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Received July 18, 1995

We have synthesized and characterized a series of novel compounds of  $\alpha,\alpha'$ -bis(aminomethyl)oligothiophenes and their related compounds whose degree of polymerization spans two (dimer) to five (pentamer). The compounds presented in our studies are  $\alpha,\alpha'$ -bis[(2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl)methyl]oligothiophene,  $\alpha,\alpha'$ -bis(aminomethyl)oligothiophene dihydrochloride and  $\alpha,\alpha'$ -bis(aminomethyl)oligothiophene. These compounds exhibit desired chemical activity while maintaining controllable electronic properties. The synthetic processes of the oligothiophenes are as follows: 2-aminomethylthiophene is first 'protected' and the thiophene rings are coupled using standard Grignard methods. The protected groups are removed at the final stage of the reaction. The compounds show unique properties; for example  $\alpha,\alpha'$ -bis(aminomethyl)oligothiophene dihydrochloride is soluble in water. The results of electronic spectra and titration are also presented.

*J. Heterocyclic Chem.*, 33, 173 (1996).

## Introduction.

A variety of oligothiophenes has been synthesized and investigated as a well-defined model of a conducting polymer polythiophene [1]. Electroactivity of these oligothiophenes can be modulated by varying their degree of polymerization. Systematic studies of electrochemistry and spectroscopy of the oligothiophenes have been carried out [2-6]. Efforts toward applying the oligothiophenes to electronic devices, especially FETs (field-effect transistors) [7-9] and LEDs (light-emitting diodes) [10,11] also have been extensively made by many researchers. Among the oligothiophenes, those blocked at molecular terminal positions ( $\alpha$  and  $\beta$  positions) [2-6,12,13] are characterized by enhanced chemical stability and good crystallizability, these features being responsible for their unique electronic properties (*e.g.* high mobility and photosensitivity) [5,12,13].

In contrast, if the oligothiophenes have chemically convertible groups, these oligothiophenes would be further modified into useful materials and/or interact with other materials, while maintaining controllable electronic properties. Syntheses of such oligothiophenes, therefore, are of major importance and interest and various approaches to this have been made. If one intends to directly modify oligothiophenes with chemically convertible groups, substitution with such groups, in most cases, occurs solely at  $\alpha$  and  $\omega$  positions of the two terminal oligothiophene rings because of the high chemical reactivity on those positions. The substitution, therefore, only leads to the compounds  $\alpha$ - and/or  $\omega$ -substituted with the convertible groups. Examples include syntheses of terthiophene derivatives (*e.g.*  $\alpha$ -carboxyl [14],  $\alpha,\omega$ -dicarboxyl [14],  $\alpha$ -formyl [14-15],  $\alpha,\omega$ -diformyl [15],  $\alpha$ -hydroxymethyl

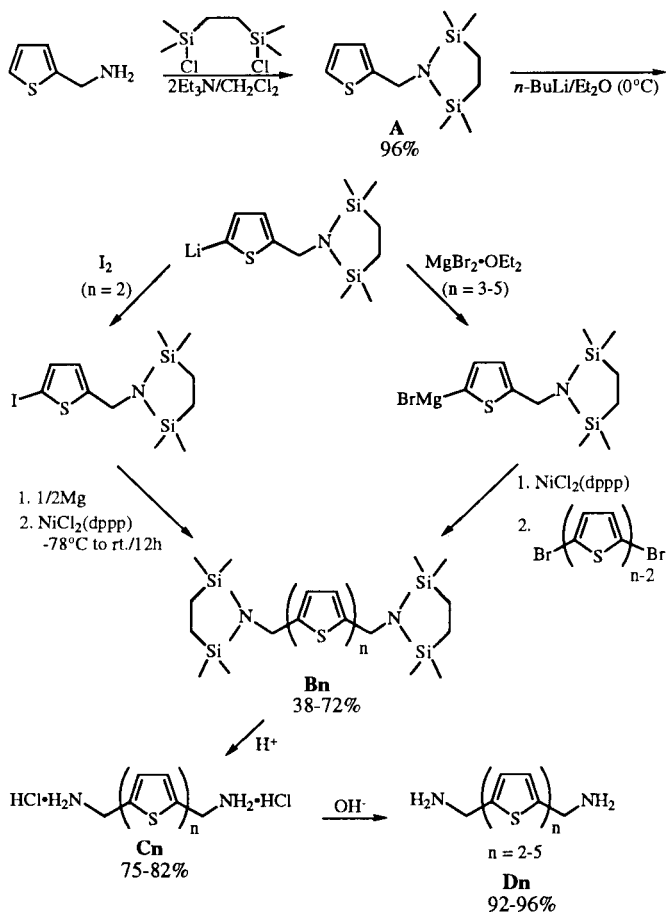
[15,16],  $\alpha$ -amino [17],  $\alpha$ -cyanoterthiophene [15] and terthiophene- $\alpha$ -propionic acid [16,17] and  $\alpha$ -acetic acid [16] and quaterthiophene compounds [18].

If, on the other hand, the chemically convertible groups are introduced beforehand, one can appropriately design a variety of molecular forms. To do this, however, the chemically convertible groups should be "protected" during courses of organic synthesis. In the final stages of the organic synthesis the protecting groups will be removed to obtain the desired compounds. For this purpose various reagents and synthetic techniques developed up to this date may be utilized.

As an initial attempt, we have synthesized a series of oligothiophene compounds with amino groups at the molecular terminals and their related intermediates. To this end, we chose 1,1,4,4-tetramethyl-1,4-dichlorodisilylethylene (Lancaster) as a protecting reagent [19-21]. By using this reagent we first protected 2-aminomethylthiophene and derived 2-(2,2,5,5-tetramethyl-1-aza-2,5-disila-1-cyclopentyl)methylthiophene (see A in Scheme 1). This makes the aza position of this compound inert to subsequent steps of the organic syntheses, while maintaining the reactivity of the other  $\alpha$ -position of the thiophene ring in A. For instance, lithium can be easily introduced at this position, and various compounds can be readily derived using the resulting highly reactive intermediate. Making the best use of this method, we synthesized a series of oligothiophene compounds with polymerization degrees spanning two (dimer) to five (pentamer).

In general, it would be difficult directly to modify the oligothiophenes with chemically convertible groups, because solubility of these compounds becomes poor with their increasing polymerization degrees. In this regard, to

Scheme 1



use compounds protected with bulky chemical groups such as those used in the present studies is advantageous, since these chemical groups dramatically enhance the solubility of the resulting oligothiophene compounds. This enables us to readily obtain in the subsequent reaction steps the oligothiophenes of higher polymerization degrees. After these procedures the protecting groups can be removed so as to be a dihydrochloride of the amino compound and finally a compound having amino groups on both the molecular terminals. We note that the  $\alpha,\alpha'$ -bis(aminomethyl)oligothiophene dihydrochlorides are soluble in water. This is an outstanding feature among the oligothiophene family; most of the oligothiophene compounds are insoluble in water because of hydrophobicity of the oligothiophene backbone. In this paper, we report synthesis and characterization of  $\alpha,\alpha'$ -bis(aminomethyl)oligothiophenes and the related intermediates.

### Results and Discussion.

Scheme 1 shows the synthetic routes that involve a series of organic reactions providing each oligothiophene compound stepwise. 2-Aminomethylthiophene is

first protected to be 2-[(2,2,5,5-tetramethyl-1-aza-2,5-disila-1-cyclopentyl)methyl]thiophene (**A**) so that the terminal amino groups can be non-reactive against organolithium and Grignard reagents [19-21]. After treating **A** with butyllithium, the Grignard coupling of the thiophene rings is carried out following literature methods [22,23] to give the intermediate, 5,5'-bis[(2,2,5,5-tetramethyl-1-aza-2,5-disila-1-cyclopentyl)methyl]-2,2'-bithiophene, -terthiophene, -quaterthiophene and -quinquethiophene (**B<sub>n</sub>**, where **n** means a polymerization degree and the same notation will be used henceforth). The protecting groups are removed in the final steps that successively produce the dihydrochloride of the  $\alpha,\alpha'$ -bis(aminomethyl)oligothiophene (**C<sub>n</sub>**) and the  $\alpha,\alpha'$ -bis(aminomethyl)oligothiophene (**D<sub>n</sub>**).

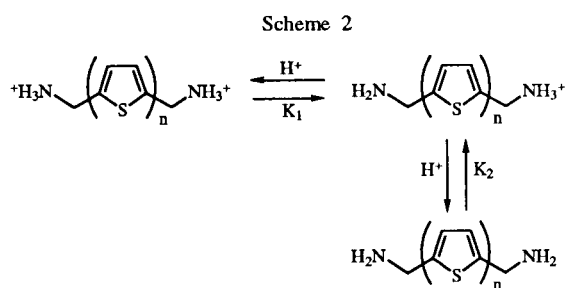
Of these, **B<sub>n</sub>** is particularly soluble in non-polar solvents; for instance solubility of **B<sub>4</sub>** in chloroform was more than 5% w/w at rt. This is because the bulky groups of (2,2,5,5-tetramethyl-1-aza-2,5-disila-1-cyclopentyl)methyl are present on both terminals. Large needle-shaped crystals of **B<sub>n</sub>** were readily accessible through recrystallization from the appropriate solvent. The hydrophobic interaction between the bulky terminal groups is probably responsible for the good crystallizability [4]. Of these, the crystal structure of **B<sub>4</sub>** has been successfully determined; the results are reported elsewhere [24]. **C<sub>n</sub>** was readily dissolved in water; the solubility of **C<sub>2</sub>** was more than 1% w/v at rt. However, the greater the degree of polymerization, the lower the solubility. As a similar example, synthesis of water-soluble poly(3-thiophene- $\beta$ -ethanesulfonate) was reported by Patil *et al* [25]. Of a series of compounds **D<sub>n</sub>**, on the other hand, **D<sub>4</sub>** and **D<sub>5</sub>** were difficult to dissolve both in water and in common organic solvents.

For the sake of variety in the syntheses, for example, 2-(2-aminoethyl)thiophene can be utilized as the starting material instead of 2-aminomethylthiophene. In this case, Scheme 1 undergoes slight modification correspondingly. Following the modified scheme we synthesized  $\alpha,\alpha'$ -bis(aminoethyl)quaterthiophene and its related com-

Table 1  
Electronic Spectra of **B<sub>n</sub>**, **C<sub>n</sub>** and **D<sub>n</sub>**

	<b>B<sub>n</sub></b>	<b>C<sub>n</sub></b>	<b>D<sub>n</sub></b>	Dimethyl-[a]
Polymerization degree	$\lambda_{\max}$ CH <sub>2</sub> Cl <sub>2</sub> [nm, log $\epsilon$ ]	$\lambda_{\max}$ H <sub>2</sub> O [nm]	$\lambda_{\max}$ CH <sub>2</sub> Cl <sub>2</sub> [nm]	$\lambda_{\max}$ CH <sub>2</sub> Cl <sub>2</sub> [nm]
Dimer	327 (4.18)	310	320	316
Trimer	367 (4.34)	359	367	364
Tetramer	404 (4.43)	394	400	397
Pentamer	422 (4.53)	417	422	422

[a] Dimethyl-substituted oligothiophenes from ref [4].



pounds. Their physicochemical properties (*e.g.* electronic properties) were similar to those of **Bn**, **Cn** and **Dn** as expected.

We have examined the electronic spectra of the oligothiophenes. The results are summarized in Table 1. Note that the spectra of **Cn** were measured in water. The spectral profile and the peak position of **Bn**, **Cn** and **Dn** were virtually the same and were closely related to those of  $\alpha,\alpha'$ -dimethylsubstituted oligothiophenes [4]. This implies that the electronic structure defined by the oligothiophene backbone was retained throughout the synthetic processes. This is because the terminal groups are linked to thiophene rings through the medium of electronically inert methylene groups. Interestingly enough, the absorption maxima of **Bn** are slightly but significantly red-shifted relative to the other compounds as well as the

$\alpha,\alpha'$ -dimethylsubstituted compounds, even though **Bn** has the bulky terminal groups. This seems to be opposite to that anticipated, because the bulky side groups may well result in variation in the rotational conformation of the oligothiophene backbone, causing a blue-shift in the spectrum [26]. The observed red-shift implies the presence of an ordered conformation in its backbone.

Since **Cn** is a bifunctional acid, dissociation of **Cn** in water is expected to take place as in Scheme 2. There  $K_1$  and  $K_2$  denote the dissociation constant in each equilibrium. As typical examples, **C2** and **C3** were titrated in order to determine these constants. Figure 1 displays titration curves of **C2** and **C3**. In this figure, the theoretical first and second end points for **C2** and **C3** correspond to 4 ml and 8 ml of sodium hydroxide (see Experimental), respectively. Although the second end point (around 8 ml) was resolved both in **C2** and **C3**, the first end point was not clearly observed. This indicates that  $K_1$  and  $K_2$  are rather close to each other for both cases, in other words the ratio  $K_1/K_2$  is probably smaller than 100 [27]. From the relationships  $\text{p}K_{a1} = -\log K_1$  and  $\text{p}K_{a2} = -\log K_2$ , we estimated  $\text{p}K_{a1}$  and  $\text{p}K_{a2}$  of **C2** to be both *ca.* 8-9 and those of **C3** at both *ca.* 6.5-7.5. The corresponding values  $\text{p}K_{a1}$  ( $\text{p}K_{a2}$ ) of ethylenediamine and hexamethylenediamine are 7.08 (9.89) and 9.83 (10.93) (at 25° under an ion strength of 0.1) [28], respectively. This implies that **C3** is a stronger acid than **C2** and also then the typical aliphatic diamine dihydrochlorides such as ethylenediamine dihydrochloride.

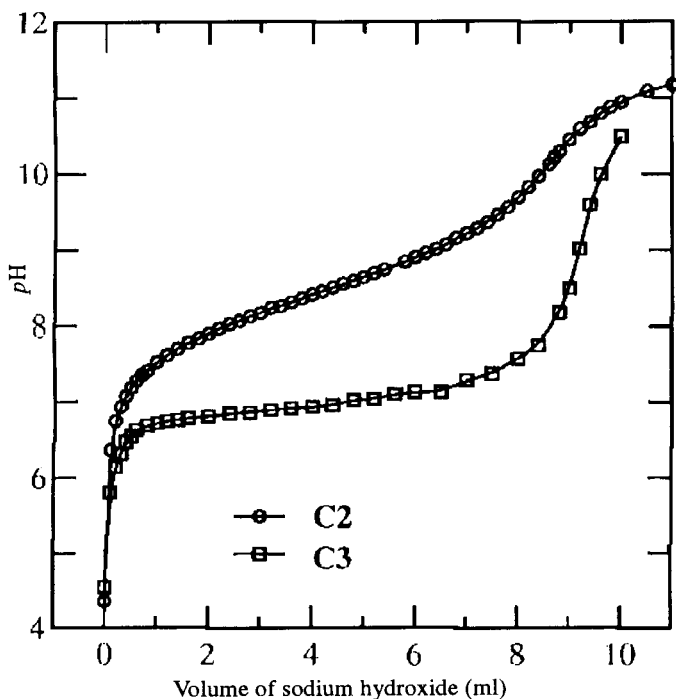


Figure 1. Titration curve of **C2** and **C3**. A 50 mM sodium hydroxide solution was used to titrate 20 ml of 10 mM **C2**. A 25 mM sodium hydroxide solution was used to titrate 20 ml of 5 mM **C3**.

## Conclusion.

We have synthesized the novel amino compounds and their intermediate oligothiophenes. The electronic spectral data show that these oligothiophene compounds retain the controllable electronic properties that are characteristic of the oligothiophenes. The diamine dihydrochloride compounds are soluble in water, so these compounds were titrated in aqueous solution. The results indicate that the diamine dihydrochlorides are co-existent in equilibrium with the corresponding diamines. Since the amino groups are chemically active, the oligothiophenes having these groups are expected to be useful in the synthesis and preparation of additional useful materials that include unique compositions and hybrids based upon these oligothiophene compounds.

## EXPERIMENTAL

### General.

Proton nmr spectra were collected on either a JEOL FT-NMR JNM-A500 instrument or a Hitachi FT-NMR R-1900. The ir spectra were observed on a Hitachi FT-IR I-5040 using a pow-

dered material dispersed in a potassium bromide matrices. Electronic spectra of the oligothiophenes were recorded with a Hitachi U-4000 spectrometer either in dichloromethane or in aqueous solution.

2-[(2,2,5,5-Tetramethyl-1-aza-2,5-disila-1-cyclopentyl)methyl]-thiophene (**A**).

A magnetically stirred solution (200 ml) including 2-aminomethylthiophene (22.6 g, 0.2 mole, Lancaster) and triethylamine (40.5 g, 0.4 mole) in 300 ml of dichloromethane was prepared and cooled in an ice/water bath. Then a solution of 1,1,4,4-tetramethyl-1,4-dichlorodisilylene (43.1 g, 0.2 mole, Lancaster) dissolved in 400 ml of dichloromethane was added dropwise. After removing the ice/water bath, the reaction mixture was stirred for 2 hours at rt under dry nitrogen. The mixture was filtered and evaporated to eliminate precipitates; the remaining liquid extracted with hexane and again filtered and evaporated. The resulting pale yellow product was distilled at 91° under reduced pressure, 2-3 mm Hg, giving a viscous colorless liquid, yield 49.0 g, 96%; <sup>1</sup>H-nmr (500 MHz, deuteriochloroform): δ (ppm) 7.14 (dd, 1H, J<sub>5,4</sub> = 4.9 Hz, J<sub>5,3</sub> = 1.2 Hz, H-5 of thiophene), 6.88 (dd, 1H, J<sub>4,5</sub> = 4.9 Hz, J<sub>4,3</sub> = 3.7 Hz, H-4 of thiophene), 6.85 (dd, 1H, J<sub>3,4</sub> = 3.7 Hz, J<sub>3,5</sub> = 1.2 Hz, H-3 of thiophene), 4.18 (s, 2H, CH<sub>2</sub>N), 0.75 (s, 4H, SiCH<sub>2</sub>), 0.03 (s, 12H, SiCH<sub>3</sub>).

5,5'-Bis[(2,2,5,5-tetramethyl-1-aza-2,5-disila-1-cyclopentyl)-methyl]-2,2'-bithiophene (**B2**).

A solution of **A** (5.1 g, 20 mmoles) in 80 ml of ether under dry nitrogen was cooled to 0°. *n*-Butyllithium/hexane (1.6 M, 13.75 ml, 22 mmoles, Aldrich) was added dropwise, causing the solution to turn dark purple. After 30 minutes, iodine (5.58 g, 22 mmoles) was added and allowed to warm to rt. After another 30 minutes, magnesium (0.243 g, 10 mmoles) was added and disappeared completely in 60 minutes. The solution was cooled down to -78° in a dry ice/methanol bath and [1,3-bis(diphenylphosphino)propane]nickel(II) chloride (0.16 g, 0.033 mmole, Aldrich) was added. The solution was stirred overnight while the solution was allowed to warm gradually to rt. The solution was then heated to reflux for 4 hours. The resulting substance was in the solution. Hexane (200 ml) was added and washed with water. The solution was dried over calcium chloride and evaporated. The residue was washed with methanol and recrystallized from ethanol to give white needle-shaped crystals, yield 1.9 g, 38%; <sup>1</sup>H-nmr (90 MHz, deuteriochloroform): δ (ppm) 6.88 (d, 2H, J = 3.9 Hz, ring), 6.70 (d, 2H, J = 3.7 Hz, ring), 4.11 (s, 4H, CH<sub>2</sub>N), 0.74 (s, 8H, SiCH<sub>2</sub>), 0.04 (s, 24H, SiCH<sub>3</sub>); ir (potassium bromide): aromatic ν (CH) 3072, 3061; aliphatic ν (CH<sub>2</sub>)/ν (CH<sub>3</sub>); 2951, 2921, 2909, 2884, 2840; ν (ring): 1532, 1456; γ (CH) 781 cm<sup>-1</sup>; uv-vis (dichloromethane): λ<sub>max</sub> 327 nm.

*Anal.* Calcd. for C<sub>22</sub>H<sub>40</sub>N<sub>2</sub>S<sub>2</sub>Si<sub>4</sub>: C, 51.91; H, 7.92; N, 5.50; S, 12.60. Found: C, 51.64; H, 7.87; N, 5.80; S, 12.92.

5,5''-Bis[(2,2,5,5-tetramethyl-1-aza-2,5-disila-1-cyclopentyl)-methyl]-2,2':5',2''-terthiophene (**B3**).

A solution of **A** (5.1 g, 20 mmoles) in 80 ml of ether under dry nitrogen was cooled to 0°. *n*-Butyllithium/hexane (1.6 M, 13.75 ml, 22 mmoles, Aldrich) was added dropwise, causing the solution to turn dark purple. After 30 minutes, magnesium bromide etherate (5.68 g, 22 mmoles) was added and allowed to warm to rt. After an additional 30 minutes, [1,3-bis(diphenyl-

phosphino)propane]nickel(II) chloride (0.16 g, 0.033 mole) was added and 2,5-dibromothiophene (2.25 g, 9 mmoles) in 5 ml ether was added dropwise. The solution was stirred overnight and heated to reflux for 4 hours. The resulting substance was in the solution. Hexane (200 ml) was added and washed with water. The solution was dried over calcium chloride and evaporated. The residue was washed with methanol and recrystallized from ethanol to give yellow needle-shaped crystals, yield 2.7 g, 51%; <sup>1</sup>H-nmr (500 MHz, deuteriochloroform): δ (ppm) 6.99 (s, 2H, ring), 6.94 (d, 2H, J = 3.6 Hz, ring), 6.72 (d, 2H, J = 3.6 Hz, ring), 4.12 (s, 4H, CH<sub>2</sub>N), 0.73 (s, 8H, SiCH<sub>2</sub>), 0.04 (s, 24H, SiCH<sub>3</sub>); ir (potassium bromide): aromatic ν (CH) 3065; aliphatic ν (CH<sub>2</sub>)/ν (CH<sub>3</sub>): 2948, 2917, 2888, 2840; ν (ring) 1522, 1445; γ (CH) 779 cm<sup>-1</sup>; uv-vis (dichloromethane): λ<sub>max</sub> 367 nm.

*Anal.* Calcd. for C<sub>26</sub>H<sub>42</sub>N<sub>2</sub>S<sub>3</sub>Si<sub>4</sub>: C, 52.82; H, 7.16; N, 4.74; S, 16.27. Found: C, 52.61; H, 7.36; N, 4.91; S, 16.64.

5,5'''-Bis[(2,2,5,5-tetramethyl-1-aza-2,5-disila-1-cyclopentyl)-methyl]-2,2':5',2''':5''',2''''-quaterthiophenes (**B4**).

The processes up to adding [1,3-bis(diphenylphosphino)propane]nickel(II) chloride were the same as that of **B3**. After those processes, 5,5'-dibromo-2,2'-bithiophene (2.6 g, 8 mmoles) was immediately added which was prepared beforehand by mixing 2,2'-bithiophene (Aldrich) and *N*-bromosuccinimide (NBS) in methanol and subsequently recrystallizing the white precipitates from acetone [29]. The solution was stirred overnight and heated to reflux for 4 hours. The resulting deposits were filtered and recrystallized from hexane to give yellow thin needle-shaped crystals (5 mm x 0.3 mm x 0.05 mm), yield 3.9 g, 72%; <sup>1</sup>H-nmr (500 MHz, deuteriochloroform): δ (ppm) 7.02 (d, 2H, J = 3.7 Hz, ring), 6.99 (d, 2H, J = 3.7 Hz, ring), 6.94 (d, 2H, J = 3.7 Hz, ring), 6.73 (d, 2H, J = 3.7 Hz, ring), 4.12 (s, 4H, CH<sub>2</sub>N), 0.73 (s, 8H, SiCH<sub>2</sub>), 0.03 (s, 24H, SiCH<sub>3</sub>); ir (potassium bromide): aromatic ν (CH) 3061; aliphatic ν (CH<sub>2</sub>)/ν (CH<sub>3</sub>) 2950, 2911, 2888, 2843; ν (ring) 1512, 1439; γ (CH) 779 cm<sup>-1</sup>; uv-vis (dichloromethane): λ<sub>max</sub> 404 nm.

*Anal.* Calcd. for C<sub>30</sub>H<sub>44</sub>N<sub>2</sub>S<sub>4</sub>Si<sub>4</sub>: C, 53.52; H, 6.59; N, 4.16; S, 19.05. Found: C, 53.35; H, 6.59; N, 4.40; S, 19.52.

5,5''''-Bis[(2,2,5,5-tetramethyl-1-aza-2,5-disila-1-cyclopentyl)-methyl]-2,2':5',2''':5''':2''''-quinquethiophene (**B5**).

Compound **B5** can be synthesized using 5,5''-dibromo-2,2':5',2''-terthiophene instead of using 5,5'-dibromo-2,2'-bithiophene in the tetramer synthesis. 5,5''-Dibromo-2,2':5',2''-terthiophene was prepared by using 2,2':5',2''-terthiophene in place of 2,2'-bithiophene in a manner similar to the synthesis of 5,5'-dibromo-2,2'-bithiophene [29], yield 3.2 g, 53%; <sup>1</sup>H-nmr (500 MHz, deuteriochloroform): δ (ppm) 7.05 (s, 2H, ring), 7.04 (d, 2H, J = 4.2 Hz, ring), 7.01 (d, 2H, J = 3.7 Hz, ring), 6.96 (d, 2H, J = 3.0 Hz, ring), 6.75 (d, 2H, J = 3.7 Hz, ring), 4.14 (s, 4H, CH<sub>2</sub>N), 0.75 (s, 8H, SiCH<sub>2</sub>), 0.05 (s, 24H, SiCH<sub>3</sub>); ir (potassium bromide): aromatic ν (CH) 3061; aliphatic ν (CH<sub>2</sub>)/ν (CH<sub>3</sub>) 2951, 2913, 2888, 2840; ν (ring) 1505, 1451; γ (CH) 780 cm<sup>-1</sup>; uv-vis (dichloromethane): λ<sub>max</sub> 422 nm.

*Anal.* Calcd. for C<sub>34</sub>H<sub>46</sub>N<sub>2</sub>S<sub>5</sub>Si<sub>4</sub>: C, 54.06; H, 6.14; N, 3.71; S, 21.22. Found: C, 54.34; H, 6.16; N, 3.93; S, 21.29.

5,5'-Bis(aminomethyl)-2,2'-bithiophene Dihydrochloride (**C2**).

Compound **B2** (1 g, 2.0 mmoles) was dissolved in 100 ml of ethanol and 1 ml of concentrated hydrochloric acid was added dropwise with stirring. This immediately produced a white precipitate. The precipitate was filtered and dried to yield white

powder, yield 0.46 g, 79%;  $^1\text{H-nmr}$  (500 MHz, deuterium oxide),  $\delta$  (ppm) 7.19 (d, 2H,  $J = 3.7$  Hz, ring), 7.12 (d, 2H,  $J = 3.7$  Hz, ring), 4.71 (s, 6H,  $\text{NH}_3^+$ ), 4.33 (s, 4H,  $\text{CH}_2\text{N}$ ); ir (potassium bromide):  $\nu$  ( $\text{NH}_3^+$ ) 3100-2400;  $\delta$  ( $\text{NH}_3^+$ ) 1595;  $\nu$  (ring) 1447;  $\gamma$  (CH)  $787\text{ cm}^{-1}$ ; uv-vis (water):  $\lambda_{\text{max}}$  310 nm.

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{14}\text{N}_2\text{S}_2\text{Cl}_2$ : C, 40.40; H, 4.75; N, 9.42; S, 21.57; Cl, 23.85. Found: C, 40.20; H, 4.88; N, 9.39; S, 21.36; Cl, 24.11.

5,5''-Bis(aminomethyl)-2,2':5',2''-terthiophene Dihydrochloride (**C3**).

The preparation of **C3** was carried out as described for the preparation of **C2**, except that **B2** was replaced with **B3** (1 g, 1.7 mmoles), yield 0.48 g, 75%;  $^1\text{H-nmr}$  (500 MHz, deuterium oxide):  $\delta$  (ppm) 7.13 (s, 2H, ring), 7.11 (d, 2H,  $J = 3.7$  Hz, ring), 7.05 (d, 2H,  $J = 3.7$  Hz, ring), 4.65 (s, 6H,  $\text{NH}_3^+$ ), 4.27 (s, 4H,  $\text{CH}_2\text{N}$ ); ir (potassium bromide):  $\nu$  ( $\text{NH}_3^+$ ) 3100-2400;  $\delta$  ( $\text{NH}_3^+$ ) 1593;  $\nu$  (ring) 1443;  $\gamma$  (CH)  $781\text{ cm}^{-1}$ ; uv-vis (water):  $\lambda_{\text{max}}$  359 nm.

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_{16}\text{N}_2\text{S}_3\text{Cl}_2$ : C, 44.32; H, 4.25; N, 7.38; S, 25.36; Cl, 18.69. Found: C, 44.04; H, 4.39; N, 7.18; S, 25.60; Cl, 18.99.

5,5'''-Bis(aminomethyl)-2,2':5',2''':5'',2'''-quaterthiophene Dihydrochloride (**C4**).

Compound **B4** (1 g, 1.5 mmoles) was dissolved in 50 ml of chloroform and 10 ml of 3 *N* hydrochloric acid was added dropwise with stirring. The chloroform solution immediately became colorless and produced a yellow precipitate in the aqueous phase. The precipitate was filtered to give a yellow powder, yield 0.53 g, 78%; ir (potassium bromide),  $\nu$  ( $\text{NH}_3^+$ ) 3100-2400;  $\delta$  ( $\text{NH}_3^+$ ) 1593;  $\nu$  (ring) 1441;  $\gamma$  (CH)  $771\text{ cm}^{-1}$ ; uv-vis (water):  $\lambda_{\text{max}}$  394 nm.

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{18}\text{N}_2\text{S}_4\text{Cl}_2$ : C, 46.84; H, 3.93; N, 6.07; S, 27.79; Cl, 15.36. Found: C, 46.57; H, 3.95; N, 6.18; S, 27.59; Cl, 15.34.

5,5''''-Bis(aminomethyl)-2,2':5',2''':5'',2''':5''',2''''-quinquethiophene Dihydrochloride (**C5**).

The preparation of **C5** was carried out as described for the preparation of **C4**, except that **B4** was replaced with **B5** (1 g, 1.3 mmoles), yield 0.59 g, 82%; ir (potassium bromide),  $\nu$  ( $\text{NH}_3^+$ ) 3100-2400;  $\delta$  ( $\text{NH}_3^+$ ) 1588;  $\nu$  (ring) 1441;  $\gamma$  (CH)  $787\text{ cm}^{-1}$ ; uv-vis (water):  $\lambda_{\text{max}}$  417 nm.

*Anal.* Calcd. for  $\text{C}_{22}\text{H}_{20}\text{N}_2\text{S}_5\text{Cl}_2$ : C, 48.61; H, 3.71; N, 5.15; S, 29.49; Cl, 13.04. Found: C, 48.30; H, 3.66; N, 5.05; S, 29.37; Cl, 12.93.

5,5'-Bis(aminomethyl)-2,2'-bithiophene (**D2**).

Compound **C2** (0.4 g, 1.3 mmoles) was dissolved in 100 ml of water and 3 ml of 3 *N* sodium hydroxide was added dropwise with stirring. This immediately produced a white precipitate which was filtered providing white blade-shaped crystals, yield 0.28 g, 92%;  $^1\text{H-nmr}$  (500 MHz, deuteriochloroform):  $\delta$  (ppm) 6.95 (d, 2H,  $J = 3.7$  Hz, ring), 6.79 (d, 2H,  $J = 3.1$  Hz, ring), 4.02 (s, 4H,  $\text{CH}_2\text{N}$ ), 1.57 (br, 4H,  $\text{NH}_2$ ); ir (potassium bromide),  $\nu$  ( $\text{NH}_2$ ) 3312, 3268; aromatic  $\nu$  (CH) 3090, 3074; aliphatic  $\nu$  ( $\text{CH}_2$ ) 2919, 2853;  $\delta$  ( $\text{NH}_2$ ) 1522;  $\nu$  (ring) 1453, 1408;  $\gamma$  (CH)  $795\text{ cm}^{-1}$ ; uv-vis (dichloromethane):  $\lambda_{\text{max}}$  320 nm.

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{12}\text{N}_2\text{S}_2$ : C, 53.54; H, 5.39; N, 12.49; S, 28.59. Found: C, 53.36; H, 5.52; N, 12.44; S, 28.17.

5,5''-Bis(aminomethyl)-2,2':5',2''-terthiophene (**D3**).

The preparation of **D3** was carried out as described for the preparation of **D2**, except that **C2** was replaced with **C3** (0.4 g, 1.1 mmoles). The resulting material **D3** was recrystallized from 2-propanol, yield 0.31 g, 95%;  $^1\text{H-nmr}$  (500 MHz, deuteriochloroform):  $\delta$  (ppm) 7.01 (s, 2H, ring), 7.00 (d, 2H,  $J = 3.7$  Hz, ring), 6.82 (d, 2H,  $J = 3.7$  Hz, ring), 4.04 (s, 4H,  $\text{CH}_2\text{N}$ ), 1.71 (br, 4H,  $\text{NH}_2$ ); ir (potassium bromide):  $\nu$  ( $\text{NH}_2$ ) 3359, 3283; aromatic  $\nu$  (CH) 3086, 3061; aliphatic  $\nu$  ( $\text{CH}_2$ ) 2911, 2853;  $\delta$  ( $\text{NH}_2$ ) 1584;  $\nu$  (ring) 1518, 1443;  $\gamma$  (CH)  $793\text{ cm}^{-1}$ ; uv-vis (dichloromethane):  $\lambda_{\text{max}}$  367 nm.

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_{14}\text{N}_2\text{S}_3$ : C, 54.87; H, 4.60; N, 9.14; S, 31.39. Found: C, 54.59; H, 4.80; N, 9.19; S, 31.63.

5,5''''-Bis(aminomethyl)-2,2':5',2''':5'',2''':5''',2''''-quaterthiophene (**D4**).

As soon as 3 ml 3 *N* aqueous sodium hydroxide solution was added to a 100 ml aqueous suspension of **C4** (0.4 g, 0.87 mmole), **C4** turned bright yellow. This was filtered and recrystallized from DMF, yielding bright yellow blade-shaped crystals, yield 0.32 g, 95%; ir (potassium bromide):  $\nu$  ( $\text{NH}_2$ ) 3333, 3281; aromatic  $\nu$  (CH) 3081, 3058; aliphatic  $\nu$  ( $\text{CH}_2$ ) 2909, 2851;  $\delta$  ( $\text{NH}_2$ ) 1601;  $\nu$  (ring) 1509, 1443;  $\gamma$  (CH)  $795\text{ cm}^{-1}$ ; uv-vis (dichloromethane):  $\lambda_{\text{max}}$  400 nm.

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{16}\text{N}_2\text{S}_4$ : C, 55.63; H, 4.15; N, 7.21; S, 33.01. Found: C, 55.35; H, 4.07; N, 7.30; S, 33.38.

5,5''''''-Bis(aminomethyl)-2,2':5',2''':5'',2''':5''',2''''-quinquethiophene (**D5**).

The preparation of **D5** was carried out as described for the preparation of **D4**, except that **C4** was replaced with **C5** (1 g, 0.74 mmole). This was recrystallized from *m*-dichlorobenzene, yielding red-brown blade-shaped crystals, yield 0.33 g, 96%; ir (potassium bromide):  $\nu$  ( $\text{NH}_2$ ) 3359, 3275; aromatic  $\nu$  (CH) 3079, 3058; aliphatic  $\nu$  ( $\text{CH}_2$ ) 2911, 2851;  $\delta$  ( $\text{NH}_2$ ) 1597;  $\nu$  (ring) 1507, 1441;  $\gamma$  (CH)  $792\text{ cm}^{-1}$ ; uv-vis (dichloromethane):  $\lambda_{\text{max}}$  422 nm.

*Anal.* Calcd. for  $\text{C}_{22}\text{H}_{18}\text{N}_2\text{S}_5$ : C, 56.13; H, 3.85; N, 5.95; S, 34.06. Found: C, 55.91; H, 4.03; N, 5.84; S, 33.80.

2-[(2,2,5,5-Tetramethyl-1-aza-2,5-disila-1-cyclopentyl)ethyl]-thiophene (**Ae**).

The preparation of **Ae** was carried out as described for the preparation of **A**, except that 2-(2-aminoethyl)thiophene (25.5 g, 0.2 mole, Lancaster) was used instead of 2-aminomethylthiophene. The boiling point was 99°/2-3 mm Hg, yield 49.8 g, 93%;  $^1\text{H-nmr}$  (500 MHz, deuteriochloroform):  $\delta$  (ppm) 7.10 (dd, 1H,  $J_{5,4} = 4.9$  Hz,  $J_{5,3} = 1.2$  Hz, H-5 of thiophene), 6.92 (dd, 1H,  $J_{4,5} = 5.2$  Hz,  $J_{4,3} = 3.3$  Hz H-4 of thiophene), 6.78 (dd, 1H,  $J_{3,4} = 2.4$  Hz,  $J_{3,5} = 1.2$  Hz, H-3 of thiophene), 3.08 (t, 2H,  $J = 8.2$  Hz, methylene group), 2.87 (t, 2H,  $J = 7.9$  Hz, methylene group), 0.71 (s, 4H,  $\text{SiCH}_2$ ), 0.05 (s, 12H,  $\text{SiCH}_3$ ).

5,5''-Bis[(2,2,5,5-tetramethyl-1-aza-2,5-disila-1-cyclopentyl)ethyl]-2,2':5',2''-quaterthiophenes (**Be4**).

The preparation of **Be4** was carried out as described for the preparation of **B4**, except that **A** was replaced with **Ae** (5.38 g, 20 mmoles). Blade-shaped orange crystals (2 mm x 2 mm x 0.1 mm) were obtained by recrystallization from hexane, yield 3.5 g, 62%;  $^1\text{H-nmr}$  (500 MHz, deuteriochloroform):  $\delta$  (ppm) 7.03 (d, 2H,  $J = 3.7$  Hz, ring), 6.99 (t, 4H,  $J = 4.3$  Hz, ring), 6.69 (d, 2H,  $J = 3.1$  Hz, ring), 3.09 (t, 4H,  $J = 7.9$  Hz, methylene), 2.84 (t, 4H,  $J = 8.2$  Hz, methylene), 0.72 (s, 8H,  $\text{SiCH}_2$ ), 0.07 (s, 24H,  $\text{SiCH}_3$ ); ir (potassium bromide): aromatic  $\nu$  (CH) 3071, 3063;

aliphatic  $\nu$  (CH<sub>2</sub>)/ $\nu$  (CH<sub>3</sub>) 2951, 2909, 2886, 2853;  $\nu$  (ring) 1510, 1464;  $\gamma$  (CH) 777 cm<sup>-1</sup>; uv-vis (dichloromethane):  $\lambda_{\max}$  401 nm.

*Anal. Calcd.* for C<sub>32</sub>H<sub>48</sub>N<sub>2</sub>S<sub>4</sub>Si<sub>4</sub>: C, 54.80; H, 6.90; N, 3.99; S, 18.29. *Found:* C, 54.80; H, 7.11; N, 4.02; S, 18.30.

5,5'''-Bis(aminoethyl)-2,2':5',2'':5'',2'''-quaterthiophene dihydrochloride (**Ce4**).

The preparation of **Ce4** was carried out as described for the preparation of **C4**, except that **B4** was replaced with **Be4** (1 g, 1.4 mmoles), yield 0.55 g, 78%; ir (potassium bromide):  $\nu$  (NH<sub>3</sub><sup>+</sup>) 3100-2400;  $\delta$  (NH<sub>3</sub><sup>+</sup>) 1595;  $\nu$  (ring) 1443;  $\gamma$  (CH) 781 cm<sup>-1</sup>; uv-vis (water)  $\lambda_{\max}$  396 nm.

*Anal. Calcd.* for C<sub>20</sub>H<sub>22</sub>N<sub>2</sub>S<sub>4</sub>Cl<sub>2</sub>: C, 49.07; H, 4.53; N, 5.72; S, 26.20; Cl, 14.48. *Found:* C, 48.81; H, 4.43; N, 5.65; S, 26.49; Cl, 14.44.

5,5'''-Bis(aminoethyl)-2,2':5',2'':5'',2'''-quaterthiophene (**De4**).

The preparation of **De4** was carried out as described for the preparation of **D4**, except that **C4** was replaced with **Ce4** (0.4 g, 0.82 mmole), yield 0.32 g, 93%; ir (potassium bromide):  $\nu$  (NH<sub>2</sub>) 3344, 3273; aromatic  $\nu$  (CH) 3088, 3063; aliphatic  $\nu$  (CH<sub>2</sub>) 2924, 2867;  $\delta$  (NH<sub>2</sub>) 1593;  $\nu$  (ring) 1512, 1442;  $\gamma$  (CH) 790 cm<sup>-1</sup>; uv-vis (dichloromethane):  $\lambda_{\max}$  401 nm.

*Anal. Calcd.* for C<sub>20</sub>H<sub>20</sub>N<sub>2</sub>S<sub>4</sub>: C, 57.65; H, 4.84; N, 6.72; S, 30.78. *Found:* C, 57.30; H, 4.96; N, 6.56; S, 30.45. Repeated analyses failed to improve the carbon and sulfur value.

Titration.

Twenty ml of a solution of 10 mM **C2** was prepared. The titration was carried out by adding dropwise 50 mM of sodium hydroxide to the above solution and monitoring pH by a pH meter at 25°. Similarly 20 ml of a solution of 5 mM **C3** was titrated by using 25 mM sodium hydroxide.

Acknowledgments.

We would like to thank Professor Masao Saito for his helpful suggestions and continuous encouragement. Thanks are also due to Professor Maurice Comtat, Dr. Regine Devaux and Dr. Ryohei Nagata for their fruitful discussions. This work was supported by the Ministry of Education, Science and Culture through Scientific Grant-in-Aid, A Grant-in-Aid for Scientific Research International Scientific Research Program Joint Research, and Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists.

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