RESULTS AND DISCUSSION

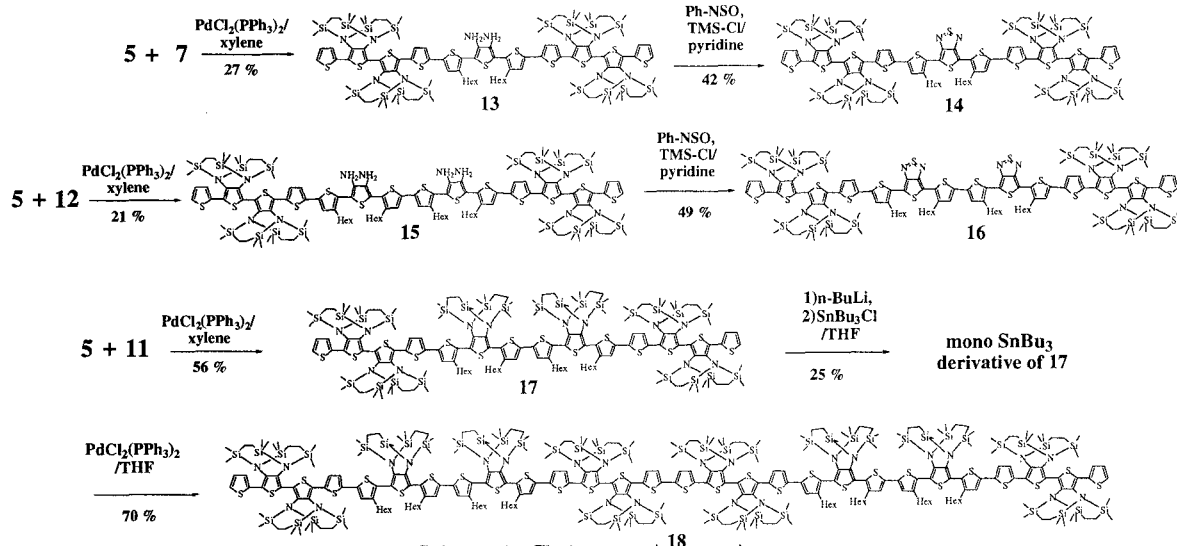
As shown in Scheme 2 and 3, we synthesized the stannyl and bromo derivatives as building blocks for Stille cross-coupling reaction. Scheme 4 shows the chain-extension reactions which gave the α -11T (**13-14**; $l \sim 4$ nm), α -14T (**15-17**; $l \sim 5$ nm) and α -28T (**18**; $l \sim 10$ nm) derivatives. All of the obtained oligomers are more soluble in dichloromethane, chloroform, and tetrahydrofuran compared with the unsubstituted oligothiophenes. So the purification of these new oligomers was easily achieved by gel permeation chromatography. The purity of the products was clearly revealed by MALDI-TOF mass spectroscopy using dithranol as matrix. All of the highly oligomers **13-18** only displayed the molecular ion $[M+]$ peak as the parent peak as shown in Fig. 2.



Scheme 2: Synthesis of the stannyl derivatives.



Scheme 3 : Synthesis of the bromo derivatives.



Scheme 4 : Chain extension reactions.

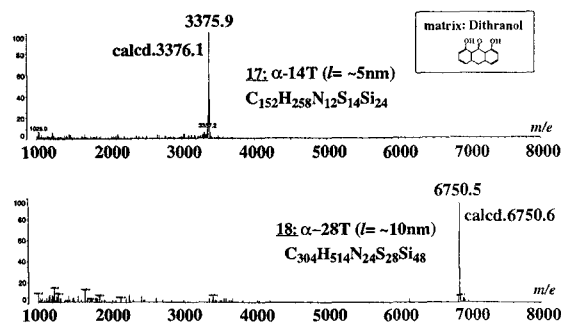


Fig. 2. MALDI-TOF mass spectra of 17 and 18.

In order to get insights into the electronic features of these extended oligomers, we compared their optical absorption spectra with those of typical oligothiophenes. The oligomers 13, 15, 17, and 18 exhibit the lowest-energy absorption maxima nearly at the same position of the unsubstituted thiophenes estimated by the fitting equation proposed by Meier et al. [10]. These results suggest that the effective conjugation length of these oligomers can be comparable to those of unsubstituted thiophenes. On the other hand, the chemical modification of the amino groups of 14 and 16 to thiadiazole ring induces an appreciable red shift of the absorption band due to the low HOMO-LUMO gap feature of nonclassical thiophene [9]. Detailed investigations of the structural and physical properties is now in progress.

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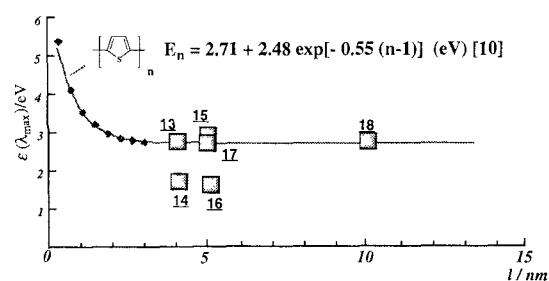


Fig. 3. Correlation of the absorption maxima of the oligothiophenes with the chain length.

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(Received December 8, 2000; Accepted December 18, 2001)